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# Nanoporous Organic Frameworks for Biomass Conversion

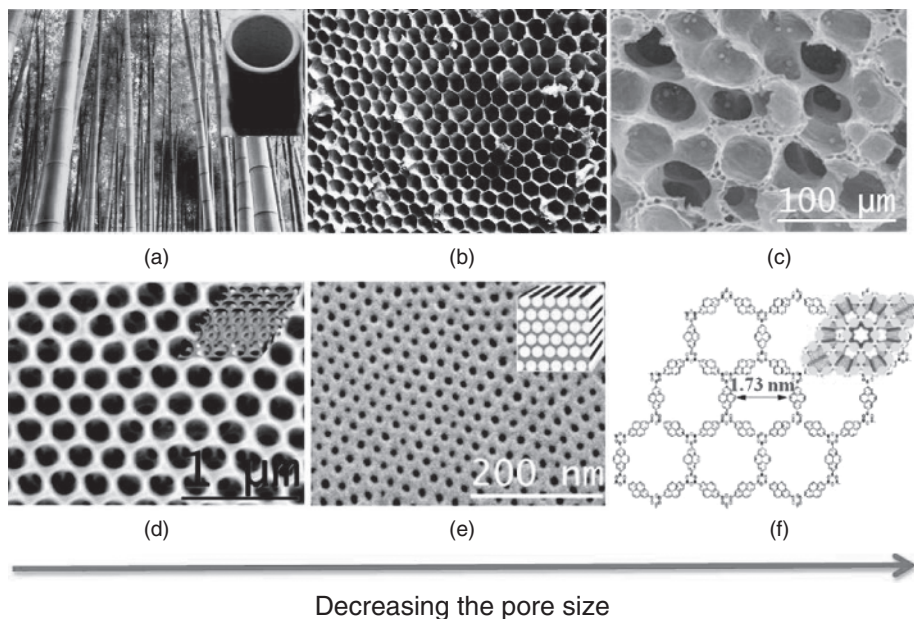
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## 1.1 Introduction

Porosity, a profound concept that helps to understand Nature and create novel fascinating architectures, is inherent to natural processes, as seen in hollow bamboo, hexagonal honeycomb, and the alveoli in the lungs (Figure 1.1) [1,2]. These advanced natural porous frameworks and their promising applications have widely inspired scientists with the idea of mimicking them in artificial structures down to the micro- and nanoscale range [1,2]. The rational design and synthesis of advanced nanoporous materials, which play a crucial role in established processes such as catalysis and gas storage and separations and catalysis [3–12], have long been an important science subject and attracted tremendous attention. During the past two decades, the linking of molecular scaffolds by covalent bonds to create crystalline extended structures has afforded a broad family of novel nanoporous crystalline structures [13] such as like metal–organic frameworks (MOFs) [14] and covalent organic frameworks (COFs) [15]. The key advance in this regard has been the versatility of covalent chemistry and organic synthesis techniques, which give rise to a wide variety of target applications for these extended organic frameworks, for example, the use of MOFs and COFs in the context of biomass conversion. In addition to crystalline frameworks, nanoporous organic resins have long been extensively studied as heterogeneous catalysts for the conversion of biomass because of their commercial synthesis [16].

Upgrading biomass into fuel and fine chemicals has been considered a promising renewable and sustainable solution to replacing petroleum feedstocks, owing to the

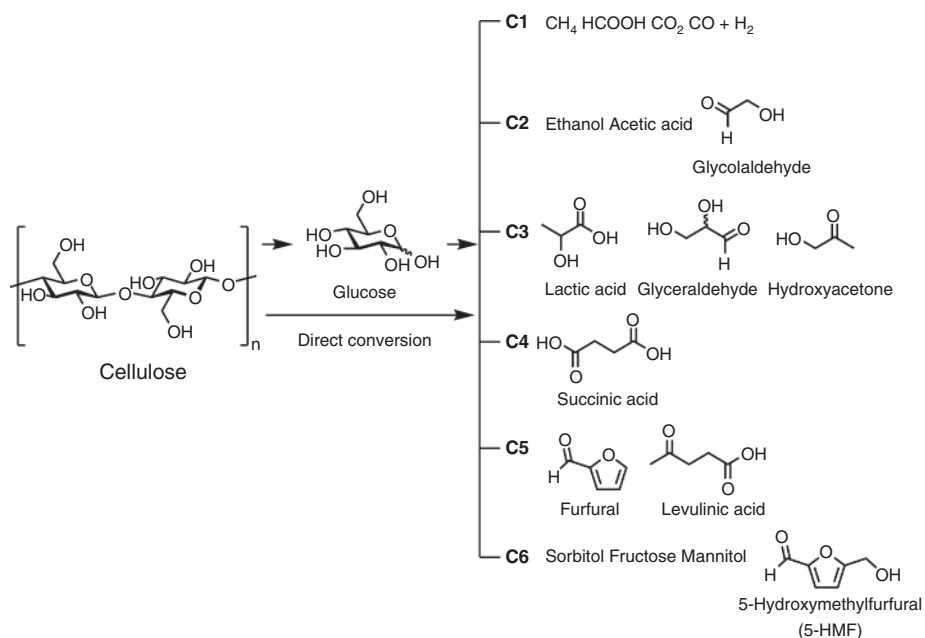


**Figure 1.1** Illustration of porosity existing in Nature and synthesized frameworks with a decreasing pore size. (a) Bamboo; (b) honeycomb; (c) scanning electron microscopy (SEM) image of alveolar tissue in mouse lung; (d) SEM image of an ordered macroporous polymer; (e) SEM image of an ordered mesoporous polymer from self-assembly of block copolymers; (f) structural representation of the COF structure. (See color plate section for the color representation of this figure.)

