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INVITED REVIEW PAPER

Periodic mesoporous organosilica (PMO) for catalytic applications

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Abstract−Surfactant-templated binuclear alkoxysilane precursors or cyclic silsesquioxane precursors have led to a new class of nanocomposites with bridging organic groups (R) inside the channel walls, known as periodic mesoporous organosilica (PMO). These PMO materials facilitate chemistry of the channels and provide new opportunities for controlling the chemical, physical, mechanical, and dielectric properties of the materials. This review provides an overview of recent papers on the synthesis of PMOs and their applications as catalysts published after the year 2000.

Keywords: Periodic Mesoporous Organosilica, Catalyst, Organometallic Complex, Morphology, Precursors

INTRODUCTION

A fundamental breakthrough in porous materials was reported in 1992 when the first periodic mesoporous silica was discovered by Mobil Co. [1]. Since the invention of the MCM series, there has been considerable effort in creating zeolite-like materials with ordered and uniform pores larger than 2 nm because this would allow for host-guest chemistry with large molecules and polymers, nanoscale clusters and wires as well as enhanced diffusion rates of molecules within the pores [2]. Intense interest in surfactant-mediated synthesis and the modification of periodic mesoporous organosilica (PMO) soon took shape after its discovery in 1999 [3-5]. Unlike surface-functionalized mesoporous silica materials, the organic moieties in PMO are built directly into the channel walls.

The introduction of organic functionalities into the framework of mesoporous silica materials is potentially advantageous for various applications, including catalysis, ion exchange, encapsulation of transition metal complexes, chemical sensing, nano-material fabrications, and the adsorption of metal ions and drugs [4-11]. The properties, such as adsorption capacity for metal ions, ion exchange capacity, surface hydrophobicity, reactivity and thermal as well as mechanical properties can be controlled by changing the nature and distribution of organic groups within the hybrid mesoporous silica. Although many reports on the synthesis of PMOs with various types of organic spacer groups, including alkanes, alkenes, phenyls, and aromatic molecules, are available, the incorporation of multifunctional long chain organic moieties as bridging groups has been reported, albeit in a limited capacity [11-17]. Although the development of PMO has prompted great interest in the material sciences, owing to their specific composition and function, the synthesis of PMO with large and flexible organic bridging groups within the mesoporous wall remains a challenge [11,18].

In PMOs, the organic groups are located within the channel walls as bridges between Si centers ($(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ (R'=methyl or ethyl, R=the bridged organic groups)). Organic-inorganic hybrid materials can be synthesized by hydrolysis and condensation reactions of bridged organosilica precursors via the self-assembly process of structure-directing agents, corresponding to the similar process for the preparation of mesoporous silica materials.

In 2005, the Ozin group [2] first discussed the discovery and development of PMOs emphasizing the most important advances regarding their compositions, structures, morphologies, and properties. After that report, several review papers were published, such as Fröba et al. [9], Jaroniec et al. [10], Inagaki et al. [12], Lin et al. [13], Ozin et al. [14], Corma et al. [15] and Van der Voort et al. [16]. The current authors published a comprehensive overview of these materials, discussing the functionalities, morphology and advanced applications by referring to approximately 100 references on PMO materials [19]. Fig. 1 illustrates the research trends on the applications of PMOs with a number of papers.

The number of papers published on the application field of PMOs

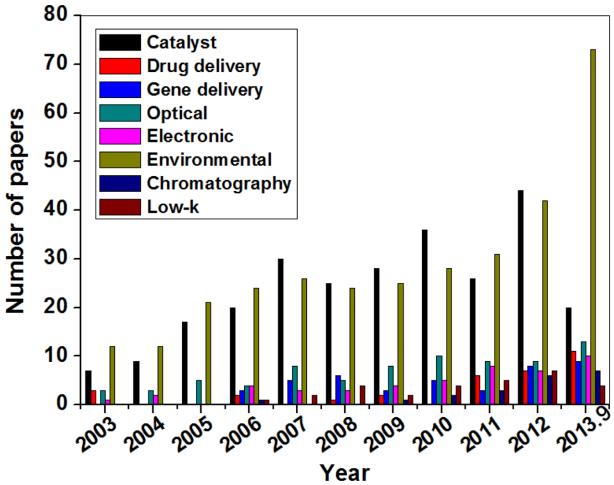


Fig. 1. Number of papers in the field of "periodic mesoporous organosilicas (PMOs)" and their applications in either "catalyst" or "drug delivery" or "gene delivery" or "optical" or electronics" or "environmental" or "chromatography" or "low-k" over the last 10 years. Statistics obtained from Scifinder Scholar (https://scifinder.cas.org/, accessed September 2013).

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increased steadily to 2013. Environmental studies rank top among the many application categories, such as catalysis, drug delivery, gene delivery, optical and electronic, environmental, chromatography, and low-*k* materials. PMOs with high surface areas, nanopores and various functional groups are useful for removing contaminants from a range of contamination sources, whereas the applications as a catalyst also rank relatively high compared to other uses. Therefore, this review is limited to the applications of PMOs as catalysts. The amount of research data is far too large to cover all the areas in a single review. Nevertheless, we try to present as much information as possible with reference to the original papers published mainly after the year of 2000. We hope that this review will encourage readers to enter this exciting but still young field.

SYNTHESES AND PROPERTIES OF PMOs

1. Syntheses of PMOs with Tunable Pore Walls

The hybridization of inorganic and organic species on the molecular to mesoscopic scale is a powerful tool for developing functional materials because cooperative and synergetic effects, as well as the compatibility of different functionalities, can be induced in such materials [4].

Generally, organic-inorganic hybrid mesoporous silica materials can be synthesized in three pathways depending on the supramolecular templating mechanism [4] (Fig. 2): (1) subsequent modification of the pore surface of a purely inorganic silica material (grafting), (2) simultaneous condensation of the corresponding silica and organosilica precursors (co-condensation), and (3) the incorporation of organic groups as bridging components directly and specifically into the pore walls using bissilylated single-source organosilica precursors (production of PMOs) [4].

PMO materials that are synthesized by the simultaneous use of a soft template and a hydrolyzable bis-silane, condensing around the template have been known for a long time from sol-gel chemistry [18,20,21]. A wide variety of functional groups and synthesis conditions can be applied to hydrothermal or via evaporation induced self-assembly (EISA). In this respect, all these methods are similar

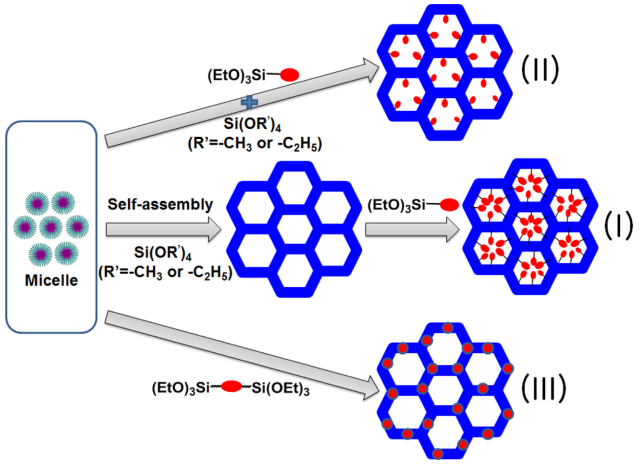


Fig. 2. Synthetic pathways of organic-inorganic hybrid mesoporous silica: (I) Post-synthesis functionalization or post grafting, (II) Co-condensation or in situ grafting, and (III) Periodic mesoporous organosilica.

