

Low-Cost Hypercrosslinked Polymers by Direct Knitting Strategy for Catalytic Applications

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Direct knitting of nucleophilic arene monomers in the presence of electrophilic cross-linker, like formaldehyde dimethyl acetal, is proven to be a cost-effective and versatile method for the synthesis of porous organic polymers. The resulting hypercrosslinked polymers (HCPs) are featured by hierarchical porous structure, high surface area, and pore volume. Coordinating functional groups can be easily installed with this method into the rigid aryl network. Direct knitting to HCPs has therefore been widely used in preparing heterogeneous solid catalysts. Wise selection of monomers with rational design of 3D structure and the synergy between the HCP support and the catalytically active species often lead to high efficiency of tailor-made catalysts without sophisticated operations. On account of all these excellent properties, enthusiasm of researchers to use HCPs in catalysis is increasing rapidly. This review documents the necessity, feasibility, and the great contributions of using HCPs as invaluable tools for catalysis research, and summarizes state of the art of this chemistry. Similar type catalysts obtained by one-step Scholl reaction are also included in this review.

1. Introduction

A homogeneous catalyst is characterized by highly active and selective reactions, mild conditions, and free or weak effect of diffusion control. A heterogeneous catalyst is characterized by easy separation from the products and easy adaptation to continuous flow processes, but sometimes restricted by a diffusion problem. Heterogenizing a homogeneous catalyst by immobilization is a trend toward the development of

chemically homogeneous but physically heterogeneous catalysts.^[1] However, some bottlenecks, such as reduced catalytic activity, lack of stability, and increase of catalyst cost, are hampering the application of immobilized molecular catalysts in industry.^[2]

The reduced catalytic activity perhaps resulted from an altered chemical environment and decreased accessibility of the substrates to active sites. The immobilization may also negatively affect stability of the catalyst, which often results from some changes of coordinating model and microenvironment around the active sites. To implement the immobilization, pre-functionalized precursors or supporting materials have to be used, which were often prepared through multistep reactions with tedious synthetic procedures. The anchoring reaction often involves the use of complex and expensive catalyst. It

is sometimes associated with special instruments and sophisticated operations.^[3] Combining one or a number of these factors together resulted in an increase of cost and diminished significantly the advantages of using a heterogenized homogeneous catalyst for chemical synthesis.

On the basis of aforementioned factors, heterogenizing a homogeneous catalyst by immobilization should be implemented by a wise method, which should not only involve only the use of low-cost and designable supporting material, but is also characterized by simple operation and great compatibility with most of the research areas of modern catalysis. Additionally, the procedure to anchor active sites onto solid supports should allow the high possible stability of catalyst structure in order to keep or increase their original catalytic abilities. All these requirements put together tended to narrow the possibility of finding a suitable method to implement heterogenization of a homogeneous catalyst. Fortunately, fast development of material chemistry allowed us to find an ideal choice without sweat.

Porous organic polymers (POPs) have gained much attention because of their huge surface area, tunable pore size distribution, high hydrothermal and mechanical stability, flexible synthetic strategy, and readily modifiable functionality.^[4] The enthusiasm of researchers to study POPs was mostly triggered by covalent organic frameworks^[5] and conjugated microporous polymers (CMPs),^[6] which however has to be prepared using well-designed building blocks that are generally expensive or not commercially available. Synthesis of some POPs relies

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heavily on the use of precious metal catalysts, and due to the difficulty of recycling the metal catalysts, the costs of POPs were further increased. Therefore, POPs are facing great difficulty for scale-up although many promising results have been achieved.

Hypercrosslinked polymers (HCPs) are known for many years, and can be synthesized easily via Friedel–Crafts reaction. The first generation of HCPs was introduced by Davankov, who distinctly installed numerous structural bridges by means of a Friedel–Crafts reaction between neighboring aromatic rings of linear polystyrene (PS). In Davankov's process, the starting PS was in a highly swollen/expanded state, and yielded resins having a hypercrosslinked 3D structure, high micropore content, and very high S_{BET} (up to $\approx 2000 \text{ m}^2 \text{ g}^{-1}$).^[7] Since the original synthetic procedure was disclosed by Davankov, several variables have been developed. Basically, Davankov's process is a post-crosslinking method for the production of porous PSs, and the extensive cross-linking established with an external reagent prevents the polymer chains from collapsing into a dense, nonporous state. The significant contributions of Jerábek^[8] and Sherrington^[9] cannot be overlooked.

A big breakthrough in HCPs development came in 2011, during which, one of the authors of this review, Tan, developed a novel strategy, on the basis of Friedel–Crafts reaction, namely one-step knitting method by using simple arenes as monomers and chloromethyl ether (CME) or formaldehyde dimethyl acetal (FDA) as an external cross-linker.^[10] To differentiate with the conventional Davankov's cross-linked resins, the newly obtained HCPs were specified as knitting aryl network polymers. HCPs constructed by Tan's knitting approach have gained much attention because of their easy preparation, high chemical–physical stability, and low cost.

Particularly, the uses of HCPs in heterogeneous catalysis are fashionable, which opened an avenue for chemists to design a tailor-made catalyst in a cost-effective and time-saving manner. Why HCPs obtained by one-step knitting approach are so interesting for heterogeneous catalysis may encompass multiple basis: i) designable ability and great diversity with tunable property; in order for the researchers to prepare heterogeneous catalysts, HCPs with different functional groups as coordination sites for catalytic metal species have been synthesized by virtue of this bottom–up direct knitting approach; the structural integrity of HCPs can be easily tuned by varying the selection of monomers and the reaction conditions; ii) inherent compatibility with heterogeneous reaction and catalysis; HCPs have stable, rigid, and porous structure; some of them are featured by two main pore size distributions with micro- and mesopores; such a structure with mixed-sized pores has been found to be beneficial to enhance the mass transfer of substrate and product; iii) low-cost and time-efficient synthesis and amenable to modern physical characterization methods; such method for constructing microporous HCPs directly from readily available arene monomer offered significant advantages for large-scale production and applications;^[11] even solid-grafted arene fragment, which normally is flexible, can be knitted, allowing the fabrication of HCP on solid surface; most of the spectroscopic methods that have been used in conventional heterogeneous catalysis are effective for investigating the physicochemical properties of HCPs; therefore this innovation arising

from polymer chemistry can be easily adopted by catalysis researchers.

HCPs from direct knitting approach have been widely used in gas storage,^[12] separation,^[13] and heavy metal removal in wastewater treatment.^[14] Some excellent reviews already gave a comprehensive overview about this area.^[15] Although HCPs have been widely used in catalysis, there is still a lack of comprehensive review to summarize state of the art of this chemistry. Here, we will focus on the applications of HCPs constructed by direct knitting approach in the major area of catalysis. Performances of these materials will all be shown in each individual example. For easy understanding of the readers, the synthesis of HCPs will be discussed in the beginning part, with which the intrinsic advantages stem upon the easiness of preparation and structural design, as well as the great diversity, can be fully displayed.

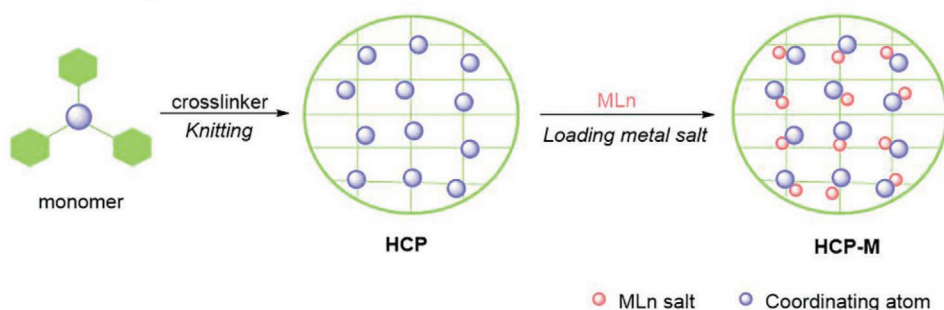
2. Synthesis of Hypercrosslinked Polymers by a Direct Knitting Strategy

Generally, the reaction system to implement hypercrosslinking via acid-catalyzed Friedel–Crafts alkylation involves an electrophilic species, one or more arene-based nucleophilic species, a Lewis acid catalyst, and reaction solvent. To prevent occurrence of side reaction, the knitting step was generally performed under a nitrogen or an argon atmosphere. After finishing the knitting step, HCPs can be directly isolated as a solid, which were then subjected to washing and removing of the Lewis acid catalyst. A metal species can be introduced in two routes (**Figure 1**): i) by post-modification of HCP with metal salt or complex after the formation of HCP; this route allowed the metal to be anchored in the most accessible place, thus facilitating mass transfer of the catalytic reaction; and ii) by using metal complex as a monomer or comonomer in the knitting reaction; because the original structure of the metal complex retained in large extent in the HCP skeleton, this route enabled the researchers to predict the molecular properties of the supported catalyst on the basis of their homogenous counterpart; in addition, if the metal complex is stable during the knitting reaction, the metal active sites can be atomically dispersed in the porous matrix of HCP support. Most of the HCP-based metal catalysts were prepared by the first route. We will discuss all these components one by one in this part.

2.1. Electrophiles

The electrophiles commonly used for the fabrication of HCPs are dihalomethanes, formaldehyde, CME, FDA, alkyl orthoformates, 2,4,6-trichloro-1,3,5-triazine, benzyl halides, dihalomethylbenzenes, and trihalomethylbenzenes. The electrophiles should be able to react with the nucleophile to construct a bridge between the two arene units. It seems like a very short chain segment confined between the branching points that are spatially non-planar cycles. When dihalomethylbenzene-type electrophiles were used, self-polymerization is also possible without adding the nucleophilic component because the phenyl ring can act as the nucleophile. However, in this case, hydrogen

The first knitting model:



The second knitting model:

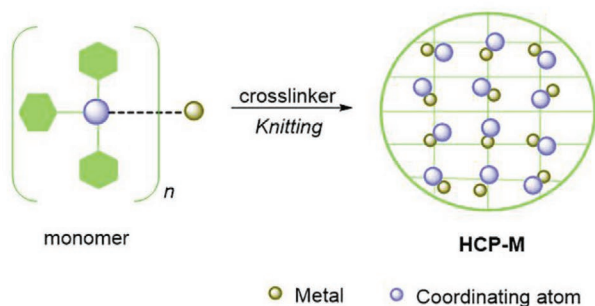


Figure 1. Schematic illustration of two knitting models for incorporating metal species onto the skeleton of HCPs.

halide was generated as by-product, and chlorination or bromination of the arene system may be possible, which may show adverse impact, probably, on the performance of the cross-linking reaction and the quality of the HCPs. Because free formaldehyde is too reactive and tends to form solid polyformaldehyde, FDA and CME are often employed as the electrophile in conjunction with using anhydrous FeCl_3 as catalyst. The use of FDA as external cross-linker has an additional advantage, namely, the coproduct methanol which is much less reactive and can be easily removed from the reaction systems.^[16]

2.2. Arene Nucleophiles

Many arenes can be used as the nucleophilic components of synthesizing HCPs, including substituted benzene derivatives, pyrroles, and carbazoles. Although the aryl groups in triphenylphosphine (PPh_3), triphenylamine, and their corresponding salts are electron-deficient and thus have relatively low reactivity, they were proven to be viable precursors of HCPs. Some highly reactive nucleophiles, such as electron-rich aromatics even reacted themselves under strongly acidic conditions, offering an alternative way to form HCPs (e.g., AlCl_3 -catalyzed Scholl reaction).^[17] To facilitate the synthesis or to endow the HCP specific multifunctionalities, two or more arenes could be mixed together. In this case, the two nucleophilic arenes that have nearly the same nucleophilicity reacted simultaneously with an external cross-linking reagent, forming a rigid porous material with incorporation of two kind of fragments into the polymer network. By means of wisely selecting the arene monomer, some specific function-

alities can be induced, endowing the resulting HCP with some anticipated properties.

2.3. Catalysts

The metal halides, such as FeCl_3 , AlCl_3 , SnCl_4 , and ZnBr_2 , can all be used as Lewis acids. Their choice and dosage depend on the reactivities of electrophile and arene nucleophile.^[18] In the most cases, mole of catalyst and the number of bridging group between aromatic ring and halogen functional group is in $\approx 1:1$ ratio.^[19] To ensure the knitting of monomer to be successful, the catalyst can be added portion by portion. Because the Lewis acid catalyst was used in a large amount, after finishing knitting reaction, the metal catalyst has to be removed carefully; otherwise the catalytic performance may be interfered by residual Lewis acid. It was generally realized by washing with methanol in a Soxhlet extractor for 24–48 h.^[20] Brønsted acid, trifluoromethanesulfonic acids, such as trifluoromethanesulfonic acid (TfOH) and H_2SO_4 , can also be used as catalysts for the knitting reaction.^[21]

2.4. Solvents

During the course of Friedel–Crafts alkylation, the formation of carbocation intermediates was involved mechanically, to stabilize them; polar aprotic solvents, such as chlorinated solvents (dichloroethane, dichloromethane, and chloroform), acetonitrile, and nitromethane, was generally used in the knitting procedure.^[22] The selection of solvent should also consider

the issues of solubility, product isolation, and energy transfer. With the aid of mechanosynthesis technique, solvent-free cross-linking is also possible, in which the mixture composed of monomer and cross-linker played the role of solvent.^[23]

3. Characterization of Hypercrosslinked Polymers

As organic porous solid materials, many spectroscopic methods can be used to investigate the structure of HCPs, including solid NMR, FT-IR, Raman spectra, and elemental analysis. Their morphology can be studied by optical microscope, field emission scanning electron microscope (FESEM), and transmission electron microscope (TEM). Study of thermal stability of HCPs was often implemented by thermo gravimetry analysis. Nitrogen adsorption isotherms and Brunauer–Emmett–Teller (BET) surface area measurements are common methods to characterize the textural property (surface area and pore size distribution) of HCPs. Other regular measurements for heterogeneous catalyst, such as X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectroscopy (ICP-MS), and energy dispersive X-ray spectroscopy, are also necessary to get useful information of HCPs. In general, almost all of the instruments that were commonly used for characterizing a solid catalyst can be employed to study the relationship between the structure and the catalytic activity.

4. Catalytic Applications of Hypercrosslinked Polymers Constructed by Direct Knitting Strategy

4.1. Hypercrosslinked Polymers–Metal Complex Catalysts

The enthusiasm of researchers to use HCPs in catalysis may be triggered by immobilization of a homogeneous metal complex catalyst with this easily accessible and designable material. Phosphine ligands were widely used in homogeneous catalysis, which were naturally selected as model systems to study the feasibility. However, the phenyl ring in aromatic phosphine ligand is generally electron-deficient. In order to make knitting successful, a large amount of FeCl_3 has to be used. Because of the oxidizing ability of FeCl_3 , a part of phosphine may be oxidized to phosphine oxide. However, by carefully controlling the reaction conditions, most of the phosphines can be retained after knitting, facilitating its catalytic uses. The first example to show a promising capacity of one-step knitting strategy for immobilizing homogeneous metal complex catalyst was established by using PPh_3 . In 2012, Li and Tan et al. fabricated,^[24] on the basis of the first knitting model, a rigid HCP with a fragment of PPh_3 by knitting this ligand with benzene in the presence of FDA in one step (Figure 2). With the obtained HCP material, a stable, highly active, and recoverable palladium–phosphine heterogeneous catalyst, $\text{HCP-PPh}_3\text{-Pd}$, was prepared. The S_{BET} was high up to $1025 \text{ m}^2 \text{ g}^{-1}$ with 0.7 wt% loading of Pd. Thereby obtained catalyst was examined in a Suzuki–Miyaura coupling reaction in an aqueous ethanol solution. Under mild conditions (80°C), excellent yields of biaryl products were obtained although some less-reactive chloroarenes were used as the counterpart reagents of arylboronic acids. By physicochemical

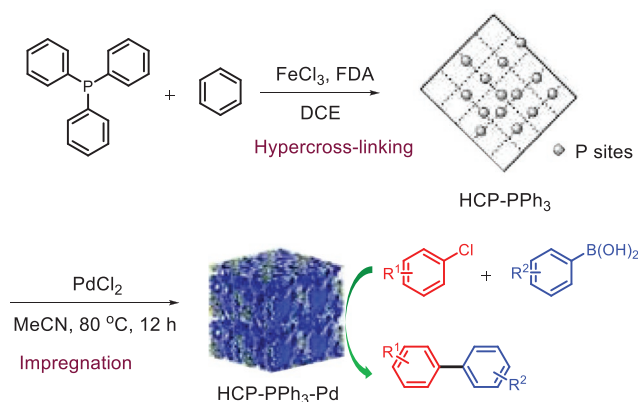
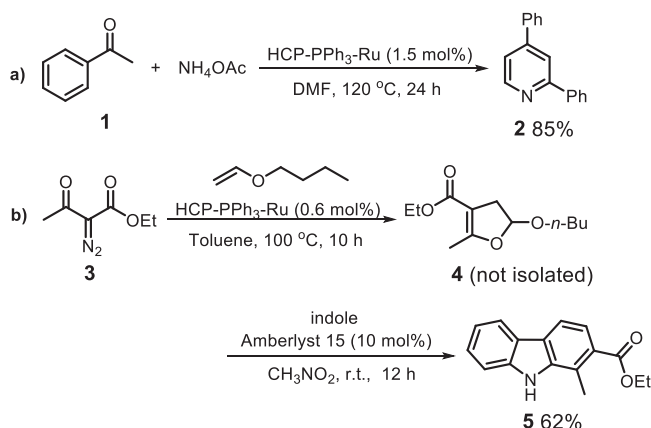


Figure 2. Schematic illustration of knitting of PPh_3 and benzene for the preparation of an $\text{HCP-PPh}_3\text{-Pd}$ catalyst. Reproduced with permission.^[24] Copyright 2012, Wiley-VCH.

characterizations of the solid catalyst, it was conferred that the microporous structure of the HCP support allowed a high dispersion of the metal species, confining Pd inside each micropore alone. This avoided the possible Pd^0 aggregation, and ensured the superior activity, stability, and recyclability of the $\text{HCP-PPh}_3\text{-Pd}$ catalyst. Indeed, the catalyst can be recycled at least five times without significant loss of its activity. During the reaction, metal leaching is also negligible. A similar type of $\text{HCP-PPh}_3\text{-Pd}$ catalyst has also been used in aminocarbonylation of aryl iodides with amines.^[25]

This HCP material was also used in immobilizing other metal catalysts. An $\text{HCP-PPh}_3\text{-Ru}$ developed by Tan and Gu et al. can be used in the construction of many heterocyclic compounds (Scheme 1).^[26] The metal loading of the $\text{HCP-PPh}_3\text{-Ru}$ is 0.15 mmol g^{-1} . In the synthesis of pyridine 2 from aromatic ketone 1 and ammonium acetate (NH_4OAc), the $\text{HCP-PPh}_3\text{-Ru}$ catalyst exhibited outstanding catalytic performance, even than that of the homogeneous counterpart, $\text{PPh}_3/\text{RuCl}_3$ (Scheme 1a). It might be attributed to the coordination ability of the phosphine ligand and the multistage porous structure of the support. The catalyst can be easily recovered and reused several times without significant loss of catalytic activity. During the reaction, metal leaching into the reaction mixture hardly happened, indicating again the robustness of HCP material. The



Scheme 1. An $\text{HCP-PPh}_3\text{-Ru}$ as efficient catalyst in some organic reactions.

