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Task-Specific Design of Porous Polymer Heterogeneous Catalysts beyond Homogeneous Counterparts

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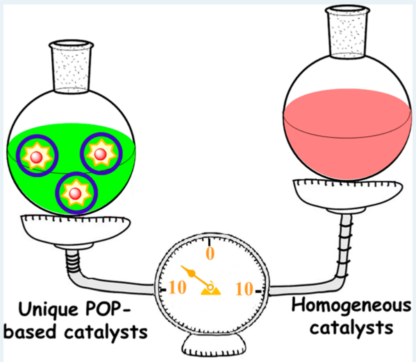
ABSTRACT: Porous organic polymers (POPs), which feature high surface areas and designable pore walls, have attracted much attention recently as a result of combining the advantages of both heterogeneous and homogeneous catalysts. Because of the diversity of chemical reactions, one could design polymer frameworks with unique functionalities used as active sites and ligands in catalysis. In the view of green chemistry, this perspective is focused mainly on rational preparation of the porous organic polymers under metal-free conditions and their applications in heterogeneous catalysis. It is observed that many POP-based heterogeneous catalysts demonstrate superior catalytic properties, even better than the homogeneous counterparts. The strategies for designing highly efficient heterogeneous catalysts are briefly assessed.



KEYWORDS: *porous organic polymers, covalent organic frameworks, heterogeneous catalysis, metal-free polymerization, adjustable wettability*

1. INTRODUCTION

Catalysis plays critical roles in modern society, and improvements in catalytic processes could not only increase efficiency of chemical transformations but also reduce wastes and environmental impact.[1−3] The search for highly selective and active catalysts, especially those that can be readily recycled, is vital for the development of sustainable chemical processes. Continuous efforts in catalysis have been devoted toward developing heterogeneous catalysts with easy recyclability as well as fully accessible and highly designable active sites.[4−8] To this end, a series of porous organic polymers (POPs) with high surface areas, excellent stabilities, controllable chemical composition, and designable pore walls have been successfully developed.[9−16] These POPs have unique features listed in the following: (1) Similar to homogeneous catalysts, POPs inherit excellent chemical tunability afforded by the wide range of functionalized groups employed in their construction. (2) Like a heterogeneous catalyst support, POPs are insoluble in the reaction media, thereby enabling them to be easily recycled. (3) The wettability of POPs is easily adjusted, which is very favorable for improving mass transfer and catalyst performance. (4) The nanosized pores in the POPs could effectively enrich the reactants, thus enhancing catalytic activities. Obviously, the POP-based catalysts combine the best features of both homogeneous and heterogeneous catalysts. As a result, they even exhibit better catalytic performance than the homogeneous counterparts.

POPs generally constructed with strong covalent bonds could be mainly divided into crystalline and amorphous phases. The crystalline POPs represented by covalent organic frameworks (COFs) constructed by linking light elements, such as carbon, boron, oxygen, and silicon, exhibit large surface areas and uniform porous structures,[17−20] whereas the amorphous POPs usually give disordered porous structures and relatively wide pore size distributions.[21−27]

The past decade has witnessed an expansion of synthetic methodologies of porous polymers owing to the flexibility of molecular design, coupled with the diversity of chemical reactions developed in the organic synthesis. Numerous metal-catalyzed couplings, such as Yamamoto,[28−30] Sonogashira-Hagihara,[31] oxidative couplings,[32] Suzuki-Miyaura,[33] Friedel—Crafts,[34−36] nitrile cyclotrimerization,[37,38] terminal alkyne trimerization,[39,40] olefin metathesis,[41] and CuAAC click,[42] have been well established and provide a wealth of opportunities to yield POPs with predesignable structures and functions. Despite these rapid advances, a long-term goal for the preparation of porous polymers is to develop polymerization protocols that are more environmentally friendly and economically beneficial. Notably, the employment of metal catalysts inevitably increases the cost of preparation and the environmental burden because a large amount of metal catalysts are usually needed to achieve highly cross-linked porous polymers. For example, stoichiometric bis(1,5-cyclooctadiene)nickel catalyst is often required to obtain high-quality polymers polymerized via the Yamamoto reaction.[28−30] In addition, the residual metal species may contaminate the polymer, and complete removal of these metals is not easy, even using treatment under harsh conditions, such as strong

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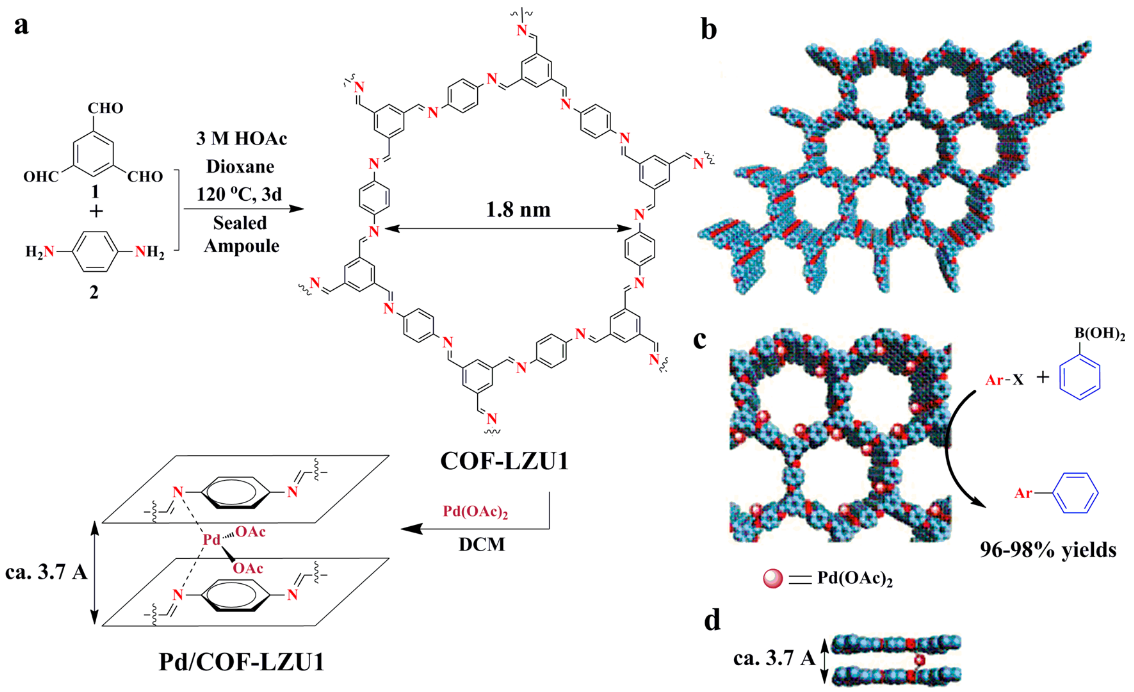
Scheme 1. Construction of COF-LZU1 and Pd/COF-LZU1[a]



[a](a) Schematic representation for the synthesis of COF-LZU1 and Pd/COF-LZU1 materials. (b) Proposed structure of COF-LZU1 and (c,d) Pd/COF-LZU1 possessing regular microporous channels (diam. 1.8 nm), simulated with a 2D eclipsed layered-sheet arrangement. C, blue; N, red; brown spheres represent the incorporated $Pd(OAc)_2$. H atoms are omitted for clarity. Reprinted with permission from ref 56. Copyright 2011, American Chemical Society.

acid conditions.[43] Fortunately, in addition to these couplings involving metal catalysts, a variety of metal-free processes, such as free-radical polymerization,[44,45] keto-enamine,[46,47] benzodioxane formation reaction,[48] superacid-catalyzed nitrile cyclotrimerization,[49] amine anhydride condensation,[50] boronate ester,[51] imine,[52] boronate anhydride,[53] hydrazone,[54] and borosilicate[55] condensations, have been successfully developed. In these cases, customized functionalities have also been rationally introduced for target applications.

