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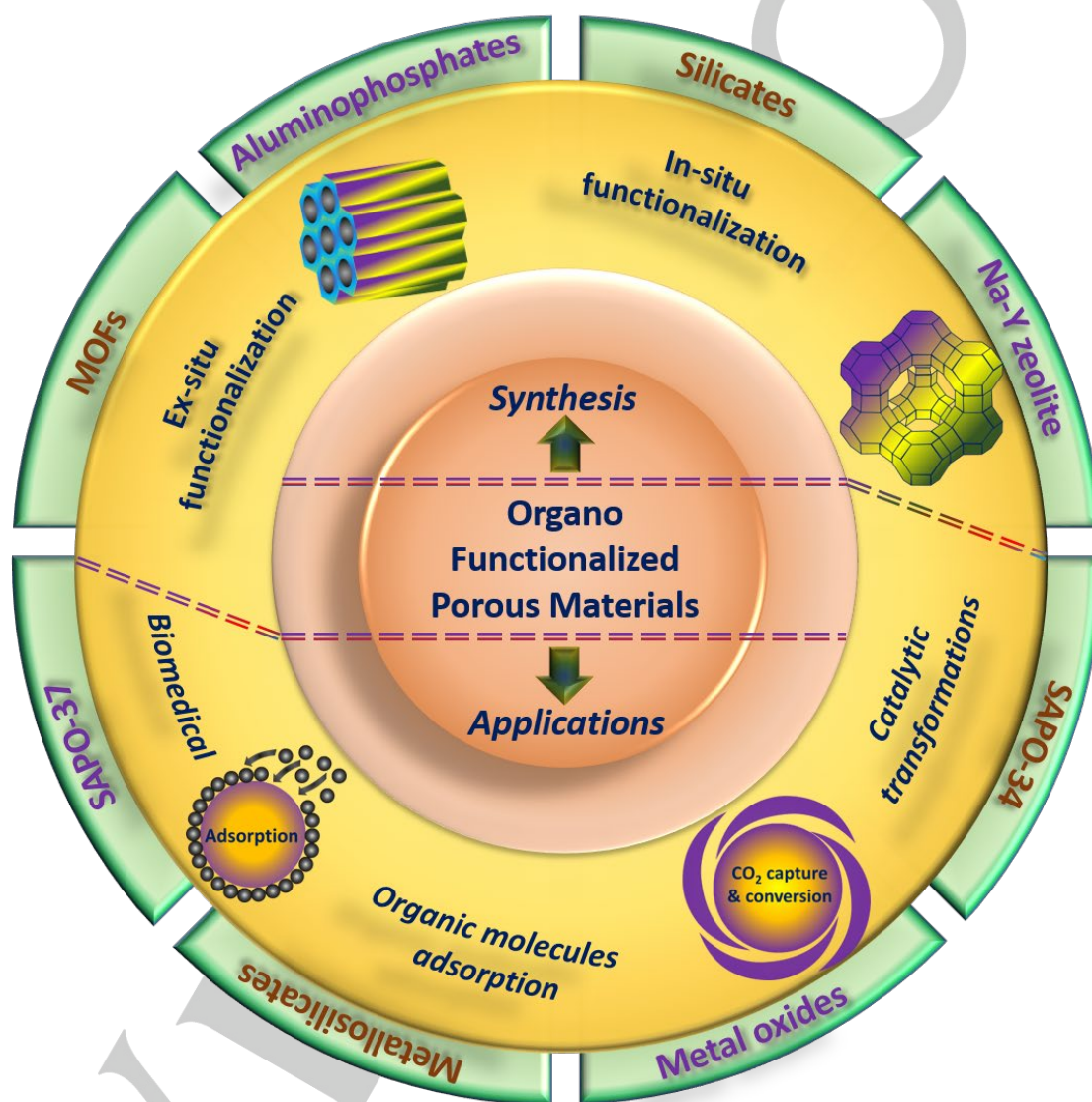
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Recent Advances in the Preparation and Applications of organo-functionalized Porous Materials

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Dedication ((optional))



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Abstract: Organo-functionalized materials with porous structure offer unique adsorption, catalytic and sensing properties. These unique properties make them available for various applications, including catalysis, CO₂ capture and utilization, and drug delivery. The properties and the performance of these unique materials can be altered with suitable modifications on their surface. In this review, we summarize the recent advances in the preparation and applications of organo-functionalized porous materials with different structures. Initially, a brief historical overview of functionalized porous materials is presented, and the subsequent sections discuss the recent developments and applications of various functional porous materials. In particular, the focus is given on the various methods used for the preparation of organo-functionalized materials and their important roles in the heterogenization of homogeneous catalysts. A special emphasis is also given on the applications of these functionalized porous materials for catalysis, CO₂ capture and drug delivery.

1. Introduction

Advanced materials and technologies play a dynamic role in the research and development of novel physical and chemical approaches that are employed in several industries, including petrochemical, fine chemical, pharmaceutical, and pesticide. Especially, porous materials have been receiving much attention owing to their exciting textural properties including high specific surface area, large pore volume and tunable pore size.^[1] New properties can be introduced in these materials through functionalization with organic and inorganic moieties. This approach is considered as one of the effective ways of tuning the specific properties of the porous materials for selective applications including catalysis, adsorption, separation and drug delivery.^[2] In particular, the introduction of organic functionalities into porous inorganic frameworks affords organic-inorganic hybrid molecular sieves with high porosity and a range of unique properties.^[3] Such materials with the surface-exposed organo-functionalized active species offer an easier manipulation of the overall physicochemical properties which extend their

application scope into a wide range of fields. Therefore, the functionalized porous materials have emerged as one of the core subjects of multidisciplinary studies, attracting tremendous interest and investment, and inspiring numerous research and development investigations.^[1] The significance of this research field is marked by a growing rate of high impact research which is continuously evolving and new materials with exciting properties are developed.

In particular, organo-functionalized mesoporous materials containing well-ordered and tunable porous nanostructures have shown high promise for catalysis, adsorption and molecular

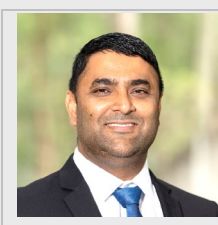
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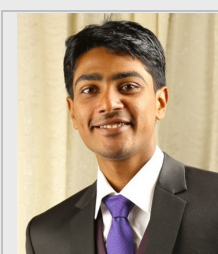
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Dr Gurwinder Singh is a research fellow at the Global Innovative Centre for Advanced Nanomaterials (GICAN), the University of Newcastle, Australia. He received his PhD in Materials Science under the supervision of Prof. Ajayan Vinu and his research interests include the development of porous materials for CO₂ capture/conversion and energy storage.



Dr Stalin Joseph is a Research Associate at the Global Innovative Center for Advanced Nanomaterials (GICAN), The University of Newcastle, Australia. His research interests focus on the conversion of industrial wastes into functional nanoporous carbon based materials for energy storage devices such as supercapacitors and batteries, and CO₂ capture and conversion.



Prof. Ajayan Vinu is currently working as a Global Innovation Chair Professor and the Director of Global Innovation Chair Professor for Advanced Nanomaterials, the University of Newcastle. He is a pioneer in the field of advanced nanoporous materials and is author of more than 400 research articles with an h-index of 72 (google scholar).



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separation applications owing to their interesting properties including high porosity and tunable surface chemistry which can be controlled through a simple manipulation with organic/inorganic guest species^[1a-c] These unique materials with the specific functional groups and properties find special use in several environmentally friendly organic transformations that have led to significant progress in the field of organocatalysis. The organic functional groups can also be introduced in both micro and mesoporous materials,^[4] and they are well suited for heterogeneous catalysis,^[5] and other applications including heavy metal sorption, drug delivery, wastewater treatment and photocatalysis.^[6] The emergence of these attractive materials and their unique and specific application possibilities has understandably resulted in the publication of numerous review articles. There have been several review articles published recently on the synthesis of functionalized SBA (Santa Barbara Amorphous) mesoporous silica materials, organically modified hybrid materials (including those containing primary, secondary and tertiary organo-amine functionalities) and their applications in various organic transformations.^[7] Recently, the theoretical investigations of hybrid materials based on density functional theory and the role of van der Waals forces in determining the properties of sexiphenyl films, the growth and morphology of which are strongly influenced by the subtle interplay between intermolecular and molecule-substrate interactions can also be found in recent reviews.^[8] Different hybrid materials, including structural characteristics with physicochemical properties and their application for coagulation- and flocculation-based wastewater treatment under different conditions has also been systematically covered.^[9] However, it should be pointed out that the properties of these hybrid materials mainly depend on the synthesis strategies adopted and therefore, the design of these new hybrid materials is giving new momentum to the family of organic-inorganic hybrid porous materials. The organic functionalization is a unique strategy to produce multifunctional hybrid organic-inorganic porous materials with multifaceted advantages. Owing to their larger pore size, the mesoporous materials are well suited for organic functionalization with groups such as trialkoxysilyl-organosilanes (R'O)₃Si-R as compared to microporous materials.^[10] The grafting of the organic groups to porous inorganic matrix imparts good thermal and mechanical stability to structure as well allows for easier surface

manipulation for enhancing the activity for a particular application. The combination of organic and inorganic constituents in the hybrid allows for the co-existence of porosity and surface functional groups due to which such materials present an enormous potential for a wide array of applications.^[11] Metal organic frameworks possess highly crystalline structure and are used for several applications owing to the presence of high surface areas and unique properties imparted by the presence of organic linkers and metal species.^[12] The functionalization of the porous materials with inorganic functional groups is also an attractive approach to fabricate materials that could be applied for various applications^[13], however, these might not be suitable application in technologically advanced areas. Eni carbon silicates (ECSs) is a class of hybrid organic-inorganic materials formed by covalent bonding between organic functional groups and aluminosilicate layers.^[14] The grafting of organic groups inside the inorganic framework results in the highly porous systems due to the enhanced spacing of the CSiO₃ units by the AlO₄ inorganic tetrahedral units.^[15] The modification of the zeolites with the organic functional groups is an effective strategy to enhance their application potential by tuning their hydrophilicity or hydrophobicity.^[16] Several ECSs such as ECS-1-3, ECS5-7, and ECS-14 have been reported with variations in the spatial arrangement of the organic and inorganic components.^[17] This unique class of crystalline materials with combined properties of organic functional groups embedded in the inorganic layers presents are an attractive prospect for different applications including catalysis.^[18]

Several pristine strategies for the preparation of hybrid inorganic-organic porous solids with different surface functionalities and micro and mesoporous structures with unique morphological and surface features have emerged recently.^[1e, 3, 4f, 4g, 5-6, 7-9] These materials with the fine control of functionalities and unique structural features fabricated through advanced nano approaches, including soft and hard templating strategies have been making a significant impact in the field of porous hybrid nanostructures.^[6a, 7] They have displayed a tremendous potential for various applications including organocatalysis, carbon capture and drug adsorption and delivery. Recently, vast advancements have been witnessed in the novel organic-inorganic hybrid porous materials and a wide range of high surface area micro- and mesoporous materials functionalized with organic moieties, synthesized via *in-situ* and *ex-situ* processes displaying a high degree of recyclability and recoverability and their use in a diverse range of applications have been reported.^[7] Although there are a few review articles on these organic-inorganic hybrid porous materials with a special emphasis on their synthesis and characterization,^[1e, 7a, 7d, 8-9] there are no review articles on the application of these materials with the special emphasis on catalysis, environmental and health. Therefore, it is highly critical to summarize the recent advancement in the synthesis strategies for organic-inorganic hybrid porous materials and offer collective information about their potential application possibilities. In this review, we discuss on the significant advancements in different synthesis strategies for designing organo-functionalized porous materials, together with the brief history of the porous materials, and the efficiency of these materials for useful applications covering environmental and health sectors (Figure 1).

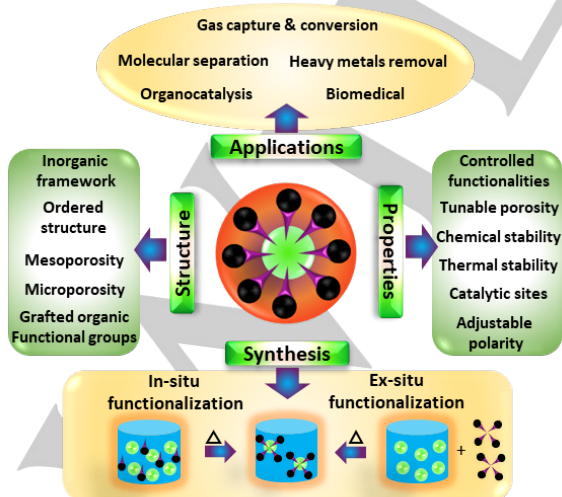


Figure 1. An overview of the contents covered in this review.

2. Porous Materials and their classification

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Porous materials are solid materials with a defined porosity and are naturally available or can be synthesized through simple self-assembly of structure-directing agents (SDA) and the required precursors using hydrothermal or solvothermal or ionothermal approaches. Typically, a material is called as porous if its internal pores are accessible for gas molecules or, in some cases, for liquids or solids.^[19] Depending on the nature of the pores, the textural parameters, and the adsorption properties of these materials will be changed. Examples of these porous materials include zeolites, zeotypes, metal-organic frameworks, mesoporous materials, and covalent organic frameworks. These materials offer excellent textural properties including high surface area and tunable pore sizes which can distinguish molecules based on their shape and size, therefore exhibiting selective adsorption (“sieving”) properties that allow the separation of molecules and can also be used for shape-selective catalytic reactions.^[1a]

Broadly speaking, porous materials are a subset of catalytic materials with a unique surface, structural, and porous properties which make them suitable for a broad range of applications including ion exchange, separation, catalysis, sensing, biomolecule isolation/purification, drug delivery and photocatalysis.^[20] Generally, pores are classified into open and closed ones, depending on whether they are connected to the outside of the material. Compared with non-porous materials, porous materials typically exhibit lower densities and higher surface areas. In addition to these surface features and pores, the nature of the framework structure of these materials offers unique catalytic, sensing, electronic and magnetic properties which can play an important role in expanding the application possibilities to various fields. The nature of these materials can be classified based on the structure and pore diameters. According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials are classified as (i) microporous materials whose pore size is < 2 nm, (ii) mesoporous materials with the pore size in the range of 2–50 nm, and (iii) macroporous solids with the pore size above 50 nm, as shown in **Figure 2**.^[21]

Porous materials are also called as nanoporous materials, whose pores (or voids) are of the order of ~1–100 nm. The materials with open pores are used in several industrial processes including separation, catalysis, and bioreactor operation, while those with closed pores are mainly used as low-density materials and also for insulation application.^[22] Based on the nature of framework structures, porous materials can be classified as inorganic (example zeolites, SAPO, AIPO, etc.), organic-inorganic hybrids (example organosilane silicates, organophosphate etc.) and

purely organic materials including polymers and carbonaceous materials. Although various porous materials have been developed, the discovery of mesoporous materials with an ordered porous structure, high specific surface area and large pore volume by the researchers in Japan and USA in the early 1990s was considered as special as it has made a huge revolution in the field of porous inorganic solids.^[23] These mesoporous materials were prepared by following two slightly different routes with the use of a silica source and alkyl ammonium surfactants as structuring and self-assembling agents.

The porous molecular sieves having mesopore range can be classified as ordered and disordered based on the distribution of pores, channels widths and atomic arrangements. The ordered mesoporous components (e.g., MCM-41/48 and SBA-15) lack ordered atomic arrangements, whereas the pores and channel widths are uniform and regular.^[20a] On the other hand, disordered mesoporous solids (e.g. KIT-1^[24]) exhibit uniform channel widths but both pores and atomic arrangements are not regularly arranged. Notably, microporous zeolites possess uniform pores and proper atomic arrangements.^[25]

Ordered molecular sieve with mesoporous structure (MCM-41) was synthesized by replacing conventional small organic molecules used in the synthesis of zeolites with surfactants as structure-directing agents (SDA) (**Figure 3**). The preparation of the mesoporous molecular systems is governed by the energetically-dictated formation of solution-based molecular assemblies which induce the assembly of inorganic precursors. In particular, SDA molecules with a lipotropic liquid crystalline phase induce the precursor's assembly. The obtained materials are then subjected to surfactant removal via extraction or calcination to get the desired mesoporous materials. After the successful replacement of small organic templates by long-chain surfactants, the synthesis routes have been explored in the preparation of different silica/non-silica-based materials.^[26] Since its discovery, the area of supramolecular templating has been expanded tremendously, and this has been reflected by the number of review articles published on this topic.^[27] However, the detailed account on the chemistry and the mechanism on the formation of functionalized mesoporous materials is quite limited. In the following section, we present a brief discussion on mechanisms involved in the surfactant-assisted synthesis of functionalized mesoporous materials and review their applications in specific areas covering environment and health.