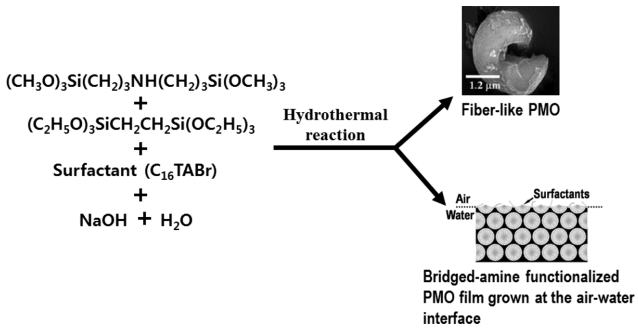


Fig. 3. Schematic diagram of the preparation of bi-functionalized PMOs with a bridged amine group in the frameworks.

to those of silica materials. Moreover, the general synthesis methods of PMOs were well reviewed in several review articles [4,9,22].

Ha et al. [23,24] synthesized bi-functionalized PMOs in the mesopore walls using the ethane-bridged organosilica (1,4-bis(triethoxysilyl) ethane, BTSE) as the main composition and the amine-bridged organosilica bis[(3-trimethoxysilyl)propyl]amine precursors as a co-precursor via a self-assembly and hydrothermal process in alkylammonium surfactant as structure-directing agent under basic conditions. PMOs materials were obtained as a powder and free-standing film type with different reactant ratios, different reaction temperatures and times (Fig. 3). In another approach, Thiel et al. [25] generated a PMO material with the successful cohabitation of two antagonistic functional groups in a single PMO material.

Ha et al. [24] also synthesized organic-bifunctionalized mesoporous silica materials by the co-condensation of BTSE with a variety of trialkoxysilanes, such as 1-[3-trimethoxysilyl)propyl]urea (uredo), vinyl, ethyl, glycidoxypropyl, and cyanopropyl units, via a hydrothermal reaction at 80 °C using mixed surfactant systems under basic conditions [Cetyltrimethylammonium bromide (CTAB)/polyethylene glycol dodecyl ether=5.74, w/w; surfactant/6 M NaOH=0.73, w/w; water/6 M NaOH=12.4, w/w; BTSE=10 mmol; co-organosilica precursor=10(1−x), x=0.05-0.25 for PMO-3-cyanopropyltriethoxysilane (cps), PMO-amine, PMO-vinyl, PMO-ethyltriethoxysilane, PMO-(3-glycidoxypropyl)trimethoxysilane, PMO-3-(trimethoxysilyl) propyl isocyanate, and PMO-uredo]. The PMO materials had well-defined rope-based and fiber-shaped morphologies as well as ordered pore structures.

Van der Voort et al. [26] prepared a thiol functionalized bis-silane incorporated PMO with 1,2-bis(triethoxysilyl)ethane through acid-ene click chemistry using poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$) as a structural directing agent. The targeted materials were then obtained by an aminolysis reaction process to produce SH- groups onto the material surface. The resulting materials retained their good mesostructural ordering with 100% thiol functionalization in the PMO materials. Although several materials have been synthesized using the post-functionalization method, this approach is simple and can produce a large amount of complex functional groups in the materials pore walls. Hence, the resulting materials would provide better efficiency for many applications.

Corma et al. [27] also synthesized bifunctional mesoporous hybrid materials containing both proton sponges and acid groups though a sol-gel or post-synthetic grafting method. They used a 1,8-bis(dim-

ethylamino)napthalene precursor as a proton sponge along with 3-mercaptopropyltriethoxysilane and the pendant precursor of sulfonic acid groups. The resulting materials were used as heterogeneous catalysts for various C-C bond formation reactions, including deacetalization-Knoevenagel condensation or deacetalization-nitroaldol (Henry) reaction.

Zhang et al. [28] designed PMO materials integrated with fluorescent resonance energy transfer (FRET) cascade components in the material pore walls at different loading ratios along with TEOS. The resulting materials exhibited multifluorescent emission behavior with single wavelength excitation. The materials produced monodisperse and nanometer-sized particle, and the framework properties were quite different from the hydrophilic silica framework or hydrophobic carbon framework, and the pore surface properties could be tunable by loading fluorophore amounts. The materials investigated had the capability of color-tunable drug release as well as strong barcoding applications [29-32].

2. PMOs with Crystal-like Pore Walls

The synthesis of PMOs with crystal-like pore walls is one class of PMO materials bridged with aliphatic and aromatic bridged functionalities, such as benzene [33], biphenyl [34,35], ethane [36], divinyl benzene [37], and napthalene [38]. According to the reported materials, several other functional bridged organic molecules also produce crystal-like silica pore walls. Ha et al. [39] prepared a free-standing benzene-silica PMO film with phenyl group-bridged functionalities. The obtained film type PMOs with a uniform thickness of 3.5 μm were optically semitransparent. Huh and Kim produced a PMO material with a single crystal wall structure using different 1,4-bis(triethoxysilyl)benzene precursors. Crystal pore walls were formed via the π-π stacking interactions between the two adjacent benzene moieties [40]. Inagaki et al. synthesized a PMO material with densely packed pyridine within the framework with crystal-like molecular scale periodicity [41]. The same group also prepared Ru and Ir metal complex bridged phenyl pyridyl PMO using 100 mol% phenyl pyridyl silane precursors. The resulting PMO material is a good example of the chelating ligand bridged framework with crystal-like and belt-like layer pore walls with an interval of 1.17 nm [42]. Gao et al. synthesized a rhodamine derivative-bridged PMO material with crystal-like pore walls [43].

Ferreira et al. [44] reported a crystal-like PMO material that had been achieved successfully by the N-alkylation reaction of amine functionalized phenylene moieties using a microwave synthetic process. This approach could be useful for preparing PMO materials with a range of amino-alkyl groups in the PMO pore walls. Recently, Inagaki et al. reported pyridinium group-integrated crystal PMO materials for electrochemical applications. Owing to the presence of a high density of pyridinium groups within the pore wall frameworks, the obtained PMO showed enhanced electrochemical properties, such as ionic conductivity (14 mS cm^{-1}) at 90 °C under 100% relative humidity [45].

CATALYTIC APPLICATIONS OF PMOs

PMOs were prepared from organosilica bridged precursor using a sol-gel process. Owing to the combined advantages of an ordered mesoporous structure, the unique distribution of organic functionalities in the mesopore walls and tunable mesopore surface properties give them potential for a range of catalytic applications [46].

Accordingly, considerable efforts have been directed towards the synthesis of PMOs for catalytic applications, because of their advantages, such as a decrease in the reactant diffusion lengths, increase in the accessibility to active sites, thereby enhancing the catalytic activities. Tuning the pore wall properties of PMOs with desirable reactive catalytic active sites, such as metal nanoparticles and metal-complexes, can be a real advantage for the enhanced uniform dispersion of active nanoparticles, stabilization, and their catalytic activation.

1. Mesoporous Organosilica Catalyst

The synthesis of a very large number of mesoporous materials has been reported. These include SBA-15, MCM-41, CMK-1, HMS, KIT, MSU-1 and KSN. Although considerable progress has been made in the fields of periodic mesoporous silica (PMS) and PMO materials, there are a limited number of examples showing some current trends in the applications of PMO materials in the heterogeneous catalytic field.