From the concept of green chemistry, the development of sustainable preparation strategies of porous polymers has already become and will continue to become a thriving area of research. In this Perspective, we present a comprehensive summary of POPs synthesized under metal-free conditions and their properties in heterogeneous catalysis, with an emphasis on the substantial benefits of the pore structures and polymer matrix to the catalytic performance of active sites.

2. CRYSTALLINE POROUS ORGANIC POLYMERS AS PLATFORMS FOR HETEROGENEOUS CATALYSIS

COFs have exhibited superior potentials in gas adsorption and separation, photoelectricity, and catalysis since the pioneer contributions made by Yaghi and co-workers.[17] Wang et al. first realized the application of COF materials in catalysis.[56] They rationally synthesized a 2D imine-linked framework (COF-LZU1) by condensation of 1,3,5-triformylbenzene and 1,4-diaminobenzene (Scheme 1). The resultant framework adopts a nearly eclipsed layered crystal with 1.8-nm-wide pores, which not only makes the COF-LZU1 material an ideal scaffold for incorporating a variety of metal ions but also offers efficient access to the active sites and fast diffusion for the bulky products. As a proof-of-concept, Pd species were introduced through bidentate coordination of proximal N atoms in adjacent layers. The yielded catalyst Pd/COF-LZU1 exhibits excellent performance in catalytic Suzuki reactions as elucidated by the broad substrate tolerance, high activity (the products yields are often >96%), and good recyclability (at least 4 times).

Later, inspired by the pioneer work demonstrated by Jiang and co-workers that a squaraine-based COF can be utilized in the light-induced activation of oxygen,[57] Lotsch et al. developed a hydrazone-based COF (TFPT-COF) photocatalyst.[58] The TFPT-COF was constructed from 1,3,5-tris(4-formylphenyl)-triazine (TFPT) and 2,5-diethoxyterephthalohydrazide (DETH), giving a layered structure with a honeycomb-type lattice featuring mesopores of 3.8 nm and a very high surface area (1603 m^2/g). Interestingly, this framework is competitive with the state-of-the-art nonmetal photocatalysts in hydrogen evolution under visible light irradiation in the presence of Pt as a proton reduction catalyst. More importantly, the COF scaffold exhibits great opportunities for modification, which is very important for the underlying mechanism and enhancing its light harvesting capability.

Yan and co-workers[59] designed and synthesized two new 3D microporous base-functionalized COFs by imine-bond condensation of 1,3,5,7-tetraaminoadamantane (TAA) and 1,3,5-triformylbenzene (TFB) or triformylphloroglucinol (TFP). The obtained COFs exhibit high catalytic activities and excellent recyclability in catalytic Knoevenagel condensation. Particularly, they also show superior shape selectivities in the catalysis, which is very similar to those in zeolite catalysis.

Despite these achievements, it is widely recognized that the synthesis of COFs is very difficult because the microscopic reversibility of the crystallization of monomers into such COFs is necessary, where harsh experimental conditions such as reaction in a sealed pyrex tube and inert atmosphere are required.[19] This feature is not favorable for a large scale preparation and practical operations. More importantly, their relatively high sensitivity to moisture, especially in the presence of acidic chemicals, still remains an important issue to be addressed for their real applications.

3. AMORPHOUS POROUS ORGANIC POLYMERS AS PLATFORMS FOR HETEROGENEOUS CATALYSIS

Compared with COFs, amorphous POPs usually connected by irreversible covalent bonds have very high chemical stabilities. This feature is critical for their catalytic applications. In addition, the preparation of amorphous POPs can be operated under relatively mild conditions, which is desirable for scalable production. In the following section, we give an overview on the current research in the amorphous POPs as catalysts and/or organic ligands, which are synthesized under metal-free conditions.

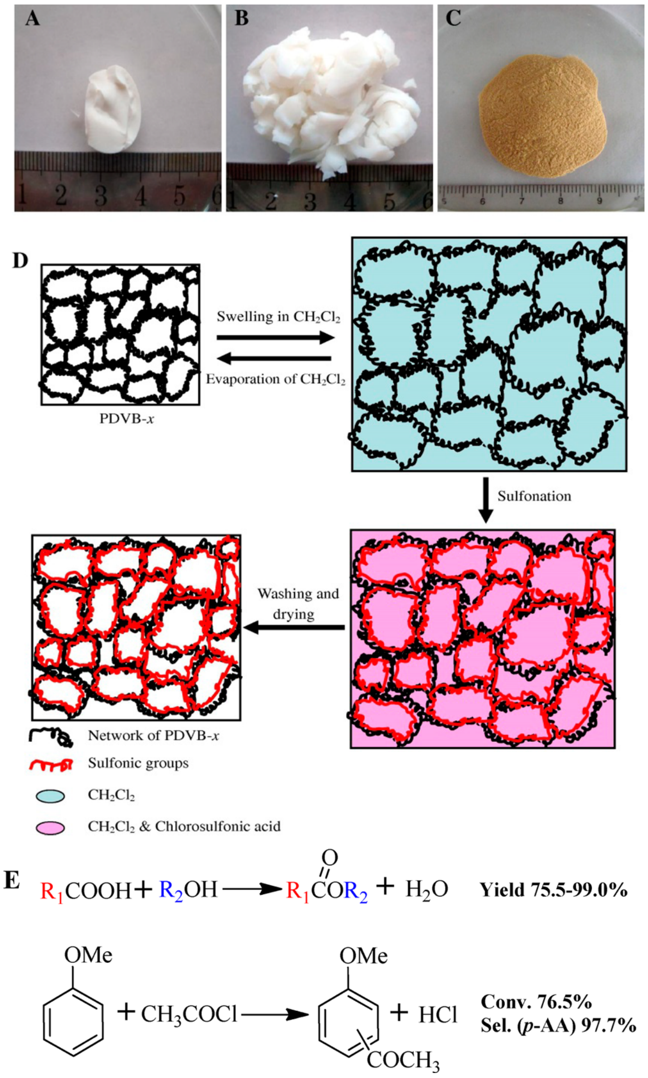
3.1. Stability and Functionalization. The extraordinary stability of the POPs is verified by their exceptional tolerance to a variety of postgrafting processes. For example, after treatment of polydivinybenzene (PDVB) with a strong oxidizing reagent, $ClSO_3H$, a large amount of SO_3H groups can be loaded in the porous PDVB structures (Scheme 2).[60] Nitrogen sorption isotherms reveal that the SO_3H-functionalized PDVB sample still retains its porous structure (SO_3H-PDVB). In the context of esterifications of hexanoic acid with ethanol, acetic acid with cyclohexanol, and lauric acid, the SO_3H-PDVB exhibits a much better catalytic performance than Amberlyst-15 and Beta. Particularly, even if multitreatments include nitration, reduction, aldimine condensation, and coordination, the obtained Cu metalated Schiff base-modified PDVB (PDVB-SB-Cu) still maintains its porous structure (Scheme 3).[61] In contrast, the porous structure of the COFs could be completely destroyed by similar treatments.[62,63] These results confirm the excellent stability of the porous structures in the amorphous PDVB-based POPs. Notably, the resultant PDVB-SB-Cu shows comparable catalytic activities with soluble copper salt in the context of Cu-catalyzed Ullmann biaryl ether coupling.

From the aforementioned examples, it is worth noting that POPs are easy to functionalize with various organic groups because of the reactivity of the organic framework and diversity of organic reactions as well as the stability of the POPs, which provides great opportunities for designing efficient heterogeneous catalysts with required active sites and ligands.

