Review

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Design and Synthesis of Porous Organic Polymers: Promising Catalysts for Lignocellulose Conversion to 5-Hydroxymethylfurfural and Derivates

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Abstract: In the face of the current energy and environment problems, the full use of biomass resources instead of fossil energy to produce a series of high-value chemicals has great application prospects. 5-hydroxymethylfurfural (HMF), which can be synthesized from lignocellulose as raw material, is an important biological platform molecule. Its preparation and catalytic oxidation of subsequent products have important research significance and practical value. In the actual production process, porous organic polymer (POPs) catalysts are highly suitable for biomass catalytic conversion due to its high efficiency, low cost, good designability, and environmentally friendly features. Here, we briefly described the application of various types of POPs (including COFs、PAFs、HCPs、CMPs) in the preparation and catalytic conversion of HMF from lignocellulosic biomass, and analyzed the influence of the structural properties of catalysts for the catalytic performance. Finally, we summarized some challenges that POPs catalysts will face in biomass catalytic conversion, and prospected the important research directions in future. This review would provide valuable references for the efficient conversion of biomass resources into high-value chemicals in practical applications.

Keywords: Porous organic polymer; biomass conversion; lignocellulose; 5-hydroxymethylfurfural; eco-friendly catalysts

1. Introduction

Facing the current global energy and environmental problems, it is urgent to replace fossil energy with renewable and environmental alternatives to produce a series of high-value chemicals and clean fuels. The effect of biomass resources in these two aspects can effectively overcome the dependence on fossil energy [1,2]. Lignocellulose, the main structural component of plants, is by far the most abundant renewable resource. It is capable of being converted in significant quantities into biofuels such as bioethanol [3] and other commercial chemicals like 5-hydroxymethylfurfural (HMF), sugars and phenols.

HMF is a biological platform molecule that can be produced from lignocellulose, that is, lignocellulose is hydrolyzed into six-carbon sugars (glucose and fructose) and further dehydrated [4]. It is an intermediate as well as a raw material for many important chemicals and can be converted into high value-added chemicals by oxidation, hydrogenation, polymerization and ring-opening reactions by its own furan rings, aldehyde groups and hydroxyl groups, some of the products are showed in Figure 1 [5–7], such as cross-linking agents of polyvinyl alcohol (PVA) for batteries manufacturing [8] and γ-valerolactone (GVL), which produces high value-added fuels. In particular, 2, 5-furanodicarboxylic acid (FDCA) for the substitution of petroleum-based aromatic compounds can be produced by the oxidation path of HMF [9]. It can be polymerized with ethylene glycol to produce polyrthylene furandicarboxylate (PEF), which can replace polyethylene terephthalate (PET) synthesized from petroleum-based compounds as precursors [10]. Furthermore, other polyester products synthesized by FDCA are also promising, such as bio-based copolyesters, which can be used as 3D printing materials [11].

The existing catalytic preparation of HMF can be roughly divided into two categories. Homogeneous catalysts are represented by inorganic acid [12], ionic liquid [13], metal salt [14], etc. In this kind of catalyst system, although the active center of the catalyst is uniform and the structure is clear, the separation of catalyst in reaction mixture is difficult, which may be accompanied by side reactions, and the recovery performance of catalyst is greatly reduced. Consequently, from the industrial perspective of product separation and equipment maintenance, etc., heterogeneous catalyst is more advantageous. Due to various defects and local environment of active sites, the coexisting environment of multiple active sites created is beneficial to improve catalytic efficiency, but attention should also be paid to product selectivity. Some researchers use metal oxides [15], metal carbide [16], functional carbon materials [17], etc., as catalysts for achieving HMF. And the study of catalytic active site, pore size, solvent environment and other aspects also often carried out to improve the catalytic efficiency of the whole reaction. Similarly, the above discussion of catalysts is also applicable to the catalytic conversion of HMF.

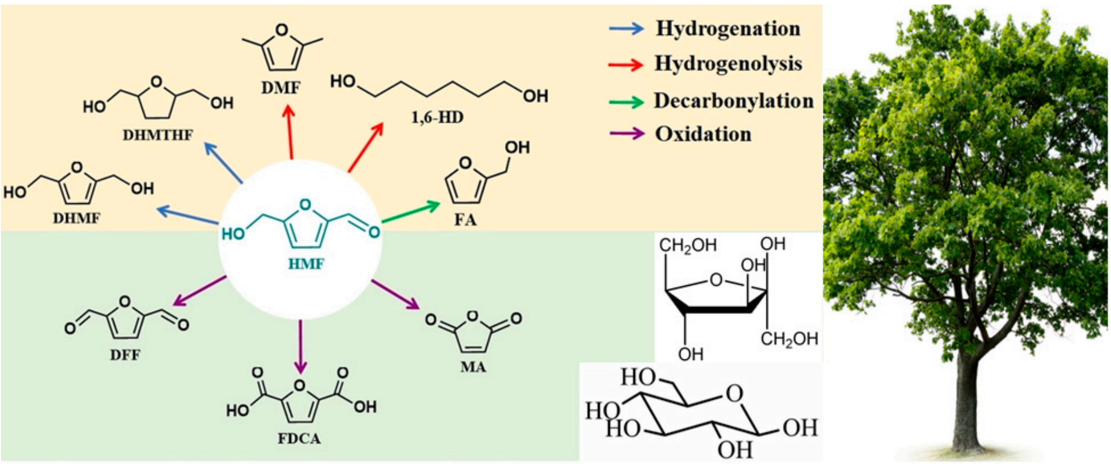

Figure 1. Partial transformation route of HMF [7].

Supported catalysts as the typical heterogeneous catalyst have naturally become a hot option for catalyst structures, which not only can be combined with precious metals to further improve efficiency, but also can achieve efficient conversion by combining non-precious metals [18] or even environmentally friendly non-metallic components [19] with suitable carriers. Here, the selection of catalyst support and active ingredients (sites) are very important. For the support, they are often a class of solid porous materials with high surface areas, suitable pore size and distribution, and adequate pore volume. Of course, for some porous supports, it also can be directly used as a catalyst or as a cocatalyst itself [20].

