

Chapter 2

Chemical Conversion of Biomass to Green Chemicals

Yijun Jiang, Xicheng Wang, Quan Cao, Linlin Dong,
Jing Guan and Xindong Mu

Abstract Biomass has the potential to serve as a sustainable source of energy and organic carbon for our industrial society. The focus of this chapter is to provide a survey of different strategies to achieve chemical catalytic conversion of biomass-derived oxygenated feedstocks to value-added chemicals and fuels. The key reactions involved in the processing of biomass are hydrolysis, dehydration, isomerization, aldol condensation, reforming, hydrogenation/hydrogenolysis, and oxidation. Here, a few specific examples, namely efficient hydrolysis of cellulose over novel solid acids and synthesis of polyols by hydrogenation/hydrogenolysis of cellulose and sugar have been chosen for this review. Further, the selective conversion of platform molecules, such as furan, HMF, and biogenic carboxylic acids into intermediates, specialties, and fine chemicals has been considered. While many challenges are involved in biomass processing, understanding of fundamental reaction chemistry for different types of reactions can lead to the development of new approaches for specific processes.

Keywords Biomass · Green chemicals · Chemical conversion techniques

2.1 Introduction

Production of chemicals highly depends on non-renewable fossil resources such as petroleum, coal, and natural gas in modern society, which is widely acknowledged as unsustainable. The diminishing fossil fuel reservoirs together with ever-deteriorating environment associated with the worldwide fossil-fuel-based industry makes the use of alternative feedstock imperative [1–3]. Biomass, which has utilized directly via combustion to produce heat for thousands of years, has

Y. Jiang · X. Wang · Q. Cao · L. Dong · J. Guan · X. Mu (✉)

CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 266101 Qingdao, China
e-mail: muxd@qibebt.ac.cn

been recalled for its renewable ability and enormous reserves. Biomass has been regarded as a sustainable alternative to fossil resources, and therefore, the effective utilization of biomass has greatly attracted the interest of the scientific and industrial communities [4–6].

The transformation of biomass to chemicals and fuels can be generally realized by three different techniques: thermal, biochemical, and chemical routes. Thermal techniques, like pyrolysis and gasification, can take full advantage of the entire organic substance of this resource. Nevertheless, these techniques still suffer from the disadvantages of low selectivity and high energy input which are unacceptable. Bioconversion of biomass possesses the advantage of good selectivity, but sometimes suffers from low efficiency. Reasonable routes to promote biomass converted into high value-added chemicals under relative mild circumstance in liquid phase at a high selectivity are required. A variety of processes for the production of green chemicals derived from biomass have been developed in the last few years, which will be discussed in this chapter.

2.2 Depolymerization of Polysaccharide with Catalytic Method

As we all know, glucose is an important platform compound which can be converted into various value-added chemicals with the fermentation or chemical processes. Cellulose is a polysaccharide with glucose as its monomer, which needs to be hydrolyzed into glucose before being used as feedstock in most chemical and bioprocesses. Therefore, the hydrolysis of cellulose into glucose is a key technology for efficient biomass utilization. However, due to its highly crystalline structure, together with the strong inner β -1,4-glycosidic bonding and complex hydrogen bonding, the hydrolysis of cellulosic biomass is quite difficult [7].

Currently, although a lot of efforts have focused on the hydrolysis of biomass by enzymes, liquid acid, and supercritical water, drawbacks still exist in these processes. Liquid acid hydrolysis including dilute acid [8], concentrated acid [9], and organic acid [10, 11] has a long industrial history, but is not recyclable and corrosive, which leads to various environmental problems. Enzymatic hydrolysis [12] is one of the most promising hydrolysis technologies, but suffers from the low hydrolysis efficiency and high cost of the enzyme. The utilization of supercritical water faces the problem of high energy consumption [13].

Compared with traditional mineral acid, solid acids are environment-friendly catalysts that are less corrosive, easy to handle, separable and recyclable, which have already been widely used to catalyze a variety of organic reactions. Recently, the solid acid catalysts have attracted considerable attention in biomass conversion and several solid acids have been developed to facilitate the hydrolysis of cellulose, starch, or other polysaccharides with moderate to good glucose yield. Solid acid catalysts such as carbonaceous solid acids (CSAs) [14, 15], inorganic oxides [16, 17],

zeolites [16, 18–20], cation-exchanged resins [16, 17], clays [16], and hetero polyacids [21–23] have been reported for the hydrolysis of cellulose due to their merits of retrievability. Among them, the CSA bearing SO_3H , COOH , and phenolic hydroxyl (OH) groups in the framework of the amorphous carbon has been proven to be an excellent candidate for the cellulose hydrolysis due to its high catalytic activity and retrievability [20, 21]. The activity of CSA was reported to be much higher than sulfuric acid and could be reused without obvious loss of activity. In order to enhance the performance of CSA for the hydrolysis of cellulose, several groups including us did some basic work to optimize the preparation of the CSA catalyst or to study the mechanism of the solid-solid reaction. CSA prepared via sulfonating the amorphous carbon or active carbon prepared at high temperature showed considerable catalytic activity for the hydrolysis of cellulose [14, 15]. While these carbonaceous solid acid still have the disadvantages of relative low activity and high energy consumption.

Highly dispersed carbonaceous spheres with sulfonic acid groups were successfully prepared from glucose by hydrothermal method [14] (Fig. 2.1). Under hydrothermal conditions, the sugar was first incompletely carbonized to carbon nanospheres by dehydration. Then, the resulting carbon spheres were sulfonated to form highly dispersive uniform CSA. More importantly, the uniform size and high aqueous dispersibility of the CSA improve the accessibility to the polysaccharides, and thus it exhibits excellent catalytic performances for the polysaccharides hydrolysis. In the cellulose hydrolysis, ZrO_2/WO_3 and H-ZSM5 showed negligible glucose yield less than 1 %; while Amberlyst-15 and C-673 gave glucose in 25.6, 49.0 % yield, respectively. Similarly, our CSA C-453 gave the highest glucose

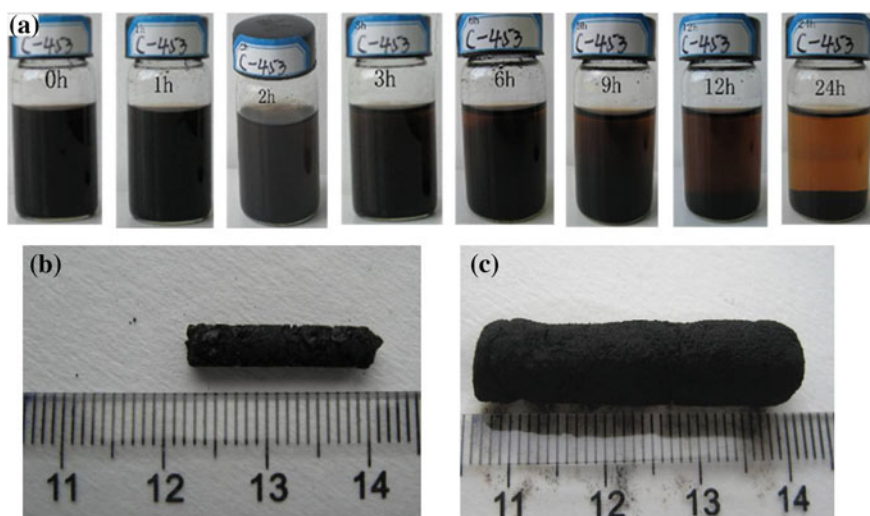


Fig. 2.1 Stability of the CSA in the water solution (a), the cylinder of CAS powders before (b) and after water wetting (c)

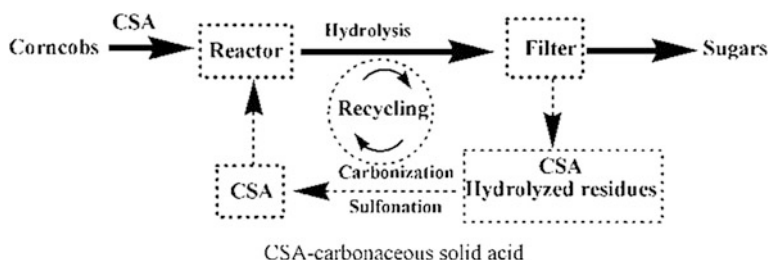
yield of about 74.0 %, which is much higher than previous reported sulfonated activated carbon solid acid (40.5 %) [15], indicating that our CSA exhibits considerably high activity for cellulose hydrolysis.

However, in most reports, microcrystalline cellulose was always used as the model feedstock which is far away from real industrial applications due to the different compositions and structures between natural lignocellulosic biomass (mainly composed of cellulose, hemicellulose, and lignin) and microcrystalline cellulose. Additionally, the hemicellulose in the natural lignocellulosic biomass has always been ignored as target feedstock for solid acid hydrolysis, although it is also the main component in many plants and easier to be hydrolyzed. Therefore, it is imperative to investigate the hydrolysis performance of CSA aiming at real biomass substrates, especially the biomass containing significant amount of hemicellulose.

Corncoobs containing about 30 % hemicellulose are the popular and abundant agricultural waste, which have been used as industrial raw material to produce xylose and furfural by liquid acid hydrolysis. However, the environmental problems from the large amount of liquid acids used and solid residues generated limit its sustainable industrial application. A green and effective approach for the comprehensive utilization of corncoobs (Scheme 2.1) was developed [24]. During this process, the CSA catalyst was prepared from the hydrolyzed corncoobs residue and was used for the hydrolysis of corncob with only a small amount of water under microwave irradiation. After reaction, the CSA and hydrolyzate can be easily separated and recycled. There are two value-added products during the whole process. One is sugars produced by hydrolysis, the other is CSA derived from the unconverted solid residue, which can also be used as catalyst in the hydrolysis.

However, challenges still exist in this process; both the cellulose and the solid acids are presented in solid state in this reaction and have resulted in difficulties for cellulose to get access to the active catalytic sites. Mass transfer between substrates and catalysts is the main difficulty in hydrogenolysis of cellulose. Generally, the hydrolysis reaction catalyzed by solid acids needs higher temperature and gives low glucose yield. In a word, despite the success of these techniques for the hydrolysis of cellulose, each has its own pros and cons with respect to the economy, recyclability, and activity.

To mimic the functional sites in the real enzyme, sulfonated copolymer poly (acrylic acid)-co-poly(styrene sulfonic acid) which showed high performance for



Scheme 2.1 Procedure for the corncoobs hydrolysis by CSA derived from the hydrolysis residue

the hydrolysis of polysaccharides were also managed to be designed and synthesized [25]. However, the separation of the catalyst is still a main problem to block its application. Well-defined sulfonated block copolymer poly(acrylic acid)-block-poly(styrene sulfonic acid) (PAA-*b*-PSSH) and random copolymer poly(acrylic acid)-random-poly(styrene sulfonic acid) (PAA-*r*-PSSH) were prepared by direct thermolysis of the precursor copolymers poly(*tert*-butyl acrylate)-block-poly(neopentyl styrenesulfonate) (PtBA-*b*-PNSS) and poly(*tert*-butyl acrylate)-random-poly(neopentyl styrenesulfonate) (PtBA-*r*-PNSS), which were synthesized by living radical polymerization (MWD < 1.10) catalyzed with CuBr. As shown in Table 2.1, the well-defined sulfonated polymers exhibited excellent catalytic performance for polysaccharide hydrolysis under microwave irradiation at the low effective acid concentration (0.4 mmol mL⁻¹). The best result was obtained by using PAA-*r*-PSSH as a catalyst, with the glucose yield of 94.5 % for the hydrolysis of starch at 373 K and 35 % for cellulose hydrolysis at 393 K. The remarkable performance of PAA-*r*-PSSH for polysaccharide hydrolysis was achieved through the synergetic combination of SO₃H and COOH. The mechanism of the hydrolysis of polysaccharide by the polymer acid catalyst established here will guide the design of new acid catalyst for the polysaccharide hydrolysis.

