Review

Advances in catalytic conversion of lignocellulose to chemicals and liquid fuels

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Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, CAS, China.

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A B S T R A C T

In response to the awareness of limited fossil resources and environmental concerns, catalytic conversion of renewable lignocellulose biomass to value-added chemicals and fuels is of great significance and attractive for sustainable chemistry. Division of Biomass Conversion and Bio-Energy attached to Dalian National Laboratory for Clean Energy has devoted themselves to valorization of lignocellulose biomass since launched in 2011. Our research interests focus on breeding of biomass resources (inulin and microalgae), exploration of catalytic and biological technologies, and production of energy chemicals and fuels. Although lignocellulose biomass is renewable and abundant, the way of utilization should be reasonable according to its structural characteristics in view of efficiency and economy. In this review, to celebrate the DICP’s 70th anniversary, we will highlight the major fundamental advances in DICP about the conversion of lignocellulose to value-added chemicals and liquid fuels. Particular attention will be paid to the transformation of cellulose and its derivatives to glycols, acids and nitrogen-containing chemicals, hemicellulose-derived platform molecule furfural to jet fuels and lignin to aromatics using catalytic technologies.

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1. Introduction

Fossil resources such as oil, coal and natural gas, contribute to the foundation of the modern society by providing energy and materials for our daily life. However, the fossil resources are non-renewable and their reserves are limited. With the increasing energy demand of human society and the decreasing of the fossil reserves, it is urgent to develop renewable resources for the sustainable development in the future. Biomass resources, which are originally formed via biological photosynthesis from readily available atmospheric carbon dioxide (CO₂), water and sunlight, can provide energy and carbon resource. Nature provides large amounts of biomass each year. Globally, 170 billion metric tons of biomass sources are produced [1]. Thus, biomass is a promising feedstock for production of chemicals and fuels in the future.

Lignocellulose is the most abundant biomass resource, which consists of 35%–50% of cellulose, 20%–35% of hemicellulose and 10%–25% of lignin [2]. Cellulose is an organic polymer consisting of D-glucose units connected with 1,4-glycosidic bond. Hemicellulose is a polysaccharide composed not only of glucose but also pentose (xylose, mannose, galactose, rhamnose and arabinose). The most abundant monomer present in hemicellulose is xylose. Unlike the cellulose and hemicellulose, lignin is an aromatic polymer and lacks a defined primary structure. Generally, lignin is formed via p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

The catalytic conversion of lignocellulose and its derivatives to various value-added chemicals has aroused a great attention [3–9]. In order for most effective utilization of the lignocellulose resources, the product should be rationally designed based on its native structure [10,11]. Considering there are plentiful oxygen atoms in the structure of lignocellulose, it is desirable to convert lignocellulose to oxygen-containing compounds, which are usually obtained from oxygen-deficient fossil resources via the insertion of oxygen to the inert C–H or C–C bond under the harsh reaction conditions. For example, ethylene glycol (EG) is an important monomer for synthesis of polyester resins of poly(ethylene terephthalate). The selective cleavage of the C–C bond in each D-glucose unit of cellulose can produce three ethylene glycols. It is an economical and renewable way to produce EG from cellulose [12]. Cellulose derived product 5-hydroxymethylfurfural (HMF) is one of the top platform chemicals from biomass [13], which can be further converted to polymer monomers such as diols [14–16], diadile [17–20], diacid or diester [21–26], and anhydride [27]. Considering lignin is an aromatic polymer, the production of phenols is a high value way of lignin utilization [28].

Another option is to convert lignocellulose to liquid fuels via removing excess oxygen atoms to increase their energy density [29–31]. Although the conversion of lignocellulose to fuels is in debate from the viewpoint of energy, in some cases, the conversion of biomass to high energy density fuels, such as jet fuels, is significant. At present, there is no other alternative energy for the airplanes. Moreover, compared to the fuels for the cars, the jet fuels have the characteristics of higher value and lower consumption. Thus, it may be economically competitive with the fossil route.

Division of Biomass Conversion and Bio-Energy is attached to Dalian National Laboratory for Clean Energy, which was launched in 2011. The mission of our division is to convert lignocellulose biomass to value-added chemicals and fuels. Research interests include breeding of biomass resources (inulin and microalgae), exploration of catalytic and biological technologies, and production of energy chemicals and fuels. In this review, it is to demonstrate our concerned fundamental advances in DICP about the synthesis of liquid fuels and value-added chemicals from lignocellulose and lignocellulose-derived platform chemicals using catalytic technologies but not biological technologies. More specifically, we will highlight the major advances in the catalytic conversion of lignocellulose to chemicals and liquid fuels, including cellulose and its derivatives to glycols, acids and nitrogen-containing chemicals, hemicellulose-derived platform molecule furfural to jet fuels and lignin to aromatics. What needs illustration is that the advances reviewed previously will not be emphasized in this manuscript to avoid rehashing [5,10,32,33].

