

Review Article

Functionalized Metal-Organic Framework Catalysts for Sustainable Biomass Valorization

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Currently, pristine and functionalized metal-organic frameworks (MOFs) are introduced in heterogeneous catalysis for biomass upgrading owing to the specific texture properties including regular higher-order structure, high specific surface area, and the precisely tailored diversity. The purpose of this review is to afford a comprehensive discussion of the most applications in biomass refinery. We highlight recently developed four types of MOFs like pristine MOFs and their composites, MOF-supported metal NPs, acid-functionalized MOFs, and biofunctionalized MOFs for production of green, sustainable, and industrially acceptable biomass-derived platform molecules: (1) upgrading of saccharides, (2) upgrading of furan derivatives, and (3) upgrading of other biobased compounds.

1. Introduction

Rapid population growth and enhanced living quality requirements led to an improvement in energy demand and fossil feedstocks containing coal, petroleum, and natural gas. Another mainstream of the current generation is the increasing motivation to protect the environment from greenhouse gas emissions aroused by the tremendous consumption of fossil fuels [1, 2]. This concern is an irritation for the researchers for renewable and replaces sustainable resources instead of non-renewable fossil-based fuels. Because biomass is a green, highly abundant, and carbon-natural process available, it is served as a promising and replacing one to be transformed through bio-refinery and catalytic valorization into an extensive series of value-added chemicals, which has a relatively low impact on the environment [3–11].

Various technologies including biological, thermal, and chemical procedures have been explored for biomass upgrading. Among those, chemical processes (e. g., dehydration, hydrolysis, esterification, alcoholysis, isomerization, and etherification) of biomass conversion have drawn

increasing researchers' attention, which resulting in petro-based products. While reaction rates, high yields of target molecules depend on catalysts.

Numerous heterogeneous catalysts for the efficient conversion of biomass feedstocks into platform molecules and high-energy fuels have been explored [12, 13]. Solid catalysts developed for biomass upgrading are commonly divided into four categories: (a) porous materials [14], (b) metal oxides [15–17], (c) immobilized metal nanoparticles, and (d) sulfonated materials [18, 19]. Among them, high specific surface areas, tunable acidity, porous nanostructures, and bifunctionality such as Brønsted-Lewis acidic, acidic-basic, and metal nanoparticle-acidic or basic play a pivotal role in efficient heterogeneous catalytic procedures. Generally, the biomass conversion processes are composed of a series of tandem reactions [20–24].

Metal-organic frameworks (MOFs), also identified as micro- and mesoporous coordination polymers (PCPs), are a class of crystalline porous materials produced by metal centers or metal-containing secondary building units (SBUs) and bi- or multimodal functional organic linkers [25, 26]. MOFs are of particular research topics for biomass valorization owing to the

proverbial texture properties such as changeable pore/cage size, high surface area, large cavity diameter and volume, the tunable diversity, and high hydrothermal stability [27]. In addition, the MOFs afford to functionalized anxious acid-base groups ($-\text{SO}_3\text{H}$, $-\text{NH}_2$, etc.), excellent support of active metal nanoparticles (Ru, Pt, Cu, etc.) on particular sites, and immobilization of high-efficient homogeneous catalyst (POMs, ILs, et al.). The obtained functionalized MOFs could be an arbitrary choice application in diverse catalytic strategies with the existence of synergistic active moieties (Figure 1).

Among more than 20,000 well-known MOFs, MIL (Material of Institut Lavoisier), consisting of rigid terephthalate organic linkers and trimeric octahedral metal-oxo clusters, possesses kinds of quasispherical mesoporous cages (20–35 Å), with 5–20 Å windows and large surface areas (2000–5900 m^2/g). UiO (UiO for University of Oslo), zirconium terephthalate, which has 3D microporous cubic pore system and relatively high stability ($\sim 500^\circ\text{C}$), is combined with large accessible pore volumes. ZIF (zeolitic imidazolate frameworks), having 3D structural feature with nanometre pore size and large Brunauer–Emmett–Teller (BET) surface area ($< 2000 \text{m}^2/\text{g}$), has been reported to act as a template/precursor to give porous carbon.

2. MOFs for Biomass Valorization

2.1. Pristine MOFs and Their Composites

2.1.1. Upgrading of Saccharides. Catalytic hydrolysis of carboxymethyl cellulose was investigated by MIL-53(Al) [28]. The HMF and total reducing sugar molar yielding high up to 40.3% and 54.2% were achieved with 200°C , 4 h, respectively. The aluminum-based MOF acted as a reuse catalyst for three cycles without obvious activity loss, and the HMF yield (40.3%) decreased to 38.4%, which was ascribed to MIL-53(Al) mass weightlessness in cleaning proceeds and plugging of active sites by unexpected byproducts.

The preparation of lactic acid and derivatives from carbohydrates are important processes in biomass valorization. Lactic acid is a worthy platform molecule for the development of degradable bioplastic manufacture and towards the preparation of multiple noticeable chemicals like acrylic acid, propylene glycol, 1,2-propanediol, poly(lactic acid) and linear esters (alkyl lactic acids). Two zeolitic imidazole frameworks (ZIFs) Zn-ZIF-8 and Co-ZIF-67 were synthesized and acted as a catalyst for the transformation of carbohydrates (sucrose, glucose, and fructose) to lactic acid derivatives for the first time [29]. The ZIFs processed by zeolite-type topology, 3D-porous rigid framework and high chemical and thermal stability are obtained facile, providing 42% methyl lactate using the prepared Zn-ZIF-8 for the ever-smaller crystal particles and higher content of Lewis acidic. Reusability studies indicated the reduction of methyl lactate yields from 34.8% to 27.2% after the fourth recycling catalyzed by ZIF-8, on account of active site absence and structural difference. Furthermore, the metal node effect of catalysts M-MOF-74 ($M = \text{Co}, \text{Ni}, \text{Mg}, \text{and Zn}$) on the performance of the transformation of carbohydrates to methyl lactate was studied [30]. Among these, it expressed

the optimal performance for 35% and 47% yields of the product based on glucose and sucrose under the optimal reaction conditions with 220°C and 6 h, respectively. Meanwhile, the Mg-MOF-74 catalyst exhibited excellent stability that could be reused three cycles without deactivation. Similarly, Huang et al. [31] revealed an efficient one-pot conversion of fructose to lactic acid via catalyst Fe-MOF. Lactic acid yielding high up to 32% was achieved with fructose as the substrate, benefitting from the particular porous feature of catalyst MIL-100(Fe), while relatively low yields of 18% and 20% lactic acid were found with other MOFs, such as Cu-BTC and MIL-100(Cr), respectively. Derived from hexose-based carbohydrates including glucose, sucrose, inulin, and cellobiose, moderate lactic acid yields were effectively converted over MIL-100(Fe). The existed pores or active sites blockage and the absence of partial active sites and the catalytic performance of MIL-100(Fe) evidently reduced after the fourth recycle. Modifying the regeneration method of catalyst MIL-100(Fe), lactic acid yield maintained 28% from fructose.

In another work, the possible mechanism accounting for the preparation of methyl lactate with glucose as the reactant was revealed. MIL-101(Cr) combined with activated fly ash complex was developed to be effectual for furfural synthesis over xylose dehydration [32]. Compared to the bare MOF, 71% and 80% high yield and selectivity of furfural were acquired at optimized reaction conditions; the excellent performance was retained after ten times continuous recycling. The synergistic action of Cr Lewis acidic and $-\text{OH}$ Brønsted acidic belonging to composite laid the foundations for application in other biomass valorization.