To solve the problems of activity and recycling for solid acid, concentrated H₃PW₁₂O₄₀ (HPW) was also employed to decompose cellulose under microwave irradiation at low temperature [26]. 75.6 % yield of glucose was obtained at 90 °C under microwave irradiation for 3 h, which was considerably high under such mild condition using phosphotungstic acid as catalyst. With the same effective acid concentration, HPW gave the highest cellulose conversion and glucose yield among the Brønsted acid catalysts, indicating that the strong Brønsted acid played an important role during cellulose hydrolysis. In the hydrolysis of cellulose with HPW

Table 2.1 Microwave-assisted hydrolysis of starch catalyzed by various catalysts^a

Temp (°C)	Catalyst	Y _{GI} /%	Rate of glucose formation (μmol h ⁻¹)	TOF (h ⁻¹) ^b
80	PSSH	7.2	44	0.11
	PAA- <i>b</i> -PSSH	12.6	78	0.19
	H ₂ SO ₄	14.4	89	0.22
	PAA- <i>r</i> -PSSH	16.2	100	0.25
90	PSSH	20.7	128	0.31
	PAA- <i>b</i> -PSSH	29.7	183	0.45
	H ₂ SO ₄	31.5	194	0.47
	PAA- <i>r</i> -PSSH	38.7	238	0.58
100	PSSH	76.5	472	1.15
	PAA- <i>b</i> -PSSH	88.2	544	1.33
	H ₂ SO ₄	90.9	561	1.37
	PAA- <i>r</i> -PSSH	94.5	583	1.43

^aStarch: 100 mg; effective acid amount: 0.4 mmol; distilled water: 1 mL; reaction time: 60 min.

^bTOF is estimated from glucose formation per mole effective acid sites (SO₃H) per hour

as catalysts, microwave irradiation led to higher glucose yields than the conventional heating method. The recovery and reusability of HPW were investigated by extraction with diethyl ether from the reaction solution. In order to investigate the performance of the concentrated HPW for the hydrolysis of real lignocellulosic biomass, corncob, corn stover and bagasse were also employed to serve as feed-stock under microwave irradiation. Before the reaction, the composition of the lignocellulosic biomass was first analyzed following the modified NREL laboratory analytical procedures (NREL). Table 2.2 gives the results for the hydrolysis of corncob, corn stover, and bagasse catalyzed by 88 % HPW solution at 90 °C for 3 h under microwave irradiation. For the hydrolysis of cellulose in corncob, corn stover, and bagasse, 37.2, 43.3, and 27.8 % yields of glucose were obtained, respectively, which were lower than that of microcrystalline cellulose (75.6 %) under the same reaction conditions because of the recalcitrance of lignocellulose. It is well established that the hydrolysis of hemicellulose (xylan + araban) is easier than that of cellulose, but only 2.96, 2.30, and 3.94 % yields of xylose were obtained from the xylan in corncob, corn stover, and bagasse, respectively, which was attributed to the side reactions of xylose (xylose to furfural) under the reaction condition. The yields of the side product for furfural were detected to be 11.6, 7.26, and 7.47 %, respectively. The effect of the amount of corn stover on the glucose yield was also evaluated by varying the amount of cellulose from 0.06 to 0.5 g. With increasing the amount of corn stover from 0.06 to 0.5 g under the reaction conditions, the yield of glucose decreased from 43.4 to 25.6 % because of the saturation of the catalytic sites. After hydrolysis, the reusability of HPW in corn stover hydrolysis was investigated just as that in microcrystalline cellulose hydrolysis and the yield of glucose gradually decreased from 31.8 (the 2nd run), 19.9 (the 3rd run) to 12.6 % (the 4th run). It is believed that the by-products (furfural and HMF) and the impurities such as extractives in the corn stover (proteins, fat) generated in the hydrolysis reaction could be extracted by the diethyl ether with HPW and damaged the catalytic site in the HPW.

In a word, despite the success of these techniques for the hydrolysis of cellulose, each has its own pros and cons with respect to the economy, recyclability, and activity. Therefore, it is imperative to develop some novel hydrolysis technologies which not only can decompose the rigid cellulose structure effectively like cellulase under mild temperature, but also can be recycled like solid acids.

Table 2.2 Hydrolysis of real lignocellulosic biomass catalyzed by HPW^a

Biomass	Y _{Gl} (%) ^b	Y _{Xy} (%) ^b	Y _{Ar} (%) ^b	Y _{Ts} (%) ^b	Y _{Fu} (%)	Y _{HM} (%) ^c
Corncob	37.2	2.96	28.0	24.6	11.6	0.24
Corn stover	43.4	2.30	26.5	30.0	7.26	0.21
Bagasse	27.8	3.94	34.1	19.0	7.47	0.29

^aBiomass: 60 mg; HPW solution: 3 mL; temperature: 90 °C; reaction time: 180 min

^bY_{Gl}, Y_{Xy}, Y_{Ar}, and Y_{Ts} were the carbon-based yield of glucose, xylose, arabinose, and total sugar respectively

^cY_{Fu} (%) and Y_{HM} (%) were the carbon-based yield of furfural and HMF, respectively

2.3 Production of Polyols from Lignocellulosic Biomass and Biomass-Derived Compounds

Biobased polyhydroxy compounds, including sugars, sugar alcohols, and glycerol can be converted into high value-added chemicals via catalytic conversion [27–30]. However, unlike petroleum, biomass possess high oxygen content and specific carbon skeleton. In order to transform the biobased polyhydroxy compounds into high value-added chemicals, the selective removal of oxygen is the key step. Catalytic hydrogenolysis is an efficient way for biomass valorization. Here, we will provide a general overview of the catalytic conversion of polyhydroxy compounds into high value-added chemicals via hydrogenolysis. Figure 2.2 illustrated the value-added glycols with carbon chain in the range of 2–6, which can be derived from fatty acid esters and lignocellulose.

2.3.1 Cellulose Hydrogenation and Hydrogenolysis

Cellulose, mainly from agricultural and forestry residues, is one of the world's largest organic raw material resource (nearly 40 billion tones production every year). Different from starch, cellulose cannot be digested by human. Therefore instead of starch, human's main food source, cellulose was regarded as a promising resource that can be transformed into energy and chemicals in the post-petroleum era. To date, the one-pot chemical transformation of cellulose to polyols over heterogeneous catalyst is one of the most promising routes for the effective

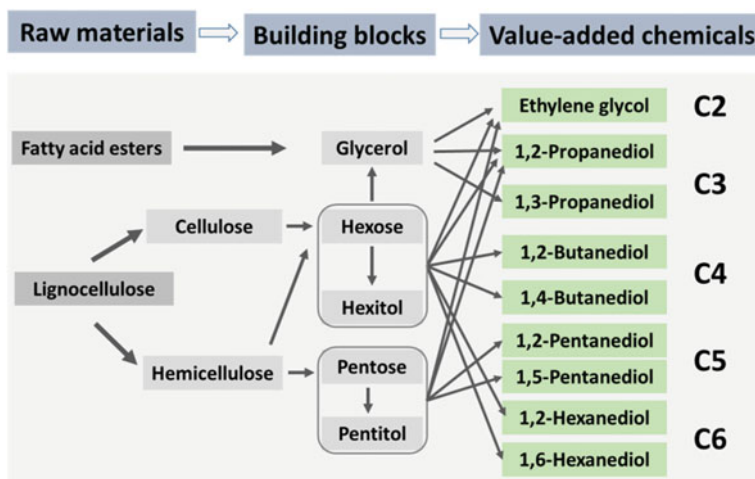


Fig. 2.2 Value-added glycols with carbon chain in the range of 2–6 from fatty acid esters and lignocelluloses

utilization of cellulose in a more efficient and convenient manner [31]. In this part, we will focus on the recent advances of one-pot hydrogenation and hydrogenolysis of cellulose.

Supported metal catalyzed hydrogenation of cellulose was first reported by Fukuoka in 2006 [32]. Among the metal catalysts they had tested, Pt and Ru showed superior activity in conversion of cellulose at 463 K under 5 MPa H_2 . A yield of 30 % sugar alcohol was obtained over Pt/ γ - Al_2O_3 . The reaction of cellulose hydrolysis to glucose was catalyzed by in situ generated acid sites, while noble metals catalyze the following process of glucose hydrogenation. In order to reduce the crystallinity and particle size of cellulose which impeded the conversion of cellulose into high value-added chemicals via heterogeneous catalytic transformation, ball milling was applied in their experiment for the purpose of degradation the cellulose more efficiently. To improve the efficiency, the in situ generated protons produced by high temperature liquid water (above 473 K) was employed to act as acid catalyst in Liu's research [33]. The acid will disappear when the reaction system is cooled down to the room temperature, making it a green process. Ru/C was chosen as the hydrogenation catalyst in this research for its superior glucose hydrogenation activity. After 30 min, yield of hexitol was 39.3 % at the conversion of 85.5 % under the reaction of 518 K, 6 MPa H_2 . Zhang et al. [34] performed the hydrogenation of cellulose under the catalysis of tungsten carbide in order to replace the high-price noble metal catalysts used previously. Tungsten carbide was found to give a higher yield of ethylene glycol (EG) than platinum and ruthenium catalysts at the reaction condition of 518 K, 6 MPa H_2 , 30 min. Furthermore, the yield of EG increased from 27 to 61 % significantly with the promotion of a small amount of nickel. The following study showed that H_xWO_3 was the authentic active species which promoted the C–C cleavage of cellulose for the formation of EG in this reaction [31]. Tungsten trioxide promoted ruthenium catalysts was also proved to show high activity in hydrogenolysis of cellulose to yield glycols by Liu et al. [35]. WO_3 was found to promote the hydrolysis of cellulose as well as the C–C bond cleavage of the sugar. EG and propylene glycol were produced by selective hydrogenolysis of glucose and fructose, respectively.

Although non-noble nickel is generally considered as efficient hydrogenation and hydrogenolysis catalyst, supported nickel catalysts investigated currently and consistently exhibited poor performances towards the production of target polyols. In order to explore a catalyst that can effectively convert cellulose at low cost, Mu et al. [36] evaluated Ni catalysts supported on a series of supports and found that 20 % Ni/ZnO catalyst can convert the cellulose completely and give a 70.4 % yield of total glycols. The main drawback of this catalyst lies in its poor hydrothermal stability, resulting in the decrease of catalytic activity after repeated reaction runs. Further study showed that Ni–Cu/ZnO bimetallic catalysts could be successfully applied to the hydrogenolysis of cellulose and real biomass substrates (including cornstalk and corncob) for the purpose of producing 1,2-alkanediols as the major products [37]. The mole ratio of Ni and Cu not only dominated the activity, selectivity, and product distribution, but also played synergetic roles for the formation of 1,2-alkanediols during the reaction. Other than nickel, non-noble metal

copper was also employed in the reaction of hydrogenolysis of cellulose. Concentrated cellulose (up to 15 wt%) can be converted into 1,2-propylene glycol and EG through the reaction of hydrogenolysis with no coke-like precipitates formed over CuCr catalysts promoted by $\text{Ca}(\text{OH})_2$ [38]. 1,2-propylene glycol and EG was obtained at the yield of 42.6 and 31.6 % under the reaction condition of 518 K, 6.0 MPa H_2 , respectively.

Apart from acid sites from solid acid, water with high temperature and pressure, mineral acids like phosphoric acid and sulfuric acid were also introduced into cellulose hydrogenation under the catalysis of supported noble metal catalysts based on Pt, Ru, and Pd at relatively low temperature and short reaction time [21, 39–41]. The reaction network of cellulose hydrogenolysis is shown in Fig. 2.3.

Based on the progress made in cellulose hydrogenolysis, the real biomass was also used as starting materials for the production of polyols over similar catalysts used in cellulose conversion. However, researches still focus on the pure cellulose feedstocks because the real cellulose raw material contained some components that are difficult to transform or some elements that are poisonous to the catalysts. It is significant to spare additional efforts to investigate the influence of feedstocks in hydrogenolysis of cellulose.