Porous material is a kind of functional material which is composed of interconnected or closed holes. According to the pore size, it can be divided into micropore materials (<2 nm), mesoporous materials (2–50 nm) and macropore materials (>50 nm). We are familiar with porous materials such as metal-organic frameworks (MOFs), porous organic polymers (POPs), activated carbon, silica, clay, and so on [21]. They have been used in a wide range of fields, nowadays, such as porous silicon for the manufacture of photoelectric components, porous membranes and porous adsorbents for separation, thermal and sound insulation materials, biomedical materials and so on [22]. Porous materials not only could improve the utilization of volume of material based on the stability and screening characteristics of pores, but also provided more space for the contact between active sites and reaction substrates, which will greatly promote the performance of catalysts[23]. When the metal components are the important active sites, the supported porous catalyst can ensure high efficiency, but there are also side reactions, low selectivity and metal leaching into the product [24]. Hence, as one of the hot topics in catalysis research, nonmetallic porous carbon materials have the advantages of low density, no metal leakage pollution, good structural ductility and strong acid and alkali resistance [25], they are often used as a kind of catalytic materials with great potential for energy storage and conversion [26], and can realize efficient conversion through functionalization and loading of active components. It has excellent application in catalytic biomass valorization and environmental remediation [27]. However, since porous carbon materials are usually prepared by high-temperature pyrolysis, it is relatively difficult to predict and control the structural features [28]. In addition, its energy consumption and equipment cost are relatively high. Therefore, the development of high performance catalysts with well-defined synthetic structures, low cost, and environmentally friendly feature is of paramount importance, specially, for the catalytic field of the preparation and conversion of HMF.

With the pursuit of the above desired characteristics, researchers are starting to pay more attention to the gradual update of catalyst structure from inorganic skeleton to organic skeleton [29]. At present, POPs are widely used in the field of catalysis due to their excellent physical and chemical properties, good thermal stability, large specific surface area, and controllable pore size and designable chemical structure [30]. Specifically, in the field of photocatalysis [31,32] and photoelectrocatalysis [33], they had showed good performance. Compared with other inorganic porous materials, the advantages of POPs is that, first of all, they are mainly composed of light elements C, H, O, N and B, and has low skeletal density [34]. Secondly, it has rich organic synthesis strategies and various types of monomers, and it is connected by high-energy covalent bonds, has inherent porosity and high physical and chemical stability. Therefore, it can effectively avoid the above mentioned catalyst recovery and product separation problems, and in the design of catalyst structure, compared with the popular carbon materials, more accurate control can be achieved [35]. It can even achieve high efficiency metal-free catalytic conversion by virtue of its special structure. Depending on the framework features and the synthesized way, the POPs mainly included COFs (covalent organic frameworks) [36], PAFs (porous aromatic frameworks) [37], HCPs (hypercrosslinked polymers) [38], CMPs (conjugated microporous polymers) [39] and other types. It not only has many applications in catalysis, but also has certain advantages and effects in gas storage, molecular separation, drug delivery and sensing [40,41]. Likewise, the heterogeneous catalytic system for the preparation of HMF from biomass resources, and the subsequent conversion of HMF discussed in this paper also showed good performance and provided important enlightenment for subsequent research. It is essential value and significance to explore the potential application of POPs in the catalytic conversion of biomass. This paper mainly considered the preparation of biomass-based HMF, focused on the catalytic conversion of fructose and its subsequent transformation on different types of POPs catalysts, and explored the unique advantages of the specific structure of catalyst on the reaction, analyzed the problems and research direction of POPs in catalytic process of biomass, and looks forward to more uses of POPs in the field of catalysts.

2. Synthesis and Structure of POPs

POPs is a kind of organic porous functional material with microporous and mesoporous structure. As shown in Figure 2, according to its structural characteristics, it could be divided into amorphous categories (representing PAFs, CMPs, and HCPs) and crystalline categories (representing COFs and covalent triazine frameworks (CTFs) [42]). POPs can be classified into different categories and achieve various functions based on different monomers and synthesis routes, such as Suzuki coupling [43], Friedel-Crafts alkylation reaction [44], Schiff-base condensation [45] and Hagihara cross-coupling [46], etc. Its unique physical and chemical properties have been enabled POPs to achieve good results in adsorption, catalysis, sensing, battery production, energy storage, biomedicine, film material and other fields [47-51].

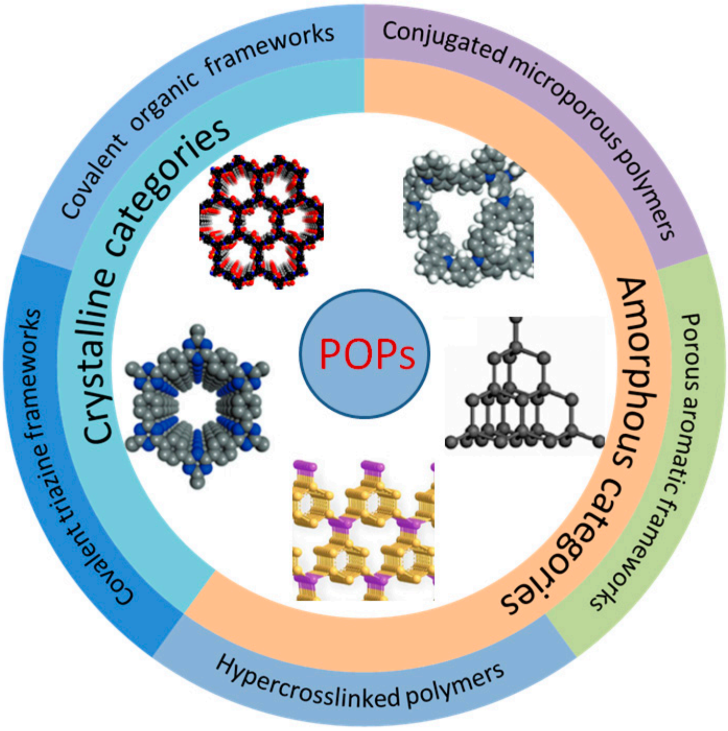

Figure 2. Partial classification of POPs.

COFs are an emerging crystalline porous molecular material composed of organic molecules linked by strong covalent bonds (such as B-O, C=N, C-N, C=C, etc.), which is mainly composed of two main components: covalent bond skeleton and modifiable functional group. It was first synthesized and reported by Omar Yaghi et al. in 2005 [52]. On account of its large specific surface area, periodicity, regular and adjustable channel structure, the functional surface and the inner wall of the channel could be used for catalysis after loading the active component. From the perspective of topological structure, COFs could be divided into two categories: 2D COFs have unique layered morphology, namely conjugate planes and π-π structures stacked between layers, which form regular channels in the longitudinal direction. 3D COFs were connected by covalent bonds to form a network, so that they were highlighted by many open sites and low density [53]. Both structures could ensure the stability of COFs crystallinity by placing active sites into their own structures, which was also a very representative case in heterogeneous catalysis. The polymerization is generally carried out according to the principles of dynamic covalent chemistry and reticular chemistry, and the final product is determined by the thermodynamic stability of the substrate. However, due to its dependence on dynamic reversible reaction synthesis, its stability is not only lower than that of other POPs subclasses, but also due to the limitations of reversible reaction types, so its synthesis scheme and structural diversification need to be developed.