Apart from the post-treatments, functional groups can also be introduced into the POPs by polymerization of the functionalized monomers in the synthesis, in which both the functional groups and polymer matrix could be precisely adjusted. These adjustments could obtain controllable wettability and hierarchical porosity of the samples. The catalyst-suitable wettability is beneficial for access of reactants, and the catalyst hierarchical porosity is favorable for mass transfer of reactants and products. For convenience, we will give a brief summary according to the functional groups in the following parts, mainly including acidic and basic sites, ionic liquids, organometallic groups, and organocatalysts.

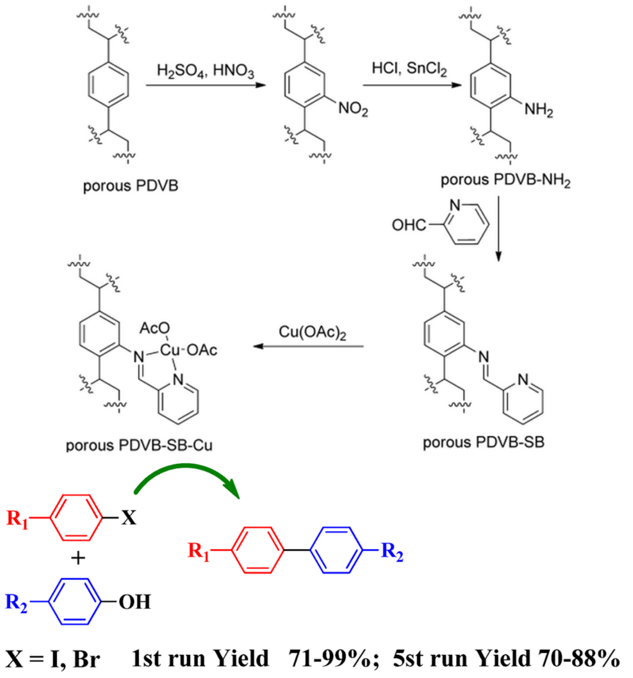
3.2. Acid and Base Catalysis. It is well-known that water usually acts as a byproduct in many acid-catalyzed reactions, which not only easily poisons the active sites but also gives rise to side reactions.[64] Liu et al. have rationally designed and synthesized a series of solid acid catalysts with controllable hydrophobicity by copolymerization of sodium *p*-styrenesulfonate and divinylbenzene in different ratios, followed by the treatment of H_2SO_4 solution.[65] Particularly when the molar ratio of sodium *p*-styrenesulfonate to divinylbenzene is lower than 0.05, the resultant acid catalyst (H-PDVB-0.05-SO_3H) exhibits a superhydrophobic feature. The performances of these solid acid catalysts were evaluated in the context of esterification of acetic acid with cyclohexanol, esterification of acetic acid with 1-butanol, and condensation of benzaldehyde with ethylene glycol. Notably, the superhydrophobic H-PDVB-0.05-SO_3H catalyst affords the highest activity in terms of turnover frequency. This acid catalyst also exhibits much higher activities than other solid acid catalysts, such as Amberlyst-15, SBA-15-SO_3H, and zeolites, which imply that the catalyst superhydrophobicity is very helpful to isolate water from the active sites, then shifting the reaction equilibrium.

Scheme 2. Photographs of PDVB-0.1 (A) before and (B) after Swelling in CH_2Cl_2; (C) Sulfonated PDVB-0.1 as well as (D) Proposed Sulfonation of PDVB-*x* Samples by Chlorosulfonic Acid in CH_2Cl_2 and (E) Catalytic Esterifications and Acylation of Anisole with Acetyl Chloride over PDVB-0.1-SO_3H Catalyst[a]



[a] The weight amount of polydivinylbenzene (PDVB) in the samples of A, B, and C is the same. Reprinted with permission from ref 60. Copyright 2010, Elsevier.

Scheme 3. Synthesis of Copper-Incorporated Porous Organic Polymer Catalyst and Its Catalytic Properties in the Ullmann Couplings[a]



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It has been reported that acid-catalyzed conversion of fructose to 5-hydroxymethylfurfural (HMF) is often accompanied by the side reaction of HMF hydrolysis to byproducts of levulinic acid (LA) and formic acid (FA), which significantly reduces HMF yield.[66] Interestingly, when the superhydrophobic H-PDVB-0.05-SO_3H catalyst was employed to catalyze this reaction, the hydrolysis of HMF was successfully suppressed, giving the HMF as sole product. In contrast, a considerable amount of byproducts was detected over hydrophilic Amberlyst-15. These results suggest that the creation of a superhydrophobic barrier can hinder the water from interacting with the acid sites, thereby preventing the acid-catalyzed hydrolysis of HMF.[67]

Furthermore, Liu et al. reported successful fabrication of a superhydrophobic and porous solid base catalyst (PDVB-VI-0.5) via copolymerization of divinybenzene and 1-vinylimidazolate under solvothermal conditions.[68] Catalytic tests in the methanol transesterification of tripalmitin show that the superhydrophobic solid base catalyst is much more active than the corresponding homogeneous analogue and a variety of hydrophilic base catalysts such as basic resin, hydrotalcite, CaO, and NaOH. The superhydrophobicity of the catalysts should be responsible for the superior catalytic performance, as evidenced from the contact angle measurements. Superhydrophobicity of the PDVB-VI-0.5 is expected to be very favorable for the miscibility of the reagents methanol and tripalmitin, whereas relatively hydrophilic byproduct of glycerol quickly leaves the hydrophobic catalysts along with the reaction progress, which results in the promotion of the transesterification. In contrast, it is speculated that hydrophilic catalysts should be a benefit to the miscibility of hydrophilic reactants, thereby accelerating the conversion of these reactants. As expected, Wang et al. show that the superhydrophilic base catalysts formed by copolymerization of divinylbenzene, 1-vinylimidazole, and *N*,*N*-methylenediacrylamide exhibit excellent activity and selectivity in the isomerization of hydrophilic glucose to fructose, as compared with other base catalysts.[66]

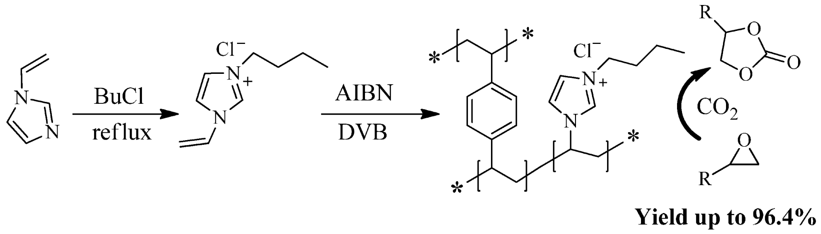
Generally, for the acid and base catalysts, it is mainly focused on the investigation of their density, strength, and type, and their wettability is sometimes ignored.[69] In this perspective, importance of the catalyst wettability is noted because catalysis is strongly related to the adsorption and desorption of the reactants and products, which are remarkably influenced by the catalyst wettability.

