

# Chapter 1

## Fundamentals of Bifunctional Catalysis for Transforming Biomass-Related Compounds into Chemicals and Biofuels

Hu Li, Xiao Kong, Zhen Fang, and Richard L. Smith Jr.

**Abstract** Multi-step catalytic processes are generally required in chemoselective conversion of biomass derivatives into chemical products. Integration of different types of transformations into a single catalytic system with a bifunctional catalyst can be used to improve reaction efficiency, enhance product selectivity and to promote specific reaction pathways. In this chapter, the fundamentals of bifunctional catalysis are introduced to understand some of the specific roles in designing catalytic materials for biomass transformations. Acid-mediated hydrolysis of polysaccharides to mono- and oligosaccharides in combination with successive isomerization is one of the effective strategies for valorization of sugar-containing solutions, wherein the type of acid catalyst (i.e., Lewis and Brønsted acids) can be used to control product distribution. Catalytic production and upgrading of furanic compounds (e.g., 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, and 2,5-dimethylfuran) with bifunctional materials via corresponding tandem reaction pathways is another effective strategy. Emphasis can be placed on the synthesis of organic acids (e.g., levulinic acid and lactic acid) from carbohydrates through either anaerobic or aerobic oxidation, integrated with preprocessing reactions. This chapter provides an overview of bifunctional catalytic systems and a perspective outlook on bifunctional catalytic pathways for biomass transformations.

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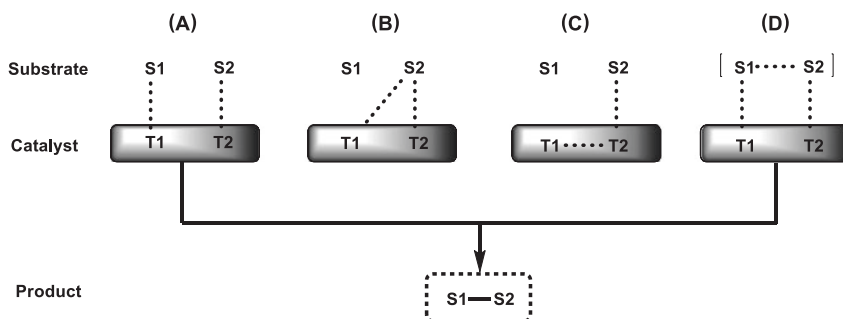
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## 1.1 Bifunctional Catalysis

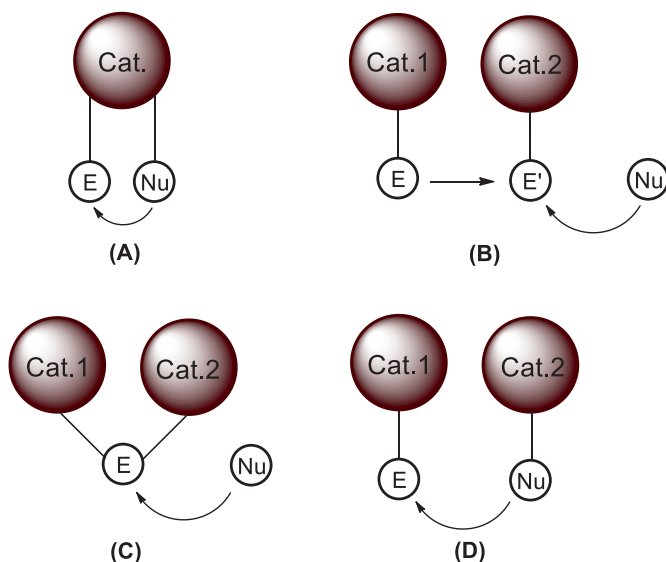
In comparison with monofunctional catalytic systems, bifunctional catalysts with Brønsted/Lewis acid, acid-base, or metal-containing acid/base sites have been demonstrated to exhibit remarkably high performance in both gas-phase (e.g., syn-gas to hydrocarbons or alcohols) and liquid-phase (e.g., aqueous-organic) conversions [1–7]. Bifunctional catalysis may be in use, more commonly than is generally recognized, because a certain number of monofunctional catalysts are most likely bifunctional in nature [8]. For instance, the surfaces of transition metal oxides (e.g.,  $\text{MoO}_2$  and  $\text{Cr}_2\text{O}_3$ ) have been found to possess both types of hydrogenation-dehydrogenation and acidic sites, implying that the apparently single-site catalysts possibly have bifunctional activities, in spite of their relatively lower activity than their tailor-designed two-site counterparts [8].

To mimic enzymatic catalysts, materials can be designed with functionalities (e.g., metal centers, basic and acidic sites, nucleophiles, hydrogen bond donors/accepter groups) that are spatially organized around active sites to promote efficient transformations [9]. Some reported heterogeneous catalysts have unprecedented performance unattainable with homogeneous catalysts [9]. Typically, the cooperation between the active sites or groups (T1/T2 as in Fig. 1.1) of a bifunctional material surface in catalyzing a reaction with two substrates (S1/S2 as in Fig. 1.1) can be divided into four different modes (Fig. 1.1) that possibly include dual activation (A), sequential activation (B), self activation (C), and multiple point transition state stabilization (D) [9, 10]. All of these strategies have been adopted as references for the design of synthetic catalysts that are able to take full advantage of multifunctional cooperation in catalytic processes [9].

