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Porous Polymer Catalysts with Hierarchical Structures

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Abstract: The emergence of porous organic polymers (POPs) has provided great opportunities for new applications in heterogeneous catalysis owing to their unprecedented intrinsic structural features such as high surface areas, extraordinary framework stabilities and chemically adjustable compositions. In this tutorial review, representative recent developments in the POPs-based catalysts with hierarchically porous structures are presented. Various strategies for the syntheses of the hierarchically porous polymers including hard-templating, soft-templating and template-free approaches and designs of the catalytically active porous polymers including post-modification, co-polymerization and self-polymerization have been discussed. In addition, their catalytic properties are compared. Finally, we emphasize the importance for the synthesis of the hierarchically porous polymers based heterogeneous catalysts from the sustainable routes under template-free and metal-free conditions.

1. Introduction

1.1 Porous materials

Since the discovery of zeolites and their successful industrial applications, the porous materials have become one of the most exciting frontiers in modern chemistry because the porous materials are endowed with the ability to interact with guest species not only at their surfaces but also throughout the bulk of the materials owing to their permanent porosity. In the past decade, the field of porous materials has undergone revolutionary growth. A number of new porous materials such as metal-organic frameworks (MOFs),[1] crystalline covalent-organic frameworks (COFs),[2] and amorphous porous organic polymers (POPs)[3,4] have been well developed and intrigued much attentions not only owing to their high porosity like conventional porous materials such as zeolites or activated carbons, but also their capable of incorporating targeted or multiple chemical functionalities into the porous framework by bottom-up or post-synthetic modification approach. They have been recently explored as promising candidates for applications in gas storage, gas separations and catalysis and as useful platforms for the design of advanced functional materials.[5,6] Particularly, the catalysts based on these designable porous frameworks exhibit the potentials to unify the best features of homogeneous catalysts (ease of modification) and heterogeneous catalysts (ease of recovery and recycling).

1.2 Importance of stability

The stability of the porous materials is an essential prerequisite for their practical applications, that is, these porous materials need to be stable enough to a variety of conditions that they may encounter. The wide applications of zeolites in industrial processes are reasonably contributed to their excellent thermal and hydrothermal stabilities. COFs and MOFs owing to their crystallinity, have absolutely uniform pore sizes to those of zeolites, nevertheless, their practical applications are readily hampered by their relatively high sensitivity to moisture, especially in the presence of acid or base chemicals. One possibility for these disadvantages is that the periodic networks of COFs and MOFs linked by molecular building blocks are assembled through reversible chemical bond-forming reactions.[1,2] Whereas, POPs comprising chemically stable covalent bonds should not suffer from such framework degradation, exhibiting high chemical and hydrothermal stabilities. In addition, they also show good thermal stability (normally higher than 300 °C), withstanding a wide range of reaction temperatures, although that is much lower than for inorganic zeolites. These features render POPs with potentially advantageous over COFs and MOFs as platform for deployment of heterogeneous catalysts because of their enhanced stabilities, which greatly facilitate the recovery and reuse of heterogeneous catalysts based on POPs.[3-9]

1.3 Importance of hierarchical porosity

The pores of materials are classified into micropores (<2 nm), mesopores (2- nm), and macropores (>50 nm) according to the IUPAC recommendation. The hierarchical porosity means that the porous materials contain two or more kinds of pores, even one kind of pores have more than one pore size distributions. For catalytic applications, catalysts with a sole micropore is very favorable for increasing catalytic selectivity, but the relative small micropores might limit the diffusion of the reactants, leading to low catalytic activity. The solution for this problem is to introduce meso/macropores into the sole microporous catalysts. As a result, the hierarchical porous catalysts exhibit both excellent catalytic performance and superior diffusive properties.[10] For example, it has been reported that the small and sole micropores in the zeolites strongly influence the mass transfer in catalytic organic transformation, and an introduction of hierarchical porosity in the zeolites significantly enhance their catalytic performance, in particular to the catalytic conversion of heavy oil-based bulky molecules.[10] Therefore, as distinguishable from recent excellent reviews on POPs,[3,4] this tutorial review will focus on highly stable and hierarchically porous POPs-based catalysts, briefly summarizing their synthetic strategies, targeted functionalization, and performance in catalysis.

2. Synthetic strategies for highly stable and hierarchically porous polymers

The POPs constructed by stable covalent bonds mainly include microporous hyper-cross-linked polymers (HCPs), conjugated microporous polymers (CMPs), polymer of intrinsic microporosity (PIMs), covalent triazine-based frameworks (CTFs), porous aromatic frameworks (PAFs), and porous polymer networks (PPNs).[11] They could be readily formed by irreversible chemical reactions such as condensation of precursors in the presence or absence of metal catalysts and polymerization of monomers with double bonds. The generation of the hierarchical porosity in the POPs is usually performed with hard-templating, soft-templating, and template-free methodologies.

2.1 Hard-templating

Hard-templating is essentially a casting technique for the replication of the inverse structure of the hard template. A large number of mesoscale materials such as silica nanoparticles, mesostructured silicas, and anodic aluminum oxides (AAO), have been successfully employed as hard templates, and after etching these templates, well defined pores can be finally obtained. Right now, the hard-templating technique is recognized as a direct and versatile approach for preparation of porous polymers. For example, Johnson *et al.*[12] reported a successful preparation of ordered mesoporous polymers from replication of a matrix made from nanosized silica spheres by monomer such as divinylbenzene (DVB), ethyleneglycol dimethacrylate (EDMA), or a mixture of the two. After polymerization and subsequent dissolution of the silica template, networks of interconnected pores were finally achieved. Recently, Nguyen *et al.*[13] demonstrated that hierarchically porous organic polymers containing both meso- and micropores can be realized by cobalt-catalyzed trimerization of 1,4-diethynylbenzene inside a mesoporous silica aerogel template, followed by removal of the hard-template, as shown in Figure 1. Interestingly, the broad range of pores is very favorable for transport of molecules through the hierarchically porous POPs, resulting in drastically increased diffusion rates and fast gas uptake, compared with those containing only micropores.

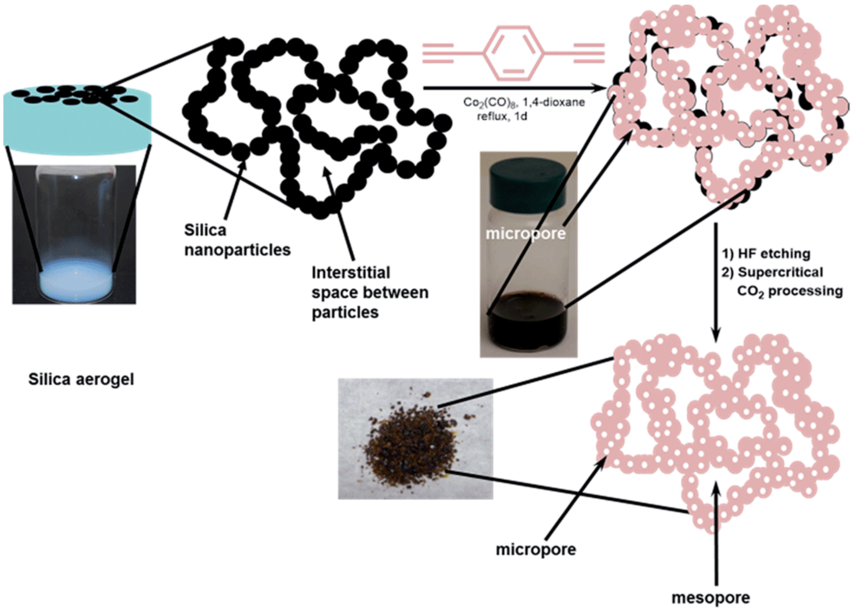


Figure 1. An illustration of the synthesis of a POP possessing a hierarchy of pores. From left to right: a silica aerogel template is infiltrated with a solution of the monomer and catalyst. After polymerization, HF etching and supercritical CO_2 processing of the resulting monolith afford the desired POP as a powder. In this scheme, the interstitial spaces between the silica nanoparticles that made up the monolithic aerogel template are responsible for the formation of mesopores. Reproduced from Ref. 13.

2.2 Soft-templating

Compared with hard-templating, the soft-templating approach is relatively versatile. As one of the most useful soft-templates, block copolymers are widely applied for the fabrication of sophisticated architectures, especially for those with well-defined ordered mesoporous structures. There are two different roles for block copolymers in the procedures employed for the synthesis of nanostructured porous polymers. One is that the block copolymers serve as the pore templates. In this process, block copolymers self-assemble with polymer precursors through various noncovalent interactions, followed by removal of these block copolymers as sacrificial components, leaving the pores in the resultant polymers. There are a number of successful examples for soft-templating synthesis of hierarchically porous polymers including phenolic resins, melamine resins, and urea-phenol-formaldehyde resins. Particularly, a series of phenolic resins with various ordered mesostructures such as body centered cubic, 2D hexagonal, and face-centered cubic have been developed through cooperative assembly of resols and commercial ethylene oxide/propylene oxide triblock copolymers (*e.g.,* F127 and P123).[14] Notably, the soft-templates in the resulting polymers could be successfully removed by washing in ethanol or calcinations at high temperature. Figure 2 displays a typical scheme, illustrating the preparation of the ordered mesoporous polymers from the surfactant-templating process of solvent evaporation induced self-assenbly (EISA).