2. Cellulose and its derivatives to glycols, acids and nitrogen-containing chemicals

Cellulose is homopolysaccharide of β-1,4-glycosidic bonds linked D-glucose units. Depolymerization processing is always the prerequisite for biomass-based chemicals or fuels production, and cellulose is no exception. Due to the presence of plentiful intra- and inter-molecular hydrogen bonds, cellulose is insoluble in most solvents which challenges the catalytic transformation process. Zhao and co-workers have been focusing on the acid catalyzed cel- lulose hydrolysis in the ionic liquid over the last decade [34,35]. The combination of HCl with 1-butyl-3-methylimidazolium chloride ([C₄mim][Cl] IL) was found to be an efficient system for the selective hydrolysis of lignocellulose toward total reducing sugars
(TRS) [35]. Later, to circumvent the difficulty in recovering mineral acids, zeolites with Brønsted acid sites were used, and demonstrated as efficient systems for hydrolysis of cellulose in ionic liquid [36]. Zhang and co-workers found that carbon sulfonated at proper temperature has a high acid density and a reasonably large surface area, which selectively catalyzed the hydrolysis of cellulose into glucose with 75% yield [37]. Recently, an oxidation-hydrolysis strategy was developed by Yang and co-workers for depolymerization of cellulose. Part of the hydroxymethyl groups on glucose units were oxidized to carboxyl groups which acted as the catalytic active sites for the following depolymerization of cellulose. After pretreating α-cellulose in air at 210 °C for 48 h, 23% yield of glucose was produced upon hydrolysis in water at 150 °C for 8 h in the absence of additional catalyst [38].

2.1. Glycols

Glycols, a class of alcohols having two hydroxyl groups, play an important role in sustaining the fields like chemicals, automobiles, textiles, transportation, and manufacturing [39–42]. Considering the challenge of limited fossil resources and increasing greenhouse gas emission, catalytic transformation of cellulose and its derivatives to glycols represents a particularly attractive process for biomass valorization. EG, 1,2-propylene glycol (1,2-PG) and isosorbide are value-added products with large market demand. In addition, the furan-based diols of 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyltetrahydrofuran (DHMTF) produced by dehydration-hydrogenation process of C6 carbohydrates, can be used as monomers for specialty polymer materials and intermediates for biofuels [43–45].

2.1.1. Ethylene glycol and 1,2-propanediol glycol

Sugar alcohols, which can be produced via hydrogenation of glucose, are important sources for producing biomass-based EG and 1,2-PG (Fig. 1). In 2006, the hydrogenolysis technique developed by Xu’s group was applied to a 5000 t/y scale production of EG and 1,2-PG from glucose-derived sorbitol. Two years later, a 200 kt/y scale sorbitol to EG and 1,2-PG production line went to operation. At the same year, the industry application test has been finished and examined. Based on the industrial experience, Xu and coworkers further developed Ni-Re/C catalyst for the selective hydrogenolysis of C–C bonds in sorbitol under nitrogen atmosphere to produce EG and 1,2-PG [46]. Lately, it was found that the addition of La(OH)₃ resulted in an increased selectivity for the C2 and C4 products in the hydrogenolysis reaction of sorbitol over Ni/C catalyst [47]. Eterification of EG with methanol produces dimethoxyethane, which can be used as green solvent or potential diesel fuel additive. Via a continuous flow experiment, up to a 79% selectivity for dimethoxyethane at 97% conversion of EG was archived over SAPO-34 catalyst [48].