HCP-PPh₃-Ru catalyst displayed good catalytic activity also in cycloaddition reactions of diazodicarbonyl compounds to olefins to synthesize dihydrofuran derivatives. Because of the easy separation of HCP-PPh₃-Ru catalyst, carbazole derivatives can be synthesized by combining this reaction together with an Amberlyst-15-catalyzed benzoannulation to establish a one-pot, step-wise protocol. In more detail, diazodicarbonyl compounds 3 first reacted with vinyl ethyl ether to form dihydrofuran 4, which then acted as starting material without isolation to react with indole to generate the corresponding carbazole derivative 5. The use of HCP-PPh₃-Ru as a catalyst not only facilitated the recycling of the metal catalyst, but also effectively simplified the operational procedure (Scheme 1b). A chiral phosphine-containing ligand, 2,2-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) was also amenable to the knitting strategy using FDA as a cross-linker.^[27] The prepared HCP-BINAP-Ru catalyst showed excellent activities and enantioselectivities in asymmetric hydrogenation of methyl acetoacetate. However, a slight decrease of enantioselectivity was observed, which can be ascribed to the possible effect of residual Lewis acid, FeCl₃. Direct knitting of 1,1'-bis(diphenylphosphino)ferrocene with FDA is also successful, and the obtained HCP contains an iron center which can be used as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol.^[28]

To demonstrate the great ability of this one-step knitting strategy for catalysis uses, various arene-based ligands were then tested. A great success was achieved with commonly used *N*-heterocyclic carbenes (NHCs). Through incorporation of different NHC units into the HCPs backbone by the first knitting model followed by a post-modification to induce Pd²⁺, Tan and Li et al. fabricated an HCP-NHCs-Pd catalyst with high *S*_{BET} up to 569 m² g⁻¹ (Figure 3).^[29] The easiness of changing the monomer to affect physicochemical property of the resulting HCPs enabled the researchers to finely optimize the catalytic ability of the catalyst from molecular level. It was found in this example

that, in Suzuki-Miyaura coupling reactions, electronic effect of ligand has significant influence on the activity and recyclability of catalysts.^[30] Stronger electron-withdrawing ability of the substituent leads to more efficient stabilization of the lone pair of electrons on NHC, resulting in better catalytic activity and cyclic stability. The NHCs-based HCP support also played a key role in enhancing metal species stability under thermal and oxidative conditions. For example, an HCP-NHC-Cu, prepared by Tan and Gu,^[31] showed quite good thermal stability, and can be used eventually in Glaser oxidative coupling and Ullmann C-N coupling reactions. A planar trimer indole called triazatruxene has also been used as the monomer of HCP, and after loading Pd(OAc)₂, the resulting material showed reasonably good catalytic activity in Suzuki-Miyaura cross-coupling reaction.^[32]

Lai et al. tried to use the second knitting model to incorporate metal complex onto HCP skeleton, and the proof-of-concept was verified by knitting Pd(PPh₃)₄ and benzene with FDA to prepare an HCP. The resulting material has nearly single-atom dispersed Pd species in its 3D network.^[33] An interesting electro-beam irradiation-induced metal atoms aggregation-crystallization was also observed under HRTEM imaging process with this material, indicating partially the spatial isolation of Pd species in the HCP support. It is beneficial to catalysis uses because Pd(0) and Pd(II) both exist in this HCP. This HCP-supported Pd material exhibited excellent activity in many reactions, including Suzuki cross-couplings, reductive homo-coupling of aryl halides, and oxidative homo-coupling of aryl boronic acid for biaryl synthesis. The HCP catalyst can be easily recycled with no detectable metal leaching and activity loss. With the similar strategy, Lai and Huang prepared a heterogeneous Ru pincer HCP framework with single-atomic sites by using a phosphorus-nitrogen PN³P-pincer ruthenium complex as the monomer component.^[34] It can efficiently catalyze dehydrogenates formic acid in both organic and aqueous media, and a turnover number (TON) of 145 300 was attained in a continuous experiment with no significant decline in catalytic activity. The second knitting model was also used to heterogenize ruthenium and gold PPh₃ complexes, [RuH(CO)PPh₃]₃ or AuXPPPh₃ (X = Cl, NTf₂), and the resulting HCPs can be used as highly efficient catalysts in imination of alcohols, intermolecular hydrations, and hydroamination of alkynes.^[35] All these results demonstrated that direct knitting of metal complex monomer is indeed an effective way to prepare immobilized metal catalyst with active single-atom site.

Tu et al. found that it is possible to make HCP-NHC-M by direct knitting of the NHC-metal complexes with the second knitting model.^[36] This is probably the only example that uses a metal complex as the monomer component in the second knitting model while all the skeleton and coordination environment of the metal species remained to be unaltered. Characterizations of the obtained HCPs with many spectroscopic methods fully verified the uniform dispersion of bis-chelating NHC-M metal species in the matrices of HCPs. It means that there are only bis-NHC-Ir species, no mono-NHC-Ir model was observed in the HCP matrix. This clearly showed the advantages of the second knitting model compared with the first knitting model, namely the post-modification strategy. With the latter one, a mixture of mono- and bis-chelating model would be obtained. Then, Tu et al. investigated their activities as single-site catalysts in the hydrogenation of biomass levulinic

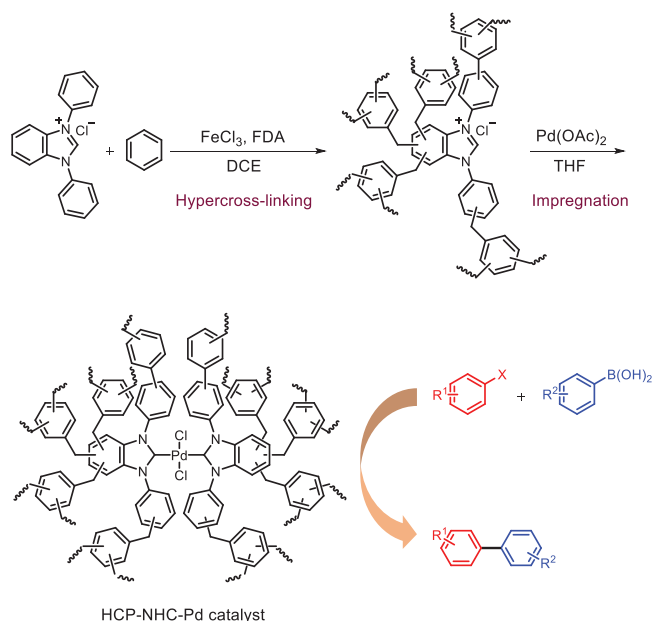
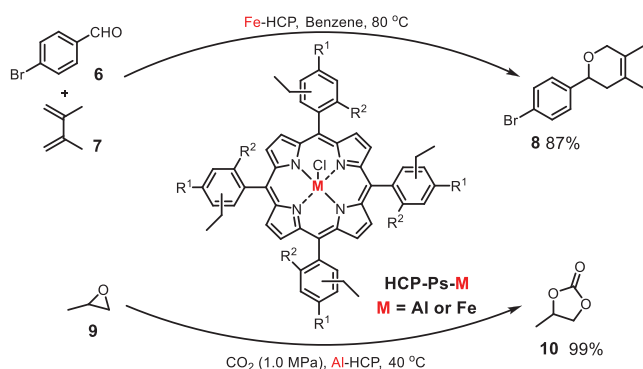


Figure 3. Schematic illustration of preparation of an HCP-NHC-Pd catalyst with the one-step knitting strategy.^[29]



Scheme 2. Metalloporphyrin-based HCPs as catalyst in some transformations.^[37,38]

acid to γ -valerolactone. Under optimized reaction conditions, a high yield was obtained with the newly obtained HCP catalyst. The solid could be used for 15 consecutive runs under the optimized reaction conditions. TEM images and XPS analysis clearly demonstrate that no iridium agglomeration or cluster formation occurred during recycle of the catalyst.

The arene structure of porphyrins ensured these ligands are weakly nucleophilic and amenable to a Friedel–Crafts-type reaction. Based on this reactivity, Dou and Liu used iron(III) porphyrins as building blocks to construct a series of metalloporphyrin-based HCP (HCP–FePs) through a one-step knitting strategy promoted by anhydrous FeCl_3 .^[37] By using FDA as a cross-linking reagent, the HCP–FePs can be synthesized easily, which featured by inherent hierarchical porosity and fine distribution of single iron porphyrin sites. Powder X-ray diffraction measurements revealed that HCP–FePs are amorphous, with no evident definite signals. Because of the rich distribution of iron porphyrin, it can be used as excellent heterogeneous catalyst for cycloaddition of aldehydes 6 to 2,3-dimethyl-1,3-butadiene (Scheme 2). A high yield (872%) was also afforded in the scaled-up reaction. The TON reaches 4359 with a turnover frequency (TOF) of 91 h^{-1} after 48 h. The catalyst can be easily separated by centrifugation. The recovered HCP–FePs catalyst can be reused at least five times without any significant loss of catalytic activity and original shape.

Proceeding on the same line, Ji et al. constructed some aluminum(III) porphyrin-based HCPs (HCP–Al–Ps),^[38] which could be used as an efficient solid catalyst for the cycloaddition of CO_2 to epoxide (Figure 4). The synthesized HCP–Al–Ps possess not only high S_{BET} , excellent thermal stability, and superior CO_2/N_2 adsorptive selectivity, but are also characterized by relatively uniform hollow nanotube structure, thus favoring the enrichment of CO_2 and facilitating substrate transfer. All these structural properties combined with a large amount of Lewis acid sites, aluminum cation center, and the weakly basic porphyrin skeletons, which can partially absorb the acidic CO_2 by the acid–base interactions, ensured HCP–Al–Ps to be excellent catalysts for the cycloaddition of CO_2 to epoxide. A high TOF value ($14\,880 \text{ h}^{-1}$) was obtained with PO at 100°C and 3.0 MPa (Scheme 2). When using flue gas composed of 15% volume of CO_2 and 85% N_2 as the raw material, the reaction proceeded also quite well under ambient conditions.

Homogeneous porphyrin-based bimetallic Lewis acid–base pair, $[\text{M–Ps}]^+[\text{Co}(\text{CO})_4]^-$, were well known as efficient catalysts

for the ring-expansion carbonylation of epoxides. To facilitate their recycling, Yoon and coworkers established a simple heterogenization strategy by means of direct knitting of Al(III)–porphyrin or Cr(III)–porphyrin with or without cross-linking reagent.^[39] The basic framework was subjected to an anion exchange to incorporate $\text{Co}(\text{CO})_4^-$ into the porous material. Although the incorporation of $\text{Co}(\text{CO})_4^-$ led to the decrease of total pore volume available, the framework still retained high porosity, facilitating mass transfer of the substrates and products. The obtained porous porphyrin aluminum(III) tetracarbonylcobaltate bimetallic material, $[\text{HCP–Al–Ps}][\text{Co}(\text{CO})_4]$, can effectively catalyze transformation of epoxides to the β -lactones with an excellent site time yield, 360 h^{-1} (Figure 5). This is comparable with several homogeneous analogues. With the same knitting method, Al(III)–4,5-bis(2-di-iso-propylphenoxy)phthalonitrile and metallosalen complexes can also be heterogenized, and the obtained HCP after incorporating with $[\text{Co}(\text{CO})_4]^-$ anion can also be used as a recyclable catalyst in the ring-expansion carbonylation of epoxides.^[40]

Quite recently, Zhu et al. established a simple and low-cost method for heterogenizing Pd–Salen complex by means of a one-step knitting strategy using FDA as an external cross-linking reagent.^[41] The resulting HCP–Salen–Pd catalyst exhibited excellent catalytic performance in C–H bromination and chlorination reactions, even better than the homogeneous counterpart (Figure 5). HCP–Salen–Pd can be reused at least ten times without significant loss of catalytic activity. A hot filtration test revealed that the reaction was really heterogeneous in nature. Furthermore, ICP–OES analysis showed only traces of Pd ($<0.1 \text{ ppm}$ were recognized) in either the conversion or the yield. The similar catalyst displayed also excellent catalytic performance under the mild conditions and aqueous reaction media for the Suzuki coupling reaction.^[42] 2,2′-Bipyridine, a commonly used nitrogen-containing bidentate ligand, is also amenable to the knitting conditions, leading to an HCP that can also immobilize Pd efficiently.^[43]

4.2. Hypercrosslinked Polymers–Metal Nanoparticles for Catalysis

Metal nanoparticle (NP) catalysts often use porous solid and coordinating material as support. Metal NPs can be readily stabilized and encapsulated in nanoporous channel of HCPs by introducing coordination groups into metal precursors. Normally, the metal was introduced after finishing the knitting step, and the following reducing step allowed the formation of metal NPs. The synergy of HCPs bearing metal-coordinating sites and NPs often offer high activity with limited agglomeration and leaching of NPs. We will summarize the literature results based on the classification of ligand.

4.2.1. Hypercrosslinked Polymers with P-Containing Ligands for Metal Nanoparticle Catalysts

Fan and Zhang recently used HCP–PPh₃ as a support to stabilize Rh NPs. They found that the Rh NPs were uniformly dispersed on the solid surface, and the average particle size of Rh NPs is 2.1 nm.^[44] The obtained Rh NP–HCP–PPh₃ was

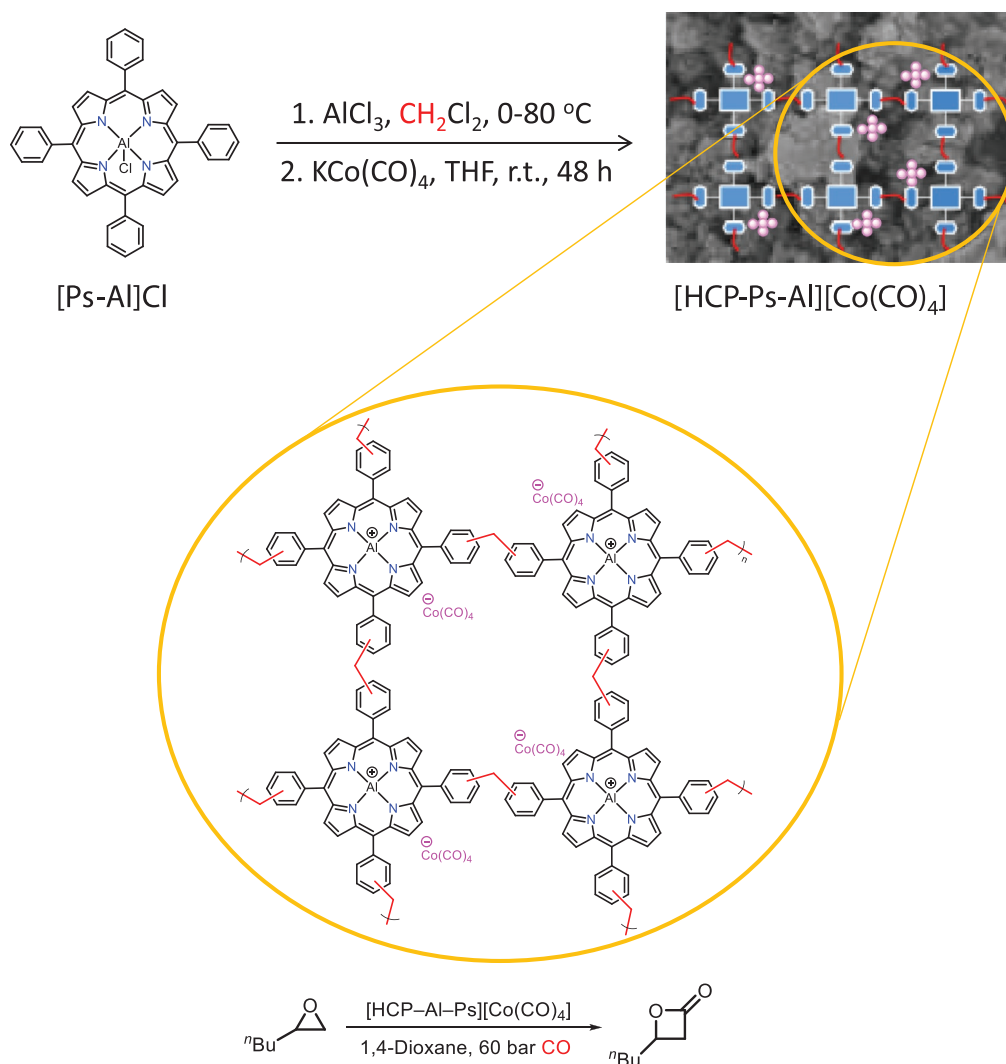


Figure 4. Schematic illustration of synthesis of [HCP-(TPP)Al][Co(CO)₄] and its utilization in the ring-expansion carbonylation of epoxides. Reproduced with permission.^[39a] Copyright 2019, ACS.

proven to be an active catalyst for hydrogen generation from ammonia–borane hydrolysis. Under mild conditions, this catalyst exhibited a high TOF of 481 mol H₂ (mol Rh min)^{−1} for ammonia–borane hydrolysis. The same reaction was also examined by a Ru NPs fabricated with the same HCP–PPh₃ support, but the efficiency is slightly inferior.^[45]