Kaskel's group reported synthesis of element organic frameworks (EOFs) with acidic properties.[70] These materials contain elements such as tin, antimony, and bismuth as nodes connected through covalent bonds to the carbon atoms of the aromatic linker synthesized from the treatment of lithiation of 4,4′-dibromobiphenyl and the corresponding element chloride in a one-step procedure. The structural and functional "defects" of the resultant porous polymers are responsible for these acidic properties. For example, open metal centers provide Lewis acidic sites, whereas hydroxyl groups at the metal centers could function as weak Brønsted acidic sites. As a result, in the cyanosilylation of benzaldehyde, all of the aforementioned EOFs demonstrated good catalytic performances in terms of activities and recyclabilities. These EOFs thereby offer a great opportunity to be useful alternatives to highly toxic molecular Lewis acid catalysts.[70]

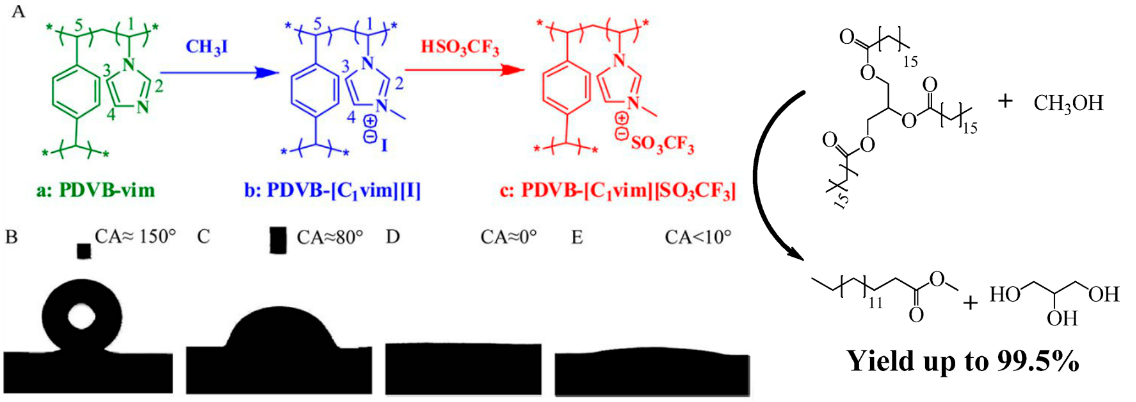
3.3. Ionic Liquid Catalysis. The ionic liquid-based catalysts have generated much interest owing to their diverse structures and potentially tunable properties. However, a relatively low solubility, high viscosity, and separation difficulty of the catalysts from the products still restrict their wide application.[71] Incorporation of ionic liquid moieties into porous organic polymers could not only overcome the aforementioned issues but also inherit the advantages of unique polymeric matrixes.

Han et al. demonstrated for the first time the incorporation of ionic liquid moiteties into a highly cross-linked polymer through free-radical copolymerization of 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) and divinylbenzene (DVB) as a

Scheme 4. Synthesis of the Cross-Linked-Polymer-Supported Ionic Liquid and Its Catalytic Activity in the Conversion of Epoxide to Carbonate with CO_2

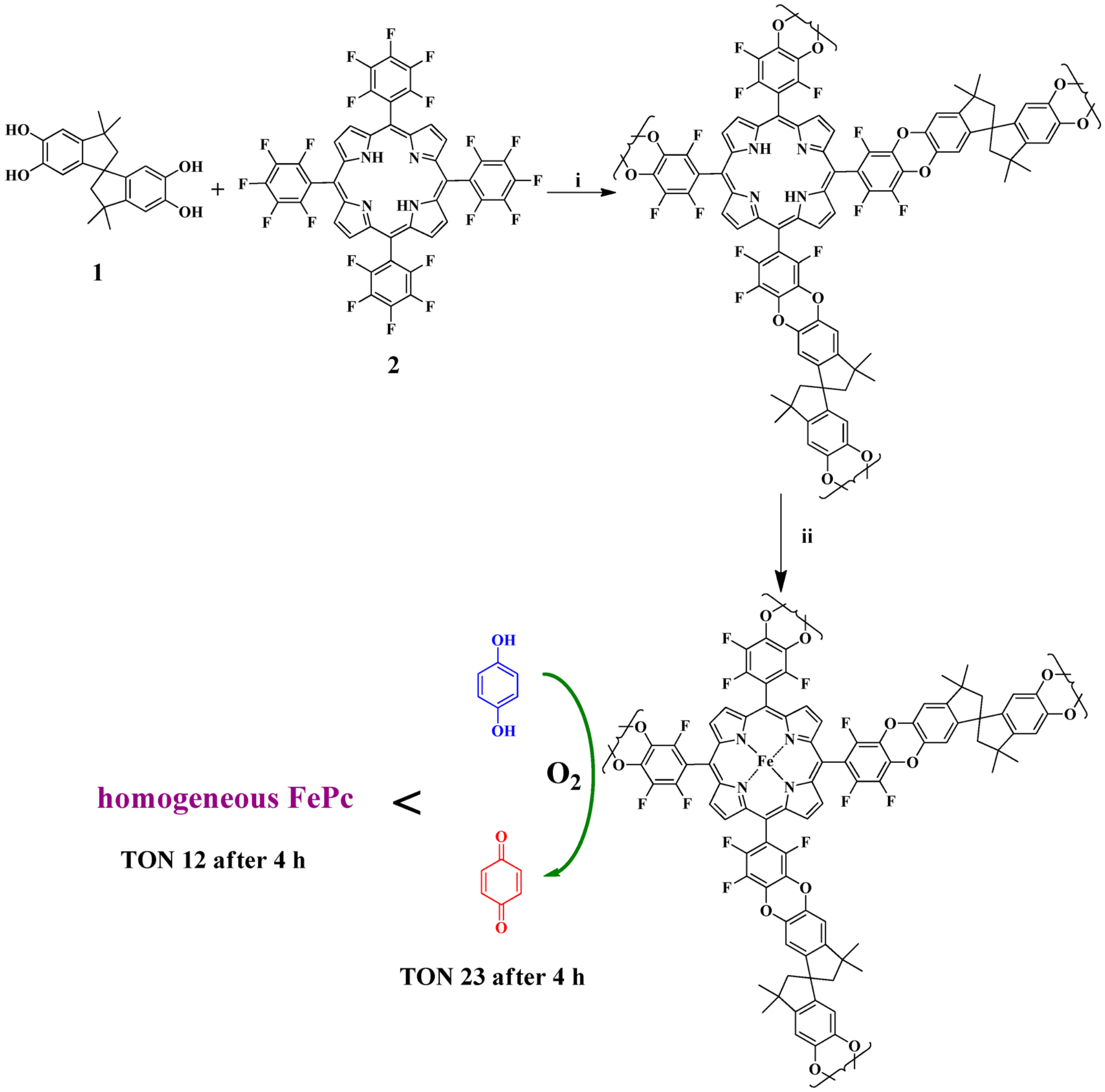


Scheme 5. (A) Scheme for the Synthesis of PDVB-[C_1vim][SO_3CF_3] from PDVB-vim.; (B, C) Contact Angle for a Water Droplet on the Surface of (B) PDVB-vim and (C) PDVB-[C_1vim][SO_3CF_3]; and (D, E) Contact Angle of a Droplet of (D) Methanol and (E) Tripalmitin on the Surface of PDVB-[C_1vim][SO_3CF_3] and Its Catalytic Activity in Transesterification[a]



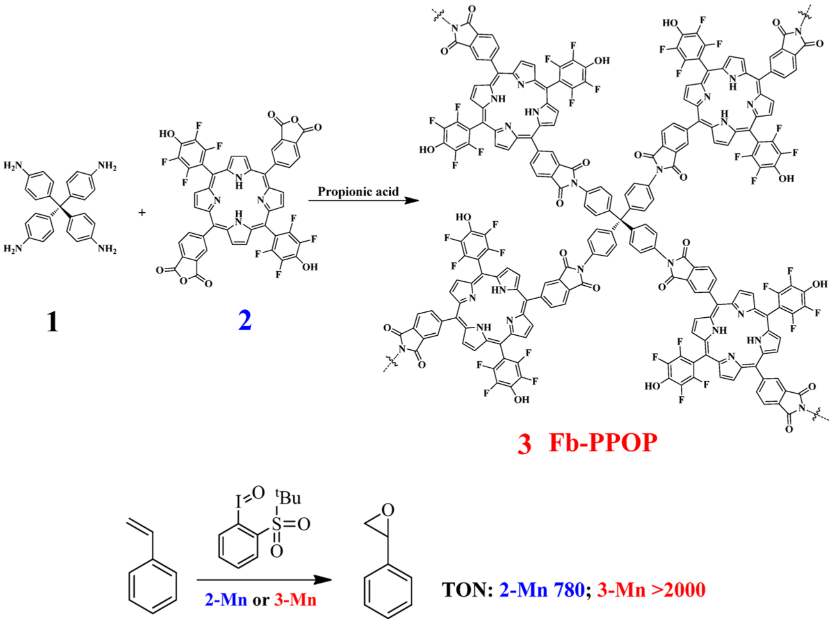
[a]Reprinted (adapted) with permission from ref 73. Copyright 2012, American Chemical Society.