The covalent organic frameworks (COFs) is another class of porous materials which are crystalline porous polymeric materials consisting of lighter elements (H, B, C, N and O) connected via covalent bonding.^[28] These materials possess remarkably thermal high surface areas and thermal stabilities which make them good candidates for several applications including gas capture.^[29] The COFs can be classified into 2D and 3D forms with the former consisting of atomic layers stacked using π - π interactions and the latter possess building blocks that are connected via covalent bonds.^[30] The structure of COFs can be suitably manipulated as per the requirement of the application. For example, the 2D COFs can be transformed into nanosheets with thin atomic layers that are useful for electrochemical purposes.^[31] The thin nanosheets serve as a conductive pathway for fast ion transport that leads to enhancement in the electrochemical storage. COFs are also good candidates for transforming into thin membranes to separate gold particles from solution with high recyclability.^[32] The COFs are continuously evolving and, due to their intriguing properties such

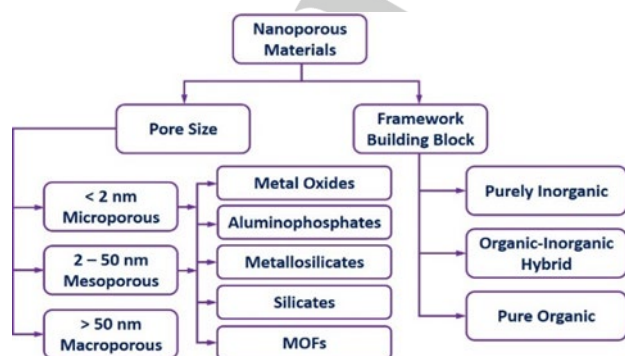


Figure 2. Classification of nanoporous materials based on pore size distribution and building blocks (reproduced with permission from ref 19 and 21).^[19, 21]

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as high crystallinity, porosity, rigidity and thermal stability, hold great promise for a variety of applications.^[33]

The functionalized porous materials, especially, the organic-inorganic porous hybrids, are interesting as they can simultaneously offer the properties of both organic and inorganic components in a single system. Such porous hybrid materials with controlled functionalities can be realized through a simple integration of different organic functionalities inside the porous inorganic frameworks owing to the availability of large voids. For example, porous materials have been utilized for the immobilization of enzymes, cells and antibodies to produce porous bio-nano hybrid materials which show a high efficiency for the targeted drug delivery applications.^[6b, 7d, 8-9, 20a, 34] Since 1916, much exploration has been devoted to the hybridization of biomolecules with porous inorganic nanostructures to improve the properties and the performance of the biomolecules. In addition, it is also used to simplify the operation of processes involving enzymatic reactions and allowing the re-use of immobilized enzymes to make these processes more cost-effective. It is also believed that the stability of enzymes in harsh reaction media can be significantly enhanced through the immobilization process.^[35] In general, enzymes are supported on polymeric organic materials including resins, organic gels and fibres, which, however, exhibit limited reusability and thus create disposal problems. Compared to organic supports, inorganic supports have been investigated quite extensively owing to their structural, chemical and thermal stability, non-hazardous nature as well as their resistant to organic solvents and microbial attack.^[35]

3. Synthesis of organo-functionalized molecular sieves

Mesoporous materials are a fascinating class of porous materials that have gained immense importance since the 1990s, due to their high surface area, narrow pore size distribution, a unique structure with a long-range ordering, and surface organo-

functionalization. A typical synthesis of mesoporous materials requires hydrothermal conditions in the presence of template or structure-directing agents (SDA) such as polymers, anionic surfactants and cationic surfactants, and a precursor such as tetramethyl orthosilicates (TMOSs), sodium silicates, etc., at a desired pH and reaction temperature. A self-assembly of these SDAs with the inorganic precursors makes highly ordered mesostructures. Through a high temperature calcination treatment in the presence of nitrogen and air, the SDAs can be removed, leaving the highly ordered mesoporous structure. By varying the nature of the surfactants, amount and the nature of the inorganic precursors, pH of the synthesis medium and the synthesis temperature, the pore structure and the size of the pores can be controlled. These calcined mesoporous materials have been extensively used as catalysts and catalytic supports but the scope of mesoporous materials can be extended by introducing the functionality on the mesoporous walls/ surface. The incorporation of organic functionalities on porous materials offers a convenient approach to design porous hybrid materials that can offer the control over the polar/non-polar surface with unique functional groups, as well as high specific surface area, controlled morphology, and tunable pore structures. Various functionalities including chirality, acidic, basic, redox, superacid, biomolecules and drug can be introduced either on the pore walls or inside the pores to generate new properties to the porous materials. The following section describes the synthesis and the characterization of different types of organo-functionalized meso and microporous materials. In addition, various strategies that have been adopted for the introduction of these functionalities will be described in the below section.

3.1 Synthesis of functionalized porous materials

During the last several years, considerable progress has been made on the development of various synthesis strategies for the functionalized porous, more specifically, mesoporous materials. In particular, the synthesis of porous inorganic-organic hybrid

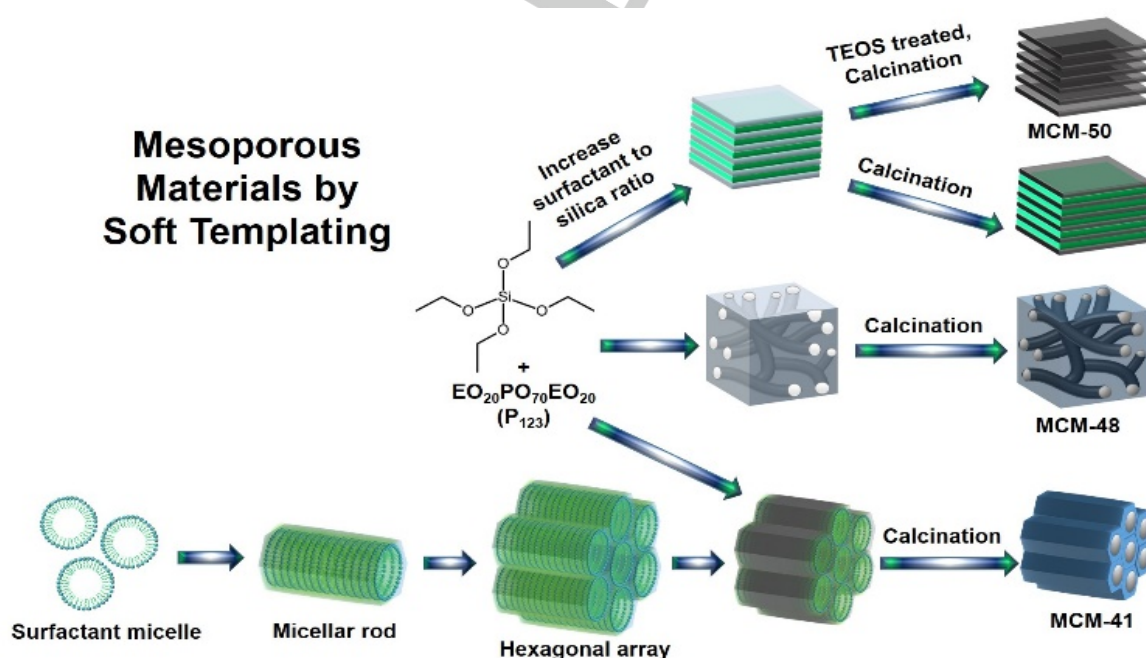


Figure 3. Synthesis of mesoporous materials by soft templating routes

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molecular sieves based on organo-linkers can be performed in three ways including (i) post-synthesis surface modification of pores of silica matrix, (ii) co-condensation of silica and organo-silica linker and (iii) the direct and specific introduction of the organic linker as bridging molecules into the pore walls using bis-silylated single-source organosilica precursors.^[36] Each strategy has its advantages, including the control of functionalities, pore size and morphology control, and the disadvantages such as the reduction in the structures features and large scale production. Therefore, it is highly critical to understand each strategy in more detail as the balance between the unique functionalities, and the structure, pore size, and morphological is needed to obtain the best functionalized porous materials. In this section, we mainly focus on the synthesis of organo-functionalities introduced by post-synthetic and co-condensation approaches. The *in-situ* route involves the direct addition of a functionalized precursor to the synthesis gel, whereas the *ex-situ* method offers the post-synthesis incorporation of functional groups into porous materials under specific conditions.^[37] In other words, *ex-situ* techniques feature an initial synthesis of the porous material followed by treatment with functionalized precursors to afford “dangling” functionalities attached to the external surface. Conversely, *in-situ* synthesis provides the introduction of organic functionalities onto the porous material during the synthesis itself. The *in-situ* synthesis relies specifically on the identity of the organic functional precursor, which may be incorporated into the walls of the materials or attached to the external surface.^[38]

From the viewpoint of materials science, the ability to combine the features of organic and inorganic components in a single hybrid matrix using either *in-situ* or *ex-situ* synthesis schemes is considered as quite interesting as it allows varied functionalities of organic substrates on the surface together with the amazing thermal stability of the inorganic matrix in a heterogeneous media. The physico-chemical properties of such organic-inorganic hybrids are significantly different from those of their components which enhance their application efficacy. For example, the addition of organic building blocks allows the adjustment of the polarity of the porous surface of inorganic matrices that find potential application in chromatography.^[39] Moreover, the functionalization of these hybrids with different organic groups including amines, carboxyl and thiols allows them to be utilized for the selective organic and/or biochemical transformations which require highly stable but selective catalytic sites.

3.2 Post-synthetic or *ex-situ* functionalization

The post-synthetic approach is generally adopted for the grafting of the functional groups on the surface of the synthesized materials. This approach is quite simple and straightforward. The advantage of this approach is that the functional groups can be attached on the surface of the walls of the mesoporous materials and can be easily accessible for various applications. Post-synthetic or grafting based surface modification is generally conducted by silylation. Esterification with different alcohols on the surface of silanol groups is another interesting method which is seldom used for the organic functionalization of mesoporous materials. It is widely recognized that the post-synthetic functionalization process requires free and geminal silanol groups but sometimes hydrogen bonded silanol groups are also used even though they are not accessible for the modification process. By tuning the amount of the surface silanol groups, the density of

the organic or other functional groups to be attached through the post-synthetic or grafting process can be controlled. Therefore, it is highly critical to have a huge number of silanol groups on the surface of the walls of the mesoporous materials for the attachment of functional groups through the post-synthetic process. The number of silanol groups on the surface of the mesoporous materials can be controlled by treating the calcined materials with boiling water or steam treatment. It should be mentioned that the surfactant extracted samples that are calcined at low calcination temperature (400 to 450 °C) are preferred for the post-synthetic or grafting process as the high-temperature calcination process decreases the number of silanol groups on the surface as it enhances the condensation process.

Organic moieties such as propyl amino-/chloro-/azenes could be anchored with the silanol groups on the surface of mesoporous materials.^[40] In principle, varying the length of the carbon chain or the number of functional groups allow synthesizing materials with different properties. Additionally, the hybrid mesoporous materials usually retain the mesostructure of the parent inorganic component.^[41] However, a major drawback of the post-synthetic procedure is the blockage of the pore entrance by organosilanes during the synthesis, which might prevent further molecular diffusion into the porous channels. This would lead a non-homogeneous distribution of organic functional moieties on the surface, which might be helpful for the removal of environmentally toxic contaminants, and for the separation of bulk biomolecules by restricting their freedom of diffusion. The surface functionalization also depends on the size of the functional groups to be attached on the surface and pore size of the host material. Sometimes, the presence of the surface silanol groups on the host materials may affect the movement of the functional groups along the porous channels. Therefore, for the post-synthetic functionalization, the choice of the functional groups, nature and pore size of the template and the surface silanol groups of the host is highly critical and needs to be carefully considered.

Feng *et al.*^[42] described the post-synthesis grafting of 3-MPTS onto MCM-41. They found that the obtained material could be used to selectively remove mercury and other heavy metal ions from an aqueous stream. The above behaviour was ascribed to the formation of covalent bonds between the soft sulphur atoms of MPTS and soft metals on the right side of the *d*-element block. Additionally, these materials were characterized by adsorption measurements, which reveal that the prepared materials have a large surface area. Besides, they have the MPTS functional groups which can form a close-packed high-density surface monolayer and the unhindered diffusion of mercury species through the regular pore network without any pore blockage.^[43] In this case, the pore size of the MCM-41 was small, and the movement of Hg atoms inside the porous channels with the bulky MPTS groups was not hindered due to the small size of the Hg atoms.

The access and the release of the functional groups are highly critical for certain applications. As the functionalized moieties inside the porous channels may come out of the pores due to the weak bonding between the surface silanol groups and the functional groups, the selective functionalization of the external surface of the pore entrance is needed to close the functionalized porous channels. For example, Mal *et al.*^[44] suggested a molecular gate at the entrance of the pore channels to control not only the access of the functional molecules inside the mesochannels but also their release from the porous channels.

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They synthesized a photo-chemically controlled system by fixing coumarin to the entrance of uncalcined MCM-41 silica phases for compound uptake and release. The use of SDA-containing MCM-41 resulted in the specific reaction of coumarin with the external surface, and subsequently, the SDA in the post modified samples was extracted. This technique helps on the selective incorporation of active compounds like cholestane derivatives inside the channels of porous materials. The UV light irradiation (<310 nm) resulted in grafting of the external surface with polymerized coumarin, which blocks pore entrance and facilitates permanent encapsulation of active species. Subsequently, the sample was irradiated again with the UV light at 250 nm, which led to the depolymerization of coumarin dimers and thus allowed for the diffusion-controlled release of active cholestane derivatives. This unique strategy may also be adopted for the selective functionalization on the pore entrance, leaving the inner part of the pore channels free of functional groups. As the functionalization of porous channels with the organic groups may block the pore channels, the selective functionalization on the external surface of the pore entrance is needed for the specific applications that require both functional groups and the surface areas and the pore channels.

Yu et al., functionalized mesoporous nanoparticles using two types of bromo-tetraphenylethene derivatives and explored their luminescence properties. They found that the materials showed strong blue fluorescence.^[45] These functionalized materials were found to be the potential candidates for the selective sensing of nitroarenes explosives and antibiotics with low detection limits. The high sensing capability of these fluorescent chemosensors based on functionalized mesoporous materials can be attributed to the photo-induced energy transfer quenching. Fluorescence properties could be introduced in the pure and phenyl substituted MCM-41 with Rhodamine B (RhB) molecules.^[45] It was reported that the surface charge on the walls, which could dictate the interaction between the surface functional groups of MCM-41 and RhB, is a crucial element that controls the intensity of fluorescence.

In order to introduce dual properties including magnetic and fluorescence, we introduced Rhodamine molecules (fluorophore) over 3D iron substituted mesoporous silica functionalized with 3-chloropropyltrimethoxysilane, which is a magnetic material, through the post-synthetic approach. With the help of trace, track and separate approach, we could use these fascinating materials with dual properties for the selective detection of mercury ions in living cells.^[46] Chatterjee et al. also demonstrated the synthesis of fluorescent active mesoporous silica materials with anthracene based compound and cubic structure via a post-synthetic approach. This unique material had the capability of not only sensing but also adsorption of toxic elements such as Hg^{2+} and Cu^{2+} ions from the real food samples and living organisms with the detection limits of 37 ppb for Hg^{2+} and 6 ppb for Cu^{2+} ions.^[47] The same group also used a similar approach and prepared safranin O-functionalized cubic mesoporous silica and applied them successfully for the sensing and adsorption of permanganate ions from the living organisms.^[48] Similar approach has also been applied for the preparation of RhB functionalized over Ag loaded SBA-15 films which showed enhanced selectivity for the detection of Hg ions. The addition of Ag instead of Fe significantly enhances the intensity of fluorescence and helps to extend the sensing for other metal ions such as Cd and Pb.^[49] Very recently, Wang et al. prepared pyrene based mesoporous

SBA-15 materials through post-synthetic approach and successfully applied for the selective detection of Hg^{2+} ion with a low detection limit of 1.02×10^{-7} M through aggregation-induced emission method. They also demonstrated that the aggregation or disaggregation properties could be easily tuned by varying the concentration of the pyrene compounds.^[50]

Similarly, various functional groups such as chalcones, salicylidene, dithizone, di-N-salicylidene-o-phenylenediamine, chromotropic acids, 2-mercaptopyrimidine, 2-mercaptothiazoline and/or other functional groups were introduced in the pore channels of mesoporous silica materials with different pore diameters and structures. They were found to be excellent chemosensors for the selective detection of various toxic metal ions such as Fe, Hg, Ag, and Pb.^[51] El Sayed et al. used a unique approach for the detection of cyanide ions using mesoporous silica nanoparticles with $[\text{Ru}(\text{bipy})_3]^{2+}$, coupled with Ni complex and the hexametaphosphate anion. In this approach, the demetallation of nickel(II) complexes and the removal of capping anions from the silica surface are induced by the cyanide ions, which increased the fluorescence intensity of the released dye molecules.^[52] Liu et al. reported pyrene functionalized mesoporous silica with Cu^{2+} ions through the post-synthetic approach. Originally, these materials are nonfluorescent, but when they interacted with the H_2S molecules, they produced a strong fluorescence as the Cu^{2+} ions from these complexes forms a stable CuS, releasing the pyrene-mesoporous silica which is fluorescence. This turn-on detection of H_2S is a unique approach and could be used as a logic gate for the selective detection of toxic gases.^[53]

In another interesting study, Li et al. prepared organic-inorganic hybrid materials based on europium luminescent mesoporous materials functionalized with the derivative of phenanthroline (2-(2-hydroxyphenyl)-imidazo[4,5-f]-1,10-phenanthroline). The coordination of pyridine groups with the Eu ions offered much better fluorescence when it interacted with fluoride ions. This could help to have the detection limit of 1.6×10^{-9} M for the fluoride ions.^[54] In another study, Schiff base complex was immobilized over salicylidene functionalized SBA-15 materials which were later employed as fluorescent chemosensors and showed a great promise for the selective detection of even a trace amount of Zn ions.^[51a] In another report, Karimi et al. demonstrated the synthesis of naphthalene-1-amine functionalized over 3-(isocyanatopropyl)trimethoxysilane linked SBA-15 through the post-synthetic approach.^[55] The prepared material was found to be highly selective for the detection of $\text{Cr}_2\text{O}_7^{2-}$ ions due to the strong binding affinity between the functional groups and the chromate ions.

Recently, mesoporous materials with tunable pore diameters are used as a controlled medium to tune the density and the arrangement of organic functional groups on the surface of the porous materials via post-synthetic approach. It was reported that the parent materials with a small pore diameter offer heterogeneously functionalized groups on the surface but the monolayers of organic groups could be decorated on the materials with the pore diameter less than 20 nm. If the pore size is larger than 30 nm, multilayered organic groups can be functionalized.^[56] This method seems to be a facile and straightforward approach as it can have unprecedented control over the density of functional groups. From this report, it is clear that it is crucial to choose the right materials with the right pore diameter if the nature of the organic functional groups needs to

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be controlled through the post-synthetic approach. This strategy may be applied to mesoporous materials with 1D, 2D and 3D porous structures whose pore diameters can be easily tunable. The pore size of the mesoporous materials can be easily controlled by either varying the hydrophobic chain length of the SDA or reaction temperature or the addition of the swelling or polar solvents.

Similarly, various functional groups such as amine, thiol and glycidyl groups were introduced in the porous channels of MCM-41, which were further explored for sustainable release of metronidazole drug.^[57] To introduce basic catalytic properties in the SBA-15, Wellei and Hu introduced biguanide groups on the surface of organic modified SBA-15 and further utilized these catalysts for the transesterification of soybean oil.^[58] The biguanide groups were strongly bonded with the surface of SBA-15, which increased the stability of the catalysts. The prepared catalyst showed excellent activity for was functionalized in the In another report, amine groups were functionalized in the mesoporous materials derived from rice husk. These functionalized materials were used for the removal of polyaromatic hydrocarbons in the range of 81-98%.^[59] Very recently, Selvaraj and Assiri prepared Schiff base ligand on the surface of mesoporous molecular sieves by two-step method and subsequently treated with copper nitrate to get surface grafted copper-based Schiff base complex (CSASBA-15).^[60] Similarly, Co and Fe Schiff base complexes were encapsulated over MCM-41 molecular sieves and utilized them for the conversion of sulphides to sulfoxides and thiol to disulphides, respectively.^[61] By varying the nature of the metal ions in the encapsulated Schiff base complexes in MCM-41, the nature of the catalytic sites which controls the oxidation process could be finely tuned. The resultant heterogenized copper-based Schiff based complexes were used as potential catalysts for the complete conversion of substituted phenols to the corresponding quinone with the selectivity in the range of 91-99%.^[61] These findings indicate that post-synthesis modification procedures allow organic functional groups to be attached to both the internal and external porous surface of mesoporous silica walls. Importantly, the external surface of the mesoporous silica can be selectively decorated by performing the condensation of organosilanes with the as-prepared mesoporous silica. In this case, the extent of external surface functionalization and functional group density can be controlled by varying functional silica to silica source ratio during synthesis.^[62] A similar approach has been adopted for the functionalization of the Schiff-base complexes of zirconium oxide and copper over MCM-41 which were successfully applied for the synthesis of sulfoxides and tetrazoles.^[63] The catalysts were found to be highly active, and the rate of the reaction over these catalysts is much faster than that of Cd-Salen-MCM-41 and Cu-Salen-MCM-41 catalysts, revealing the role of the metal cation and the complexes.