2.1.2. Upgrading of Furan Derivatives. The catalytic oxidation of HMF providing a series of great value platform molecule for chemical engineering industries includes 2,5-diformylfuran (DFF), 5-hydroxymethylfuran-2-carboxylic acid, 2,5-dimethyltetrahydrofuran, and 5-ethoxymethylfurfural. The conversion and selectivity of the aforementioned molecules can be adjusted by regulating catalyst active sites' constitutions and experiment conditions. Lucarelli et al. [33] verified the oxidation process of HMF-DFF over Ni-based MOFs including Ni(BDP), Ni(BPEB), and $\text{Ni}_3(\text{BTP})_2$, which were equipped with square planar and accessible metal centers. Among the base-free catalysts, $\text{Ni}_3(\text{BTP})_2$ exhibited the optimal catalytic activity, yielding 27% DFF under mild reaction conditions (120°C , 30 bar O_2 , in water). The satisfactory catalytic performance attributed to the accessibility of the metal centers, which depend on the crystal texture of the MOF. Following, an efficient MOF was applied in another conversion of one-pot two steps processes, which was investigated to prepare furilydenepropanenitrile derivatives, the key polymer basic entities [34]. The first oxidation procedure of HMF was explored by Fe-based MOFs (MIL-100(Fe), Cu-based MOF, Fe-HY zeolite, and Fe salts with 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) acting as cocatalyst, NaNO_2 serving as an additive, and O_2 as the terminal oxidant. Post-treated by NH_4F , MIL-100(Fe) explained the highest catalytic activity, giving a full yield of DFF converted from HMF, which ascribe to the

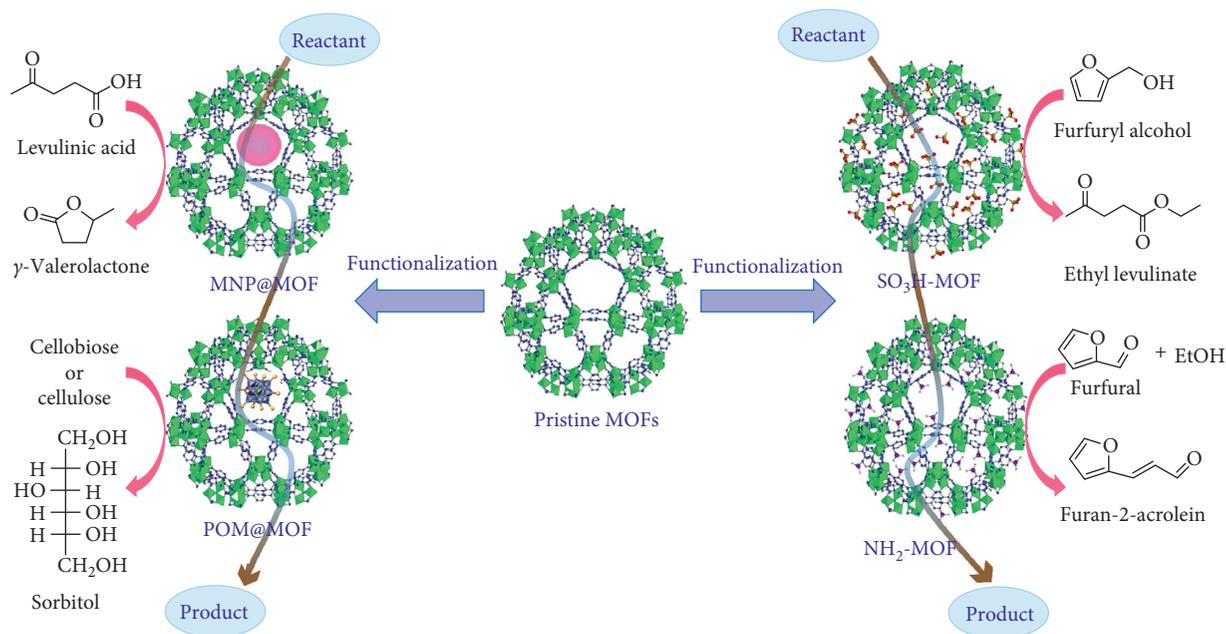


FIGURE 1: Application of MOFs for partial biomass upgrading.

existence of accessibility of Fe(III) active sites for reactants. The following Knoevenagel condensation step of DFF catalyzed by malononitrile or ethyl cyanoacetate was carried out under the basic medium.

Through aldol condensation, aldehydes and ketones react to provide high-value-added products from simple and inexpensive ones. On account of which, Kikhtyanin et al. [35] contrasted the catalytic effect of Lewis acidic MOFs (Cu-BTC, Fe-BTC) with zeolites including both Lewis acidity and Brønsted acidity to inquire the aldol condensation reaction of furfural with acetone. As demonstrated, acidic sites have the advantage to proceed aldol condensation rather than basic ones. It is worth noting that catalysts possessing weak Brønsted acidity, which are obtained by the mutual effect of Fe^{3+} with coordinated H_2O or the presence of structural defects, showed the best performance at 100°C .

The oxidative condensation reaction of furfural with alcohols- O_2 can promote double-carbon molecules to synthesize longer hydrocarbon chains acting as transport bio-fuels. In recent years, furfural reacting with alcohol to proceeding the aerobic oxidative condensation was explored by multiple Co-MOF catalysts [36]. Generally, two tactics were surveyed for the production of effective catalytic sites in MOFs: (1) removal of a coordinated small organic molecule or water molecules at 300°C , issuing in exposed and available metal active species; (2) thermolysis at 700°C , obtaining carbon-matrix nanometer and porous composites. Both types of Co-MOF exhibited satisfactory catalytic activity in the oxidative condensation with 84.9% and 99% furfural conversion and selectivity under optimal reaction conditions.

Except that, Zr-based MOFs (UiO-66 or UiO-66- NH_2), were further examined on the esterification reaction of levulinic acid with the amount of biomass-derived various alcohols [37]. The gained catalytic performances are

comparable to have published heterogeneous acidic catalysts' activities, and the data exhibit the excellent activity, thanks to the synthesis conditions, defect sites, and particle size in these MOFs.

2.1.3. Upgrading of Other Biobased Compounds. Because of the consumption of petrochemical energy, the development of transformation of biomass to biodiesel over esterification and transesterification reaction become an attractive topic. Larasati et al. [38] examined the catalytic performance of the synthesized Zr^{4+} -BTC based MOF by the solvothermal and reflux method for the esterification of palmitic acid and ethanol. The solvothermal prepared MOF affords the maximum 69.2% palmitic acid conversion with 0.6% catalyst loading. In addition, Zr-MOFs, like UiO-66 and UiO-66- NH_2 , are also inquired as heterogeneous acids for fatty acids with short-chain alcohols to carry out the esterification reaction [39]. With the optimized reaction condition, excellent outputs of fatty acid alkyl esters (94–99%) were provided over the superior UiO-66- NH_2 , which was ascribed to cooperative acid-base catalytic properties. The investigation further proved that Zr-MOFs possess the potential to catalyze other biobased feedstock conversions.

2.2. MOF-Supported Metal NPs

2.2.1. Upgrading of Furan Derivatives. Implementing aerobic oxidative condensation with furfural combined alcohols acts as great important techniques for stabilizing furan derivatives and upgrading furan derivatives for desirable components for gasoline. Pt nanoparticles supported on MOFs like Pt@MOF-5, Pt@UiO-66, and Pt@UiO-66- NH_2 were prepared by the impregnation and gas-phase reduction process [40]. The catalytic performance was detected in the

oxidative process of furfural for furan-2-acrolein in the presence of O₂. Among which, material Pt@MOF-5 exhibited the optimal efficiency as furfural converted up to 84.1% and furan-2-acrolein yielded 75.7% under 150°C, 4 h. Under the optimized reaction condition, Pt@MOF-5 demonstrated significant stability and five times reusability without any loss in furan-2-acrolein yields. Uniform dispersion of Pt nanoparticles proved the synergetic effect with the MOF-5 channel for superior catalytic performance.

In addition, for furfuryl alcohol which can be hydrogenated to form tetrahydrofurfuryl alcohol and can further polymerize, selective hydrogenation of readily produced furfural has drawn increasing attention. Yuan et al. studied the hydrogenation procedure via Ru nanoparticles immobilized on a range of Zr-MOFs [41]. Among the evaluated catalysts, such as Ru/UiO-66, Ru/UiO-67, Ru/Zr₆-NDC, MIL-140A, MIL-140B, and MIL-140C, Ru/UiO-66 provided the maximum yield with 94.9% furfuryl alcohol, which can reuse five consecutive times without obvious activity loss. Similarly, Hester et al. [42] explored the PtNP@UiO-67 application in the hydrogenation and oxidation of HMF, which are thermally stable consisting of Pt nanoparticles embedded in the UiO-67 channel. The results implied that PtNP@UiO-67 catalyst was more efficient for the hydrogenation than the oxidation of HMF with the same conditions.