Scheme 6. Preparation of Spiro-Linked Iron Porphyrin Network Polymer (FePorph-PIM) and Its Catalytic Performance in the Oxidation of Hydroquinone by Molecular Oxygen[a]



[a]Reagents and conditions: (i) K_2CO_3, NMP, 170 °C, 5 h; (ii) $FeCl_3$, NMP, 120 °C, 24 h.

Scheme 7. Synthesis of Fb-PPOP and Its Catalytic Activity in the Oxidation of Styrene after Metalation with Mn Species



cross-linker (Scheme 4).[72] The afforded polymer exhibits excellent performance in catalytic cycloaddition of CO_2 to epoxides, giving an activity comparable to that of the homogeneous analogue ([BMIM]Cl) and much better than that of the nonporous counterpart poly[VBIM]Cl synthesized from direct polymerization of [VBIM]Cl. Particularly, it can be readily separated from the products and recycled.

Xiao et al. have introduced a series of acid ionic liquid moieties into a superhydrophobic porous polymer matrix (Scheme 5). The combination of the ionic liquid activity and the matrix superhydrophobicity endows the superhydrophobic porous ionic liquid polymer catalysts with exceptional activities in the context of the transesterification of tripalmitin and methanol, outperforming the soluble ionic liquid analogues.[73] Contact angle measurements and catalytic tests suggest that the superhydrophobic catalysts have miscibility with the reactants that is superior to that of the products. As a result, the reactants can be enriched in the catalyst domain, giving an accelerated reaction rate.

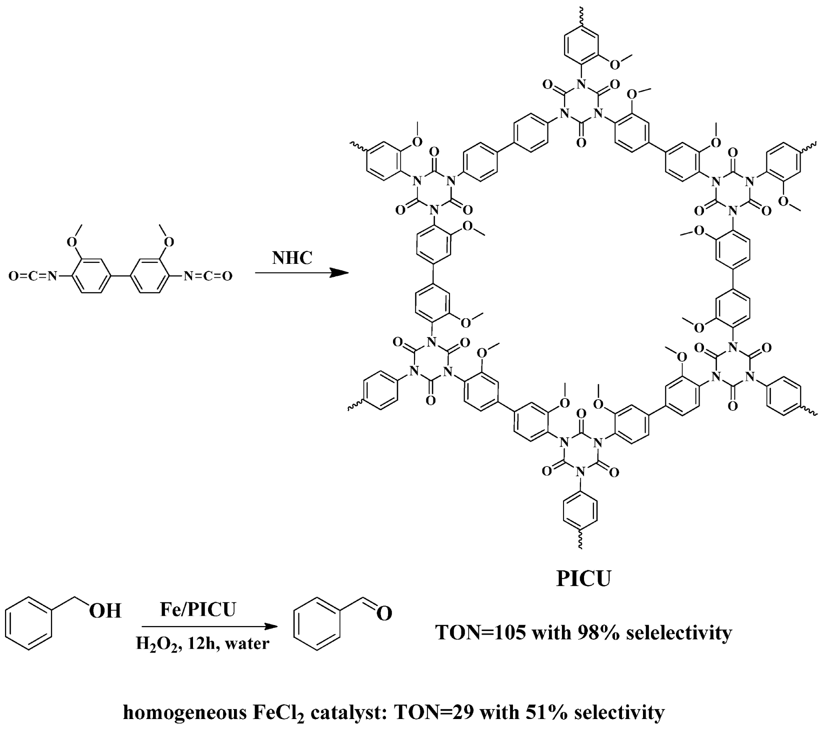
3.4. Organometallic Catalysis. Homogeneous organometallic catalysts play an extremely important role in the field of catalysis. Some of them have achieved wide acceptance in terms of selectivity and activity, and a few of them are even applied in industry. Despite a huge number of works being devoted to this subject, the complicated synthesis and difficult recycling still remain a challenge for their wide applications.[74]

Porphyrin derivatives as typical organometallic compounds have been used as organic linkers to build the POPs in pursuance of mimicking their biological functionalities, such as light-harvesting, oxygen transportation, and catalysis.[75] When the POPs work as platforms to immobilize porphyrins, their designable structures with high surface areas can not only make porphyrins fully accessible by substrates but also hinder the formation of catalytically ineffective dimeric porphyrin species.

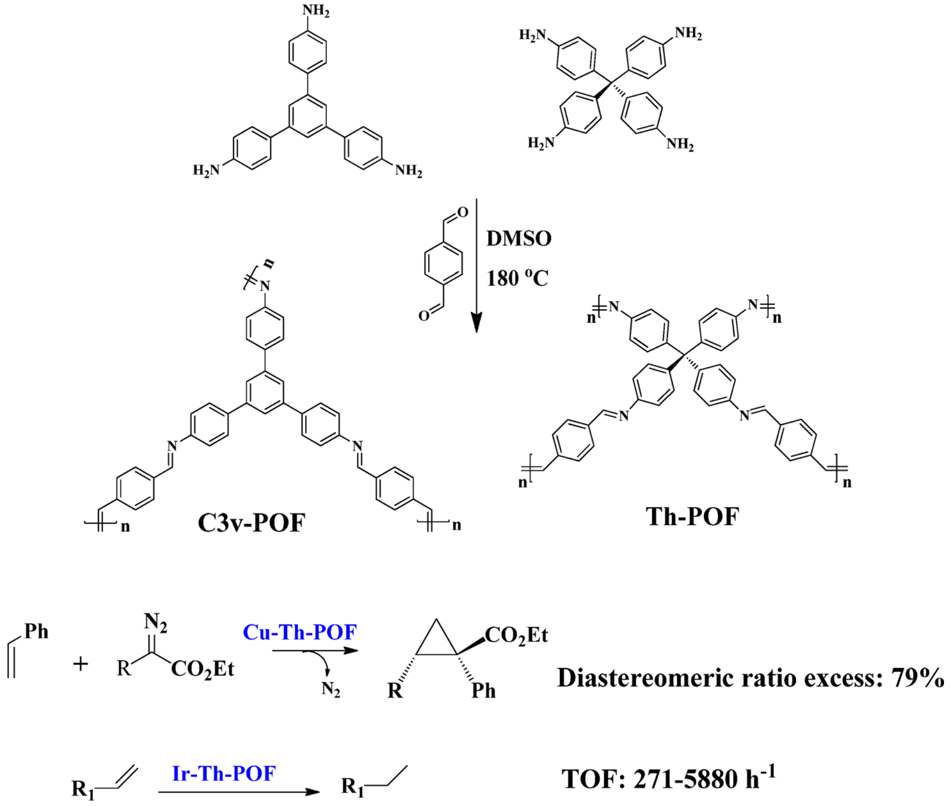
McKeown et al. first incorporated porphyrin groups in a network polymer Porph-PIM by a dibenzodioxane-forming reaction between 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane **1** and a preformed fluorinated porphyrin **2** with open metal chelating site, as shown in Scheme 6.[76] The metalation of Porph-PIM to form FePorph-PIM was realized in the presence of $FeCl_3$ and NMP solvent at 120 °C under N_2 for 24 h. The selected rigid nonplanar comonomer **1** is expected to separate and force porphyrin groups to different directions in the resultant polymer as well as create space to allow access by small molecules. The spiro-linked Fe porphyrin polymer network has a BET surface area of 866 m^2/g. Catalytic tests in oxidation of hydroquinone show that the spiro-linked Fe porphyrin outperforms the corresponding homogeneous analogues. They ascribe this phenomenon to the combined contributions of highly accessible Fe porphyrin species and effectively suppressed dimerization of reaction centers, which block the catalysis pathway. Meanwhile, they have successfully extended this strategy to the synthesis of microporous Co phthalocyanine network polymers via condensation reactions between **1** and 4,5-dichlorophthalonitrile, followed by introducing Co species or direct condensation of a preformed Co phthalocyanine with **1**. The yielded polymer networks also exhibit a significant enhancement of catalytic activities, compared with the homogeneous counterpart in the context of H_2O_2 decomposition, cyclohexene oxidation, and hydroquinone oxidation.