In 2008, Zhang and co-workers reported a catalyst system of nickel-tungsten carbide for the direct conversion of cellulose to EG and 1,2-PG (Fig. 2) [12]. Via a balanced cascade reactions of hydrolysis, isomerization, retro-aldol condensation and hydrogenation, EG can be obtained from cellulose in 61% yield over a Ni-W₃C/AC catalyst. Afterwards, a series of tungsten-containing catalysts were developed, which further resulted in an improved EG yields at around 75% [49–51]. In addition, significant progress has been made in the nickel catalyst. Zhang’s group developed a binary nickel–lanthanum(III) catalyst for the conversion of cellulose to EG and 1,2-PG in an overall yield of 64% [52]. For these catalyst systems, the tungsten or other metal additives created acidic or basic hydrothermal environment is/are critical for the cellulose hydrolysis and further cleavage reaction of in situ formed carbohydrates. Thus, the durability of nickel in the harsh hydrothermal reaction environment is a great concern [53]. In their further research, Zhang’s group combined nickel and metallic tin powders to in situ form NiSn alloy during the conversion of cellulose, and this catalyst system acted as stable heterogeneous catalyst with rather low amount of leaching [54]. Very recently, they proposed a high-loading Ni–N–C single atom catalyst (Ni content 7.5 wt%) for the conversion of cellulose [55]. This catalyst exhibited remarkable durability under the typical reaction conditions (245 °C, 60 bar H₂ in the presence of tungstic acid) and can be reused for at least 7 times without deactivation.

In nature, cellulose coexists with hemicellulose and lignin as rigid structure in raw lignocellulosic biomass, which is protected from degradation in many cases. Zhang’s group proposed a variety of strategies to unlock the (hemi)cellulose from biomass for EG production [56–58]. By pretreating with base solvents, micaschust was effectively converted to EG in 39% yield even under 10% concentration of feedstock [57]. Very recently, they found ball milling pretreatment as an efficient method to promote the catalytic conversion of lignocellulosic biomass to ethylene glycol (EG) [58].

2.1.2. Isosorbide

Apart from hydrogenation processing, dehydration is another strategy to obtain glycols from sorbitol. Isosorbide, recognized as an alternative to bisphenol A, can be synthesized via double dehydration of sorbitol [59]. However, selectivity control over the intramolecular etherification of sorbitol remains a challenge. Very recently, Xu’s group proposed a strategy of ketalization for the catalytic selective dehydration of sorbitol to afford isosorbide over H-beta zeolite (Fig. 3). The in situ generated 1,3-dioxolane structure with the terminal vicinal hydroxyl groups in sorbitol and ketone facilitates subsequent intramolecular etherification, thus resulting in the improved synthesis of isosorbide in a yield of up to 93% [60].

2.1.3. 2,5-Dihydroxymethylfuran and 2,5-dihydroxymethyltetrahydrofuran

HMF is widely viewed as versatile biomass-based platform molecules, which is obtained from the dehydration reaction of C6
hexoses [61–63]. However, the uncontrollable formation of humins or levulinic acid in the presence of acid catalysts as well as the cumbersome process for product separation still challenge the production of HMF. Thus, timely isolation of HMF from acid catalysts or mild reaction conditions is desired. In 2006, Dumesic and co-workers reported a two-phase reactor system for the dehydration of fructose in aqueous phase over acid catalyst, and continuous extraction of HMF into an organic phase from the reactive aqueous solution [64]. Later, Du's group proposed the solid acid catalyst of tantalum hydroxide in water-2-butanol biphasic system for the saccharide dehydration to HMF with high catalytic activity and excellent stability [65,66]. Zhang and co-workers reported chromium (II) chloride in [EMIM][Cl] to produce HMF in high yield at around 70% from glucose, and the acid catalyzed decomposition of HMF to levulinic acid and formic acid was negligible [67]. Zhao's group reported a catalytic system based on germanium(IV) chloride in [BMIM][Cl] ionic liquid for the conversion of carbohydrate to HMF under mild conditions. D-Fructose, D-glucose, sucrose, maltose, and even cellulose were successfully converted into HMF with mild to good yields [68]. Recently, it was further demonstrated that ternary biphasic system of ionic liquid-organics-water was efficient in promotion of the HMF yield and separation at high glucose concentration [69].