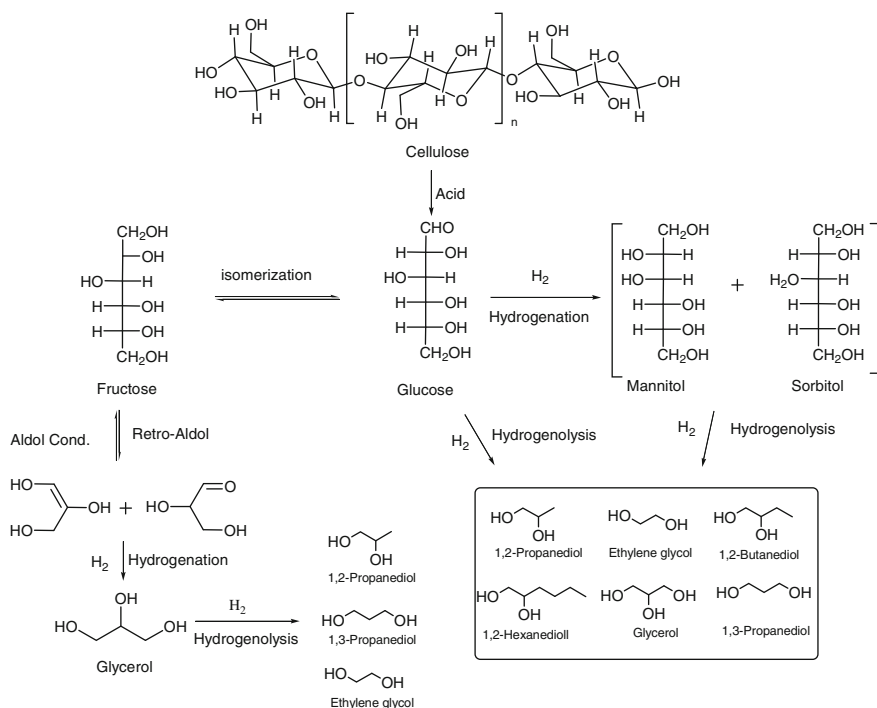


Fig. 2.3 Typical pathways for the hydrolytic hydrogenation of cellulose to glycols

Though great advances have been made in the conversion of cellulose to polyols, challenges still exist in this process. For example, both the substrate and the catalysts are presented in solid state in this reaction, resulting in difficulties for cellulose to get access to the active catalytic sites. Mass transfer between substrates and catalysts is the main difficulty in hydrogenolysis of cellulose.

2.3.2 Hydrogenolysis of Sugars and Sugar Alcohols

Glucose hydrogenation/hydrogenolysis is an important step not only in one-pot hydrogenation/hydrogenolysis of cellulose but also in cellulose utilization step by step. Study on catalytic hydrogenation and hydrogenolysis of glucose is essential for it can give an insight in the process of glycols production, thus leading us to gain insights how to coordinate the reaction rate of glucose production and rate of hydrogenation/hydrogenolysis reaction in one-pot catalytic reaction. Until now, the hydrogenolysis of sugars and sugar alcohols has been abundantly investigated. Glycols such as propanediol, EG, and butanediol can be obtained by hydrogenating sugars or sugar alcohols under the transition metal catalysts with Ni, Ru, and Pt as major active components and other catalysts via selective cracking of C–C and C–O bonds [42]. Nickel- and copper-based catalysts usually suffer from disadvantages of nickel leaching, activity deactivation, and challenges in product purification, which restricted their application. To avoid the problems, the robust noble metal catalysts were generally used for their high hydrogenation activity and high stability [43].

In the conversion of sugar alcohols to glycols, base promoters such as NaOH or $\text{Ca}(\text{OH})_2$ were always needed in hydrogenolysis of sugar alcohols because base can catalyze the C–C cleavage of dehydrogenation intermediate products. However, the use of alkali brings about problems like difficulties in recycle of the alkali. MgO , a kind of solid base was employed to support the metal of nickel to promote the hydrogenolysis of sorbitol under a relative mild condition [44]. Bimetallic catalysts promoted by solid bases were rational materials for the upgrading of sugar alcohols to lower polyols, which is under intensive study [45].

2.3.3 Hydrogenolysis of Glycerol

Glycerol is produced by hydrolysis of vegetable oil as a by-product of soap and by transesterification of oil and fats in the production of biodiesel [46, 47]. Due to the intensive interest in biofuels, the production of glycerol has increased enormously and the disposal of glycerol waste in biodiesel manufacture has limited the spread of the use of biodiesel. In this context, several ways of glycerol valorization have been described. One of the most promising ways to generate value-added products is hydrogenolysis especially 1,2-propanediol, 1,3-propanediol, and also EG (see Fig. 2.4) [48].

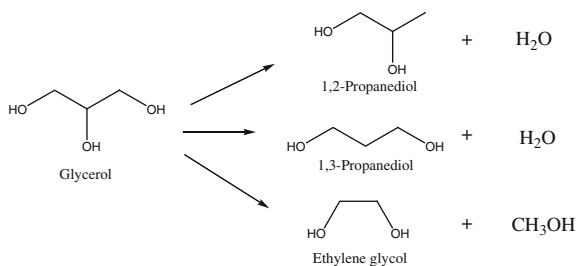


Fig. 2.4 Conversion of glycerol to 1,2-propanediol, 1,3-propanediol and ethylene glycol

The hydrogenolysis of glycerol involves the dissociation of the C–C bonds and the C–O bonds followed by hydrogen addition. C–C hydrogenolysis of glycerol generates EG. On the other hand, in the C–O hydrogenolysis, 1,2-propanediol or 1,3-propanediol could be obtained depending on the catalyst used. The general challenge in the hydrogenolysis of glycerol lies in the selective cleavage of C–O versus C–C bonds. Effective catalytic systems have been developed to selectively discriminate between C–C and C–O bonds. Cu-based catalysts were found to be selective for the formation of 1,2-propanediol with over 95 % selectivity, while with the more active Ni and noble metal based catalysts, both 1,2-propanediol and EG can be obtained due to the capability of cleaving both C–O and C–C bonds. However, the selective hydrogenolysis of the secondary hydroxyl group in the cleavage of C–O bonds is a different problem. Several catalyst systems have been described which resulted in a significant selectivity for 1,3-propanediol [48]. For example, WO_3 promoted Pt catalysts and ReO_x promoted Ir or Rh catalysts were especially effective in 1,3-propanediol formation among the reported materials.

2.4 Catalytic Synthesis of Value-Added Furanic Products from Biomass

The dehydration of pentose (xylose) and hexose (fructose or glucose) can yield furfural and 5-hydroxymethylfurfural (HMF), which are both promising intermediates to synthesize high-value products. By now, numerous works have been carried out on their conversion and a lot of value-added products have been successfully synthesized. Their detailed synthetic methods are described below.

2.4.1 Furfural Derivatives

Furfural has been produced in million tons annually all over the world from the hydrolysis of hemicellulose and subsequent dehydration of the intermediate xylose.

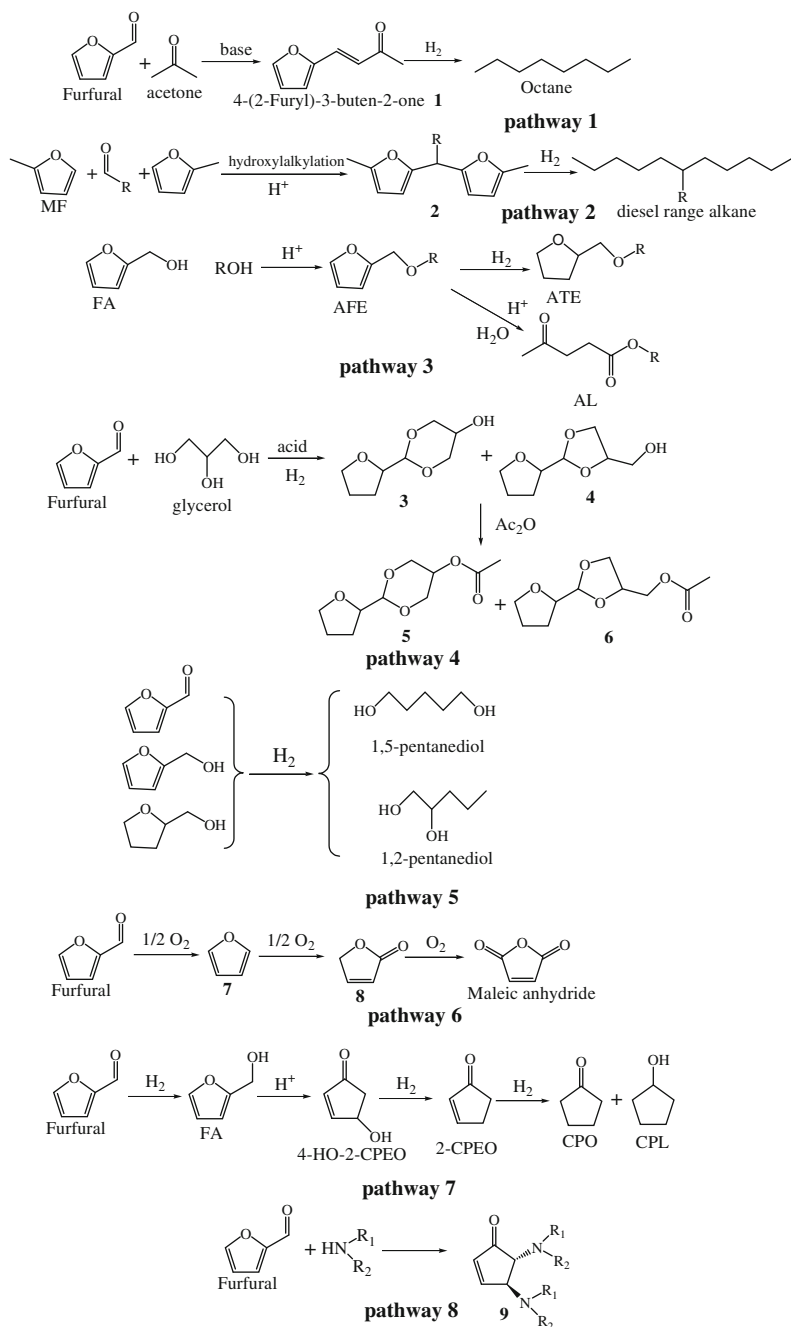
Therefore, scientists are keen to develop methods on furfural conversion for its easy availability and acceptable price. By hydrogenation, furfural can be converted into furfuryl alcohol (FA), 2-methylfuran (MF), and tetrahydrofurfuryl alcohol with their synthetic method very mature in industry [49]. Scheme 2.2 shows the compounds that have been successfully synthesized from furfural, FA and MF. Those compounds can be divided into two categories, fuels (pathways 1–4) and fine chemicals (pathways 5–8).

Due to the high polarity and instability of furfural from the presence of aldehyde group, it cannot be added directly into gasoline or diesel. Therefore, converting furfural into fuels is a process that can obtain a molecule with low polarity and long-term stability. Moreover, the octane number or cetane number of the products should be considered to meet the requirement of gasoline or diesel. Such molecules as alkane, ether, ester, and acetal have been designed and synthesized.

Base-catalyzed aldol reaction occurred between furfural and acetone to produce compound 1 (4-(2-furyl)-3-buten-2-one) as an intermediate. Subsequent hydrodeoxygenation of 1 yields octane, which is used in gasoline (pathway 1) [50]. The yield of 1 can be improved by increasing the molar ratio of acetone to furfural, aiming at avoiding the formation of difurfurylideneacetone (double aldol adduct). The Pt/NbOPO₄ catalyst was reported to achieve ca. 76 % octane yield from 1 under a mild condition, in particular, $P = 2.5$ MPa, $T = 175$ °C, and WHSV = 0.6 h⁻¹.

Through acid-catalyzed hydroxyalkylation with carbonyl-containing compounds and subsequent hydrodeoxygenation, MF was converted to a diesel-range alkane (pathway 2). Acid catalysts such as strong Brønsted inorganic, organic and solid acid can all catalyze hydroxyalkylation reaction with more than 90 % yield achieved. Hydrodeoxygenation could be realized by Pt catalyst supported on active carbon, TiO₂, SiO₂–Al₂O₃, Nb₂O₅, and ZrP [51–53].

It is notable that 6 mol of hydrogen were needed to synthesize alkanes (pathways 1 and 2) when furfural was adopted as the primary substrate. Besides, all the oxygen atoms of the reactants are removed, against the atom economy. Therefore, pathways 3 and 4 were put forward that could consume less hydrogen and keep more atoms. In pathway 3, FA first etherifies with monohydric alcohol to produce the intermediate alkyl furfuryl ether (AFE). AFE was then hydrogenated to alkyl tetrahydrofurfuryl ether (ATE), a promising cetane number improver for diesel. Further hydration of AFE can synthesize alkyl levulinate (AL) for gasoline additive. Mu et al. developed a synthetic method of methyl tetrahydrofurfuryl ether (MTE) and ethyl tetrahydrofurfuryl ether (ETE) using acidic ZSM-5 zeolite and Raney Ni catalytic system. The highest selectivity of the intermediates methyl furfuryl ether (MFE) and ethyl furfuryl ether (EFE) reaches 59 and 45 %, respectively. Nearly quantitative hydrogenation of MFE and EFE to MTE and ETE was achieved by Raney Ni catalyst⁶. However, the main drawback of MTE and ETE lies in their low flash point [54]. The one-pot conversion of FA to AL has been performed using various acidic catalysts in the corresponding alcohol solution with more than 80 % AL yield achieved [55–58].