Later, Hupp et al. developed an alternative strategy to incorporate metalloporphyrin building blocks.[77] As outlined in Scheme 7, by taking advantage of the reaction of amines and acid anhydrides to form robust diimide bonds, the porphyrin groups with open coordinated sites can be readily achieved (Fb-PPOP) via the condensation of tetraamine monomer **1** and an acid anhydride-functionalized porphyrin monomer **2** in the presence of propionic acid. Treatment of Fb-PPOP with either $FeCl_2$ or $MnCl\cdot 4H_2O$ in DMF gives rise to Fe- or Mn-metaled Fb-PPO (Fe-PPOP or Mn-PPOP). Interestingly, the metalation process has little impact on the surface area of the pristine polymer, giving in the range of 376−453 m^2/g. It is also worth mentioning that the polymer-based metalloporphyrin catalysts exhibit a long catalyst life, superior to the homogeneous analogues, as evidenced by the observed higher turnover numbers. For example, in the case of homogeneous (TPFPP)-Mn, deactivation and degradation of the catalyst occur after 780

Scheme 8. Synthesis of PICU and Its Catalytic Performance in the Selective Oxidation of Benzyl Alcohol to Benzaldehyde



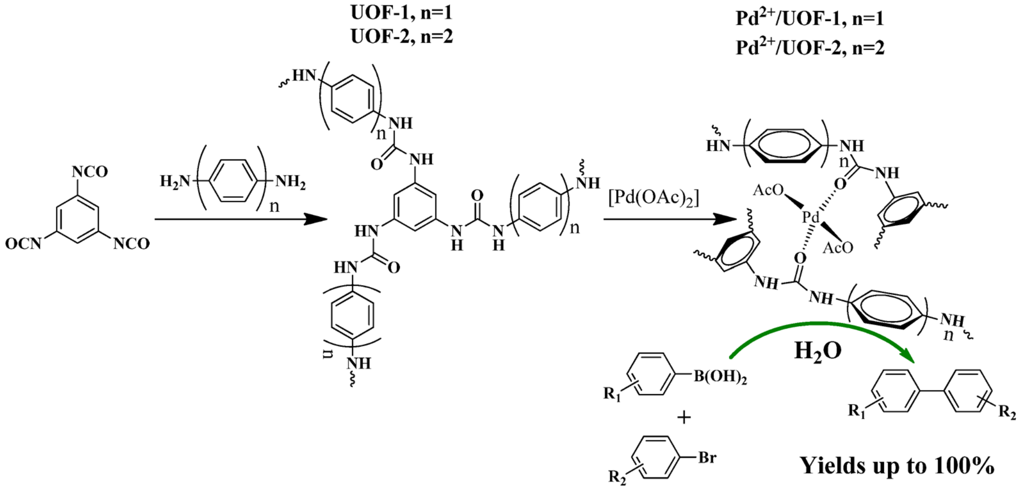
Scheme 9. Synthesis of the Imine-Linked Mesoporous Polymer Organic Frameworks (POFs) and Their Catalytic Properties in the Cyclopropanation and Hydrogenation after Metalation with Cu and Ir Species, Respectively



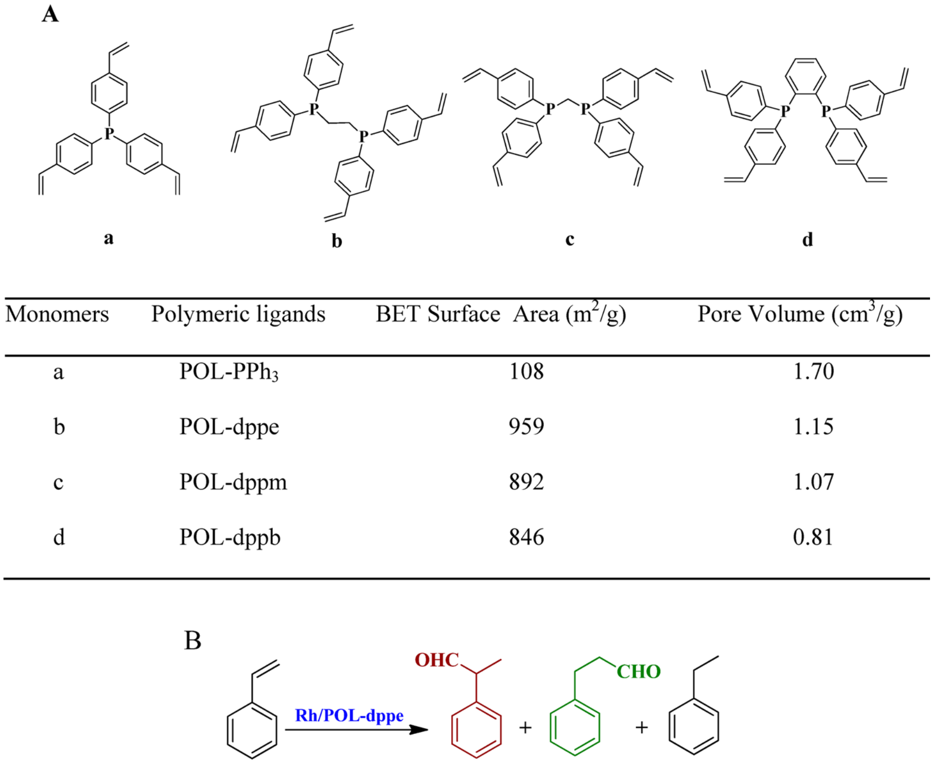
turnovers. In contrast, Mn-PPOP fully retained its activity for more than 2000 turnovers. These results further highlight the importance of the polymer network to prevent the dimerization of the metalloporphyrin species.