Many types of asymmetric organocatalysts have been developed for applications in a wide range of methodologies. On the other hand, the majority of developed metal complexes are generally hindered owing to their homogeneity and the requirement for high catalyst loading and the difficulty in separating the catalyst from the product. On the other hand, immobilization or integration of organocatalyst in solid supports, such as polymers, porous materials and magnetic nanoparticles [47-49], has been explored to achieve heterogeneous conditions. To rationalize the catalytic applications of PMOs, they were classified based on their main catalytic functions.

The ionic bridged organosilica ($[(R'O)_3Si\text{-}R^+\text{-}Si(OR')_3X^-]$) precursors lead to advanced materials for heterogeneous catalysis, adsorption and photochemical processes (Fig. 4). Garcia et al. [50]

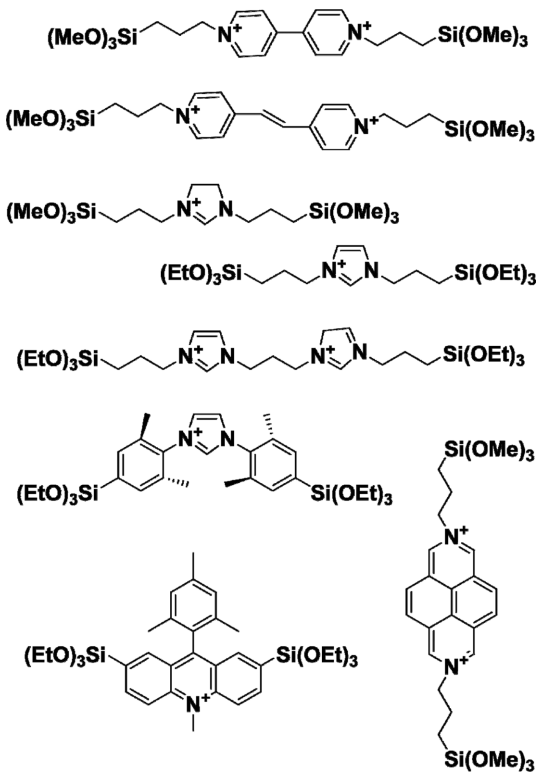


Fig. 4. Ionic bridged PMO precursors [50-56].

reported the synthesis of a new PMO with electron-acceptor viologen units (4,4'-bipyridinium) incorporated into the pore walls. They extended their photochemical studies to PMOs containing trans-1,2-bis(4-pyridyl)ethylene units into the frameworks. These materials were found to be photoresponsive, showing trans-to-cis isomerization of their double bonds [51]. In addition, PMOs were synthesized successfully using precursors containing imidaimidazolium or dihydroimidazolium units as the silica source by several researchers [52-56] and used for anion exchange resins and heterogeneous catalysts.

The PMO materials with chiral centers also aroused interest for high-tech applications, such as chiral chromatography, chiral separations and asymmetric catalysis. After the pioneering work by Polarz and Kuschel [57], a range of organosilica precursors with chiral centers were reported [58-70]. Inagaki et al. [59] produced PMOs from 100% bis-silylated chiral bridged precursors using novel chiral precursors. The enantiomeric purity of the organosilicas was determined to be >95% ee in materials obtained under acidic conditions. The researchers extended their studies to integrate tartrate derivatives as a chiral building block. From the co-condensation reactions of modified bis-silylated tartramide precursor with tetraethoxysilane (TEOS) or tetramethoxy silane (TMOS), Li et al. [68] and Gordillo et al. [69] achieved materials with good properties in asymmetric catalysis. A range of metals have already been included in PMOs with a metal complex. The metal complexes are also interesting in the field of catalysis.

In addition to the development of new PMOs using new precursors, the morphological control of the PMOs is also important for applications including catalysts, because the morphology of materials often controls their function and utility. [70-86]. Among the morphologies, hollow spheres have attracted attention because of their many applications in catalysis, as well as in drug delivery systems, microcontainers, etc. [87,88]. Mesoporous hollow spheres with organic moieties in the shell are attractive owing to their outstanding properties of organic functional groups in addition to the advantages of mesoporous hollow silica. Several studies have reported the synthesis of organic moieties containing mesoporous silica with a hollow structure. Lu et al. [89] reported the successful synthesis of PMO hollow spheres with tunable wall thickness by a new vesicle and a liquid crystal "dual templating" approach using co-structure directing agents (fluorocarbon surfactant and cationic surfactant) and 1,2-bis(trimethoxysilyl)ethane (BTME) as the hybrid silica precursor.

Ha et al. [90-93] examined the effects of an inorganic salt on the synthesis of large-pore PMO materials with a range of bridged organic groups (amine, benzene, and biphenyl) inside the channel wall. The triblock copolymer template with the aid of an inorganic salt could provide a new method for preparing mesoporous organosilica materials with hollow sphere morphology. The materials are used for the adsorption of protein (cytochrome c) [91] enzyme (lysozyme) and amino acid (glycine, L-lysine and isoleucine) [92], and nicotine [93].

2. PMOs with Acidic or Basic Functional Groups

PMO materials containing acid groups, such as sulfonic acid and carboxylic acid groups, are used widely as acid catalysts. The PMO materials that contain bifunctional catalytic functionalities are utilized effectively as a bifunctional catalyst. Thiel et al. [94] prepared bifunctional PMOs with sulfonic acid groups in the pore frameworks and amine groups in the pore surfaces. The resulting PMO catalyst works on the chemical conversion of benzaldehyde dimethyl acetate to 2-nitro vinylbenzene, called the nitro aldol reaction. Polarz et al. [95] prepared a $[VO]^{2+}$ and amine containing bifunctional PMOs for the active cleavage of an acetal-like benzyldioxolan catalyzed by $[VO]^{2+}$ sites acting as Lewis acids. Similarly, the existing amine groups act as a Lewis base that can catalyze the benzaldehyde to cyan-acetic ethyl ester. The reaction rates of both reactions are comparable. The maximum sulfonic acid content loaded in the PMO materials used is ca. 1.8 mmol g^{-1}. In addition to the content of acidic functional sites, a range of other factors, such as hydrophobicity, acidic strength, structure, and stability, also affect the catalytic activity of PMO-based catalysts.

The resulting PMO material could behave as an efficient bifunctional acid-base PMO catalyst for the chemical conversion of benzaldehyde dimethyl acetate to 2-nitro vinyl benzene via an acid-base catalyzed nitro aldol reaction because of the presence of sulfonic acid groups in the pore wall framework and amine groups in the pore surfaces. Do et al. [96] prepared sulfonic acid ethane-silica for the liquid phase acetylation of heptanal by 1-butanol and compared its catalytic activity with that of Amberlyst-15. The sulfonic acid functionalized PMO material exhibited good catalytic activity. Yang et al. [97] obtained disulfide-bridged PMO material using a co-condensation method and further derived sulfonic acid on the PMO walls by a post-oxidation method. The prepared sulfonic acid containing PMO exhibited high catalytic activity for the oxidation of aliphatic acid in high yield (Fig. 5).