rich family of biomass raw materials, which mainly includes cellulose, hemicellulose, and lignin [17,18]. For example, the carbohydrates, present in the cellulosic and hemicellulosic parts of biomass, can be converted into renewable platform chemicals such as 5-hydroxymethylfurfural (HMF), via acid-catalyzed dehydration for the production of a wide variety of fuels and chemical intermediates [19]. Despite great progress, including unprecedented yields and selectivities, having been made in biomass conversion using conventional homogeneous catalysts, the cycling abilities have long been the main drawbacks that inhibit their large-scale applications. As a result, heterogeneous nanoporous solid catalysts hold great promise in these diverse reactions [16]. High porosities of nanoporous catalysts may help to access reactants, mass transfer, and functionalization of task-specific active sites, such that the product selectivities can be easily controlled. To this end, nanoporous materials with high surface areas, tunable pore sizes and controllable surface functionalities have been extensively prepared and studied. Significantly, nanoporous crystalline organic frameworks, with well-defined spatial arrangements where their properties are influenced by the intricacies of the pores and ordered patterns onto which functional groups can be covalently attached to produce chemical complexity, exhibit distinct advantages over other porous catalysts. For instance, post-synthetic modification (PSM) techniques [20] provide a means of designing the intrinsic pore environment without losing their long-range order to improve the biomass conversion performance. The inherent ‘organic effect’ enables the architectures to function with task-specific

moieties such as the acidic sulfonic acid ( $-\text{SO}_3\text{H}$ ) group. The desired microenvironment can also be generated by rationally modifying the organic building units or metal nodes. In addition, the attractive large porosity allows the frameworks to become robust solid supports to immobilize active units such as polyoxometalates and polymers [21]. In essence, nanoporous crystalline organic frameworks including MOFs and COFs have demonstrated strong potential as heterogeneous catalysts for biomass conversion [21]. The ability to reticulate task-specific functions into frameworks not only allows catalysis to be performed in a high-yield manner but also provides a means of facile control of product selectivity.

HMF, as a major scaffold for the preparation of furanic polyamides, polyesters, and polyurethane analogs, exhibits great promise in fuel and solvent applications [19,22]. The efficient synthesis of HMF from biomass raw materials has recently attracted major research efforts [23–29]. Via a two-step acyclic mechanism, HMF can be prepared from the dehydration of C-6 sugars such as glucose and fructose. First, glucose undergoes an isomerization to form fructose in the presence of either base catalysts or Lewis acid catalysts by means of an intramolecular hydride shift [30]. Subsequently, Brønsted acid-catalyzed dehydration of the resultant fructose affords the successful formation of HMF with the loss of three molecules of  $\text{H}_2\text{O}$  (Scheme 1.1) [31]. The development of novel nanoporous acidic catalysts for the catalytic dehydration of sugars to HMF is of great interest, and is highly desirable. Hence, design strategies for the construction of nanoporous crystalline organic frameworks that are capable of the efficient transformation of sugars to HMF are discussed in this chapter, and some nanoporous organic resins for the conversion of raw biomass



**Scheme 1.1** Possible valuable chemicals based on carbohydrate feedstock.

materials are highlighted. By examining the common principles that govern catalysis for dehydration reactions, a systematic framework can be described that clarifies trends in developing nanoporous organic frameworks as new heterogeneous catalysts while highlighting any key gaps that need to be addressed.