Unlike COFs, PAFs were usually formed through irreversible coupling reactions, such as Ullmann coupling. The term PAFs was first proposed in 2009 [54]. Diamond-like structure was formed by rigid benzene ring, as shown in Figure 2. Charmingly, in addition to large internal surface area, the very strong skeleton formed by bottom-up C-C bond between aromatic structural units enabled it to show excellent structural stability even under some extreme conditions [55]. In summary, there are three important aspects that determine the synthetic diversity and performance of PAFs materials, which are symmetrical structures-containing monomers, efficient coupling reactions, and the topological design of the framework. By modifying the functional group of the framework unit, the specific function of a certain substance can be realized. For example, the capture of CO_2 could be realized through the amino group on the aromatic structure [56]. At the same time, its adjustable physical and chemical properties and large specific surface area could also be well used in biomass catalysis.

Porous materials with good structural properties often had higher requirements for the preparation cost, but HCPs differed from other types of POPs in that they could be directly synthesized by post-modified easily through FC (Friedel-Crafts) reactions in mild conditions [57]. As a kind of polymer material with permanent microporous structure, HCPs can achieve specific structure depending on the choice of monomer, crosslinking agent and appropriate reaction routes. Figure 3 showed the specific hypercrosslinked process [58]. At present, there are mainly three synthetic ways: post-crosslinking [59], direct polycondensation [60] and external crosslinking [61]. Its large surface area, light weight and mild prepared condition make it particularly outstanding in the fields of adsorption and catalysis.

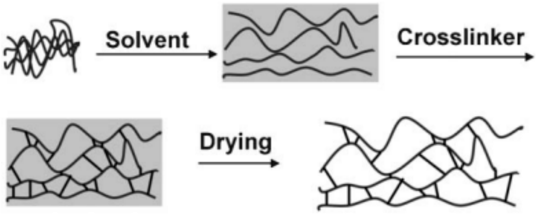

Figure 3. Schematic diagram of hypercrosslinked process [58].

Analogously, Conjugated microporous polymers (CMPs) are porous organic materials that combine extended π conjugated structure with permanent microporous framework, and are basically three-dimensional conjugated networks [62]. CMPs can be formed from several different monomers through coupling reactions, and can be tuned by changing the geometry of the monomer or combining with other atoms. Substitution of aromatic structures by alkenes, alkynes, halogens, aldehydes, and other groups is already available for the synthesis of CMPs, and many more groups are waiting to be discovered. Figure 4 showed part of its various routes. As a result, CMPs also became the broadest subcategory of POPs material development. The CMP catalyst that directly introduced the active groups into the framework were convenient for recycling due to its insoluble property, and had made great progress in the field of heterogeneous catalysis in recent years [63]. However, highly cross-linked networks and π-conjugated rigid structures also greatly reduced the machinability of CMPs and limited its application scope.

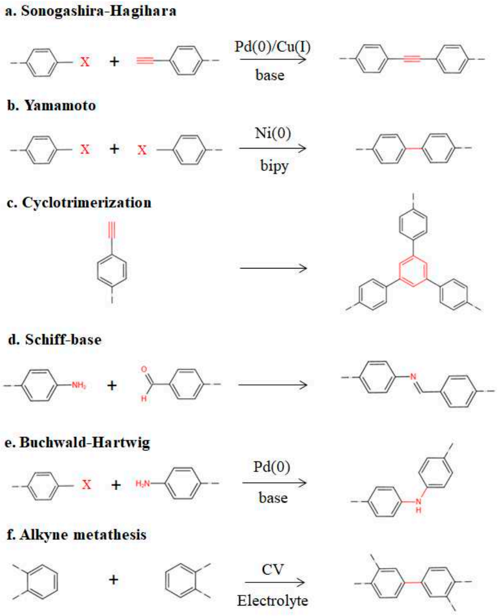

Figure 4. Partial synthetic strategies of CMPs (X = Cl, Br, I, OTf). (a) Sonogashira-Hagihara, (b) Yamamoto, (c) Cyclotrimerization, (d) Schiff-base, (e) Buchwald-Hartwig, (f) Alkyne metathesis.

To sum up, POPs has become an important part of porous supports or catalysts with its excellent physical and chemical properties, and each subclass also had good results in catalytic conversion of biomass after functionalization and loading of active components with its unique structural properties.

3. Catalytic Conversion of Fructose on POPs

Natural wood after simple treatment can get non-toxic, tasteless, pollution-free lignocellulose, the use of biomass resources mostly concentrated on its treatment [64] The hydrolysis of cellulose into glucose is the starting point of its high-value transformation. Glucose can not only produce the most widely used industrial raw material ethanol, but also isomerize to fructose for producing lactic acid, HMF and other important platform compounds. Hemicellulose can also be converted into furfural, xylitol and other compounds after acid hydrolysis. Lignin is the most abundant renewable aromatic compound in nature and can also be used in the production of fuel and high value chemicals. How to overcome the complexity and obstinacy of its structure and realize efficient utilization, which needed us to continue to study. Using efficient catalytic technology to transform lignocellulose into high value-added chemical platform compounds and derive downstream green chemicals on the basis of platform molecules, which will accelerate the arrival of the era of carbon neutrality. This section will focus on the conversion path of lignocellulose to fructose and subsequent HMF.

At present, there were researchers using cellulose as raw material to prepare HMF by one-pot method [65] or multi-step method, and also used mannose with the same intermediate as glucose as raw materials and other polysaccharides for conversion [66]. Here, we mainly introduce two preparation paths of HMF. One is directly prepared by removing three molecules of water from glucose. The second is fructose as a starting point, under certain conditions to generate a specific intermediate, gradually remove three molecules of water collocation [67]. Wang et al. proposed the mechanism of C_6 dehydration to prepare HMF, and reasonably concluded that the precondition for glucose to HMF was to convert into fructose firstly [68]. Structurally, glucose with pyran ring structure was more stable and more difficult to convert to HMF than fructose with furan ring structure [69]. In the specific study on the preparation of HMF from lignocellulose derived fructose, the results and analysis also verified the reliability of the above transformation mechanism [70]. If the efficient catalytic technology can be used to convert biomass resources into high value-added chemical platform compounds, and let these platform molecules derive downstream green chemicals, it will accelerate the arrival of the era of carbon neutrality [71]. Moreover, fructose, as an isomer of glucose, is one of the most common hexose. It is an excellent biomass product, which can be converted into polyester monomers and additives [72] through a series of transformations, and has been widely used in food and medicine production [73]. Therefore, most studies had designed green and efficient catalytic systems using fructose as raw material. Among them, the most popular route was the catalytic reaction of dehydration to prepare HMF. Figure 5 showed the conversion mechanism of fructose to prepare HMF by removing three molecules of water with acid catalyst [74].