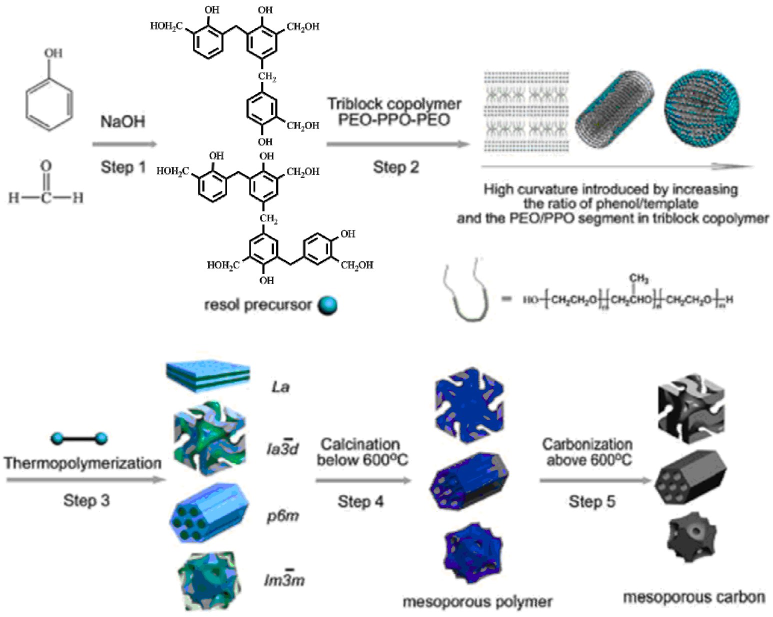


Figure 2. Scheme for the preparation of ordered mesoporous polymer resins and carbon frameworks from the surfactant-templating process of EISA. Reprinted (adapted) with permission from Ref. 14. Copyright © 2006, American Chemical Society.

Another role of the block copolymers is to become the porous polymer framework, which provides a promising strategy for fabricating hierarchical structures with long-range order. For examples, block copolymer membranes with graded meso- and macroporous substructures can be formed through a process termed spinodal-decomposition induced macro- and meso-phase separation plus extraction by rinsing (SIM^{2}PLE).[15] One-pot approach for the preparation of hierarchically porous polymer scaffolds can be successfully performed with spinodal decomposition induced phase separation plus extraction by rinsing, as demonstrated in Figure 3. Particularly, the hierarchical porosities of the polymer can be tuned by controlling the casting temperature.

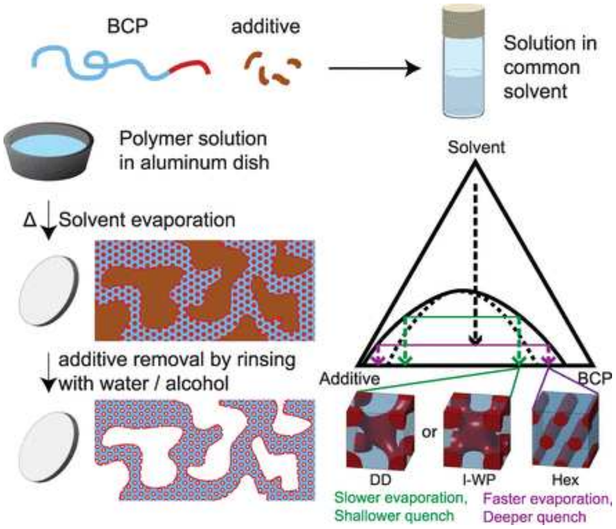


Figure 3. Scheme for the synthesis method and ternary phase diagram. Synthesis of hierarchically porous polymer scaffolds with ordered mesostructure using the SIM^2 PLE method. Red color on the surface of the pores suggests PEO lining. Schematic ternaryphase diagram shows paths to hexagonal and network mesostructures *via* solvent evaporation. Reprinted with permission from Ref. 15. Copyright © 2013, American Association for the Advancement of Science.

2.3 Template-free methodology

Generally, the templates in the synthesis of porous polymers are costly, and removal of these templates from the porous polymers is not only energy-consuming but also productive of polluted wastes. Therefore, it is strongly desirable to synthesize hierarchically porous polymers in the absence of any templates, based on the concept of sustainable chemistry. Fortunately, the diversity of functionalized groups, coupled with the wide availability of different covalent-bond forming reactions in organic synthesis provide a wealth of opportunities to control the porous structures as well as framework, yielding a wide range of advanced porous organic polymers under the template-free conditions. Recently, a number of metal-catalyzed couplings such as Yamamoto reaction, Sonogashira-Hagihara reaction, oxidative coupling reaction, Friedel-Crafts reaction, phenazine ring fusion reaction, and cyclotrimerization have been well-established for the synthesis of porous organic polymers. Normally, these reactions performed in the presence of metal catalysts, and their complete removal form the product is not easy. As a result, a trace of metal may still exist in the porous polymers, which makes the catalytic processes more complicated, although some of them are proven to be beneficial for the enhancement of the catalytic properties. For example, Cooper *et al.* demonstrated that the residual Pd species in the organic photocatalysts fabricated from Pd-catalyzed Suzuki reaction are good for visible-light-driven hydrogen evolution.[16] In addition, the transformation efficiency of these reactants to the porous polymer products is usually not quantitative due to their incomplete condensations. To overcome these problems, it is developed novel template-free and metal-free routes for synthesis of hierarchically porous polymers.[17] Typically, hierarchically porous polydivinylbenzene polymers with nearly quantitative yields have been synthesized from a radical-induced polymerization of divinylbenzene monomer under solvothermal conditions, as shown in Figure 4. Particularly, it is worth mentioning that the pore size distribution and hierarchically porous structure could be rationally controlled by changing the solvents. When THF is used as sole solvent, it is obtained very narrow pore size distribution at 3.9 nm; when a small amount of water (molar ratio of H_2O/THF at 0.05) is introduced, it is shown uniform pore size distribution at 4.2 nm; when further increase the water in the THF (molar ratio of H_2O/THF at 0.08), it is exhibited a hierarchically porous structure centered at 4.0 nm and 8.6 nm. [17]

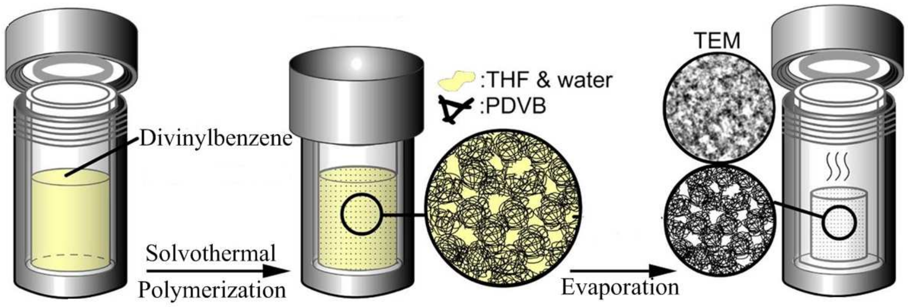


Figure 4. Synthetic scheme of polydivinylbenzene under solvothermal conditions.

3. Targeted functionalization of hierarchical porous polymers

Currently, a variety of porous polymers with different nanostructures and functionalities have been successfully fabricated. The strategies for targeted functionalization of hierarchical porous polymers can be summarized in the following: (1) post-modification, (2) co-polymerization of skeleton molecules with functional groups; (3) self-polymerization of functional organic groups.

3.1. Post-modification

Although homogeneous catalysts have been extensively investigated, their practical applications still has a challenge due to their high-cost and difficult separation from the catalytic systems. To address these issues, a great effort has been devoted to heterogenizing the homogeneous catalysts by attaching them to solid supports. Post-modification has been recognized as a highly versatile methodology, which allows for control over the number and types of functional groups introduced into a pre-made framework, especially for which is difficult to achieve through one-step framework synthesis. A number of porous solid materials, such as porous carbons, porous polymers, mesoporous silicas, and microporous zeolites have been employed as supports for post-modification of the homogeneous catalysts. Notably, the inherent disadvantages of these conventional supports limit their more extensive applications. For examples, the carbon materials are difficult to be modified because of their inert structures; the silica-based materials are not stable in alkaline media; the organic supports such as polystyrene normally have relatively low exposure degree of active sites due to their low surface areas. Therefore, there is still a need to search for new types of platforms for heterogenizing the homogeneous catalysts. These supports should include advantages of (i) robust framework structures with high hydrothermal and chemical stabilities under typical reaction conditions, (ii) high surface areas with a high concentration of the functionalized groups, (iii) ease of functionalization to facilitate the tailoring of active sites.