## 1.2 Nanoporous Crystalline Organic Frameworks

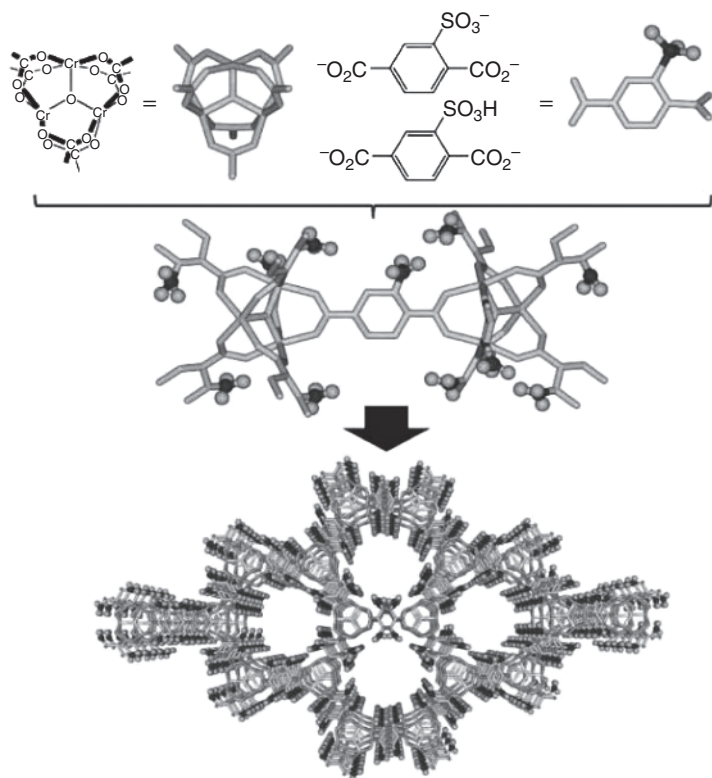
### 1.2.1 Metal–Organic Frameworks

The Brønsted acidity of nanoporous catalysts is very essential for the dehydration of carbohydrates towards the formation of HMF [32–34]. One significant advantage of metal–organic frameworks (MOFs) is their highly designable framework, which gives rise to a versatility of surface features within porous backbones. Whereas, a wide variety of functional groups has been incorporated into MOF frameworks, exploring the Brønsted acidity of MOFs [14], the introduction of sulfonic acid groups in the framework remains a challenge and less explored, mainly because of the weakened framework stability. In this regard, several different synthetic techniques have been developed and adopted to introduce sulfonic acid ( $-\text{SO}_3\text{H}$ ) groups for MOF-catalyzed dehydration processes: (i) de-novo synthesis using organic linkers with  $-\text{SO}_3\text{H}$  moiety; (ii) pore wall engineering by the covalently postsynthetic modification [20] (PSM) route; and (iii) modification of the pore microenvironment through the introduction of additional active sites. These novel MOF materials featuring strong Brønsted acidity show great promise as solid nanoporous acid catalysts in biomass conversion.

#### 1.2.1.1 De-Novo Synthesis

Inspired by the framework MIL-101 [35], which possesses strong stability in aqueous acidic solutions and is fabricated from a chromium oxide cluster and terephthalate ligands in hydrofluoric acid media, Kitagawa *et al.* for the first time reported the rational design and synthesis of a MIL-like MOF material for cellulose hydrolysis [36]. By, adopting the MIL-101 framework as a platform, these authors created a novel nanoporous acid catalyst with highly acidic  $-\text{SO}_3\text{H}$  functions along the pore walls by the innovative use of 2-sulfoterephthalate instead of the unsubstituted terephthalate in MIL-101 (Figure 1.2). The resultant Cr-based MOF MIL-101- $\text{SO}_3\text{H}$  was shown to exhibit a clean catalytic activity for the cellulose hydrolysis reaction, thus opening a new window on the preparation of novel nanoporous catalysts for biomass conversion. On account of the unsatisfactory yields of mono- and disaccharides from cellulose hydrolysis being caused by the poor solubility of crystalline cellulose in water, the same group further studied isomerization reactions from glucose to fructose in aqueous media, where MIL-101- $\text{SO}_3\text{H}$  not only shows a high conversion of glucose but also selectively produces fructose [37]. A catalytic one-pot conversion of amylose to fructose was also achieved because of the high stability of the framework in an acidic solution, which suggests promising applications of compound in the biomass field.

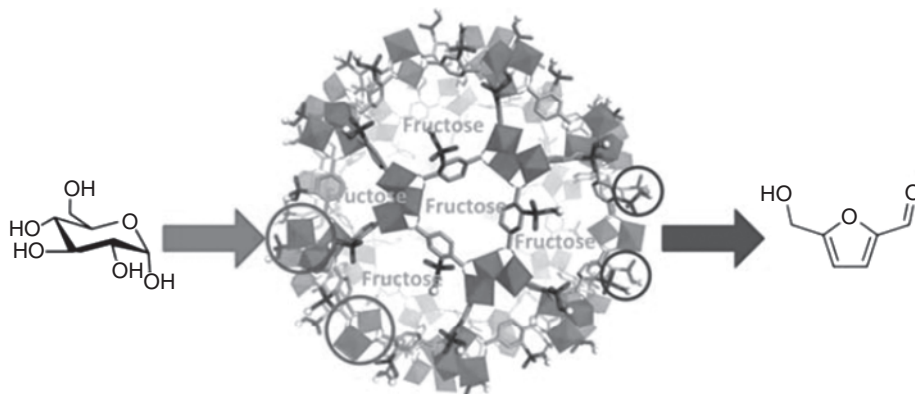
On account of the HMF formation mechanism, the Lewis acid featuring metal center – for example, chromium (II) – allows for a high-yield isomerization because of the coordinate effect between the Lewis acidic metal sites and glucose [24]. In addition