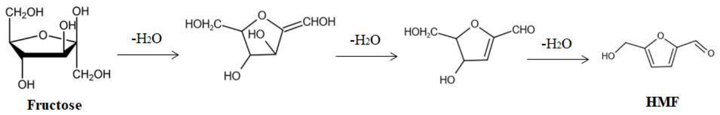

Figure 5. Conversion mechanism of fructose in preparation of HMF [74].

In a reaction system with POPs as the main component of the catalyst, strong covalent bonds were connected between monomers to ensure the stability of the structure in solvent, and ensured that the substrate could fully contact the active site in the catalytic reaction [75]. After multifunctional acids functionalization, it had corresponding groups, which could ensure high conversion and selectivity. Subclasses of POPs had been gained favor among scientists. For example, amorphous PAFs and HCPs, the former has extremely high surface area, while the latter has economical and mild synthesis conditions, both of which achieved extremely high conversion rate in biomass conversion, especially fructose. Periodic COFs with their unique crystal structure and synthesis methods have not only been applied in traditional thermal catalysis, but also have the possibility of realizing efficient biomass conversion through electrocatalysis, hence, its development was worth our deep thinking.

Due to the fact that most COFs are synthesized by reversible reactions, they are not only less stable than other POPs types, but also limited to the symmetry of structural monomers. Therefore, it needs to be extended to improve its synthesis scheme and topological structure to improve its stability [76]. Peng et al. prepared irreversible enol-ketone intervariant structures with significant chemical stability by alkali condensation reaction, and treated with 1, 3, 5-triformyl-phloroglucinol (TFP) and 2, 5-diaminobenzene sulfonic acid (DABA) to obtain solid acid catalyst, called TFP-DABA [77]. 2D COFs could enhance the degree of sulfonation and increased the number of Brønsted acid sites by their virtue of the pore structure formed by the accumulation of layered structures. With this characteristic, the catalytic system reacted in dimethyl sulfoxide (DMSO) at 100℃ for 12 hours to obtain 97% HMF from fructose and 65% of its subsequent oxidation product 2, 5-formylfuran (DFF). No significant decreased in activity was observed after 3 cycles. Most of the fructose catalytic conversion systems with POPs as catalyst could not get rid of their dependence on DMSO, which could stabilize HMF and inhibited the occurrence of side reactions, but it was also a very harmful solvent to the environment.

Here, by exploring the influence of non-covalent interaction on catalytic performance, Sun et al. modified the environment around the active site of catalyst by using the movable and aggregable properties of the groups on the highly flexible linear polymer, and even achieved better conversion efficiency without DMSO. As shown in Figure 6, they prepared novel COF with large mesoporous channels by condensation reaction of 1,3,5-tris(4-aminophenyl)-benzene (TPB) and 2,5-dimethoxyterephthalaldehyde (DMTA) [78]. We could clearly see that the perfluoroalkyl chain with sulfonic acid groups was confined to the pore through the reaction of the sultone ring with the hydroxyl group on the COF framework, and then through hydrogen bond interaction to create the desired solvent environment. When PVP@$[SO_3H]_{0.17}$-COF was inserted into the highly flexible polymer synthesis catalyst, the fructose conversion rate was greater than 99.5% and the HMF yield was as high as 99.1% at 100℃ for only 30 minutes. The catalyst could still maintain the fructose conversion rate after 5 cycles, and the HMF yield only decreased by 2%.The studies carried out by Bhanja et al. had not been limited to monocatalytic centers [79], they used 2,2′-benzidinedisulfonic acid and 4,4′-diaminostilbene-2,2′-disulfonic acid with cyanuric chloride to synthesize catalysts (POPDS and POPSDS) containing sulfonic acid and secondary amine, and became the excellent catalyst to prepare HMF. The reaction at 130℃ for 20 minutes could achieve 98% fructose conversion and 86% and 89% HMF yield, the catalyst could maintain 6 cycles of experiments. Figure 7 showed the mechanism of the conversion of glucose and fructose to HMF. We can find in the figure that the two groups had different functions. Amino group was mainly responsible for isomerization transformation, while sulfonic acid group played a role in subsequent transformation. Their presence guaranteed the high catalytic performance of the reaction.

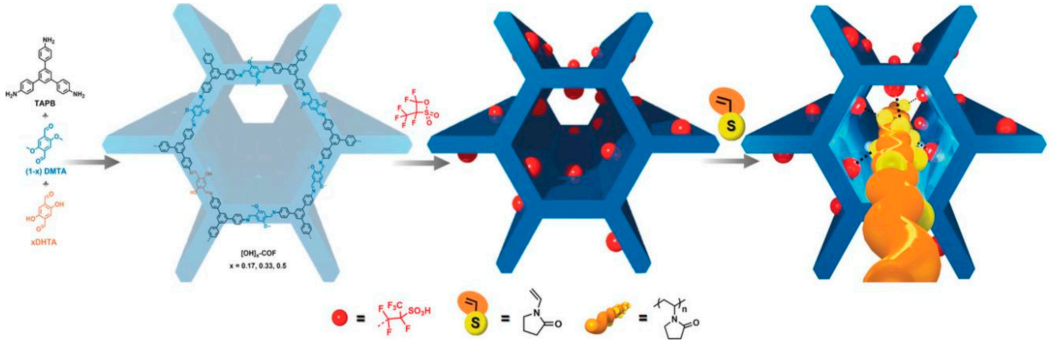

Figure 6. The concept of changing the local environment of the active site in porous materials by inserting linear polymers and the synthesis strategy of PVP@$[SO_3H]_{0.17}$-COF [78].