With these aforementioned advantageous properties, porous organic polymers offer a great opportunity to serve as a promising platform for designing heterogeneous catalysts. As an illustration, it is prepared a swollen porous polydivinylbenzene (PDVB) with hierarchically porous structure from free radical polymerization of divinylbenzene monomer under unique solvothermal conditions.[17] The PDVB constructed from tailorable phenyl ring-derived building blocks with the features of robust structure and high surface area, offers a promising platform for targeted post-modification of various organic groups. For example, sulfonic acid functionalized PDVB-*x* (PDVB-*x*-SO_3Hs, where *x* stands for the volume ratio of H_2O to THF used for the synthesis of PDVB) can be easily obtained by treating dried PDVB with chlorosulfonic acid in CH_2Cl_2, as shown in Figure 5.[18] The sample nitrogen sorption isotherms reveal that the PDVB-*x*-SO_3Hs still have high surface areas and hierarchical porosity. Thanks to a high-density of accessible phenyl ring in PDVB, elemental analysis and acid-base titration showed that abundant of sulfonic groups (as high as 4.1 mmol/g) have been successfully introduced into the PDVB framework. Catalytic tests of esterifications and Friedel-Crafts acylations indicate that the PDVB-0.1-SO_3Hs are more active than the sulfonic groups functionalized mesoporous silicas, zeolite, and Amberlyst-15 catalysts. Particularly, in esterification of bulky lauric acid with ethanol, the PDVB-0.1-SO_3Hs gave very high conversion (99%). In contrast, Beta zeolite and Amberlyst-15 showed relatively low conversion at 11% and 75.2%, respectively due to small micropores (0.67 nm) of Beta zeolite and low surface area (45 m^2/g) of Amberlyst-15. These results demonstrate that the hierarchically porous structure and high surface area in the PDVB-0.1-SO_3Hs are very helpful to enhance the catalytic performance, especially the transformations involving bulky molecules.

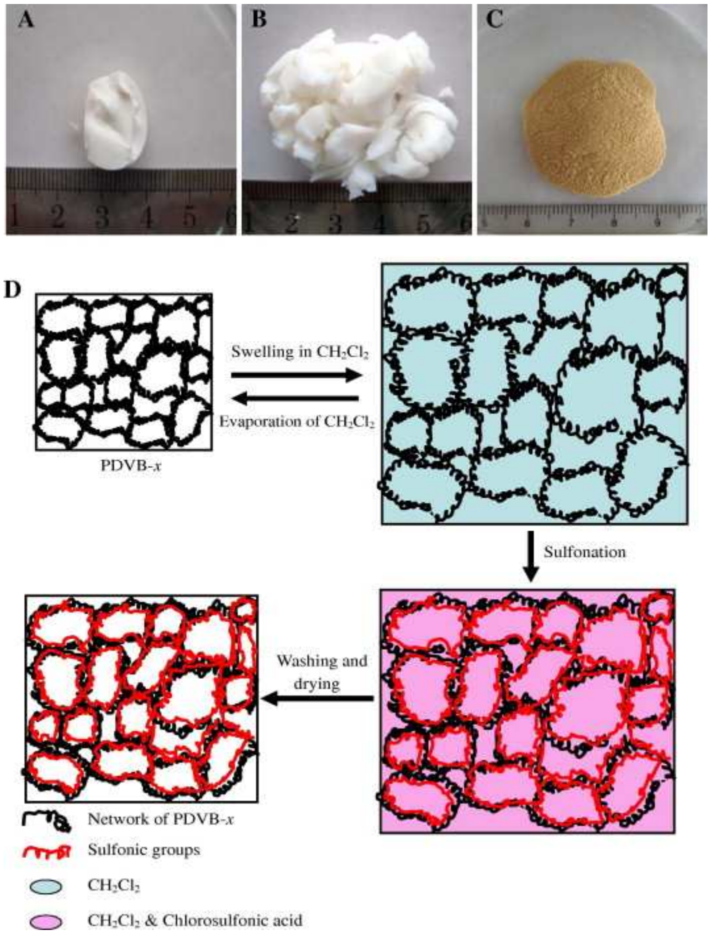


Figure 5. Photographs of PDVB-*0.1* (A) before, (B) after swelling in CH_2Cl_2, and (C) sulfonated PDVB-*0.1* as well as (D) proposed sulfonation of PDVB-*x* samples by chlorosulfonic acid in CH_2Cl_2. The weight amount of polydivinylbenzene (PDVB) in the samples of (A), (B), and (C) is the same. Reprinted with permission from Ref. 18. Copyright © 2010, Elsevier.

Very importantly, pore blocking arising from the post modification can be suppressed even if the PDVB experiences multistep chemical modifications. For example, the hierarchically porous structure of the PDVB is well retained from two-step post-modification of nitration and reduction. The well-preserved hierarchically porous structure is expected to be beneficial for the access of the active sites and mass transfer of the reactions. The PDVB-NH_2 supported metallic Au particles (Au/PDVB-NH_2), exhibit high activity and excellent recyclability in the aerobic oxidation of styrene.[19] Furthermore, the PDVB-NH_2 can be further treated with 2-byridinecarboxaldehyde to afford hierarchically porous Schiff base-modified polydivinylbenzene (PDVB-SB). After metalation with Cu species, the PDVB-SB-Cu gave comparable activity with corresponding homogeneous analogues in Ullmann biaryl ether couplings, which is also assigned to the presence of hierarchical porosity. Notably, this catalyst also exhibits good retention of catalytic activity for at least 5 cycles.[20]

3.2 Co-polymerization of skeleton molecules with functional monomers

Compared with post-modification, the co-polymerization of skeleton molecules with functional monomers has obvious advantages such as uniform distribution of the functional groups in the framework and simple process. Typically, the co-polymerization of hierarchical porous polymers is fabricated from cross-couplings and olefin polymerization. According to the type of catalytically active sites, these porous copolymer catalysts mainly contain (1) small organic molecular groups, (2) organometallic groups, (3) chiral organometallic groups, (4) ionic groups, (5) acidic and basic groups, and (6) metal nanoparticles.

3.2.1 Small organic molecular groups

Small organic molecules (organocatalysts) have emerged as complement biocatalysts and transition metal catalysts, providing distinct reactivity, activity, and selectivity. Despite fruitful advancements in academia, further application of organocatalysts in industry is still hampered by their separation problem.

Heterogenization of these homogeneous organocatalysts presents an interesting solution to both separation and recycling. Porous organic polymers as versatile platforms provide new possibilities in connecting porous polymer networks and organocatalysts.

Wang *et al.* synthesized Tröger's-base-functionalized polymer *via* palladium-catalyzed Sonogashira-Hagihara cross-coupling reaction of Tröger's base derivative (2,8-diiodo-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine, **1**) and 1,3,5-triethynylbenzene as the cross linker in one-pot process (Figure 6).[21] The obtained polymer has a large surface area (750 m^2/g), and evidently contains hierarchical porosity. Interestingly, this hierarchically porous polymer as a heterogeneous catalyst shows comparable activity in the catalytic addition of diethylzinc to 4-chlorobenzaldehyde to that of the corresponding homogeneous analogue.

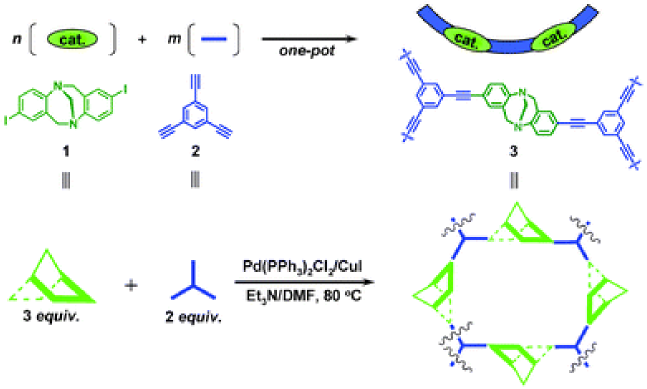
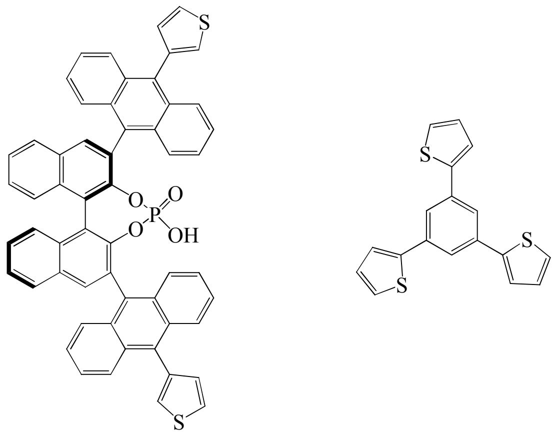


Figure 6. Schematic of "bottom-up" approaches for functionalizing nanoporous materials *via* covalent bonding. An organic nanoporous polymer **3** was constructed in this work by using Tröger's base derivative (one enantiomer **1** is depicted) as the functional groups (catalytic moieties) and 1,3,5-triethynylbenzene **2** as the linkers. Reproduced from Ref. 21.