Hydrogenation of the aldehyde group in HMF provides a facile way to furan-based glycols (Fig. 4). Xu and co-workers reported a highly dispersed Ru clusters supported on zirconium silica for the hydrogenation of HMF in aqueous solution at room temperature, affording 2,5-dihydroxymethylfuran (DHMF) in around 90% yield [70]. Considering the low stability and difficult isolation of HMF, starting from carbohydrates to synthesize DHMF or 2,5-dihydroxymethyltetrahydrofuran (DHMTF) via a one pot reaction is more intriguing. Carbohydrates contain the C=O groups which are tend to be reduced via hydrogenation, making the direct dehydration-hydrogenation cascade reaction of carbohydrates to DHMF or DHMTF a challenge. Xu's group reported the direct synthesis of DHTMF from fructose by using a combination of acid and hydrophobic Ru/SiO₂ in a water/cyclohexane biphasic system. The hydrophobicity of the hydrogenation catalyst ensured itself to remain in the organic phase, and prohibited the undesired hydrogenation of fructose in water [71]. Zhang's group reported the production of both DHMF and DHMTF from carbohydrates via one-pot tandem reactions [72]. First, in ionic liquid, HMF was obtained via dehydration reaction; afterwards water was added, and the subsequent hydrogenation reaction of HMF over supported noble metal catalyst gave diols. Ir/TiO₂ afforded 71% yield of DHMF based on fructose, and around 63% yield of DHMTF based on fructose was obtained in the case of Pd/C.

2.2. Diacid and diester

The importance of polyester material industry has been driving chemists to explore diacid monomers from renewable resources. 2,5-Furandicarboxylic acid (FDCA) and its diester, which can be obtained by the selective oxidation of HMF (Fig. 5), has been well recognized as a potential alternative to terephthalic acid (TA).

In 2011, Xu and co-workers reported an efficient catalyst system of VOSO₄/Cu(NO₃)₂ for the aerobic oxidation of HMF to 2,5-diformylfuran (DF) [73]. Further oxidation of DF provided a facile way to the synthesis of FDCA with adequate purity for further polymerization with a variety of diols [74,75]. For example, the poly(butylene 2,5-furandicarboxylate) (PBF) obtained by esterification of DFF-derived FDCA and 1,4-butylene glycol (1,4-BG) possessed a polymerization degree of about 125 [74]. In addition, copolymerization of the FDCA with EG and 1,4-BG resulted in the copolymesters with tunable thermal properties [75]. Next, Xu’s group reported the Au/HY catalyst which catalyzed the direct aerobic oxidation of HMF to FDCA quantitatively [76]. In comparison with FDCA which is insoluble in most solvents, furan-2,5-dimethylcarboxylate (FDMC) has the advantage of high solubility and facile purification in normal solvents [77]. Besides, the polymerization of FDMC with diols could be handled under mild conditions relative to that of FDCA, which is desirable considering the relatively low thermal stability of furan modif in FDCA [78]. Recently, Xu and coworkers combined manganese oxide and CoO₂-N/C catalyst for the aerobic oxidative esterification of HMF to FDMC in high yield (96%) [79]. The reaction proceeds via fast oxidation of HMF to DFF over the manganese oxide catalyst, and then oxidative esterification of in situ formed DFF to FDMC by CoO₂-N/C.

In addition, synthesis of biomass-derived TA has been attracting the chemists’ interest over the last decades. A promising reaction
route is the Diels–Alder reactions with ethylene and muconic acid (TTMA) followed by dehydrogenation. However, the presence of two electron-withdrawing carboxylic acid groups renders muconic acid low solubility and deactivates the Diels–Alder reaction, making this reaction process a challenge. Recently, Xu's group proposed an alternative synthetic route to obtain diethyl terephthalate from ethylene and muconic acid by using ethanol as both solvent and reagent for esterification reaction (Fig. 6). The in-situ occurred esterification reaction with ethanol notably promoted the Diels–Alder reaction by improving the solubility and modulating the electronic properties of muconic acid. And a total diethyl terephthalate yield of 81% based on the amount of muconic acid was archived by silicotungstic acid catalyzed esterification and Diels–Alder reaction followed by palladium-catalyzed dehydrogenation reaction [80]. Afterwards, a series of pioneering work concerning pyromellitic acid and trimellitic acid, 1,4-cyclohexanedicarboxylic acid and 1,2-cyclohexanedicarboxylates synthesis from biomass-derived dienophiles and dienes was reported by Zhang's group (Fig. 7) [81,82].

More recently, Xu and co-workers reported the production of phthalate and its hydrogenated derivative, which are widely used in polymer industry, from bio-based malic acid and erythritol (Fig. 8). In this process, dehydration-esterification of malic acid and deoxydehydration (DODH) of erythritol initially gave fumarate and 1,3-butadiene, respectively; and the in-situ generated dienophile and diene was applied to construct a substituted cyclohexene structure via Diels–Alder reaction. A 74% yield of dibutyl trans-4-cyclohexene-1,2-dicarboxylate was obtained starting from erythritol and dibutyl fumarate. Further dehydrogenation or hydrogenation of the cycloaduct afforded phthalate in 78% yield or its hydrogenated derivative quantitatively [83].