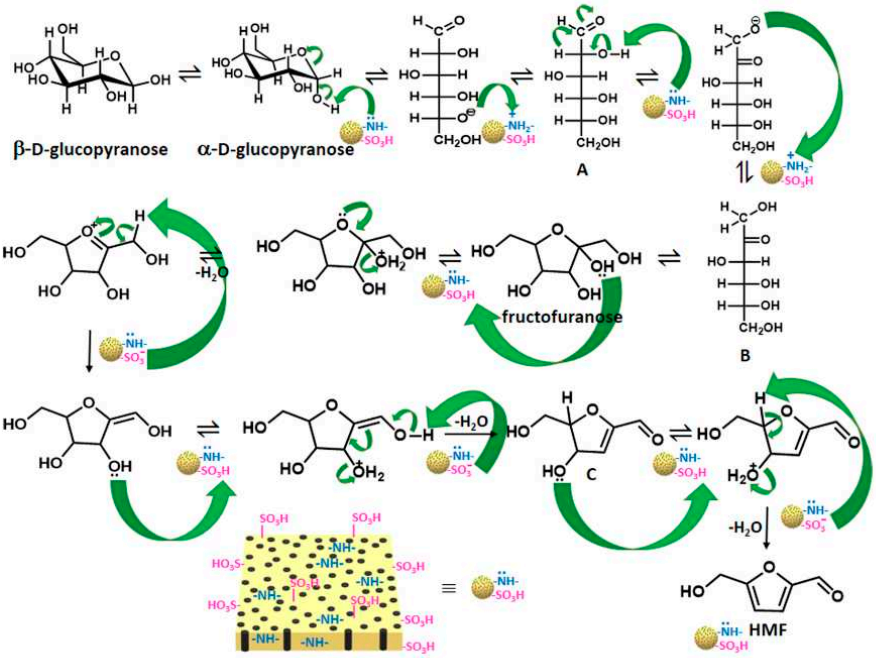

Figure 7. Mechanistic pathway for the conversion of glucose and fructose to HMF over bifunctional porous organic polymers [79].

The synthesis system of COFs endowed them with unique structural properties. In the formation and connection of covalent bonds, the high synthesis rate speeded up the nucleation process in the synthetic system, which leaded to a great reduction in the crystallinity of COFs, and made it difficult to obtain single crystal COFs. This structure made its stability weaker than that of other subclasses. This characteristic was reflected in the catalytic reaction which shortened the catalyst life and affected the economic and time benefits [80]. Therefore, the development of a new synthetic approached to discuss the stability and crystallization of COFs was worthy of further study.

In addition to increasing the specific surface area and the number of acid sites of the catalyst, the catalytic activity and product selectivity in converting fructose into HMF should also be considered due to the low diffusion of fructose molecules in the cellular structure [81]. Subsequently, some PAFs had recently been reported for this catalytic reaction, Du et al. used rigid tetrahedrons and triangles to construct porous aromatic framework PAFs to ensure the suitable pore size and the availability of active sites [82]. Their catalyst HO_3S-POP was highly adapted to the substrate with high specific surface area, could achieve 100% fructose conversion within 15 minutes under microwave heating to 140°C, and 70% HMF selectivity.

Unlike crystalline framework materials such as COFs, PAFs are composed of irreversible structures, we would pay more attention to the uniqueness of topological design. The structure formed by the appropriate coupling reaction could realize the high product selectivity. In the local structure, aromatic groups with certain rules can rotate and combine to deform, thus forming structural defects that fit with the reaction system. Therefore, it is necessary to clearly study framework of PAFs, in-depth understand its structural composition, and further broaden the scope of its heterogeneous catalysis.

Although HCPs with permanent microporous structure could not be dominant in fructose diffusion, the preparation and application of HCPs with low threshold was still one of the best choices for porous catalytic materials. Das et al. synthesized microporous polymer TrzDBTH by Friedel-Crafts reaction of 2,4,6-tris[4-(bromomethyl)phenyl]-1,3,5-triazine and dibenzothiophene (DBTH), and then sulfonated it with chlorosulfonic acid to obtain solid acid catalyst STrzDBTH with sulfonic acid groups [83]. The complete conversion of fructose and 96.2% yields of HMF were achieved after 20 minutes reaction at 140°C under atmospheric pressure. The catalyst could maintain five reaction cycles. Dong et al. verified the effect of sulfonation treatment and reaction solvent on the dehydration of fructose into HMF by self-polymerization of benzene monomer into HCP-x [84]. The HMF yield of 96.7% was obtained at nearly 140℃ for half an hour, and the catalyst could be cycled for more than 4 times.

Porous organic polymers of other HCP structures with different monomers and synthesis methods also had been used in biomass catalytic conversion, such as porous polytriphenylamine (PPTPA), which was self-polymerized from trianiline, could be used as adsorbent for aromatic compounds and hydrogen bonding compounds because of its conjugated system and a large number of nitrogen atoms [85]. Mondal et al. obtained SPPTPA-1 after sulfonation from the PPTPA-1 material prepared above. Acid-base titration showed that SPPTPA-1 had strong acidity, which could be used as solid acid catalyst for the preparation of HMF by dehydration of fructose [86]. The fructose was completely transformed in organic solvent system at 140℃ for 20 minutes, and HMF with yield of 94.6% was obtained. The activity of the catalyst did not decrease significantly after four catalytic cycles. In addition, Sebati et al. formed a solid acid catalyst SPPTPA by adding chlorosulfonic acid [87]. In order to further facilitate recycling, they used Fe_3O_4 nanoparticles to synthesize the catalyst FeSPPTPA for fructose preparation of HMF, achieved a higher specific surface area than other catalysts, reaching 95% yields of HMF at 100℃ for 20 minutes. In the process of separation and recovery, magnetic characteristics could be effectively used for intelligent processing, the activity of catalyst did not decrease obviously in 4 reaction cycles, which also had a certain reference for subsequent research and innovation.

Sulfonic acid functionalized materials are widely used in the field of catalysis [88]. In the dehydration reaction of fructose preparation of HMF, POPs catalyst was almost sulfonated in the synthesis process and contained sulfonic acid sites, which proved to be able to improve the reaction efficiency. For broaden the research direction, Ravi et al. [89] used phosphate-functionalized POPs for biomass conversion to HMF for the first time, they synthesized the HCP-structured catalyst (B-POP) by replacing the sulfonic acid site with the phosphoric acid site. The reaction was carried out in DMSO at 160℃ for 30 min to obtain 100% fructose conversion and 85% HMF production. The catalytic effect was further to convert HMF into oxidation product DFF and ring-opening product Levulinic acid (LA). In addition, the fructose conversion rate was only reduced by less than 5% after 10 cycles, and the HMF yield did not change visibly.