**Figure 1.2** Schematic representation of the structure of MIL-101-SO<sub>3</sub>H. (See color plate section for the color representation of this figure.)

to strong Brønsted acidity caused by the  $-\text{SO}_3\text{H}$  moieties, MIL-101-SO<sub>3</sub>H also bears Cr(III) sites within the structure, which is similar to  $\text{CrCl}_2$  and may act as active sites for the isomerization of glucose to fructose, whereas the fructose dehydration can be initiated with the aid of  $-\text{SO}_3\text{H}$  groups. Bao *et al.* carried out an integrated process using nanoporous MIL-101-SO<sub>3</sub>H as the catalyst and biomass-derived solvent ( $\gamma$ -valerolactone; GVL) for the conversion of glucose into HMF (Figure 1.3) [38]. The batch heterogeneous reaction was shown to give a HMF yield of 44.9% and a selectivity of 45.8%. The glucose isomerization in GVL with 10 wt% water was found to follow second-order kinetics, with an apparent activation energy of  $100.9 \text{ kJ mol}^{-1}$  according to the reaction kinetics study. Clearly, the bifunctional MIL-101-SO<sub>3</sub>H framework can serve as a potential platform for the dehydration reaction of biomass-derived carbohydrate to generate platform chemicals.

Solvents play another crucial role in the green biomass conversion processes, and the development of water-based heterogeneous systems for dehydration is important for the industrial reaction of fructose conversion to HMF [19]. Janiak *et al.* adopted MIL-101Cr (MIL-SO<sub>3</sub>H) as the heterogeneous catalyst and achieved a 29% conversion of glucose to HMF in a THF : H<sub>2</sub>O (39 : 1, v : v) mixture [39]. Recently, Du *et al.* reported a 99.9%



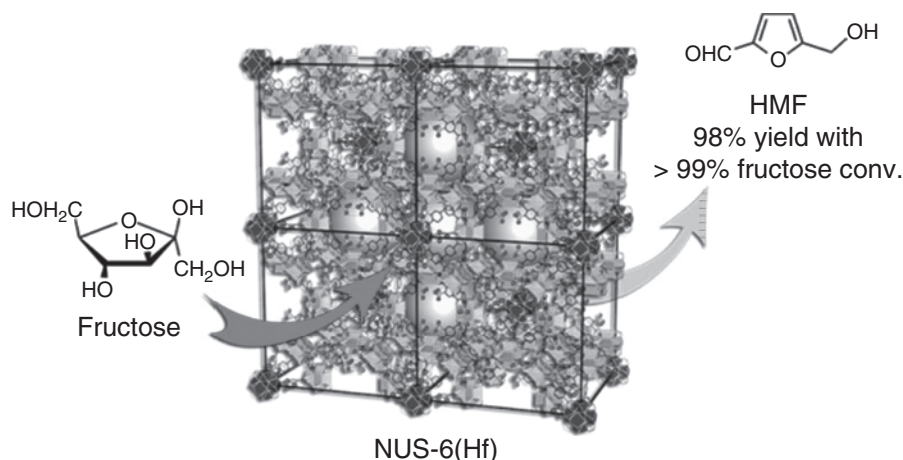
**Figure 1.3** Bifunctional catalyst MIL-101(Cr)-SO<sub>3</sub>H used for glucose conversion to HMF. Reproduced with permission from Ref. [38]. Copyright 2016, American Institute of Chemical Engineers. (See color plate section for the color representation of this figure.)

glucose conversion and an excellent HMF yield of 80.7% in water using a new bifunctional PCP(Cr)-SO<sub>3</sub>HCr(III) material [40]. These authors showed that the sulfonic acid group in the framework was the essential function center, and more Lewis acid sites resulted in a better catalyst activity.

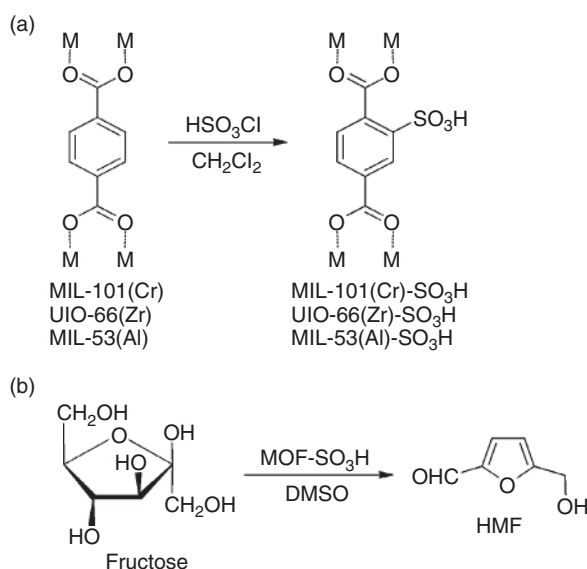
Despite the aforementioned nanoporous Cr-based MOF materials displaying promising applications in dehydration processes, the stringent synthetic conditions and toxic inorganic reagents of Cr MOFs greatly limit their real use. Recently, the research group of Zhao reported a modulated hydrothermal (MHT) approach that can be used to synthesize a series of highly stable Brønsted acidic NUS-6(Zr) and NUS-6(Hf) MOFs in a green and scalable way, although the linker 2-sulfotherephthalate was previously reported to make unstable UiO-type frameworks. The hafnium (Hf)-based material NUS-6(Hf) exhibited a superior performance for the dehydration of fructose to HMF (Figure 1.4) [41], outperforming all other presently known MOFs or heterogeneous catalysts with a yield of 98% under the same reaction conditions. Nevertheless, although such a high transformation yield can be achieved in organic dimethyl sulfoxide (DMSO), the attempts at dehydration with the same MOF material in aqueous media resulted in only negligible amounts of HMF (ca. 5%). Therefore, it is very valuable and significant to rationally design and develop stable Brønsted acidic MOF materials for high-performance dehydrations to prepare HMF in green aqueous media, even though this is an enormous challenge.