To reduce the dependence on petroleum resources, γ -valerolactone (GVL) as the sustainable production from renewable biomass was identified as significant target chemicals. 5 wt.% Ru/MIL-101(Cr) catalyst afforded above 99% GVL yield with 100% conversion of levulinic acid compared to a Ru/zeolite catalyst at mild reaction conditions (70°C, 5 h, 1.0 MPa H₂ pressure) [43]. The higher catalytic performance is due to the synergistic effect between the MIL-101(Cr) supporter and the well-dispersed Ru sites.

2.2.2. Upgrading of Other Biobased Compounds. The oxidation of glycerol provides sustainable routes for value-added chemicals, such as polyglycerol, glyoxylic acid, and glycerolaldehyde [44]. Li et al. [45] studied M-NPs/Fe-MIL-101 (M = Pd, Pd-Ce, Ce, and Au) for the production of dihydroxyacetone by adjusting the reaction time and metal types. Test results indicated that the longer reaction time better catalytic activity of the Pd-Ce NPs/Fe-MIL-101 for the glycerol oxidation to produce derivative dihydroxyacetone. Intriguingly, the modalism of Fe-MIL-101-NH₂ is slightly reliance on the preparation time, while the crystal structure maintained. With the MOF-supported metal-particles catalysts, bimetallic ones afforded higher yields of target compounds compared with the monometallic Pd-based MOF.

Furthermore, palladium nanocatalyst incorporated the hybrid support constituting the novel Pd/PRGO/Ce-MOF, among which the supports composed of Ce-MOF crystals and partially reduced graphene oxide (PRGO) nanosheets [46]. Results highlighted the developed 5 wt.% Pd/PRGO/Ce-MOF exhibited excellent catalytic performance for the transformation of vanillin to synthesize 2-methoxy-4-methylphenol by successive hydrogenation-deoxygenation

reactions. The desired performance is due to the reason of Pd nanoparticles' uniform dispersion on support and the existence of acidic active sites.

2.3. Acid-Functionalized MOFs

2.3.1. Upgrading of Saccharides. Utilization of renewable and abundant reserve resources like biomass caters to the development of sustainable production of chemicals. Biomass-derived saccharides (e.g., cellulose, sucrose, glucose, and fructose) can be catalyzed into bio-platform molecules, for instance, HMF was catalyzed and applied in medicine, fuel additives, and various fine chemicals which were applied to polymers and solvents [47, 48]. Generally, fructose bearing a five-membered ring can be easily transformed into HMF by dehydration reaction, while glucose with a more stable six-membered ring is the direct product of lignocellulosic biomass and is cost efficient; its conversion and application remain challenging. The transformation of glucose-HMF process carries out through two steps, I) the isomerization reaction of glucose over Lewis acid to fructose and II) the dehydration process for HMF catalyzed by Brønsted acid [49]. Considering the catalytic activity, the catalyst combined Brønsted and Lewis acidity would be superior over the separated ones.

In view of the situation, Oozeerally et al. [50] investigated the prominent stable and strong acidic UiO-66-MSBDC catalyst for the transformation of glucose-HMF, among which the catalyst was prepared via partially substituting the organic linker of UiO-66 by MSBDC. For the obtained catalyst constructed with Lewis (Zr⁴⁺) and Brønsted (-SO₃H) acidities, the synergistic effect of the catalyst guaranteed prominent catalytic performance for the production of HMF in aqueous solution under optimized reaction condition.

Considering a more stable pyranose form of glucose reduces the efficiency of HMF yield; Oozeerally et al. [49] and Yabushita et al. [50] demonstrated PO₄/NU as an efficient catalyst for the production of HMF derived from glucose, which is synthesized by partial phosphate modification of Zr-MOF NU-1000 to provide strong acidic sites to accomplish the glucose-to-HMF conversion. Results verified the maximum yield of 64% HMF with 1 mM glucose concentration in water/2-propanol hybrid medium. The high yield and selectivity attributed to the reduced Lewis acidity combined Brønsted acidity, which are favorable for the glucose-fructose isomerization and the followed dehydration process.

Similarly, selective products of glucose catalyzed by nitro- or sulfo-modified functionalized MIL-101(Cr) catalysts and MOF derivatives were explored in depth [48]. Research has found that the MIL-101(Cr)-SO₃H catalyst afforded the highest yield (29%) of HMF derived from glucose with 24 h, which is the maximum value over MOF so far. The solvent effect was studied and it was revealed that the distribution of the products over MIL-SO₃H was different with sulfuric acid or Amberlyst-70 in pure THF or THF-H₂O. Furthermore, Su et al. developed a similar functionalized MOF, MIL-101(Cr)-SO₃H, possessing both

Lewis and Brønsted acidity, which was evaluated for glucose conversion to synthesize HMF with optimized reaction conditions and GVL-combined 10 wt.% water acted as the reaction medium [52]. The HMF yield reaching up to 45% with full conversion of glucose was achieved with Cr^{3+} centers as Lewis acid and $-\text{SO}_3\text{H}$ as the Brønsted one. The wonderful catalytic performance ascribed to the synergistic effect of Lewis and Brønsted acid and combined solvents, and the solvent effect was further proved by kinetic reactions, which revealed that the isomerization step obeyed second-order kinetics and GVL- H_2O decreased the E_a value from 114 to $100.9 \text{ KJ mol}^{-1}$.

With the same functionalized MOF- SO_3H , Chen et al. prepared various sulfonic acid-functionalized MOFs using the postsynthetic modification method of functionalized organic linkers by chlorosulfonic acid, realizing the fructose dehydration for HMF production (Figure 2). [53]. The grafting level of $-\text{SO}_3\text{H}$ groups affected the Brønsted acid density and the acidic strength of catalysts and further determined the output of the ultimate product HMF. The HMF yield reached up to 90% with the full conversion of fructose with the optimized MIL-101(Cr)- SO_3H (15.0%) catalyst, which is superior to the UiO-66 and MIL-53. About 55 KJ mol^{-1} activation energy was achieved through kinetic reaction, and at the same time, the fructose-HMF conversion process possibly followed the pseudo-first-order kinetics. Results showed that the product yields did not remain stable after five recycles, which indicated that the catalyst channel may accumulate oligomeric products derived from side reaction.

Followed, Hu et al. [54] directly synthesized the high stability and strong Brønsted acidity NUS-6, including two types of Zr and Hf clusters with modulated hydrothermal (MHT) approach. The novel catalysts NUS-6(Zr) and NUS-6(Hf) possessed high specific surface areas of 550 and $530 \text{ m}^2 \text{ g}^{-1}$, respectively, which increases the interaction sites between reactants and active acidic sites. As a consequence, the NUS-6(Hf) MOF exhibited the optimal HMF yield of 98% in the fructose dehydration process, which was also attributed to the strong Brønsted acidity and the appropriate pore size that suppressed secondary reactions.

Furthermore, the acidic adjustability played an increasing remarkable role in the catalytic conversion of biomass. A hybrid MOF-based solid acidic catalyst PVP-HNTs@UiO-66- $\text{SO}_3\text{H}-x$ prepared with polyvinylpyrrolidone-modified halloysite nanotubes incorporated in a $-\text{SO}_3\text{H}$ group-functionalized UiO-66(Zr) revealed good catalytic property for fructose dehydration reaction with high HMF yield (92.4%) [55]. The acidic site density in the PVP-HNTs@UiO-66- SO_3H can be tuned by altering the dosage of support and $-\text{SO}_3\text{H}$ groups. The catalyst can be facilely and effectively reused for successive five cycles without obvious loss in its activity and stability.

2.3.2. Upgrading of Furan Derivatives. Research has shown that γ -valerolactone (GVL) can act as a plasticizer, fuel additive for gasoline, aviation kerosene that can reduce the dependence on the petrochemical energy, and can be further

converted to liquid long-chain hydrocarbon fuels for diesel. Considering this situation, Kuwahara et al. [56] developed an SO_3H -functionalized Zr-MOF (UiO-66-Sx) for the production of GVL through converted hydrogenation from levulinic acid and its corresponding esters. Owing to the strong connection of Brønsted acidic $-\text{SO}_3\text{H}$ groups and Lewis-basic $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters existed in the UiO-66 framework, the highest yield of GVL reaches up to 85% at 140°C . Meanwhile, UiO-66- S_{60} containing 60 mol% fraction of $-\text{SO}_3\text{H}$ maintained relatively high BET surface area although functionalization leads to the reduction of crystallinity and BET surface area.