From the point of view of organic chemistry, bifunctional catalysis is defined as both nucleo- and electrophilic substrates being separately activated by discrete active sites present on a single catalytic material (Fig. 1.2a) [11]. In line with bifunctional catalysis, both cascade and double activation catalysis may be present,



**Fig. 1.1** Cooperative modes between active sites or groups (T1/T2) of a bifunctional catalyst in the activation of two substrates (S1/S2) (Adapted with permission from Ref. [9], Copyright © 2008 Royal Society of Chemistry) (A) Dual activation, (B) Sequential activation, (C) Self activation, (D) Multiple point transition state stabilization

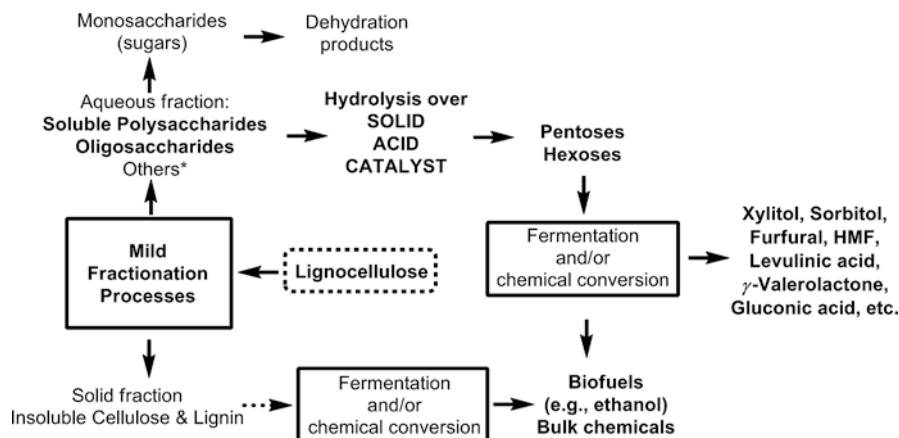


**Fig. 1.2** Schematic representation of bifunctional catalysis (Adapted with permission from Ref. [11], Copyright © 2014 Royal Society of Chemistry) (A) Bifunctional catalysis, (B) Cascade catalysis, (C) Double activation catalysis, (D) Synergistic catalysis

wherein two or more catalysts activate the identical substrate sequentially or in a concerted manner, respectively (Fig. 1.2 b–c). On the contrary, the nucleo- and electrophilic substrates may be concurrently activated by two or multiple separate catalysts such that synergistic catalysis occurs (Fig. 1.2d). In this chapter, acid-participated bifunctional catalytic hydrolysis of polysaccharides to mono- and oligosaccharides will be introduced. The key step of glucose isomerization involved in the valorization of sugar-containing solutions mediated by dual functional groups is depicted. Further, discussion is made on application of the techniques to the production of biofuranic platform molecules (e.g., 5-hydroxymethylfurfural and furfural) and the upgrading of these compounds to oxygenated and hydrogenated furans (e.g., 2,5-furandicarboxylic acid and 2,5-dimethylfuran) tandem reaction pathways. Finally, the synthesis of organic acids (e.g., levulinic acid and lactic acid) from carbohydrates is introduced through either anaerobic or aerobic oxidation via bifunctional catalysis.

## 1.2 Hydrolysis of Oligo- and Polysaccharides

Simple sugars hydrolyzed from biomass over chemical and enzymatic catalysts have been used to study the production of liquid/gas fuels (e.g., ethanol, butanol, hydrogen, and methane) or formation of chemical products (e.g., organic acids, furanic/aromatic compounds, and polyols), as illustrated in Fig. 1.3 [12, 13]. In the



**Fig. 1.3** Schematic representation of a catalytic strategy for biomass upgrading (Adapted with permission from Ref. [12], Copyright © 2012, Elsevier)

conversion of oligo- and polysaccharides (e.g., cellobiose and cellulose) into monosaccharides such as glucose via hydrolysis, homogeneous chemical catalysts generally show good activity, but they require harsh reaction conditions ( $> 180\text{ }^{\circ}\text{C}$ ), and have recycle and waste treatment issues especially for when mineral acids (e.g.,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$ ) are used. Enzymes, on the other hand, have good selectivity but are generally inefficient, expensive and are susceptible to impurities [14]. In this regard, the use of solid acids or supported catalysts that are stable and recoverable could address the issues inherent in both homogeneous catalysts and enzyme catalysts to promote hydrolysis reactions that are selective and efficient that can be performed at mild conditions without environmental wastes.