Juneja et al. [98] reported an alternate route to the production of sulfonic acid functionalities in PMO materials by the covalent attachment of 2(3,4-epoxycyclohexyl)ethyltrimethoxysilane followed by a reaction with sulfite ions under mild acidic conditions. The material obtained showed superior catalytic performance in esterification, acetylation and condensation reactions. Kaliaguine et al. [99] produced fluorine-containing sulfonic acid groups by the post grafting of 1,2,2-trifluoro-2-hydroxy-1-trifluoromethyl ethane functional groups onto the ethane-bridged PMO materials. The liquid phase

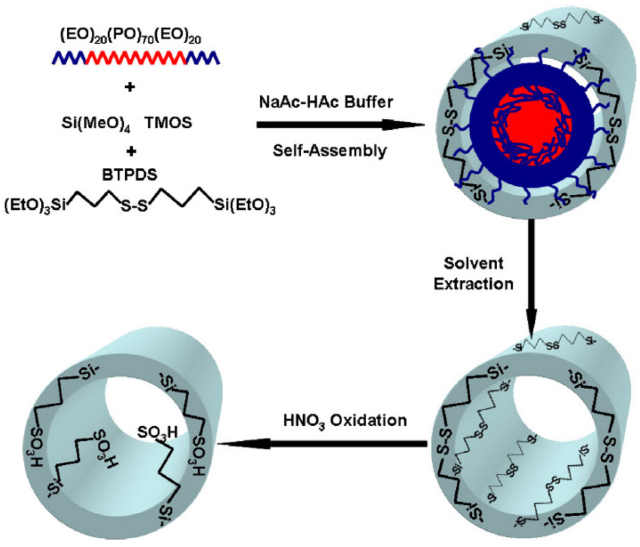


Fig. 5. Schematic diagram of the synthesis and oxidation process of bis[3-(triethoxysilyl)propyl]tetrasulfide (TSSn) [97].

self-condensation of heptanal and the acetalization of heptanal by 1-butanol were performed at 30 °C and 75 °C in the presence of the catalyst, and results were compared with those obtained with several other heterogeneous hydrophobic acid catalysts. The catalyst exhibited efficient catalytic performance on the catalytic reactions.

3. Gold Nanoparticle-supported PMOs

The incorporation or integration of catalytic organic sites/metal atoms in the mesoporous framework walls of the mesoporous materials is normally considered to be more efficient than the surface modifications.

Gold has long been disregarded for catalytic applications because of its inert nature. On the other hand, Yamada et al. [100] discovered the remarkable catalytic activity of supported Au nanoparticles (AuNP) for CO oxidation, which has received considerable interest. Khorasani et al. [101] synthesized gold nanoparticle-supported PMOs with a two-dimensional (2D) hexagonal structured imidazolium ionic liquid framework for a highly selective catalyst for the three component coupling reactions of aldehydes, terminal alkynes and amine. In addition, the bridged organosilane consisting of phenyl groups and ethane groups together with a gold nanoparticle-encapsulated mesoporous silica framework [102] exhibited high catalytic activity for the aerobic oxidation of various types of alcohols into their corresponding aldehydes and ketone at room temperature (Fig. 6).

Zhao et al. [103] prepared gold nanoparticles, 2-4 nm in size, dispersed on ordered mesoporous silica through a one-pot synthesis route in the presence of organosilane mercaptopropyl trimethoxysilane (MPTMS). In this study, MPTMS played a dual role: coordination of the Au precursor ($AuCl_4^-$) via its thiol ligands, and the formation of a covalent bond with the silica matrix. The synthesized mesoporous silica nanoparticles showed high catalytic activity and selectivity in the solvent-free selective oxidation of cyclohexane in the presence of molecular oxygen.

Similarly, the selective oxidation of cyclohexane with molecular oxygen was used to evaluate the catalytic properties of the AuNP catalyst prepared using Au catalyst through the hydrogen reduction method. The AuNP catalyst exhibited outstanding catalytic performance on the cyclohexane oxidation reaction [104]. Wei et al. [105] also reported cyclohexane oxidation reactions that were performed by the Au/SiO_2 catalyst with the conversion of cyclohexane and the total selectivity of cyclohexanone and cyclohexanol of up to ~10 and ~92%, respectively.

Furthermore, gold nanoparticles (AuNPs)-supported on PMOs (Au-PMOs) have also been prepared as an efficient and highly selective catalyst in the three-component coupling reaction of aldehydes, terminal alkynes and amines under mild reaction conditions [103]. In such a way, the AuNPs were incorporated with HS ($HS-CH_2-CH_2-CH_2$ group) incorporated ethylene-bridged PMO by the in situ reduction of Au^{3+}. This approach has advantages, such as (1) producing very tiny nanoparticles (1-2 nm), (2) stabilizing the Au nanoparticles against aggregation/leaching, and (3) oxidizing HS to produce SO_3H in the PMO network [106]. Li et al. [107] reported the catalytic activity of gold nanoparticles confined in PMOs modified by an external passive route and the resulting PMOs exhibited good catalytic properties in methylene blue reduction. The resulting Au-PMOs were applied to alkene hydration, intramolecular hydroamination, styrene oxidation and coupling reactions, and olefins epoxidation [108] with high catalytic efficiency.

4. Catalytic PMOs Containing Metal Complexes

Integrating metal complexes into the PMO frameworks is particularly important because metal complexes have unique features in a range of fields, particularly in catalysis. A range of homogeneous metal complexes have been applied widely for catalysis applications [109-111]. On the other hand, the separation and recycling of the rather expensive catalyst has inherent difficulties. The heterogenization of such homogeneous catalysts on solid supports can mitigate these problems. In this sense, a range of metal complexes were integrated in the PMO framework through bridged organosilane-metal complexes.

4-1. Rh-, Cu- and Cr-PMO

In addition, allyl imidazolium-based PMOs with rhodium metal complex (Rh@PMO-IL) are suitable for the conversion of a wide range of either primary or secondary benzyl alcohols into corresponding aldehydes or ketones in good to excellent yield. The catalyst was reported by Hunt et al. [112]. Xu et al. [113] reported a novel copper (II) ion-containing bisimidazolium ionic liquid bridged PMO (Cu-BIM-PMO) as a heterogeneous catalyst for the decomposition of cyclohexyl hydroperoxide. Through electrostatic binding between the bisimidazolium cation and $CuCl_4^{2-}$ complex, the stability of the catalyst improved and metal leaching was negligible under the reaction conditions. In the decomposition of cyclohexyl hydroperoxide (CHHP), this catalyst exhibits high catalytic

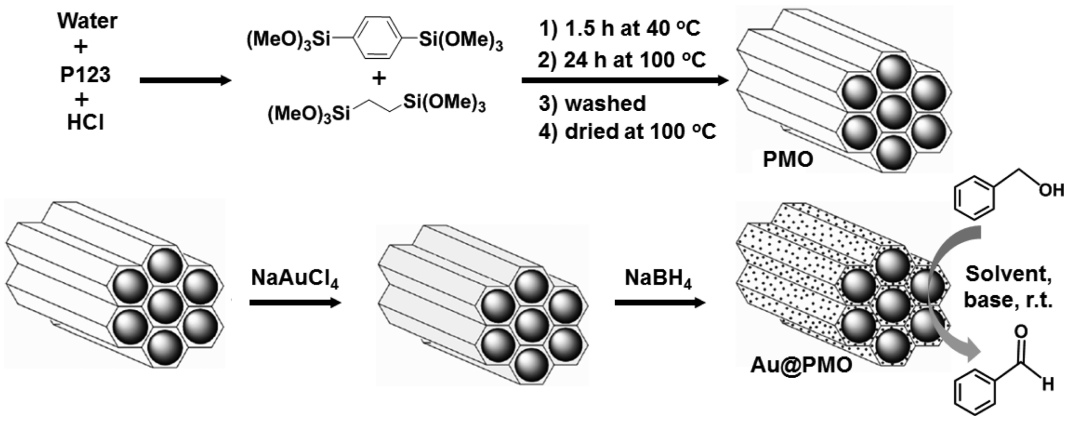


Fig. 6. Typical schematic pathway for the preparation of Au@PMO 1 [102].