The post-synthetic approach can also be used for the introduction of dual and tri functionalities inside the porous materials. Aryan et al. introduced piperazine into the mesochannels of MCM-41 decorated with magnetic iron oxide nanoparticles.^[64] The piperazine groups acted as catalytic sites for the synthesis of pyrimidine derivatives whereas the iron oxide offered magnetic properties which are used for the effective removal of the catalysts from the reaction mixture, supporting the recyclability. The combination of catalytic sites and the magnetic properties is considered as an effective approach for the design of the robust and recyclable catalysts. Amino acid-functionalized ionic liquids

were also introduced in the mesoporous silica to create surface basicity which is the key parameter for basic catalysis and the adsorption of CO₂ molecules.^[65] By varying the nature of the amino acids, the amount of basicity and the total amount of CO₂ adsorption can be controlled. Supported with the theoretical calculation, it was reported that the energy required for the CO₂ adsorption over lysine functionalised ionic liquid in ordered mesoporous silica is high and therefore, it was found to be the best adsorbent for the CO₂ adsorption. Not only the functional groups but also porous organic frameworks have also been functionalized with mesoporous silica materials in order to combine the properties of these two porous materials in a single system. Soltani et al. demonstrated that covalent triazine framework could be functionalized over the phenyl functionalized mesoporous silica molecular sieves through a simple covalent attachment. The prepared material showed excellent adsorption capacity for the methylene blue, which is due to the presence of a large number of aromatic groups on the surface of these hybrid materials. These groups offered strong hydrophobic interactions which significantly enhanced the adsorption capacity of these hybrids for the methylene blue dye.^[66]

Not only basic sites but also organic acidic or redox groups can be introduced in the mesoporous materials through a simple functionalization through post-synthetic strategy.^[67] Organic sulfonic acids and sulfamic acids are the two major acidic groups that have been widely used for the generation of super acidity in the mesoporous materials with different structures including SBA-15, KIT-5 and KIT-6. For example, Mirsafaei et al. successfully used mesoporous KIT-5 functionalized with organic sulfonic or sulfamic acids for the synthesis of 1,4-dihydropyridines, 2,4,5-triaryl-1H-imidazoles and benzimidazole quinazolinones whereas Chermahini et al. used functionalized KIT-6 for the synthesis of aryl tetrazoles.^[68] As these functional groups are attached on the surface of the pore walls, they are readily available and can provide super acid sites which are highly useful for the selective production of the final products with excellent yields, revealing the importance of the addition of functional groups on the mesoporous silicas. Similarly, propyl or phenylsulfonic acid groups were also introduced on the mesoporous hybrid materials for the transesterification of soybean lecithin with methyl caprate. The catalysts were found to be highly stable and selective and could be recycled for several numbers of time.^[69] Various other catalytic functional groups such as piperazine-ethyl urea, Cu(II)-Schiff base complexes, organotin, cobalt salophen, etc have been introduced on the mesoporous silica materials for different catalytic reactions including oxidation, reduction, addition reactions involving the synthesis of fine chemicals, confirming the widespread application possibilities of these organic-inorganic mesoporous hybrid materials.^[58, 70]

Although post-synthetic functionalization is quite interesting owing to the selective functionalization on the surface of the walls, there is a possibility that the pores may be blocked after the functionalization. Therefore, researchers tried to functionalize organic moieties through different approaches including co-condensation or in-situ functionalization and the direct synthesis routes as they may offer porous organic-inorganic hybrid materials with much better textural parameters than the hybrid materials prepared from the post-synthetic routes.

3.3 Co-condensation or *in-situ* functionalization

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In-situ functionalization is based on the addition of the functional groups in the porous materials during their synthesis. This method introduces functional groups throughout the samples as a result of the direct reaction between the inorganic precursors and the organic precursors. These organic-inorganic hybrid materials can be prepared by a one-step co-condensation method, which involves the reaction of tetraalkyl orthosilicate with organo-silanes having a terminal functional group in the presence of a surfactant/template. Co-condensation approach is generally applied for the direct or *in-situ* synthesis of organo-functionalized porous nanostructures. Although this approach requires tedious synthesis steps and the control of the functional groups on the surface of the porous materials is very difficult, many research groups have adopted different strategies for the synthesis of organo-functionalized porous materials through co-condensation routes. For example, mesostructured silica phases with organic residues covalently anchored to pore walls can be prepared by the reaction of tetraethoxysilane with propyl-amine/ chloro/thiol functionalized terminal silane linker of the type $(R'O)_3SiR$ in the presence of surfactant (Figure 4). The utilization of suitable SDA for the synthesis of pure mesoporous silica phases (e.g., MCM or SBA) allows the formation of varying pore sizes which can be modified with suitable organic groups.

As these functional groups are embedded directly on the internal surface of the mesoporous silica matrix, the materials prepared through the co-condensation method do not suffer from the issue of pore blockage. Generally, porous organic-inorganic hybrid materials with a more homogeneous distribution of organic units can be obtained through the direct synthesis route than that are achieved with the *ex-situ* technique. However, it does suffer a reduction in the degree of crystallinity of the materials with the increased concentration of functional silane introduced in the initial gel. The maximum number of organic functional groups can be introduced by the co-condensation method, and the concentration of surface-exposed organo-functionality concentration is generally much less as compared to the amount of organic functionality used in the starting gel composition. This could be due to the increase in the concentration of terminal functional organosilane that facilitates the self-condensation rather than cross-linking via co-condensation with silica sources. The extent of self-condensation of functional terminal organosilane depends on the rate of hydrolysis and condensation of the starting materials used for the synthesis. It should be mentioned that the co-condensation approach does not guarantee a uniform dispersion of functionalities in the framework and an increase in the concentration of terminal silane groups could lead to a reduction in the textural parameters of the materials. The potential destruction of organic functionalities during surfactant removal is also considered as another disadvantage for the co-condensation approach. This explains the predominant use of extractive methods and the unsuitability of calcination in most cases.^[71] However, there is a growing interest in the use of hybrid organic/inorganic porous materials^[72] in a range of applications such as multistep catalysis^[36, 73] and adsorption-based separation.^[74]

As previously discussed, the syntheses of these hybrids involve the chemical grafting of organic groups (typically organosilanes) onto the surface of inorganic frameworks,^[75] and the acidity, basicity, and surface charge of the obtained materials are therefore determined by the properties of the grafted functional groups. The introduction of various functionalities in the

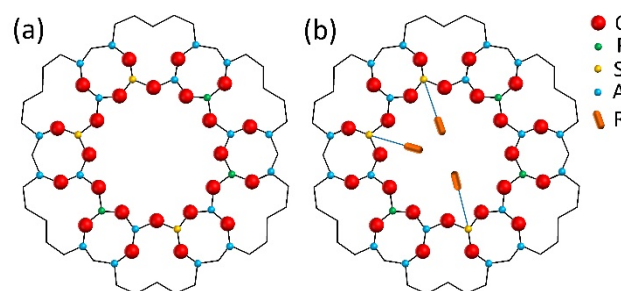


Figure 4. (a) Organic-inorganic hybrid microporous molecular sieves, and (b) molecular sieves containing organic frameworks.

framework (i) helps to generate a broad range of functionalities ($-SH$, $-NH_2$, $-COOH$, $-SO_3H$, etc.) within the functional material, (ii) facilitates the host-guest chemistry, and (iii) results in integrated functional properties causing the framework to behave as a multi-functional component.

3.3.1 Functionalized zeolites and zeotype materials

Chemical grafting affords organic-inorganic hybrid molecular sieves of two types (Figure 4), with type I characterized by a pendant-like attachment of organic groups and type II characterized by the incorporation of organic groups into the inorganic material framework.^[76] Three-dimensional framework materials bearing organic groups were first reported in 1994 by Maeda *et al.*, who fabricated a methyl group-functionalized aluminophosphate molecular sieve via *in-situ* hydrothermal synthesis.^[77] The properties of these materials are different from the pure microporous aluminosilicate materials as the channel walls of the hybrid materials are made of organic groups that are directly attached with the P in the skeleton. Especially, the hydrophobic character of the hybrid material is much better than non-functionalized materials. Another interesting feature is that the micropore size and shape of the final materials can be controlled with the simple change of the chain length of the alkyl phosphonic acid groups. In another report, Zhou *et al.*^[78] prepared vinyl-functionalized SAPO-5 using a water-ethanol mixture as the reaction medium. The presence of SDA molecules occluded in microporous channels along with organic functional groups limits the applications of these materials, as SDA molecules are difficult to be removed without disturbing the co-present organic functionalities.

Similarly, researchers tried to incorporate organic functional groups directly into the microporous zeolite samples through direct synthesis method. The approach that was used for the zeotype samples was also adopted for the microporous zeolite materials. However, it was not quite simple as many researchers failed to specifically functionalize the organic molecules within the porous channels of the zeolite materials and were not successful in achieving higher shape selectivity in the catalysis reactions. Jones *et al.* synthesized a phenylethyl group-functionalized beta zeolite that was subsequently sulfonated and used in the acid-catalyzed condensation of cyclohexanone and glycol.^[79] In this approach, they first attached phenylethyl groups with the silicon atoms in the aluminosilicate framework and then removed the SDA and the functional groups attached outside the framework structure in order to create the microporosity. With the subsequent functionalization of phenyl groups with sulphonic acid groups, highly acidic sites could be generated and used for the shape-selective catalysis. The scope of functional groups and material

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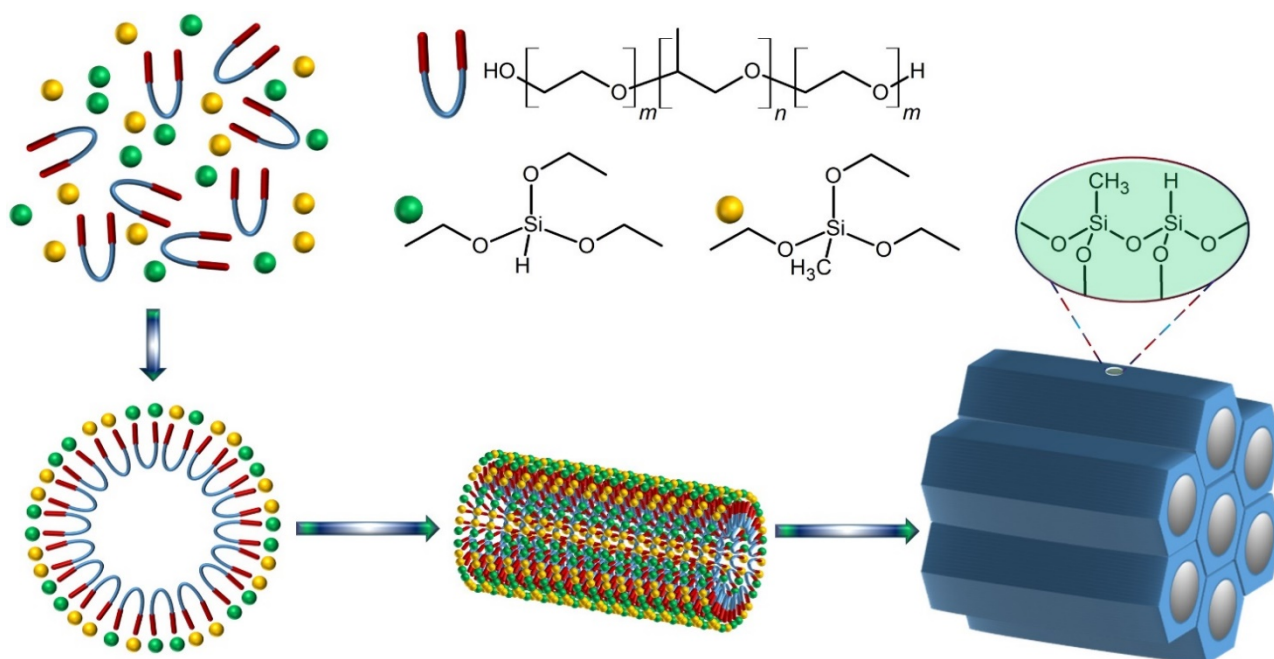


Figure 5. Schematic representation of the synthesis of functionalized mesoporous silica (reproduced from ref 85).^[85]

frameworks is not limited by the above examples and is very broad, encompassing groups such as Si-(CH₂)₂-C₆H₅, Si-(CH₂)₂-C₆H₉, Si-(CH₂)₂-CH=CH₂, Si-(CH₂)₃-SH, Si-(CH₂)₃-NH₂, Si-C₆H₅, Si-CH=CH₂, P-CH₃, and P-C₆H₅ and zeolite frameworks such as zeolite beta (BEA), Zeolite Socony Mobil-5 (MFI), aluminophosphate-eleven (AEL), and aluminophosphate-five (AFI).^[80] For example, Yamamoto *et al.*^[108] synthesized a methyl group-containing BEA organic-inorganic hybrid molecular sieves and demonstrated the shape-selective lipophilicity and structure stability of ZOL (zeolite with the organic group as lattice) material. Zhou *et al.*^[76] used dry gel conversion to synthesize methylene-bridged MOR-1 and MOR-2 hybrid materials using pure bis(triethoxysilyl)methane and its mixture with fumed silica, respectively. González *et al.*^[81] used the similar approach but used the microwave technique for the synthesis of sulphonic acid-functionalized commercially available zeolites viz., Beta, ZSM-5, mordenite, and montmorillonite K-10 clay using a one-step method and their application for the etherification of glycerol with isobutene. It was reported that the degree of acid functionalities could be controlled by varying the amount of sulphonic acid groups. However, the nature of the formed acid groups varied quite significantly with the structure of the zeolites or clays. For example, zeolites with one-dimensional structure and pores, which showed much lower activity than the functionalized zeolites with 3D structure, exhibited lower external surface area and the acidity. Besides, the materials with the higher external surface area, Beta zeolite, which have the functional groups both inside the porous channels and the external surface registered much better activity than the functionalized ZSM-5 catalyst. Similarly, various organic functional groups, well-defined clusters or nanoparticles have been introduced in the porous channels of the inorganic materials by coupling the soft chemistry processes and intelligent coding in order to fine-tune the surface charges, reactivity, and protection, as well as to modify the bulk properties of the original materials.^[82]

3.3.2 Functionalized mesoporous materials

The effectiveness of hybridization can be enhanced when the organic functional groups are introduced into the mesoporous materials as they can offer a large pore diameter, large pore volume and a high specific surface area. Mesoporous organic-inorganic hybrid materials synthesized through in-situ approach have been extensively studied owing to their enormous potential for various applications including adsorption and separation, catalysis, sensing and drug delivery.^[83] Stein *et al.* and Sanchez *et al.* summarized the earlier reports on the organic-inorganic hybrid mesoporous materials and how the organic functional groups alter the specific properties of the mesoporous materials and extend the application possibilities of these hybrid nanostructures with both active and inert functional organic groups prepared via grafting or co-condensation under SDA control.^[83f, 83g, 84] As mentioned previously, co-condensation method is generally used for the direct synthesis of mesoporous organic-inorganic hybrid materials with different organic functional groups both in the internal pores and the external surface. For instance, Xie *et al.*^[85] synthesized organic functionalized periodic mesoporous silicas (PMSs) via co-condensation using (R'O)₃Si-H and (R'O)₃Si-R type terminal trialkoxyorganosilanes. This synthetic route, shown in **Figure 5**, resulted in materials with higher co-condensation of methyltriethoxysilane (MTES) and triethoxysilane (TES). The prepared PMSs reached ca 78% incorporation of CH₃-SiO₃ units by extending the length of organic groups. Further, PMSs with a large number of vinyl groups (ca 48%) was also achieved. It is considered as one of the most effective methods that provided an efficient way to prepare PMSs with different organic functional groups. Notably, the above method allows organic functionality to be incorporated either on the surface of the pores or the walls. Such functionalized hybrid mesoporous silicates are especially important for catalysis, metal ion sorption, and optoelectronics, and are also employed in several organic processes and fixation of biological species. Importantly, the high stability, selectivity and binding site density of these organic-inorganic hybrid materials, as well as their ease

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of modification, are also the reason for their widespread usage in various applications.

3.3.3 Periodic mesoporous organosilica (PMO)

Self-organization in organic-inorganic hybrid mesoporous materials may or may not lead to molecular- and mesoscale periodicities depending upon the synthesis conditions. For example, Fujita *et al.*^[39] summarized different synthesis approaches for the periodic mesoporous organosilica (PMO) materials with ordered porosity and high crystallinity. It was described that the molecular and mesoscale periodicity in the PMO materials could be obtained through the self-organization of molecular building blocks that contain a variable organic component with two or more functional silyl groups such as bis-silylated organic monomers with or without using any additional templates. The difference between the organic functionalized mesoporous silica and the PMOs is that the organic groups in the PMO are homogeneously distributed due to the two-point attachment with the silica matrix through covalent bonding which offers unique thermal, optical, electronic and surface properties. The properties of the PMOs can be altered by varying the nature of the organic groups in the building blocks. It is also believed that the pore surface blockage can be significantly avoided in PMOs. The unique distribution of functionality, mesoporous structure and the excellent surface properties widen their potential use in molecular separation, catalysts, sensor, optoelectronics etc. As mentioned above, the organic-inorganic hybrid materials can be directly synthesized by using a large number of organosilane molecules viz., $(R'O)_3Si-R-Si(OR')_3$ (e.g., R = ethyl, methyl, benzyl etc.), where R is linker connected with two trialkoxysilyl groups.^[85] These materials are categorized by the nature of the organic fragments and silica moieties that are available on the framework structure. It is also possible that the surface functional groups can be designed as per need of the chemical reactions, which may include either simple or bulky functionalities. To incorporate the organic bridging groups, which include benzenes or heterocyclic^[86] or fluorophore moieties,^[85] soft templating routes are used.