In addition, metal-catalyzed couplings, such as Suzuki[33] and Yamamoto[78,79] reactions, are also successful for the construction of porphyrin-based porous polymers. However, because of the strong affinity of the porphyrin to the metal species, the metal catalysts are easily maintained in the resultant

Scheme 10. Synthesis of UOFs and the Corresponding Palladium Polymers and Its Catalytic Activities in Suzuki Reactions Using Water As a Green Solvent



Scheme 11. (A) Structures of Vinyl-Functionalized Phosphine Ligand Monomers and Textural Parameters of the Corresponding Porous Polymers: (a) Triphenylbenzene, (b) 1,2-Bis(diphenylphosphino)ethane (dppe), (c) Bis(diphenylphosphino)methane (dppm), and (d) 1,2-Bis(diphenylphosphino)benzene (dppb),; and (B) Catalytic Performance in the Hydroformylation of Styrene As Exemplified by Rh-Metalated POL-dppe



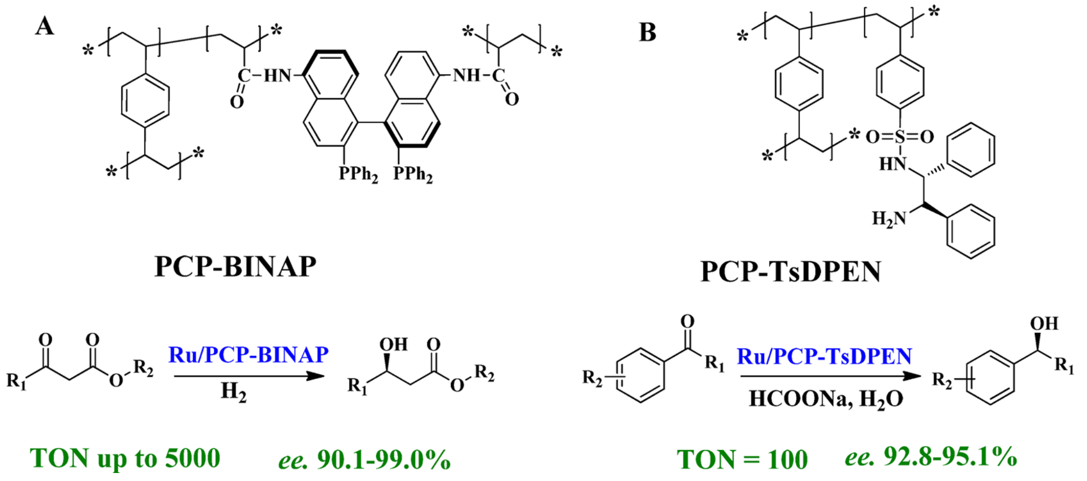
Monomers	Polymeric ligands	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
a	POL-PPh_3	108	1.70
b	POL-dppe	959	1.15
c	POL-dppm	892	1.07
d	POL-dppb	846	0.81

Quantitative aldehydes yield, 94.9% regioselectivity for branched aldehyde

polymers. In contrast, in the absence of metal catalysts (metal-free), free base porphyrin subunits can be obtained, and the desired metal species can be introduced into the resultant porphyrin-based POPs for task-specific applications through postsynthetic metalation.[76,77,80] Therefore, the metal-free synthetic strategies are more versatile to introduce catalytically active sites in the polymers because of the complete elimination of the metal effect in the synthetic process.

Ying et al. prepared a novel polyisocyanurate (PICU) polymer via N-heterocyclic carbene-catalyzed diisocyanate cyclotrimerization reaction (Scheme 8).[81] The obtained polymer possesses BET surface areas ranging from 320 to 569 m^2/g. The combined advantages of a porous structure and isocyanurate functional units could make the PICU serve as a promising insoluble ligand. After metalation with $FeCl_2$, the resultant Fe/PICU catalyst shows outstanding activities and

Scheme 12. Structures of Porous Chiral Polymer Bearing (A) BINAP and (B) TsDPEN and Their Properties in the Asymmetric Catalysis



selectivities in the oxidation of benzyl alcohol with H_2O_2 using water as a green solvent.

Iglesias et al. described two imine-linked porous polymer frameworks with different geometries and mesoporous structures through condensation of 1,4-benzenedicarbaldehyde with 1,3,5-tris(4-aminophenyl)benzene and tetra(4-aminophenyl)methane, yielding C3v-POF and Th-POF, respectively (Scheme 9).[82] These covalent imine frameworks offer abundant metal binding sites to postsynthetic metalation. Because the Th-POF has strong metal-binding ability and large surface area, Cu and Ir species were successfully introduced into the Th-POF framework [Cu(I)−Th−POF and Ir−Th−POF], turning out to be effective catalysts in the cyclopropanation and hydrogenation. More significantly, these catalysts are readily recyclable because of the good stability of the coordinated complexes and the porous frameworks.

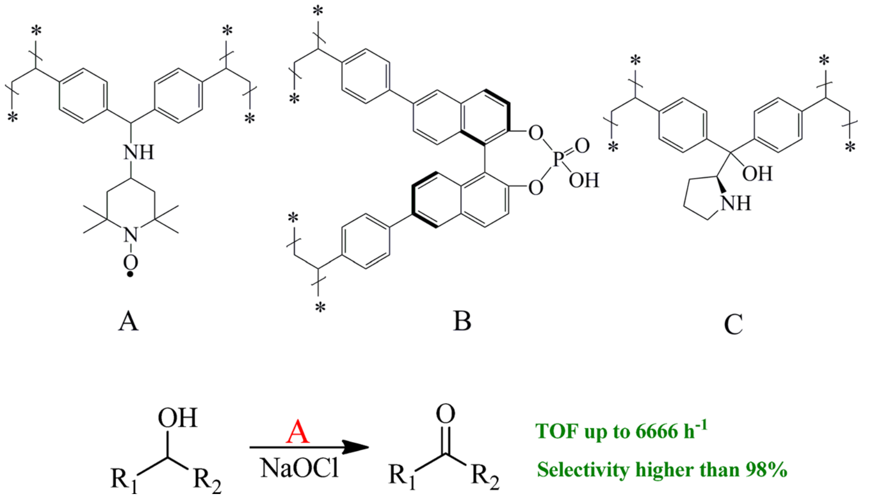
Li et al. reported two urea-based porous organic frameworks (UOF-1 and UOF-2) synthesized from a urea-forming condensation of 1,3,5-benzenetriisocyanate with 1,4-diaminobenzene and benzidine (Scheme 10).[83] After coordination with $Pd(OAc)_2$, the achieved Pd^{2+}/UOF-1 and Pd^{2+}/UOF-2 catalysts demonstrated excellent substrate tolerance and good recyclability in the context of Suzuki−Miyaura cross-couplings and reduction of nitroarenes using water as a sustainable solvent. Good dispersion of urea-based frameworks in water and a microenvironment with a high concentration of organic substrates inside the frameworks resulted from the presence of a hydrophilic urea linkage and hydrophobic void are responsible for the superior performances.

Although heterogenization of homogeneous catalysts onto solid supports has been well proven to be more desirable for industrial applications owing to the convenience of catalyst recycling, there are still many important industrial processes controlled by homogeneous catalysts, such as hydroformylation of olefins. Currently, the conventional rhodium-based heterogeneous catalysts are suffering mainly from their low activity and selectivity[84] because the conventional heterogeneous catalysts cannot easily obtain a high concentration of freely movable organic ligands in the vicinity of metal species. The POPs provide a good opportunity for bridging the gap owing to their tailorable pore walls, controllable chemical composition, and relatively flexible frameworks.

Sun et al. demonstrated a facile and universal route for synthesizing phosphine ligand-constructed porous polymers with high ligand concentration and outstanding framework flexibility via free-radical polymerization of the corresponding vinyl-functionalized phosphine monomers.[85,86] It should be pointed out that the vinyl-functionalized phosphine monomers, such as triphenylphosphine (PPh_3), 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm), and 1,2-bis(diphenylphosphino)benzene (dppb), are obtained from one-pot processes of commercially available chlorophosphines with (4-vinylphenyl) magnesium bromide. Moreover, these monomers can be transformed into highly polymerized polymers in nearly quantitative yields under mild conditions (free-radical polymerization at 100 °C). These easy-to-get features make a number of porous phosphine ligand polymers easily scale up (Scheme 11). The resultant polymerized phosphine ligands have large surface areas (846−1086 m^2/g) and hierarchical porosity, which not only make the coordinated sites more accessible but also minimize transport limitations in the catalytic processes.