From the view point of atomic economy, the fulfilling strategies for the biomass processing should make full use of the existing oxygen [84,85]. Via oxidative decarboxylation of sugar derived malic or levulinic acid, aliphatic diesters could be produced (Fig. 9) [84]. Xu and co-workers used phosphovanadomolybdate as a bifunctional catalyst to achieve the oxidative decarboxylation and subsequent esterification of malic acid to synthesize dimethyl
malonate in 68% yield. Later, Xu and co-workers employed MnAc$_3$ as catalyst for the aerobic oxidation of levulinate with preserving the oxygen in the substrate to produce succinate [85].

2.3. Nitrogen-containing compounds

Despite the various strategies for the degradation of cellulose, the derived chemicals made up of C/H/O are still not enough to substitute or supplement the chemicals from fossil resources. Implanting N atom during the conversion of cellulose would produce a series of renewable N-containing chemicals with high value or difficult to be obtained alternatively from fossil resources.

2.3.1. Ethanolamine and pyrazine derivatives

Zhang and co-workers reported a catalyst system of Ru/ZrO$_2$ for the reductive amination of biomass-derived aldehydes and ketones using aqueous ammonia as nitrogen source [86]. And combined with H$_2$WO$_4$ catalyst, ethanolamine could be produced via a two-step approach from lignocellulose in an overall yield of 10%. Next, they synthesized 2-hydroxymethyl-5-methylpyrazine from biomass derived 1,3-dihydroxyacetone in a yield of 72% via adopting di-ammonium phosphate as nitrogen source [87].

2.3.2. Furan-based nitrogen-implanted compounds

Recently, catalytic implantation of nitrogen into HMF or DFF was found as a fruitful reaction pathway toward furyl diamine, dinitrile, diamide, diamidine, diimide and dioxime which are hardly obtained from fossil resources (Fig. 10) [88–92]. In 2016, Xu and co-workers used manganese oxide catalyst of OMS-2 for the aerobic ammoxidation-Pinner reaction of HMF to synthesize dimethyl furan-2,5-dicarboximidate in around 88% yield [88]. And the imidate could be further transformed into 2,5-furandiamidine dihydrochloride with ammonium chloride. Next, 2,5-furandicarboxamide was synthesized by Xu and co-workers via ammoxidation of HMF over manganese oxide catalyst [89,90]. By contrast, dinitrile is highly desired owing to its promising application in polymer chemistry. However, the direct ammoxidation of HMF or DFF could not selectively give 2,5-dicyanofuran due to its high reactivity to hydration in the presence of water [89,90]. Very recently, Xu’s group realized the practical synthesis of 2,5-dicyanofuran from DFF via a two-step procedure, 2,5-Diformylfuran was first converted to 2,5-diformylfuran dioxime in around 90% isolated yield in water with hydroxylamine as nitrogen source [91]. The obtained dioxime could be dehydrated to 2,5-dicyanofuran in 82% isolated yield over Amberlyst-15 catalyst. More recently, Xu and co-workers used Rh/HZSM-5 catalyst for the direct reduction of the dioxime to produce 2,5-bis(aminomethyl)furan in around 94% yield [92]. The high selectivity was realized by the efficient dehydration-hydrogenation cascade of the dioxime owing to the surface acidity and highly dispersed Rh on the catalyst, respectively. Different from ammonia and hydroxylamine, reductive amination with organic amines affords secondary or tertiary amines. Zhang’s group applied homogeneous Ru complex as catalyst for the
selective reductive amination of HMF with H₂ and a broad range of primary and secondary amines [93,94].

3. Hemi-cellulose derived furfural to branched alkanes

Furfural is derived from the hydrolysis-dehydration of hemicellulose [95], and its hydrogenation product 2-methylfuran (2-MF) [96] was proposed to be used as the feedstock for the production of diesel (C₉–C₂₁) and jet fuel (C₄–C₁₆) range alkanes [97–101]. And Due to the five-membered ring structure of furfural and 2-MF, synthesis of renewable diesel or jet fuel is achieved through hydroxyalkylation-alkylation (HAA) coupled with hydrogenation/hydrodeoxygenation (HDO) [102].

Usually, the first step is HAA which constructs the oxygenates with expected carbon chain length and structure with furan (2-MF) and carbonyl compounds, which can be aldehydes (such as furfural, butanal), ketones (e.g., acetone, cyclopentanone and hydroxyacetone) as well as levulinic acid or esters through aldol condensation [102–105]. A series of solid-acid catalysts were investigated for the HAA step of 2-MF with furfural, butanal, acetone and hydroxyacetone. Among the investigated catalysts, Nafion-212 resin exhibits excellent activity and stability [102,103,105,106].