Later, they successfully prepared the porous polymer (denoted as **JH-CPP**) contained asymmetric organocatalyst of diarylprolinol silyl ethers (Jørgensen-Hayashi catalysts) *via* the $Co_2(CO)_8$-mediated trimerization reaction.[22] The resultant polymer has abundant microporosity and a small amount of mesoporosity. The efficiency of **JH-CPP** catalyst compares well to that of the homogeneous counterpart in catalytic asymmetric Michael addition of aldehydes. The recycling tests indicate that the **JH-CPP** catalyst can be reused at least four times without the loss of enantioselectivity and diastereoselectivity. But, the reaction yield decreased to 51% from 96% in the third recycling experiment. They ascribed the deactivation to partial blocking of the polymeric nanopores, which is reflected by decreasing BET surface area from 750 m^2/g of the fresh catalyst to 578 m^2/g after reused for four times. In this context, construction of polymeric catalysts with abundant mesopores may be of importance for retaining high efficiency of the catalyst. Therefore, they have incorporated a versatile organocatalyst of 4-(*N,N*-dimethylamino)-pyridine (DMAP) into the network of the porous polymer with broader mesopore size distributions (**DMAP-NCP**). The recyclability tests of **DMAP-NCP** in acylation reaction of 1-phenylethanol and acetic anhydride showed that it can be reused for at least 14 iterative runs without loss of activity. The ^{13}C CP/MAS NMR spectrum and the N_2 sorption studies reveal that these parameters recorded after the 14th run are almost identical to that of the fresh catalyst. More importantly, the **DMAP-NCP** catalyst can be easily adopted in fix-bed reactor and there is no activity loss over 536 h, indicating its extraordinary persistent catalytic ability. These results suggest that mesopores throughout the catalyst networks could provide efficient mass transport for the reactants and products, which is very favorable for maintaining the catalytic activity.[23]

Binol-derived phosphoric acid catalysis has intrigued considerable attentions for their excellent catalytic performance in many asymmetric organic transformations, such as transfer hydrogenation, hydrocyanations, and aldol-type reactions. Recently, binol-derived phosphoric acid [(*R*)-3,3-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1-binaphthalen-2,2-diyl-phosphoric acid, BNPPA, Figure 7a] has been successfully embedded into microporous organic ploymers *via* oxidative coupling with thiophene groups using $FeCl_3$ as a catalyst.[24]

The resultant catalyst exhibits superior performance in a series of asymmetric reactions. Furthermore, a family of polymer attached BNPPA were prepared from copolymerization of the BNPPA with 1,3,5-tris(2-thienyl)benzene [TTB, Figure 7b] in different ratios.[25] The surface areas and pore volumes of these copolymers can be adjusted by the polymerization ratio of the BNPPA and the TTB. These polymers have proved to be catalytically active in asymmetric transfer hydrogenation of 2-phenylquinoline. Interestingly, it is observed that the reaction rate can be enhanced by increasing the accessible surface areas and pore volumes of these catalysts. For example, the copolymer network with hierarchical porosity, highest surface area and largest pore volume, constructed by BNPPA/TTB mole ratio at 1/5, affords much higher conversion rate than that of pure BNPPA-constructed microporous polymer network. This experiment confirms that the accessibility of active sites and the diffusion rate of substrates within the network reflected by the surface area and pore structure directly influence the catalytic performance.



(a) (b)

Figure 7. Monomers used for the co-polymerisation of (a) BNPPA and (b) TTB.

3.2.2 Organometallic groups

Organometallic catalysts play an extremely important role in the field of modern catalysis. Driven by the motivation to mimic ubiquitous biological functions of metalloporphyrins and their related compounds in nature such as photo-synthesis and oxygen transportation, porphyrin/metalloporphyrin-based linkers are of increasing interest for incorporation into porous polymer frameworks to afford porphyrin-based heterogeneous catalysts. Budd and McKeown incorporated porphyrin and phthalocyanine molecules into robust nanoporous materials (coexistence of micro- and meso-porosity) with high surface area (500-1000 m^2/g) by covalent binding using the aromatic nucleophilic substitution reaction.[26] Notably, spiro-linked Co phthalocyanine polymer networks with apparent surface areas in the range of 120-612 m^2/g and hierarchical porosity showed considerably enhanced catalytic activities in catalytic H_2O_2 decomposition and cyclohexene oxidation (Figure 8), compared with the insoluble and nonporous analogues. These results presumably indicate that the presence of hierarchical porosity in the heterogeneous catalysts leads to enhanced accessibility of reactants to catalytic sites, giving improved reaction rate.

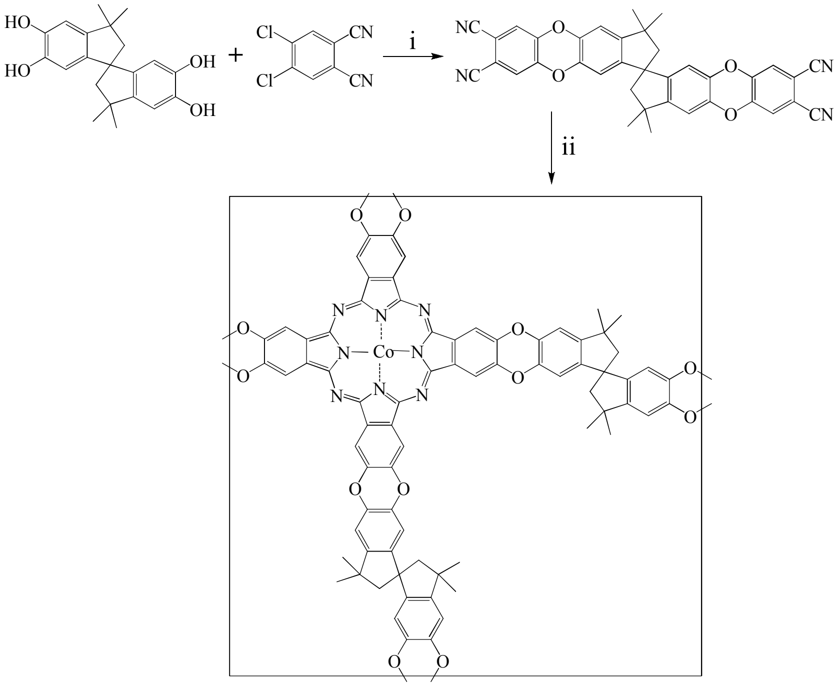
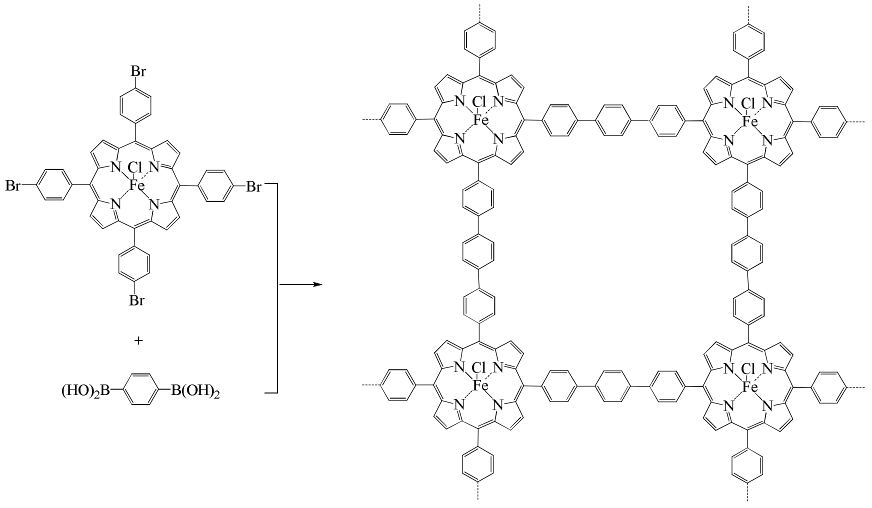


Figure 8. Preparation scheme of spiro-linked cobalt phthalocyanine network polymer (CoPc-PIM-A) utilizing a phthalocyanine-forming reaction. Reagents and conditions: (i) K_2CO_3, DMF, 70 °C; (ii) $Co(CH_3COO)_2$, quinoline, 220 °C.

Jiang *et al.* gave an alternative route for incorporation of porphyrin units into porous polymer networks *via* a Pd catalyzed Suzuki polycondensation of tetrakis(4-bromophenyl)porphyrin derivative and 1,4-phenyldiboronic acid (Figure 9).[27] The achieved polymer designated as FeP-CMP, has high surface area (1270 m^2/g) and hierarchical pores distributed at 0.47 and 2.69 nm, respectively. The FeP-CMP is catalytically active and selective for converting various sulfides to the corresponding sulfoxides using O_2 as the oxidant. Large molecules such as diphenylsulfide can also be efficiently oxidized owing to the presence of mesopores in the FeP-CMP catalyst. Furthermore, in a large scale experiment, the FeP-CMP gives turnover number as high as 97,000 in 40 h, suggesting that mass transport of reactants and products are very fast in the catalyst with hierarchical porosity. This catalyst can be reused at least for 3 times with good retention of catalytic activity.



FeP-CMP

Figure 9. Schematic representation of the synthesis of nanoporous polymer with metalloporphyrin built-in skeleton (FeP-CMP).