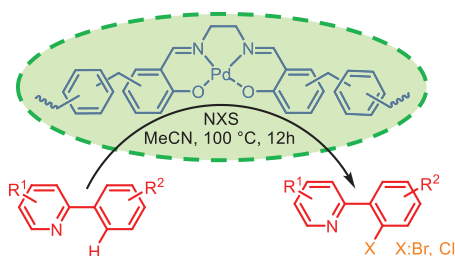


Figure 5. HCP–Salen–Pd catalyst and its application in C–H halogenation.^[41]

Direct knitting of arene via Friedel–Crafts alkylation produced normally amorphous HCP, which possess large content of microporous structure. Owing to the less distribution of mesoporous structure, the mass transfer of substrate and product was sometimes limited, restricting their applications in catalysis. To solve this problem, effort was also made to increase the content of mesoporous structure of HCP. In this context, Huang et al. provided a viable protocol. A honeycomb-like bicontinuous P-doped porous polymers were prepared via anhydrous FeCl₃-catalyzed Friedel–Crafts alkylation of polylactide-*b*-polystyrene/4-diphenylphosphinostyrene (PLA-*b*-P[S/DPPS]) diblock copolymer precursor (**Figure 6**).^[46] Because no external cross-linking reagent was added, this mesoporous HCP was in fact synthesized via a PPh₃-guided hyper-cross-linking self-assembly strategy. And, the PPh₃ functional groups not only act as the cross-linkable monomer but also serve as a strong ligand to bind the metal species. It was conjectured that the space effect from the three aromatic rings on the P atom might positively influence the hyper-crosslinking self-assembly process,

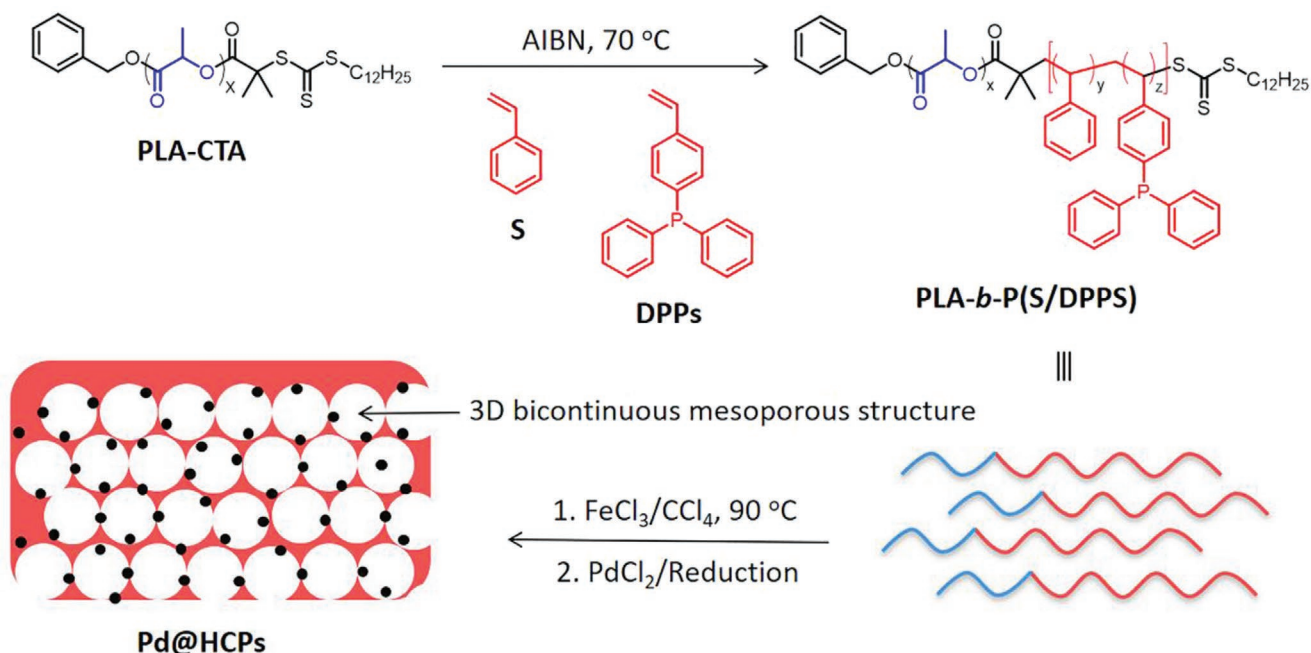


Figure 6. Schematic illustration of synthesis of Pd@HCPs from PLA-b-P(S/DPPS) diblock copolymer precursors (small balls represent Pd NPs). Reproduced with permission.^[46] Copyright 2017, ACS.

allowing the honeycomb-like bicontinuous mesoporous structure to be formed. Pd NPs can be encapsulated into the synthesized HCP via impregnation reduction method to generate a PdNP@HCP material. Owing to the distinct structure, Pd@HCPs also performed good catalytic activity, recyclability, and stability in the selective hydrogenation of nitroarenes.

With the similar method, a NP-encapsulated hollow porous polymeric nanosphere frameworks (HPPNFs) were prepared by Huang et al. via hyper-cross-linking mediated self-assembly method of polylactide-*b*-polystyrene diblock copolymer

precursor (PLA-*b*-PS) (Figure 7).^[47] By using the obtained HPPNFs as supporting materials, yolk-shell structured catalysts M@HPPNFs (M = Pd, Ru, or Pt) were prepared by adding metal ions to the HPPNFs followed by reduction with NaBH₄ (Figure 7). Among them, Pd@HPPNFs were examined for the catalytic activity in hydrogenation of styrene, and a full conversion of styrene with TON of 2500 within 25 min was achieved, which is significantly higher than commercial Pd/C. The evaluation recyclability shows a high TON without significant decrease in the catalytic activity over 15 cycles. Interestingly,

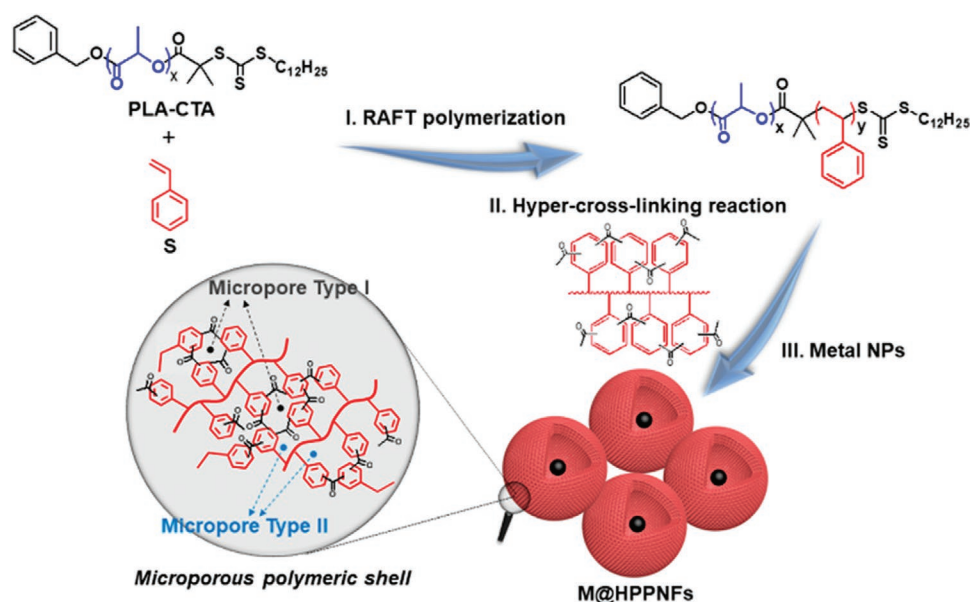


Figure 7. Schematic illustration of synthesis M@HPPNFs (M = Pd, Ru, or Pt). Reproduced with permission.^[47] Copyright 2019, ACS.

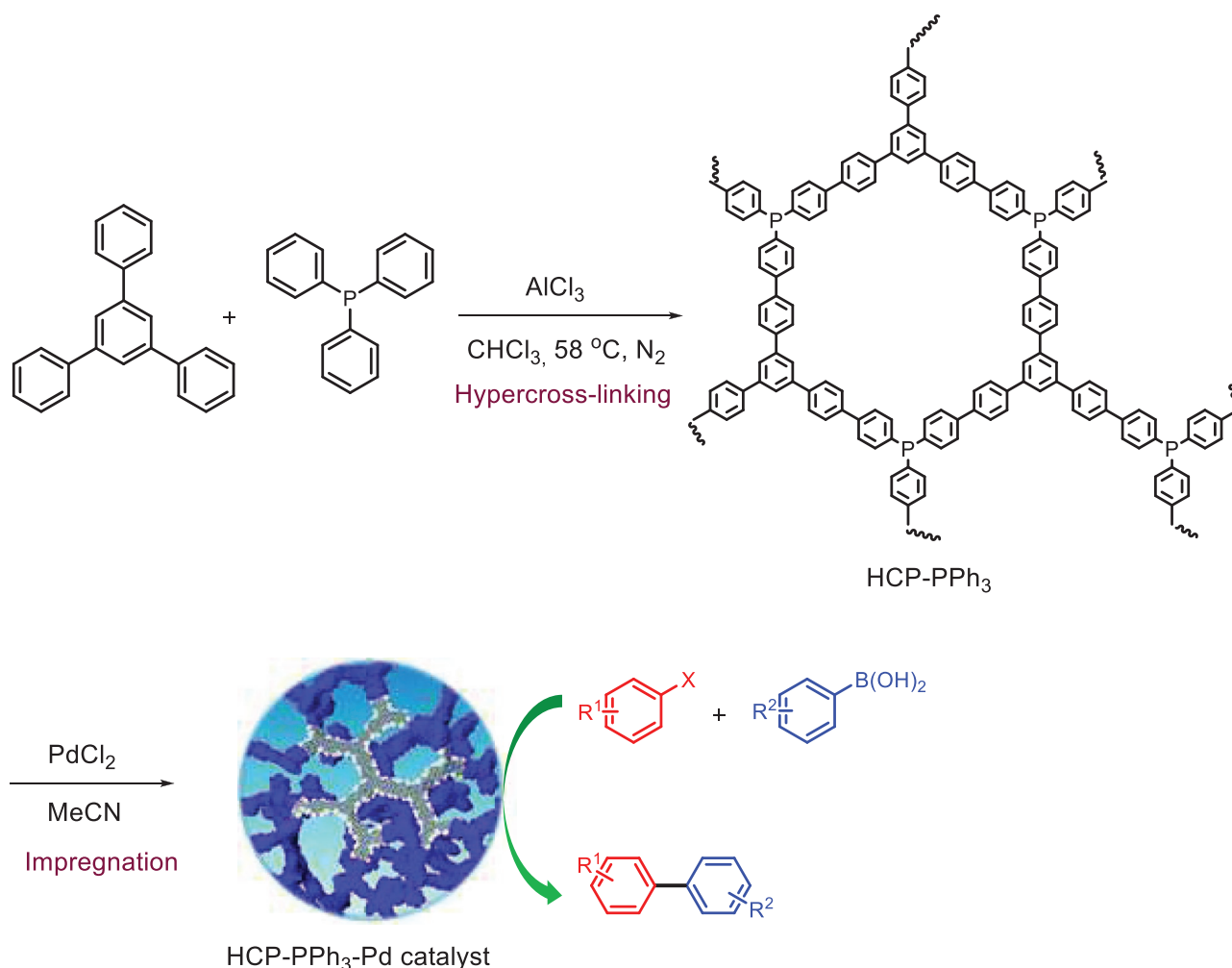


Figure 8. Schematic illustration of direct knitting of triphenylphosphine to form a MOP by acid-catalyzed Scholl reaction. Reproduced with permission.^[49] Copyright 2014, RSC.

Pd@HPPNFs achieved high conversion of styrene in all the solvents, whereas high conversion of *N*-vinyl carbazole could only be obtained in solvents with low polarity and the conversion of *N*-vinyl carbazole increased with enhancing swelling degree of the HPPNFs. This provided a possible means to precisely adjust the bimodal micropore sizes of the HPPNF shell by changing the polarity of the solvent media, and in turn the performance of catalyst.

Tris(2-thienyl)phosphine can also be used as monomer to prepare HCP in conjunction with using FDA as the cross-linker. With this kind of HCP, a supported Ru NP catalyst was prepared and used in nitrobenzene reduction.^[48] Knitting PPh₃ to form a microporous organic polymer can also be realized by acid-catalyzed Scholl reaction, which involves the elimination of two aryl-bound hydrogen atoms accompanied by the formation of a new aryl–aryl bond. This method avoided the use of external cross-linking reagent, and the generated MOP featured by a conjugated framework with a low skeleton density. Li and Tan et al. obtained a series of conjugated MOPs based on this strategy by using AlCl₃ as catalyst.^[49] Typically, MOP with ligand function was obtained via reaction of *sym*-PhPh₃ and PPh₃, followed by immobilization of Pd(II) to

form coordinating Pd(II) heterogeneous catalysts in Suzuki–Miyaura coupling reaction (Figure 8). The obtained Pd–MOP has a high *S*_{BET} (651 m² g^{−1}) and contains 2.98 wt% of P and 1.2 wt% Pd. In a selected model Suzuki reaction, this catalyst gave a 99% conversion of aryl halide within 5 min at 80 °C and a very high TOF up to 59 400 h^{−1}. Hot filtration test demonstrated that catalytic active Pd species can strongly hold in the MOP supports, suggesting the great stability of heterogeneous system. Less Pd-loading, shorter reaction time with higher products yields, revealed that abundant micropore structure and highly dispersed PPh₃ groups stabilized Pd species, thus avoiding Pd⁰ aggregation as well as loss of Pd. The facile method to embed small molecular ligands as a part of the microporous polymer scaffold gives a novel design strategy for heterogeneous catalysts.

Huang et al. reported a mild method for preparing Ag NPs supported on the framework of well-designed HCP, which was prepared by a one-step Friedel–Crafts reaction using PPh₃ and pyrrole as the precursors and FDA as an external cross-linking reagent. The dispersion of Ag NPs onto the HCP was realized by means of a reduction of silver tricyanomethanide (Figure 9).^[50] The XPS and HRTEM analysis of

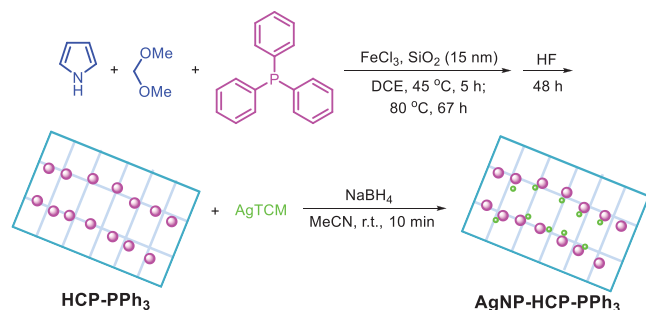


Figure 9. Schematic illustration of synthesis of Ag/HCP-PPh₃ catalyst for carboxylation of phenylacetylene. Reproduced with permission.^[50] Copyright 2017, ACS.

AgNP-HCP-PPh₃ confirmed the silver species was homogeneously dispersed in the amorphous matrix of HCP in a zero oxidation state with a smaller size (4.1 ± 1.4 nm). The AgNP-HCP-PPh₃ was tested as catalyst in a direct carboxylation of CO₂ with phenylacetylene to phenylpropionic acid. In the absence of the Ag NPs catalyst, the target product was obtained only in 37% yield after 6 h of reaction at 60 °C in the presence of Cs₂CO₃. AgNP-HCP-PPh₃ can impose a significant positive effect on the transformation, and the yield was promoted to 74%. By performing the reaction at 80 °C and increasing the reaction time to 10 h, the yield of phenylpropionic acid can be promoted to nearly 90%. Reusability of AgNP-HCP-PPh₃ catalyst was also demonstrated.