Certainly, in the application of POPs as catalysts in the conversion of fructose, there were still some aspects to be investigated, such as avoiding side reactions, reducing the use of raw materials or making the reaction conditions more moderate, etc. Here, we mainly discussed the influence of solvent system on the reaction. Table 1 summarized the catalytic system of fructose conversion to HMF with POPs as catalyst mentioned in this section. The data showed that most of the systems could work under atmospheric pressure, the working conditions were relatively mild. In about half an hour, they could achieve the raw material conversion rate was more than 95%, and the product yield was between 70% and 98%. Furthermore, it was not difficult to find that in the conversion of fructose to HMF, the solvent used was basically DMSO, not only that, in other biomass conversion reactions, it was also commonly used as a solvent [90]. From a green point of view, it was undoubtedly better to reduce the harm of DMSO or not used DMSO in reaction.

Table 1. Summary of reactive systems for the conversion of fructose to HMF using POPs as catalyst.

Catalyst	Substrate	Solvent system	Time (min)	Temperature (℃)	$X_{substrate}$ (%)	HMF Yield (%)	Reference
TFP-DABA	Fructose	DMSO	60	100	>99	97	[77]
PVP@$[SO_3H]_{0.17}$-COF	Fructose	Tetrahydrofuran	30	100	>99.5	97.6	[78]
POPDS	Fructose	DMSO	20	140	98	86	[79]
POPSDS	Fructose	DMSO	20	140	98	89	[79]
HO_3S-POP	Fructose	Dioxane aqueous	15	140	100	>70	[82]
STrzDBTH	D-Fructose	DMSO	20	140	100	96.2	[83]
HCP-x	Fructose	DMSO	30	139.85	>99	96.7	[84]

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SPPTPA-1	Fructose	DMSO	20	140	100	94.6	[86]
FeSPPTPA	Fructose	DMSO	20	100	95	96.6	[87]
B-POP	Fructose	DMSO/ Dioxane	30	130	100	85	[89]

4. Catalytic Conversion of HMF on POPs

The growing depletion of non-renewable energy and climate changes are putting enormous pressure on all sectors of the world, forcing economies to scale up to meet demand [91], and the chemical industry, which relies on fossil fuels to run, urgently needs to change this status. As mentioned above, PEF using FDCA as the precursor has the potential to replace PET, but the current process route for FDCA production is not mature, and it has not been able to achieve large-scale production of degradable polyester for practical application [92]. The most possible way of large-scale production was to prepare FDCA by catalytic reaction of HMF, which could be converted from biomass resources. For different oxidation ways, the catalytic methods for preparing FDCA from HMF could be divided into thermal catalysis [93], photocatalysis [94], electrocatalysis [95] and biocatalysis [96]. According to the current production level, thermal catalysis was the most compatible method in industry. Among the catalysts selected, the most effective ones were those with precious metal components [97]. However, due to the scarcity of precious metals, industrialization could not be realized according to the current industrial level. The catalysis of non-noble metal or even non-metallic components with porous carrier for the preparation of FDCA from HMF had always been an interest of scholars. Solid acid catalysts with POPs as the carrier showed considerable potential in this conversion route and other conversion routes of HMF, but there were also some research areas worth improving to enhance the competitiveness with existing catalysts for conversion of HMF.

2D COFs could be designed from symmetric and asymmetric topologies to order layered stacked lattice patterns, and regular carrier channels would be formed along the longitudinal axis, so there were also space for application in the field of electrocatalysis [98]. Since most COFs were non-conductive materials, in order to improve the catalytic efficiency, their unique structures could be used to carbonize the pyrolysis treatment template, and ingenious design could also be made in their utilization forms. Cai et al. used nickel acetate, triformyl-phloroglucinol-5,5-diamino-2,2-bipyridine and toluene sulfonic acid to obtain 2D COF-structured containing films by interfacial crystallization, and stamped it on the fluorine-doped tin oxide (FTO) to prepare the catalyst TpBpy-Ni@FTO [99]. It could achieve up to 96% HMF conversion and obtained 58% and 34% oxidation products FDCA and FFCA separately. As the first case of electrocatalytic oxidation of HMF with COF structure, the product yield of this system was not ideal. We considered that the catalyst might be gradually covered by nickel element with low surface electroactivity during the reaction process [100]. Nevertheless, it provided some basis and optimization reference for the subsequent biomass electrocatalysis with COF structure.

FDCA was not the only important substance in the oxidation path of HMF, such as DFF, 5-hydroxymethyl-2-furan carboxylic acid (HMFCA), 5-formyl-2-furan carboxylic acid (FFCA), which also could be widely used in the preparation of fine chemicals, pharmaceuticals, chiral catalysis and polyester industry [101–103]. Similarly, the oxidation route was not the only one worth discussing in the utilization of HMF. HMF, known as "the sleeping giant" [104], could activate itself C=O, C=C and C-O for high-value conversion in green sustainable chemistry. 2,5-dihydroxymethylfuran (DHMF) is an important chemical in the production of artificial fibers and resins, which can be produced by hydrogenation of HMF [105]. Most studies relied on the synergistic system of Cu^0 and Cu^+ to improve the catalytic activity in hydrogenation treatment [106]. However, due to the existence of reducing gases, the stability of the system needed to be strengthened [107]. Therefore, it had been very important to develop a stable structure of Cu-supported catalyst in this direction. Sarkar et al. [108] synthesized the catalyst Cu@C-POP by the FC reaction with catechol and dimethoxymethane. Figure 8a showed the as-synthesized catechol-functionalized C-POP. The copper nanoparticles were then fixed to the polymer by the reduction deposition of two copper salts, respectively. The C-POP had a stable framework and formed a space structure that restricted the agglomeration and leaching of copper nanoparticles. The system achieved 98% selectivity of DHMF at 150°C and 20 bar H_2 for 10 hours, and the catalyst could be reused seven times. Figure 8b showed the reaction energy distribution of hydrogenation process of HMF conversion to DMHF. In addition to the conversion process at the location, we also could see the presence of Cu vacancy on the catalyst surface. The presence of vacancy increased the electron density of CuO surface, thus improving the adsorption capacity of substrate molecules.