Hupp and Nguyen also developed a synthetic route for embedding free-base porphyrin units into the porous polymers by a condensation of bis(phthalic acid)porphyrin and tetra(4-aminophenyl)methane using propionic acid as both catalyst and solvent. After post-synthetic metallation with Fe or Mn species, the obtained catalysts show high activities and excellent recyclabilities for both olefin epoxidation and alkane hydroxylation reactions.[28]

In 2011, Lin *et al.* first introduced phosphorescent $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ building blocks into hierarchically porous cross-linked polymers through $Co_2(CO)_8$-mediated trimerization of the metal complexes of $[(ppy)_2Ir(debpy)]Cl$ and $[(bpy)_2Ru(debpy)]Cl$ (debpy =5,5-diethynyl-2,2-bipyridine) with tetra-(4-ethynylphenyl)methane (Figure 10).[29] Both of the obtained materials possess high surface areas (1547 and 1348 m^2/g for Ir-PCP and Ru-PCP, respectively), broad pore size distributions, and remarkable chemical stabilities. They are efficient catalysts for light-driven reactions such as Aza-Henry reaction, α-arylation of bromomalonate, and oxyamination of 3-phenylpropanalal. Notably, in the mentioned reactions these catalysts exhibit comparable, even higher yields than those catalyzed by corresponding homogeneous catalysts.

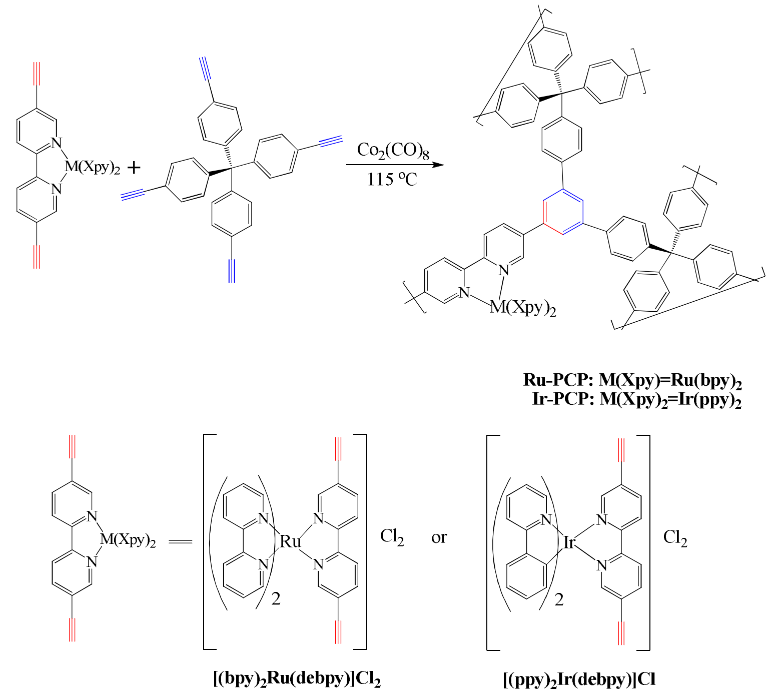


Figure 10. Scheme for synthesis of Ir-PCP and Ru-PCP.

In the same year, Cooper and co-workers also provide a versatile strategy for preparing phenylpyridine/bipyridine-functionalized metal-organic conjugated microporous polymers (MO-CMPs).[30] The MO-CMP networks were prepared by the direct cross coupling of 1,3,5-triethylbenzene, 1,4-dibromobenzene, and a halogenated metal-organic co-monomer *via* palladium catalyzed Sonogashira-Hagihara coupling. Interestingly, this synthetic methodology can rationally adjust the porosity and the metal-organic complexes density. Experimental results indicate that all of the networks were found to be catalytically active in reductive aminations. It is important to mention that CMP-CpIr-3 with hierarchical porosity comprised of micropores and mesopores, gives higher activity than those samples with sole micropores, although the relatively low surface area is given, highlighting the importance of the presence of hierarchical structures to the substantial increase in the catalytic activities.

Later, Li and coworkers reported a "*knitting*" strategy for synthesizing PPh_3 functionalized porous polymer KAPs(Ph-PPh_3) *via* $FeCl_3$ catalyzed Friedel-Crafts reaction of PPh_3, benzene, and cross-linker formaldehyde dimethyl acetal.[31] After metalation with Pd precursor, the obtained heterogeneous catalyst of KAPs(Ph-PPh_3)-Pd exhibits excellent activity and recyclability for the Suzuki-Miyaura cross-coupling of aryl chlorides under mild conditions and aqueous media. This work also emphasizes the importance of hierarchical porosity for the enhancement of catalytic performance and the stabilization of active sites. The microporous structure ensures the high dispersion of Pd active sites and coexistence of mesoporosity and macroporosity improves the diffusion of organic reactant molecules. When the PPh_2-Pd functional groups were grafted on the skeleton of the polystyrene spheres with sole large inter-pore channels (PS-PPh_2-Pd), the catalyst turned black immediately at the beginning of the reaction, which indicates the formation of Pd black and the deactivation of the catalyst. As a result, low activity was observed and the catalyst can not be reused.

Li *et al.* described a controllable synthesis of N-heterocyclic carbene gold(I) functionalized porous organic polymers (Au-NHC@POPs) *via* Sonogashira coupling.[32] The surface areas and pore size distributions of the porous polymer can be turned by varying the co-monomer structural length and concentration of the monomers during the polymerization process (Figure 11). These obtained Au-NHC@

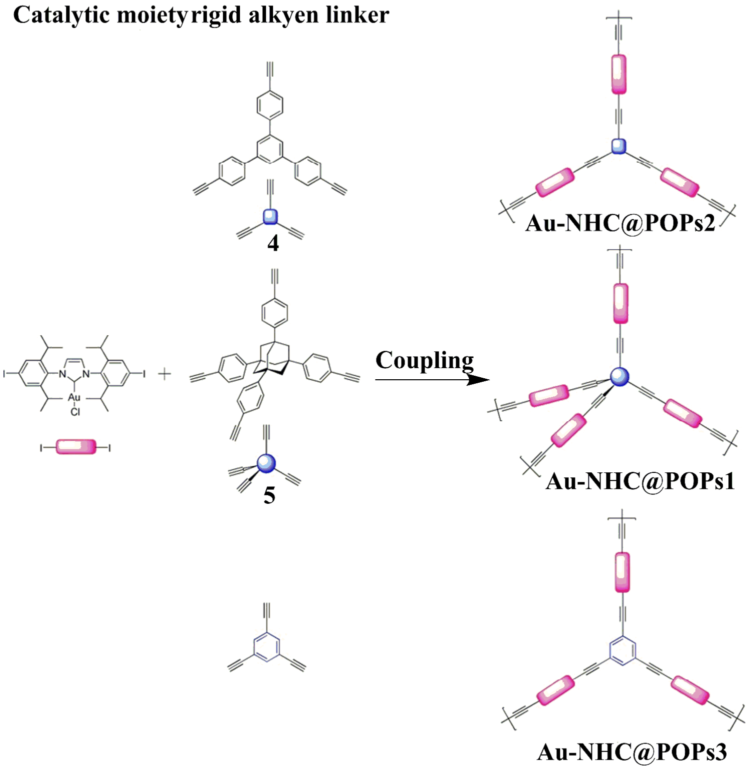


Figure 11. Synthesis of Au-NHC@POPs using the Pd-catalyzed Sonogashira coupling. Reprinted (adapted) with permission from Ref. 32. Copyright © 2014, American Chemical Society.

POPs have been found to be efficient heterogeneous catalysts for alkyne hydration reactions with good substrate tolerance. Interestingly, they give strong evidence that the pore size distributions of the heterogeneous catalysts could severely impact their catalytic performance of bulky molecules. For instance, Au-NHC@POPs1 with hierarchical porosity (coexistence of micropores and mesopores) and moderate surface area (506 m^2/g) has superior catalytic activities involving large alkyne hydration reactions than that of microporous Au-NHC@POPs3 with higher surface areas (798 m^2/g), but they show comparable activities for the smaller substrates. Additionally, catalytic efficiency of Au-NHC@POPs with porosity is much higher than nonporous counterpart with the same molecular composition.

3.2.3 Chiral organometallic groups

It is worth mentioning that asymmetric catalysis has been recognized as one of the most attractive routes to produce enantiomerically pure compounds. Currently, homogeneous chiral organometallic catalysts have been achieved wide acceptance in terms of selectivity and activity, and a few of them are even applied in industrial processes. However, despite a huge amount of works have been devoted to this subject, a plenty of asymmetrically catalytic processes are still limited to laboratory, mainly owing to the scale-up processes suffered from costly preparation of the chiral catalysts/ligands. A promising solution to this task is to use heterogeneous chiral catalysts, which can be recovered and then, potentially, be recycled.

Sun *et al.* provided a universal route for incorporating chiral organic ligands into hierarchically porous organic polymer *via* free radical copolymerization of vinyl-functionalized chiral ligands and divinylbenzene (DVB) under solvothermal conditions. The resultant polymers exhibit obvious chirality, confirmed by their solid (circular dichroism) CD spectra. Variation of the mass ratio of chiral ligands and DVB gives rise to polymers with different concentration of chiral ligands, surface areas, pore volumes, and pore size distributions. For example, chiral 2,2-bis(diphenylphosphino)-1,10-binaphthyl ligand (BINAP), one of the most important and efficient ligands in asymmetric reactions, was incorporated into the hierarchically porous polymer framework (PCP-BINAP, Figure 12a) for the first time.[33] After metalation with $[RuCl_2(benzene)]_2$ species, the heterogeneous chiral catalysts (Ru/PCP-BINAP) show comparable catalytic activities and enantioselectivities in asymmetric hydrogenation of a series of β-keto esters to those of the corresponding homogeneous analogues. Notably, bulky reactants such as 4-methoxyphenyl-3-oxopentanoate can also be efficiently transformed into corresponding chiral alcohols, indicating the importance of the relatively large pores existed in the catalysts. Elemental analysis of the solution after the reaction gave Ru concentration below 0.1 ppm, indicating that Ru species in the catalysts are almost leaching-free. Accordingly, the Ru/PCP-BINAP catalyst could be recycled, retaining both of the activity and the enantioselectivity for at least 6 cycles.