Scheme 2.2 Reaction pathways for the conversion of furfural

Glycerol is the by-product yielded during the production of biodiesel. Expanded use of biodiesel will generate large amount of glycerol [59]. The pathway 4 presents a way of utilizing both furfural and glycerol in fuel production. The acetal reaction of glycerol with furfural and subsequent hydrogenation produced compounds 3 and 4. To further reduce the polarity of the final products, the hydroxyl group in 3 and 4 reacts with acetic anhydride to produce compounds 5 and 6. In the acetal reaction, ZnCl_2 was proved to be the best choice from the pool of Lewis acids with 90 % of acetal products obtained. The solid acids aluminosilica MCM-41 ($\text{Al} = 3\%$) and montmorillonite K-10 clay could achieve around 80 % acetal yield. Hydrogenation of the furan ring can be carried out using Pd/C catalyst. Acetylation of the free hydroxyl group was performed by combining 3 and 4 with two equivalents each of acetic anhydride and triethylamine [60]. Although the targeted products 5 and 6 showed no problems with solubility, cloud point, density and flash point in diesel, the more significant parameter cetane number was not investigated.

Furfural contains five carbon atoms and two oxygen atoms. Hydrogenation of furfural and its downstream products FA and tetrahydrofurfuryl alcohol (THFA) produces 1,2-pentanediol (1,2-PeD) or 1,5-pentanediol (1,5-PeD) depending on the substrate and catalyst employed (pathway 5). The Ru/ MnO_x catalyst was reported to hydrogenate FA to 1,2-PeD in aqueous solution with 42.1 % yield achieved [61]. The hydrotalcite-supported Pt nanoparticles (Pt/HT) was capable of achieving 73 % yield of 1,2-PeD from furfural in isopropanol [62]. No work has been reported to hydrogenate tetrahydrofurfuryl alcohol into 1,2-PeD. With respect to 1,5-PeD, the Pd–Ir– $\text{ReO}_x/\text{SiO}_2$ catalyst showed good performance from furfural obtaining the maximum yield of 71.4 % [63]. The Pt/ Co_2AlO_4 catalyst prepared by co-precipitation method was able to achieve 35 % 1,5-PeD yield from FA [64]. The most efficient way of preparing 1,5-PeD is by hydrogenating tetrahydrofurfuryl alcohol. More than 90 % 1,5-PeD selectivity could be obtained using Rh– MoO_x , Ir– MoO_x , Rh– ReO_x , and Ir– ReO_x supported on SiO_2 or carbon [65–69]. Recently, we developed a highly efficient and green catalytic system comprising MoO_3 and a supported Rh catalyst for the hydrogenolysis of THFA with 1,5-PeD selectivity up to 80 % is achieved [70]. Moreover, a very interesting phase-transfer behavior for MoO_3 during the reaction was observed with the assistance of different characterization techniques. In this process, MoO_3 dissolves partially in the liquid phase under the reaction conditions and is transformed into the soluble hydrogen molybdenum oxide bronzes (H_xMoO_3) in the presence of H_2 , which are recognized as the genuinely active sites for the secondary C–O bond breaking of THFA. The furan ring and aldehyde group of furfural were both sensitive to oxygenation. Oxygenation of furfural yields maleic anhydride (MA) using $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts (pathway 6). The highest selectivity to MA reached 73 % [71].

Copper and nickel supported on Co_3O_4 and ZrO_2 prepared by co-precipitation or sol-gel method can catalyze hydrogenation of FA into cyclopentanone (CPO) and cyclopentanol (CPL) as main products in aqueous solution [72]. Possible mechanism is presented in Scheme 2.2 pathway 7.

Erbium (III) chloride [73] in ethyl lactate is used for the reaction of furfural and amines at room temperature to yield diastereoselectively differently N,N-substituted

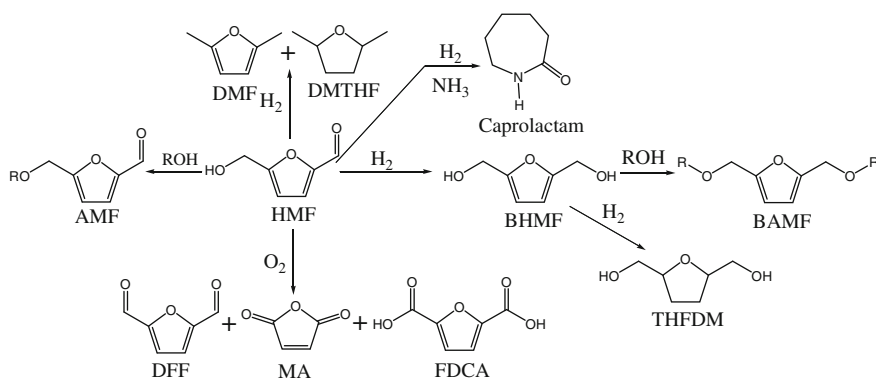
trans-4,5-diaminocyclopent-2-enones as versatile synthetic intermediates to the formation of densely functionalized derivatives as shown in pathway 8.

2.4.2 HMF Derivatives

Different from furfural, there are two substituents in the furan ring of HMF, aldehyde, and hydroxymethyl, which are both active during hydrogenation or oxygenation. Hence, HMF is considered to be more valuable than furfural especially in the synthesis of polymer monomer [74]. Scheme 2.3 shows some value-added products that have been synthesized from HMF. They can be divided into two categories. One is fuel and the other is monomer.

As HMF itself is highly polar, oxygen-rich, and non-volatile, it is necessary to lower the polarity and the boiling point to obtain liquid fuels or fuel additives. By hydrogenation, HMF can be converted into 2,5-dimethyl-furan (DMF) and 2,5-dimethyl-tetrahydrofuran (DMTHF), which possess both a high octane number and high energy content to replace gasoline directly [75–81]. Dumesic et al. developed a CuRu/C catalyst that could in situ hydrogenate HMF produced in a water/1-butanol biphasic system into DMF [76]. The neat HMF can be converted into DMF using most of the precious metal catalysts such as Pd, Pt, Ru, and Rh supported on active carbon [79]. In the case of HMF conversion to DMTHF, RhCl_3 in aqueous solution can be used as catalyst to in situ hydrogenate HMF from fructose dehydration into DMTHF with more than 80 % DMTHF yield achieved [81].

The processes to DMF and DMTHF consume 3 and 5 mol of hydrogen, respectively, and remove two oxygen atoms in HMF, which are not favorable from the viewpoint of atom economy. Therefore, work was carried out on the conversion of HMF into 2,5-bis-alkoxymethylfurans (BAMF), which could consume less hydrogen and retain more mass than those of DMF and DMTHF [82, 83].



Scheme 2.3 Reaction pathways for the conversion of HMF

As shown in Scheme 2.3, such a process needs hydrogenation and etherification catalysts. Mu et al. employed a low-cost supported Cu/SiO₂ catalyst in the efficient hydrogenation of HMF into 2,5-bis-hydroxymethylfuran (BHMF) and acidic ZSM-5 zeolite in the etherification of BHMF with methanol. In their work, 97 % BHMF and 70 % 2,5-bis-methoxymethyl-furan (BMMF) yield could be achieved. The high cetane number of 80 (much higher than that of the commercial diesel), high flash point (90 °C), and low cold filter plugging point (<−37 °C) make BMMF a good candidate for diesel [83]. Although direct etherification of HMF with monohydric alcohol can produce 5-alkyloxymethyl furfural (AMF), the presence of aldehyde group in AMF makes its stability and solubility in diesel limited. Furthermore, its cetane number has not been measured [84].

The monomer production from HMF can be carried out by hydrogenation, oxygenation, or hydrogenation and subsequent amination. The hydrogenation of HMF can produce BHMF and 2,5-bis-hydroxymethyltetrahydrofuran (THFDM) [83, 85]. Except the aforementioned Cu/SiO₂ catalyst, Pt or PtSn supported on active carbon or Al₂O₃ demonstrated good performance in hydrogenation to BHMF [82]. Nearly quantitative hydrogenation of HMF to THFDM can be realized by Raney Ni catalyst [85].

Oxygenation of HMF can synthesize three products using different catalysts. The Cu(NO₃)₂/VOSO₄ catalyst was reported to selectively oxidize the hydroxymethyl to aldehyde with 99 % 2,5-di-formylfuran (DFF) yield achieved only at room temperature [86]. Besides, Fe₃O₄/Mn₃O₄ and V₂O₅/C also exhibited high selectivity in HMF oxygenation to DFF [87]. Deeper oxygenation of HMF to 2,5-furandicarboxylic acid (FDCA) was performed typically using supported platinum catalysts with the aid of homogeneous base, resulting in near quantitative FDCA yield [88]. Gorbanev et al. demonstrated that Au/TiO₂ could oxidize HMF into FDCA in 71 % yield. At near room temperature [89], Casanova et al. showed that Au/CeO₂ was more active and selective [90]. However, these catalysts require addition of homogeneous base (1–20 equiv. NaOH) and high oxygen pressure (10–20 bar). Navneet et al. reported a base-free oxidative system using hydrotalcite-supported gold nanoparticle catalyst [91].

Using vanadium compounds, the furan ring of HMF can be further oxidized to MA. About 30–50 % yields of MA were obtained using VO(acac)₂, VO(pic)₂ [bis (pyridine-2-carboxylato) oxovanadium (IV)], VO(mal)₂ [bis (maltolato) oxovanadium (IV)], and VOSO₄ catalysts [92].

Vries et al. developed a route that could convert HMF into caprolactone, which needed four steps with THFDM, 1,2,6-hexanetriol (1,2,6-HT), 1,6-hexanediol (1,6-HD) as the intermediates. Caprolactone was considered to be the intermediate of caprolactam, the monomer for nylon-6, a widely used polymer [85].

It should be noted that although HMF may be converted into a lot of high-value compounds, the bottlenecks that hinder the industrial application of those products is the availability of HMF in large scale. The price of HMF precursor fructose is too high. In addition, the high boiling point and high polarity of HMF make it difficult to be separated from the reaction system.

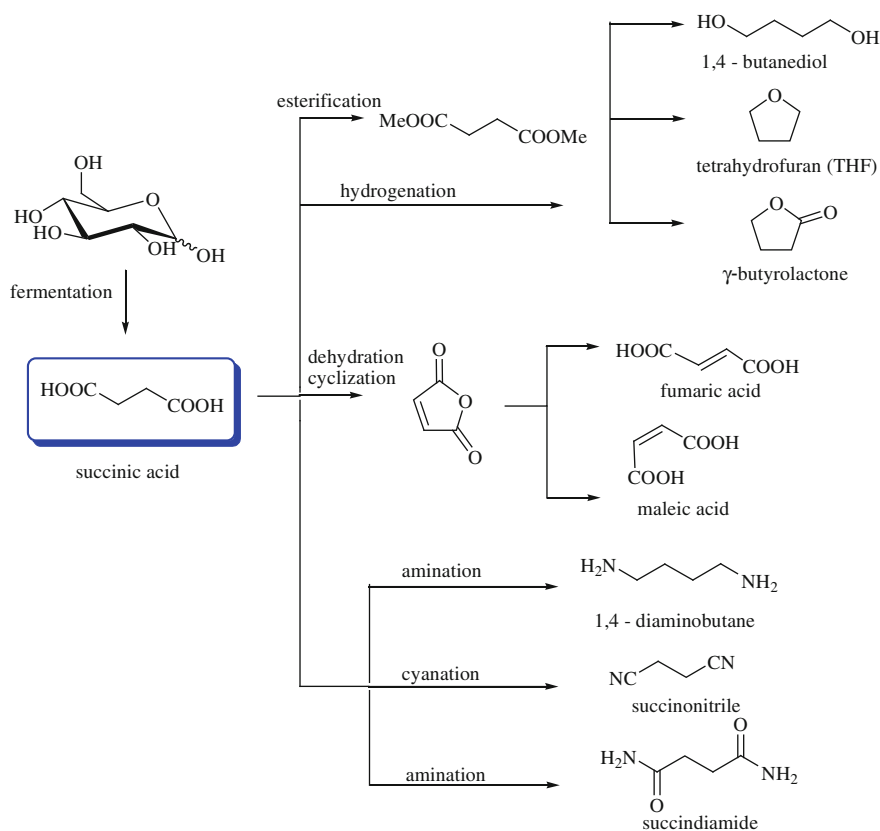
2.5 Catalytic Conversion of Biological Fermentation Products into Value-Added Chemicals

A core part of modern biotechnology is the modern fermentation engineering like genetic engineering. The fermentation products can be used in drug, cosmetics, food, and other chemical industries. Biotechnology itself as a hot research field has significant advantages: high selectivity in the biological fermentation; high conversion efficiency, mild reaction conditions. However, the existing biological conversion technology based on microbes and enzymes has its inherent limitations, such as the enzyme specificity, serious environmental pollution, and expensive equipments. The problems greatly limit the large-scale application of biological technology. Chemical catalytic conversion can realize flexible product structures. With breakthroughs in bio-fermentation technology and reduction in the production costs, succinic acid, lactic acid (LA), itaconic acid (IA), etc., have become a cheap and abundant supply of raw material products [93–95]. Selective conversion of biogenic carboxylic acids has become an important biorefinery transformation concept based on platform chemicals. With the development of science and technology, the combination of biological technology and chemical conversion technology to produce chemical products would be gradually applied into industrial productions.