In addition, among the various studies on biomass valorization, the preparations of alkyl levulinates have attracted much attention in recent years. The transformation of furfuryl alcohol to ethyl levulinate was investigated with the SO_3H -functionalized Cr-MOF MIL-101(Cr)- SO_3H in ethanol (Figure 3). [57] The as-prepared catalyst materials possessed special textural properties including high BET surface area, porous mesopore size, high hydrothermal/chemical stability, and increased approachability of $-\text{SO}_3\text{H}$ Brønsted acidic sites. By the reason of the aforementioned satisfying characteristics, the catalyst MIL-101(Cr)- SO_3H afforded good catalytic performance with a yield of 79.2% ethyl levulinate and 100% furfuryl alcohol conversion. Re-usability experiments further proved the material stability with a slight loss of activity was showed.

2.3.3. Upgrading of Other Biobased Compounds. Esters, the products of esterification, are widely applied for fragrances, lubricants, plasticizers, drugs, pharmaceuticals, and solvents. At the same time, dehydration of alcohol is a significant reaction to industrial development. Based on these, novel acid-functionalized MOF attracted numerous interests for the application in various areas. Hasan et al. [58] published the esterification reaction of oleic acid with MeOH to produce biodiesel using porous and strong acidic MIL-101(Cr)- SO_3H in order to improve process efficiency and energy conservation. Remarkably, the maximum yield of methyl oleate up to 93% was gained within only 20 min by microwave heating, which was superior compared to the conventional heating with 10 h, resulting in similar product yield.

For the sake of modification of vegetable oils in a friendly and environmentally pattern, the high catalytic activity and excellent stability $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}@ \text{UiO-66}$ were synthesized by facile solvothermal approach, which method encapsulated the Keggin-type $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ heteropolyacid into microporous UiO-66 crystal with enhanced Lewis acidity [59]. Results demonstrated that functionalized MOF exhibited good catalytic activity for soybean oil proceeding the acidolysis reaction towards low-calorific lipids.

2.4. Bifunctionalized MOFs

2.4.1. Upgrading of Saccharides. For the purpose of understanding the effect between the acid and metal centers in the hydrothermal stable Ru-PTA/MIL-100(Cr) (PTA-phosphotungstic acid), Chen et al. [60] studied catalysts

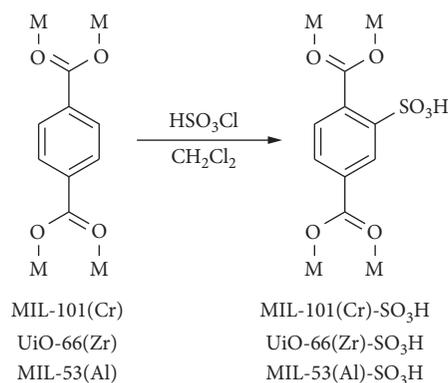


FIGURE 2: Preparation of MOF-SO₃H for the conversion of fructose into HMF.

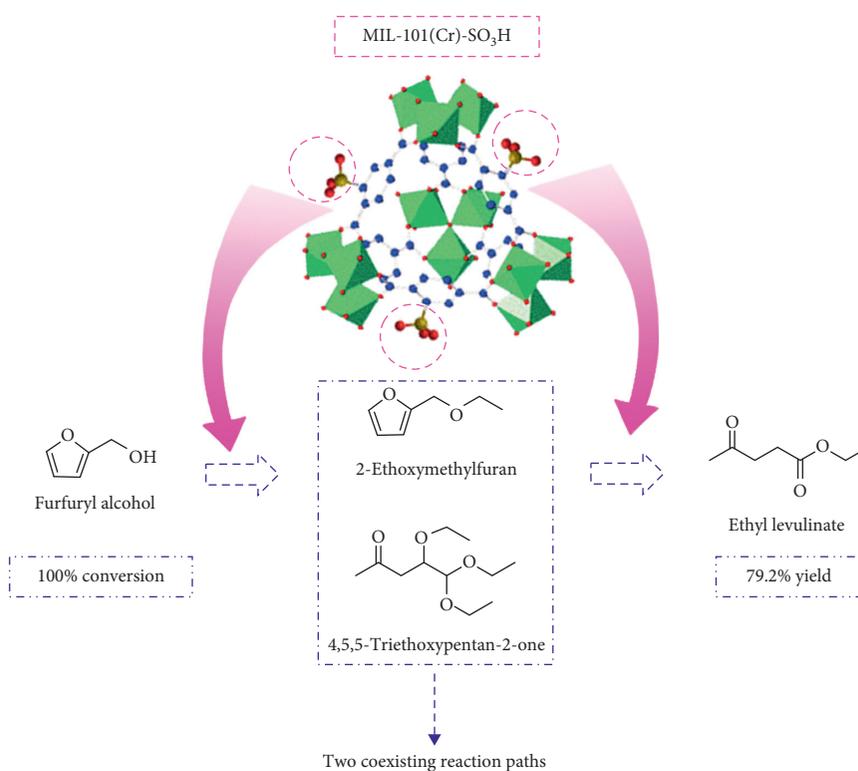


FIGURE 3: Possible mechanisms for the synthesis of ethyl levulinate from ethanolysis of furfuryl alcohol over MIL-101(Cr)-SO₃H.

during the conversion of cellulose and cellobiose for polyol preparation. Adjust the incorporated PTA dosage in MIL-100(Cr) to optimize the optimum amount of acidic sites (Figure 4). Under the optimal parameter, the Ru-PTA/MIL-100(Cr) catalyst supported 3.2 wt.% Ru and 16.7 wt.% PTA exhibited a high yield of 63.2% hexitols and 57.9% selectivity for sorbitol with 100% cellulose conversion. Meanwhile, yielding 97.1% hexitols combined 95.1% selectivity for sorbitol with full conversion of cellobiose. Uniform dispersion of metallic Ru NPs (<2 nm) played a pivotal part during the hydrogenation conversion, whereas acidic sites of PTA/MIL-100(Cr) are answerable for the hydrolysis course.

The efficient transformation of cellulose for the synthesis of polyols has attracted much attention owing to the polyols

acting as significant platform chemicals. With the similar catalysts, Wang et al. developed the metallic Ru nanoparticles embedded into NENU-3 (composing of PTA functionalized HKUST-1), applied in cellulose transformation to prepared ethylene glycol [61]. With the optimized parameters, 2.4 wt.% Ru and 34.8 wt.% PTA, the maximum ethylene glycol yield attained 50.2% under 4.0 MPa pressure and at 245°C for 4 h. The best catalytic activity attributed to the synergistic effect of acid sites and the well-dispersed Ru nanoparticles, which promoted hydrolysis and subsequent C-C bond fragmentation and hydrogenation reaction, respectively. Leaching of catalyst active species in the recycle reaction can be explained by partial decomposition of NENU-3, which further affects the decrease in product yields to a certain extent.

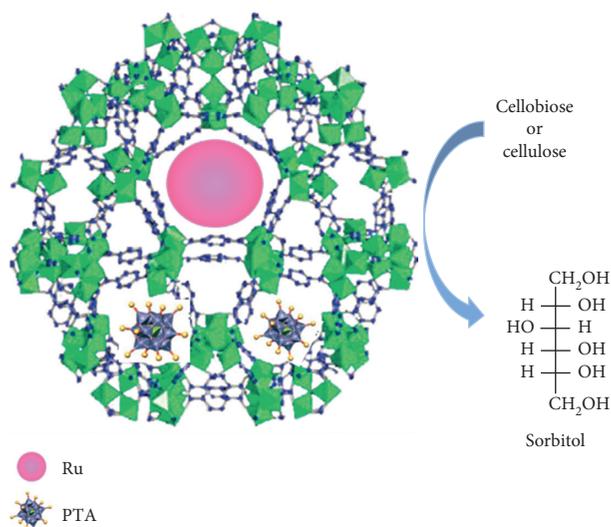


FIGURE 4: Metal-acid bifunctional catalyst Ru-PTA/MIL-100(Cr).