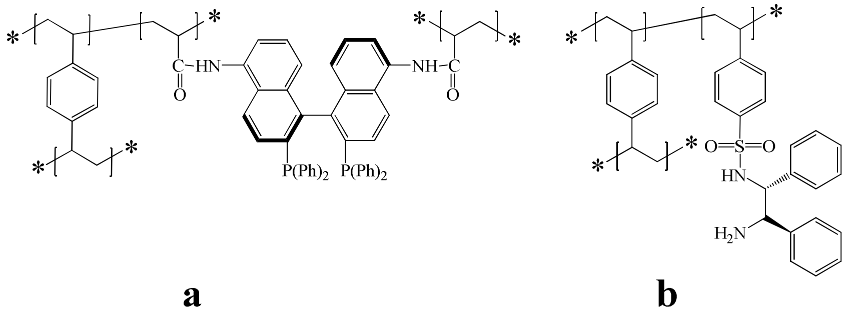


Figure 12. Structures of (a) PCP-BINAP (b) and PCP-TsDPEN.

Furthermore, they rationally designed superhydrophobic heterogeneous chiral catalysts (PCP-TsDPEN-Ru, TsDPEN means N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine, Figure12b), featuring excellent wettability to the lipophilic reactants and easy transfer hydrophilic products from the catalyst into water phase, by controlling the polymerization ratios of the two monomers, DVB and TsDPEN. As a result, the reactants can be highly enriched in the pores of the catalyst. Endowed with these unique features, PCP-TsDPEN-Ru exhibits significantly enhanced catalytic performance in asymmetric transfer hydrogenation (ATH) of ketones, compared with that of the corresponding homogeneous chiral catalyst.[34] More importantly, the PCP-TsDPEN-Ru exhibit extraordinary recyclability, and negligible drops in activity and enantioselectivity are observed after recycling for 14 times.

3.2.4 Ionic groups

Ionic liquids (ILs), a class of compounds consisting of organic cations and anions, show a series of unique properties in chemistry. Besides as solvents, ILs could be also served as catalysts for chemical transformations. However, ILs are relatively costly, and their high viscosity may result in low diffusion rate. An effective methodology to overcome these limitations is immobilization of ILs on porous materials.

Han *et al.* firstly anchored ionic liquids into highly cross-linked porous polymer matrix (PSIL) *via* free radical copolymerization of 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) and the cross-linker divinylbenzene (DVB).[35] The polymer-supported ionic liquid is very active, selective, and stable for the cycloaddition of CO_2 to epoxides. Also, these catalysts can be easily separated from the products and reused. The catalytic activity of the PSIL was comparable or even better than those of the corresponding homogeneous ionic liquid catalysts.

Later, Liu *et al.* successfully incorporated a series of acid ionic liquids into the superhydrophobic hierarchically porous polymer (polydivinybenzene, Figure 13).[36] The achieved catalysts displayed much higher activities in transesterification to form biodiesel than heterogeneous catalysts of ionic liquid supported SBA-15 as well as homogeneous catalysts of the ionic liquids themselves. The unique feature was ascribed to the good miscibility of the reactant in the porous polymers, and the reactant was highly enriched in the catalyst domains and the reaction rate was obviously enhanced.

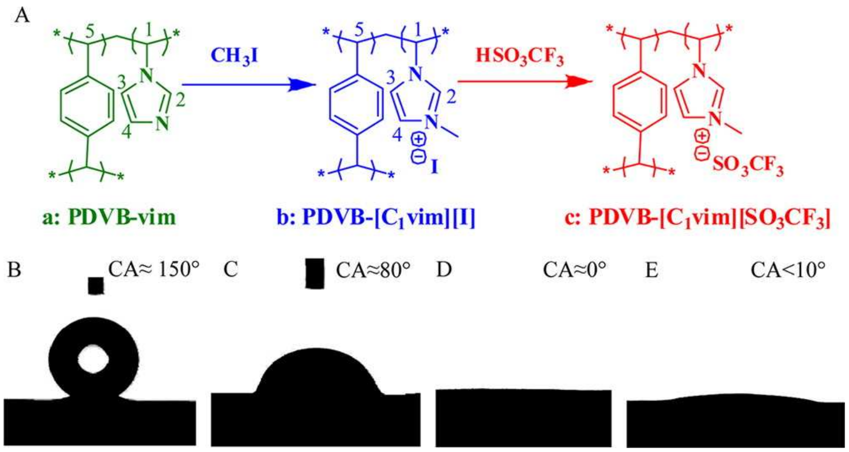


Figure 13. (A) Scheme for the synthesis of PDVB-[C_1vim][SO_3CF_3] from PDVB-vim. Contact angle for a water droplet on the surface of (B) PDVB-vim and (C) PDVB-[C_1vim][SO_3CF_3]. Contact angle of a droplet of (D) methanol and (E) tripalmitin on the surface of PDVB-[C_1vim][SO_3CF_3]. Reprinted with permission from Ref. 36. Copyright © 2012, American Chemical Society.

Thomas *et al.* reported an anion porous anion containing weakly coordinating tetraphenylborate ions fabricated by copolymerization of $Li[B(C_6F_4Br)_4]$ and 1,3,5-triethynylbenzene though Sonogashira coupling.[37] The obtained polymer is expected to have the combined features of porous networks and the intrinsically charged character, in which the counter cations would be mobile and fully accessible, similar to the extra-framework cations in zeolites. Consequently, the anionic polymer network can act as a solid counter ion for immibilization catalytically active cationic species. In addition, the hierarchy of pore sizes of the anion framework is expected to enhance the efficiency of ions exchange as well as potentially anchor bulky ions. As a typical example, $[Mn(bpy)^2]^{2+}$ was immobilized using a "ship-in-the bottle" approach and the resultant network is a promising catalyst for the aerobic oxidation of alkenes.

Apart from the formation of porous polymerized ionic liquids (PPILs) by the covalent bonds, it is also reported a poly(ionic liquid) complex solid (PILC) with spontaneous micro/mesoporosity formed by electrostatic interaction *via in-situ* ionic complexation between imidazolium-based polymerized ionic liquids and poly(acrylic acid) in various alkaline organic solvents (Figure 14).[38] The charged network endows the PILC with the ability to immobilize metal ions, salts, and nanoparticles. As an example, Cu supported PILCs (Cu@PILC) can be easily obtained by treating the PILC and $CuCl_2$ overnight under refluxing. It should be mentioned that after

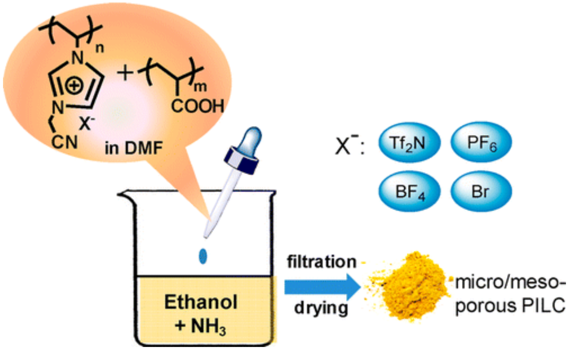


Figure 14. Synthetic route to micro/mesoporous PILC based on PCMVImX PILs and PAA. Tf_2N: bis(trifluoro methanesulfonyl)imide. Reprinted with permission from Ref. 38. Copyright © 2012, American Chemical Society.

metallation, the Cu@PILC still gave a relative high specific surface area of 220 m^2/g and hierarchically porous structure, indicating that this kind of electrostatic interaction is stable under the immobilization process. With the assistance of N-hydroxyphthalimide (NHPI), the Cu@PILC can efficiently catalyze the oxidation of hydrocarbons using air as oxidant under mild conditions.