Besides, the reactivities of different lignocellulose-derived furans and carbonyl compounds were studied and compared. Furfural and 2-MF were found to be the most reactive furan and carbonyl compounds [102], respectively. Butanal is more reactive than acetone in the HAA reaction with 2-MF [103]. Due to the electron-withdrawing effect of the hydroxyl group, hydroxyacetone affords a higher yield of the HAA product than acetone (42% vs. 25%) (Fig. 11) [105].

HDO is performed over a noble metal catalyst of Pt/ZrP. A 94% carbon yield of diesel and a 75% carbon yield of C₁₅ hydrocarbons were achieved, respectively [102]. Besides, the non-noble metal catalyst Ni-W₆C/C exhibited good performance and stability which is similar to Pt/C and Pd/C in the HDO of HAA products of 2-MF with butanal and acetone [103]. As for the high energy consumption needed for the ring-opening of the furan compounds, non-noble metal catalyst Ni supported on Hβ-(394) with strong acid sites, which is necessary for the ring-opening of the furan compounds, was proved to achieve high performance (~90% carbon yield of diesel range alkanes) at a much lower temperature (503 K) [107].

Usually, external hydrogen resource is indispensable for the hydrogenation/HDO process. However, as much as 67% of 1,1,3-trimethylcyclohexane has been achieved at 533 K through the loading of Pt catalyst, which is active for both HDO reactions and aqueous phase reforming of lignocellulose derived glycerol that can be utilized as renewable hydrogen source (Fig. 12) [108].

4. Lignin to aromatics

Lignin is one of the major components of lignocellulose with a percentage of 15%–30% [109]. The structure of lignin can be viewed as an amorphous polymer with the aromatic build blocks connected with various linkages (Fig. 13). Three primary building blocks are: H (p-hydroxyphenyl), G (guaiacyl), and S (syringyl), all of which are methoxylated phenylpropane. And the main linkages could also be divided into C–O (e.g., β–O–4, α–O–4 and 4–O–5) or C–C (e.g., β–5 and 5–5). Lignins from different woods vary in the percentage of the building blocks and the linkages. In recent years, valorization of lignin to aromatic fine chemicals has received great attention [5,110–113]. Currently, the method for the valorization of lignin could be divided into the following three parts, namely (i) lignocellulose fractionation, (ii) lignin depolymerization, and (iii) upgrading towards targeted chemicals (Fig. 14).

4.1. Lignocellulose fractionation

In the raw lignocellulose, cellulose, hemicellulose and lignin are connected tightly by different linkages. The lignin fractionation
Fig. 12. Synthesis of jet fuel range cycloalkane from isophorone with glycerol as renewable hydrogen source [108].

from the raw lignocellulose is not only a critical step for the valorization of lignin, but also an important step for the utilization of the remaining polysaccharides. One pioneering work on the lignin fractionation was the activated carbon supported nickel (Ni/AC) catalyzed fragmentation–hydrogenolysis process reported by Xu and co-workers [114]. In this work, the native birch lignin was firstly fragmented with methanol into smaller intermediate species with molecular weights from m/z ca. 1100 to ca. 1600, which proved that the alcoholsysis was an effective way for the lignin fractionation (Fig. 15). In the following hydrogenation, the lignin species were further converted into monomeric phenols with a best selectivity of 97% at conversion of 50% based on birch wood lignin. Furthermore, this strategy was also applied in the lignosulfonate and lignin model conversion [115,116]. Inspired by this work, series of work have been developed with alcohol as solvent when fractionation lignin. Recently, a new fractionation strategy was also reported by Xu and co-workers, which can generate both high-quality cellulose and lignin simultaneously based on alcoholsysis [117]. In this work, tetrahydrofurfuryl alcohol (THFA) and water were used as the thermal treatment solvent. With this special alcohol, a 94% purity of cellulose could be obtained with a yield of 93%. Meantime, 77% pure lignin could be also obtained.
4.2. Lignin depolymerization

The key for the lignin depolymerization lies in the breaking down of the linkages between the aromatic building blocks. Although there are kinds of linkages in the lignin, their amount differs largely (Fig. 13). The β-O-4 linkage accounts for almost 50% of all lignin linkages. As the predominant linkage in lignin, this crucial unit has been seriously studied in our division for its selective cleavage. One interesting work on the lignin depolymerization is the two-step strategy aiming at weakening the β-O-4 linkage by modifying the adjacent functional group in the first step. The strategy was mainly focused on the β-O-4 linkage, which was named as “sell a dummy” by Wang and co-workers [119]. The strategies reported to date can be divided into three categories, namely (i) Ca-OH oxidation to Cα=O, (ii) methylation of Cα-OH and (iii) dehydroxylation of Cα-OH.