### 1.2.1.2 Postsynthetic Modification

In addition to direct synthesis using building linkers to modify MOF materials *in situ*, the PSM route is becoming an important technique to introduce various functions inside the MOFs for diverse applications, such as heterogeneous catalysis and gas storage and separation [20]. Therefore, PSM provides another means of introducing Brønsted acid groups to MOF backbones for the dehydration of biomasses to HMF. The presence of organic scaffolds in MOFs allows for a convenient employment of a variety of organic transformations. Furthermore, the acid strength on the surface can be precisely controlled



**Figure 1.4** NUS-6(Hf) used as a heterogeneous catalyst for fructose conversion to HMF. Reproduced by permission of Ref. [41]. Copyright 2012 American Chemical Society. (See color plate section for the color representation of this figure.)



**Figure 1.5** Synthetic routes to MOF-SO<sub>3</sub>H and the conversion of fructose into HMF.

by the PSM through varying the grafting rate of the reaction. As shown in Figure 1.5, Chen *et al.* reported the synthesis of a family of MOF frameworks functionalized with the -SO<sub>3</sub>H group through the PSM of the organic linkers, using chlorosulfonic acid [42]. The resultant framework MIL-101(Cr) [MIL-101(Cr)-SO<sub>3</sub>H] exhibited a full fructose conversion with a HMF yield of 90% in DMSO. The -SO<sub>3</sub>H groups was found to have a significant effect on fructose-to-HMF transformation [42]. Both the conversions of fructose

and selectivities towards HMF were increased with the sulfonic acid-site density of the MOF material. Kinetics studies further suggested that the dehydration of fructose to HMF using MIL-101(Cr)-SO<sub>3</sub>H followed pseudo-first-order kinetics with an activation energy of 55 kJ mol<sup>-1</sup>.

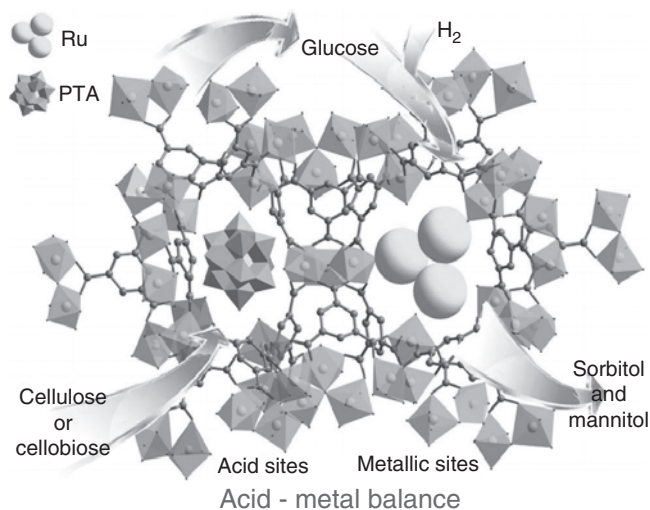
### 1.2.1.3 Pore Microenvironment Modification

Pore microenvironment engineering inside MOF frameworks via either the physical impregnation of acidic compounds or *in-situ* polymerization, allows for the hybrid material to obtain promising catalytic activities towards the formation of HMF. MOF materials featuring large porosities not only give rise to easy access of voluminous reactant molecules diffusing into the pores, but also provide an appropriate channel for the product molecules to move out, and thereby improve the catalytic performance. Li and coworkers first introduced this concept to construct MOF materials for the dehydration of carbohydrates to HMF by introducing phosphotungstic acid, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PTA), to the network of MIL-101 [43]. PTA and other transition metal-substituted polyoxometalates have been widely encapsulated into MIL-101 for other catalysis processes, such as the oxidation of alkanes and alkenes and esterification of n-butanol with acetic acid in the liquid phase. Using ionic liquids as reaction media, PTA(3.0)/MIL-101 showed the best catalytic performance in fructose dehydration with a HMF yield of 79% [43]. The immobilization of PTA significantly changed the pore environment, which promoted the initiation of the proton-catalyzed dehydration. The exchange of protons between the PTA and the organic cations of the ionic liquid led to the presence of partial protons in the ionic liquid medium [43].