Chirality can also be introduced in the PMOs through the self-assembly of the SDAs and the chiral molecules. For example, Baleizão *et al.* synthesized a chiral PMO using vanadium-containing chiral Schiff base molecules (containing trimethoxysilyl groups as the organo-linker precursor) with 2D hexagonal periodicity^[87] and showed that cyanosilylation of benzaldehyde, promoted by this chiral PMO, could be performed with enantioselectivity of 30%. Chirality in the PMOs has also been introduced by varying the nature of the precursors and the SDAs in order to introduce the improved photonic and catalytic properties. Recently, MacLachlan reported that PMO films with chiral nematic structures could be prepared by bridging urea molecules and alkylene groups using cellulose nanocrystals as SDAs. The self-assembly of CNCs with the organosilica precursors offered chiral nematic nanostructures which exhibited excellent photonic properties together with a high thermal stabilities.^[88] Chiral resolution can also be obtained in mesoporous silica particles with guanosine monophosphate and folic acid. The additional organic functionalization offers chirality on the surface of the mesopores, which are effectively used for the separation of enantiomeric pairs. This provides a fantastic opportunity for the enantiomeric catalysis.^[89]

The properties of the PMOs can be significantly enhanced upon further functionalization with organic or inorganic functionalities.^[90] For example, gold nanoparticles have been incorporated into the PMO with phenylene-ethylene bifunctional groups through a simple impregnation of $NaAuCl_4$ and a further reduction with sodium borohydride.^[91] The presence of the aromatic ring in the PMO stabilizes the formation of highly dispersed gold nanoparticles within the channels of the organic functional groups. The prepared catalysts also showed excellent performance in the homocoupling of aryl halides to yield biaryl products. In another report, the same group has introduced ionic liquids (ILs) in the PMOs through simple hydrolysis and condensation reaction of the 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride and the TMS using Pluronic P123 as an SDA.^[92] The ILs linked PMOs were effectively utilized for the immobilization of Pd nanoclusters for the Suzuki-Miyahara coupling and Heck cross-coupling of different aryl halides.^[93] Similarly, gold nanoparticles supported PMOs functionalized with ILs were prepared through a simple ion-exchange of gold source with the Cl^- ions in the parent material. The prepared materials have been effectively utilized for the synthesis of propargylamines through A3 coupling reaction of alkynes, amines and aldehydes.^[94] Fukuoka *et al.* also synthesized gold nanoparticles in PMO with bipyridine-silica using $HAuCl_4$. It was suggested that the gold precursor makes a complex with PMO, which further undergoes reduction with hydrogen gas to produce highly dispersed gold nanoparticles. It was demonstrated that these catalysts showed excellent activity in aerobic oxidation of benzaldehyde with the selective production of benzoic acid.^[95]

Not only inorganic nanostructures but also other functional groups such as amines, organotin, graphene, rare earth metal oxides, etc can also be functionalized with PMOs.^[96] For instance, Lourenco *et al.* demonstrated that amine groups could be functionalized in the PMOs through mononitration with nitric acid in the presence of sulphuric acid, followed by the reduction with tin chloride and HCl. The amine-functionalized samples showed higher selectivity for the adsorption of CO_2 molecules in comparison with the CH_4 molecules.^[96a-c] The same group also manipulated the amine-functionalized PMOs for the formation of dialkylated amine through the microwave-assisted approach. The newly formed dialkylated amine PMO could be used for various applications including catalysis and adsorption.^[96e] In another report, it was demonstrated that amine groups can be introduced in bi-functional PMOs with phenylene and isocyanurate bridging groups synthesized through a simple co-condensation route.^[96i] The prepared materials showed a significant enhancement in the adsorption of CO_2 molecules as compared to pure mesoporous silica and the unfunctionalized PMOs. These results reveal that the properties and the performances of the PMOs can be significantly altered with an introduction of suitable functional groups which can easily be attached in PMOs. PMOs can also be used as the templates as well as the carbon source for the fabrication of new nanoporous carbon nanostructures with a high specific surface area and ordered pores.^[96f] For instance, PMO with phenylene or biphenylene organic linkers have been used as the source of carbon and treated at different temperatures from 800 to 1200 °C. This simple process offered nanoporous carbons with tunable pore diameters.

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Table 1. Labels for ordered mesoporous solids, type of surfactant used and crystallographic structure (reproduced from ref 97a)^[97a]

Sample Name	Organic-Surfactant-used	Structure
2D Mesoporous Silica	Tetraalkyl substituted ammonium salt with the formula of $RN^+(CH_3)_3X^-$ (Where R is an alkyl group having a carbon chain length of 12, 14, 16 or 18 and X = halide ion)	p6mm, hexagonal
3D Mesoporous Silica	Tetraalkyl substituted ammonium salt with the formula of $RN^+(CH_3)_3X^-$ (Where R is an alkyl group having a carbon chain length of 12, 14, 16 or 18 and X = halide ion)	la-3d, cubic
FSM-16 ^a	Tetraalkyl substituted ammonium salt with the formula of $RN^+(CH_3)_3X^-$ (Where R is an alkyl group having a carbon chain length of 12, 14, 16 or 18 and X = halide ion)	p6mm, hexagonal
Hexagonal Mesoporous Silica	Uncharged amine surfactant $C_nH_{2n+1}NH_2$	Wormhole framework structure
Large pore Mesoporous Silica	P123-type polymeric surfactant	p6mm, hexagonal
Large cage structure	F127-type polymeric surfactant	Im3m, cubic
KIT-6 ^b	P123-type polymeric surfactant	la-3d, cubic
FDU-1 ^c	B50-6600-copolymer derived from Poly-(EO)-poly(BO)-poly(EO) (EO ₃₉ BO ₄₇ EO ₃₉ ; where EO-ethyleneoxide and BO butylene oxide)	polymer Fm3m, cubic
COK-12 ^d	P123-type polymeric surfactant	p6m, hexagonal

As the treatment temperature was increased, the amount of the micropores was significantly increased with the concomitant reduction of the pore size. The higher calcination temperature offered nanoporous carbons with a lot of micropores which are important for the selective capture of the CO₂ molecules. The important factor is that the presence of the aromatic ring in the PMS helps to get the highest Henry's constant which is better than amine-functionalized porous adsorbents for carbon capture. It should also be pointed out that the aromatic rings in the PMOs could also be effectively used for the preparation of highly graphitic porous carbons which might be useful for energy storage applications.

3.4 Synthesis of functionalized mesoporous materials using different surfactant types (anionic, cationic and non-ionic)

New properties can also be introduced into mesoporous materials with different organic functional groups. The properties and the performance of these materials not only depend on the functional groups but also the structure and the pore diameter of the materials. The structure and the pore diameter of the materials can be controlled by varying the nature of the SDAs. The SDAs play a major role in the synthesis of mesoporous materials^[97] and have the unique function to tune the structure, morphology, particle size and shape of the final materials. As mentioned previously, the nature of the surfactant, molecular weight, concentration and the functional groups on the surfactants have a direct relation with the final structure and morphology of the materials (**Table 1 and 2**).

These structural features can also be further tuned by varying other synthesis parameters, including solution pH, temperature, the addition of co-surfactants, and the stirring speed. **Table 2** summarizes the methods and conditions for the syntheses of various functionalized mesoporous solids with uniform pore structures. The following section provides the summary on the role of different surfactant types (anionic, cationic, neutral and

non-ionic forms) in controlling the formation of functional mesoporous materials and their significance.

3.4.1 Anionic surfactants

Anionic surfactants are widely used in a range of applications, including soap manufacturing because of the easy availability and low cost. These are typically weak acids and possess negatively charged head groups including alkyl carboxylate, phosphate, sulphate and sulphonate groups. The solution pH is a crucial parameter when working with synthesis of functionalized porous material using anionic surfactants as it controls the porous dimensions of the final product. These surfactants also have the switchable charging state which can easily allow the change in the area of the hydrophilic head group and the surface packing parameters. As these surfactants can be easily fine-tuned by varying the solution pH or modifying the effective head group area, the physicochemical properties of mesostructures derived from these surfactants could be easily controlled and tuned into desired characteristics. Above mentioned unique characteristics of anionic surfactants make them different from other surfactants including cationic and non-ionic surfactants.

Table 3 briefly summarizes the functional mesoporous solids synthesized using anionic surfactants and their applications. For example, Yokoi *et al.*^[98] reported the synthesis of mesoporous silica via the $S^-N^+~I^-$ pathway, employing APTES as the silica source and sodium laurate as the anionic surfactant. During the synthesis, the APS amine group ($pK_a \approx 10.6$ at 298 K) can be protonated to interact with the head group of the anionic surfactant that could be subsequently removed using acid extraction. Also, the obtained material showed a higher amine loading than MCM-41 synthesized using a cationic surfactant. Additionally, these researchers described the hydrothermal preparation of mesoporous materials having amine-functionality by co-crystallization and grafting methods using three different amines (APTS, 6-amino-4-azahexyltrimethoxysilane, and 9-amino-4,7-diazanonyltrimethoxysilane) in the presence of

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Table 2. Synthesis protocols and parameters on the preparation of various uniform mesostructured materials.

Mesophase solids	Molar gel ratio	Synthetic conditions	Average-pore (nm)
Large cage structure	TEOS: 4.0 HCl: 0.004 F127: 130 H ₂ O	Hydrothermal	5.6
FDU-12	1.0TEOS:0.5TMB:3.36KCl:0.0037F127: 6.08HCl:165H ₂ O	Hydrothermal	12.2–21.6
2D Mesoporous Silica	1.0SiO ₂ : 0.5NaOH:40.5H ₂ O: 0.167MTAB: 0.835EG	Microwave	2.1
Large cage structure	3.17×10 ⁻⁴ F127: 1SiO ₂ : 6.68 HCl: 137.9 H ₂ O	Hydrothermal	7.7
Large pore mesoporous silica	SiO ₂ : 0.017 P123: 0–2330NaCl: 6HCl: 4400EtOH: 188H ₂ O	Microwave	5.2–6.2
FDU-1	10TEOS: 0.0735B50 – 66000: 60HCl: 1550H ₂ O	Hydrothermal	9.6
AMS	5APTES: 5TEOS: 1SDS: 1800H ₂ O: 200EtOH	Hydrothermal.	3.2–3.3
AMS-10	15TMPS: 150TEOS: 19830H ₂ O: 7.5NaOH: 10C ₁₄ GIA	Hydrothermal	4.7
2D Mesoporous Silica	1CTAB: 2.36TEOS: 0.0223F127: 234H ₂ O: 12NH ₄ OH	Hydrothermal	2.1
2D Mesoporous Silica	1CTAB: 2.36TEOS: 0.0223F127: 234H ₂ O: 12NH ₄ OH	Hydrothermal	1.8–2.9

* TEOS: tetraethylorthosilicate, EG: ethylene glycol, CTMACl/Br: Hexadecyltrimethylammonium chloride/ bromide, TMACl: tetraalkylammonium chloride (alkyl = methyl), TMB: 1,3,5-trimethylbenzene, MTAB: myristyltrimethylammonium bromide, EtOH: Ethanol, APTES: 3-aminopropyltriethoxysilane, SDS: sodium dodecyl sulfate, TMPS: N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, C14GIA: N-myristoyl-L-glutamic acid,

hexadecyltrimethylammonium bromide, TEOS and tetramethylammonium hydroxide.

The positions of the functional (amino-) groups incorporated onto the silica depend on the type of synthesis methods, for example, co-condensation or post-synthesis modification, adopted for the synthesis.^[99] A schematic representation of the various synthetic approaches for the amine-functionalized mesoporous silica is shown in **Figure 6**. Gai *et al.*^[99] introduced novel methods for synthesizing large pore mesoporous silica nanoparticles (MSNs) with amine functional groups via co-condensation using APTS and the conventional silica source such as TEOS. The obtained material exhibits large pore diameter (10.3 nm) and small particle size (ca 50 nm). Mixed anionic surfactants sodium dodecylbenzene sulfonate (SDBS) and sodium dodecyl sulphate (SDS) were used for this approach. The ratio of these anionic surfactants was varied to control the size, morphology and the pore structure of the hybrid mesoporous materials. MSNs were also functionalized with organic compounds such as Schiff base and utilized for the sensing of Fe³⁺ in water through fluorescence

technique. As the assembly between anionic surfactant and precursor is based on electrostatic interactions and is carried out in acidic medium, a high amount of amine loading on the materials can be achieved.

Chiral anionic surfactants are unique SDAs that offer not only the ordered structure but also the chiral functions to the materials which may be effectively used for the chiral catalysis and enantio-separation. For instance, mesoporous amino-functionalized chiral mesoporous silica nanoparticles were prepared by using C16-L-alanine as a chiral anionic surfactant. The prepared materials were successfully used as drug delivery carrier for the delivery of indomethacin which is generally used for the treatment for anti-inflammation and showed significant improvement with the drug intestinal permeability.^[100] Similarly, Wang *et al.* reported the preparation of amine-functionalized chiral mesoporous silica nano-cocoon, which has 2D mesopores with curled nanoporous channels.^[101] This unique material could adsorb more drugs into the nanochannels than the pure MSNs as the curled chiral channels offer more space for holding a large amount of the drugs.

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Table 3. Synthesis protocols and parameters on the preparation of various uniform mesostructured materials

Material	Functional Group	Synthesis route	Application	Ref
Meso-porous silica (AMS)	Amino-propyl, <i>N</i> -(2-aminoethyl)-3-aminopropyl and 3-[2-(2-aminoethylamino) ethylamino]propyl-functionalities	co-condensation	CO ₂ adsorption/desorption measurement	[71b]
Mesoporous silica nanospheres	3-aminopropyltrimethoxysilane (APTS)	Simultaneous condensation	--	[71c]
Meso-porous silica (AMS)	3-aminopropyl (AP) or <i>N</i> -trimethoxysilylpropyl- <i>N,N,N</i> -trimethylammonium cation denoted as TMAPS	co-condensation method	--	[71d]
Meso-porous silica	<i>N</i> -trimethoxysilylpropyl-, - <i>N,N,N</i> -trimethylammonium ion (TMAPS)	Simultaneous condensation	--	[71e]
Meso-porous silica	<i>N</i> -trimethoxysilylpropyl-, - <i>N,N,N</i> -trimethylammonium cation or 3-aminopropyl	Simultaneous condensation method	Hard template for Preparation of chiral metal wire	[73]
Mesoporous aminopropyl silica	3-trimethoxysilyl)propylamine	grafting	sorption of anionic reactive dyes	[74a]
Mesoporous silica nanoparticles (MSNs)	3-aminopropyltrimethoxysilane Followed with Schiff base	Condensation method followed by grafting	fluorescence sensing of Fe ³⁺ in water	[75a]

Peng *et al.* demonstrated that the chiral PMOs could be effectively used for the separation of racemates. They have successfully separated more than 18 racemates including organic acids, alcohols and aldehydes with high selectivity, revealing the powerful role of the chirality in the PMOs prepared by the anionic surfactants.^[102] All these results confirm the potential practical applications possibilities of these PMOs in adsorption, drug delivery and enantio-separation.

3.4.2 Cationic surfactants

Functionalized mesoporous materials can also be prepared by cationic surfactants which are organic SDAs with a quaternary ammonium structure and a long hydrophobic alkyl chain length (> C10). These generally form micelles and liquid crystals and are used as potential surfactants for the preparation of several porous inorganic materials. With the careful control of the synthesis conditions, various MSNs including hollow silica nanoparticles with the size range of 100 nm can be synthesized.^[103] Through a simple post-synthetic or cocondensation approach, various mesoporous organic-inorganic hybrid materials with different functional groups, including sulphonic acids, amines and chiral molecules can be prepared using cationic surfactants. A summary of different functionalized mesoporous systems synthesized in the presence of cationic surfactants is given in **Table 4**.^[104]

Xiang *et al.*^[104b] introduced a chiral tartaric acid derivative on the surface of titanium species grafted MCM-41 using cationic surfactant using post surface modification method. The catalytic system used in the enantioselective epoxidation of allyl alcohol showed enantioselectivities of up to 80%. The observed high catalytic activity with high enantioselectivity is due to the presence

of highly active monomeric titanium species that are complexed with the hybrid chiral material which behaves like the Sharpless catalyst.^[104b] On the other hand, Zhao *et al.* modified the surface of MCM-41 with trimethylchlorosilane to obtain a more hydrophobic surface which did not show pore filling or capillary condensation of water. However, good adsorption properties for benzene were observed for these samples. The modified materials were also identified as good adsorbents for the selective

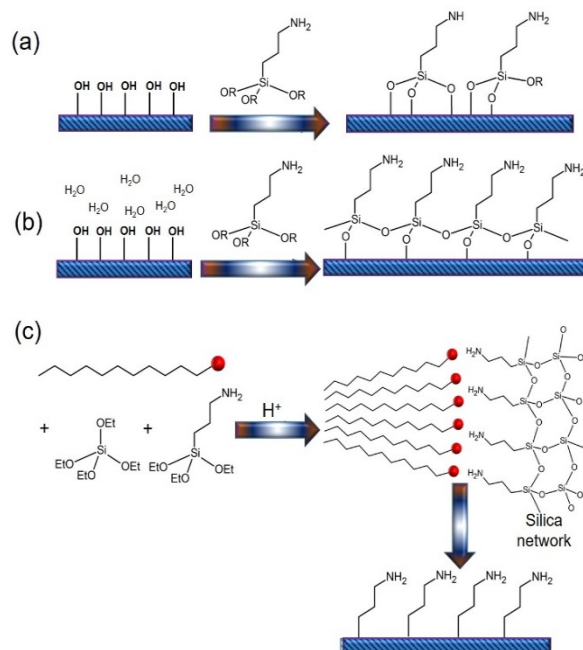


Figure 6. Synthesis principles of amine-functionalised mesoporous silica: (a) grafting; (b) filming and (c) anionic surfactant template method (reproduced with permission from ref 99b).^[99b]

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Table 4. Functionalized mesoporous solids, synthesis route using cationic surfactant and application.