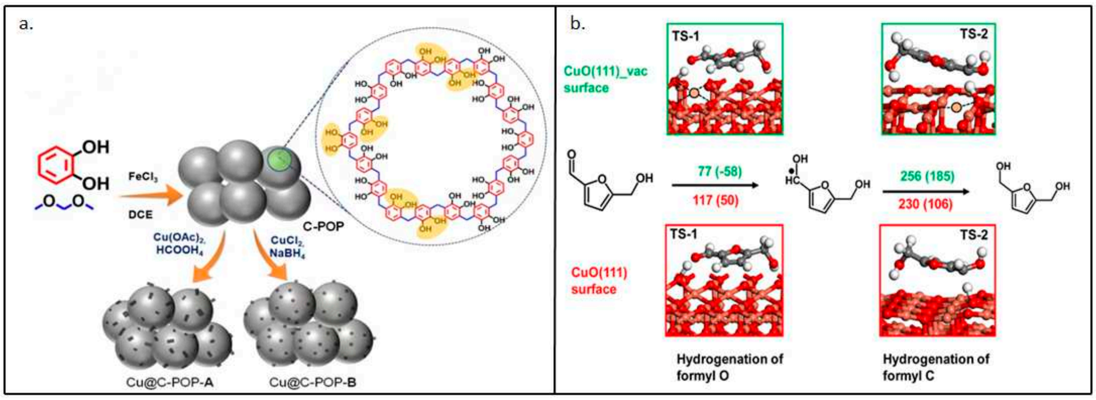

Figure 8. (a) Synthetic strategy of as-synthesized catechol-functionalized POP (C-POP), Cu@C-POP-A and Cu@C-POP-B. (b) Reaction energy profile of hydrogenation process of HMF conversion to DMHF [108].

In particular, 5-ethoxymethylfurfural (EMF), the etherification product of HMF not mentioned in the Figure 1, had been identified as an important substance for the preparation of biodiesel and could produce a change from the currently used petroleum-based energy systems [109]. Wang et al. used soft template method to synthesize ordered mesoporous carbon (OMC) from resorcinol and pluronic F-127 and then sulfonated it to produce a catalyst OMC-SO_3H. The fructose was converted into EMF with a yield of 55.7% by a one-pot method [110]. On this basis, Zhang et al. used sulfonic acid functionalized HCPs instead of OMC as catalyst for the direct reaction of one-pot method into a mixed solvent system of ethanol and DMSO, and obtained EMF and HMF with yields of 78.9% and 15.4% by reaction at 104.85°C for 480 minutes, respectively. The activity of catalyst HCP-x did not decrease significantly after 5 catalytic cycles [111]. In this reaction, the high density sulfonic acid groups and stability of HCPs-based catalysts ensured the activity of fructose etherification. Its abundant Brφnsted acidic site and high mobility given by its structure guaranteed the efficient conversion of the product with the addition of Lewis acid.

Sulfonic acid sites-containing POPs catalysts and surface properties that can be regulated as required have great potential for biomass conversion. In the synthesis of EMF, fructose as raw material could not avoid the problem of time consuming and low efficiency, while using HMF as raw material could shorten the reaction time, achieved higher selectivity and even solvent-free conversion, which was more valuable and feasible from the perspective of green sustainable chemistry [112]. There were various synthetic ways, and the most kinds of CMPs combined with sulfonic acid groups also had some application space in the catalytic conversion of HMF. Xiang et al. used divinylbenzene (DVB) and triallylamine (TAA) to synthesize porous organic polymer PDVTA with CMP structure by solvothermal copolymerization. The catalyst PDVTA-SO_3H was obtained after sulfonation. As shown in the Figure 9, the structure of the sulfonated CMPs provided a large number of reactive sites, and HMF was etherized into EMF under the action of these acidic sites. The catalytic system at 110°C reaction for 30 minutes to achieve 87.6% EMF yield and could maintain 5 catalytic cycles [113].

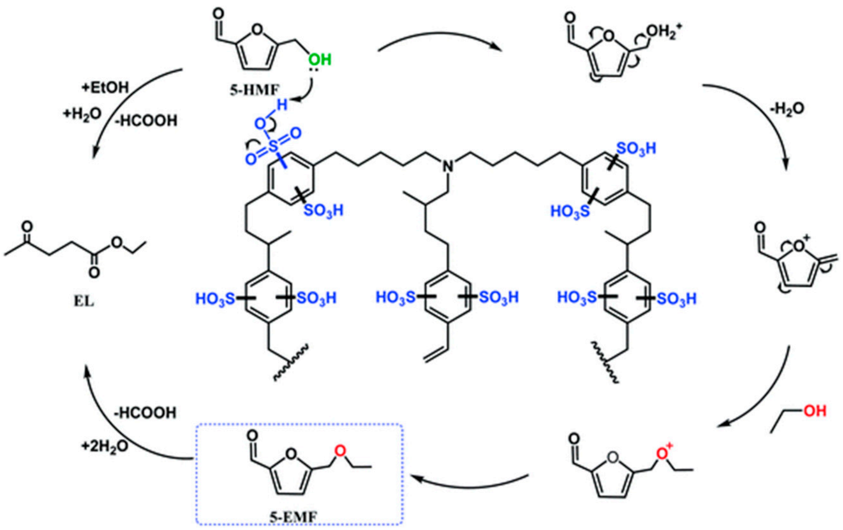

Figure 9. Reaction mechanism of the catalytic conversion of HMF on PDVTA-SO3H [113].

In addition to the functional modification of POPs, the supported catalyst prepared with active components could achieve higher performance than the catalyst composed of only active components. In the utilization of PDVTA, Lai et al. loaded Cu-doped MnO_2 nanowires to prepare Cu-MnO_2@PDVTA, which achieved up to 96.8% FDCA yield at 80°C for 12 hours, and the catalyst could achieve 7 cycles [114]. Figure 10 showed the reaction mechanism of HMF oxidation to FDCA. The conversion of HMF to DFF and FFCA could also occur in the absence of catalyst, and FFCA was gradually transformed to FDCA under the action of Mn^{4+}. In addition, the doping of Cu^{2+} in the catalyst was conducive to the exchange between Mn^{3+} and Mn^{4+}. It also promoted the transfer of lattice oxygen. Since the addition of alkali was required in most non-precious metal catalytic systems, here they took advantage of the excellent performance of Mn-based catalyst, considered the influence of its crystal structure on the catalytic oxidation of HMF [115], and improved the stability of the catalyst by using the CMP structure to provide more basic groups, so as to realized the alkyl-free catalysis.