4.2.2. Hypercrosslinked Polymers with Nitrogen-Containing Ligand for Metal Nanoparticle Catalysts

Bhaumik and coworkers prepared RuNP-HCPs that can catalyze transfer hydrogenation of nitroarenes with NaBH₄ as reducing agent to produce aniline derivatives. In this work, the

HCP supports with amine coordination sites was first prepared through Friedel-Crafts alkylation of benzylamine and benzene by using FDA as a cross-linker (**Figure 10**).^[51] Ru³⁺ ions were introduced and stabilized by coordination bonds between Ru³⁺ with -NH₂ groups of HCPs support. The *S*_{BET} of RuNP-HCPs is quite high, ranging from 523 to 607 m² g⁻¹. Although RuNP-HCPs have a relatively large particle size distribution, from 3.5 to 7.0 nm with a certain degree of agglomeration, compared with traditional Ru@C, Ru@SiO₂, and Ru@TiO₂ catalysts, RuNP-HCPs exhibited excellent catalytic performance with high conversion, selectivity, stability, and recyclability in transfer hydrogenation of nitroarenes at ambient temperature. It was declared that the synergetic effect of nano-confinement and electron donation offered by the 3D HCPs network guaranteed the distinct catalytic performance. A calix[4]resorcinarene-based HCP has also been used as support to anchor pendant primary amine, and the obtained material was then used to immobilize copper(I) for catalyzing [3+2] Huisgen cycloaddition in water.^[52]

By using α, α' -dibromo-*p*-xylene and carbazole as electrophilic and nucleophilic reagent couple, Bhaumik and Islam prepared an HCP by using anhydrous FeCl₃ as catalyst.^[53] A supported Pd NP catalyst was then prepared with using this nitrogen-containing HCP as the support. FESEM image analysis revealed that the PdNP-HCP is characterized by spherical particle morphology with dimensions of ≈ 80 –90 nm. The *S*_{BET} and the pore volume of the PdNP-HCP were 384 m² g⁻¹ and 0.2171 cc g⁻¹, respectively. The palladium NPs in the surface of HCP have an average diameter of ≈ 10 –15 nm. The PdNP-HCP material was proven to be an efficient catalyst for the formylation of *N*-methylaniline with CO₂ using dimethylphenylsilane as a reducing agent. After 9 h of reaction in a water-containing 1,4-dioxane at 60 °C, the formylation product was obtained in 87% of yield. A wide range of aromatic and non-aromatic amines, such as substituted aniline, morpholine, and piperidine, were all amenable to the transformation and successfully

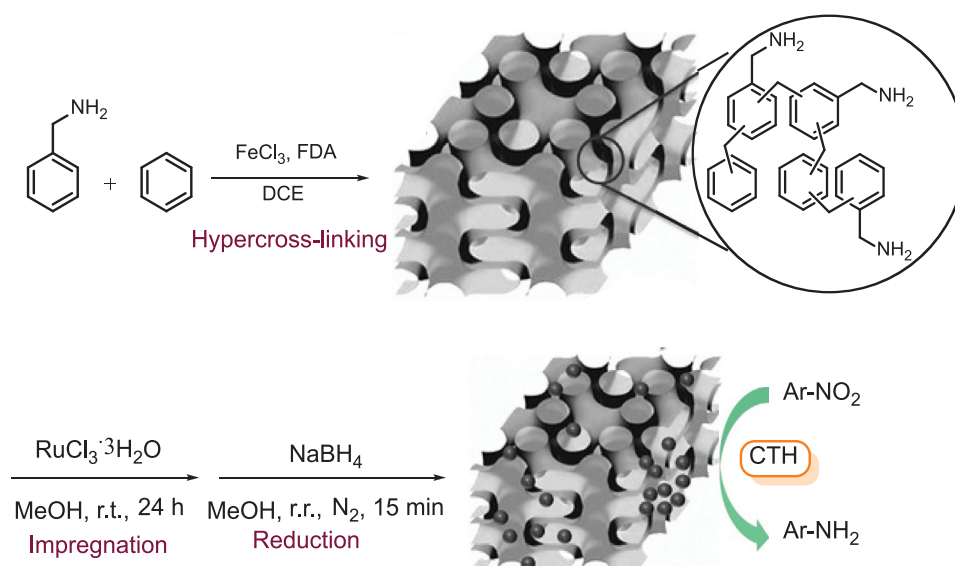


Figure 10. Schematic illustration of synthesis of a RuNP-HCPs by knitting of benzylamine with FDA. Reproduced with permission.^[51] Copyright 2015, Wiley-VCH.

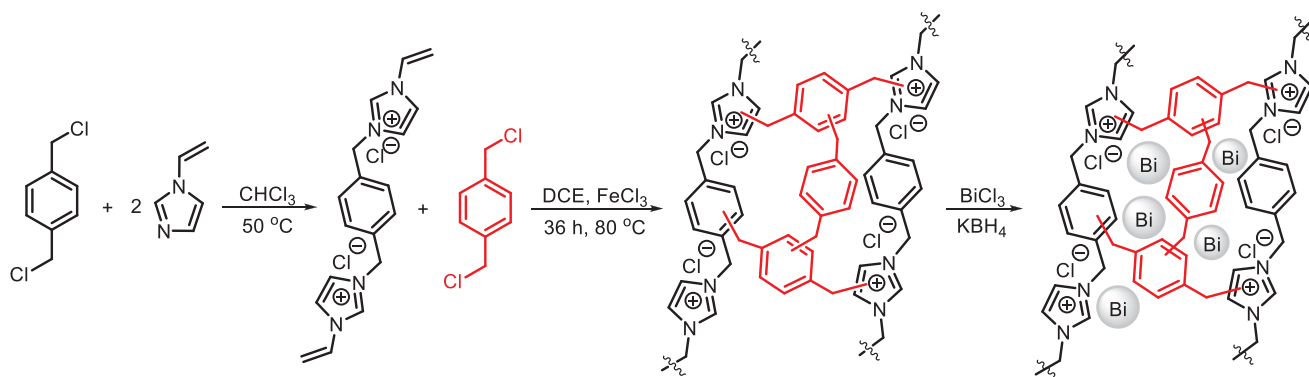


Figure 11. Schematic illustration of synthesis of an ionic HCP-stabilized BiNP catalyst. Reproduced with permission.^[56] Copyright 2020, Elsevier Inc.

afforded the corresponding formamide products in excellent yields. An alternative way was also developed by Han et al. who prepared a porous polycarbazole by a FeCl_3 -promoted oxidative coupling copolymerization with 1,3,5-tri(9*H*-carbazol-9-yl) benzene that was then utilized as a support to encapsulate AuNPs.^[54] In a reduction of 4-nitrophenol to 4-aminophenol, the catalytic activity of this supported AuNP catalyst is found to be outstanding with an activity factor of up to $1757 \text{ s}^{-1} \cdot \text{g}^{-1}$. An HCP fabricated by knitting 5,10,15,20-tetraphenylporphyrin with FDA was also used to support AuNPs, and the obtained catalysts were used in alkyne hydration and alcohol oxidation in water.^[55]

It was generally recognized that using heteroatom-doped carbon materials as metal support, the heteroatom-induced defects will favor the dispersibility of metal NPs and charge transfer between metal and supports. Because the knitting aryl networks of HCPs are mainly composed of carbons, and some of them also involve doping of metal or heteroatoms, HCPs can be considered as suitable precursors for carbon materials. The low-cost synthesis, tunable and designable structure, and high diversity of HCPs are the most attractive points for making carbon-based catalysts with this kind of material. Indeed, these properties allowed researchers to establish a new facet of carbon catalysis with HCPs. Imidazolium-based ionic liquids are well known to stabilize metal NPs. In order to make knitting of the ionic liquids successful, Chen et al. used 1,4-bis(chloromethyl) benzene to react with 1-vinylimidazole to prepare a dicationic ionic liquid with two vinyl group.^[56] Then, by treating a mixture composed of this ionic liquid and 1,4-bis(chloromethyl)benzene with anhydrous FeCl_3 , an imidazolium-functionalized HCP was obtained, which has a S_{BET} of $950 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $1.2 \text{ cm}^3 \text{ g}^{-1}$ (Figure 11). It should be noted that, with the

conventional radical polymerization method, such a porous ionic liquid material with a high S_{BET} can be hardly obtained. This HCP can be used to prepare a BiNP–HCP catalyst by an impregnation of BiCl_3 solution and the following reduction with KBH_4 . The Bi NPs were uniformly dispersed in the HCP support with small diameter 1.0–3.0 nm. In the reduction of 4-nitrophenol, it showed excellent catalytic activity and good stability. Considering the designable structures and great diversity of ionic liquids, it is conceivable that many metal NP catalysts can be prepared with conjunction of generating HCP support.^[57]

Wang and Li tried to carbonize carbene-based HCPs, and they found that the rigid aromatic building blocks in HCPs skeleton, to some extent, function as a self-template to retain the high surface area and regular pore distribution during carbonization.^[58] These propensities of HCPs enabled the formation of high quality microporous carbon framework. The authors prepared a carbon-supported Pd NP catalyst and then examined its electrochemical performance (Figure 12). Compared with commercial carbon products, the newly synthesized Pd NP catalyst displayed superior activity in oxygen reduction reaction (ORR). It was conjectured that heteroatom-induced altering of electronic structures should play pivotal role in addition to the effect of the stable skeleton.

Similarly, Mondal et al. designed and prepared a Pd NP encapsulated a nitrogen-rich HCP material through a Friedel–Crafts alkylation reaction of triphenylamine with α, α' -dibromo-*p*-xylene.^[59] The Pd NPs were loaded onto the HCP support by immobilization and the following solid phase H_2 reduction at 400°C (Figure 13). The S_{BET} and the total pore volumes of the HCP support were found to be $1165 \text{ m}^2 \text{ g}^{-1}$ and $1.033 \text{ cm}^3 \text{ g}^{-1}$, respectively. After loading the Pd NPs, the values dropped to

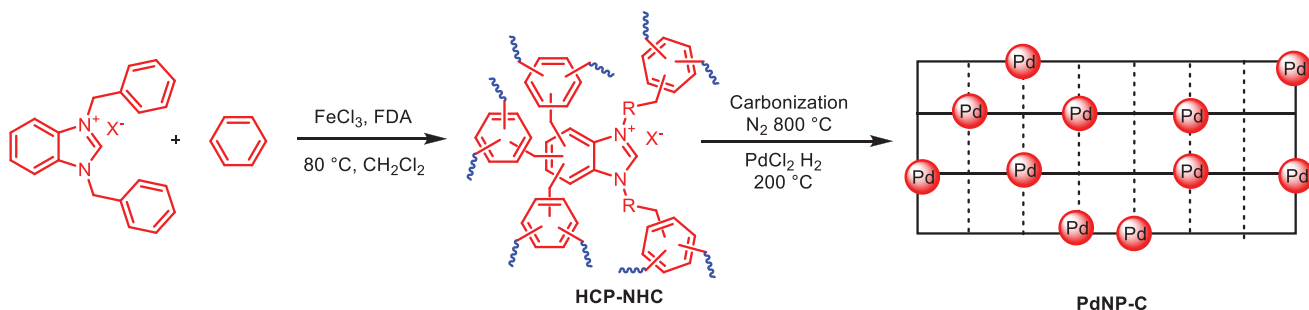


Figure 12. Schematic illustration of a carbene-based HCP for the preparation of PdNP–HCP. Reproduced with permission.^[58] Copyright 2020, ACS.

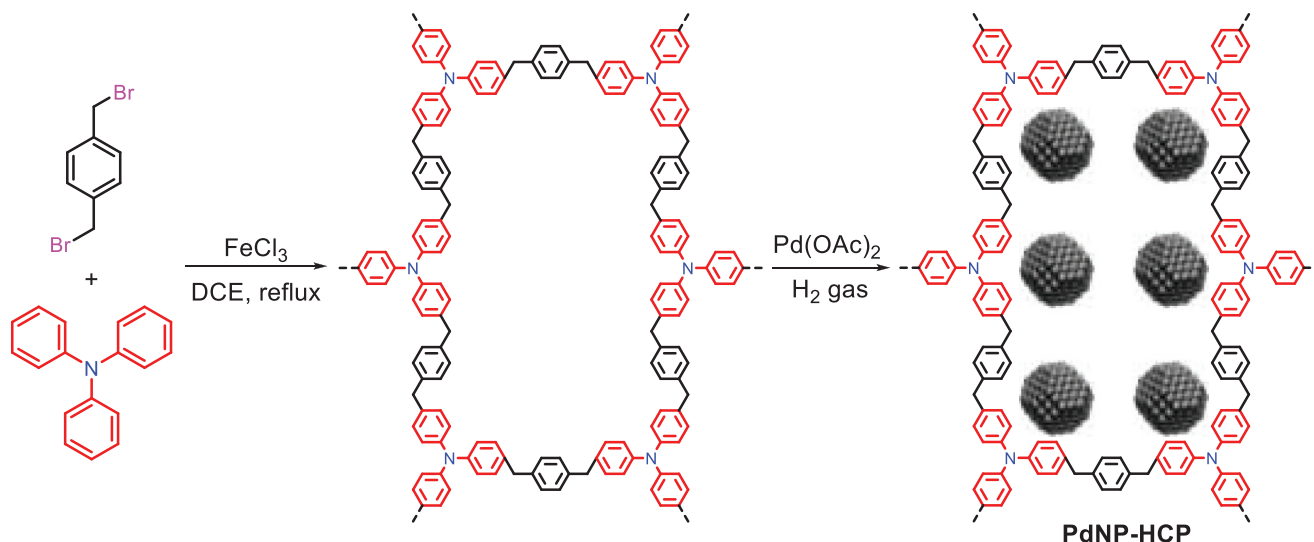


Figure 13. Schematic illustration of the synthesis of HCP from *N,N*-diphenylaniline and the corresponding Pd loaded polymer (PdNP-HCP). Reproduced with permission.^[59] Copyright 2020, RSC.

679 m² g⁻¹ and 0.825 cm³ g⁻¹. Interestingly, a dual PdNP size distribution was found in this PdNP-HCP, and the mean diameters are $\approx 1.86 \pm 0.36$ and 2.89 ± 0.25 nm. This catalyst was examined in hydrodeoxygenation of fatty acids to long chain alkanes, which were potential biofuel additives. Upon 20 bar of H₂, up to 90% conversion with 83% selectivity to C17-alkane was obtained after 14 h of reaction at 150 °C by using this PdNP-HCP using stearic acid as model substrate. However, a significant loss of its catalytic activity was observed in the reuse of the catalyst. The size of the NPs also increased apparently. Fortunately, hot filtration test validated that there was an insignificant leaching of the Pd species. PdNP-HCPs can also be prepared by Friedel-Crafts alkylation reaction using 4-tritylaniline,^[60] substituted 1,2,3-triazoles,^[61] and 5-, 10-, 15-, and 20-tetraphenylporphyrin^[62] as the monomer and FDA or dichloromethane as the cross-linker, respectively. And the resulting materials were proven to be a suitable catalyst for promoting Suzuki coupling reaction, and hydrogenation of ammonia borane, nitro compounds, or α,β -unsaturated aldehydes.^[63]

4.2.3. Hypercrosslinked Polymers with S-Containing Ligand for Metal Nanoparticle Catalysts

Triphenylmethanethiol (TPMT) contains not only three arene fragments but also a thiol group, which is well known to coordinate with gold salt. By using TPMT as monomer and FDA as cross-linker to prepare HCP thus facilitated preparation of AuNP-HCP. Although the thiol group may also react with the electrophilic FDA, a part of free -SH exist and allows binding of Au NPs onto the HCP to be feasible. With this protocol, Jin and Tan established a size-controllable method to support Au NPs onto HCP support. A thermal reduction method was employed without adding external reductant.^[64] The obtained AuNP-HCP showed high catalytic activity and recyclability in reduction of 4-nitrophenol. The Au NPs could be controlled within the size range of 1.7–5.1 nm by modulating the loading

mass ratio of H₂AuCl₄·4H₂O/HCP-TPMT and the confinement effect of porous structure in the microporous organic materials played a vital role. It thus offers an effective strategy to produce size-tunable metal NPs in HCPs that can be used as effective heterogeneous catalysts for chemical processes (Figure 14). With the aid of strong coordination of gold and thiol group, HCP-supported Au NPs can also be synthesized by direct knitting of core-shell bottlebrush copolymer precursors containing a disulfide bond, which was broken before loading gold species. This method allowed Au NPs (the diameter is $\approx 3.0 \pm 1.0$ nm) to be loaded in 18% with uniform dispersion.^[65] This Au NPs exhibited a high catalytic activity and excellent stability for the selective oxidation of benzyl alcohol in water.

4.2.4. Hypercrosslinked Polymers without Coordinating Site for Metal Nanoparticle Catalysts

Metal NPs can also be well stabilized by an HCP support without prefunctionalization of coordinating site in the framework. To realize this goal, confinement of the HCP support is crucial. Davankov's process intrinsically has advantage as the precursor, linear PS, is already linked together, allowing the fine control of the aggregation state.^[66] To find an alternative method, Li and Tan et al. were dedicated to fabricating an HCP-based carbon material in order to improve the size, stability, and dispersion degree of Pd NPs.^[67] Initially, an HCP was prepared using 1,3,5-triphenylbenzene and FDA as the monomer and external cross-linker, respectively. The expected catalysts with encapsulated palladium species were obtained by the following carbonization and H₂ reduction (Figure 15). The monomer structure and carbonization temperature have great influence on the *S*_{BET}, pore size, and Pd NPs size. Fortunately, by using 1,3,5-triphenylbenzene as the monomer of HCP, the expected hierarchical porous structure can be obtained, and the average size of Pd NPs can be controlled at

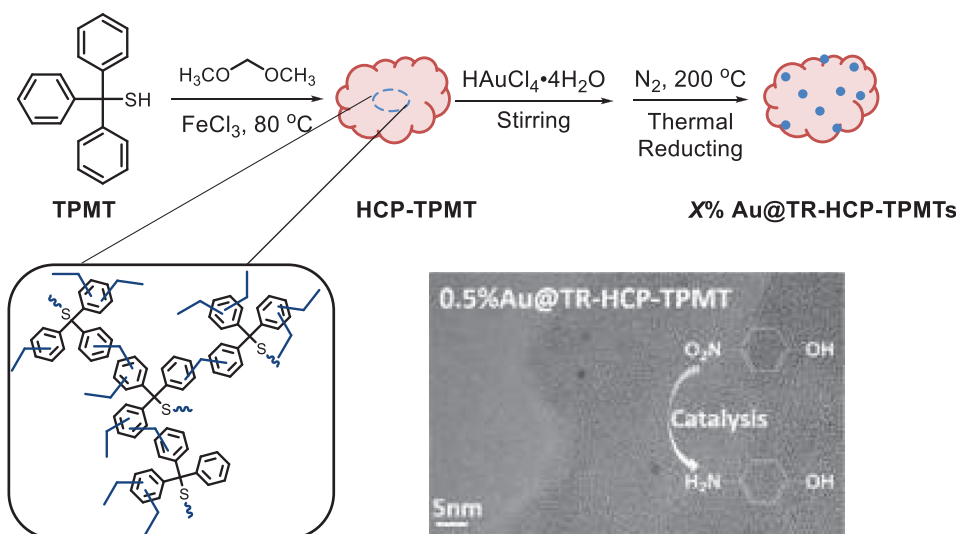


Figure 14. Schematic illustration of synthesis of HCP-TPMT and AuNP-HCP-TPMT catalysts. Reproduced with permission.^[64] Copyright 2019, ACS.