2.5.1 Succinic Acid

Succinic acid (SA, $C_4H_6O_4$) [96] produced from fermentation anaerobically with bacteria from glucose and CO_2 has been identified as one of the most important platform chemicals according to the US Department of Energy (DOE) Report in 2004 [97]. As a C_4 -dicarboxylic acid, succinic acid could be converted into some key building blocks in chemical markets and industries via hydrogenation, dehydration, esterification, amination, and cyanation reactions (Scheme 2.4) [98]. The hydrogenation of succinic acid will be discussed in details.

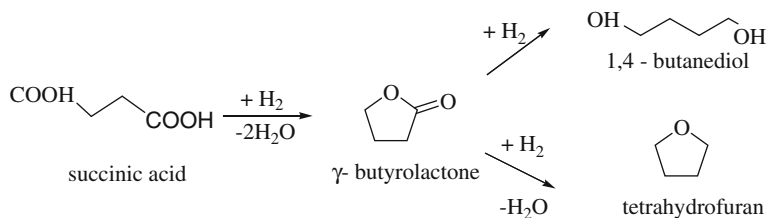
Ruthenium-based catalyst was considered as an efficient catalyst for the hydrogenation of succinic acid [99–101]. A series of important chemical products including 1,4-butanediol (BDO), tetrahydrofuran (THF), and γ -butyrolactone (GBL) could be obtained via direct hydrogenation of SA or diethyl succinate [101, 102]. BDO is an important raw material for the production of polyesters and polyurethanes. GBL could be used to produce THF, N-methyl-2-pyrrolidone (NMP), and 2-pyrrolidone. THF as an important chemical was widely used as solvent or chemical intermediate in the production of polyvinyl chloride (PVC) and paints. It was usually obtained from fossil fuels, including the dehydration of 1,4-butanediol (BDO), hydrogenation of maleic anhydride (MAN), hydrogenation of SA or diethyl succinate. The product distribution in the hydrogenation of SA is varied with different catalysts and experimental conditions. In order to obtain the



Scheme 2.4 Succinic acid as a platform chemical [94]

above chemicals more effectively, it is important to understand the hydrogenation mechanism of succinic acid. A simple reaction pathway for the hydrogenation of succinic acid was shown in Scheme 2.5 [103].

As early as 1988, DuPont Company has applied a patent for making butyrolactones, butanediols, and mixtures thereof by hydrogenating maleic acid, fumaric



Scheme 2.5 Reaction pathway for the hydrogenation of succinic acid

acid, succinic acid, IA, or mixtures thereof over palladium or combinations with rhenium using at least one support selected from the oxides of titanium, zirconium, and hafnium [104]. Piero Frediani et al. [99] studied the hydrogenation of γ -butyrolactone, succinic and fumaric acid into 1,4-butanediol with the homogeneous catalytic system $[\text{Ru}(\text{acac})_3]/\text{triphos}$ [$\text{triphos}:\text{MeC}(\text{CH}_2\text{PPh}_2)_3$]. A 96 % yield and 100 % isotopomeric selectivity of 1,4-butanediol were achieved under mild reaction conditions. In order to simplify the separation process of the products, researches committed to finding heterogeneous catalyst replacing homogeneous catalytic system. Many studies focused on finding suitable support materials for ruthenium-based catalysts. Palladium-mesoporous alumina (Pd-AX) catalysts prepared by Song et al. via sol-gel method were first used in the liquid-phase hydrogenation of SA to GBL [103]. The yield for GBL increased with increasing the acid density of Pd-AX catalysts. Lee and co-workers examined the effect of different mesoporous supports (MCM-41 and SBA-15) impregnated by palladium solutions on the product distributions for the hydrogenation of SA [105]. With the same preparation and reaction process, Pd/MCM-41 catalyst favorably produced BDO, while the Pd/SBA-15 catalyst preferred to produce cyclic compounds THF and GBL. The HRTEM results indicated that for MCM-41, larger Pd particles were located on the outside of the pore channels predominantly; for SBA-15, smaller Pd particles preferred to incorporate to the inside channels while the larger particles located on the mesopores. Besson examined the effect of 2 wt% Pd/TiO₂ catalysts for the hydrogenation of SA in aqueous phase, and titania support showed better stability than other support materials under hydrothermal conditions [106].

Nowadays, carbon is usually selected as support materials for its controllable porosity, non-toxicity, interactive functions at the surface, and hydrophobic property [107]. Song et al. introduced ruthenium-mesoporous carbon composite (Ru-XC) catalysts, which was prepared by an incipient wetness impregnation method into this system [102]. They found that ruthenium dispersion played a key role in determining the catalytic performance in the hydrogenation of succinic acid. Ruthenium particle size depended on the HCl solution concentration during the RuCl₃ impregnation process. THF yield in the hydrogenation of SA increased with decreasing average ruthenium particle size.

Ru-mesoporous carbon catalyst served as an efficient and reusable catalyst in the hydrogenation of succinic acid to GBL. Petitjean et al. studied the effect of addition of Re to Pd/C and Ru/C catalysts over the hydrogenation of 15 wt% SA aqueous solutions to BDO [108]. By addition of 4 % Re to 2 % Pd/C and 2 % Ru/C, the selectivity of BDO increased from 44 and 49 %, to 62 and 66 % at 180 °C and 150 bar H₂, respectively. Liang's group also confirmed the results above [109]. In the following studies, X-ray diffraction and TEM results illustrated that Re and Cu metals which were introduced into the carbon support step by step could improve the ruthenium dispersion significantly [110]. Re/Cu-MC catalyst showed a better catalytic activity than Re/Cu/MC catalyst in the liquid-phase hydrogenation of succinic acid to BDO. In the real reaction process, all the reactions are reversible [111], there are still some other by-products including butyric acid, propionic acid and butanol.

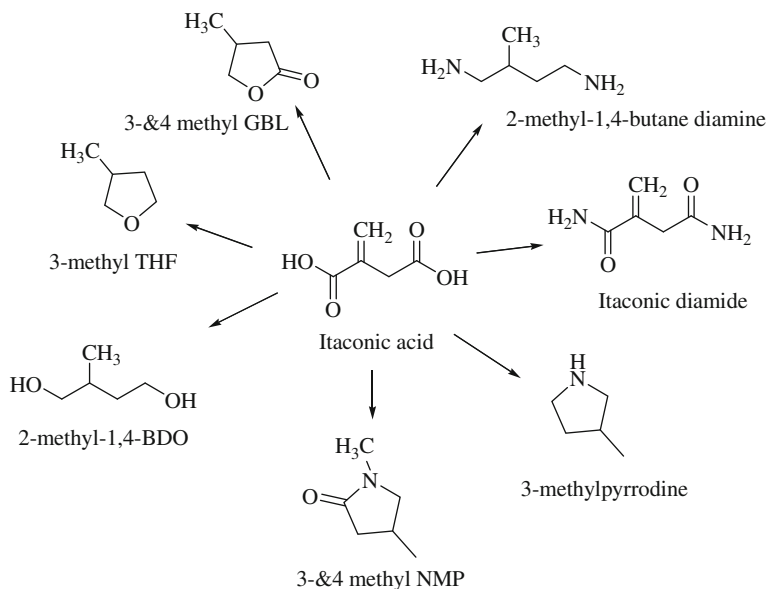
Mu et al. have also carried out the hydrogenation of SA to BDO over Pd/C catalysts. By the addition of iron, the size of Pd particles and the iron dispersion on carbon support were improved effectively. The yield and selectivity of BDO were further changed. Fan et al. have developed a new gold-catalyzed aqueous hydrogenation protocol with syngas as hydrogen source [112]. The conversion of SA reached 100 % and the selectivity of GBL reached 99 % with Au/*m*-ZrO₂ (Au 0.2 mol%) and syngas (4 MPa, H₂/CO = 2:1) at 180 °C for 6 h. Furthermore, the catalyst could also be readily adapted to IA hydrogenation.

However, there are still some problems in expanding this chemical catalytic system: harsh reaction conditions, higher reaction temperature, excess hydrogen, high cost of precious metals. Using soluble mineral acids one can realize the fast esterification of succinic acid, but it would lead to hazardous waste and complex separation process. Traditional heterogeneous solid acid catalysts including acidic zeolites, metal oxide, sulfated zirconia, heteropoly acids or resins were also considered, but the above catalysts could not keep stable in water. Hu et al. reported the esterification of valeric acid over amino acid ionic liquids catalysts. A 99.9 % yield of ethyl valerate with 100 % selectivity was obtained after 7 h at 80 °C and the catalysts kept activities after 5 recycles [113]. To resolve the catalyst stability problems, we speculate that acidic ionic liquids may help a lot in future. Furthermore, in order to obtain special products selectively, some theoretical studies about the catalytic mechanism would be considered.

2.5.2 Itaconic Acid

IA [114], also called methylene succinic acid, was firstly produced from citric acid in 1837 via dehydration reaction at high temperature. It was widely used as an important precursor to synthesis pharmaceuticals, resins, adhesives, plasticizers, coatings, deodorants, herbicides, and surfactants [115–117]. IA has conjugated double bonds and two carboxyl groups according to its structure which can be used as co-monomer with acrylamide or self-polymerized to polyitaconic acid (PIA) [115]. It could also be esterified to a series of itaconate esters using $\text{Ln} \sim \text{SO}_4^{2-}/\text{TiO}_2\text{--SiO}_2$ catalysts [118] (Scheme 2.6). Many researches paid attention to the enantioselective hydrogenation of IA. Bartvk et al. carried out a detailed study on the enantioselective hydrogenation of IA over cinchona alkaloid modified supported Pd catalyst in presence of benzylamine with the ee values up to 58 % [119].