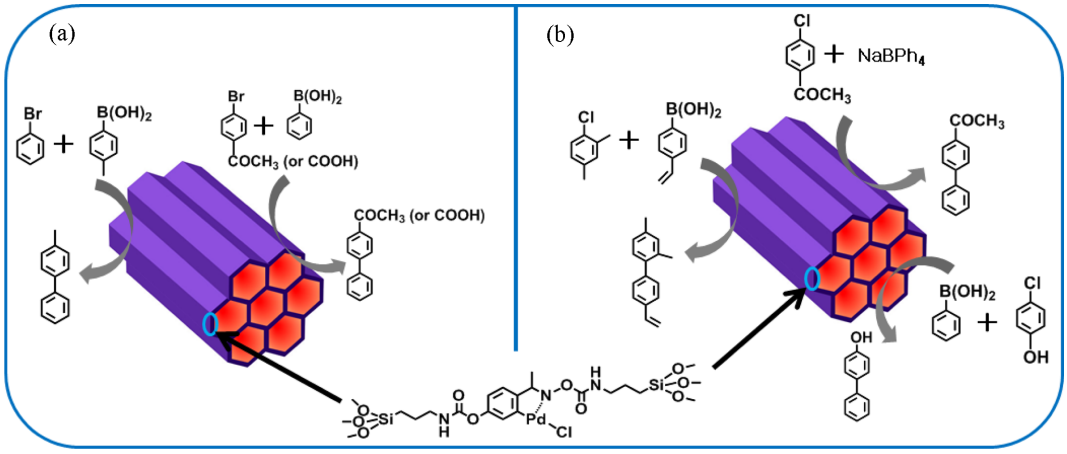


Fig. 7. PMOs with carbapalladacycle complex moieties in the frameworks: an efficient heterogeneous catalyst for the Suzuki cross-coupling reaction of phenylboronic acid with bromobenzoic acid and bromoacetophenone [115].

activity (99% conversion and 84% selectivity for cyclohexanone and cyclohexanol (K/A oil)) and can be reused at least five times without any apparent loss of activity. The Cr-PMO catalyst prepared by Anderson et al. [114] exhibited the efficient oxidation of cyclohexane in the presence of H_2O_2 and tert-butyl hydrogen peroxide. The selectivity to cyclohexanone was more efficient for Cr-PMO than the other Cr-containing catalysts.

4-2. Metal-supported Catalytic-PMOs

The palladium-catalyzed reactants for the Heck cross-coupling reaction of alkenes with aryl or vinyl halides are among the most significant and efficient transformations in a chemical process. The preparation of catalytic-active PMOs is a novel strategy for transforming into a heterogeneous form of catalyst [115-117].

Pd-supported PMOs exhibited higher catalytic performance of Pd/PMO (product yield >90%) in the Ullman coupling reaction of bromobenzene to biphenyl [118] in toluene, and a more active and selective catalytic effect in the Suzuki-Miyauro coupling reaction between aryl halides and aryl boronic acids [55]. Pd-containing aryl imidazolium PMO-IL have been synthesized and used effectively in the selective oxidation of a wide range of alcohols including benzylic and allylic alcohols [117]. In addition, vanadyl-integrated PMO exhibits the selective and direct hydroxylation of benzene to phenol owing to their intrinsic ability towards hydrocarbon oxidation [119]. The catalytic results showed that, in particular, benzene-to-phenol conversion (27.4%) and the 100% selectivity for phenol formation were observed.

Leyva et al. [115] synthesized PMOs with varying contents of the carbapalladacycle complex forming part of the walls of the hybrid. The fresh solids exhibited high activity for the Suzuki cross-coupling reaction of phenylboronic acid with bromobenzoic acid and bromoacetophenone (Fig. 7). Recently, Bhaumik et al. [116] reported that the Schiff-base organosilane precursor integrated PMOs with a Pd-grafted framework was an efficient catalyst for Hiyama coupling and Sonogashira coupling, and cyanation reactions of aryl halides under liquid phase conditions over a Pd-incorporated PMO catalyst.

Moreau et al. [54] produced Pd-containing PMOs with an ionic-liquid framework for efficient and reusable Suzuki-Miyaura coupling reaction in aqueous media due to the presence of ionic-liquid units in the material framework that efficiently control the reaction mechanism by preventing Pd agglomeration during the reaction process (Fig. 8).

The system exhibited efficient catalytic activity in the Suzuki cross-coupling reaction of aryl boronic acid with various types of aryl halides. Hunt et al. [117] also reported that the application of Pd-containing ionic-liquid PMO (PMO-IL) could be used effectively in the immobilization and stabilization of Pd nanoparticles with high catalytic efficiency for the selective oxidation of a range of alcohols, such as benzyl, allylic, alicyclic and aliphatic alcohols, in the presence of molecular oxygen/air as the oxidant.

Bhaumik et al. [119] prepared a new heterogeneous catalyst-based functionalized Ti-PMO with Ti-nanoparticle sites in the hybrid frame-

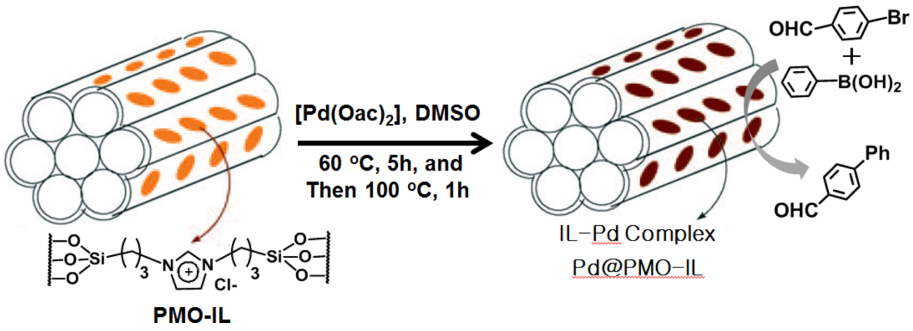


Fig. 8. Schematic diagram for the preparation and catalysis of the Pd@PMO-IL catalyst [54].

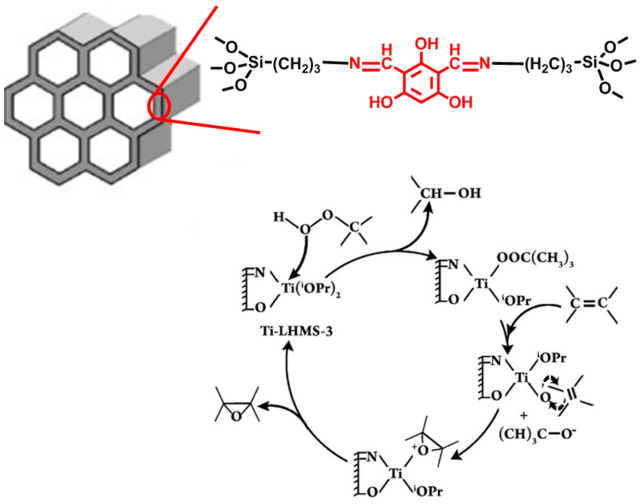


Fig. 9. PMOs with the bis(propyliminomethyl)phloroglucinol moiety in the frameworks and proposed mechanistic pathways over Ti-LHMS-3 for the epoxidation of different olefins [119].

work and demonstrated the catalytic activity of Ti-nanoparticles for the epoxidation of olefins over the hybrid mesoporous titanosilicate materials (Ti-LHMS) catalyst (Fig. 9).