4.2.1. Ca-OH oxidation to Cα=O

As shown in Fig. 16 [119–121], the oxidation of Ca-OH to Cα=O can reduce the BDE of the Cα-OAr bond from 247.9 to 161.1 kJ/mol which facilitates the following depolymerization. And this strategy has been proved to be effective for producing carbonyl-containing aromatics that could not be obtained from depolymerization of native lignin [122]. There are various methods developed for the Ca–OH oxidation. Wang and co-workers reported the photocatalytic oxidation of Ca–OH to Cα=O with Pd/ZnInS4 catalyst under the light of 455 nm [123]. In addition, VOSO4/TEMPO was also reported to be an effective catalyst system to accomplish this oxidation [124]. Stoichiometric oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was also reported to realize the Ca–OH oxidation to be reproducible and applicable [125].

For the oxidized β-O-4 linkages, methods have been reported to depolymerize it including oxidation, hydrogenolysis and even NH3OH-mediated strategy. In the oxidation cleavage, Cu110-phenanthroline was firstly developed to catalyze the oxidized β-O-4 linkages into organic acids and phenols [124]. The detailed investigations suggested that the cleavage was mainly through the C–C bond cleavage via the hydrogen-abstraction from Cβ–H bond. Furthermore, a BF3·OEt2 assisted copper catalyst also showed high activity towards the C–C bond cleavage with a similar mechanism via Cβ–H bond activation [126]. The existence of BF3·OEt2 reduced the Cβ–H bond energy via the coordination of the carbonyl group in the oxidized motif (Fig. 17). Recently, Xu and co-workers also reported that the covalent triazine framework (CTF) could act as a metal-free catalyst for the oxidative cleavage of the oxidized β-O-4 linkages [127]. In the report, both C–C bond and C–O bond cleavage existed during the catalytic process.

For the depolymerization of oxidized β-O-4 linkages using the hydrogenolysis strategy, a TiO2–NaOAc system was developed via photocatalysis with 365 nm light [123]. Mechanism study illustrated that the in-situ formed Ti3+ activated the C-O bond which was the main cleavage position for the oxidized β-O-4 motifs. A detailed cleavage mechanism on Pd[111] was investigated by DFT method [128]. The favorable route was as follows: 2-phenoxy-1-phenylethanone (β-O-4 motif) becomes dehydrogenated to 2-phenoxy-1-phenylethano (oxidized β–O-4 motif); this ketone motif will tautomerize to its enol (2-phenoxy-1-phenylethanol), which will again be dehydrogenated at the position of the hydroxy group, after which the C–O ether bond breaks (Fig. 18). During the hydrogenolysis process, a competitive reaction of the carbonyl hydrogenation and the C–O bond cleavage always exist. To avoid the
carbonyl hydrogenation, several catalysts were developed. A special NiMo sulfide catalyst was reported preferring the cleavage of the Cβ–O bond rather than the carbonyl hydrogenation [129]. It was believed that the replacement of the edge Mo atoms by the less active Ni2+ was the main reason for the high selectivity (Fig. 19). A carbon modification of nickel catalyst was also effective for the C–O bond cleavage without the carbonyl hydrogenation [130]. The positively charged nickel was responsible for the weak activation of the carbonyl group.

Except for oxidation and hydrogenolysis, one special strategy was the NH₂OH–mediated strategy [131]. In this method, the oxidized motif was converted into isoxazole and nitrile with various catalysts. This work provided a new route toward the fine chemicals from the lignin.

4.2.2. Methylations of Cα–OH

As shown in Fig. 16, the methylation of Cα–OH can reduce the BDE of the Cα–OAr bond from 289.0 to 269.0 kJ/mol. By using Ni/C as catalyst, a 39 wt% yield of phenolic alcohols from woody biomass was gained [120]. In addition, this modification strategy could also break the hydrogen bond. Further research showed that breaking the intramolecular hydrogen bonds would accelerate the C–O cleavage (Fig. 20). This work provides another important structure modification method in lignin depolymerization, which may open a new route for the lignin valorization.