	Functional Group	Synthesis Route	Application	Ref
2D Mesoporous Silica	Chiral tartaric acid derivative	Post-modification	Asymmetric epoxidation of allyl alcohol	[73]
2D Mesoporous Silica	Trimethylchlorosilane	Post-modification	Selective adsorption for removal of organic compounds (benzene)	[74a]
2D Mesoporous Silica	Sulfonic acid group	Post-modification	Bisphenol A synthesis	[74b]
2D Mesoporous Silica	Sulfonic acid group	Post-modification	Bisphenol A synthesis	[74b]
2D Mesoporous Silica	(3-aminopropyl)-triethoxysilane, n-octyltriethoxysilane, n-octyldimethyl chlorosilane, (3-mercaptopropyl) trimethoxysilane	Post-modification	--	[75a]
Bifunctional Mesoporous silica nanoparticles	(3-aminopropyl)-trimethoxysilane (APTOS) and sulfonic acid group	Co-condensation followed by post-modification	Henry reaction	[75b]
Periodic mesoporous organosilicas (PMOs)	Bis-(triethoxysilyl)ethane & N-(2-aminoethyl)-3-aminopropyl-functionalities	Co-condensation	-	[76]
Mesoporous silica	(3-aminopropyl)-triethoxysilane	Co-condensation	CO ₂ sorption	[77]
2D Mesoporous Silica	Trimethoxysilylpropylethylenediamine, ethylenediamine-triacetic acid sodium salt	diethylenetriamine, Post-modification method	Cyclic voltammetry	[78]
Ordered mesoporous silica	3-(anilinopropyl)-trimethoxysilane	Post-modification method	Glyceryl tributyrate with methanol to methyl esters	[79]
2D Mesoporous Silica	(3-cyanopropyl)dimethylchlorosilane, propyltriethoxysilane, n-octyldimethylchlorosilane, and n-octyltriethoxysilane	(3-amino- Post-modification method	--	[80]
Mesoporous silica	diimine organosilane with oxo-vanadium Schiff base	Co-condensation	Oxidation of alcohols	[105]
2D Mesoporous Silica	phenyltriethoxysilane (PTES), aminopropyltriethoxysilane (APTES), 11-bromo- undecyltrimethoxysilane (BUTMS)	Co-condensation and grafting	--	[81]

adsorption of organic compounds from a stream of wastewater.^[104c] Das *et al.* synthesized sulfonic acid-modified MCM-41 and MCM-48 and utilized them for synthesizing Bisphenol A. It was found that these super acidic catalysts exhibited much better catalytic activity than the commercially available Amberlite-120 catalysts. Both MCM-41 and MCM-48 catalysts modified with sulfonic acid groups showed much better selectivity towards the desired p,p-bisphenol-A.^[104c] Antochshuk *et al.* studied the interfacial reactivity of self-assembled MCM-41 toward different organosilanes. The authors observed that it is possible to directly replace the template through a simple displacement approach by reacting with organosilanes which make a strong bonding with the silica surface. For this approach to be highly effective, it is required to use the organosilane with at least one reactive group in its structure.^[104d] A similar approach was adopted for the removal of the surfactant for the cerium substituted mesoporous silica materials, and it was found that a

long reaction time with the organosilane is required for the complete removal of the surfactants.^[104j]

In another interesting report, Huang *et al.* synthesized bifunctional mesoporous silica nanoparticles functionalized with Brønsted acidic and Brønsted basic sites.^[104d] At first, APTS was introduced via co-condensation followed by insertion of sulfonic acid to the external surface via a post-modification method. The obtained materials were applied in the two-step Henry reaction, which involves both Brønsted acidic and basic sites. Burleigh *et al.* synthesized PMOs with bis (triethoxysilyl)ethane and APTS and studied their accessibility of functional sites via adsorption of Cu(II) trizma complexes.^[103] A high amount of the adsorption of this Cu complex confirms that these organic ligands are accessible for different applications. Osei-Prempeh *et al.* synthesized amine-functionalized mesoporous silica using fluorinated cationic surfactants and CTAB as the SDA.^[104g] The resulting mesoporous silica having amine-functionality was

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utilized for CO₂ sorption. The interaction of surface amine functionality with CO₂ resulted in the sorption of a higher amount of CO₂ than non-functionalized silica. A high degree of amine functionality can be exposed on the surface when the materials are templated by the fluorocarbon.

Similarly, Diaz *et al.* introduced a series of silane (ethylenediamine (ED), diethylenetriamine (DET), and ethylenediaminetriacetic acid) on MCM-4.^[104h] The attached functional groups on the surface of MCM-41 were effectively utilized for the covalent coupling of cobalt(II) complexes which were then employed as composite electrodes. The complex modified materials showed electroactivity, whereas the silane only modified materials showed no electroactivity. On the other hand, Guerrero *et al.* synthesized a series of highly stable amine-functionalized MCM-41 with ordered porous structures and employed them as catalysts for the conversion of glyceryl tributyrates to methyl esters.^[104i] The prepared catalysts showed the activity similar to that of free amines, and most importantly, they were found to be stable even after repeated cycles.

Verma *et al.* investigated the preparation of diimine functionalized organic-inorganic hybrid with the mesoporous structure using cationic surfactant and used them as the platform for the functionalization of oxovanadium complex inside the mesoporous channels of the support. They found that the catalyst was highly reactive and selective towards the oxidation of various carbonyl compounds to their corresponding aldehydes using TBHP as an oxidant.^[104k] Kecht *et al.* achieved a site-selective functionalization of mesoporous nanoparticles using the co-condensation approach (Figure 7).^[106] Oligosilicates were added at different stages of the synthetic process to give functional

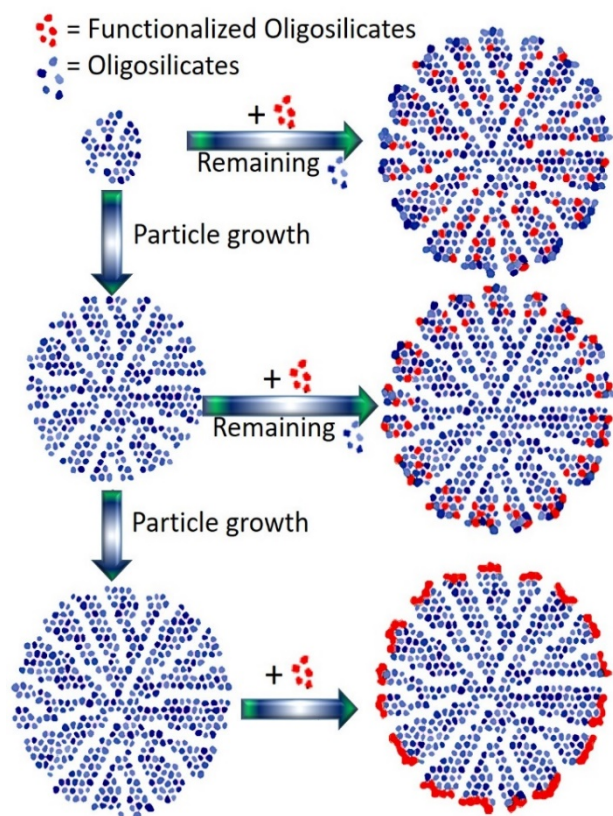


Figure 7. Distribution of functional groups depending on the addition time of the oligosilicates component during synthesis (Reproduced with permission from ref.106).

groups dispersed in different parts of the mesopores. It has been demonstrated that the density of the functional groups can be finely tuned with the simple adjustment of the ratio of organosilane-to-silane. Similar to anionic surfactants, the assembly between cationic surfactant and precursor is based on electrostatic interactions but is mostly carried out in alkaline medium. Although several materials, including SBA-1, were synthesized in highly acidic medium using cationic surfactants, the reports on the functionalization of these materials using organic groups are quite limited. Clemans and Reiner successfully functionalized SBA-1 and SBA-2 molecular sieves with amine groups, which have a three-dimensional porous structure with a cage type pore and the pore size smaller than MCM-41 (<2.5 nm).^[107] Even after the functionalization, the structure of these materials was maintained. As the pore size of these materials is small, the functional groups blocked the pores which limit their application possibilities in catalysis or adsorption and separation. Therefore, it may be concluded that the pore size of the support is one of the critical factors that should be considered for the functionalization of different organic moieties through post-synthetic modification.

3.4.3 Neutral and non-ionic surfactants

In addition to the cationic and anionic templated mesoporous organic-inorganic hybrid materials, non-ionic or neutral surfactants can be used as low-cost templates for the preparation of large pore hybrid materials. Non-ionic surfactants are a class of neutral surfactants which contain a hydrophilic head group and a hydrophobic tail and possess zero net charges. When cationic or anionic surfactants are used, the electrostatic assembly approach of SDA and silica species is a crucial step for obtaining ordered mesoporous structure. However, in non-ionic templating route, mesostructure formation is governed by hydrogen bonding and the self-assembly between the non-ionic surfactants and neutral inorganic precursors.^[108] Most common nonionic surfactants used in the synthesis of materials are petroleum derived ethylene oxide/propylene oxide (EO/PO) copolymers, polyoxyethylene alkyl ethers, Brij, polyglycerol alkyl ethers, crown ethers, ester-linked surfactants, etc. SBA-15, SBA-16, FDU-12, and KIT mesoporous materials are synthesized using EO/PO copolymers. Among these materials, SBA-15 is one of the most studied materials synthesized using pluronic P123 (EO₂₀PO₇₀EO₂₀) surfactant. SBA-15 possesses thick pore walls with excellent textural properties like surface area and pore volume and exhibits both micro and mesoporosity with the walls covered with many silanol groups. These groups can be easily functionalized by using a grafting technique that was explained previously.

The nature of the functional groups is vital for introducing new properties to the porous organic-inorganic hybrid materials. For instance, the different functional groups including triflic acid (TFA),^[109] sulfonic acid,^[110] 12-tungstophosphoric acid,^[111] triethylenetetramine,^[112] APTS,^[113] guanine^[114] etc. have been incorporated on materials and applied for different catalytic activities. Role of different metal ions in the framework of functionalized materials has also been explored. For example, super acidity functions can be introduced on the surface of the mesoporous silica materials prepared using non-ionic surfactants which tend to offer more surface silanol groups. Vinu *et al.* introduced different amounts of TFA on the wall structure of SBA-

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15 through post-synthetic approach in order to create super-acidity for the synthesis of coumarin under solvent-free conditions. TFA functionalized SBA-15 with the largest pore diameter showed the lowest activity due to the presence of the low number of silanol groups on the surface of the samples as it was synthesized at a high temperature. The TFA functionalized small pore SBA-15 was found to be the best and showed much better activity than the zeolites and other mesoporous materials.^[109a] In another report, super-acids were functionalized over ionic acids functionalized SBA-15 molecular sieves through the post-synthetic approach. In this approach, it was shown that ionic acids not only stabilized the superacid molecules but also enhanced the dispersion of the same on the porous surface, which helped to achieve high conversion and selectivity for the alkylation of 1-dodecene.^[182] On the other hand, Wang et al. prepared sulfonic acid functionalized SBA-15 using non-ionic surfactant through post-synthetic approach for the dehydration of fructose to 5-hydroxymethylfurfural (HMF). The prepared catalyst was found to be the best catalyst to date, which showed the highest yield and the selectivity of HMF from fructose.^[110b]

A similar strategy was also applied for the introduction of TFA on to mesoporous materials with cage type and 3D porous structure, KIT-5, which showed superior activity for the synthesis of coumarin through Pechmann reaction.^[109b] It was reported that the 3D mesoporous materials can not only offer more active sites but also better diffusion for the reactant molecules than the mesoporous materials with 1D or 2D porous structure. Although these superacids functionalized mesoporous molecular sieves exhibited a high acidity, the stability of these superacids inside the mesochannels of the support is a big concern. We proposed that the metal oxides can be used to stabilize the structure of the super-acids in the meso-channels of SBA-15. For example, Sawant-Dhuri *et al.*^[115] reported TiO₂ nanoparticles stabilized 12-tungstophosphoric acid (TPA) in SBA-15 using wet impregnation method with different TPA/TiO₂ ratio. It has also been demonstrated that these catalysts are highly active and selective for the hydroamination of ethyl acrylate with different aromatic and aliphatic amines, and offered 100% atom efficient. The presence of the metal oxides significantly enhanced the stability of the superacids at a high temperature. Very recently, Vinu *et al.* successfully prepared mesoporous superacids made of heteropoly acids using F127 as an SDA in the presence of heteropoly acids and KCl. It was proposed that the addition of KCl during the synthesis helps to reduce the interference and facilitates the long-range ordering. These materials could be applied as acid catalysts for various acid-catalyzed organic transformation as these are found to be highly stable and acidic.^[116]

Not only acidity but hydrophobicity can also be introduced on the surface of the mesoporous silicas or metallosilicates prepared through non-ionic surfactants using hydrophobic organic molecules. For instance, Melero *et al.*^[108d] synthesized titanium-substituted mesoporous molecular sieves modified with hexamethyldisilazane (HMDS) using non-ionic surfactants including Pluronic 123, Brij56, and Brij76 and titanocene dichloride under strongly acidic conditions. The materials were found to yield good conversion and selectivity for epoxidation of 1-octene using ethyl benzyl hydroperoxide as an oxidant. The surface functionalization with the hydrophobic HMDS promoted the selectivity of the epoxide in the epoxidation of 1-octene. On the other hand, Wang et al. introduced hydrophilicity in SBA-15

through a simple hybridization with a hydrophilic polysulfone blended with poly[poly(ethylene glycol) methyl ether methacrylate]. The hydrophilic property helped to enhance the water flux of this unique hybrid system which also exhibited antifouling properties.^[112] Basicity can also be introduced on the surface of the SBA-15 materials through functionalization with triethylenetetramine chelating agent. After the amine functionalization, the adsorption capacity of these materials for the toxic metal ions such as Cu and Zn can be enhanced.^[111] Similarly, Gupta et al. reported that amino acids can be functionalized on the surface of SBA-16, which has a three-dimensional structure. The amino acid groups can introduce the basicity which is effectively utilized for the selective removal of the toxic heavy metal ions such as Pb²⁺, Hg²⁺ and Cd²⁺.^[114] It is possible that various functional groups could be introduced on the surface of the porous inorganic oxides, and these strategies could be extended to fabricate various other porous materials and hybrids.

Although there are a lot of reports on the functionalization of porous silica using cationic, anionic or neutral surfactants, the reports on the surface modification of inorganic materials other than silica are quite limited. Various researchers tried the synthesis of phosphates based inorganic-organic,^[186] molecular sieves with polymers, and metal-organic frameworks (MOFs).^[117] In particular, hybrid phosphates and phosphonates were synthesized using either a single molecule as a template or no templates. Kimura synthesized several organic-inorganic hybrid mesoporous aluminophosphates via surfactant templating.^[118] For example, methylene group functionalized aluminum organophosphonate was synthesized using Brij 56, Brij 58, Pluronic F68, Pluronic F127, and Pluronic P123 as SDA. Importantly, some of these materials exhibit ordered pore arrangements and can therefore potentially be used in adsorption, ion-exchange and catalytic applications. Bagherzadeh et al.^[119] introduced the nitrosyl derivative of a polyoxomolybdate (NH₄)₁₂[Mo₃₆(NO)₄O₁₀₈(H₂O)₁₆] over amine-functionalized SBA-15. The functionalization of polyoxomolybdate was successful as it was carried out over the protonated amine functional groups of SBA-15 which offered strong electrostatic interaction. This was reflected by the fact that the prepared materials were found to be highly stable and showed much better activity for the epoxidation of alkenes as compared to pure periodic mesoporous materials. Similarly, 2,2'-Pyridil complex or chelate complexes have been introduced in pure or functionalized SBA-15 using ethyl alcohol reflux with a trace amount of acetic acid. These hybrids materials were employed as the adsorbents for the effective removal of Cu(II) from water samples. It was found that the pyridyl groups provided excellent binding sites through the nitrogen and oxygen atoms for the selective removal of Cu ions.^[120] These results further reveal the role of both organic and inorganic functionalities for designing an excellent catalytic system for organic transformations as well as the adsorbents for the selective removal of toxic ions.

Supported metal or metal nanoparticles have been receiving much attention in the field of heterogeneous catalysis owing to their unique catalytic functions which make them as active and reusable catalysts for various organic transformations and magnetic applications. For example, Vinu et al. introduced the nano sieve approach for the synthesis of iron oxide nanoparticles with different sizes with simple control of the nanopore size of SBA-15 molecular sieves.

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Table 5. Functionalized microporous solids, synthesis routes and applications

	Functional Group	Synthesis Route	Application	Ref
Na-Y zeolite	3-aminopropyltrimethoxysilane (APTS) with Pt and Pd nanoparticles	Post-modification	Arylation of styrene with iodobenzene	[82a]
SAPO-34	[3-(trimethoxysilyl)propyl]-octadecyldimethyl-ammonium chloride (TPOAC)	Co-condensation method	Methanol to olefin	[82b]
SAPO-37	Propyl]ethylenediamine moiety	Co-condensation method	Epoxide ring opening	[83a]
SAPO-37	3-aminopropyl, propyl-ethylenediamine, and propyl]aniline moiety	Co-condensation method	Epoxide ring opening	[83b]

Further, they demonstrated that the size of the nanoparticles plays a critical role in controlling the magnetic properties of these hybrid nanostructures.^[192] The same materials were also found to be as excellent catalysts for the synthesis of diphenylmethane.^[121] These performances are related to the mesoporous support that provides room for not only the fine control of the nanoparticles but also their dispersion over the mesoporous support. Similar strategies have also been adopted for the introduction of various nanostructures, including metal nanoparticles over ionic liquid functionalized SBA materials.^[122] These ionic liquids help to avoid the aggregation and minimize the formation of large particles inside the meso-channels of SBA-15. By varying the nature and the quantity of the ionic liquids, the size and shape of these nanoparticles in the mesoporous channels of SBA-15 can be controlled. For example, AuPd nanoparticles have been synthesized over SBA-15 functionalized with imidazolium groups which showed excellent activity toward the hydrogenation of 4-nitrophenol.^[122a] These results reveal that non-ionic surfactants can be effectively used for the introduction of varieties of functional groups in the mesoporous inorganic oxides to develop a series of porous organic-inorganic hybrid materials with different properties and also for different applications. In addition to their low cost and easy availability, non-ionic surfactants do not ionize in water and hence establish hydrogen bonding with inorganic precursors. The absence of electrostatic interaction in non-ionic surfactants implies that it can be easily removed from the material. This is one of the major advantages of the non-ionic surfactants which make them as a favourable choice for the commercialization of these advanced nanohybrid structures. Neutral amines are another interesting class of SDAs and come under the neutral surfactants. Neutral amine (S_0) species can form hydrogen bonding with uncharged inorganic species (I_0) which is helpful with the formation of self-assembled nanostructures through S_0I_0 approach. Corriu *et al.*^[123] reported the incorporation of the phosphorus-containing organic group by a co-condensation method using neutral amine templating route (*n*-hexadecylamine). The resulting material showed no change in the ordered structure during the chemical reaction. Tanev *et al.*^[108b] prepared mesoporous silica using primary amines based neutral surfactant $C_nH_{2n+1}NH_2$, where $n = 8, 10, 12, 14, 16, 18$) with different hydrocarbon chain length. The framework of mesoporous silica synthesized with a neutral surfactant, hexagonal mesoporous silica (HMS) was similar to that of mesoporous MCM-41 which was prepared by cationic surfactant in a highly basic medium. However, the wall thickness of the HMS (1.7-3.0 nm) is much larger than that of MCM-41 (1.2-1.5 nm). One of the most interesting features of HMS is its high thermal stability due to cross-linking framework with short-range hexagonal order. Zhang *et al.*^[108c] studied the effect of water and ethanol solvent mixture on the framework and textural properties

of HMS molecular sieves. The HMS material was prepared using water-rich (water:ethanol ratio of 90:10 (v/v)) and ethanol rich (water:ethanol ratio of 35:65 (v/v)) solutions in the presence of dodecylamine and tetradecylamine surfactants. The authors concluded that both surfactants, dodecylamine and tetradecylamine can afford a high textural mesoporosity. Besides, the framework of HMS prepared by using this method is highly polar.