A one-pot hydrogenation conversion procedure of methyl levulinate into GVL was investigated with a bifunctional hybrid catalyst preparing by metallic Ru nanoparticles incorporated on functionalized UiO-66-SO₃H [62]. Under mild reaction conditions (0.5 MPa, 80°C, 4 h), 81% high yield of GVL was attained owing to the synergistic effect of Ru NPs and plenty of Brønsted acidic sites of catalysts that promoted the intermediates converted efficiently. Reusability experiments demonstrated the stability of the catalyst with five coherent times maintained no remarkable loss of activity, while the significantly decreased catalytic performance of two-stage processes further confirmed the indispensable role of -SO₃H groups.

A hybrid Pd/UiO-66@SGO (SGO-sulfonated graphene oxide) material was studied for the one-pot transformation of monosaccharides into 2,5-dimethylfuran [63], which was prepared by supporting the Pd nanoparticles on UiO-66@SGO. The abundant Brønsted acidity existing in UiO-66@SGO guaranteed the high yield of HMF, while the succeeding hydrogenation/hydrogenolysis for the product 2,5-dimethylfuran was catalyzed by uniform dispersed Pd nanoparticles. Direct conversion from fructose afforded the maximum 2,5-dimethylfuran yield of 70.5 mol% under the optimized reaction conditions, while surprisingly, glucose acted as the substrate provided 45.3% mol yield for 2,5-dimethylfuran.

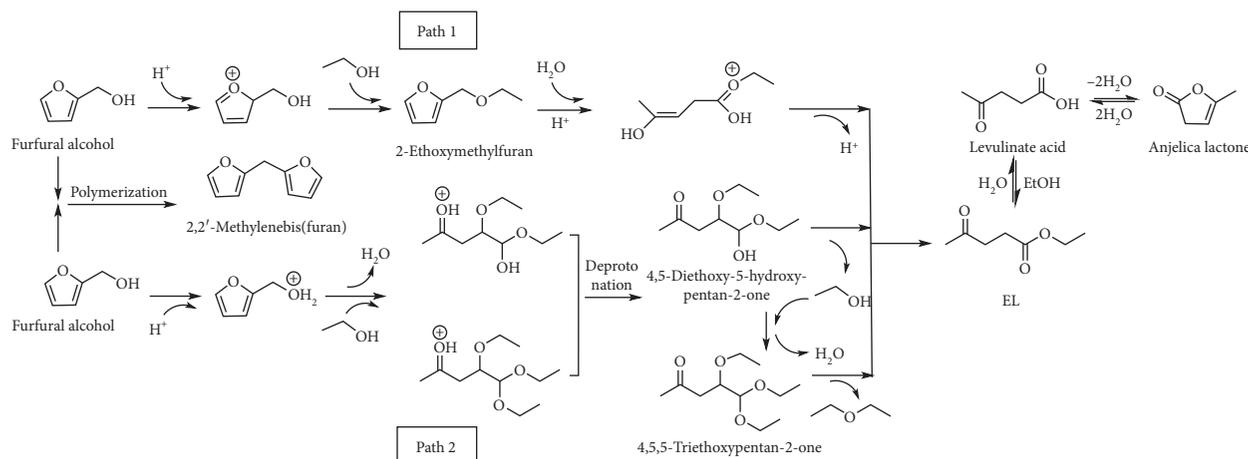
2.4.2. Upgrading of Furan Derivatives. Zhang et al. [64] introduced the ligand-based solid solution for MOF functionalization with the insertion of -SO₃H Brønsted acidic groups into the Cr-MOF and loading of Pd nanoparticles on MIL-101-SO₃H. The -SO₃H acidic density played a pivotal positive correlation role in the ring-open activity of γ -valerolactone and the succeeding hydrodeoxygenation to provided ethyl pentanoate, which was then catalyzed by the Pd NPs of bifunctional Pd/MIL-101-SO₃H to ethyl valerate (83% yield). Reusability experiments indicated a sudden reduction in target chemical yields from

83% to only 10% after the third recycle, owing to the aggregation of Pd NPs under enhanced reaction temperatures in acidic medium.

A bifunctional Pd/MIL-101(Al)-NH₂ was explored for the selective hydrogenation of HMF to produce 2,5-dihydroxymethyl-tetrahydrofuran (DHMTFH) [65]. The catalyst was prepared via direct anionic exchange procedure and then the reduction step was introduced for the Pd nanoparticles immobilized on MIL-101(Al)-NH₂. The existence of isolated amine groups of the catalyst guaranteed the constitution of well dispersion of Pd nanoparticles avoiding the aggregation of Pd NPs. With the explored catalyst, the conversion process HMF-DHMF (2,5-dihydroxymethyl-furan)-DHMTFH afforded a 96% high yield of DHMTFH and 100% conversion of HMF at only (30°C). The excellent catalytic activity partially ascribed to the hydrophilic nature of DHMF and the interaction of DHMF and MOF, which further promoted the transformation of DHMF to the target product. The investigation exploited the perspectives of functionalized Al-MOF-NH₂ for sustainable biomass valorization.

2.4.3. Upgrading of Other Biobased Compounds. As the ordinary component of lignin-derived bio-oil, vanillin was converted through hydrodeoxygenation reaction using bifunctional Pd/SO₃H-MIL-101(Cr), which was developed by immobilization of Pd nanoparticles on mesoporous functionalized Cr-MOF [66]. The existing Brønsted acidic groups -SO₃H of the MOF acted as the activator of the reactants guaranteeing the catalytic efficiency. Results showed that the 2 wt.% Pd/MIL-101(Cr)-SO₃H catalyst indicated excellent capability in the hydrodeoxygenation of vanillin for the product 2-methoxy-4-methylphenol. Meanwhile, the reusability of the catalyst proved the stability that can be continuously reused for no less than seven recycles without a decrease of catalytic effect. Comparable studies of the hydrodeoxygenation of vanillin were published with a similar catalyst Pd@NH₂-UiO-66, which was prepared by ultramicro Pd nanoparticles (1.5–2.5 nm) incorporated in a basic-functionalized MOF (NH₂-UiO-66) [67]. Until now, the maximum 100% yield of 2-methoxy-4-methylphenol was obtained higher than 2 wt.% Pd@NH₂-UiO-66 with mild reaction conditions as 0.5 MPa and 100°C for 60 min. The synergistic effect of uniform Pd sites and the NH₂-UiO-66 support played a critical role in the wonderful catalytic performance of Pd@NH₂-UiO-66.

The comparison study of Pd/UiO-66 and NH₂-functionalised Pd/UiO-66 catalysts was conducted for phenol hydrogenation to prepare cyclohexanol [68]. Interestingly, the introduction of NH₂ groups verified a destroyed crystalline structure in UiO-66, providing weak chemical interaction between Zr and Pd in prepared Pd-UiO-66-NH₂. Based on that, the Pd-UiO-66 catalyst exhibited preferable catalytic performances in phenol hydrogenation than Pd-UiO-66-NH₂ with complete conversion of phenol for only 2 h in 120°C. Chemical kinetic results exhibited that the activation energies with Pd-UiO-66 and Pd-UiO-66-NH₂ are 50.44 ± 3.20 and 43.11 ± 5.98 kJ/mol, respectively, which further proved the aforementioned conclusion.



SCHEME 1: Proposed mechanism for the transformation of furfuryl alcohol to ethyl levulinate in EtOH.

The presence of oxygen-containing C16-C18 fatty acids causes polymerization, weak oxidation stability, and low calorific value, even when cannot efficiently utilize the alga-derived bio-oil for transportation fuel. Considering this, Fang et al. [69] researched the facile conversion of palmitic acid to hexadecane catalyzed by the bifunctional PTA@PdCu@Fe^{III}-MOF-5, which was prepared by immobilizing phosphotungstic acid into the MOF structure. The explored catalyst demonstrates an enhanced acidity and efficiently facilitates palmitic acid for hexadecane with relatively high selectivity. The preferable catalytic activity was explained by its particular yolk-shell structural feature, increased acidity, and the superior supercritical fluid medium.

2.5. Determinant of MOF Catalytic Performance in Biomass Valorization. The multiplicity of metal centers and functional/nonfunctional organic ligands combined the chemical interactions grants MOFs to act as active catalysts, catalyst carriers, or catalyst precursors. Because of the stable SUB coordinated networks, MOFs possess adjustable pore size, high specific surface areas, and multiple topology structures compared to traditional heterogeneous solid catalysts.