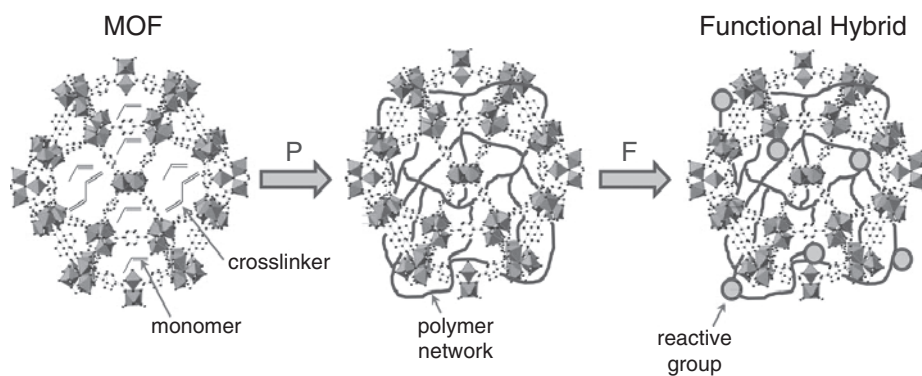
Inspired by this innovative finding, Chen *et al.* further reported the synthesis of PTA/MOF hybrid ruthenium catalysts, Ru-PTA/MIL-100(Cr), to selectively convert cellulose and cellobiose into sorbitol under aqueous hydrogenation conditions (Figure 1.6) [44]. It was shown that a 63.2% yield in hexitols, with a selectivity for sorbitol of 57.9% at complete conversion of cellulose, and 97.1% yield in hexitols with a selectivity for sorbitol of 95.1% at complete conversion of cellobiose, could be achieved with the creative use of a Ru-PTA/MIL-100(Cr) catalyst with loadings of 3.2 wt% for Ru and 16.7 wt% for PTA. This opened new avenues for the rational design of acid/metal bifunctional MOF catalysts for biomass conversion.

In addition to the physical incorporation of metals and the phosphotungstic acid, Hatton and coworkers described a straightforward strategy for the construction of novel hybrid materials consisting of MOFs and polymer networks [45]. The porous MIL-101(Cr) framework was impregnated with organic monomers (maleimide) and crosslinkers for an *in-situ* free-radical (co)polymerization (P), and thereby the functionalization (F) of the pore environment with poly(N-bromomaleimide) (Figure 1.7). Although the porosity of the composite material was decreased because of the presence of polymers, the pore of the MOF material was still large enough to enable ready access of the reactants to the active sites inside the framework. As a result, the resultant MOF-brominated polymer hybrids exhibited potential applications for the industrially important reaction of fructose conversion to HMF, suggesting an innovative and effective method for controlling the pore environment for target applications and thus promoting the development of MOF materials for biomass conversion.





**Figure 1.6** Ru-PTA/MIL-100(Cr) used as a heterogeneous catalyst for biomass conversion. Reproduced with permission from Ref. [44]. Copyright 2013, Wiley.



**Figure 1.7** Scheme of fabrication of functional hybrids of MOFs and polymer networks. Reprinted with permission from Ref. [45]. Copyright 2014, American Chemical Society. (See color plate section for the color representation of this figure.)

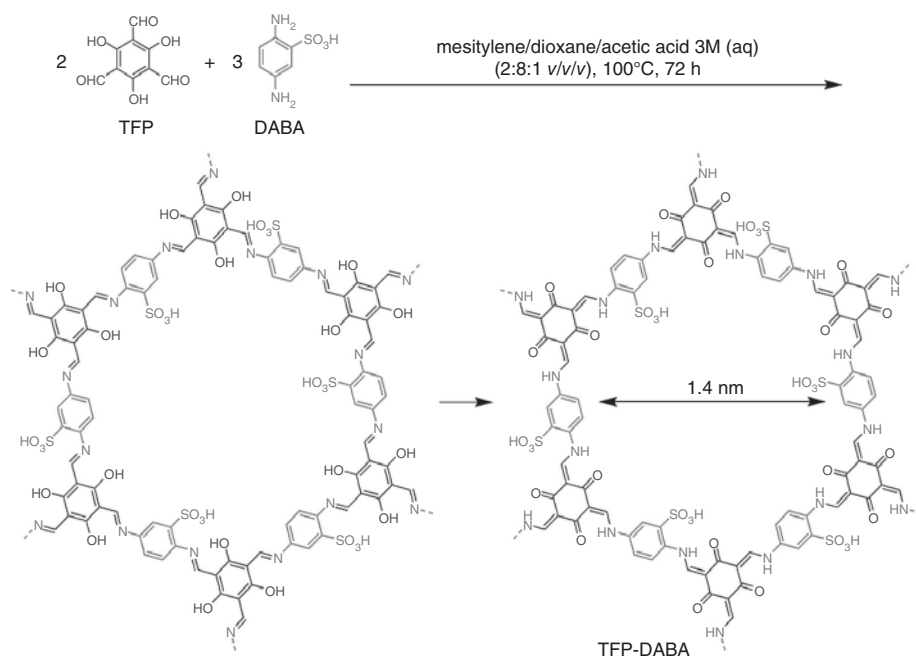
Even though MOF compounds show significant advantages for biomass conversions over other heterogeneous catalysts such as zeolites and metal oxides, only a handful of studies have been reported dealing with the conversion of biomass using MOF catalysts. Herbst and Janiak recently highlighted the promising potential in the field of MOF-catalyzed biomass conversion [21]. These authors discussed the synthetic conditions of MOF materials, mechanisms of biomass reactions, product yields, and the corresponding selectivity in detail. Meanwhile, in-depth reviews by Jiang and Yaghi which focused on Brønsted acidic MOFs were recently published [14,46]. Clearly, there exist great opportunities and potential to address investigations into MOF catalysis in the context of biomass-based fine