3.4.4 Mixed surfactants

By mixing the different SDAs, which can change the phase or the structure of the self-assembled micellar structures, new mesoporous materials with different structures, morphologies and properties could be obtained. For instance, Ikari *et al.*^[104a] studied the effect of a binary surfactant system wherein a mixture of a cationic surfactant, cetyltrimethylammonium chloride (CTMACl) with polymeric surfactants for the preparation of mesoporous silica with small particle size. The small size particle with mesoporous structure was obtained with a simple concept of inhibiting the grain growth using polymeric surfactants through hydrogen bonds. This concept was followed for the preparation of mesoporous organic-inorganic hybrid materials. In another interesting report, the concept of the mixed precursor was applied for the introduction of simultaneous control of acidity and the particle size. Díaz *et al.*^[124] prepared sulfonic acid functionalized MCM-41 using a mixture of neutral and cationic surfactants. The neutral surfactant *n*-dodecylamine was considered to have a stronger interaction with thiol group through polar amine head. The addition of neutral surfactant with cationic surfactant resulted in a material with thicker walls and smaller particle sizes. Zhou *et al.* reported the preparation of HMS using dodecylamine and modified the prepared materials with polyethyleneimine, which significantly changed the polar characteristics. The prepared HMS hybrid showed the highest adsorption for water molecules due to the strong hydrogen bonding between the water molecules and the amine groups in HMS. The amino groups in the surfactants also helped to adsorb water molecules, revealing the importance of using the neutral surfactants, which help not only to provide ordered structure but also change the surface charge of the final materials.^[125]

3.5 Synthesis of functionalized microporous materials

Although the organo-functionalized porous materials are more prevalent in the mesoporous category, their counterparts with microporous character have also jumped alongside and gained importance in several applications. Functionalization of microporous materials through *in-situ* or post-synthetic modification with inorganic or organic functional groups extended

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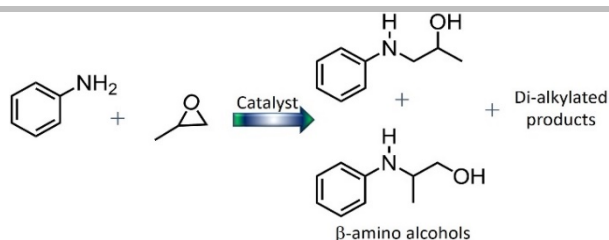


Figure 8. Epoxide ring opening reactions of aniline promoted by amine-functionalized SAPO-*n* materials (Reproduced with permission from 127).^{127b)}

the application possibility of these materials as it offers unique and selective properties to the materials that are required for the applications. A few selected functionalized microporous materials with different functional groups and their catalytic applications are summarized in **Table 5**. For instance, Mandal *et al.*^[200] reported on the preparation of Pt, and Pd nanoparticles over the amine-functionalized Na-Y zeolite. The presence of amine groups not only helps to reduce the nanoparticles but also support the high dispersion and further limits the agglomeration of the nanoparticles inside the microchannels. The synthesized materials were applied for hydrogenation and Heck coupling reactions. The highly dispersed nanoparticles and the microchannels helped to achieve much better activity for the prepared materials as compared to that of the conventionally prepared catalysts. On the other hand, Mu *et al.*^[126] successfully used the functionalization strategy to minimize the defects in the zeolite membranes based on SAPO-34. They used a simple vacuum-assisted deposition method and prepared bis(triethoxysilyl)ethane (BTESE) derived organosilica over defective SAPO-34 membranes supported on tubular porous alumina. This approach was found to be highly effective for healing the defects in SAPO-34, which was subsequently used for the selective capture of CO₂ molecules. However, it was found that the amount of the loading of the BTESE over SAPO-34 is highly critical as the excessive loading of the BTESE groups over the SAPO-34 decreases the permeation of the CO₂ molecules through the microchannels. These results reveal again the importance of the specific functional groups in the zeo-type materials.

Similarly, different organic functional groups have been introduced in the porous matrix of zeotype materials. Recently, Yadav *et al.* reported the *in-situ* preparation of functionalized SAPO-37 molecular sieves with different *N*-[3-(trimethoxysilyl)propyl]ethylenediamine contents via template removal by simple extraction with NaNO₃ and employed the synthesized materials for epoxide ring-opening reactions in the

Table 6. Functionalized SAPO-37 and its importance on epoxide ring opening using aniline.

Catalyst	Conversion (%)	Selectivity (%)	
		Mono-alkylated	Di-alkylated
SAPO-37-0.16N-ex	81.2	73.8	26.2
SAPO-37-0.16NN-ex	78.4	81.8	16.7
SAPO-37-0.24AN-ex	85.0	70.8	29.2

presence of aniline (**Figure 8**).^[127] The increased activity of these molecular sieves was explained by the homogeneous distribution of organosilane moieties in the framework achieved by the *in-situ* approach. Later, the same group reported the syntheses of SAPO-*n* (SAPO-37, SAPO-5, and SAPO-34) materials with different amino functionalities including APTES and APTS and compared their performances in epoxide ring-opening reactions at room temperature.^[128] The covalent grafting of organo-functional groups and the presence of -NH and -NH₂ functionalities were confirmed by FT-IR, ¹³C MAS NMR, and ²⁹Si MAS NMR analyses. Materials prepared using organo-functional precursor concentrations of 0.16–0.24 M exhibited a uniform functional group distribution and achieved excellent conversions at room-temperature for epoxide ring-opening reactions (**Table 6**). These findings again support the importance of the functionalization of microporous materials with the tunable amount of organic functional groups and their influence on the final performance of these catalytic materials for various catalytic transformations.

4. Applications of organo-functionalized porous materials

As discussed in the previous section, unique functionalities can be introduced both in the walls of the mesoporous materials or inside the pores with different functional groups having different properties. In addition, the size, shape, structure of these organic-inorganic hybrid materials can be altered by modifying the nature of the surfactants and the synthesis conditions. These unique functions of these organic-inorganic porous materials can be effectively used for various applications, including catalysis, drug delivery, and adsorption and separation of toxic elements. In the following section, we will discuss how the nature of the functional groups can control the efficiency of these functionalized materials in various applications, including catalysis, adsorption and biomedical applications.

4.1 Catalytic organic transformations

The functionalization of porous materials with the organic frameworks (**Figure 9**) is a convenient approach to devise hybrid

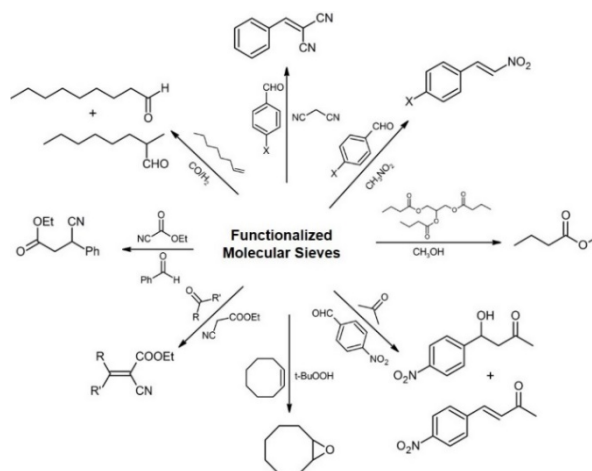


Figure 9. Diverse organic transformations promoted by functionalized molecular sieves

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Table 7. Different organo-functionalized molecular sieves and their applications in organic transformations

Molecular sieves	Functional groups	Applications	Ref.
Large pore mesoporous silica	Aminopropyltrimethoxysilane	Flavanone synthesis	[99h]
Large pore mesoporous silica	Aminopropyltriethoxysilane	Claisen-Schmidt and Knoevenagel condensation	[99i]
Large pore mesoporous silica	3-methyl-amino-propyl and methyl-amino-propyl-[3-(2-amino-ethyl amino-propyl)] functionalities	Flavanone synthesis, and Knoevenagel condensation	[100]
Aluminium-Large pore mesoporous silica	<i>Tertiary</i> -butyl 2-(3-(triethoxysilyl)-propyl-carbamoyl)-pyrrolidine-1-carboxylate	Nitro-aldol and Knoevenagel condensation	[101]
Large pore mesoporous silica and 2D Mesoporous silica	3-aminopropyltriethoxysilane	Cyclohexene oxidation	
2D Mesoporous Silica	3-trimethoxysilylpropylethylene diamine	Aldol, and Knoevenagel condensation	[103]
2D Mesoporous Silica	3-aminopropyltrimethoxysilane	Nitro-aldol condensation	[104a]
2D Mesoporous Silica	N-(2-aminoethyl)-3-aminopropyl and 3-(diethylamino) propyl functionalities	Aldol condensation	[104b]
Zeolite-Y	Propyl-amine, -ethylene-diamine, and diethylene-triamine functionalities	Transesterification of glyceryl tributyrate	[83c]
SAPO-37	N-[3-(trimethoxysilyl) propyl] ethylenediamine	Epoxide ring opening	[83d]
Mesoporous silica	(3-mercaptopropyl) trimethoxy-silane	Esterification of fatty acids	[83f]
Mesoporous silica	3-aminopropyltriethoxysilane	Knoevenagel reaction	[83g]
SiO ₂	3-aminopropyltrimethoxysilane	Knoevenagel condensation	[83h]
Mesoporous silica sphere	3-aminopropyltrimethoxysilane, [3-(2-aminoethylamino) propyl]trimethoxysilane	Nitro-aldol condensation	[104c]
Silicate intercalated MgAl-HT	Ethylene-diamine functionality	Nitro-aldol condensation	[104d]
Ti(Al)-SBA-15	3-Cl/3-aminopropyltriethoxy silane	CO ₂ utilization	[104e]

materials with unique catalytic functions, thermal and chemical stability, and textural parameters which find potential use in catalysis. The development of solid heterogeneous catalysts with different organic functionalities is considered as a topic of particular interest, given the abundant availability of the precursors containing organic functionalities. Samart *et al.* successfully functionalized zeolite-Y with various amino silanes via a direct condensation method and probed the catalytic activity of the obtained materials for esterification of glyceryl tributyrate and methanol.^[129] Among the functionalized zeolites Y, N-[3-(trimethoxysilyl)propyl] diethylenetriamine functionalized zeolite Y, which has registered the highest basic strength, showed the highest activity with a large selectivity to methyl butyrate. The functionalization of mesoporous silica (SBA-15,^[126] MCM-41,^[130]

and HMS^[131]) has also been extensively studied because of its wider pore channel system. In contrast, the functionalization of zeolite-type microporous materials has been underexplored because of problems with template extraction and structure control. As mentioned above, a wide variety of organo-functionalities can be incorporated into the framework of various molecular sieves via different techniques, with the choice of the exact functionality depending on the nature of the desired catalytically active site (Table 7). A few of the examples of the catalysis of functionalized organic-inorganic hybrid porous materials are discussed in the below section.

Margelefsky *et al.*^[132] discussed the cooperative action of different functional groups on an inorganic silica surface, showing that some of these groups act as linkers between the homogeneous

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catalyst and support. Along with periodic mesoporous silica, the development of chiral PMOs by utilizing chiral bridging organosilane ligands has received much attention^[133] as they have found numerous applications in catalysis and chromatography.^[134] In particular, organic- functionalized molecular sieves have been used in transesterifications,^[129, 135] Knoevenagel reactions,^[136] epoxidation of cyclooctene,^[137] cyano-ethoxy carbonylation,^[138] flavanone synthesis,^[139] and aldol condensation.^[134a] They have also been employed as metal ion (Fe^{2+} and Co^{3+}) scavengers^[98, 140] and the support for the noble metals (e.g., Rh).^[141] Some important reactions promoted by functionalized molecular sieves are summarized in Figure 8. Table 7 also lists different organo-functionalized molecular sieves and their applications in organic transformations.^[142] Hakiki *et al.*^[143] prepared mono-, di-, tri- amine-functionalized SBA-15 and applied for Michael addition of 1,3-dicarbonyl derivatives with β -ketoesters. Among several catalysts screened, diethylenetriamine functionalized SBA-15 catalyst showed a high yield of 98% Michael products within 30 minutes over microwave-assisted reaction using THF as a solvent. Mesoporous materials generally have poor acidity, but their treatment with superacids offers a high number of highly acidic acid sites. For instance, mesoporous silica functionalized with the sulphonic acid group has attained much attention due to the presence of strong acidic active sites exposed on the surface of the materials^[67b] and have been explored for numerous reactions. Chaudhuri *et al.*^[144] prepared sulfonic acid functionalized SBA-16 material using MPTMS in the presence of H_2O_2 and Pluronic F127. The catalyst was applied for Beckmann rearrangement of oximes (benzophenone oxime, salicylaldehyde oxime) and esterification of benzoic acid. In both reactions, the catalyst showed excellent activity up to six cycles, and the observed high activity resulted from the presence of strong acidic active sites. On the other hand, Doustkhah *et al.*^[145] introduced Pd^{2+} ions to highly stable, air and moisture insensitive N-propyliminodiacetic acid (PIDA) functionalized SBA-15 (SBA-15/PIDA), and the formed Pd^{2+} @SBA-15/PIDA catalyst was used for Suzuki-Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid at 80 °C under aqueous conditions. The use of iodoaryl versus bromoaryls in the presence of 2 mmol of potassium carbonate as a base significantly helped to improve the activity of the catalysts in Suzuki-Miyaura coupling reaction. Importantly, it has been noticed that the catalyst showed remarkable recyclability for 15 runs with a turn over number (TON) of 1309. In another report by Vandarkuzhali *et al.*^[146] copper nanoparticle (4-7 nm) dispersed on amine-functionalized SBA-15 (Cu/NH_2 -SBA-15) was tested for Mannich reaction and dye reduction. The catalyst showed excellent β -amino carbonyl compounds (90 %) yield for aromatic aldehyde, ketone and amines with various substituents. Similarly, a reduction of triphenylmethane dyes to their corresponding leuco forms within a short time (< 5 min) was possible with Cu/NH_2 -SBA-15 catalysts. Recently, researchers have focused on the incorporation of single organic functionalities within meso- and microporous zeolitic silicas to facilitate the immobilization of homogeneous catalysts.^[147] Since the discovery of M41S and SBA-15, the immobilization of homogeneous catalysts has become a major research focus of heterogeneous catalysis. This is because the high surface area, wide pore openings and free surface silanol groups of the thus obtained materials make them well suited for them to be used as supports for homogeneous catalysts, such as

transition metal complexes.^[148] Although homogeneous catalysts show much better catalytic activity than heterogeneous ones, the applications of the former are limited by several inherent problems, such as the difficulty in separation of the products from the reaction mixture, and the complicated regeneration of expensive catalysts. Noble metals (e.g., Rh) supported mesoporous silica via organosilane linkers are good catalysts for the hydroformylation reaction. Similarly, amine-^[141] and phosphine-modified mesoporous silicas^[147a] have been utilized as supports for the immobilization of Rh and its organometallic complexes for the selective hydroformylation to produce linear aldehyde with the selectivity of more than 94% nonanal which was then subsequently hydrogenated to obtain selective product 1-nonanol. One of the interesting features of these catalysts is that the nature of the products could be switched reversibly by changing the synthesis conditions. Interestingly, the catalysts were found to be highly stable and could be recycled several times. In another report, Grubbs catalysts have also been incorporated on to the mesoporous silicas including SBA-15 and MCM-41 via phosphine and pyridine linkers for various organic transformations including ring-closing of metathesis of citronellene, linalool and diallylphtalate, ring-opening of metathesis polymerization of cyclooctene and metathesis of methyl oleate.^[147b] The authors have found that the pore size of the supports played a critical role in controlling the activity of the metathesis of methyl oleate. It was demonstrated that the support with the largest pore diameter was found to be the best, showing better activity than support with the small pore diameter. These results confirmed that the increased rate of reactant and the diffusion of the products are favoured for the support with the largest pore diameter, encapsulated with the Grubbs catalysts.

Recently, Anjali *et al.* reported the preparation of rhodium containing macromolecules such as Calix[4]pyrrole (RhCP) and tetraphenylporphyrin (RhTPP) and their subsequent grafting on the surface of diamino-functionalized SBA-15.^[147c] The anchoring of homogeneous complexes (RhTPP & RhCP) on the surface of

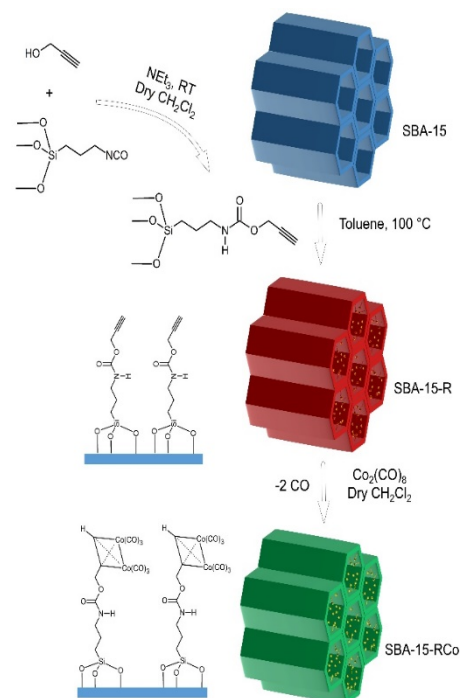
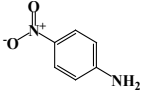
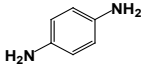
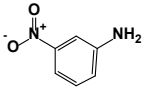
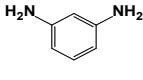
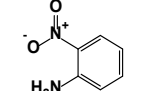
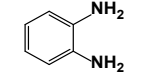
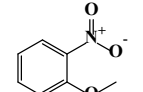
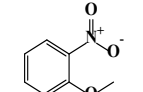
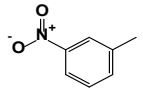
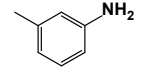
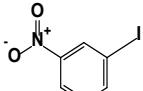
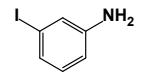
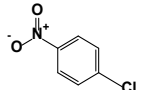
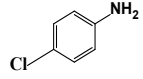
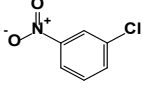
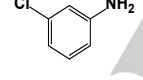
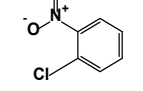
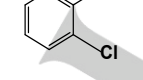
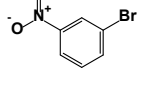
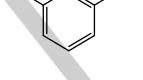
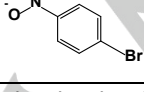
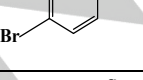


Figure 10: A possible route for the covalent grafting of Co carbonyl on the walls of SBA-15

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Table 8. Nitroarene conversion using heterogenized RhCP and Rh TPP catalyst

Sl. No.	Reactant	Compound yield	Yield of aniline (%)	
			SBA-15-Fu-Rh-TPP	SBA-15-Fu-Rh-CP
1			100	100
2			100	100
3			100	100
4			100	100
5			100	100
6			95.82	100
7			94.70	100
8			100	100
9			98	100
10			100	100
11			90	100

functional molecular sieves was confirmed via ^{13}C MAS NMR, N_2 sorption and SEM-EDAX studies. The heterogenized novel macromolecules were found to catalyze nitrobenzene reduction with complete conversion and retained their catalytic activities for

several runs.^[147c] The catalyst promoted the complete conversion of nitroarene derivatives with both electrons donating and electron-withdrawing groups. This has been confirmed by the formation of substituted aniline products, as given in Table 8. Additionally, electrostatic interactions between the support and homogeneous catalysts have been utilized for immobilizing transition metal catalysts on MOFs.^[147d] The inherent drawbacks of homogeneous catalysts can be overcome by their heterogenization via immobilization of inorganic complexes on the surfaces of micro and mesoporous materials,^[147d-g] hydrotalcites^[147h, 147i] and the basic metal oxide nanoparticles (ZnO and MgO). The covalent interactions of the homogeneous catalysts with the walls of mesoporous materials can be promoted by prior functionalization using thiols,^[147j] amines^[132, 147j] and phosphines^[147k-m] as organic ligands and alkoxy silanes as linkers. Thus, the utilization of these methods would allow one, for example, to support Co carbonyl clusters on the surface of mesoporous silica using a phosphine-free organosilane ligand as a linker.