Considering the conversion of biomass feedstocks which usually involves larger molecules, appropriate pore size, and morphologies which are needed to be serious-minded adjusted for the reactants, intermediates and productions efficiently diffuse towards catalytic active sites. For example, Li et al. [45] demonstrated that the morphology of Fe-MIL-101-NH₂ can be ameliorated by altering the preparation time, resulting in desired catalytic activities in glycerol oxidation.

The independent metal ions or clusters and functional/nonfunctional organic ligands can afford required acid-base properties. The unsaturated or defected metal centers in MOFs generally provide Lewis acidity. By the reason of Lewis acidic, MOFs can act as heterogeneous acid catalysts for glucose isomerization into fructose [50]. Owing to the necessity of Brønsted acid in various biomass-upgrading reactions, several feasible approaches have been explored to introduce Brønsted acidic functional sites onto specific sites of the MOFs [45, 70]. Up to now, the functionalization of MOFs

with Brønsted acid mainly including the post-synthetic modified method, [53] one-pot synthesis through organic ligands containing substituent groups [57] and active component supported on MOFs [60]. The functionalized MOFs integrate the superiorities of MOFs and encapsulated functional active sites facilitating cascade catalytic conversion for efficient biomass valorization (Scheme 1).

The rigid coordination textural properties of frameworks are fatal determinants used as catalyst supports to synthesize highly stable heterogeneous catalysts. The easily regulated porous textures of MOFs supply strategies for the incorporation of catalytic metal NPs, avoiding agglomeration and enhancing catalytic performance [40, 71].

Furthermore, MOFs have also been employed as matrixes for the production of carbon matrixes over pyrolysis procedure for supporting metal catalysts [72–75]. The obtained carbon templates can further work as a high S_{BET} and stability carrier, which bore the generated metal nanoparticles, forming novel and well-dispersed active site catalysts. Wang et al. [73], tailoring the MOF-templated strategy, published an efficient bimetallic CuCo/C catalyst for the furfural conversion with the maximum 96.4% yield of furfuryl alcohol.

3. Conclusions and Perspectives

Taking the global warming impact into consideration, the sustainable and renewable resources such as biomass have become the hot research topic in the 21st century. With appropriate approaches (biological, thermal, or chemical processes), biomass can be derived into various value-added chemicals and fuels.

Addressing challenges in MOF preparation and application include concerns of availability, cost, toxicity, safety, and environmental impact, which are critical to evaluate the introduction of MOF materials for biomass upgrading. The exploitation of multifunctional solid catalysts with an abundance of acidic, basic, or redox-active sites is significant for performing superior reaction efficiency, notably in tandem biomass procedures. Several promising approaches investigated for the fixation of acid-base and redox

functional groups on specific sites of the abovementioned materials were argued at great length. Eventually, the succeeding impacts of functionalization on one-pot tandem procedures and other procedures that generally generated in biorefineries were thoroughly argued. More interesting research endeavors are therefore needed to develop novel functionalized solid catalysts, with multiple active sites and particular morphologies.

Although enormous procedures have been accomplished upon the investigation of effective functionalized heterogeneous catalysts for biomass upgrading, further enhancements are still essential on account of continuable and renewable manufacturing. There are challenges needed to be faced towards MOF-based catalyst handy applied in biomass valorization. For instance, (i) the fertile preparation method for cost-efficient MOFs as one-pot synthesis precesses; (ii) more stable MOFs and active sites; and (iii) effective analysis of structure-function relationships. Hence, in the future investigation, we would focus on minimizing catalyst production costs, improving production yields and hydrothermal stability, tailoring the selectivity towards a target product, and enhancing efficient reusability.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

- [1] W. Schutyser, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G. T. Beckham, and B. F. Sels, "Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading," *Chemical Society Reviews*, vol. 47, no. 3, pp. 852–908, 2018.
- [2] B. Malleshham, P. Sudarsanam, G. Raju, and B. M. Reddy, "Design of highly efficient Mo and W-promoted SnO₂ solid acids for heterogeneous catalysis: acetalization of bio-glycerol," *Green Chemistry*, vol. 15, no. 2, pp. 478–489, 2013.
- [3] X. Zhang, L. Chen, Y. Li et al., "Palladium NPs supported on sulfonic acid functionalized metal-organic frameworks as catalysts for biomass cascade reactions," *Dalton Transactions*, vol. 48, no. 17, pp. 5515–5519, 2019.
- [4] T. Guo, M. Qiu, and X. Qi, "Selective conversion of biomass-derived levulinic acid to ethyl levulinate catalyzed by metal organic framework (MOF)-supported polyoxometalates," *Applied Catalysis A: General*, vol. 572, pp. 168–175, 2019.
- [5] S. Dostagir, M. Awasthi, A. Kumar et al., "Selective catalysis for room-temperature hydrogenation of biomass-derived compounds over supported NiPd catalysts in water," *ACS Sustainable Chemistry & Engineering*, vol. 7, no. 10, pp. 9352–9359, 2019.
- [6] L. T. Mika, E. Cséfalvay, and Á. Németh, "Catalytic conversion of carbohydrates to initial platform chemicals: chemistry and sustainability," *Chemical Reviews*, vol. 118, no. 2, pp. 505–613, 2018.
- [7] S. Van de Vyver, J. Geboers, P. A. Jacobs, and B. F. Sels, "Recent advances in the catalytic conversion of cellulose," *ChemCatChem*, vol. 3, no. 1, pp. 82–94, 2011.
- [8] J. A. Geboers, S. Van de Vyver, R. Ooms, B. Op De Beeck, P. A. Jacobs, and B. F. Sels, "Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls," *Catalysis Science & Technology*, vol. 1, no. 5, pp. 714–726, 2011.
- [9] D. M. Alonso, J. Q. Bond, and J. A. Dumesic, "Catalytic conversion of biomass to biofuels," *Green Chemistry*, vol. 12, no. 9, pp. 1493–1513, 2010.
- [10] P. S. Reddy, P. Sudarsanam, B. Malleshham, G. Raju, and B. M. Reddy, "Acetalisation of glycerol with acetone over zirconia and promoted zirconia catalysts under mild reaction conditions," *Journal of Industrial and Engineering Chemistry*, vol. 17, no. 3, pp. 377–381, 2011.
- [11] S. Santoro, F. Ferlin, L. Luciani, L. Ackermann, and L. Vaccaro, "Biomass-derived solvents as effective media for cross-coupling reactions and C-H functionalization processes," *Green Chemistry*, vol. 19, no. 7, pp. 1601–1612, 2017.
- [12] H. Zhang, H. Li, C. Xu, and S. Yang, "Heterogeneously Chemo/enzyme-functionalized porous polymeric catalysts of high-performance for efficient biodiesel production," *ACS Catalysis*, vol. 9, no. 12, pp. 10990–11029, 2019.
- [13] H. Zhang, H. Li, Y. Hu, K. T. Venkateswara Rao, C. Xu, and S. Yang, "Advances in production of bio-based ester fuels with heterogeneous bifunctional catalysts," *Renewable and Sustainable Energy Reviews*, vol. 114, p. 109296, 2019.
- [14] S. Zhang, J. Zhang, Y. Zhang, and Y. Deng, "Nanoconfined ionic liquids," *Chemical Reviews*, vol. 117, no. 10, pp. 6755–6833, 2017.
- [15] H. Li, Q. Zhang, X. Liu et al., "Immobilizing Cr³⁺ with SO₃H-functionalized solid polymeric ionic liquids as efficient and reusable catalysts for selective transformation of carbohydrates into 5-hydroxymethylfurfural," *Bioresource Technology*, vol. 144, pp. 21–27, 2013.
- [16] P. Sudarsanam, B. Hillary, M. H. Amin, S. B. A. Hamid, and S. K. Bhargava, "Structure-activity relationships of nanoscale MnO_x/CeO₂ heterostructured catalysts for selective oxidation of amines under eco-friendly conditions," *Applied Catalysis B: Environmental*, vol. 185, pp. 213–224, 2016.
- [17] B. Hillary, P. Sudarsanam, M. H. Amin, and S. K. Bhargava, "Nanoscale cobalt-manganese oxide catalyst supported on shape-controlled cerium oxide: effect of nanointerface configuration on structural, redox, and catalytic properties," *Langmuir*, vol. 33, no. 8, pp. 1743–1750, 2017.
- [18] M. Besson, P. Gallezot, and C. Pinel, "Conversion of biomass into chemicals over metal catalysts," *Chemical Reviews*, vol. 114, no. 3, pp. 1827–1870, 2014.
- [19] M. Hara, K. Nakajima, and K. Kamata, "Recent progress in the development of solid catalysts for biomass conversion into high value-added chemicals," *Science Technology Advanced Materials*, vol. 16, Article ID 034903, 2015.
- [20] I. Fechete, Y. Wang, and J. C. Védrine, "The past, present and future of heterogeneous catalysis," *Catalysis Today*, vol. 189, no. 1, pp. 2–27, 2012.
- [21] P. Ferrini and R. Rinaldi, "Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions," *Angewandte Chemie International Edition*, vol. 53, no. 33, pp. 8634–8639, 2014.
- [22] Y.-D. Chiang, S. Dutta, C.-T. Chen et al., "Functionalized Fe₃O₄@Silica core-shell nanoparticles as microalgae