4 nm by tuning the porous structure and calcination temperature. Investigation on the catalytic activity manifested that the HCP-carbon-based catalysts have outstanding performance to promote a Heck reaction of styrene and halobenzene. With this carbon-supported Pd NP catalyst, high yields up to 95% were achieved after ten times of recycling using iodobenzene as the counterpart reagent of styrene. No significant size change of the Pd NP can be observed on the carbon support after the reaction, indicating the good stability of this catalyst. The catalyst displayed excellent catalytic activity also in Suzuki cross-coupling reaction even at a loading of 0.05 mmol% Pd, and the TOF for the reaction reached remarkably $61\,353\text{ h}^{-1}$.^[68] These works demonstrated that it is indeed possible to prepare

a highly active and stable metal NP catalyst without doping of a coordinating site in the framework of HCP. Loading of Pd NPs on a carbon material derived from carboxylic acid- and sulfonic acid-functionalized HCP allowed the synthesis of PdNP-HCP, which can cooperate with iron-containing ZSM-5 zeolite to implement the oxygenation of methane by tandem H_2O_2 formation from H_2 and O_2 and partial oxidation of methane.^[69]

Confining metal NPs in the hollow spheres to make yolk-shell structure is an effective way to avoid the aggregation of metal NPs and ensure a high catalytic activity. Because HCPs are amorphous porous material with rigid and organic framework, if the yolk-shell structure of HCP can be constructed, the

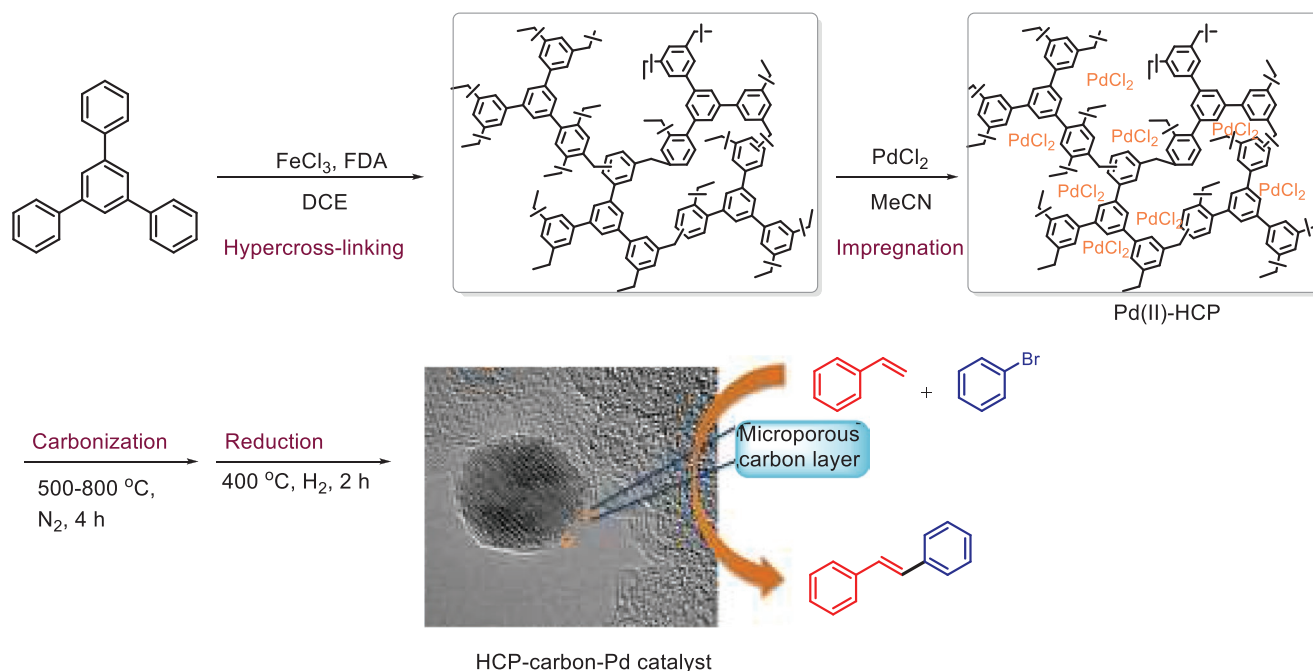


Figure 15. Schematic illustration of a porous carbon fabricated by using HCP as a precursor. Reproduced with permission.^[67] Copyright 2015, RSC.

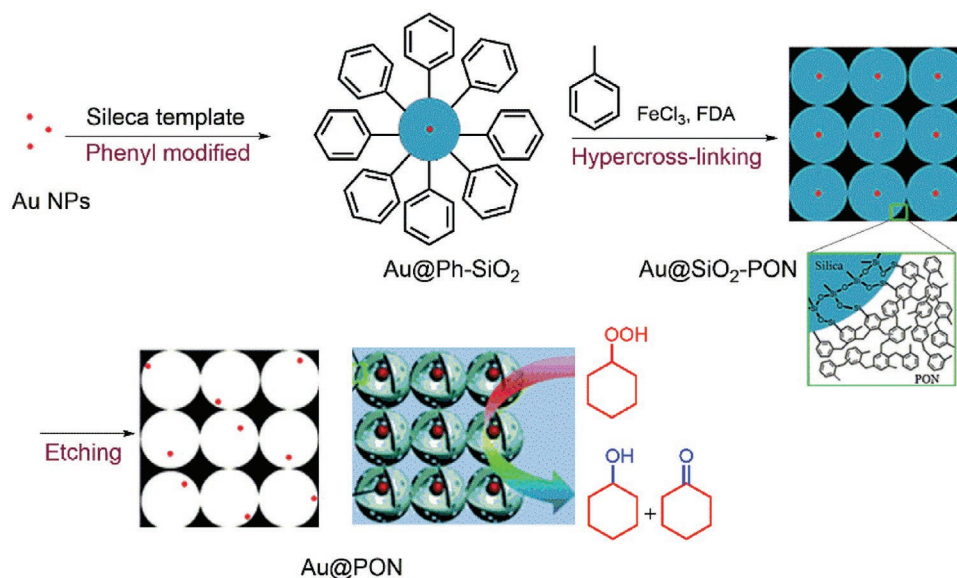


Figure 16. Schematic illustration of an AuNP@HCP catalyst for decomposition of cyclohexyl peroxide. Reproduced with permission.^[70] Copyright 2014, RSC.

inside cavities, was expected to function as a hydrophobic nano-size reactor. Xu et al. prepared a yolk-shell type HCP-supported gold NPs.^[70] To facilitate the formation of hollow morphology, a phenyl-modified SiO₂ was used as template. Au NPs were first covered with phenyl-modified silica shells to give AuNP@Ph-SiO₂. Afterward, HCPs were fabricated on the surface of the silica template by knitting phenyl groups together with toluene and FDA. Finally, the expected AuNP@HCP was obtained by etching silica shells with aqueous HF (Figure 16). The yolk-shell catalysts containing a movable core and a rigid outer shell yielded a nanoreactor. The separate confinement of the Au NPs in the HCP cavities is protected to some extent from sintering and aggregation. The prepared AuNP@HCP catalysts were employed in decomposition of cyclohexyl peroxide. Excellent activity with 90% of cyclohexyl peroxide conversion and 86% selectivity to K/A oil (a mixture of cyclohexanone and cyclohexanol) was obtained with this catalyst. The AuNP@HCP catalyst can be recycled at least three times without significant loss of its activity. The yolk-shell structure remained well after the reaction and no evident Au aggregation was observed due to the protection effect.

Knitting of toluene on the surface of a phenyl-decorated magnetic Co/C nanosphere allowed coating of a thin layer of HCP on the support (Figure 17).^[71] An encapsulated Pd NP with the resulting material displayed excellent activity in hydrogenation reactions of carbon-carbon unsaturated bonds, and nitrobenzenes with TOFs up to 3000 h⁻¹. The advantages of integrating HCP with this magnetic material displayed not only high catalytic activity, but also the easiness of structural modification. Indeed, by 2,2'-biphenol as an alternative monomer to toluene in the knitting process enabled the introduction of hydroxyl groups into the HCP, minimizing the leaching of palladium and cobalt from the catalyst.

Sheng Dai et al. synthesized a hypercrosslinked β -cyclodextrin porous polymer via a two-step method including i) complete benzylation of β -cyclodextrin (the obtained product

was denoted as BnCD); and ii) Friedel-Crafts alkylation of the obtained benzylated β -cyclodextrin using FDA as external cross-linking reagent.^[72] Although the monomer, BnCD, is a flexible molecule, the obtained BnCD-HCP possess surprisingly an S_{BET} as high as 1225 m² g⁻¹ and a total pore volume of 1.71 cm³ g⁻¹. It should be noted that the inherent cavitation of β -cyclodextrin should also be responsible for the high S_{BET} . Because of the strong binding interaction between the aromatic ring and β -cyclodextrin, BnCD-HCP can be used as an efficient adsorbent for aromatic molecular removal. Absorption and catalytic transformation of phenolic compounds, such as 4-nitrophenol to 4-aminophenol, was realized by AuNP@BnCD-HCP (Figure 18). It was conjectured that the existence of porous BnCD-HCP not only helps to stabilize the gold particles, but also promotes the diffusion of reactants. The stability of the catalyst was also examined by applying the same catalyst into the reduction reaction. After five cycles, the catalyst was still highly effective in reducing 4-nitrophenol by nearly 100% conversion in 3 min.

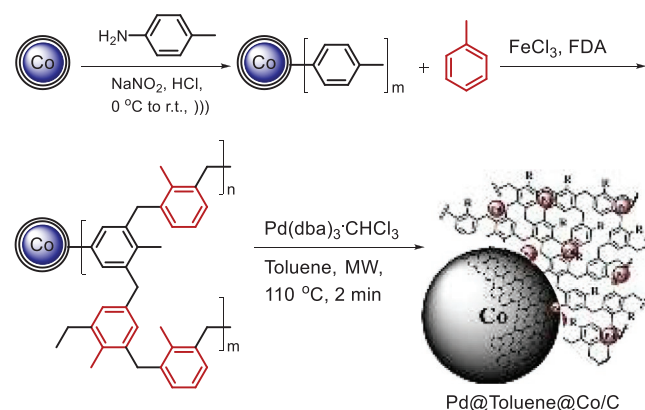


Figure 17. Schematic illustration of HCP on the surface of Co/C nanosphere. Reproduced with permission.^[71] Copyright 2019, ACS.

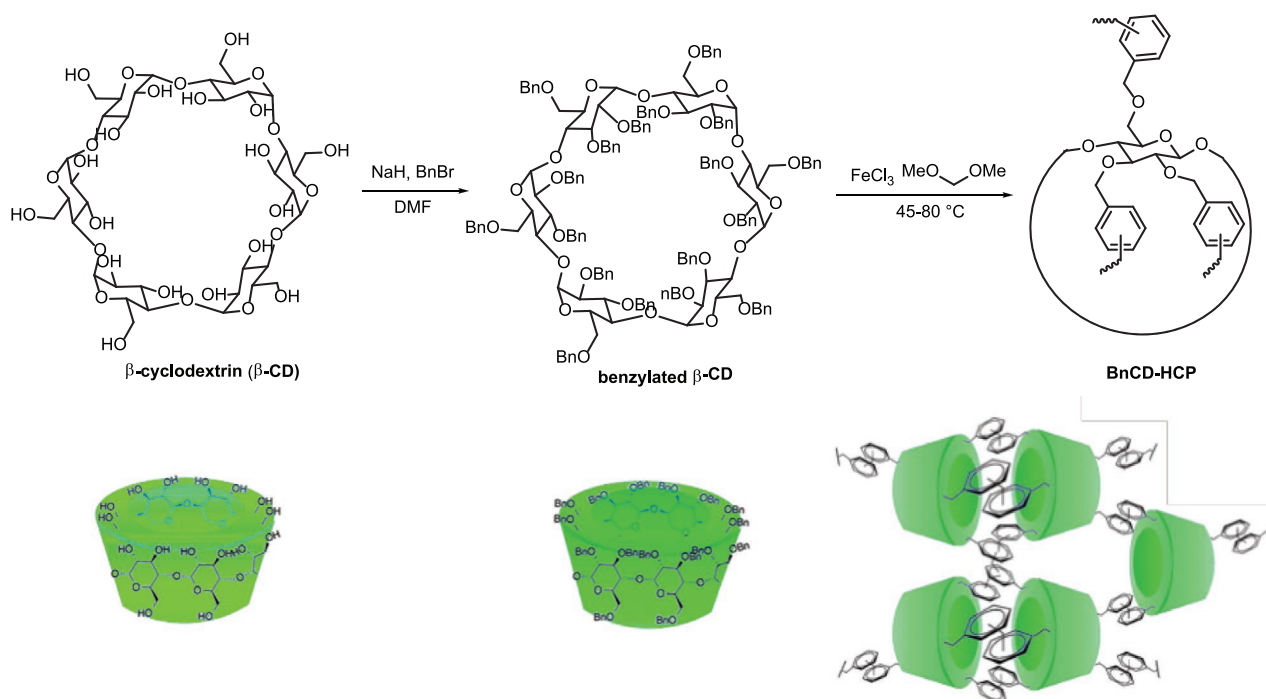


Figure 18. Schematic illustration of synthetic strategy of the hypercrosslinked β -cyclodextrin porous polymer (BnCD-HCPP).^[72]

4.3. Hypercrosslinked Polymers for Acid/Base Catalyst

Because of the unique microporous structure, HCPs obtained with direct knitting method are good supporting materials for heterogenizing acid or base catalysts. By using dichloromethylbenzenes as starting materials and anhydrous FeCl_3 as catalyst, Wang et al. synthesized some porous HCPs,^[73] which underwent a sulfonation with chlorosulfonic acid to give some heterogeneous solid acid catalysts (**Figure 19**). FT-IR and ^1H - ^{13}C CP/MAS NMR spectra indicated the successful introduction of sulfonic groups onto the framework of porous HCPs. Each peak of Raman spectroscopy does not shift after sulfonation. It implies that the skeleton structure in the functionalized HCPs materials maintained quite well. Energy dispersive spectrometer mapping for S element indicated also the presence and uniform distribution of $-\text{SO}_3\text{H}$ groups in the porous 3D network. The acidic HCPs showed excellent catalytic performance in Friedel-Crafts alkylation of anisole with

benzyl alcohol. A quantitative yield can be obtained at 120 °C with the aid of an optimal HCP-based acid catalyst. It was conjectured that the supporting material also contributed a special nano-constraint effect on the reaction, enhancing the reaction selectivity. Beckmann rearrangement reaction of cyclohexanone oxime proceeded also very well, and 83.4% of yield can be obtained. The recycling experiments demonstrated that the catalysts are robust enough and can be reused for five cycles in the model reaction with a good and stable performance. A solid acid was prepared by sulfonation of HCP, which was fabricated by direct knitting strategy of benzene with FDA. In DMSO solvent, this solid acid can effectively catalyze dehydration of fructose to 5-hydromethylfurfural (HMF).^[74] However, the S_{BET} and pore volume decreased slightly after two times of reuse, probably due to the micropore blockage by the unreacted fructose and products during the catalytic process. Performing the dehydration reaction of fructose in ethanol with the aid of HCP-supported sulfonic acid catalyst is also very successful. An

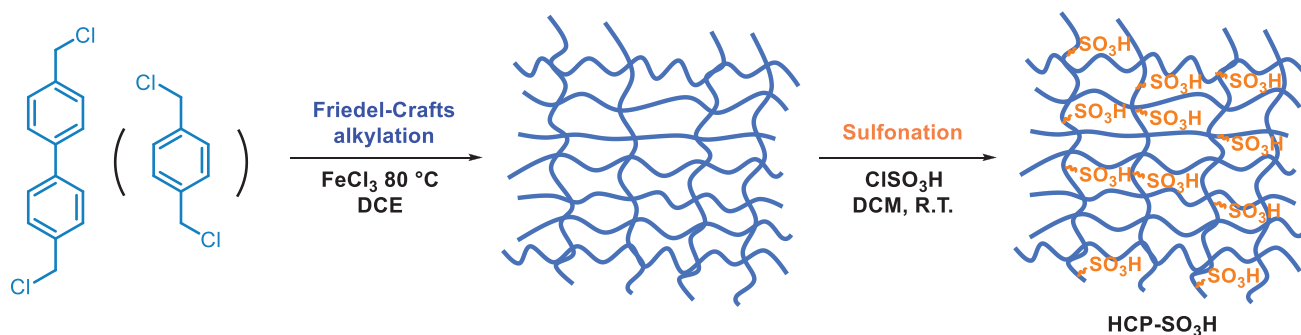


Figure 19. Schematic illustration of synthesis of sulfonic acid functionalized hypercrosslinked bischloromethyl-based porous organic polymers.^[73]

ethanol ether of HMF was generated in this case with up to 78.9% of yield.^[75] With this catalyst, overreaction of fructose, if it is selective, will produce ethyl levulinate.^[76]

Phenol and bisphenol have also been used as precursors to make SO₃H-functionalized HCPs in conjunction with employing FDA as cross-linking reagent and chlorosulfonic acid as sulfonation reagent.^[77] The obtained HCPs with bisphenol precursor displayed excellent catalytic activity for the esterification of various long chain free fatty acids and transesterification of vegetable oils. 2,2'-Biphenol has also been used to prepare a solid acid with the similar knitting and sulfonation procedure. The obtained HCP-SO₃H has a S_{BET} of 452 m² g⁻¹. In a three-component reaction of aniline, triethyl orthoformate, and dialkyl phosphite, this catalyst showed excellent catalytic activity, and is able to synthesize *N*-containing bisphosphonates in over 90% of yields.^[78] It should be noted that, the sulfonation of HCPs prepared by knitting of phenol monomer and FDA cross-linker with chlorosulfonic acid may result in the formation of two types of acid sites, including -SO₃H and -OSO₃H.^[79] The former was linked directly to the arene ring, and the latter was bonded with the -OH group of the phenol. Both of them are strongly acidic, but the former acid species is generally more stable than the latter. In order to arrange the acid site to be easily accessible, an HCP that contains chloro-

methyl groups has been used as support to react with imidazole under basic conditions. A supported Forbes's ionic liquid can be synthesized with the obtained HCP. Because the presence of a long bridge (composed by the imidazolium and alkyl chain) between the -SO₃H group and the HCP support, the supported acid ionic liquid can be an alternative choice when an acid catalyst is needed.^[80]

Bhaumik et al. developed HCP-based solid acid catalyst, HMP-SO₃H, via a two-step procedure including i) Friedel-Crafts alkylation between carbazole and α,α' -dibromo-*p*-xylene;^[81] and ii) a post sulfonation modification with chlorosulfonic acid (Figure 20). HMP-SO₃H featured distinguished physicochemical parameters, such as S_{BET} = 346 m² g⁻¹ and total acidity concentration of 3.7 mmol g⁻¹. In an esterification of lauric acid with methanol, the yield of methyl laurate reached $\approx$ 99% after 10 h of reaction at room temperature. In this reaction, methanol played the roles of both solvent and reactant. There was no significant decrease in catalytic activity after five recycles. But the authors did not comment on the possible swelling of the HCP-based catalyst, which normally was a problem for resin-based catalyst, particularly used in methanol. Anyway, the above results reflected that the prepared acid catalyst, HMP-SO₃H, has benign activity and recyclability in the esterification of lauric acid. In addition to the HCP sulfonation,