A possible route for the covalent grafting of Co carbonyl on the walls of SBA-15 is shown in **Figure 10**. Grafted materials have been extensively applied in various organic transformations, i.e., for olefin metathesis (grafted Grubbs catalysts),^[147n] alkene epoxidation (grafted Mo carbonyl)^[147o] and hydroformylation (immobilized Rh nanoparticles).^[142g, 147p-r] In particular, Rh-based organometallic complexes were grafted onto the surface of several porous materials, including SBA-15. Heterogenized homogeneous catalysts show the inherent properties of homogeneous catalysts as well as the excellent textural properties of the heterogeneous support. **Table 9** lists some examples of homogeneous organometallic complexes heterogenized on the surfaces of functionalized molecular sieves and the catalytic applications of these hybrids.^[136, 147i, 147n, 147s-x, 148] Bhaumik et al. reported that C-S coupling reactions can be carried out with the Cu anchored PMO materials under microwave irradiation.^[147s] Various alkenes and aromatic compounds have been tried for the synthesis of a series of thioethers. The synthesized catalysts were found to be superior to those of other reported catalysts for the synthesis of thioethers. This approach of a combination of active catalysts and the microwave irradiation could be extended for the syntheses of various other fine chemicals through C-S coupling pathway using these unique catalysts. In another interesting work, Sakthivel et al. employed cobalt carbonyl functionalized SBA-15 materials for the hydroformylation of 1-octene. The prepared catalyst showed more than 97% conversion of 1-octene with high selectivity for hydroformylated products.^[147v]

Similarly, various other homogeneous complexes and their combinations have been tried in the porous organic-inorganic hybrid system for catalysis. For instance, Niakan et al.^[259] prepared palladium (II) Schiff base complex on amine-functionalized SBA-16 surface and studied for Heck Mizoroki reaction of aryl halides (iodobenzene) and alkene (n-butyl acrylate) using water as a green solvent. The catalyst containing 1 mol % Pd showed 97 % yield of butyl cinnamate in 1 hr with K_2CO_3 base at 80 °C in water. This is considered as a potential green catalyst for industrial and biomedical applications. Recently, Jin et al.^[149] reported tungsten chelate complex in organic moieties (diphenyldichlorosilane)-functionalized mesoporous silica SBA-15. The catalyst was applied for the oxidation of cyclopentene using H_2O_2 as an oxidant. The catalyst showed an

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Table 9. Selected examples and applications of homogeneous complexes heterogenized on functionalized supports

Molecular sieve	Functional groups/ metal complexes	Applications	Ref.
2D Mesoporous Silica & Large pore mesoporous silica	N(β -aminoethyl) γ -amino-propylmethyl dimethoxysilane and 3-aminopropyl triethoxysilane/(Rh ₄ (CO) ₁₂)	1-octene hydroformylation	[99g]
Mesoporous silica	N-heterocyclic ligand/ Ru complex	Olefin metathesis	[109b]
Large pore mesoporous silica	3-(2-aminoethylamino)propyl-dimethoxymethylsilane / CuCl ₂ .H ₂ O	C-S coupling	[112]
Large pore mesoporous silica	3-Aminopropyltriethoxysilane / Cu(OAc) ₂ .H ₂ O	Synthesis of aryl thioethers via a coupling reaction	[115]
Large pore mesoporous silica	Ethylenediamine functionality / Hexacarbonyl Molybdenum	Olefin epoxidation	[111]
Large pore mesoporous silica	N-(3-Triethoxysilyl) propylamine/ Co-complex	Alcohol oxidation	[116]
Large pore mesoporous silica	[(2-Propynylcarbamate)propyl] Triethoxysilane/Co ₂ (CO) ₈ cluster	Hydroformylation of 1-octene	[150]
Large pore mesoporous silica	N-(2-aminoethyl)-3-aminopropyltrimethoxysilane/ Cu (OAc) ₂	Aldehyde to amide conversion	[117]
Large pore mesoporous silica	3-aminopropyl-trimethoxysilane/ Schiff complex with polyoxometalates	Oxidation of styrene	[118]
Silicate intercalated CoAl-hydratalcite	Ethylenediamine functionality / Hexacarbonyl Molybdenum	Hydroformylation of octene	[108d]

excellent conversion of 99 % at 35 °C with *tert*-butanol (t-BuOH) as a solvent and offered 73 % selectivity towards glutaraldehyde. In the catalytic reaction, *tert*-BuOH was *in-situ* generated from *tert*-butylhydrogen peroxide (*t*-BuOOH). Molaei *et al.*^[151] reported 3-chloropropyltrimethoxysilane functionalized mesoporous SBA-15 and subsequently immobilized of creatinine groups for the introduction of yttrium and cerium catalysts. These catalysts were employed as catalysts for the oxidation of sulphides and also for the synthesis of 5-substituted 1*H*-tetrazoles. In both the reaction, the excellent yield was obtained using both yttrium and cerium-based catalysts. These studies reveal that the catalytic activity of the mesoporous organic-inorganic hybrid materials can be altered with suitable functional groups or homogeneous catalysts for specific reactions. These functionalized catalysts are found to be much better, in terms of the activity and stability, than those of non-functionalized mesoporous catalysts, revealing the importance of the hybridization.

4.2 CO₂ adsorption and conversion

The past few decades have been marked by an increasing level of greenhouse gases (GHGs) in the atmosphere that has resulted in climate change and global warming. Carbon dioxide is the major greenhouse gas and is produced by the combustion of fossil fuels, industrial emissions, and other anthropogenic activities. Carbon capture and storage is a widely accepted technology that has the potential to reduce the amount of CO₂ through its capture, followed by appropriate storage measures. Amine solvents are used for commercial CO₂ capture operations. The recent past has also witnessed significant developments in porous materials such as zeolites, MOF carbon, hydratalcite and amine-functionalized materials that possess the good potential for

CO₂ sorption given their excellent textural/surface properties and high surface area, pore volume and thermal stability.^[152] A wide range of porous materials is available which possess distinctive properties for either low or high-pressure CO₂ capture. Microporous materials are suited for low pressure, and mesoporous materials perform very well at high-pressure CO₂ capture. Some of the relevant examples of organo-functionalized porous materials will be discussed in this section.

The CO₂ capturing ability of porous materials can be improved by the introduction of amine-functionalized groups with an increased affinity toward the weakly acidic CO₂.^[147s, 147t] The CO₂ sorption capacity of such amine-functionalized materials depends on parameters such as amine group density, pore size, and effect of matrix heteroatoms. For example, mesoporous materials with different pore sizes, including MCM-41, SBA-15, and SBA-12) have been employed as adsorbents. Among materials studied, the highest adsorption capacity was observed for SBA-15. Zelenak *et al.*^[152b] investigated the CO₂ sorption performances of different amino silanes including aminopropyl (AP), methylaminopropyl (MAP), and phenylaminopropyl (PAP), and 3-

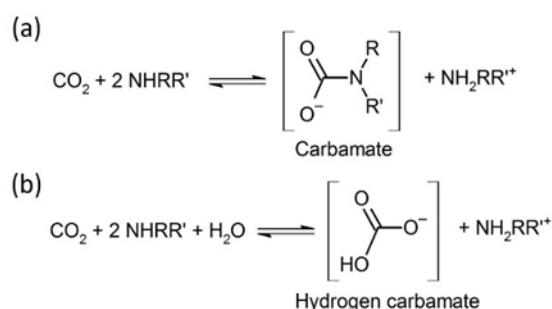


Figure 11. The general process of CO₂ absorption by amine-functionalized materials in the absence (a) and presence (b) of water (Reproduced with permission from ref 152a)^[152a]

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Table 10. Various amine-functionalized materials and their adsorption capacities

Material	Functional group	Temperature (°C)	Dry CO ₂ adsorption capacity (mg/g)	Reference
2D Mesoporous Silica	3-aminopropyl functionality	20	47	[120b]
3D Mesoporous Silica	3-aminopropyl functionality	25	50	[121]
Large pore mesoporous silica	3-aminopropyl functionality	25	70	[122a]
Large pore mesoporous silica	Diethylenetriamine functionality	60	70	[122b]
Large pore mesoporous silica	Ethylenediamine functionality	60	106	[122c]
Large cage structure	N-(2-Aminoethyl)-3-aminopropyl functionality	60	32	[122d]
Large cage structure	Ethylenediamine functionality	27	238	[123]
3D cubic Mesostructure	3-amino-propyl	25	46	[124]
HMS	Diethylenetriamine	20	53	[125]
KCC-1	3-amino-propyl	20	53	[154]
SAPO-34	3-amino-propyl	0	121	[126]
ITQ-2	3-amino-propyl	0	94	[127]
ITQ-6	3-amino-propyl	20	53	[128a]
Wider pore 2D mesoporous silica	3-[2-(2-amino-ethyl-amino)-ethyl-amino	25	117	[128b]
KIT-6	3-amino-propyl	30	69	[130]

(methylamino)propyl (MAP) grafted mesoporous SBA-12 at 25 °C using a gravimetric method. They showed that amine-functionalized high-surface-area materials might overcome the limitations of conventional CO₂ sorption materials such as regeneration, huge energy consumption, and flow viscosity problems, outperforming liquid amines. In particular, SBA-12/AP, SBA-12/MAP, and SBA-12/PAP exhibited CO₂ sorption capacities of 1.04, 0.98, and 0.68 mmol/g, respectively (indicate the temperature and pressure), and could be regenerated under heating-free conditions by purging with an inert gas. Interestingly, the fastest CO₂ desorption rate among these materials was observed for SBA-12/PAP.

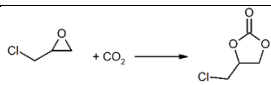
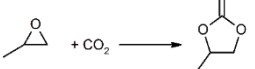
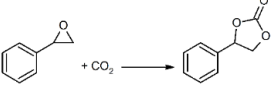
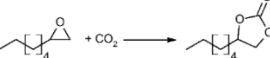
The mechanism of CO₂ adsorption by amine-functionalized materials is shown in **Figure 11**, which reveals that carbamate is produced when amine-functionalized materials (2 mol) react with CO₂ (1 mol) under dry conditions (**Figure 11a**), while hydrogen carbamate is produced in the presence of water (**Figure 11b**). Several research groups have prepared amine-functionalized porous materials and utilized them for adsorption of CO₂. **Table 10** presents various amine-functionalized meso/microporous materials and their CO₂ adsorption capacities at different temperature.^[153] It was reported that the incorporation of heteroatoms into the silica could help to tune the acidic or basic properties of the materials which may effectively be utilized to tune the adsorption capability of these materials for CO₂. Although

several dry CO₂ sorbents have been developed, a high CO₂ adsorption capacity of > 2 mmol/g is needed for practical applications.^[279] In this regard, Y-type zeolites are expected to be suitable for CO₂ capture given their well-defined pore structure and pore size is similar to that of CO₂ molecules, although the corresponding studies are rare.^[280]

On the other hand, different amine-functionalized MCM-41 materials synthesized *in-situ*^[281] and *ex-situ* methods^[268] were explored for CO₂ adsorption. It was evident that adsorbents prepared by a grafting method showed higher stability, whereas sample prepared by impregnation method showed better adsorption capacity.^[155] Further, CO₂ capture capacity of functionalized SBA-15 and MCM-41 are compared^[156] based on 100 research papers published on this field using 15 inputs (support properties, amine properties, preparation method and operational variables). This study also provides guidelines for future studies with a definite conclusion that the density of amine groups played a significant role in determining the adsorption capacity of the material. Zhang *et al.*^[157] reported a new strategy of functionalizing the surface of the mesoporous materials with two amine molecules including APTES (please provide full form) and tetraethylenepentamine and utilized for CO₂ adsorption. The functionalized material was reported to have high amine density (N content = 15.81 mmol/g) and showed CO₂ adsorption capacity of 5.687 mmol/g. In addition, it also retained CO₂ saturation

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Table 11. Preparation of cyclic carbonates on SAPO-34 having amine-functionality (Reproduced with permission from 128).^[128]

Reaction	Epoxides conversion (%)	Cyclic carbonate selectivity (%)
	98	96
	81	100
	77	97
	88	85

adsorption capacity at 5.2 mmol/g after 15 adsorption/desorption cycles. It was also reported that by carefully choosing the nature of the amine functionalities, the selectivity of the adsorption could be tuned. This was realized by Mafra *et al.*^[158] who introduced different amines including primary, secondary, tertiary and a diamine over the porous surface of the SBA-15 materials and utilized for the selective separation of CO₂ from the CO₂/CH₄ gas mixtures. At low pressures (below about 40 kPa), the primary and secondary amines supported SBA-15 favoured the chemisorption of CO₂ molecules while large mesopores do not favour physisorption of methane. At medium to high pressures, CO₂ physisorption was promoted, but these materials showed moderate adsorption for methane molecules.

Carbon dioxide (CO₂) utilization is an important method for reducing the levels of this greenhouse gas in the atmosphere. The CO₂ can be converted to valuable chemicals such as methanol, ethanol, urea, cyclic carbonates, salicylic/4-hydroxybenzoic acids etc., through catalysis process.^[67b] Srivastava *et al.*^[67b] studied the preparation of cyclic carbonates promoted by amine-functionalized materials and showed that the rate-determining step of this process corresponded to carbon dioxide activation, which could be achieved via coordination to metal and simultaneous interaction of hydroxyl ion solid bases. They prepared adenine, guanine and imidazole grafted on organo-functional (3-chloro- and 3-amino- functionalized) Ti/Al-SBA-15 materials. The synthesized materials were utilized in liquid-phase syntheses of chloropropene carbonate and styrene carbonate. It was reported that APTES functionalized TiSBA-15 materials showed better catalytic activity compared to the pristine SBA-15, revealing the role of amine groups and Ti species towards enhancing the activity of the materials. It was also concluded that the surface basic sites are key for the binding and the activation of CO₂ molecules. On the other hand, Zhang *et al.* synthesized porous silica-based catalysts with amino silane functionalities using ultrasonication under mild conditions. The number of silanol groups on the surface of the porous silica materials determines the extent of the functionalization with amino silane groups. These catalysts were found to be highly basic and active for the CO₂ coupling with an epoxide for the formation of propylene carbonate.^[159]

Metal-organic frameworks (MOF)^[160] comprise metal ions or clusters coordinated by organic ligands and are widely employed in various fields, including catalysis, separation, and gas storage.

Compared to microporous zeolites, MOF structures are more flexible as they are amenable to structural design control and pore functionalization. As these materials have ordered porous structure with unique metal ions and surface, functional groups, they are also considered as good materials for the adsorption and conversion of CO₂ molecules. For example, Ye *et al.*^[161] functionalized single cobalt (Co) atom into the porphyrin units of MOF-525 (derives from Zr₆ clusters and porphyrin'-(porphyrin-5,10,15,20-tetrayl)tetrabenzate (TCPP-H₂) and utilized for enhanced CO₂ adsorption, which also suppresses electron-hole recombination in the MOF and facilitates CO₂ reduction efficiently. Similarly, hollow porous carbon (HPC) featuring uniform N doping and Zn atoms derived from Zn-based N-rich MOF, ZIF-8 demonstrated as excellent catalysts for the CO₂ cycloaddition to epoxide under light irradiation.^[162] The presence of metal centre and organic functionality present in MOF facilitates them as promising materials for CO₂ separation and its utilization.^[160b, 163] Zhang *et al.*^[164] reported the synthesis of ionic liquid functionalized SBA-15 which showed the highest CO₂ adsorption capacity (2.12 mmol/g at 60 °C), and remained active for ten regeneration cycles with a slight decrease in adsorption.

Not only mesoporous and MOF materials but also functionalized microporous materials have been investigated for the carbon capture and conversion. Recently, Sakthivel *et al.*^[128] prepared organoamine-functionalized microporous silico-aluminophosphates (SAPO-34, SAPO-5, and SAPO-37) and utilized them for converting CO₂ into valuable products, such as cyclic carbonates, achieving promising yields of > 90%. The organo-functionalized microporous materials with surface-exposed functionalities and uniform particle size achieved better yields of cyclic carbonates and retained their catalytic activities for several runs. Catalyst performances were determined for a series of epoxides under optimum conditions, with the results presented in **Table 11**. Among the studied epoxides, the best results were obtained for epichlorohydrin, which was explained by its inductive effect, and further mechanical aspects were discussed in detail. Thus, organo-functionalized materials are promising catalysts and catalytic supports for the immobilization of various organometallic complexes, additionally possessing potential sorption properties.

4.3 NO_x, heavy metals and organic molecules adsorption

The past several decades have witnessed significant advances in the field of NO_x removal technologies, either by chemical transformation, for example, chemical reduction of NO_x molecules by hydrocarbons,^[165] nitrous oxide storage and subsequent reduction (NSR)^[166] catalysis as well as the removal of NO_x by adsorption. The absorption of NO₂ on functionalized materials synthesized using (a) grafting and (b) co-condensation methods is shown in **Figure 12**. Development of adsorption-based techniques has become more attractive since it doesn't require high temperatures or any additional reagent treatment, in contrast to SCR (Full form) and NSR (Full form). Activated carbons exhibit large specific surface areas and are amenable to surface modification by the introduction of heteroatoms or metals/metal oxides, therefore being potentially good NO_x adsorbents. However, numerous studies have reported that the adsorption of NO₂ by these materials is accompanied by a significant release of NO caused by oxidation of the carbon surface. These materials have been extensively used due to their huge adsorption capacity

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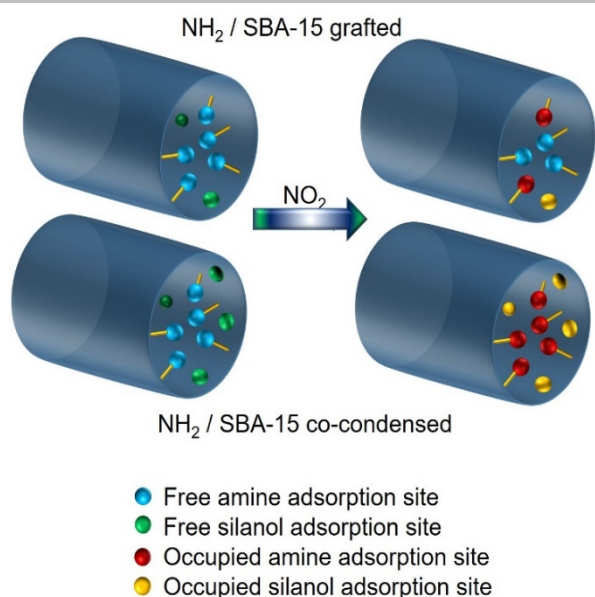


Figure 12. Representation of NO_2 binding on functionalized material synthesized using (a) grafting and (b) co-condensation methods (reproduced from ref 166a).^[166a]

of NO_2 even though they release a small amount of NO during the adsorption process. Therefore, several attempts have been made to enhance the retention of NO , which overcome the above-mentioned drawback, as exemplified by the addition of $-\text{OH}$ functional groups on the surface of activated carbons via treatment with KOH . NO retained on the adsorbent surface is oxidized to produce KNO_3 . The introduction of nitrogen-containing (e.g., urea, amine or dimethylamine) moieties on the carbon surface also represent a potential method of decreasing the amount of NO released during NO_2 adsorption. The positively charged nitrogen centre improves the stabilization of NO on the carbon materials. In addition to gas molecules sorption, the functionalized materials have also been used for the adsorption of heavy metals such as mercury, lead, cadmium, copper etc.^[119, 167] Similar, various other functional groups have been introduced to selectively adsorb different organic or inorganic vapours. For example, APTS groups were functionalized over the spherical mesoporous silica for the removal of volatile organic molecules. APTS functionalized materials showed the highest toluene adsorption capacity of 98.1 mg^{-1} .^[168] This high adsorption capacity was attributed to the formation of strong hydrophobic interaction between the APTS groups and the toluene molecule.