3.2.5 Acidic and basic groups

Currently, homogeneous acid and base catalysts have been, and still are, widely used catalysts for the production of chemicals, fine chemicals, and even oil refining processes. However, by environmental consideration and safety concerns, the replacement of hazardous and corrosive homogeneous acids or base by solid acids or base is one of the important tasks for green and sustainable production of chemicals. Particularly, the synthesis of porous solid acid catalysts with excellent hydrophobicity should be very desirable for enhancing their performance, because water usually acts as a byproduct in various acid-catalyzed reactions, which not only easily poison the acid sites but also result in the formation of the byproducts. Liu *et al.* designed and synthesized a series of hierarchically porous polymer based solid acid catalysts with excellent hydrophobicity and adjustable acidic concentration by copolymerization of divinylbenzene (DVB) with sodium *p*-styrene sulfonate under solvothermal conditions and then ion-exchange with H_2SO_4 (H-PDVB-x-SO_3Hs, x stands for the mole ratios of sodium *p*-styrene sulfonate with DVB).[39] The hydrophobicity of these H-PDVB-x-SO_3Hs catalysts was evidenced by water contact angle studies. Catalytic tests in esterification of acetic acid with cyclohexanol, esterification of acetic acid with 1-butanol, and condensation of benzaldehyde with ethylene glycol show that the H-PDVB-x-SO_3Hs are more active than those of hydrophilic heterogeneous catalysts such as Amberlyst-15, SO_3H-functionalized ordered mesoporous silicas, and Beta and USY zeolites. Impressively, the catalytic activity of H-PDVB-x-SO_3Hs catalysts is even comparable with that of homogeneous catalyst H_2SO_4. The superior catalytic performance of H-PDVB-x-SO_3Hs is attributed to the sample unique feature of excellent hydrophobicity and hierarchically porous structure.

It is well known that the acid-catalyzed conversion of fructose to 5-hydroxymethylfurfural (HMF) is often accompanied by the side reaction that HMF is tend to rehydrates to form levulinic acid and formic acid, resulting in low HMF selectivity. Interestingly, when aforementioned superhydrophobic catalyst H-PDVB-0.05-SO_3H was employed, the hydration of HMF was not detected, giving HMF as sole product. This phenomenon may be reasonably ascribed to that the unique superhydrophobicity of the catalyst can prevent water molecules contacting with acidic sites, and as a result the catalytic hydration of HMF can be completely avoided.[40]

In the base-catalyzed reactions, a great challenge is the stability of the base catalysts because conventional bases easily lose their alkalinity due to the interaction between the basic sites with CO_2 in the air. Interestingly, superhydrophobic base catalysts with hierarchical porosity formed by copolymerization of divinybenzene and 1-vinylimidazolate (PDVB-VI-*n*, where *n* is the molar ratio of 1-vinylimidazolate with divinylbenzene), are very stable, which completely avoid the interaction with CO_2 in the air.[41] As a result, catalytic tests in the methanol transesterification of tripalmitin show that the synthesized superhydrophobic solid base catalysts are highly active and exceptionally recyclable. Here, the superhydrophobicity and good oleophilicity of PDVB-VI catalysts are very favorable for the miscibility of the reagents methanol and tripalmitin, whereas hydrophilic by-product glycerol quickly leave the hydrophobic catalysts along with the reaction proceed, which result in promotion of the catalytic activity in transesterification reaction.

3.2.6 Metal nanoparticles

Conjugated microporous polymers (CMPs) developed by Cooper *et al.*[42] are unique, which allow the complementary utilization of π-conjugated skeletons and nanopores for functional exploration. However, pore sizes imposed by CMPs are predominated in the micropore regime and thus incorporation of metal nanoparticles into CMP networks appears to be rather challenging. Recently, conjugated nanoporous polymer (CNPC) with a dual pore size distribution (both micropore and mesopore) have been successfully synthesized by Guo and coworkers by taking the advantages of emulsion technique during the polymerization of poly(*p*-phenyleneethynylene) (PPE).[43] Their experimental results show that the presence of mesoporosity in the polymers is really helpful to the dispersion of Pd nanoparticles within the network. The formed Pd@CNPC composite materials are validated to have excellent catalytic activity, outstanding reusability, and exceptionally high TOF (44100 h^{-1}) for the Suzuki-Miyaura coupling.

More recently, Schüth *et al.* also gave strong evidence of the positive effect of the unique conjugated aromatic structure in the porous organic polymer on the catalytic preformance.[44] They described a solid polyphenylene synthesized from palladium-catalyzed Suzuki-Miyaura coupling reaction of 1,2,4,5-tetrabromobenzene and benzene-1,4-diboronic acid. During the catalytic polymerization, the cross-coupling catalyst, tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], was found to decompose into palladium nanoparticals. As a result, the formed palladium nanoparticals were *in-situ* confined in the porous polyphenylene network (Figure 15). Surprisingly, the resultant composite solid is in turn highly active for catalyzing Suzuki couplings, including non-activated aryl chloride. In contrast, this extraordinary activity is absent when Pd nanoparticles supported on active carbon or polydivinylbenzene. They reasonably attribute this phenomenon to the unique π-π

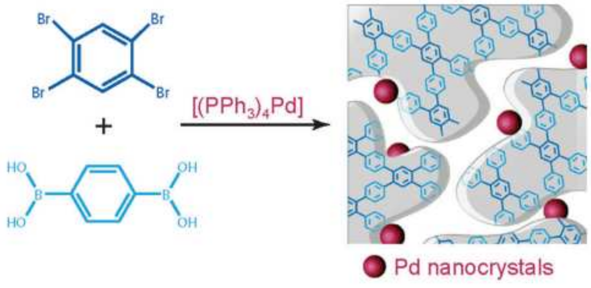


Figure 15. Formation of Pd/PPhen by [$(Ph_3P)_4Pd$]-catalyzed coupling of 1,2,4,5-tetrabromobenzene and benzene-1,4-diboronic acid. Reprinted with permission from Ref. 44. Copyright © 2014, Wiley.

interactions of the polymer framework with the substrates in the vicinity of the catalytic palladium species, which is similar to the proposed effect of conjugated aromatic ligands in C-C coupling reactions catalyzed by palladium complexes.

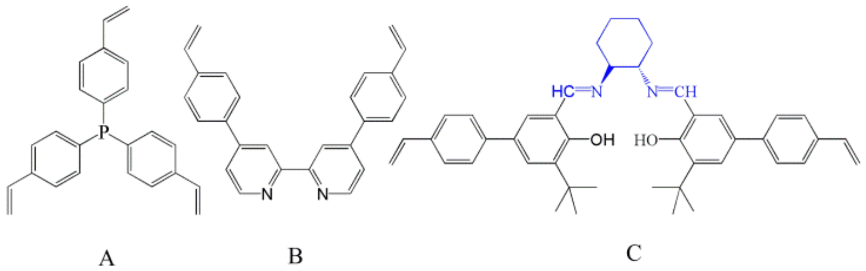
3.3 Self-polymerization of functional monomers

Compared with co-polymerization, the self-polymerization of porous polymerized polymers from functional monomers themselves has very high concentration of functional groups, which is very helpful for preparation of highly efficient heterogeneous catalysts for organic transformations. Typically, in the hydroformylation processes, a large excess of phosphine ligands (the mole ratio of phosphine ligands to metal species are normally higher than 10) in the homogeneous catalysis are usually required for realizing the high activity and selectivity, but the heterogeneous catalysts are not easy to have such high concentration due to the difficulty for immobilization of a large amount of the phosphine ligands on the supports.

Recently, Sun *et al.* reported a facile and universal route to synthesize hierarchically porous organic ligands (POLs) such as triphenylphosphine, 2,2-bipyridyl, and salen (Figure16) *via* self-polymerization of corresponding vinyl-functionalized organic ligands under solvothermal conditions.[45] The POLs constructed from organic ligand-derived building blocks, feature extremely high concentration of organic ligands, high surface areas, large pore volumes, hierarchical porosity, and robust structures with high hydrothermal and chemical stabilities. In addition, due to insolubility of the POLs in nature, they play roles as both supports and ligands. After metalation, the obtained materials could be served as heterogeneous catalysts (M/POLs), exhibiting excellent performance in their classical reactions. For instance, POLs bearing triphenylphosphine supported rhodium catalyst (Rh/POL-PPh_3, Rh loading at 2.0 wt.%) gives very high activity in the hydroformylation of 1-octene.

Moreover, the Rh/POL-PPh_3 also exhibits much higher selectivity for the corresponding aldehydes than those of homogeneous catalysts of $RhH(CO)(PPh_3)_3$

and $Rh(CO)_2(acac)$ under similar conversions. This feature is reasonably related to the high concentration of PPh_3 in the Rh/POL-PPh_3 catalysts. More importantly, the heterogeneous catalyst also shows excellent recyclability, which could be recycled at least for 6 times, without any loss of its activity. Metal leaching is also not observed, which might be assigned to that a lot of free PPh_3 in the Rh/POL-PPh_3 could act as a reservoir for these Rh species, if any, leaching into the reaction media.



POLs	Ligands	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
POL-PPh_3	A	1086	1.70
POL-bpy	B	525	0.86
POL-salen	C	490	0.38

Figure 16. Structures of vinyl-functionalized organic ligands and textural parameters of corresponding polymeric organic ligands of (A) triphenylphosphine (PPh_3), (B) 2,2'-bipyridyl (bpy) and (C) salen.

More recently, it is also synthesized a series of porous polymerized organocatalysts (PPO, Figure17) bearing 2,2,6,6-tetramethylpiperidine 1-oxyl (PPO-TEMPO), BINOL-phosphoric acid (PPO-BNPA), and 2-methyl-CBS-oxazaborolidine (PPO-CBS).[46] They also can be obtained quantitatively, showing high surface area, large pore volume, hierarchical porosity, superior stability, and extremely high concentration of active sites. Chosen as a typical example, the PPO bearing TEMPO (PPO-TEMPO) with stable radicals, exhibits high activity and excellent recyclability in catalytic selective oxidation of primary alcohols to corresponding aldehydes or ketones, using NaOCl as oxidant. Recycling tests indicate that no obvious decrease was observed in terms of catalytic activity and selectivity of recovered catalysts. In contrast, MCM-41 (a typical mesoporous silica material) grafted TEMPO could not maintain the catalyst performance because silica is liable to be dissolved and result in the leaching of active radicals under the alkaline condition.