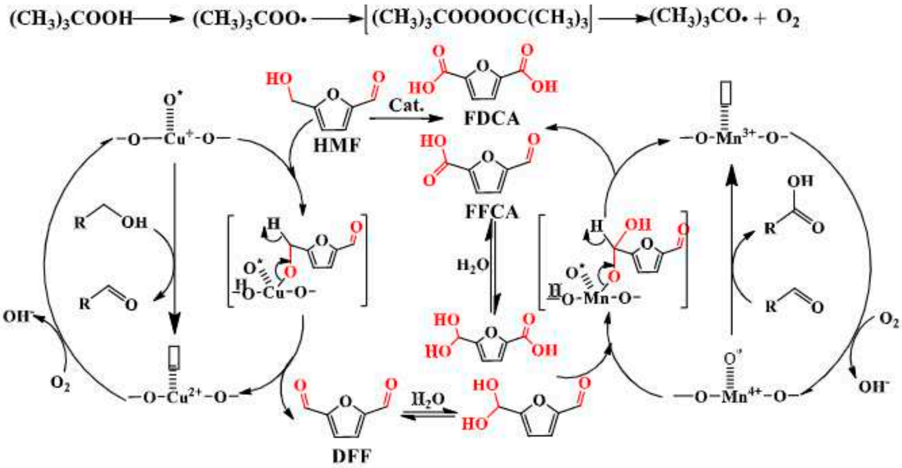

Figure 10. Mechanism for the oxidation of HMF to FDCA catalyzed by Cu-MnO_2@PDVTA [114].

Compared with other heterogeneous catalysts, the advantage of CMPs lied in its highly conjugated framework, which could effectively reduce the use of metals in conversion, but it was difficult to remove residual trace metal substances in the process of catalyst preparation [116].

In addition to performing functional modifications, POPs can achieve different functions through the composition of monomers. For example, in order to improved the adsorption capacity of CO_2, Modak et al. used porphyrinic molecules to react with phenyldialdehyde and synthesized the materials with a surface area of 875 m^2/g through one-pot method [117]. Saha et al. used this strategy in the preparation of catalyst for HMF conversion. They used pyrrole and phenylaldehydes after distillation as precursors, and added ferric chloride to acetic acid mediated through hydrothermal synthesis to obtain Fe^{III}-POP-1 catalyst. In this reaction, 100% conversion of HMF and 79% yields of FDCA could be obtained by using only water as solvent and reacting in air at 100°C for 10 h. The catalyst could maintain activity in three reaction cycles [118]. No product appeared in the system after the subsequent reaction with homogeneous Fe^{III}–porphyrin complex, this indicated the importance of large surface area and multiple active sites produced by this simple and rapid synthesis method for catalytic reaction, and also reflected the interoperability of the two fields of adsorption and catalysis.

Table 2 summarized the thermal catalytic system of HMF with POPs as the carrier. All the cases listed coule achieve a high conversion rate of 95% or above under mild reaction conditions. In the case of the same oxidant, different solvents and substrates had a large difference in the time required to convert to the target product. However, for the conversion of HMF, no matter oxidation, etherification or other conversion routes, there were relatively few studies on POPs as the catalyst. In terms of the current relatively mature thermal catalytic system of HMF, POPs still had a long way to go in terms of overall catalytic efficiency compared with other porous materials (such as zeolite) with easier access.

Table 2. Summary of reactive systems for the HMF conversion using POPs as catalyst.

Catalyst	Substrate	Solvent system	Oxidant	Pressure (Mpa)	Time (min)	Temperature (°C)	$X_{substrate}$ (%)	Yield (%)	Reference
HCP-x	Fructose	Ethanol/ DMSO	Air	0.1	480	104.85	99.8	78.9(EMF); 15.4(HMF)	[111]
PDVTA-SO_3H	HMF	Ethanol	Air	0.1	30	110	99.8	87.5(EMF)	[113]
Cu-MnO_2 @PDVTA	HMF	Tert-butyl alcohol	TBHP /Air	0.1	720	80	95	96.8(FDCA)	[114]
Fe^{III}-POP-1	Fructose	Water	Air	1	600	100	100	79(FDCA)	[118]

5. Conclusion and Outlook

It is one of the important tasks of sustainable development to rationally utilize existing energy and develop renewable energy instead of fossil energy. Biomass resources are considered as important raw materials to replace fossil based resources in the production of fuels and chemicals, which can be utilized reasonably on a large scale through catalysts with specific catalytic activities. As described above, POPs had established its position in the field of catalysis by virtue of its permanent pore structure, excellent stability and low density structure, and also demonstrated its great potential in biomass utilization. The functional groups existing on its surface could provide reaction sites and have the potential to replace metal-based catalysis. At the same time, the stable structure also guaranteed the recovery rate of the catalyst and saved the cost. The functionalization was not limited to one or some groups, but with the existing synthesis technology, to achieve stable, uniform, abundant active sites still needed more in-depth research.

This paper mainly reviewed the synthesis and the structural characteristics of POPs materials focused on the catalytic application of POPs as the main components of catalysts in lignocellulose conversion to HMF and derivates. In the preparation of HMF by catalytic dehydration of fructose and the preparation of follow-up chemicals by catalytic HMF, efficient production was not only achieved through effective functionalization combined with the unique structure of carrier materials, but also through innovative synthesis methods to improve the inherent shortcomings of some POPs materials and the unique design took into account the convenience of follow-up operations. Also, the feasibility of innovative application of some POPs materials was also discussed.

POPs have been widely used in the field of catalysis and have good effects, but their potential has not been fully realized in the catalytic conversion of biomass studied in this paper. To be specific, it basically adopts thermal and electric catalytic systems. Although it had suitable structures for other catalytic systems, it had not yet seen representative results in biomass conversion attempts. We proposed to make breakthroughs in the catalytic conversion of biomass from the design of topological structure, the orderly regulation of micro-morphology and pore structure, and the directional loading of functional groups and active sites.

In the practical application of natural resources in synthetic products, the one-step method could avoid the lengthy separation process and the purification process of intermediate compounds in the subsequent processing. Cellulose could be converted into alcohol compounds, ester compounds and organic acid compounds by homogeneous and heterogeneous catalytic systems in one-pot. However, POPs as catalyst component had not been reported. Besides, almost all existing POPs materials were synthesized under solvothermal conditions, and their requirements for synthesis environment and equipment made it hard to achieve large-scale synthesis. Although heterogeneous catalysis had improved the separation and purification efficiency of products, the applications of POPs in biomass conversion still faced great challenges in separation and purification. We need to accurately extract each of the high-value chemicals from the resulting mixture to produce a product that meets the standards.

Therefore, making full use of sustainable energy and technology combined with the structural characteristics of POPs materials to continuously innovate and developing an efficient catalytic system, so that it cannot only meet the catalytic conversion to small molecules, but also directly converts biomass macromolecules into high-value chemicals. Further, it is of great research significance to meet the needs of the times to develop green and harmless solvent systems and synthesis methods with high industrial compatibility to meet the needs of more fields.

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