4.4 Biomedical

Rapid progress in the area of porous materials for providing a platform as efficient drug delivery systems (DDS) has been witnessed in recent times. Among the different components studied for effective and controlled DDS, polymeric supports are found to be one of the compatible ones for research and commercial applications. Although polymeric particles have been widely used as drug delivery carriers, their poor textural properties, including small specific surface area and pore size, limit their performance in the drug delivery. Recently, molecular sieve-based materials as suitable drug delivery components have also attracted much attention^[83f, 169] owing to their flexible pore dimension, high surface area uniform channel of mesoporous structures and well-defined surface properties. These materials

also have other unique advantages, including tunable surface charges that allow these materials to adsorb drugs with different molecular sizes, solubility and release them in a controllable manner using functionalized surfaces. Drug molecules with different sizes can be accommodated with the simple adjustment of the pore size of the drug carrier and released via a diffusion-controlled mechanism.

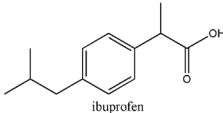
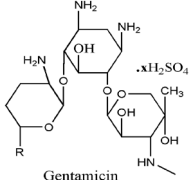
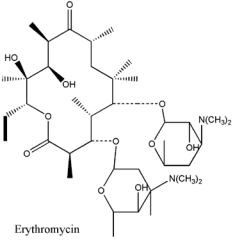
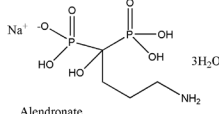
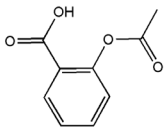
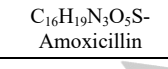
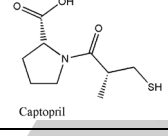
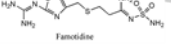
SBA-15 is considered as one of the possible candidates for DDS owing to its unique 2D porous structure, large pore size and a huge surface area with rod-shaped morphology. Besides, SBA-15 has different kinds of silanol groups on the surface which can be effectively utilized for the functionalization with different molecules both inside the wall structure as well as on the external surface. The flexibilities of these amazing materials made it available for some exciting applications including the adsorption and separation of organic contaminants and toxic metal ions,^[170] heterogeneous and biocatalysis for organic transformations^[171] and immobilization of large chelating groups or biomolecules.^[172] For potential drug delivery application, pure SBA-15 has been extensively investigated as a drug host.^[67a, 173] However, the channel walls of pure SBA-15 are covered by silanol groups which interact with drugs via hydrogen bonds and are not capable of keeping or releasing the drugs in a sustained manner. Therefore, researchers tried to modify the surface silanol groups of SBA-15 with different functional groups through direct^[170b, 171a] and post-synthesis modification (or silylation).^[174]

This was realized by Hao et al.^[175] who reported the single-stage preparation of hollow mesoporous silica with amine-functionality (HMSNs) and used them for the delivery and release of antibacterial and anticancer materials. When loaded with antibiotic or anticancer drugs, HMSNs exhibited perfect anticancer (A549) and antibacterial activities. It also successfully lowered the IC_{50} values of the corresponding drugs by several folds. The increased activity was explained based on large interior cavity and surface amine functionality which facilitate the interaction with cells. Further, the presence of uniformly defined mesoporous matrix allows sustained drug release. Moreover, these researchers showed that the difference between APTES and TEOS played an essential role in determining the aggregation of HMSNs. In particular, when the above compounds were added to a solution of CTAB which acts as SDA, the protonated APTES acted as a stabilizer, surrounding TEOS droplets (**Figure 13a and 13b**). The hydrolysis of TEOS is enhanced by the addition of ammonia and produces negatively charged silica fragments. The positively charged CTAB micelles interact with these silica species to form self-assembled structure. The addition of APTES also helps for the formation of a thin layer of silica shells (**Figure 13c**), forming a hollow structure (**Figure 13d**). When the synthesis time is progressed, the shell thickness increases, until the droplets of TEOS are fully consumed (**Figure 13e**).

Other mesoporous hybrid materials have been successfully used for DDS applications and also considered as good candidates for DDS. Sivaguru et al.^[176] synthesized cubic mesostructured KIT-6 functionalized with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine in refluxing toluene. The fully characterized material exhibited a high adsorption capacity for the drug molecule, ibuprofen in a hexane solution. In this case, solvent polarity plays a vital role in controlling the amount of drug loading into the porous support and its release from the mesoporous channels. In addition, the high hydrophobic nature and the rich basic sites on the surface of the

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Table 12. Selected matrix-drug systems reported so far for the drug loadings (Reproduced with permission from 174c).^[174c]

Drug	Mesoporous Matrix	Max Load (%)
 ibuprofen	Folded Sheet Materials	6.0
	2D mesoporous silica	23.0
	2D mesoporous silica	34.0
	Amine modified 2D mesoporous silica	23.0
	Amine modified 2D mesoporous silica	33.0
	3D mesoporous silica	28.7
 Gentamicin	LP-Ia3d	20.1
	Large pore mesoporous silica	20.0
	PLGA-SiO ₂	22.4
	PLGA-SiO ₂	45.6
 Erythromycin	3D mesoporous silica	28.0
	LP-Ia3d	28.0
	LP-Ia3d-C8	12.0
	Large pore mesoporous silica	34.0
	Large pore mesoporous silica-C8	13.0
	Large pore mesoporous silica-C18	18.0
	2D mesoporous silica	29.0
 Alendronate	2D mesoporous silica	14.0
	Amine modified 2D mesoporous silica	37.0
	Large pore mesoporous silica	8.0
 Aspirin	Amine modified large pore mesoporous silica	22.0
	2D mesoporous silica	15.0
 Amoxicillin	2D mesoporous silica	15.0
	Amine 2D mesoporous silica	15.0
	Large pore mesoporous silica	24.0
 Captopril	2D mesoporous silica	23.6
	2D mesoporous silica	34.0
	Large pore mesoporous silica	22.6
 Famotidine	MSU-3	20.0

functionalized KIT-6 helped to achieve much better adsorption and release profile of ibuprofen than pure KIT-6 materials, revealing the importance of the functionalized moieties in the DDS. Similarly, ibuprofen (anti-inflammatory) and furosemide (loop diuretic) were adsorbed onto the pure and chitosan and amino-functionalized SBA-16 with 3D porous structure and studied the release profiles of these drugs at different pH in simulating gastrointestinal tract.^[177] The authors reported no change in the bioavailability of ibuprofen for different carriers, and the functionalized materials did not show any cytotoxic effects and showed excellent releasing profile. Interestingly, the adsorption capacity of functionalized SBA-16 for furosemide is much lower than that for ibuprofen. This was attributed to the poor solubility of furosemide. Vallet-Regi et al.^[178] reported that the development of controlled DDS is significant for human healthcare and established a huge platform for biomedical materials science (Table 12). It was reported that the surface functionalization or modification of the porous DDS with suitable functional groups is the key to the development of novel DDS as it can help to control the adsorption and release of the drugs.^[179] For example, the surface of the porous DDS was functionalized with the chemical groups via the formation of ionic bonds or ester groups for the adsorption of drug molecules.^[180] In one of the studies, the adsorption of ibuprofen on functionalized porous matrices was demonstrated. In this study, the influence of textural properties including the pore size, volume and surface area on the adsorption of the drug and its release performance was explained. Moreover, Wang et al.^[181] studied the adsorption and release properties for rhodamine 6G and ibuprofen over various amine, and thiol group functionalized MCM-41 materials by co-condensation and post-synthetic methods. The hydrophobic mercaptopropyl and vinyl groups favourably have a strong interaction with the hydrophobic part of rhodamine 6G, which offer better adsorption capacity. On the other hand, amine-functionalized MCM-41 showed higher adsorption capacity for ibuprofen drugs, which was explained based on the carboxylic group present in the ibuprofen that interacts strongly with amine functionality.^[181] Patel et al.^[182] demonstrated the controlled release of poorly soluble erythromycin over SBA-15 functionalized with 12-tungstophosphoric acid (TPA). The controlled release of erythromycin was explained based on the binding of erythromycin to the terminal oxygen of TPA functionality present on SBA-15 surface. Similarly, Zeleňák et al.^[183] studied the delivery of poorly soluble indomethacin over functionalized MCM-48 and noticed that the decrease in indomethacin drug release on amine-functionalized MCM-48 and was explained based on high surface charge and pore blocking. Another study was performed by Deaconu et al.^[184] who utilized functional material for drug delivery of Doxycycline over functionalized MCM-41. The authors concluded that the release profile of doxycycline could be fine-tuned by altering the functional groups on the surface without changing its antibacterial activity. MSNs exhibit unique characters like large pore volume, surface area, tunable surface functionalities, which make them ideal nano-carrier to host, protect and act as vehicle drug to the target site.^[169f, 178, 185] For example, HMSN having structure tailored mesoporous silica-coated Au nanoparticles loaded doxorubicin hydrochloride (Dox),^[186] was effective for efficient drug delivery. It was noticed that the extend of Dox loading increases along with decreasing thickness of the shell. Similarly, the drug release also depends on shell thickness of HMSN, and the process was found

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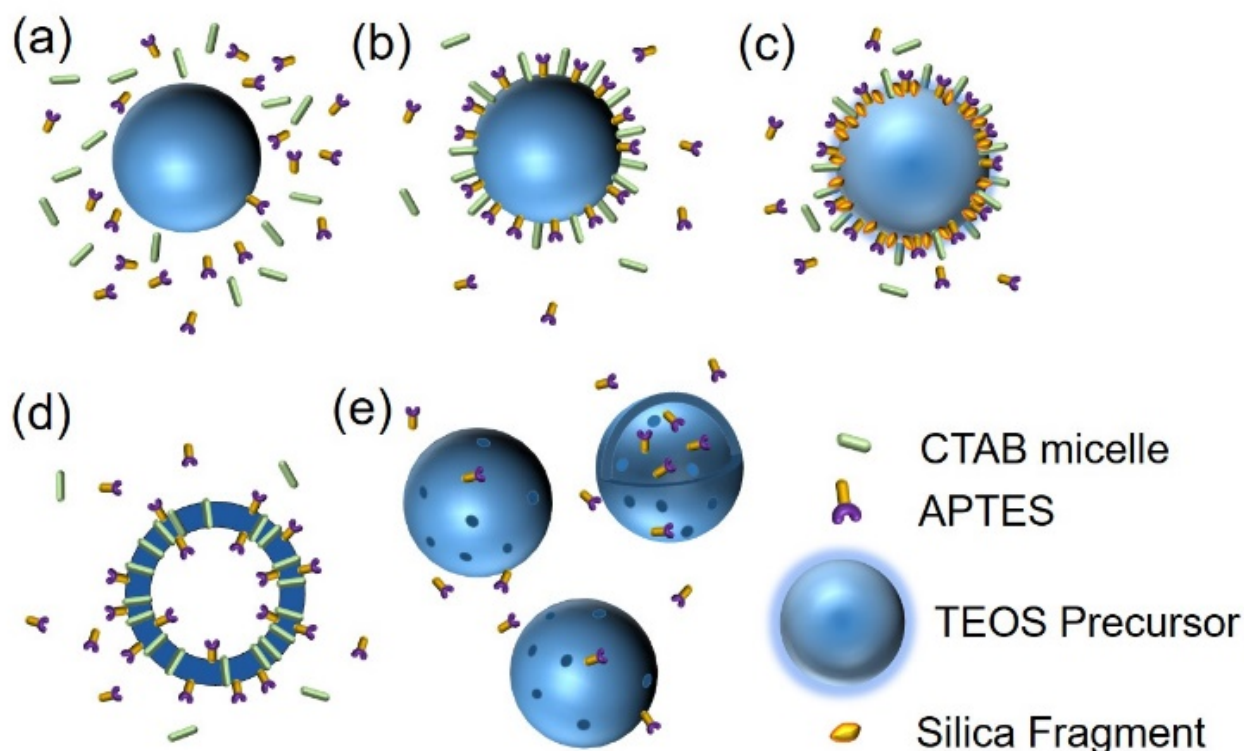


Figure 13. Proposed mechanism of HMSN formation. (a) A heterogeneous system comprising APTES and TEOS in aqueous CTAB; (b) TEOS droplets stabilized by APTES and captured CTAB micelles; (c) Formation and deposition of silica fragments; (d) Formation of a mesoporous hollow structure; (e) Amine-functionalized HMSN (reproduced with permission from ref 175,^[175]

to be purely diffusion-control.^[186] These results conclude that the mesoporous materials and their organo-functionalized derivatives are good carriers for drug molecules, which can also be tuned for the slow and the burst release and modified to target the cancer molecules specifically, and most importantly, these materials are bio-compatible.

5. Summary and Future Prospective

In summary, we have reviewed the synthesis of organo-functionalized porous materials and their application in fields including adsorption, catalysis, carbon dioxide utilization and drug carriers. We have also summarized how the introduction of organo-amine functionalities into mesoporous and microporous materials could help to generate surface basicity which is a key to promote base-catalyzed organic transformations. The addition of different functional groups, including organometallic complexes, superacids, and biomedical components, into the porous organic-inorganic hybrids, can expand the application possibilities of these materials for catalysis, adsorption and drug delivery. The methods of introducing different functionalities or ligands via *in-situ* or *ex-situ* routes, i.e., co-condensation or grafting, respectively, were discussed in detail. Surfactants play a major role in controlling the structure, size and shape of the pores. Therefore, the effect of different surfactants on the formation of an ordered porous structure with different structural features and functional moieties was reviewed in detail in this review. The function of these porous structures could be easily altered through suitable organic or inorganic modification, and the resultant materials could be applied for various applications including

multistep catalysis and the adsorption of gases including CO₂ and NO_x and adsorption of heavy metals and organic molecules. By manipulating the surface functionality and distribution of functional groups on the surface, it is also possible to influence the molecular functional materials properties such as basicity, hydrophobicity, adsorption capacity, diffusion and catalytic properties.

The ease of synthesis of organo-functional materials with variable surface functionalities, with high porosity, adsorption capacity, high thermal stability, and low raw materials cost make them robust for various applications. We have also summarised the synthesis and characterization of various organo-functionalized materials with tunable acidity or basicity that have been extensively applied for various organic transformations. By tuning the surface functionalities, the performance of these nano-hybrid catalytic materials could be altered. These organic-inorganic hybrid materials with the active catalytic species projected on the surface of the materials make them as the next-generation materials catalysts and catalyst supports. Organo-functionalized materials also found applications in controlled drug delivery systems, thus advancing their biological and biomedical applications. Similarly, these functionalized materials are bio-compatible with the ability to adapt and respond to the *in-vivo* environment and have excellent binding and diffusion control. These unique properties make them as potential alternative DDS for the capture and the release of the drug molecules. The targeted delivery of the drug molecules can also be possible after the modification of these organic-inorganic hybrid nanostructures with suitable targeting agents. Although these materials are unique for the drug delivery applications, the works on the loading of multi-drugs, with the combination of two or three different drugs,

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offering chemo, immuno and gene therapy are quite limited even though they are considered as advanced drug delivery approach. Therefore, much attention should be given on these areas using these functionalized mesoporous molecular sieves as a suitable host for delivering multi-functional different combinatorial drugs. It is also important to understand the mechanism of drug release inside the tumour environment which may be realized on attaching the imaging or targeting molecules on the surface of advanced mesoporous molecular sieves loaded with multiple drugs or different combinatorial therapies. Therefore, the research on the incorporation of different drug molecules combined with immune or gene therapeutic drugs, integrated with targeting and imaging molecules inside the porous structure or the surface of these nanostructures may be enhanced in the future.

In terms of future outlook, the field of research in organo-functionalized porous materials synthesis is continuously evolving, and the development of materials with high activity, selectivity and recyclability is highly desired. New advancements in the physicochemical properties will lead to the development of sophisticated materials that are anticipated to provide high performance in different application fields. The organo-functionalized porous materials could be hybridized with a third moiety to generate a ternary hybrid that might prove advantageous from the application perspectives. The most important criteria for their successful implementation at a commercial scale is to address their cost by using non-expensive starting precursors for their synthesis but without affecting the structure, morphologies, and the functionalities as well as the performances.

Overall, this review is a timely presentation of the recent highlights in the field of organic-functionalized porous materials. It covers recent advances related to their synthesis and their efficacy for different applications related to adsorption and drug delivery. The syntheses of these materials using *in-* and *ex-situ* methods have been given more importance which helps to understand how the anchoring organic functional groups on the surface of porous materials change the properties of the materials as well as their efficacy in various applications.

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Keywords: Mesoporous, Surface organo-functionalization; Catalysis; CO₂ utilization; Drug delivery

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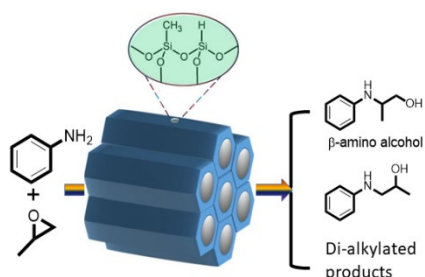
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REVIEW

Entry for the Table of Contents



In this review, we discussed the recent advances in the preparation and applications of organo-functionalized porous materials with different structures. The review starts with a brief overview of organo-functionalized porous materials followed by discussions on different methods of synthesis using different techniques. Their role in the heterogenization of homogeneous catalysts based on porous organic-inorganic hybrid materials has also been discussed in detail. A special emphasis is given on the applications of these organo-functionalized porous materials for catalysis, CO_2 capture and utilization and biomedical applications.