chemical production. Large porosity, strong acidity, and stability should be considered simultaneously when designing a novel MOF catalyst.

### 1.2.2 Covalent Organic Frameworks

Covalent organic frameworks (COFs) possess molecular ordering and inherent porosity in addition to robust stability under a wide range of conditions, and have recently been identified as versatile new platforms for a wide range of applications such as gas storage or heterogeneous catalysis. Their promising performance is due in part to the extent to which they can be rationally tuned during the preparation of their organic constituents, as comparatively gentle synthesis conditions are required for the final COF material [47–52]. Although the scope for structural diversity and high-yielding synthesis suggests potential advantages [53–61], few COFs have been investigated for biomass conversion [62].

Recently, Zhao and coworkers reported a de-novo synthesis of a sulfonated two-dimensional crystalline COF termed TFP-DABA from the Schiff base condensation reaction between 1,3,5-triformylphloroglucinol and 2,5-diaminobenzenesulfonic acid (Scheme 1.2) [63]. For the first time, remarkable fructose conversion yields (97% for HMF and 65% for 2,5-diformylfuran), good selectivity and recyclability were obtained using COF TFP-DABA as the heterogeneous catalyst. This innovative study paves a solid way towards the de-novo synthesis of novel catalytically active COFs and their applications in biobased chemical conversion.



**Scheme 1.2** Scheme of fabrication of COF-SO<sub>3</sub>H for the conversion of fructose into HMF.

### 1.3 Nanoporous Organic Sulfonated Resins

Nanoporous organic sulfonated resins, such as Amberlyst<sup>®</sup> and Nafion<sup>®</sup>, have attracted tremendous attention and show significant promise for the conversion of biomass because of their facile synthesis and high catalytic activities [16]. The intrinsic inherent porosity allows for an easy installation of the Brønsted sulfonated group ( $-\text{SO}_3\text{H}$ ) on the pore surface, thereby affording an enhanced interaction between the catalyst framework and the reactants. A high-performance transformation of sugars to HMF is therefore achieved.

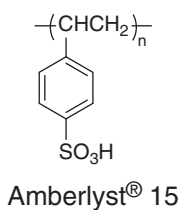
#### 1.3.1 Amberlyst Resins

A facile polymerization of styrene and further sulfonation results in the formation of one famous nanoporous resin catalyst, Amberlyst<sup>®</sup> 15 (Figure 1.8), that enables a wide variety of acid-catalyzed liquid-phase biomass conversions, for example the dehydration of fructose to HMF. Shimizu *et al.* reported a 100% yield of HMF in a water-separation reactor, using Amberlyst<sup>®</sup> 15 powder in a size of 0.15–0.053 mm [64]. The removal of adsorbed water by the small-sized resin particles resulted in an excellent yield, which was supported by the near-infrared spectroscopic characterization. It should be noted that the intrinsic nanoporous structure of Amberlyst<sup>®</sup> 15 features a relatively low stability that needs to be enhanced in future investigations.

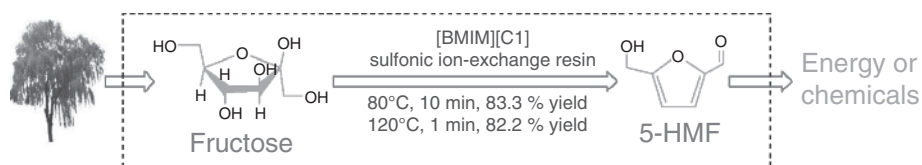
#### 1.3.2 Nafion Resins

Compared with Amberlyst<sup>®</sup> 15, Nafion<sup>®</sup> perfluorosulfonic acid resins show better stability in the nanoporous structure and bear strong acid strength that is comparable to that of pure sulfuric acid. However, unswollen Nafion<sup>®</sup> resin suffers from a serious drawback due to its very low surface area that may impede application in the conversion of sugars to HMF (Figure 1.9) [16]. Commercialized Nafion<sup>®</sup> NR50, with a pellet diameter of 0.6–1.5 mm, was used as a catalyst for the preparation of HMF from fructose, and a moderate HMF yield (45–68%) was obtained in the presence of ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) [65]. The ionic liquid and sulfonic ion-exchange resin could be recycled for seven successive trials.