More than 80 % of IA was converted to 2-methylbutanediol (MeBDO) and methyl- γ -butyrolactone (MeGBL) over a 1 % Pd and 4 % Re on titanium oxide catalyst in the itaconic hydrogenation according to DuPont Company's patent. BASF Aktiengesellschaft's invention in 2001 found that 100 % of IA could be hydrogenated to 45.2 % of MeBDO and 47.9 % of MeGBL in the presence of a catalyst comprising Pt and Re [120]. In order to prolong the life of catalyst, many itaconate esters were synthesized firstly, then, researchers tested the catalytic



Scheme 2.6 Itaconic acid as a platform chemical

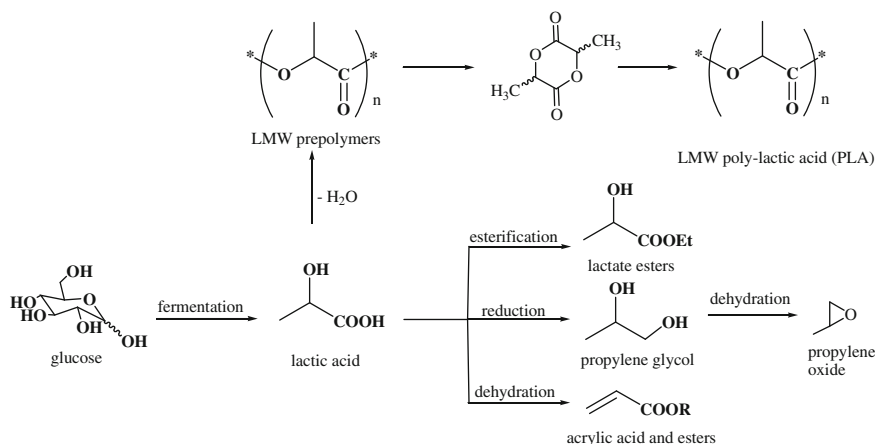
hydrogenation activity of itaconate esters over Cu–Cr–Mn–Ba or Cu₂O–ZnO composite catalysts on a fixed bed. The conversion of itaconates reached 100 % [121].

A theoretical study about the selective homogeneous hydrogenation of biogenic carboxylic acids supposed that for $[\text{Ru}(\text{TriPhos})\text{H}]^+$ as the catalytically active unit, the energetic spans for the reduction of the different functional groups follows the order: lactone \approx carboxylic acid $>$ ketone $>$ aldehyde [122]. Mu and co-workers have studied the aqueous-phase hydrogenation of biomass-derived IA to methyl- γ -butyrolactone over Pd/C catalysts. They found that the pretreatments of active carbon with concentrated nitric acid and sodium hypochlorite solution changed the properties of the carbon, and the best catalyst showed complete conversion with 89.5 % total selectivity to MeGBL [123].

Besides, decarboxylation reactions of IA were carried out with solid Pd/Al₂O₃, Pt/Al₂O₃, Pd/C, and Ru/C catalysts. The isolation of methacrylic acid reached up to 50% yield with high selectivity of 84% [124].

2.5.3 Lactic Acid

LA is one of the important biomass-derived platform chemicals, which could be industrially produced by fermentation of sugars on medium-size scale. The production is nearing 260,000 tons per year. As a platform molecule with hydroxyl group and carboxyl group, some important chemicals could be produced via



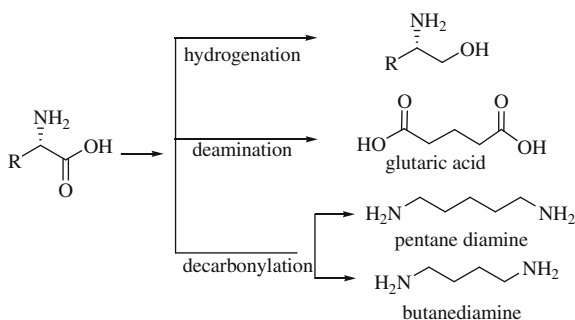
Scheme 2.7 Overview of lactic acid conversions

selective esterification, reduction, or dehydration reactions (Scheme 2.7). The chemicals were usually used as green solvents, fuel precursors, and commodity chemicals [125].

Burns et al. firstly used LA as raw material to produce acrylic acid (AA) in 1935 [126], and this was followed by Fisher and co-workers in the 1940s [127] and a patent led in 1949 by Atwood [128]. Holmen reported the one-step conversion of LA into acrylic acid via direct dehydration over $\text{CaSO}_4/\text{Na}_2\text{SO}_4$ heterogeneous catalyst, and 68 % yield of AA was obtained at 400 °C [129]. From then, NaX and NaY zeolites [130], $\text{Ca}_3(\text{PO}_4)_2\text{-Ca}_2(\text{P}_2\text{O}_7)$ [131] catalyst and NaY zeolites modified with alkali phosphates [132] have been introduced into this system.

1,2-propanediol (PeD) is a promising precursor for building unsaturated polyester resins [133]. The reduction of LA to PeD is very difficult because of the low reactivity of the carboxyl group, so that the screening of catalysts was of great importance. Ru catalysts including RuO_2 [134], Ru/C [135], $\text{MgO-NH}_2\text{-Ru}$ [136], $\text{Ru-Sn-B}/\gamma\text{-Al}_2\text{O}_3$ [137] and Ru/TiO_2 [138] for the aqueous-phase hydrogenation of LA were thoroughly studied. Dumesic et al. reported that a 88 % yield of PG was achieved at full LA conversion over a 10 wt% Cu/SiO_2 catalyst at 200 °C with a partial H_2 pressure of 0.72 MPa. The catalyst kept stable during its 22 days on stream [139]. 10 wt% Co/SiO_2 catalyst also performed good activity in the hydrogenation of ethyl lactate [140].

Poly-lactic acid (PLA) obtained from direct polycondensation of LA has numerous applications from industrial to clothes and biocompatible materials for medical application [141, 142]. The direct polycondensation yield was quite low, and therefore lactide from intramolecular esterification process was primarily separated. Then high molecular weight PLA was produced via ring-opening polymerization (ROP) of lactide. However, mainly tin-based homogeneous catalysts worked in intramolecular esterification which could not be recycled. Few studies about heterogeneous catalysts were reported [143].

Scheme 2.8 Catalytic conversion of amino acids

2.5.4 Amino Acid

As essential building blocks of proteins, amino acids could be produced in high volume from glucose via fermentation. They are important intermediates in metabolism [144] and widely applied in agriculture, medicine and industry fields [145, 146]. Aminoalcohols especially for chiral aminoalcohols are of important chiral auxiliaries to prepare pharmaceuticals or insecticidal reagents [147]. Direct hydrogenation of amino acids with hydrogen was considered as the most promising method (Scheme 2.8), and Ru/C, Ru-Re, Pd/C, and Pt/C hydrogenation catalysts were brought to this system appropriately. However, the above catalysts usually need high temperature with low activity and loss of optical purity. Tomishige et al. [144] reported selective aqueous hydrogenation of amino acids to amino alcohols with Rh-MoO_x/SiO₂ catalyst. The catalyst activity and the selectivity and ee for the product were enhanced after the modification of Rh with MoO_x.

As important precursors to synthesis polymers, glutaric acid could be prepared via deamination of glutamic acid and pentamethylene diamine via decarbonylation theoretically (Scheme 2.8). However, pentamethylene diamine was usually obtained from biological decarboxylation of 1,5-diaminopentane over lysine decarboxylase. Butanediamine was prepared similarly. Reports about the catalytic conversion of amino acid are still very limited.

2.6 Summary

So far, biomass is the only renewable carbon resources that can be converted into chemicals and liquid fuels. The global issues such as greenhouse effect and the shortage of energy can be eventually solved by the rational utilization of biomass resources. Owing to the ideal carbon skeleton and oxygen content in biomass and biomass-derived compounds, the endeavor in the industrialized catalytic transformation of biomass into high value-added chemicals via more environmentally friendly approaches would pave the way for the future chemical manufacture.

To selectively produce liquid hydrocarbon fuels, it requires oxygen removal reactions (i.e., dehydration, hydrogenolysis, hydrogenation, decarbonylation/decarboxylation, etc.) and in some cases in combination with the adjustment of the molecular weight via C–C coupling reactions (e.g. aldol condensation, ketonization, oligomerization) of reactive intermediates. In this context, the development of a new family of highly active and selective catalyst systems is an essential prerequisite for chemoselective catalytic conversion of lignocellulosic biomass into desired products.

References

1. Chheda JN, Huber GW, Dumesic JA (2007) Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew Chem Int Ed* 46:7164–7183
2. Petrus L, Noordermeer MA (2006) Biomass to biofuels, a chemical perspective. *Green Chem* 8:861–867
3. Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 106:4044–4098
4. Cortright RC, Davda RR, Dumesic JA (2002) Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 418:964–967
5. Mascal M, Nikitin EB (2008) Direct high-yield conversion of cellulose into biofuel. *Angew Chem Int Ed* 47:7924–7926
6. Binder JB, Raines RT (2009) Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *J Am Chem Soc* 131:1979–1985
7. Himmel ME, Ding SY, Johnson DK, Adney WS, Nimlos MR, Brady JW, Foust TD (2007) Biomass recalcitrance: engineering plants and enzymes for biomass production. *Science* 315:804–807
8. Deguchi S, Tsujii K, Horikoshi K (2008) Effect of acid catalyst on structural transformation and hydrolysis of cellulose in hydrothermal conditions. *Green Chem* 10:623–626
9. Kontturi E, Vuorinen T (2009) Indirect evidence of supramolecular changes within cellulose microfibrils of chemical pulp fibers upon drying. *Cellulose* 16:65–74
10. vom Stein T, Grande P, Sibilla F, Commandeur U, Fischer R, Leitner W, de Maria PD (2010) Salt-assisted organic-acid-catalyzed depolymerization of cellulose. *Green Chem* 12:1844–1849
11. Zhang M, Qi W, Liu R, Su R, Wu SM, He Z (2010) Fractionating lignocellulose by formic acid: characterization of major components. *Biomass Bioenerg* 34:525–532
12. Zhang YHP, Himmel ME, Mielenz JR (2006) Outlook for cellulase improvement: screening and selectio strategies. *Biotechnol Adv* 24:452–481
13. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Dissolution and hydrolysis of cellulose in subcritical and supercritical wate. *Ind Eng Chem Res* 39:2883–2890
14. Jiang Y, Li X, Cao Q, Mu X (2011) Acid functionalized, highly dispersed carbonaceous spheres: an effective solid acid for hydrolysis of polysaccharides. *J Nanopart Res* 13:463–469
15. Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M (2008) Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups. *J Am Chem Soc* 130:12787–12793
16. Onda A, Ochi T, Yanagisawa K (2008) Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem* 10:1033–1037
17. Takagaki A, Tagusagawa C, Domen K (2008) Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst. *Chem Commun* 5363–5365

18. Dhepe PL, Sahu R (2010) A solid-acid-based process for the conversion of hemicellulose. *Green Chem* 12:2153–2156
19. Gebboers J, Van de Vyver S, Carpentier K, Jacobs P, Sels B (2011) Efficient hydrolytic hydrogenation of cellulose in the presence of Ru-loaded zeolites and trace amounts of mineral acid. *Chem Commun* 47:5590–5592
20. Ogaki Y, Shinozuka Y, Hara T, Ichikuni N, Shimazu S (2011) Hemicellulose decomposition and saccharides production from various plant biomass by sulfonated allophane catalyst. *Catal Today* 164:415–418
21. Palkovits R, Tajvidi K, Ruppert AM, Procelewska J (2011) Heteropoly acids as efficient acid catalysts in the one-step conversion of cellulose to sugar alcohols. *Chem Commun* 47:576–578
22. Shimizu K, Furukawa H, Kobayashi N, Itaya Y, Satsuma A (2009) Effects of Brønsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose. *Green Chem* 11:1627–1632
23. Tian J, Wang J, Zhao S, Jiang C, Zhang X, Wang X (2010) Hydrolysis of cellulose by the heteropoly acid $H_3PW_{12}O_{40}$. *Cellulose* 17:587–594
24. Jiang Y, Li X, Wang X, Meng L, Wang H, Wang L, Wang X, Mu X (2012) Effective saccharification of lignocellulosic biomass over hydrolysis residue derived solid acid under microwave irradiation. *Green Chem* 14:2162–2167
25. Li X, Jiang Y, Shuai L, Wang L, Meng L, Mu X (2012) Sulfonated copolymers with SO_3H and $COOH$ groups for the hydrolysis of polysaccharides. *J Mater Chem* 22:1283–1289
26. Li X, Jiang Y, Wang L, Meng L, Wang W, Mu X (2012) Effective low-temperature hydrolysis of cellulose catalyzed by concentrated $H_3PW_{12}O_{40}$ under microwave irradiation. *RSC Adv* 2:6921–6925
27. Sheldon RA (2014) Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem* 16:950–953
28. Besson M, Gallezot P, Pinel C (2014) Conversion of biomass into chemicals over metal catalysts. *Chem Rev* 114:1827–1870
29. Olah GA (2013) Towards oil independence through renewable methanol chemistry. *Angew Chem Int Ed* 52:104–107
30. Ruppert AM, Weinberg K, Palkovits R (2012) Hydrogenolysis goes bio: from carbohydrates and sugar alcohols to platform chemicals. *Angew Chem Int Ed* 51:2564–2601
31. Wang A, Zhang T (2013) One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts. *Acc Chem Res* 46:1377–1386
32. Fukuoka A, Dhepe PL (2006) Catalytic conversion of cellulose into sugar alcohols. *Angew Chem Int Ed* 45:5161–5163
33. Luo C, Wang S, Liu H (2007) Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. *Angew Chem Int Ed* 46:7636–7639
34. Ji N, Zhagn T, Zheng MY, Wang AQ, Wang H, Wang XD, Chen JG (2008) Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. *Angew Chem Int Ed* 47:8510–8513
35. Liu Y, Luo C, Liu H (2012) Tungsten trioxide promoted selective conversion of cellulose into propylene glycol and ethylene glycol on a ruthenium catalyst. *Angew Chem Int Ed* 51:3249–3253
36. Wang XC, Meng LQ, Wu F, Jiang YJ, Wang L, Mu XD (2012) Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts. *Green Chem* 14:758–765
37. Wang XC, Wu F, Yao SX, Jiang YJ, Guan J, Mu XD (2012) Ni-Cu/ZnO-catalyzed hydrogenolysis of cellulose for the production of 1,2-alkanediols in hot compressed water. *Chem Lett* 41:476–478
38. Xiao ZH, Jin SH, Pang M, Liang CH (2013) Conversion of highly concentrated cellulose to 1,2-propanediol and ethylene glycol over highly efficient CuCr catalysts. *Green Chem* 15:891–895