- harvester and catalyst for biodiesel production,” *ChemSusChem*, vol. 8, no. 5, pp. 789–794, 2015.
- [23] H. Li, C. Wang, Y. Xu et al., “Heterogeneous (de)chlorination-enabled control of reactivity in liquid-phase synthesis of furanic biofuel from cellulosic feedstock,” *Green Chemistry*, vol. 22, pp. 637–645, 2020.
- [24] H. Li, H. Guo, Y. Su et al., “N-formyl-stabilizing quasi-catalytic species afford rapid and selective solvent-free amination of biomass-derived feedstocks,” *Nature Communications*, vol. 10, p. 699, 2019.
- [25] A. Herbst and C. Janiak, “MOF catalysts in biomass upgrading towards value-added fine chemicals,” *CrystEngComm*, vol. 19, no. 29, pp. 4092–4117, 2017.
- [26] O. Fleker, A. Borenstein, R. Lavi, L. Benisvy, S. Ruthstein, and D. Aurbach, “Preparation and properties of metal organic framework/activated carbon composite materials,” *Langmuir*, vol. 32, no. 19, pp. 4935–4944, 2016.
- [27] Y.-X. Zhou, Y.-Z. Chen, Y. Hu, G. Huang, S.-H. Yu, and H.-L. Jiang, “MIL-101-SO₃H: a highly efficient brønsted acid catalyst for heterogeneous alcoholysis of epoxides under ambient conditions,” *Chemistry—A European Journal*, vol. 20, no. 46, pp. 14976–14980, 2014.
- [28] G. Zi, Z. Yan, Y. Wang et al., “Catalytic hydrothermal conversion of carboxymethyl cellulose to value-added chemicals over metal-organic framework MIL-53(Al),” *Carbohydrate Polymers*, vol. 115, pp. 146–151, 2015.
- [29] B. Murillo, B. Zornoza, O. de la Iglesia, C. Téllez, and J. Coronas, “Chemocatalysis of sugars to produce lactic acid derivatives on zeolitic imidazolate frameworks,” *Journal of Catalysis*, vol. 334, pp. 60–67, 2016.
- [30] X. Lu, L. Wang, and X. Lu, “Catalytic conversion of sugars to methyl lactate over Mg-MOF-74 in near-critical methanol solutions,” *Catalysis Communications*, vol. 110, pp. 23–27, 2018.
- [31] S. Huang, K.-L. Yang, X.-F. Liu, H. Pan, H. Zhang, and S. Yang, “MIL-100(Fe)-catalyzed efficient conversion of hexoses to lactic acid,” *RSC Advances*, vol. 7, no. 10, pp. 5621–5627, 2017.
- [32] A. Chatterjee, X. Hu, and F. L.-Y. Lam, “Catalytic activity of an economically sustainable fly-ash-metal-organic-framework composite towards biomass valorization,” *Catalysis Today*, vol. 314, pp. 137–146, 2018.
- [33] C. Lucarelli, S. Galli, A. Maspero et al., “Adsorbent-adsorbate interactions in the oxidation of HMF catalyzed by Ni-based mofs: a drift and FT-IR insight,” *The Journal of Physical Chemistry C*, vol. 120, no. 28, pp. 15310–15321, 2016.
- [34] A. Rapeyko, K. S. Arias, M. J. Climent, A. Corma, and S. Iborra, “Polymers from biomass: one pot two-step synthesis of furilydenepropanenitrile derivatives with MIL-100(Fe) catalyst,” *Catalysis Science & Technology*, vol. 7, no. 14, pp. 3008–3016, 2017.
- [35] O. Kikhtyanin, D. Kubička, and J. Čejka, “Toward understanding of the role of Lewis acidity in aldol condensation of acetone and furfural using MOF and zeolite catalysts,” *Catalysis Today*, vol. 243, pp. 158–162, 2015.
- [36] L. Ning, S. Liao, X. Liu, L. Yu, X. Zhuang, and X. Tong, “Selective transformation of renewable furfural catalyzed by diverse active species derived from 2D co-based metal-organic frameworks,” *Journal of Catalysis*, vol. 352, pp. 480–490, 2017.
- [37] F. G. Cirujano, A. Corma, and F. X. Llabrés i Xamena, “Conversion of levulinic acid into chemicals: synthesis of biomass derived levulinate esters over Zr-containing MOFs,” *Chemical Engineering Science*, vol. 124, pp. 52–60, 2015.
- [38] I. Larasati, D. Winarni, F. R. Putri, Q. A. Hanif, and W. W. Lestari, “Synthesis of metal-organic frameworks based on Zr⁴⁺ and benzene 1,3,5-tricarboxylate linker as heterogeneous catalyst in the esterification reaction of palmitic acid,” *IOP Conference Series: Materials Science and Engineering*, vol. 214, Article ID 012006, 2017.
- [39] F. G. Cirujano, A. Corma, and F. X. Llabrés i Xamena, “Zirconium-containing metal organic frameworks as solid acid catalysts for the esterification of free fatty acids: synthesis of biodiesel and other compounds of interest,” *Catalysis Today*, vol. 257, pp. 213–220, 2015.
- [40] L. Ning, S. Liao, H. Cui, L. Yu, and X. Tong, “Selective conversion of renewable furfural with ethanol to produce furan-2-acrolein mediated by Pt@MOF-5,” *ACS Sustainable Chemistry & Engineering*, vol. 6, no. 1, pp. 135–142, 2018.
- [41] Q. Yuan, D. Zhang, L. V. Haandel et al., “Selective liquid phase hydrogenation of furfural to furfuryl alcohol by Ru/Zr-MOFs,” *Journal of Molecular Catalysis A: Chemical*, vol. 406, pp. 58–64, 2015.
- [42] P. Hester, S. Xu, W. Liang et al., “On thermal stability and catalytic reactivity of Zr-based metal-organic framework (UiO-67) encapsulated Pt catalysts,” *Journal of Catalysis*, vol. 340, pp. 85–94, 2016.
- [43] Y. Guo, Y. Li, J. Chen, and L. Chen, “Hydrogenation of levulinic acid into γ -valerolactone over ruthenium catalysts supported on metal-organic frameworks in aqueous medium,” *Catalysis Letters*, vol. 146, no. 10, pp. 2041–2052, 2016.
- [44] S. B. A. Hamid, N. Basiron, W. A. Yehye, P. Sudarsanam, and S. K. Bhargava, “Nanoscale Pd-based catalysts for selective oxidation of glycerol with molecular oxygen: structure-activity correlations,” *Polyhedron*, vol. 120, pp. 124–133, 2016.
- [45] X. Li, A. K. Tjiptoputro, J. Ding, J. M. Xue, and Y. Zhu, “Pd-Ce nanoparticles supported on functional Fe-MIL-101-NH 2: an efficient catalyst for selective glycerol oxidation,” *Catalysis Today*, vol. 279, pp. 77–83, 2017.
- [46] A. A. Ibrahim, A. Lin, F. Zhang, K. M. AbouZeid, and M. S. El-Shall, “Palladium nanoparticles supported on a metal-organic framework-partially reduced graphene oxide hybrid for the catalytic hydrodeoxygenation of vanillin as a model for biofuel upgrade reactions,” *ChemCatChem*, vol. 9, no. 3, pp. 469–480, 2017.
- [47] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, and J. G. de Vries, “Hydroxymethylfurfural, a versatile platform chemical made from renewable resources,” *Chemical Reviews*, vol. 113, no. 3, pp. 1499–1597, 2013.
- [48] Z. Xue, M.-G. Ma, Z. Li, and T. Mu, “Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts,” *RSC Advances*, vol. 6, no. 101, pp. 98874–98892, 2016.
- [49] R. Oozeerally, D. L. Burnett, T. W. Chamberlain, R. I. Walton, and V. Degirmenci, “Exceptionally efficient and recyclable heterogeneous metal-organic framework catalyst for glucose isomerization in water,” *ChemCatChem*, vol. 10, no. 4, pp. 706–709, 2018.
- [50] M. Yabushita, P. Li, T. Islamoglu et al., “Selective metal-organic framework catalysis of glucose to 5-hydroxymethylfurfural using phosphate-modified NU-1000,” *Industrial & Engineering Chemistry Research*, vol. 56, no. 25, pp. 7141–7148, 2017.
- [51] A. Herbst and C. Janiak, “Selective glucose conversion to 5-hydroxymethylfurfural (5-HMF) instead of levulinic acid with MIL-101Cr MOF-derivatives,” *New Journal of Chemistry*, vol. 40, no. 9, pp. 7958–7967, 2016.
- [52] Y. Su, G. Chang, Z. Zhang et al., “Catalytic dehydration of glucose to 5-hydroxymethylfurfural with a bifunctional metal-organic framework,” *AIChE Journal*, vol. 62, no. 12, pp. 4403–4417, 2016.