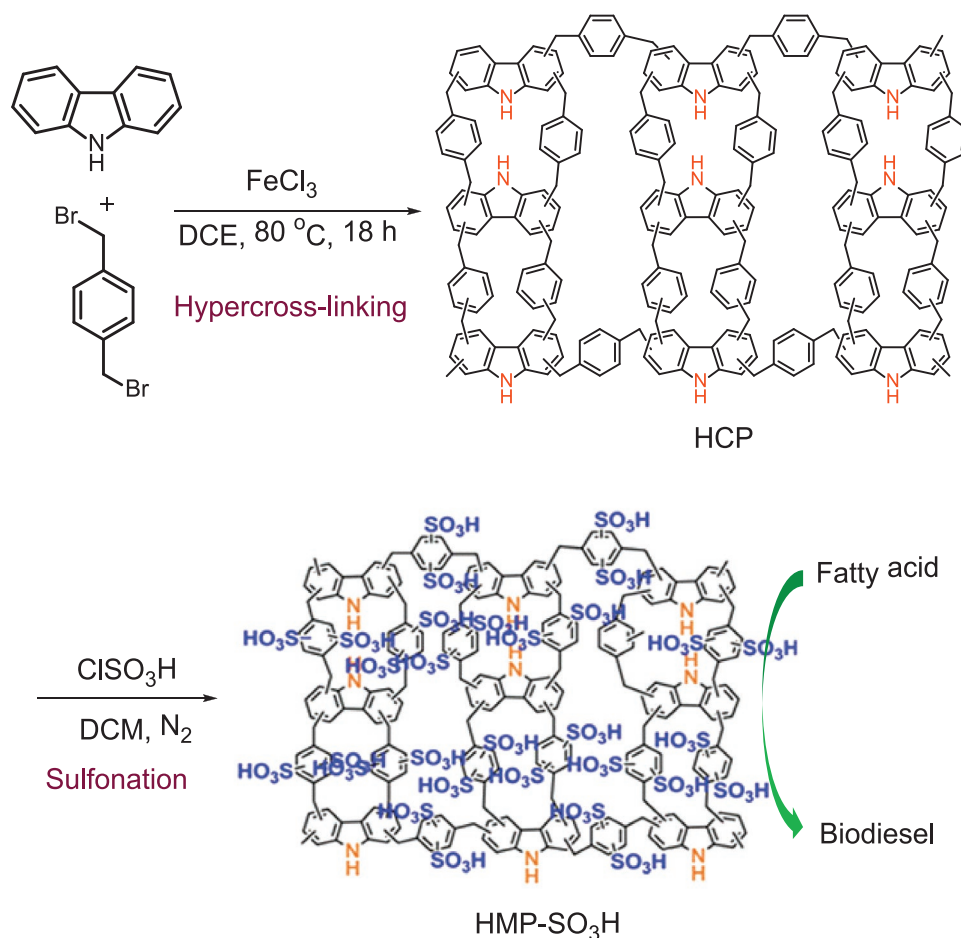


Figure 20. Schematic illustration of synthesis of a HMP-SO₃H from carbazole. Reproduced with permission.^[81] Copyright 2015, RSC.

halomethylation of the aryl network of HCP also produced an acid catalyst, but with low catalytic performance and limited application.^[82]

Generally, the methods to control the shape and polymer morphology of HCP materials are limited. But, arranging the HCPs to be regular form can hopefully modulate their performance. Therefore, researchers also pay attention to the morphology engineering of HCP. Recently, Son et al. successfully engineered HCP bearing 1,1'-bisnaphthols (BINOLs) on a shape-controlled hollow CMP, and used the resultant HCMPL@HCP-BP as heterogeneous catalytic system in the ring-opening polymerization of ϵ -caprolactones to poly(caprolactone) (PCL).^[83] In the initial stage, H-CMPL materials were synthesized through a two-step method including i) coupling of tetra(4-ethynylphenyl)methane and 1,4-diiodobenzene using silica spheres as templates, and ii) an etching of inner silica spheres with aqueous solution of HF. In the next stage, H-CMPL was subjected to Friedel-Crafts reaction of racemic BINOL with FDA, leading to the formation of H-CMPL@HCP-B, which was then used as the precursor to introduce hydrogen phosphate groups with phosphoryl chloride. The following quenching with acid provided an H-CMPL@HCP-BP (Figure 21). The hollow structure of H-CMPL retained well, and the diameter was ≈ 175 nm. But the average thickness of the shell increased after deposition of HCP with BINOL monomer. Analysis with TEM image revealed that the original hollow structure and micron-sized spherical morphologies of H-CMPL@HCP-B were completely retained after acidic quenching. The use of resultant H-CMPL@HCP-BP materials in a ring-opening polymerization of ϵ -caprolactones

to PCL showed higher isolated yields and longer chain lengths than an amorphous referential catalyst, micron-sized HCP-BP (M-HCP-BP), due to its morphology and size effect. Compared with M-HCP-BP, the H-CMPL@HCP-BP showed superior recyclability after the successive five cycles, the relatively poor recyclability of M-HCP-BP is attributed to its thicker shell thickness and the more facile clogging of diffusion pathways of monomers by the generated PCL.

Coexistence of acidic and basic sites, which are basically contradiction body, in the surface of the same solid conferred the material two different catalytic properties, thus allowing the establishment of some one-pot tandem reactions. Because of the rich distribution of arene fragment and rigid structure, acid and base species can be easily anchored onto HCP network, thus enabling the material to be good candidate of acid/base tandem catalysis. Recently, some nanospheres with the coexistence of acid and base sites were fabricated by Tan and Gu.^[84] As shown in Figure 22, the preparation of acid-base bifunctional HCP involved the following three steps: i) synthesis of a microporous hollow HCP nanosphere using nano SiO_2 as the template; ii) introducing $-\text{SO}_3\text{H}$ group by sulfonation (the acid site) after etching the template; and iii) anchoring the $-\text{NH}_2$ (the basic sites). After confirming the hollow structure of the HCP nanosphere and also the successful decoration with the acid and basic sites, the catalytic activity of the functionalized HCP nanosphere was investigated in a one-pot hydrolysis/Henry tandem reaction of 2-bromobenzaldehyde ethylene glycol acetal 11. The acetal feedstock hydrolyzed completely, and the generated aldehyde intermediate underwent the following Henry reaction to give the desired product 12 in a nearly quantitative yield. Control experiments verified that the acid-base bifunctional HCP indeed served as dual acid and base catalyst to enable the tandem reaction to proceed well. Because of the good water-stability, this bifunctional catalyst can be used in conjunction with the use of H_2O solvent, and the corresponding product was generated without significant decrease in yield. On account of remarkable water-stability, this bifunctional HCP nanosphere was found to be an ideal catalyst of a water-assisted tandem transformation of a dihydrofurans 13 to cyclohexanone 14. The HCP catalyst showed superior stability and durability in these reactions. Particularly, in the last reaction, the acid-base bifunctional HCP catalyst could be recovered and reused more than 14 times without obvious loss of activity. Owing to the rigid and stable porous structure of HCP, direct mixing an HCP- SO_3H and HCP- NH_2 in the reaction system is also able to drive the one-pot hydrolysis/Henry tandem reaction in the similar performance. The easiness of preparing these two HCP-based catalysts and also excellent water-stability endowed the established system with operational simplicity and reliable reusability.^[85]

Based on direct knitting strategy and using arylboronic acids as the monomers, Pan and Yang established a facile approach to synthesize bifunctional HCPs bearing boronic and sulfonic acids, which can be used as a new type of cellulase-mimetic solid acids for cellulose hydrolysis in water.^[86] It was expected that the boronic acid and sulfonic acid groups in these HCPs mimicked the cellulose-binding domains and the cellulose-hydrolytic domains of cellulase, respectively. Owing to the synergic effect between the boronic and sulfonic groups, the thereby obtained HCPs displayed quite promising catalytic activity and

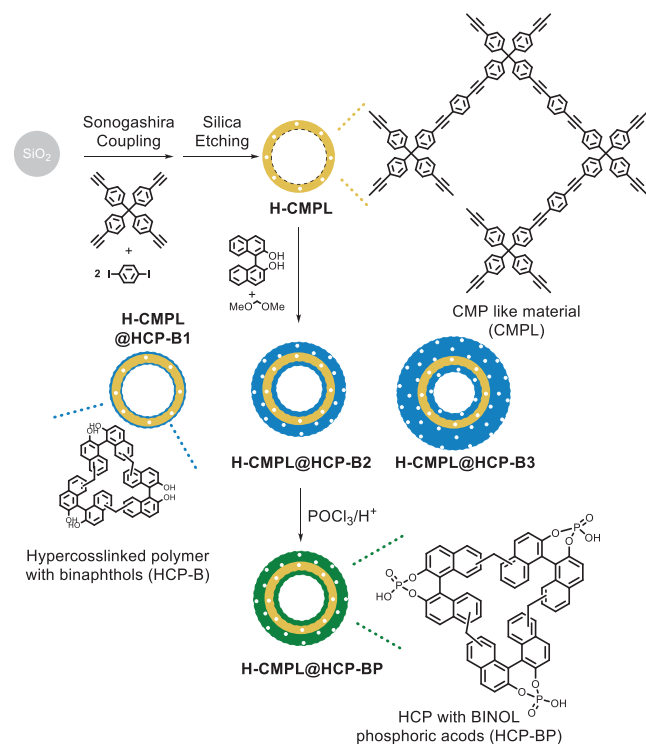


Figure 21. Schematic illustration of synthesis of H-CMPL@HCP-B, micron-sized HCP-B (M-HCP-B), and H-CMPL@HCP-BP. Reproduced with permission.^[83] Copyright 2019, ACS.

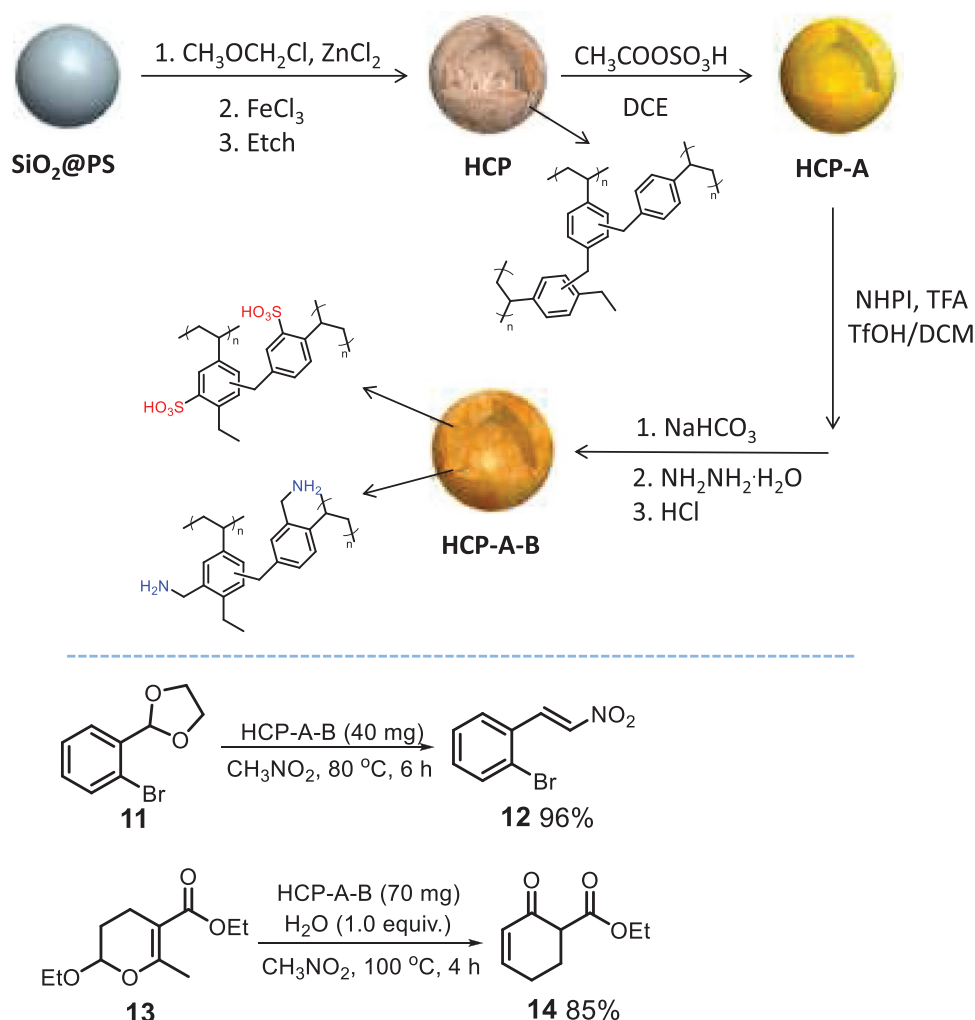


Figure 22. Schematic illustration of preparation of HCP-A-B and its application in tandem reactions. Reproduced with permission.^[84] Copyright 2017, ACS.

selectivity in hydrolysis of microcrystalline cellulose (Avicel) to glucose. An HCP from naphthalene-1-boronic acid was able to hydrolyze Avicel at 120 °C to glucose by 94.9%. But, a pretreatment with ball-milling are needed in order to get a good result. In addition, the solid acids could be reused at least four times without a dramatic drop in the hydrolysis performance.

4.4. Hypercrosslinked Polymers for Catalysis with Organic Salts or Ionic Liquids

Organic ammonium and phosphonium, including ionic liquids, are well known as catalysts for some reactions. Because most of the salt catalysts are soluble in the reaction system, to facilitate the product isolation and the catalyst recycling, anchoring the organic salt onto the surface of solid has been explored. Not surprisingly, direct knitting strategy to form HCP contributed also some options to us. The salt can be anchored before or after knitting reaction. Zhang et al. reported a new type of imidazolium salt-modified HCP,^[87] which were synthesized by Friedel–Crafts self-polymerization

of benzyl halides and the following functionalization with *N*-methylimidazole (**Figure 23**). The new material, HCP- Im^+Cl^- , have a large S_{BET} (up to 926 m² g⁻¹) and exhibit a good CO₂ capture capacity (14.5 wt%, 273 K and 1 bar). In a cycloaddition of CO₂ to propene oxide, HCP- Im^+Cl^- displayed much higher catalytic activity than the PS-supported imidazolium-based catalyst. After 8 h of reaction at 120 °C, the expected carbonate product was obtained in 92% of yield. A synergistic effect between the micropore structure and the catalytic centers, which are located in the pore structure, should be responsible for the remarkable difference. The HCP support could capture and concentrate CO₂, which results in a higher CO₂ concentration near catalytic centers and makes the catalytic reaction more efficient. Furthermore, the imidazolium-modified porous materials also exhibited high stability and excellent reusability for CO₂ capture and conversion. It is a pity that an organic solvent, ethanol, was used as solvent in the model cycloaddition. The performance of a congener ionic HCP with 1,4-bis(chloromethyl)benzene as the monomer component was also studied, and it displayed quite similar behavior in absorbing CO₂.^[88] Because of the high content

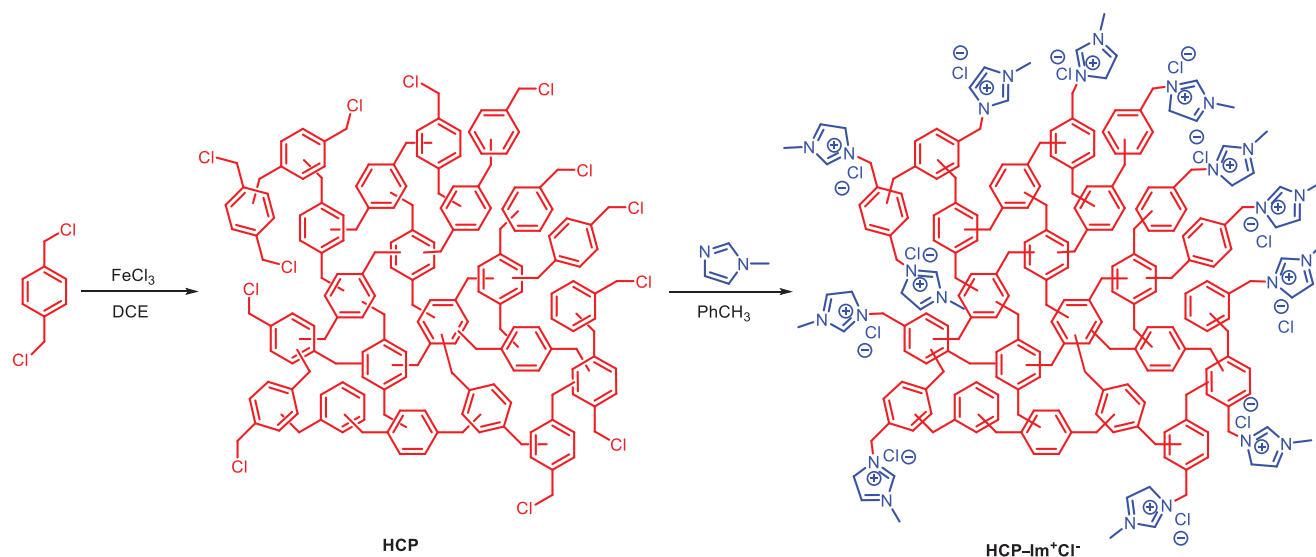


Figure 23. Schematic illustration of synthesis of supported imidazolium salts and the typical structure of HCP-Im⁺Cl⁻. Reproduced with permission.^[87] Copyright 2015, RSC.

of residual chloromethyl group, it is also possible to use the resulting ionic HCP as an acid catalyst.