39. Zhang J, Wu SB, Liu Y (2014) Direct conversion of cellulose into sorbitol over a magnetic catalyst in an extremely low concentration acid system. *Energ Fuel* 28:4242–4246
40. Palkovits R, Tajvidi K, Procelewska J, Rinaldi R, Ruppert A (2010) Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts. *Green Chem* 12:972–978
41. Geboers J, de Vyver SV, Carpentier K, de Blochouse K, Jacobs P, Sels B (2010) Efficient catalytic conversion of concentrated cellulose feeds to hexitols with heteropoly acids and Ru on carbon. *Chem Commun* 46:3577–3579
42. ten Dam J, Hanefeld U (2011) Renewable chemicals: dehydroxylation of glycerol and polyols. *ChemSusChem* 4:1017–1034
43. Sun J, Liu H (2011) Selective hydrogenolysis of biomass-derived xylitol to ethylene glycol and propylene glycol on supported Ru catalysts. *Green Chem* 13:135–142
44. Chen X, Wang X, Yao S, Mu X (2013) Hydrogenolysis of biomass-derived sorbitol to glycols and glycerol over Ni-MgO catalysts. *Catal Commun* 39:86–89
45. Alonso DM, Wettstein SG, Dumesic JA (2012) Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem Soc Rev* 41:8075–8098
46. Zhu S, Qiu Y, Zhu Y, Hao S, Zheng H, Li Y (2013) Hydrogenolysis of glycerol to 1,3-propanediol over bifunctional catalysts containing Pt and heteropolyacids. *Catal Today* 212:120–126
47. Zhou CH, Beltramini JN, Fan YX, Lu GQ (2008) Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem Soc Rev* 37:527–549
48. Nakagawa Y, Tamura M, Tomishige K (2014) Catalytic materials for the hydrogenolysis of glycerol to 1,3-propanediol. *J Mater Chem A* 2:6688–6702
49. Lange JP, Heide E, Buijtenen J, Price R (2012) Furfural-A promising platform for lignocellulosic biofuels. *ChemSusChem* 5:150–166
50. Xu WJ, Xia QN, Zhang Y, Guo Y, Wang YQ, Lu GZ (2011) Effective production of octane from biomass derivatives under mild conditions. *ChemSusChem* 4:1758–1761
51. Corma A, Torre O, Renz M (2011) High-quality diesel from hexose- and pentose-derived biomass platform molecules. *ChemSusChem* 4:1574–1577
52. Corma A, Torre O, Renz M, Villandier N (2011) Production of high-quality diesel from biomass waste products. *Angew Chem Int Ed* 50:2375–2378
53. Li GY, Li N, Wang ZQ, Li CZ, Wang AQ, Wang XD, Cong Y, Zhang T (2012) Synthesis of high-quality diesel with furfural and 2-methylfuran from hemicellulose. *ChemSusChem* 5:1958–1966
54. Cao Q, Guan J, Peng GM, Zhou JW, Mu XD (2015) Solid acid-catalyzed conversion of furfuryl alcohol to alkyl tetrahydrofurfuryl ether. *Catal Commun* 58:76–79
55. Zhang ZH, Dong K, Zhao ZB (2011) Efficient conversion of furfuryl alcohol into alkyl levulinates catalyzed by an organic–inorganic hybrid solid acid catalyst. *ChemSusChem* 4:112–118
56. Maldonado GMG, Assary RS, Dumesic JA, Curtiss LA (2012) Acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in liquid ethanol. *Energ Environ Sci* 5:8990–8997
57. Hengne AM, Kamble SB, Rode CV (2013) Single pot conversion of furfuryl alcohol to levulinic esters and γ -valerolactone in the presence of sulfonic acid functionalized ILs and metal catalysts. *Green Chem* 15:2540–2547
58. Neves P, Antunes MM, Russo PA, Abrantes JP, Lima S, Fernandes A, Pillinger M, Rocha SM, Ribeiro MF, Valente AA (2013) Production of biomass-derived furanic ethers and levulinate esters using heterogeneous acid catalysts. *Green Chem* 15:3367–3376
59. García J, García-Marín H, Pires E (2014) Glycerol based solvents: synthesis, properties and applications. *Green Chem* 16:1007–1033
60. Wegenhart BL, Liu S, Thom M, Stanley D, Abu-Omar MM (2012) Solvent-free methods for making acetals derived from glycerol and furfural and their use as a biodiesel fuel component. *ACS Catal* 2:2524–2530
61. Zhang B, Zhu YL, Ding GQ, Zheng HY, Li YW (2012) Selective conversion of furfuryl alcohol to 1,2-pentanediol over a Ru/MnO_x catalyst. *Green Chem* 14:3402–3409

62. Mizugaki T, Yamakawa T, Nagatsu Y, Maeno Z, Mitsudome T, Jitsukawa K, Kaneda K (2014) Direct transformation of furfural to 1,2-pentanediol using a hydrotalcite-supported platinum nanoparticle catalyst. *ACS Sus Chem Eng* 2:2243–2247
63. Liu SB, Amada Y, Tamura M, Nakagawa Y, Tomishige K (2014) One-pot selective conversion of furfural into 1,5-pentanediol over a Pd-added Ir–ReO_x/SiO₂ bifunctional catalyst. *Green Chem* 16:617–626
64. Xu WJ, Wang HF, Liu XH, Ren JW, Wang YQ, Lu GZ (2011) Direct catalytic conversion of furfural to 1,5-pentanediol by hydrogenolysis of the furan ring under mild conditions over Pt/Co₂AlO₄ catalyst. *Chem Commun* 47:3924–3926
65. Koso S, Furikado I, Shimao A, Miyazawa T, Kunimori K, Tomishige K (2009) Chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol. *Chem Commun* 15:2035–2037
66. Chia M, Pagan-Torres YJ, Hibbitts D, Tan QH, Pham HN, Datye AK, Neurock M, Davis RJ, Dumesic JA (2011) Selective hydrogenolysis of polyols and cyclic ethers over bifunctional surface sites on rhodium-rhenium catalysts. *J Am Chem Soc* 133:12675–12689
67. Koso S, Ueda N, Shinmi Y, Okumura K, Kizuka T, Tomishige K (2009) Promoting effect of Mo on the hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol over Rh/SiO₂. *J Catal* 267:89–92
68. Pholjaroen B, Li N, Huang YQ, Li L, Wang AQ, Zhang T (2015) Selective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol over vanadium modified Ir/SiO₂ catalyst. *Catal Today* 245:93–99
69. Nakagawa Y, Tomishige K (2012) Production of 1,5-pentanediol from biomass via furfural and tetrahydrofurfuryl alcohol. *Catal Today* 195:136–143
70. Guan J, Peng GM, Cao Q, Mu XD (2014) Role of MoO₃ on a rhodium catalyst in the selective hydrogenolysis of biomass-derived tetrahydrofurfuryl alcohol into 1,5-pentanediol. *J Phys Chem C* 118:25555–25566
71. Alonso-Fagfíldez N, Granados ML, Mariscal R, Ojeda M (2012) Selective conversion of furfural to maleic anhydride and furan with VO_x/Al₂O₃ catalysts. *ChemSusChem* 5:1984–1990
72. Li XL, Deng J, Shi J, Pan T, Yu CG, Xu HJ, Fu Y (2015) Selective conversion of furfural to cyclopentanone or cyclopentanol using different preparation methods of Cu–Co catalysts. *Green Chem* 17:1038–1046
73. Procopio A, Costanzo P, Curini M, Nardi M, Oliverio M, Sindona G (2013) Erbium(III) chloride in ethyl lactate as a smart ecofriendly system for efficient and rapid stereoselective synthesis of trans-4,5-diaminocyclopent-2-enones. *ACS Sus Chem Eng* 1:541–544
74. Saha B, Abu-Omar MM (2013) Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents. *Green Chem* 16:24–38
75. Thananathanachon T, Rauchfuss TB (2010) Efficient production of the liquid fuel 2,5-dimethylfuran from fructose using formic acid as a reagent. *Angew Chem Int Ed* 122:6766–6768
76. Ráman-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA (2007) Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* 447:982–985
77. Nishimura S, Ikeda N, Ebitani K (2014) Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported PdAu bimetallic catalyst. *Catal Today* 232:89–98
78. Chidambaram M, Bell AT (2010) A two-step approach for the catalytic conversion of glucose to 2,5-dimethylfuran in ionic liquids. *Green Chem* 12:1253–1262
79. Chatterjee M, Ishizaka T, Kawanami H (2014) Hydrogenation of 5-hydroxymethylfurfural in supercritical carbon dioxide–water: a tunable approach to dimethylfuran selectivity. *Green Chem* 16:1543–1551
80. Partenheimer W, Grushin VV (2001) Synthesis of 2,5-diformylfuran and furan-2,5-dicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural. Unexpectedly selective aerobic oxidation of benzyl alcohol to benzaldehyde with metal/bromide catalysts. *Adv Synth Catal* 343:102–111