- [53] J. Chen, K. Li, L. Chen, R. Liu, X. Huang, and D. Ye, "Conversion of fructose into 5-hydroxymethylfurfural catalyzed by recyclable sulfonic acid-functionalized metal-organic frameworks," *Green Chemistry*, vol. 16, no. 5, pp. 2490–2499, 2014.
- [54] Z. Hu, Y. Peng, Y. Gao et al., "Direct synthesis of hierarchically porous metal-organic frameworks with high stability and strong brønsted acidity: the decisive role of hafnium in efficient and selective fructose dehydration," *Chemistry of Materials*, vol. 28, no. 8, pp. 2659–2667, 2016.
- [55] M. Liu, Y. Zhang, E. Zhu et al., "Facile synthesis of halloysite nanotubes-supported acidic metal-organic frameworks with tunable acidity for efficient fructose dehydration to 5-hydroxymethylfurfural," *Chemistryselect*, vol. 2, no. 32, pp. 10413–10419, 2017.
- [56] Y. Kuwahara, H. Kango, and H. Yamashita, "Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to γ -valerolactone over sulfonic acid-functionalized UiO-66," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 1, pp. 1141–1152, 2017.
- [57] X.-F. Liu, H. Li, H. Zhang et al., "Efficient conversion of furfuryl alcohol to ethyl levulinate with sulfonic acid-functionalized MIL-101(Cr)," *RSC Advances*, vol. 6, no. 93, pp. 90232–90238, 2016.
- [58] Z. Hasan, J. W. Jun, and S. H. Jhung, "Sulfonic acid-functionalized MIL-101(Cr): an efficient catalyst for esterification of oleic acid and vapor-phase dehydration of butanol," *Chemical Engineering Journal*, vol. 278, pp. 265–271, 2015.
- [59] W. Xie, X. Yang, and P. Hu, "Cs₂.5H_{0.5}PW₁₂O₄₀ encapsulated in metal-organic framework UiO-66 as heterogeneous catalysts for acidolysis of soybean oil," *Catalysis Letters*, vol. 147, no. 11, pp. 2772–2782, 2017.
- [60] J. Chen, S. Wang, J. Huang, L. Chen, L. Ma, and X. Huang, "Conversion of cellulose and cellobiose into sorbitol catalyzed by ruthenium supported on a polyoxometalate/metal-organic framework hybrid," *ChemSusChem*, vol. 6, no. 8, pp. 1545–1555, 2013.
- [61] S. Wang, J. Chen, and L. Chen, "Selective conversion of cellulose into ethylene glycol over metal-organic framework-derived multifunctional catalysts," *Catalysis Letters*, vol. 144, no. 10, pp. 1728–1734, 2014.
- [62] Z. Lin, X. Cai, Y. Fu, W. Zhu, and F. Zhang, "Cascade catalytic hydrogenation-cyclization of methyl levulinate to form γ -valerolactone over Ru nanoparticles supported on a sulfonic acid-functionalized UiO-66 catalyst," *RSC Advances*, vol. 7, no. 70, pp. 44082–44088, 2017.
- [63] R. Insyani, D. Verma, S. M. Kim, and J. Kim, "Direct one-pot conversion of monosaccharides into high-yield 2,5-dimethylfuran over a multifunctional Pd/Zr-based metal-organic framework@sulfonated graphene oxide catalyst," *Green Chemistry*, vol. 19, no. 11, pp. 2482–2490, 2017.
- [64] D. Zhang, F. Ye, Y. Guan, Y. Wang, and E. J. M. Hensen, "Hydrogenation of γ -valerolactone in ethanol over Pd nanoparticles supported on sulfonic acid functionalized MIL-101," *RSC Advances*, vol. 4, no. 74, pp. 39558–39564, 2014.
- [65] J. Chen, R. Liu, Y. Guo, L. Chen, and H. Gao, "Selective hydrogenation of biomass-based 5-hydroxymethylfurfural over catalyst of palladium immobilized on amine-functionalized metal-organic frameworks," *ACS Catalysis*, vol. 5, no. 2, pp. 722–733, 2015.
- [66] F. Zhang, Y. Jin, Y. Fu et al., "Palladium nanoparticles incorporated within sulfonic acid-functionalized MIL-101(Cr) for efficient catalytic conversion of vanillin," *Journal of Materials Chemistry A*, vol. 3, no. 33, pp. 17008–17015, 2015.
- [67] F. Zhang, S. Zheng, Q. Xiao et al., "Synergetic catalysis of palladium nanoparticles encaged within amine-functionalized UiO-66 in the hydrodeoxygenation of vanillin in water," *Green Chemistry*, vol. 18, no. 9, pp. 2900–2908, 2016.
- [68] Q. Guan, B. Wang, X. Chai, J. Liu, J. Gu, and P. Ning, "Comparison of Pd-UiO-66 and Pd-UiO-66-NH₂ catalysts performance for phenol hydrogenation in aqueous medium," *Fuel*, vol. 205, pp. 130–141, 2017.
- [69] X. Fang, Y. Shi, K. Wu, J. Liang, Y. Wu, and M. Yang, "Upgrading of palmitic acid over MOF catalysts in supercritical fluid of *n*-hexane," *RSC Advances*, vol. 7, no. 64, pp. 40581–40590, 2017.
- [70] J. Jiang and O. M. Yaghi, "Brønsted acidity in metal-organic frameworks," *Chemical Reviews*, vol. 115, no. 14, pp. 6966–6997, 2015.
- [71] V. Pascanu, A. Bermejo Gómez, C. Ayats et al., "Double-supported silica-metal-organic framework palladium nanocatalyst for the aerobic oxidation of alcohols under batch and continuous flow regimes," *ACS Catalysis*, vol. 5, no. 2, pp. 472–479, 2015.
- [72] T. B. Čelič, M. Grilc, B. Likozar, and N. N. Tušar, "In situ generation of Ni nanoparticles from metal-organic framework precursors and their use for biomass hydrodeoxygenation," *ChemSusChem*, vol. 8, pp. 1703–1710, 2015.
- [73] Y. Wang, Y. Miao, S. Li, L. Gao, and G. Xiao, "Metal-organic frameworks derived bimetallic Cu-Co catalyst for efficient and selective hydrogenation of biomass-derived furfural to furfuryl alcohol," *Molecular Catalysis*, vol. 436, pp. 128–137, 2017.
- [74] Y. Wang, S. Sang, W. Zhu, L. Gao, and G. Xiao, "CuNi@C catalysts with high activity derived from metal-organic frameworks precursor for conversion of furfural to cyclopentanone," *Chemical Engineering Journal*, vol. 299, pp. 104–111, 2016.
- [75] P. Sudarsanam, R. Zhong, S. Van den Bosch, S. M. Coman, V. I. Parvulescu, and B. F. Sels, "Functionalised heterogeneous catalysts for sustainable biomass valorisation," *Chemical Society Reviews*, vol. 47, no. 22, pp. 8349–8402, 2018.