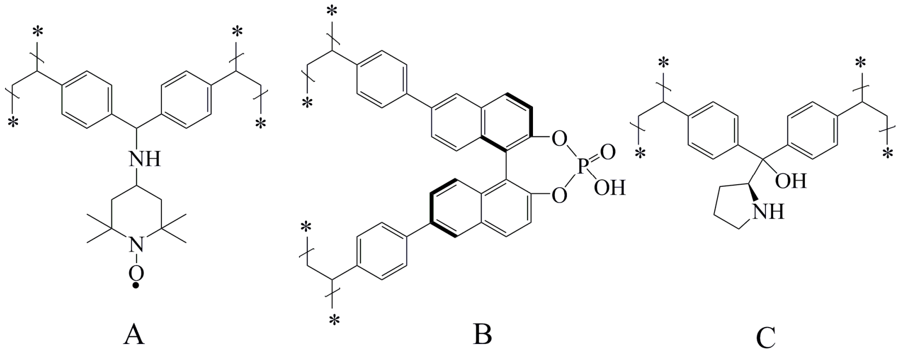


Figure 17. Structures of porous polymerized organocatalysts (PPOs) of (A) PPO-TEMPO, (B) PPO-BNPA and (C) PPO-RDPP.

Lin *et al.* have successfully synthesized porous polymerized tetra(ethynyl)

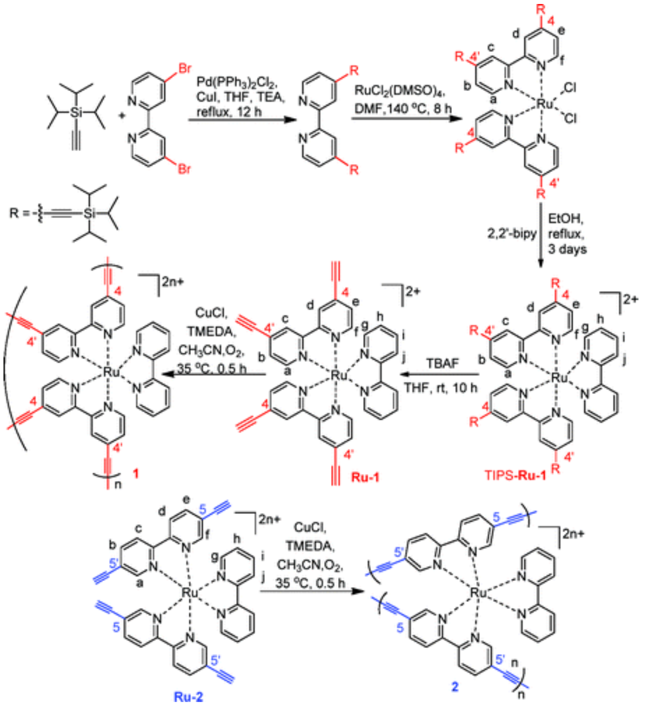


Figure 18. Synthesis of Ru(bipy)$_3$$^{2+}$-based cross-linked polymers 1 and 2. Reprinted with permission from Ref. 47. Copyright © 2012, American Chemical Society.

derivatives of $Ru(bpy)_3^{2+}$ (CP 1 and 2, Figure18) *via* Eglinton homocoupling.[47] The obtained polymers have very high $Ru(bpy)_3^{2+}$ loadings, exhibiting broad absorption bands together with relatively long excited state lifetimes. These features make them good candidates as heterogeneous photocatalysts. Catalytic tests of aza-Henry reactions, aerobic oxidative coupling of amines, and reductive dehalogenation reactions indicate that the CP catalysts are highly active and recyclable photocatalysts. The excellent photocatalytic properties is directly attributed to their high concentrations of chromophores such as $[Ru(bpy)_3]^{2+}$ in the porous materials, which can not only enhance visible light absorption but also facilitate excited state migration in the networks through Dexter triplet to triplet energy transfer.

Lin and coworkers also synthesized a series of tetraalkynyl derivatives of the chiral 1,1-binaphthyl compounds *via* Co-mediated trimerizations.[48] The resultant chiral polymers display relative high surface (689-974 m^2/g) and hierarchical porosity. Treatment of chiral dihydroxyl-containing CCPs with $Ti(O\textit{i}Pr)_4$ gives rise to CCP/Ti catalysts, which is highly active in asymmetric diethylzinc addition to aldehydes, affording secondary alcohols in quantitative yields with moderate to good *e.e.* values (55 to 81%). In addition, these catalyst systems can be recycled for up to 10 times without loss of any conversion or enantioselectivity.

Covalent triazine-based porous polymer frameworks (CTFs) formed by trimerization of aromatic nitriles in molten zinc chloride at high temperatures (normally higher than 400 °C) were first reported by Thomas *et al*. This dynamic polymerization system provides exceptionally high surface areas (up to 3300 m^2/g) with controllable pore structure in amorphous organic materials. The resultant materials exhibit rather excellent thermal and chemical stabilities. More importantly, the high nitrogen content found in these materials could yield possible coordination sites for transition metal catalysts, and the hierarchical porosity facilitates transport by orders of magnitude. The CTFs are expected as promising solid matrixes for methane oxidation owing to their excellent thermal stability as well as extraordinary resistance to strongly oxidizing conditions. The platinum-modified CTFs (Pt-CTF) can be prepared by treating $K_2[PtCl_4]$ and CTF during the reaction or by pre-coordination of platinum in a separate step (Figure 19).[49] The obtained catalysts are highly active and extraordinarily stable under harsh reaction conditions of concentrated sulfuric acid at 215 °C. They also supported Pd nanoparticles on the CTF (Pd/CTF). Compared with Pd nanoparticles supported on active carbon catalysts (Pd/AC), the Pd/CTF appeared more resistant to deactivation and more selective toward glycerate in glycerol oxidation due to the huge amount of nitrogen functionalities in the framework.[50]

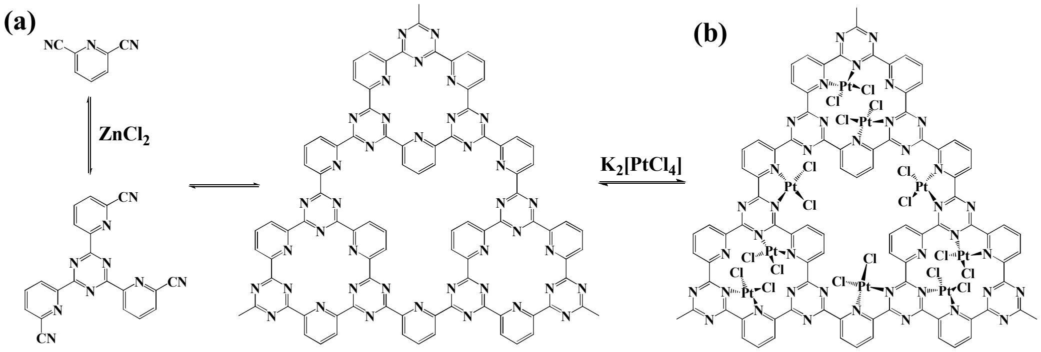


Figure 19. Synthesis of (a) Trimerization of 2,6-dicyanopyridine (DCP) in molten ZnCl$_2$, conversion to a covalent triazine-based framework (CTF) and (b) Periana's platinum bipyrimidine complex.

4. Conclusion and perspectives

Porous organic polymers formed by irreversible polymerization reactions, combining the advantages of high surface areas, excellent stabilities, designable pore walls, and hierarchical porosity, have been proved to be as one of the most promising platform for the deployment of heterogeneous catalysts. Considering the versatility of design and conditions employed for the fabrication of polymers themselves, a wealth of new tools are available for the design and construction of porous polymers, providing unprecedented possibilities for creation of novel materials, either by direct synthesis or by post-modification. In particular, the porous structures can be retro-designed based on knowledge accumulated by analyzing the correlations between porous structure, functionality, and performance. It has been verified that the presence of hierarchical porosity in the polymer is very helpful to enhancing the catalytic performance, especially for those reactions involved relatively large molecules.

It is important to note that, nowadays, a majority of template-free synthesis of porous polymers involves metal-catalysts under harsh reaction conditions. Recent successful synthesis of porous polymers formed by metal-free polymerization based on free radicals under solvothermal conditions offers a promising route for synthesizing functional hierarchically porous organic polymers on the concept of green chemistry. Particularly, the successful preparation of porous organic ligands opens a door for synthesizing efficiently heterogeneous catalysts in the organic transformations in the future. Meanwhile, continuous effort should be made to develop procedures that permit scalable fabrication of hierarchically porous organic polymers using environmentally friendly and low-cost methodologies, since a large volume of production is a prerequisite for many potential applications.

Acknowledgment

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