81. Yang WR, Sen A (2010) One-step catalytic transformation of carbohydrates and cellulosic biomass to 2,5-dimethyltetrahydrofuran for liquid fuels. *ChemSusChem* 3:597–603
82. Balakrishnan M, Sacia ER, Bell AT (2012) Etherification and reductive etherification of 5-(hydroxymethyl)furfural: 5-(alkoxymethyl)furfurals and 2,5-bis(alkoxymethyl)furans as potential bio-diesel candidates. *Green Chem* 14:1626–1634
83. Cao Q, Liang WY, Guan J, Wang L, Qu Q, Zhang XZ, Wang XC, Mu XD (2014) Catalytic synthesis of 2,5-bis-methoxymethylfuran: A promising cetane number improver for diesel. *Appl Catal A* 481:49–53
84. Lanzafame P, Temi DM, Perathoner S, Centi G, Macario A, Aloise A, Giordano G (2011) Etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol to biodiesel components using mesoporous solid acidic catalysts. *Catal Today* 175:435–441
85. Buntara T, Noel S, Phua PH, Melin-Cabrera I, Vries JG, Heeres HJ (2011) Caprolactam from renewable resources: catalytic conversion of 5-hydroxymethylfurfural into caprolactone. *Angew Chem Int Ed* 50:7083–7087
86. Ma JP, Du ZT, Xu J, Chu QH, Pang Y (2011) Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran, and synthesis of a fluorescent material. *ChemSusChem* 4:51–54
87. Liu B, Zhang ZH, Lv KL, Deng KJ, Duan HM (2014) Efficient aerobic oxidation of biomass-derived 5-hydroxymethylfurfural to 2,5-diformylfuran catalyzed by magnetic nanoparticle supported manganese oxide. *Appl Catal A* 472:64–71
88. Lilga MA, Hallen RT, Gray M (2010) Production of oxidized derivatives of 5-hydroxymethylfurfural (HMF). *Top Catal* 53:1264–1269
89. Gorbanev YY, Klitgaard SK, Woodley JM, Christensen CH, Riisager A (2009) Gold-catalyzed aerobic oxidation of 5-hydroxymethylfurfural in water at ambient temperature. *ChemSusChem* 2:672–675
90. Casanova O, Iborra S, Corma A (2009) Biomass into chemicals: one pot-base free oxidative esterification of 5-hydroxymethyl-2-furfural into 2,5-dimethylfuroate with gold on nanoparticulated ceria. *J Catal* 265:109–116
91. Gupta NK, Nishimura S, Takagaki A, Ebitani K (2011) Hydrotalcite-supported gold-nanoparticle-catalyzed highly efficient base-free aqueous oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid under atmospheric oxygen pressure. *Green Chem* 13:824–827
92. Du ZT, Ma JP, Wang F, Liu JX, Xu J (2011) Oxidation of 5-hydroxymethylfurfural to maleic anhydride with molecular oxygen. *Green Chem* 13:554–557
93. Geilen FMA, Engendahl B, Harwardt A, Marquardt W, Klankermayer J, Leitner W (2010) Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system. *Angew Chem Int Ed* 49:5510–5514
94. Werpy T, Petersen G (2004) Top value added chemicals from biomass, Volume I: results of screening for potential candidates from sugars and synthesis gas. DOE/GO-102004-1992
95. Bozell JJ, Petersen GR (2010) Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. *Green Chem* 12:9–554
96. Bechthold I, Bretz K, Kabasci S, Kopitzky R, Springer A (2008) Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chem Eng Technol* 31:647–654
97. Cok B, Tsiropoulos I, Roes AL, Patel MK (2014) Succinic acid production derived from carbohydrates: an energy and greenhouse gas assessment of a platform chemical toward a bio-based economy. *Biofuel Bioprod Bioref* 8:16–29
98. Willke Th, Vorlop K-D (2004) Industrial bioconversion of renewable resources as an alternative to conventional chemistry. *Appl Microbiol Biotechnol* 66:131–142
99. Rosi L, Frediani M, Frediani P (2010) Isotopomeric diols by "one-pot" Ru-catalyzed homogeneous hydrogenation of dicarboxylic acids. *J Org Chem* 69:1314–1322

100. Luque R, Clark JH, Yoshida K, Gai PL (2009) Efficient aqueous hydrogenation of biomass platform molecules using supported metal nanoparticles on Starbons®. *Chem Commun* 35:5303–5307
101. Hong UG, Park HW, Lee JJ (2012) Hydrogenation of succinic acid to γ -butyrolactone (GBL) over ruthenium catalyst supported on surfactant-templated mesoporous carbon. *J Ind Eng Chem* 18:462–468
102. Hong UG, Kim JK, Lee J, Lee JK, Song JH, Yi J, Song IK (2014) Hydrogenation of succinic acid to tetrahydrofuran (THF) over ruthenium–carbon composite (Ru–C) catalyst. *Appl Catal A* 469:466–471
103. Hong UG, Lee JK, Hwang S, Song IK (2011) Hydrogenation of succinic acid to γ -butyrolactone (GBL) over palladium catalyst supported on alumina xerogel: effect of acid density of the catalyst. *Catal Lett* 141:332–338
104. Rao VNM, Del W (1988) Process for preparing butyrolactones and butanediols. US4782167 A
105. Chung S-H, Park Y-M, Kim M-S, Lee K-Y (2012) The effect of textural properties on the hydrogenation of succinic acid using palladium incorporated mesoporous supports. *Catal Today* 185:205–210
106. Tapin B, Epron F, Especel C, Ly BK, Pinel C, Besson M (2013) Study of monometallic Pd/TiO₂ catalysts for the hydrogenation of succinic acid in aqueous phase. *ACS Catal* 3:2327–2335
107. Liang CD, Li ZJ, Dai S (2008) Mesoporous carbon materials: synthesis and modification. *Angew Chem Int Ed* 47:3696–3717
108. Minh DP, Besson M, Pinel C, Fuertes P, Petitjean C (2010) Aqueous-phase hydrogenation of biomass-based succinic acid to 1,4-butanediol over supported bimetallic catalysts. *Top Catal* 53:1270–1273
109. Shao ZF, Li C, Di X, Xiao ZH, Liang CH (2014) Aqueous-phase hydrogenation of succinic acid to γ -butyrolactone and tetrahydrofuran over Pd/C, Re/C, and Pd–Re/C Catalysts. *Ind Eng Chem Res* 53:9638–9645
110. Hong UG, Park HW, Lee J, Hwang S, Kwak J, Yi J, Song I (2013) Hydrogenation of succinic acid to 1,4-butanediol over rhenium catalyst supported on copper-containing mesoporous carbon. *J Nanosci Nanotechnol* 13:7448–7453
111. Zhang B, Zhu Y, Ding G, Zheng H, Li Y (2012) Modification of the supported Cu/SiO₂ catalyst by alkaline earth metals in the selective conversion of 1,4-butanediol to gamma-butyrolactone. *Appl Catal A* 443–444:191–201
112. Yu L, Du X-L, Yuan J, Liu Y-M, Cao Y, He H-Y, Fan K-N (2013) A versatile aqueous reduction of bio-based carboxylic acids using syngas as a hydrogen source. *ChemSusChem* 6:42–46
113. Dong L-L, He L, Tao G-H, Hu C-W (2013) High yield of ethyl valerate from the esterification of renewable valeric acid catalyzed by amino acid ionic liquids RSC Adv 3:4806–4813
114. Klement T, Büchs J (2013) Itaconic acid—a biotechnological process in change. *Bioresour Technol* 135:422–431
115. Willke T, Vorlop KD (2001) Biotechnological production of itaconic acid. *Appl Microbiol Biotechnol* 56:289–295
116. Levinson WE, Kurtzman CP, Kuo TM (2006) Production of itaconic acid by *Pseudozyma antarctica* NRRL Y-7808 under nitrogen-limited growth conditions. *Enzyme Microb Technol* 39:824–827
117. Zhang XX, Ma F, Lee DJ (2009) Recovery of itaconic acid from supersaturated waste fermentation liquor. *J Taiwan Inst Chem E* 40:583–585
118. Li L, Liu S, Xu J, Yu S, Liu F, Xie C, Ge X, Ren J (2013) Esterification of itaconic acid using Ln ~ SO₄²⁻/TiO₂–SiO₂ (Ln = La³⁺, Ce⁴⁺, Sm³⁺) as catalysts. *J Mol Catal A* 368–369:24–30
119. Szöllösi G, Balázsik K, Bartók M (2007) Enantioselective hydrogenation of itaconic acid over cinchona alkaloid modified supported palladium catalyst. *Appl Catal A* 319:193–201

120. Fischer R, Pinkos R, Wulff-Döring J (2001) Method for producing aliphatic alcohols. US6204417 B1
121. Xu X, Zhao Y (2010) Method for the hydrogenation of Itaconic acid. CN101781169 A
122. Geilen FMA, Engendahl B, Hölscher M, Klankermayer J, Leitner W (2011) Selective homogeneous hydrogenation of biogenic carboxylic acids with $[\text{Ru}(\text{TriPhos})\text{H}]^+$: a mechanistic study. *J Am Chem Soc* 133:14349–14358
123. Li S, Wang XC, Liu XR, Xu GQ, Han S, Mu XD (2015) Aqueous-phase hydrogenation of biomass-derived itaconic acid to methyl- γ -butyrolactone over Pd/C catalysts: effect of pretreatments of active carbon. *Catal Comm* 61:92–96
124. Le Nôtre J, Witte-van Dijk SCM, van Haveren J, Scott EL, Sanders JPM (2014) Synthesis of bio-based methacrylic acid by decarboxylation of itaconic acid and citric acid catalyzed by solid transition-metal catalysts. *ChemSusChem* 7:2712–2720
125. Martinez FAC, Balciunas EM, Salgado JM, González JMD, Converti A, de Souza Oliveira RP (2013) Lactic acid properties, applications and production: a review. *Trends Food Sci Technol* 30:70–83
126. Burns R, Jones DT, Ritchie PD (1935) Studies in pyrolysis: Part I. The pyrolysis of derivatives of alpha-acetoxy propionic acid and related substances. *J Chem Soc* 400–406
127. Ratchford WP, Fisher CH (1945) Methyl acrylate by pyrolysis of methyl acetoxypropionate. *Ind Eng Chem* 37:38–387
128. Atwood FC (1949) Process of making alkyl acrylates. US Pat 2464364
129. Holmen RE (1958) Acrylates by catalytic dehydration of lactic acid and lactates. US Pat 2859240
130. Abe T, Hieda S (1990) EP Pat 0379691
131. Hong J-H, Lee J-M, Kim H-R, Hwang Y-K, Chang J-S, Halligudi SB, Han Y-H (2011) Efficient and selective conversion of methyl lactate to acrylic acid using $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}_2(\text{P}_2\text{O}_7)$ composite catalysts. *Appl Catal A* 396:194–200
132. Zhang J, Zhao Y, Pan M, Feng X, Ji W, Au C-T (2011) Efficient acrylic acid production through bio lactic acid dehydration over NaY zeolite modified by alkali phosphates. *ACS Catal* 1:32–41
133. Krämer H (2000) Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verlag-GmbH & Co, KGaA
134. Antons S (1998) Process for the preparation of optically active alcohols. US Pat 5731479
135. Zhang Z, Jackson JE, Miller DJ (2001) Aqueous-phase hydrogenation of lactic acid to propylene glycol. *Appl Catal A* 219:89–98
136. Mao B-W, Cai Z-Z, Huang M-Y, Jiang Y-Y (2003) Hydrogenation of carboxylic acids catalyzed by magnesia-supported poly- γ -aminopropylsiloxane-Ru complex. *Polym Adv Technol* 14:278–281
137. Luo G, Yan S, Qiao M, Zhuang J, Fan K (2004) Effect of tin on Ru-B/ γ - Al_2O_3 catalyst for the hydrogenation of ethyl lactate to 1,2-propanediol. *Appl Catal A* 275:95–102
138. Primo A, Concepcion P, Corma A (2011) Synergy between the metal nanoparticles and the support for the hydrogenation of functionalized carboxylic acids to diols on Ru/TiO₂. *Chem Commun* 47:3613–3615
139. Cortright RD, Sanchez-Castillo M, Dumesic JA (2002) Conversion of biomass to 1,2-propanediol by selective catalytic hydrogenation of lactic acid over silica-supported copper. *Appl Catal B* 39:353–359
140. Huang L, Zhu Y, Zheng H, Du M, Li Y (2008) Vapor-phase hydrogenolysis of biomass-derived lactate to 1,2-propanediol over supported metal catalysts. *Appl Catal A* 349:204–211
141. Takasu A, Narukawa Y, Hirabayashi T (2006) Direct dehydration polycondensation of lactic acid catalyzed by water-stable Lewis acids. *J Polym Sci, Part A: Polym Chem* 44:5247–5253
142. Kim KW, Woo SI (2002) Synthesis of high-molecular-weight poly (L-lactic acid) by direct polycondensation. *Macromol Chem Phys* 203:2245–2250
143. Upare PP, Hwang YK, Chang J-S, Hwang DW (2012) Synthesis of lactide from alkyl lactate via a prepolymer route. *Ind Eng Chem Res* 51:4837–4842

144. Tamura M, Tamura R, Takeda Y, Nakagawa Y, Tomishige K (2014) Catalytic hydrogenation of amino acids to amino alcohols with complete retention of configuration. *Chem Commun* 50:6656–6659
145. Casalino M, Latella MC, Prosseda G (2005) Molecular evolution of the lysine decarboxylase-defective phenotype in *Shigella sonnei*. *Int J Medical Microbiol* 294:503–512
146. Kiyohiko N, Shuichi E, Yukiko M (2003) Enzymatic method for producing cadaverine dicarboxylate and its use for the production of nylon: Japan, 147688
147. Ager DJ, Prakash I, Schaad DR (1996) 1,2-Amino alcohols and their heterocyclic derivatives as chiral auxiliaries in asymmetric synthesis. *Chem Rev* 96:835–876

Sustainable Production of Bulk Chemicals
Integration of Bio-□Chemo- Resources and Processes

Xian, M. (Ed.)

2015, VII, 154 p. 69 illus. in color., Hardcover

ISBN: 978-94-017-7473-4