Zhang et al. also prepared a series of phosphonium-functionalized HCPs, HCP-P⁺Ph₃RX⁻, through a Friedel–Crafts reaction of alkyl triphenylphosphonium halide with FDA in the presence of large amount of benzene as comonomer (**Figure 24**).^[89] Elemental analysis of HCP-P⁺Ph₃RX⁻ showed that the phosphonium loading in the HCPs is in the range of 0.2–0.4 mmol g⁻¹. The *S*_{BET} are in the range from 770 to 1168 m² g⁻¹. The micropore size distribution of these materials is mainly around 1.18–1.36 nm. Mesoporous and macroporous structures were also observed. In the cycloaddition of CO₂ to propene oxide, a combination of HCP-P⁺Ph₃RBr⁻ and ZnBr₂ displayed higher activity than a congener system with the traditional PS-supported phosphonium material. The HCP-P⁺Ph₃RBr⁻/ZnBr₂ system can be recycled at least six times without significantly losing their activity. An HCP synthesized by knitting benzimidazole monomer and 1,4-bis(chloromethyl) benzene cross-linker can also act as a catalyst for the same reaction.^[90] Because of the weakly basic property of the anchored benzimidazole, this HCP played dual roles of a catalyst and a CO₂ absorption material.

4.5. Hypercrosslinked Polymers–Carbon Catalyst

Although most of HCPs have high *S*_{BET}, owing to the fact that they are organic polymers, slight swelling is inevitable. To solve this problem, Cooper et al. transferred HCPs to porous carbonaceous materials by pyrolysis. It not only increased the surface area, but also avoided the possible swelling of HCPs.^[91] Because of the great usefulness of carbonaceous materials in catalysis, considering also the fact that the choice of HCP precursor can affect the functionality in the resultant carbons, this method to use HCPs opened a new way to chemists to prepare carbon-based catalysts. Wang and Tan et al. used metalloporphyrin-containing HCPs (Fe or Co) as precursors to prepare hyperporous carbon by means of carbonization.^[92] Before the carbonization, the *S*_{BET} of HCPs-Fe-Ps and HCP-Co-Ps are less than 400 m² g⁻¹. After pyrolysis treatment by using NaOH as chemical activating reagent, the *S*_{BET} of the generated hypercarbon materials were increased to over 1600 m² g⁻¹. XPS and ICP-MS analysis revealed that the metal ions associated with nitrogen atoms and metallic NPs (Fe or Co NPs) coexisted in the nitrogen-doped graphitic carbon. This structural arrangement endowed the hypercarbon abundant effective catalytic

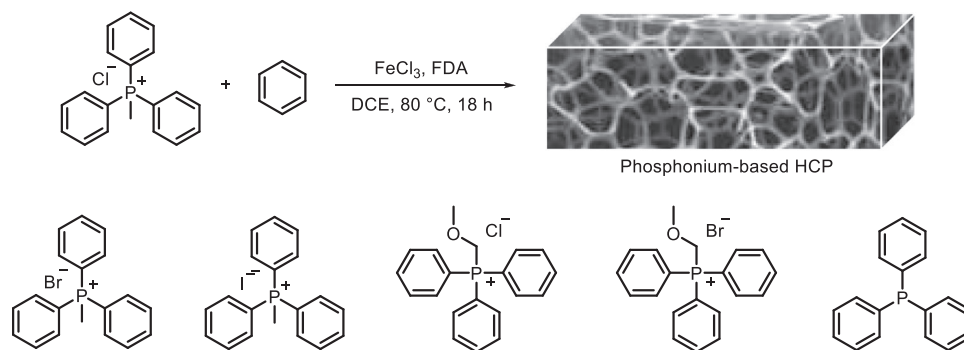


Figure 24. Schematic illustration of synthesis of hypercrosslinked phosphonium polymers. Reproduced with permission.^[89] Copyright 2015, RSC.

active centers for the ORR. Unlike the apparent impact of methanol on the Pt/C catalyst, the hypercarbon obtained from HCP–Fe–Ps can nearly avoid the methanol crossover effect. However, the electrocatalytic performance of this hypercarbon in acid medium was inferior to Pt/C and other single-atom catalyst, which can be ascribed to the etching effect of acid medium on the ORR active sites, especially on the metal NPs. An HCP synthesized by direct knitting of pyrrole monomer and FDA cross-linker was subjected to pyrolysis at 900 °C, and the obtained nitrogen-doped carbon showed outstanding catalytic activity toward ORR in alkaline medium.^[93] Therefore, pyrolysis of HCP materials may open a new possibility for the design of ORR metal-free and cost-effective catalyst of fuel-cell technologies.

4.6. Hypercrosslinked Polymers for Photocatalysis

Metal-free, visible-light active, and solid organic photocatalysts provide an environmentally friendly alternative to traditional metal-based catalysts. In this regard, direct knitting method was also explored. By using a photoactive conjugated organic semiconductor unit, 4,7-diphenylbenzo[1,2,5]thiadiazole, as the monomer and FDA as cross-linker. Zhang et al. obtained a heterogeneous photocatalyst, which possessed an S_{BET} of up to 586 m² g^{−1} and showed both high catalytic efficiency and reusability toward the bromination of a series of phenyl ether-based compounds (Figure 25).^[94] Xia and Liu also prepared a porous HCP by using 2,7-bis-(*N*-carbazolyl)-9-fluorenone (CF) as the monomer and FDA as cross-linker, which has a high S_{BET} up to 1200 m² g^{−1} with a pore volume of 0.92 cm³ g^{−1}.^[95] CF–HCP was proven to be a highly effective photocatalyst for the oxidative coupling of primary amines, dehydrogenation of inactive secondary amine substrates, and selective oxidation of sulfide under visible-light irradiation and using molecular oxygen as an oxidant (Figure 25). All the work utilized elegantly the advantages of knitting strategy to prepare porous HCP, such as simple operation, low-cost synthesis, and designable 3D aryl network.

CO₂ adsorption ability is particularly crucial to photocatalytic CO₂ conversion. However, the CO₂ adsorption on the surface of

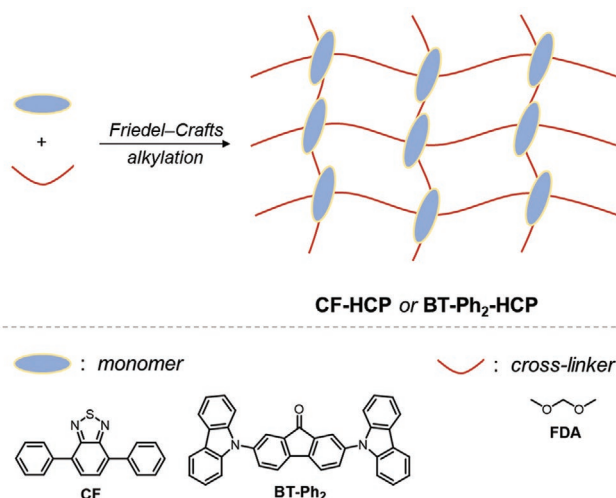


Figure 25. Schematic illustration of synthesis of two solid organic photocatalysts.

photocatalysts is generally low due to their low S_{BET} and the lack of matched pores. Given this challenge, incorporating a CO₂ capture material into the photocatalytic system has great potential to provide an opportunity for improving CO₂ conversion efficiency. In order to find a proof of concept, Wang and Tan et al. prepared a well-defined porous composite (HCP–TiO₂–FG) structure by in situ knitting HCPs on TiO₂-functionalized graphene (Figure 26).^[96] The smooth graphene nanosheets were uniformly decorated with TiO₂ crystals to the formation of TiO₂–G composite nanostructure. After in situ knitting, the graphene surface and TiO₂ crystals were covered by the ultrathin HCPs layer with a thickness of 3–8 nm. Benefiting from the high surface area and abundant microporous nature, the introduction of HCPs layers dramatically improved the S_{BET} and micropore volume of TiO₂–G to 988 m² g^{−1} and 0.306 cm³ g^{−1}, respectively, leading to the increased CO₂ uptake capacity up to 12.87 wt%. Due to the enhanced CO₂ adsorption ability of HCPs and the short diffusion length around the TiO₂ photocatalysts, such well-defined HCP–TiO₂–FG structure shows high

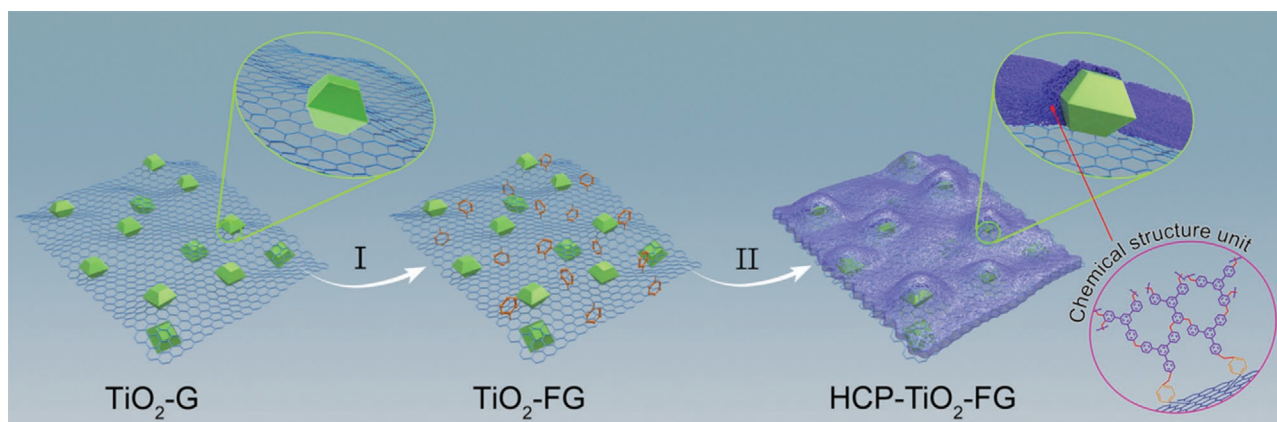


Figure 26. Schematic illustration of construction of a well-defined porous HCP–TiO₂–FG composite structure. I) The functionalization of TiO₂–G by diazonium salt formation. II) The knitting of TiO₂–FG with syn-PhPh₃ by solvent knitting method. The magnified model in the top right corner is the cross profile of HCP–TiO₂–FG composite. Reproduced with permission.^[96] Copyright 2015, Nature publishing group.

photocatalytic performance especially for CH_4 production, that is, $2762 \mu\text{mol g}^{-1} \text{h}^{-1}$, under visible-light irradiation without the use of sacrificial reagents or precious metal cocatalysts.

4.7. Hypercrosslinked Polymers-Enzyme Catalyst

Immobilization of enzyme catalyst onto solid support is always a hard and an urgent task of chemist. Because of the sensitivity of enzymatic species toward the environment, the selection of supporting material is a key factor to determine the outcome. Huang et al. prepared an organic/inorganic hybrid material,^[97] which was composed of SiO_2 and the anchored organic copolymers of methacrylic acid, divinylbenzene, and 4-chlorostyrene, $\text{SiO}_2@\text{P}(\text{MAA-co-VBC-co-DVB})$ (Figure 27). Because of the coexistence of electrophilic benzyl chloride fragment and phenyl ring in the surface of SiO_2 , treatment of this material with anhydrous FeCl_3 in DCE solvent allowed the formation of rigid HCP framework. The S_{BET} of the polymer-coated SiO_2 was increased from 141 to $487 \text{ m}^2 \text{ g}^{-1}$ after hyper cross-linking with a volume increase from 0.12 to $0.32 \text{ cm}^3 \text{ g}^{-1}$. Because of the presence of carboxylic acid group in the porous structure, the obtained HCP-coated SiO_2 was proven to be a suitable support to immobilize *Candida rugosa* lipase (CRL). Hydrophobic and weak cation exchange interactions are both important for ensuring the immobilization to be successful. The HCP-coated SiO_2 -immobilized CRL, CRL@HPC-SiO_2 , showed much better thermal stability and reusability in comparison to free CRL. CRL@HPCS was also proven to be highly efficient catalyst for esterification of phytosterol with fatty acids. High yield was obtained under mild conditions with this catalyst. CRL@HPC-SiO_2 can be recycled at least ten times without significant loss of its activity.

4.8. Hypercrosslinked Polymers for Recycling Homogenous Catalyst

Because of the excellent properties, including microporous structure, diversity of functional substitution, and intrinsic easiness of the bottom-up design and fabrication, HCP obtained by direct knitting strategy has also been used to recycle homoge-

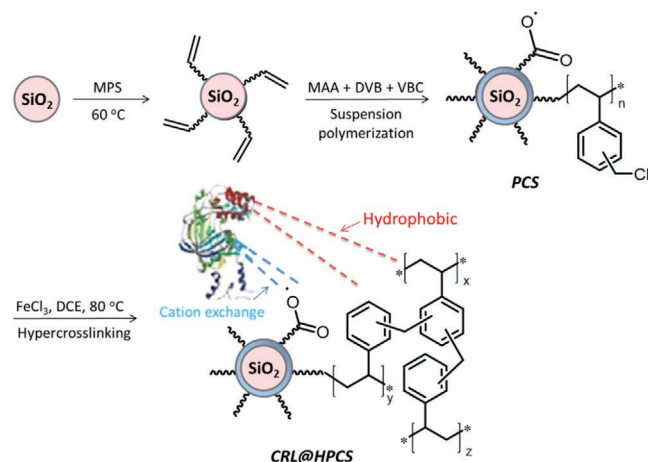


Figure 27. Schematic illustration of synthesis of a CRL@HPC-SiO_2 catalyst. Reproduced with permission.^[97] Copyright 2013, ACS.

nous catalyst from a solution. A benzene-based HCPs obtained by Friedel–Crafts reaction was proven by Palkovits et al. to be an efficient sorbent material for extraction of HMF from aqueous fructose solutions.^[98] Because of the presence of arene structure in the backbone of the HCP material, a potential π – π interaction was expected to play a key role in ensuring this protocol to be feasible. Inspired by this work, Woodward et al. synthesized a series of benzene–phenol copolymers by Friedel–Crafts reaction in conjunction with using FDA as external cross-linking reagent,^[99] and investigated its performance in the removal and recovery of toluenesulfonic acid (*p*-TSA) in degradation of α -cellulose. It was found that the apparent S_{BET} decreased gradually with increasing phenol content. The HCP obtained using pure benzene as starting material (B100) has a S_{BET} of $1483 \text{ m}^2 \text{ g}^{-1}$, but the congener HCP with pure phenol precursor (P100) has only $170 \text{ m}^2 \text{ g}^{-1}$ of S_{BET} . Interestingly, the efficiency of the *p*-TSA adsorption was improved with increasing phenol content although S_{BET} of the HCP was decreased. The B100 polymer was found to be the most promising candidate to implement the *p*-TSA adsorption. It was conjectured that the polar moieties exposed on the adsorbent surface might alleviate the electrostatic repulsion, thus allowing the adsorbed *p*-TSA species to form a loose ion-pair ($[\text{R-SO}_3^-][\text{H}_3\text{O}^+]$). In a batch process, around 97% of *p*-TSA can be removed after exposure to HCP P100. A flow-through process was also established with this material, in which HCP P100 is able to selectively remove the catalyst completely from even lower initial concentrations. The acid species can be removed from the spent adsorbent by washing with methanol. This system not only offered an efficient method for recycling homogenous *p*-TSA catalyst, but also strengthened the greenness of the acid-catalyzed process for the production of fermentable sugars.

4.9. Miscellaneous Examples

A few other examples of applying HCPs in catalysis cannot be summarized in the aforementioned catalogs. In order to comprehend the broad applications of HCPs in catalysis for the readers, we illustrate some individual examples in this part. Immobilizing phosphomolybdic acid (PMA) onto HCPs that were prepared by using PPh_3 or NPh_3 as the monomers was proven to be possible, and the degradation of PMA species was significantly inhibited with this HCP-based supporting method.^[100] The obtained HCP–PMA catalyst can be used to catalyze oxidation of olefin to epoxide in ethyl acetate using H_2O_2 as an oxidant. Doping of the HCP catalyst with cobalt increased its catalytic performance as well.^[101]

In the combustion of flue gas from fossil fuel, NO_2 and NO , both existed in a distribution in favor of the latter one (1:9). NO_2 can be absorbed relatively easier than NO because of its high Henry's law constant. Therefore, there is an increasing demand in NO_x removal, and the oxidation of NO to NO_2 is a key reaction to determine the process efficiency. The coadsorption always existed with the conventional catalyst, which decreased the performance of NO oxidation. In view of the high hydrophobicity and strong absorption ability of HCPs to some gaseous compounds, an HCP fabricated by self-polymerization of 4,4'-bis(chloromethyl)-1,1'-biphenyl was prepared

and examined by Atkinson et al. in NO oxidation.^[102] In dry conditions, the HMF provided 62% NO oxidation efficiency at 25 °C. But its performance dropped to 50% in the presence of 1.6 vol% moisture (wet conditions). The surface functionalities in HCP have significant effect. Modification with benzene to remove pendant chloromethyl groups, increased its hydrophobicity, increasing its catalytic performance in 18% under the wet conditions. However, in wet conditions, functionalization with dimethylamine decreased the NO oxidation efficiency by 30% due to increased polarity and proclivity to react with NO₂.

5. Conclusion and Perspectives

Since the first discovery of one-step knitting method in 2011 by Tan, direct knitting of arene monomers with cross-linker via Friedel–Crafts alkylation to construct HCPs has been applied in various areas of catalysis. This method allowed the use of easily available and cheap building blocks for preparing organic microporous polymers while conferring the resulting MOPs various advanced functions. The key factors that affected the catalytic performance of an HCP were also described. With in-depth development of this chemistry, the potential and beneficial effect of the one-step direct knitting strategy for catalysis has been fully demonstrated. Nowadays, the direct knitting approach has seemingly been recognized as a regular and low-cost method to implement not only the heterogenization of soluble homogeneous catalysts, but also the creation of novel catalysts with tailor-made properties. Indeed, this method enables us to synthesize some hitherto unreported functional materials directly from readily available molecules, and also the polymerization step is very simple. Therefore, HCP catalysts are expected to be highly attractive and practically scalable.

Because of the designability and a great structural diversity of HCPs, there still is a big room for developing new HCP-based catalysts with emphasis of different functions and task-specific uses. A large-scale synthesis of an HCP was proven to be possible technically.^[103] In the next decade, effort should be made to apply HCP-based solid catalysts in chemical industry.