The Ti-LHMS-x material exhibited excellent catalytic activity (conversion of 80%) and good reaction recycling (five cycling) in the epoxidation of alkenes under mild liquid phase reaction conditions using tert-butyl hydroperoxide (TBHP) as the oxidant. Similarly, Ti-PMOs were used as efficient oxidation catalysts for the epoxidation of a variety of alkenes under liquid phase conditions in the presence of TBHP as an oxidizing agent [50].

A heterogeneous Rh(I) complex integrated homogeneously into the PMO was prepared by using a surfactant-directed co-condensation method. The resulting PMOs with Rh(I) active sites exhibited high catalytic efficiency for phenyl boronic acid and butyl acrylate reaction in aqueous media [120]. Other metal complexes were also prepared, such as bipyridine-ruthenium(I) complex for the enhancement of photocatalytic CO_2 reduction [121]. PMO with a large pore diameter and high periodicity provides sufficient space to accommodate large dimeric Mn(salen) complexes with excellent catalytic activity than monomeric Mn(salen) complexes towards the alkene epoxidation reaction [122]. In addition, bridged silsesquioxanes containing various chelating groups, such as ethylenediamine derivatives and Troger-base derivatives [123] with a variety of metal complexes produced various solid hybrid metallic complexes for a range of S-arylation reactions [124].

Similarly, the bis(8-quinolinolato)dioxomolybdenum (IV) complex [125] and bridged silsesquioxane precursor consisting of a Ni(II) α-diamine complex [126] containing solid PMO-metal complex materials were prepared using a one-pot process to achieve a range of catalytic activities with high stability and well-defined materials morphology. Recent studies describe the successful synthesis of novel Ru and Ir complexes and Rh-complex [127] with triphenyl phosphine as the counter ligand for a range of applications including catalysis.

In addition, PMOs were synthesized using metal (M=Fe, Cu and Sn)-containing tetracyclic porphyrin (M-TCPP) as tetrasilanes and tetrakis (4-carboxy phenyl)porphyrin [128-130]. The obtained PMO catalyst was used successfully for the Baeyer-Villiger oxidation reaction and hydrogen transfer reaction, cyclohexane oxidant and methylene blue degradation reactions catalyzed by porphyrin-bridged PMOs [16]. Compared to other bridges, the heterogeneous complexes, such as bis(8-quinolinolato)dioxo molybdenum (IV) complex [130] and metalloporphyrene [131,132], were more active than the homogeneous complexes. In addition, bridged silica consisting of Ni(II) α-diimine complexes exhibited high catalytic activity in ethylene polymerization over a wide range of temperatures [133].

A range of bis- and tris-silylated precursors with different metal complexes, such as Pd(II), Rh(I), Ru(I) complexes were prepared with TEOS or BTEB materials, which exhibited similar catalytic activity as homogeneous complexes and could be recyclable [133, 134]. Li et al. [136] reported chiral Mn(salen) complex-modified

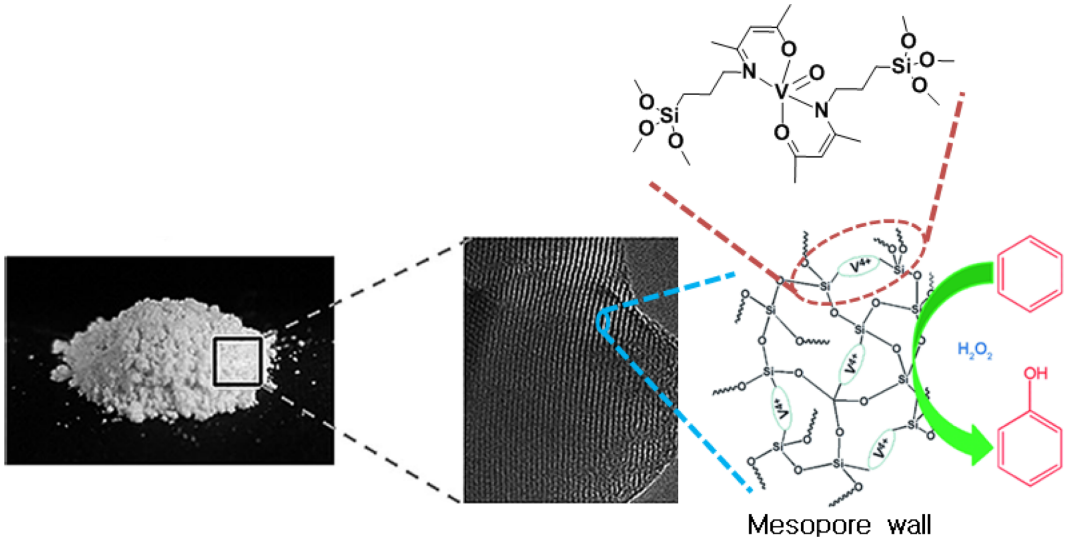


Fig. 10. Synthesis of an essential organic precursor (SB-V) and PMOs. TEOS-tetraethyl orthosilicate, CTAB-cetyltrimethylammonium bromide [135].

mesoporous materials via phenoxyl groups, phenyl sulfonic acid groups and propyl sulfonic acid groups. These materials exhibited 84% ee selective for the asymmetric epoxidation of 6-cyano-2,2-dimethylchromene.

Zhao et al. [135] reported the synthesis of new type of PMO grafted with catalytic-active vanadyl (IV) centers, and the application of the PMOs catalyst for the selective hydroxylation of benzene to phenol. The vanadium metal complex [$VO(acac)_2$] was distributed homogeneously at the molecular level as an integral part of the silica framework (Fig. 10).

5. Catalysis by Hollow PMO Spheres

The hollow mesoporous organosilica (HMOS) materials could be classified roughly into soft/hard template and self-templating methods depending on the nature of the template. The soft templates include mainly micelles [136-143], vesicles [144-148], liposomes [149], and polyamine-salt aggregates (PSAs) [150,151], and the hard templates involve polystyrene (PS) spheres [152-155] and magnetic Fe_3O_4 particles [156]. The assembly of organosilicate species around the template was performed through a sol-gel process, and the subsequent removal of templates resulted in the formation of HMOS.

Yang et al. [157] reported the successful synthesis of organosilica hollow nanospheres (OHNs) with ethylene, phenylene and 1,4-diethylphenylene bridging groups in the framework using F127 block copolymer micelles as a soft template under acidic conditions. The hydrophobicity/hydrophilicity of the silane precursor plays an important role in the structure and morphology formation of the organosilicas. The organic additive (1,3,5-trimethylbenzene) could finely tune the particle size of the nanospheres from 12 to 25 nm [157]. Fig. 11 summarizes the relationship between the morphology and the type of silane precursor.

This method was extended further to the synthesis of bifunctionalized ethane silica hollow nanospheres (ESHNSs) with -SH, $-C_6H_5$, -C=C, $-NH_2$ and -CN dangling, respectively, using a mixture of BTME with 3-mercaptopropyltrimethoxysilane (MPTMS), (trimethoxysilyl)benzene (TMSB), vinyl trimethoxysilane (VTMS), 3-aminopropyl triethoxysilane (APTES), and 3-cyanopropyltriethoxysilane (CPTES) as the initial precursor [158,159]. The preparation of hollow PMOs using large and flexible organosilane bridging groups is quite difficult and has not been explored fully. Therefore, the catalytic applications of hollow PMOs have not been investigated completely. However, the preliminary results strongly show that the unique morphology of the hollow PMOs could not enhance the accessibility of the reactants to the active sites and thereby increase the reactant diffusion rate during the catalytic process.