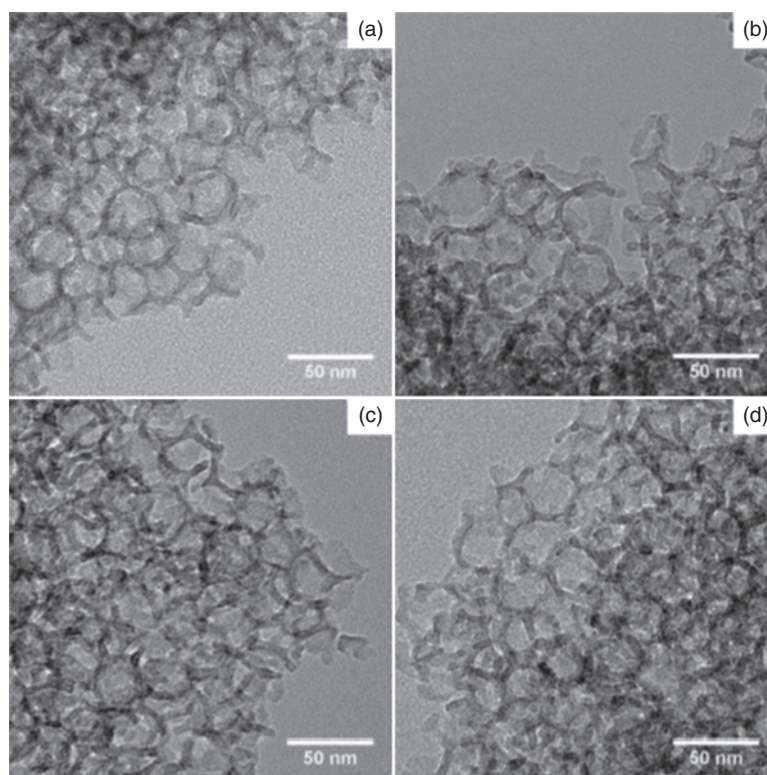
On account of these promising results and low surface areas of Nafion<sup>®</sup> resins, Shen and coworkers developed a novel Nafion<sup>®</sup>-modified mesocellular silica foam (MCF) hybrid material for the catalytic dehydration of D-fructose to HMF [66]. By using a physical



**Figure 1.8** Chemical structure of Amberlyst<sup>®</sup> 15.



**Figure 1.9** Nafion® NR50 used for the conversion of fructose into HMF.



**Figure 1.10** Transmission electron microscopy (TEM) images of (a) MCF, (b) Nafion®(15)/MCF, (c) Nafion®(30)/MCF, and (d) Nafion®(45)/MCF.

impregnation approach, the Nafion® resin was highly dispersed in the ultra-large pores of the MCFs (Figure 1.10), affording a high conversion performance with an 89.3% HMF yield and 95.0% selectivity in DMSO. It was shown that the Nafion®(15)/MCF catalyst could be easily regenerated through an ion-exchange method, and a high yield was retained after five cycles.

As discussed above, the sulfonated resins clearly hold promise as heterogeneous acidic catalysts for biomass conversion, where the nanoporous structure plays crucial roles in the acid concentration and/or strength of the resins. However, the fact must be noted that the sulfonated resin catalysts still have a relatively low thermal stability due to collapse

of the porous architectures, which greatly hinders their wide application in biomass conversion.

## 1.4 Conclusions and Perspective

This chapter has provided a brief overview of recent studies which have centered on the rational design, synthesis, and catalytic applications of nanoporous organic frameworks as acidic heterogeneous catalysts for the conversion of raw biomass materials to the renewable platform chemical HMF. Crystalline frameworks including MOFs and COFs and amorphous sulfonated resin-based networks were discussed in detail. Clearly, these novel catalysts display competitive activity towards the acid-catalyzed synthesis of HMF. The intrinsic nanoporous properties play a crucial role in the generation and dispersion of the acidic active sites, access of reactants, mass transfer, and control of product selectivity. Although in recent times extensive fundamental research and experiments have been carried out to optimize the conversion of biomass to HMF with the innovative use of these novel nanoporous organic frameworks, their commercial application for the production of HMF remains a challenge from an economic point of view. The following aspects should be considered simultaneously when designing new organic frameworks such as MOFs to improve the catalysis performance in the future: (i) better porosities consisting of hierarchical meso/macropores for faster mass transport of reactants and runoff of the products; (ii) better thermal and chemical stabilities that enable an efficient dehydration; and (iii) modulation of the degree of acidity and hydrophobicity on the surface via pore wall engineering, thereby providing a means for the controlled adsorption of substrates/intermediates. To summarize, the innovative utilization of novel nanoporous organic frameworks for the conversion of biomass to HMF as a bio-renewable energy source will lead to a sustainable and bright future.

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