It should be noted that HCP catalyst prepared by the direct knitting strategy of arene monomers is also facing some problems. Because the HCP skeleton is an organic 3D network, slight swelling often occurs during its usage. Attention should be paid to a possible structural damage and metal leaching in the recycling, particularly when it was used in high temperature. It is hard to precisely control and wisely use a synergistic effect between the HCP support and the catalytically active species. This mainly resulted from the amorphous morphology and irregular arrangement of the HCP monomer unit. In addition, the metal species in the macrospore of HCP may not readily accessible, which prevents the use of substrate with big molecular size. Because the first knitting model allows anchoring of metal species onto the most accessible places, it is unreasonable to expect that, for a reaction using big-size molecule as the substrate, the first knitting model should be the preferable choice. But, for the reactions with small-size molecules, both the first and the second knitting models are applicable. Despite all these problems, significant contributions of HCPs to heterogeneous catalysis are still expected.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

heterogeneous catalysts, hypercrosslinked polymers, immobilization of homogenous catalyst, porous organic polymers

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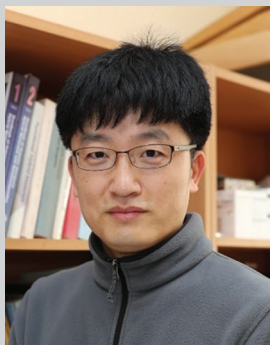
- [1] a) A. Corma, H. Garcia, *Adv. Synth. Catal.* **2006**, *348*, 1391; b) P. McMorn, G. J. Hutchings, *Chem. Soc. Rev.* **2004**, *33*, 108; c) L.-B. Sun, X.-Q. Liu, H.-C. Zhou, *Chem. Soc. Rev.* **2015**, *44*, 5092; d) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011.
- [2] S. Hibner, J. G. de Vries, V. Farina, *Adv. Synth. Catal.* **2016**, *358*, 3.
- [3] M. Rose, *ChemCatChem* **2014**, *6*, 1166.
- [4] R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.* **2012**, *37*, 530.
- [5] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166.
- [6] Y. H. Xu, S. B. Jin, H. Xu, A. Nagai, D. L. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 8012.
- [7] R. Castaldo, G. Gentile, M. Avella, C. Carfagna, V. Ambrogio, *Polymers* **2017**, *9*, 651.
- [8] P. Veverka, K. Jerábek, *React. Funct. Polym.* **1999**, *41*, 21.
- [9] J.-H. Ahn, J.-E. Jang, C.-G. Oh, S.-K. Ihm, J. Cortés, D. C. Sherrington, *Macromolecules* **2006**, *39*, 627.
- [10] B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu, B. Tan, *Macromolecules* **2011**, *44*, 2410.
- [11] S. Xu, Y. Luo, B. Tan, *Macromol. Rapid Commun.* **2013**, *34*, 471.
- [12] W. Wang, M. Zhou, D. Yuan, *J. Mater. Chem. A* **2017**, *5*, 1334.
- [13] G. Kuppan, L. J. Abbott, K. E. Hart, C. M. Colina, *Chem. Rev.* **2018**, *118*, 5488.
- [14] S. Das, P. Heasman, T. Ben, S. Qiu, *Chem. Rev.* **2017**, *117*, 1515.
- [15] a) L. Tan, B. Tan, *Chem. Soc. Rev.* **2017**, *46*, 3322; b) J. Huang, S. R. Turner, *Polym. Rev.* **2018**, *58*, 1.
- [16] S. M. Lee, W. J. Choi, K. Hwang, J.-H. Kim, J.-Y. Lee, *Macromol. Res.* **2014**, *22*, 481.
- [17] Q. Chen, D.-P. Liu, M. Luo, L.-J. Feng, Y.-C. Zhao, B.-H. Han, *Small* **2014**, *10*, 308.
- [18] N. Fontanals, R. M. Marcé, F. Borrulla, P. A. G. Cormack, *Polym. Chem.* **2015**, *6*, 7231.
- [19] V. A. Davankov, M. P. Tsyurupa, *React. Polym.* **1990**, *13*, 27.
- [20] N. Fontanals, R. M. Marcé, P. A. G. Cormack, D. C. Sherrington, F. Borrull, *J. Chromatogr. A* **2008**, *1191*, 118.
- [21] a) C. H. Lau, T.-D. Lu, S.-P. Sun, X. Chen, M. Carta, D. M. Dawson, *Chem. Commun.* **2019**, *55*, 8571; b) K. Schute, M. Rose, *ChemSusChem* **2015**, *8*, 3419.
- [22] F. Gao, R. Bai, F. Ferlin, L. Vaccaro, M. Li, Y. Gu, *Green Chem.* **2020**, *22*, 6240.

- [23] J.-S. M. Lee, T. Kurihara, S. Horike, *Chem. Mater.* **2020**, 32, 7694.
- [24] B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, *Adv. Mater.* **2012**, 24, 3390.
- [25] Y. Lei, X. Zhang, Y. Gu, J. Hu, G. Li, K. Shi, *Transition Met. Chem.* **2016**, 41, 1.
- [26] Z. Jia, K. Wang, B. Tan, Y. Gu, *Adv. Synth. Catal.* **2017**, 359, 78.
- [27] T. Wang, Y. Lyu, X. Chen, C. Li, M. Jiang, X. Songa, Y. Ding, *RSC Adv.* **2016**, 6, 28447.
- [28] C. Tang, Z. Zou, Y. Fu, K. Song, *ChemistrySelect* **2018**, 3, 5987.
- [29] S. Xu, K. Song, T. Li, B. Tan, *J. Mater. Chem. A* **2015**, 3, 1272.
- [30] Y. F. Fu, K. P. Song, Z. J. Zou, M. Q. Li, *Transition Met. Chem.* **2018**, 43, 665.
- [31] Z. Jia, K. Wang, T. Li, B. Tan, Y. Gu, *Catal. Sci. Technol.* **2016**, 6, 4345.
- [32] A. E. Sadak, E. Karakus, Y. M. Chumakov, N. A. Dogan, C. T. Yavuz, *ACS Appl. Energy Mater.* **2020**, 3, 4983.
- [33] X. Wang, S. Min, S. K. Das, W. Fan, K.-W. Huang, Z. Lai, *J. Catal.* **2017**, 355, 101.
- [34] X. Wang, E. A. P. Ling, C. Guan, Q. Zhang, W. Wu, P. Liu, N. Zheng, D. Zhang, S. Lopatin, Z. Lai, K.-W. Huang, *ChemSusChem* **2018**, 11, 3591.
- [35] A. Valverde-González, G. Marchal, E. M. Maya, M. Iglesias, *Catal. Sci. Technol.* **2019**, 9, 4552.
- [36] Y. Shen, Q. Zheng, H. Zhu, T. Tu, *Adv. Mater.* **2020**, 32, 1905950.
- [37] Z. Dou, L. Xu, Y. Zhi, Y. Zhang, H. Xia, Y. Mu, X. Liu, *Chem. - Eur. J.* **2016**, 22, 9919.
- [38] Y. Chen, R. Luo, Q. Xu, W. Zhang, X. Zhou, H. Ji, *ChemCatChem* **2017**, 9, 767.
- [39] a) V. Ganesan, S. Yoon, *ACS Appl. Mater. Interfaces* **2019**, 11, 18609; b) S. Rajendiran, V. Ganesan, S. Yoon, *Inorg. Chem.* **2019**, 58, 3283.
- [40] a) J. Jiang, S. Yoon, *J. Mater. Chem. A* **2019**, 7, 6120; b) V. Ganesan, S. Yoon, *Inorg. Chem.* **2020**, 59, 2881.
- [41] D. Meng, J. Bi, Y. Dong, B. Hao, K. Qin, T. Li, D. Zhu, *Chem. Commun.* **2020**, 56, 2889.
- [42] J. Bi, Y. Dong, D. Meng, D. Zhu, T. Li, *Polymer* **2019**, 164, 183.
- [43] C. Liu, W. Xu, D. Xiang, Q. Luo, S. Zeng, L. Zheng, Y. Tan, Y. Ouyang, H. Lin, *Catal. Lett.* **2020**, 150, 2558.
- [44] C. Xu, M. Hu, Q. Wang, G. Fan, Y. Wang, Y. Zhang, D. Gao, J. Bi, *Dalton Trans.* **2018**, 47, 2561.
- [45] C. Xu, H. Wang, Q. Wang, Y. Wang, Y. Zhang, G. Fan, *Appl. Surf. Sci.* **2019**, 446, 193.
- [46] Y. Xu, T. Wang, Z. He, M. Zhou, W. Yu, B. Shi, K. Huang, *Macromolecules* **2017**, 50, 9626.
- [47] Y. Xu, Y. Yao, H. Yu, B. Shi, S. Gao, L. Zhang, A. L. Miller, J.-C. Fang, X. Wang, K. Huang, *ACS Macro Lett.* **2019**, 8, 1263.
- [48] X. Cai, J. Nie, G. Yang, F. Wang, C. Ma, C. Lu, Z. Chen, *Mater. Lett.* **2019**, 240, 80.
- [49] B. Li, Z. Guan, X. Yang, W. D. Wang, W. Wang, I. Hussain, K. Song, B. Tan, T. Li, *J. Mater. Chem. A* **2014**, 2, 11930.
- [50] Z. Wu, Q. Liu, X. Yang, X. Ye, H. Duan, J. Zhang, B. Zhao, Y. Huang, *ACS Sustainable Chem. Eng.* **2017**, 5, 9634.
- [51] J. Mondal, S. K. Kundu, W. K. Hung Ng, R. Singuru, P. Borah, H. Hirao, Y. Zhao, A. Bhaumik, *Chem. - Eur. J.* **2015**, 21, 19016.
- [52] A. Mouradzadegun, M. A. Mostafavi, *RSC Adv.* **2016**, 6, 42522.
- [53] R. A. Molla, P. Bhanja, K. Ghosh, S. S. Islam, A. Bhaumik, S. M. Islam, *ChemCatChem* **2017**, 9, 1939.
- [54] J. Liu, Q. Chen, Y.-N. Sun, M.-Y. Xu, W. Liu, B.-H. Han, *RSC Adv.* **2016**, 6, 48543.
- [55] J. Chen, J. Zhang, D. Zhu, T. Li, *Gold Bull.* **2019**, 52, 19.
- [56] H. Zhou, Q. Chen, X. Tong, H. Liu, *Colloid Interface Sci. Commun.* **2020**, 37, 100285.
- [57] H. Song, Y. Liu, Y. Wang, B. Feng, X. Jin, T. Huang, M. Xiao, H. Gai, *Mol. Catal.* **2020**, 493, 111081.
- [58] K. Song, Z. Zou, D. Wang, B. Tan, J. Wang, J. Chen, T. Li, *J. Phys. Chem. C* **2016**, 120, 2187.
- [59] C. Sarkar, S. C. Shit, D. Q. Dao, J. Lee, N. H. Tran, R. S. K. An, D. N. Nguyen, Q. V. Le, P. N. Amaniampong, A. Drif, F. Jerome, P. T. Huyen, T. T. N. Phan, D.-V. N. Vo, N. T. Binh, Q. T. Trinh, M. P. Sherburne, J. Mondal, *Green Chem.* **2020**, 22, 2049.
- [60] A. Modak, J. Sun, W. Qiu, X. Liu, *Catalysts* **2016**, 6, 161.
- [61] C. Liu, L. Zheng, D. Xiang, S. Liu, W. Xu, Q. Luo, Y. Shu, Y. Ouyang, H. Lin, *RSC Adv.* **2020**, 10, 17123.
- [62] Z. Zou, Y. Jiang, K. Song, *Catal. Lett.* **2020**, 150, 1277.
- [63] P. Bhanja, X. Liu, A. Modak, *ChemistrySelect* **2017**, 2, 7535.
- [64] J. He, S. Razzaque, S. Jin, I. Hussain, B. Tan, *ACS Appl. Nano Mater.* **2019**, 2, 546.
- [65] A. Zhong, Y. Xu, Z. He, H. Zhang, T. Wang, M. Zhou, L. Xiong, K. Huang, *Macromol. Chem. Phys.* **2017**, 218, 1700044.
- [66] N. A. Nemygina, L. Z. Nikoshvili, V. G. Matveeva, M. G. Sulman, E. M. Sulman, L. Kiwi-Minsker, *Top. Catal.* **2016**, 59, 1185.
- [67] K. Song, P. Liu, J. Wang, L. Pang, J. Chen, I. Hussain, B. Tan, T. Li, *Dalton Trans.* **2015**, 44, 13906.
- [68] K. Song, P. Liu, J. Wang, B. Tan, T. Li, *J. Porous Mater.* **2016**, 23, 725.
- [69] J. Kang, P. Puthiaraj, W. Ahn, E. D. Park, *Appl. Catal. A* **2020**, 602, 117711.
- [70] S. Shi, C. Chen, M. Wang, J. Ma, H. Ma, J. Xu, *Chem. Commun.* **2014**, 50, 9079.
- [71] L. Stadler, M. Homafar, A. Hartl, S. Najafshirvari, M. Colombo, R. Zboril, P. Martin, M. B. Gawande, J. Zhi, O. Reiser, *ACS Sustainable Chem. Eng.* **2019**, 7, 2388.
- [72] H. Li, B. Meng, S. H. Chai, H. Liu, S. Dai, *Chem. Sci.* **2016**, 7, 905.
- [73] J. Li, X. Wang, G. Chen, D. Li, Y. Zhou, X. Yang, J. Wang, *Appl. Catal. B* **2015**, 176, 718.
- [74] K. Dong, J. Zhang, W. Luo, L. Su, Z. Huang, *Chem. Eng. J.* **2018**, 334, 1055.
- [75] J. Zhang, K. Dong, W. Luo, H. Guan, *Fuel* **2018**, 234, 664.
- [76] J. Gu, J. Zhang, D. Li, H. Yuan, Y. Chen, *J. Chem. Technol. Bio-technol.* **2019**, 94, 3073.
- [77] R. M. N. Kalla, M.-R. Kim, I. Kim, *Ind. Eng. Chem. Res.* **2018**, 57, 11583.
- [78] S. S. Reddy, R. M. N. Kalla, A. Varyambath, I. Kim, *Catal. Commun.* **2019**, 126, 15.
- [79] R. M. N. Kalla, S. S. Reddy, I. Kim, *Catal. Lett.* **2019**, 149, 2696.
- [80] B. Pei, X. Xiang, T. Liu, D. Li, C. Zhao, R. Qiu, X. Chen, J. Lin, X. Luo, *Catalysts* **2019**, 9, 963.
- [81] S. Bhunia, B. Banerjee, A. Bhaumik, *Chem. Commun.* **2015**, 51, 5020.
- [82] R. M. N. Kalla, S. C. Hong, I. Kim, *ACS Omega* **2018**, 3, 2242.
- [83] S. J. Choi, E. H. Choi, C. Song, Y.-J. Ko, S. M. Lee, H. J. Kim, H.-Y. Jang, S. U. Son, *ACS Macro Lett.* **2019**, 8, 687.
- [84] Z. Jia, K. Wang, B. Tan, Y. Gu, *ACS Catal.* **2017**, 7, 3693.
- [85] K. Wang, Z. Jia, X. Yang, L. Wang, Y. Gu, B. Tan, *J. Catal.* **2017**, 348, 168.
- [86] Q. Yang, X. Pan, *ACS Sustainable Chem. Eng.* **2016**, 4, 4824.
- [87] J. Wang, W. Sng, G. Yi, Y. Zhang, *Chem. Commun.* **2015**, 51, 12076.
- [88] S. Hao, Y. Liu, C. Shang, Z. Liang, J. Yu, *Polym. Chem.* **2017**, 8, 1833.
- [89] J. Wang, J. G. Wei Yang, G. Yi, Y. Zhang, *Chem. Commun.* **2015**, 51, 15708.
- [90] Y. Sang, J. Huang, *Chem. Eng. J.* **2020**, 385, 123973.
- [91] J.-S. M. Lee, M. E. Briggs, T. Hasell, A. I. Cooper, *Adv. Mater.* **2016**, 28, 9804.
- [92] T.-L. Zhai, C. Xuan, J. Xu, Li Ban, Z. Cheng, S. Wang, D. Wang, B. Tan, C. Zhang, *Chem. - Asian J.* **2018**, 13, 2671.
- [93] Z. Yang, J. Han, R. Jiao, H. Sun, Z. Zhu, W. Liang, A. Li, *J. Colloid Interface Sci.* **2019**, 557, 664.
- [94] R. Li, Z. J. Wang, L. Wang, B. C. Ma, S. Ghasimi, H. Lu, K. Landfester, K. A. I. Zhang, *ACS Catal.* **2016**, 6, 1113.
- [95] Y. Zhi, K. Li, H. Xia, M. Xue, Y. Mu, X. Liu, *J. Mater. Chem. A* **2017**, 5, 8697.
- [96] S. Wang, M. Xu, T. Peng, C. Zhang, T. Li, I. Hussain, J. Wang, B. Tan, *Nat. Commun.* **2019**, 10, 676.
- [97] M.-M. Zheng, Y. Lu, F.-H. Huang, L. Wang, P.-M. Guo, Y.-Q. Feng, Q.-C. Deng, *J. Agric. Food Chem.* **2013**, 61, 231.

- [98] C. Detoni, C. H. Gierlich, M. Rose, R. Palkovits, *ACS Sustainable Chem. Eng.* **2014**, 2, 2407.
 [99] R. T. Woodward, M. Kessler, S. Lima, R. Rinaldi, *Green Chem.* **2018**, 20, 2374.
 [100] X. Song, W. Zhu, Y. Yan, H. Gao, W. Gao, W. Zhang, M. Jia, *J. Mol. Catal. A: Chem.* **2016**, 413, 32.
 [101] X. Song, W. Zhu, Y. Yan, H. Gao, W. Gao, W. Zhang, M. Jia, *Microporous Mesoporous Mater.* **2017**, 242, 9.
 [102] M. Ghafari, R. Ghamkhar, J. D. Atkinson, *Fuel* **2019**, 241, 564.
 [103] W. Li, A. Zhang, H. Gao, M. Chen, A. Liu, H. Bai, L. Li, *Chem. Commun.* **2016**, 52, 2780.



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