Nanosized PMO materials, particularly with a hollow nanostructure, can decrease the diffusion length, increase the accessibilities to the active sites, and enhance the catalytic activity [153]. Despite this, only a few examples of such systems have been reported. Ha et al. [160] also prepared mesoporous ethane-silica hollow nanospheres through a hard templating route, but no catalytic applications were reported. Through further efforts on the preparation of hollow sphere mesoporous organosilicas, AuNP with the hollow silica sphere was introduced to produce Au nanoparticle-loaded cyanopropylsilsesquioxane (Au/CPSQ) hybrid nanocomposites, and highly dispersed Au nanoparticles could be loaded onto polysilsesquioxane hollow spheres for catalytic applications and used as the catalysts for the reduction of 4-nitrophenol.

Wang et al. [158] produced hollow phenylene-bridged PMO (H-PhPMO-Mac) through a hard templating route using hematite nanoparticles as the hard template, and further utilized them as a highly active MacMillan catalyst in asymmetric Diels-Alder reactions (Fig. 12).

The synthesized H-PhPMO-Mac catalyst exhibited high catalytic activity (98% yield, 81% enantiomeric excess (ee) for endo and 81% ee for exo) in asymmetric Diels-Alder reactions with water as the solvent [158].

6. Photocatalysis

Hirai et al. [161] prepared a Ti-containing mesoporous organosilica (Ti-OS) using Ti-precursors along with TEOS and BTSE as the co-precursors. The synthesized catalyst exhibited efficient catalytic activity with 21% epoxide selectivity and produced higher quan-

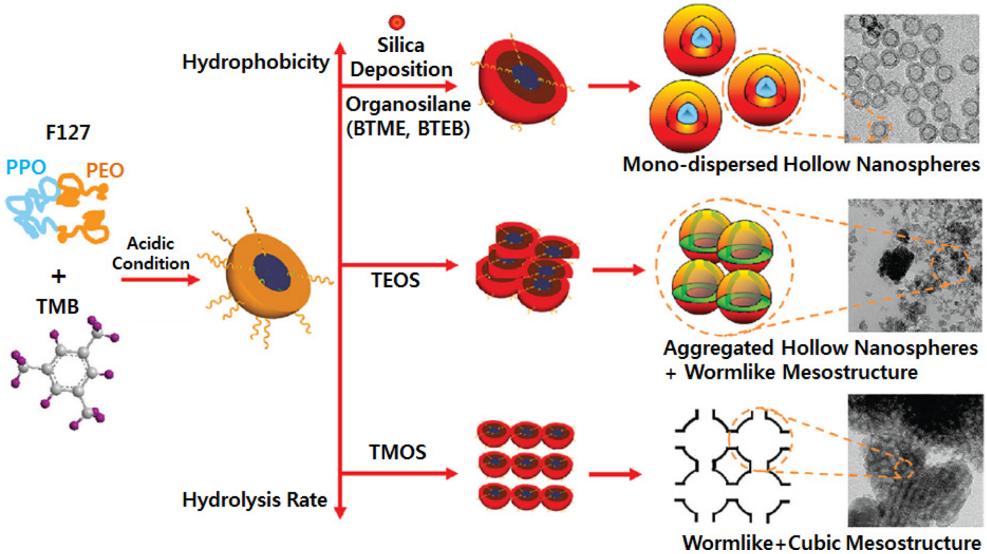


Fig. 11. Schematic diagram of the formation mechanism of organosilica hollow nanospheres and the relationship between the morphology and silane precursors, where 1,3,5-trimethylbenzene (TMB) was used as a swelling agent [157].

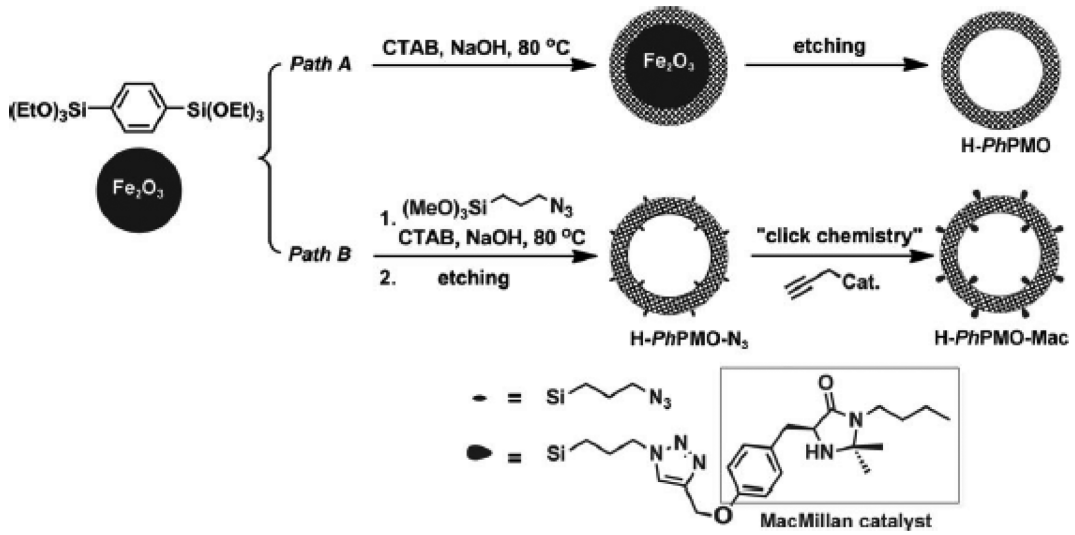


Fig. 12. Schematic diagram of the synthesis of hollow-structured phenylene PMO (H-*Ph*PMO, path A) and further functionalization with MacMillan catalyst (H-*Ph*-PMO-Mac, path B) through the co-condensation process and click chemistry post-modification [158].

tities of allylic oxidation products. Ota et al. [162] reported CdS-incorporated mesoporous organosilica used for photocatalytic applications to the generation of H_2 from an aqueous 2-propanol solution. The quantity of H_2 generation on CdS-PMO was greater than the mesoporous silica (MCM-41)-immobilized CdS nanoparticles. Diderman et al. [163] developed porphyrin-embedded PMO materials for the sun-light stimulated generation of cyclic organics, such as p-cresol, p-nitrophenol and trinitro toluene.

Hirai et al. [164] prepared two catalysts, chromium containing mesoporous organosilica (Cr/MOS) and chromium containing mesoporous organosilica, prepared by calcination (Cr/MOS-cal) with highly dispersed chromate species. Cr/MOS was synthesized by Cr impregnation onto MOS followed by calcination, whereas Cr/MOS-cal was synthesized by the calcination of MOS, followed by Cr impregnation and calcination. Both catalysts containing highly dispersed chromate species in the pore walls by chromium impregnation onto the mesoporous organosilicas followed by the calcination process promoted the partial oxidation of cyclohexane with high selectivity (>86%). Inagaki et al. [165] constructed a solid-state donor-acceptor based PMOs using Viologen (Vio) attached biphenyl (Bp)-bridged functionality. The resulting PMO showed good photocatalytic hydrogen evolution in the presence of reduced nicotinamide adenine dinucleotide (NADH) under irradiation at 400 nm (Fig. 13). The catalytic results showed that the hydrogen was produced at most linearly with time (6-7 h) with a quantum yield of approximately 0.022%.