A more important benefit is that these insoluble polymerized phosphine ligands can be swollen by a wide range of organic solvents, exhibiting behavior similar to those of soluble analogues. Furthermore, Because of the extremely high concentration and extraordinary spatial continuity of the phosphine ligands in these polymers, the ratios of the ligand to the metal in the resultant heterogeneous catalysts can be rationally adjusted by the metal loading weights, which are as alike as those of the homogeneous counterparts. As a typical example, after metalation with Rh species, the porous polymerized 1,2-bis(diphenylphosphino)ethane (POL-dppe) catalysts demonstrate unprecedented catalytic performance in the hydroformylations, such as styrene, *n*-octene, and *n*-dodecene, which are even better than those of the corresponding homogeneous analogues. For example, the Rh/POL-dppe catalyst outperforms the optimized homogeneous catalyst of Rh/5dppe (the mole ratio of dppe/Rh is 5) in terms of activity and selectivity. Through multiple experimental studies, it is reasonable to suggest that the wonderful catalytic performance of these porous polymers should be attributed to the extremely high ligand concentration and the excellent mobility of the dppe ligands in the framework in the swollen state. These Rh-metalated porous organic polymers exhibit

Scheme 13. Structures of Porous Polymerized Organocatalysts (PPOs) of (A) PPO-TEMPO, (B) PPO-BNPA, and (C) PPO-RDPP and the Catalytic Performance of PPO-TEMPO in the Oxidation of Alcohols, As Exemplified by PPO-TEMPO[a]



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"quasi-homogeneous" catalytic behavior. As solids in nature, they are also easily separated and recycled from the reaction system without loss of any activity and selectivity. Therefore, these porous phosphine ligand polymers provide new perspectives for synthesizing highly efficient heterogeneous catalysts in the future.

Notably, this synthetic approach is not limited to fabrication of porous phosphine polymers; other important ligand monomers, such as 2,2′-bipyridyl and salen, can also be transformed into insoluble porous polymers.[85] These polymers could act as both support and ligand in catalysis. After introduction of metal species, the achieved heterogeneous catalysts exhibit excellent activities and recyclabilities. For example, the Cu-supported porous polymerized 2,2′-bipyridyl (POL-bpy) affords comparable catalytic activity with the corresponding homogeneous analogue ($CuBr_2$/bpy) in oxidations of primary alcohols to aldehydes using O_2 as oxidant.

Asymmetric catalysis has been considered as one of the most attractive methodologies to produce enantiomerically pure compounds. Recently, Sun et al. showed a powerful approach to incorporate chiral organic ligand into hierarchically porous polymer with adjustable ligand concentration, as exemplified in the context of two widely studied chiral ligands 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[87] and *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN).[88] These chiral porous polymers can be achieved via the free-radical copolymerization of vinyl-functionalized organic ligand and divinylbenzene (Scheme 12). The resultant polymers have relatively high surface areas (524 and 481 m^2/g) and hierarchical porosity (coexistence of micro-, meso-, and macroporous), which are beneficial to mass transfer. The chirality of pristine ligands is well retained, as evidenced by the sample solid circular dichroism spectrum. These porous chiral polymers are expected to serve as insoluble chiral ligand for applications in asymmetric catalysis. For instance, after in situ coordination with $[RuCl_2(benzene)]_2$, the porous chiral BINAP polymer catalyst (Ru/PCP-BINAP) gives excellent catalytic performance in terms of activity, chemoselectivity, and enantioselectivity, which are comparable to those of the corresponding homogeneous analogue in asymmetric hydrogenation of methyl methacrylate.

Importantly, a wide range of ß-keto esters could be fully converted into the corresponding chiral alcohols over the Ru/PCP-BINAP catalyst with very high enantioselectivities in the range of 94−99% under a high S/C (substrate/catalyst) ratio of 2000. More importantly, this insoluble catalyst can be easily separated and recycled at least six times without obvious loss of its performance. Very interestingly, in the case of Ru-metalated porous chiral polymers functionalized with TsDPEN catalyst (PCP-TsDPEN-Ru), an accelerated reaction rate was observed in comparison with the homogeneous counterpart of Ru/TsDPEN in an asymmetric transfer hydrogenation (ATH) of acetophenone using water as a green solvent and HCOONa as a hydrogen source. Time-dependent curves of the distribution of the reactant (acetophenone) and product (1-phenyl-ethanol) in the catalyst domain and solvent phase (water) reveal that the heterogeneous catalyst of PCP-TsDPEN-Ru has a strong ability to enrich the reactant in the catalyst domain and transfer the product from the catalyst to the water phase, in good agreement with the wettability of the reactant (acetophenone) in the PCP-TsDPEN-Ru being much better than that of the product (1-phenyl-ethanol), as indicated from the contact angle tests of these compounds on the catalyst surface.

3.5. Organocatalysts.

Organocatalysts exhibit distinct activities and selectivities in a series of organic transformations. Despite fruitful advancements in academia, further applications of the organocatalysts in industry are also hampered by their separation problem. Porous organic polymers as versatile platforms provide new possibilities in connecting nanoporous polymer networks and organocatalysts, giving an interesting solution to both separation and recycling of the catalysts.

Recently, Huangfu et al. illustrated a generalized strategy to synthesize highly cross-linked organocatalyst polymers with high surface areas, large pore volumes, and hierarchical porosity via the polymerization of vinyl-functionalized organocatalyst monomers, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), (*R*)-1,1′-binaphthyl-2,2′-diylhydrogen phosphate, and α,α-diphenylprolinol under solvothermal conditions (Scheme 13).[89] Notably, the resultant porous polymers bear an extremely high concentration and high exposure degree of functional groups. As a typical example, the porous polymerized organocatalyst composed of functionalized TEMPO moieties

(PPO-TEMPO) was carefully investigated; selective oxidations of primary and secondary alcohols were chosen as the model reactions. PPO-TEMPO is very active and selective for oxidations of a wide range of aliphatic and aromatic alcohols into the corresponding aldehydes and ketones, showing activity that is competitive with or superior to the corresponding molecular catalyst TEMPO. More importantly, the PPO-TEMPO displays excellent recyclability, indicated by the negligible loss of catalytic performance over several reuses. In contrast, MCM-41-grafted TEMPO catalyst lost its catalytic activity in the second run owing to silica-based materials generally suffered from an inherent liability toward hydrolysis in the alkaline solution.

4. CONCLUSION

In this Perspective, we have briefly summarized the synthesis of porous organic polymers under metal-free conditions and their applications in heterogeneous catalysis. Clearly, the porous organic polymers have become a fascinating new type of porous materials that inherently combine designable pore walls, controllable composition, and porosity. By taking advantage of the versatility of design and conditions employed for the fabrication of polymers themselves, a diverse range of target functionalities can be precisely incorporated in the porous polymers. In addition, as a platform for designing synergistic systems in heterogeneous catalysis, POPs enable the complementary exploration of tailorable polymeric matrix properties, such as controllable wettability, to improve the performance of the catalytically active sites. More importantly, these porous organic polymers could be retro-designed according to the catalytic features, which will create more sophisticated properties in the heterogeneous catalysis. These porous organic polymers with unique features offer a good opportunity to deploy highly efficient heterogeneous catalysts in the future. Nevertheless, the strategies for construction of porous organic polymers are still developing, especially for those polymerized in the absence of metal catalysts. Therefore, continued efforts should be devoted to searching for procedures that permit scalable preparation of porous polymers using sustainable, concise, and low-cost strategies.

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Notes

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