4.2.3. Dehydroxylation of Cα–OH

The dehydroxylation strategy is a special one. Because the modified motif could not be separated. The radical intermediate from
the dehydroxylation of the $\text{C}–\text{O}–4$ existed only on the acid-redox site of a NiMo sulfide catalyst [121]. The C–H oxidation BDE decreased from 274.0 kJ/mol to 66.9 kJ/mol via this strategy, which made the C–O bond easy to be broken (Fig. 21). The synergy effect between the acid-redox site and hydrogenation site is crucial for this strategy.

Except for the two-step methods, direct lignin depolymerization method has also been studied. Xu and co-workers reported the C–C bond cleavage with acetic acid and V catalyst [132,133]. Detailed mechanism investigation investigated a distinct route of the C–H oxidation which proceeded via a hemiacetal-like structure. This intermediate was believed to facilitate $\text{C}–\text{O}–4$ bond cleavage under mild reaction conditions. Unlike the two-step method, the photo oxidation with C3N4 as the catalyst is less effective for the oxidized $\text{C}–\text{O}–4$ motif, which only worked for the original $\text{C}–\text{O}–4$ motif [134]. The process begins with the oxidation of the $\text{C}–\text{H}$ bond, and the substrate was believed to have $\pi–\pi$ interactions with the catalyst. With ZnIn2S4, the original $\text{C}–\text{O}–4$ motif could also be cleaved without additional H2 [135]. The hydrogen generated through the C–OH bond dehydrogenation process was used directly for the C–O bond cleavage. This catalyst was also effective for the unreacted dioxanols poplar lignin. With the ingenuous designed CuOx/ceria/anatase nanotube catalyst, the $\text{C}–\text{O}–4$ motif could also be cleaved, especially for the C–C bond (Fig. 22) [136]. With CuOx cluster dispersed on the ceria, it could enhance the activity via the increase of Ce3+, with CuOx cluster dispersed on the exposed anatase surface, side reactions could be suppressed. This work not only provided a new catalyst for the C–C bond cleavage but also supplied a new route to fabricate catalyst.

4.3. Upgrading

Although some depolymerization methods could give fine chemicals which can be used directly, most of the depolymerization methods give only a mixture of substituted phenolic compounds. These mixtures require additional upgrading processes to be transformed into marketable chemicals for end-use applications. Zhang and co-workers reported the hydrodeoxygenation of guaiacol to phenols with the anatase TiO2 supported gold nanoparticles [137]. In this work, the Au nanoparticle was not believed as the active site. The size of gold nanoparticles could only affect the activity, while has no effect on the selectivity. The catalyst could only hydrogenate catechol and guaiacol to phenol, but not for the hydrodegenation of phenols, anisole, and aromatics, which acted as a high selective catalyst for the lignin compound upgrading. As for the oxidation depolymerization method of lignin, it is important to develop catalytic decarboxylation method since most of the compounds from the lignin oxidation were organic acids. Wang and co-workers reported CuCl2 accounts for catalytic decarboxylation (Fig. 23) [138]. This catalyst can be applied in both converting lignin extracts and native lignin. This work provides an upgrading method to produce phenol from the organic acid substrate.

5. Conclusions and outlook

Lignocellulose is abundant in nature and renewable. However, most of the biomass resource is not well utilized. Currently, biomass derived from inedible plant is considered to be wastes and are majorly burned to provide heat, and this will inevitably cause environmental problems. For the sustainable development, a great research interest has been recently devoted to the conversion of lignocellulose to the fuels and chemicals. Although a great progress has been made, the development of a more efficient and benign process is still need to be further investigated. The process for the lignocellulose conversion should be a green process and reduce the negative environmental impact of the chemical industry. Environmentally benign reagents and green solvents should be used. Developing a highly efficient catalyst is critical to reduce the CO2 emission and energy consumption.

Presently, the depolymerization of lignin usually leads to a mixture of phenols. The isolation of each product is difficult. It is needed to develop new method to selectively remove the functionality. Further upgrading the lignin oil is a promising way to narrow the product distribution, which would facilitate the product separation. Using cascade reaction involving several steps is supposed to be an effective way for one-pot conversion of lignin to single product. Each step should simultaneously work well under the same reaction conditions, and this needs to combine several catalytic components together.

Although the raw-biomass resources such as corn stalks and sugarcane are abundant and inexpensive, their energy densities