The same group [166] prepared 2,2'-bipyridine (bpy) ligand-integrated PMOs without the addition of other silane precursors. The resulting bpy-PMO samples possessed unique pore wall structures with uniformly packed ligand groups exposed to the surfaces. The bipyridine ligand sites were efficiently coordinated with a range of metals, such as Ru, Ir, Re, and Pd, and act as a solid state heterogeneous catalyst with superior activity, durability and recyclability. Ru-complexed PMO (Ru-PMO) was found to be an efficient photosensitizer and Pt-complexed PMO (Pt-PMO) acted as a catalyst without any electron relay molecules (Fig. 14).

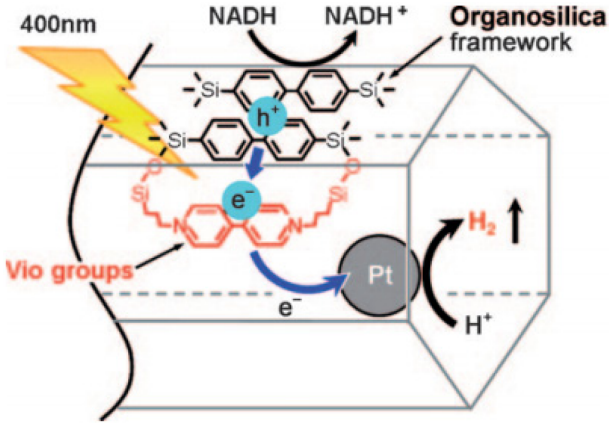


Fig. 13. Designed solid-state donor-acceptor system based on PMO for photocatalytic hydrogen evolution. Photoirradiation induces electron transfer from Bp in the framework to Vio attached covalently to the framework. Platinum in the mesochannels promotes hydrogen evolution. The holes in the framework are consumed by oxidation of the sacrificial agent [165].

In addition, the same group [167] reported that a rhenium (I) complex-based PMO material showed efficient photocatalytic CO_2 reduction. The 280 nm light was effectively adsorbed by the biphenyl groups and the excited energy was funneled into the Re-complex via a resonance energy transfer process. The excited energy caused an increase in the photocatalytic evolution of CO from CO_2 by a factor of 4.4. The designed system mimicked natural photosynthesis. Ren et al. [168] produced a PMO material with bismuth nitrate using a post modification approach. The prepared mesoporous silica materials exhibited good photocatalytic efficiency in phenol degradation (>90%) at 2 h under irradiation by Xe light.

Park et al. [169] synthesized tetrakis(4-carboxyphenyl)porphyrin (TCPP) units integrated TCPP-silsesquioxane by a co-condensation method in the presence of P123 as the structural directing agents.

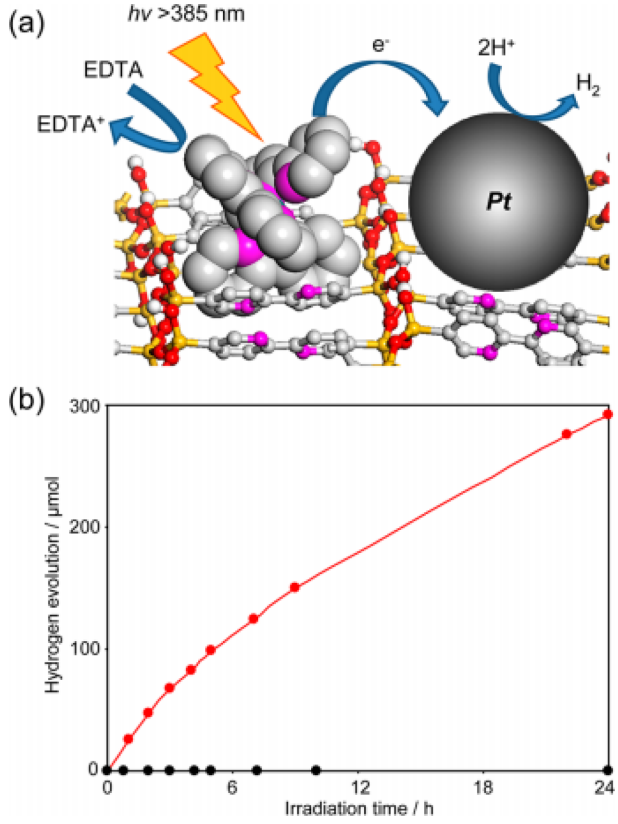


Fig. 14. (a) Schematic diagram of a hydrogen evolution system based on Pt/Ru-PMO. Ru-complex is represented as a space filling (CPK) model. (b) Time-dependent hydrogen evolution curves of Pt/Ru-PMO (red line) and homogeneous $Ru(bpy)_3Cl_2$ and colloidal platinum particles system (black line) under visible light irradiation (>385 nm) [166].

The TCPP-PMOs were superior for the hydrogen transfer reactions for various ketones and exhibited good photocatalytic degradation of methylene blue without metal incorporation. The prepared materials also worked as efficient catalysts for the oxidation of cyclohexene with good activity and selectivity. Recently, Karimi et al. [170] reported a new binary photocatalyst by the incorporation of amorphous titania into the PMO frameworks for the regeneration of carbonyl compounds from oximes under sunlight irradiation. They also studied the photocatalytic aerobic oxidation of various oximes into aliphatic and aromatic phenols in the presence of Ti-coated PMO materials under sunlight irradiation.

Recently, Bein et al. [171] designed a photoactive porphyrine based PMO thin film using tetra-substituted porphyrin silsesquioxane precursors by the EISA process. The designed PMO film has a face-centered orthorhombic porous structure with a 15 nm pore diameter suitable for the inclusion of electron-conducting species namely, [6,6]-phenyl C_{61} butyric acid methyl ester. The designed donoracceptor system has light-induced charge generation capability and hole-conducting property, highlighting the potential of PMO materials for optoelectroactive systems.

CONCLUSION

Significant developments have occurred in the design and synthesis of PMO materials with a range of pore structures, such as *p6mm*, *pm3n*, *Im3m* etc., and morphologies, such as spheres, rods and thin films, by tuning the pore wall properties of PMOs with desirable reactive catalytic active sites, including metal nanoparticles and metal-complexes. The facile synthesis and easy control of the properties and reactivity by simply changing the nature and distribution of organic groups within the hybrid mesoporous silica as well as those uniform structural and morphological features of PMOs can be real advantages for the enhanced uniform dispersion and stabilization of active nanoparticles, and their catalytic activation. These are important advantages over other porous materials, such as mesoporous silica including MCM-41 type catalysts and metal-organic framework (MOF) materials.

This review summarized selected examples of PMO materials that had been prepared and utilized for catalytic applications including soft catalysis, bifunctional catalysis, chiral catalysis, acid-base catalysis, organometallic catalysis, and chiral catalysis. The robustness, stability and properties of the PMO catalyst can be tuned by incorporating desirable organic bridging functionalities to produce a variety of PMO-based heterogeneous solid catalysts suitable for a range of applications over the homogeneous catalysts.

This account covers only the tip of the iceberg regarding the huge number of studies into mesoporous organosilica materials. More still remains to be unveiled, ranging from the remarkable design and synthesis of new bridging organosilane units to the production of the PMO architecture to demonstrate the resulting PMOs in applications. Overall, more research effort will be needed to meet the specific utilization demands at every scale. In particular, special attention will be required to design facile precursors and synthesize novel PMO materials that can be applied as multifunctional and/or universal catalysts for a variety of reactions as well as specific catalysts for a given reaction of interest.

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