### 1.2.1 Brønsted/Lewis Acid Bifunctional Solid Catalysts

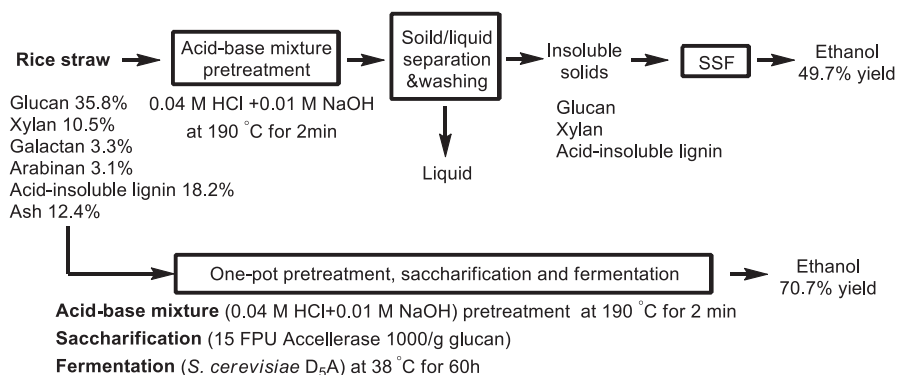
In the organosolv process, Schwiderski et al. [15] demonstrated that a Lewis acid  $\text{AlCl}_3$  was able to catalyze both ketol-endiol-tautomerism and dehydration to produce furfural from beech wood chips, showing comparable and even superior activity to that of a Brønsted acid such as  $\text{HCl}$  [15]. For both Lewis and Brønsted acid sites, the increase in acidity was found to be favorable for the cleavage of  $\beta$ -1,4-glycosidic bonds in cellobiose and in cellulose, thus enhancing their hydrolysis [16]. Typically, the distribution of Brønsted and Lewis acid sites on mixed metal oxides can be adjusted by simply changing the molar ratio of metal species or calcination temperature of the catalyst. In an in-depth study on the role of  $\text{WO}_x$  clusters in  $\text{WO}_3/\text{ZrO}_2$  catalysts, it was observed that a high  $\text{WO}_x$  loading resulted in an increase in the number of Brønsted acid sites, and prevailed over the number of Lewis acid sites of  $\text{ZrO}_2$  even at calcination temperatures greater than  $700\text{ }^{\circ}\text{C}$  [17].

One type of commercially available Brønsted/Lewis acid bifunctionalized catalysts is the H-form zeolites that show moderate activity and stability for hydrolysis of hemicellulose and cellulose. H-form zeolites forms that have relatively higher acidic (e.g., ferrierite) and hydrophobic sites with high Si/Al ratios have superior performance to others for hydrolysis of carbohydrates [18, 19]. With these types of catalysts, the polymerization of monosaccharides (e.g., glucose) to humins with zeolites is significantly inhibited, which possibly can be attributed to shape-selectivity, in comparison with other solid and homogeneous acids (e.g., sulphated zirconia and heteropoly acids) [20]. Over H-USY-15 (Si/Al = 15) in water, a moderate yield of xylose and arabinose (56%) with >90% carbon balance is obtained from hemicellulose at 170 °C in 1 h [21], while the sulfonated H-USY zeolite gives improved yields (ca. 78%) at 140 °C after 9 h [22]. These results highlight the effect of Brønsted acid sites and the importance of Lewis acid sites. Meso- and macropores created on zeolites by dealumination (e.g., treated with oxalic acid) promote the accessibility of the acid sites to the reactants, thus improving the mass transfer, with the yield of total reduced sugars increasing by tenfold [23]. Under microwave heating conditions, the hydrolysis of cellulose to glucose gives moderate yields (ca. 37%) over H-form zeolites, but only requires reaction times on the order of minutes (e.g., 8 min) [24]. The integration of bifunctional catalytic materials with auxiliaries such as microwave and ultrasound offers yet another approach to improve reaction efficiency.

As a biomass-derived polymer that has aromatic monomeric units rather than glucose monomeric units, the hydrolytic degradation of lignin into aromatic monomers can also be achieved with well-designed solid acid catalysts based on zeolites [25]. For example, H-USY affords 60% yields of monomeric aromatics from lignin at 250 °C, further demonstrating the potential of Brønsted/Lewis acid bifunctional solids (particularly zeolites) for conversion of biomass-related compounds into small components or fractions.

### 1.2.2 Base-Acid Bifunctional Solid Catalysts

The pretreatment of biomass with base (e.g., Ca(OH)<sub>2</sub>, NaOH and KOH) can be used to remove lignin at ambient to 100 °C temperatures, while the remaining polysaccharides can be hydrolyzed with acidic or enzymatic catalysts [26]. In an improved process, Chandel et al. found that crude lignocelluloses (e.g., sugarcane bagasse) consecutively pretreated with dilute H<sub>2</sub>SO<sub>4</sub> and NaOH could surmount the structural recalcitrance of the biomass, thus enhancing subsequent cellulase accessibility and hydrolysis efficiency for ethanol production [27]. Likewise, an acid-base mixture can be employed to simplify the catalytic steps for one-pot production of cellulosic ethanol, without solid/liquid separation, neutralization and detoxification (Fig. 1.4) [28]. This process integrates acid-base catalyzed hydrolysis of cellulose and subsequent fermentation of ethanol with *in situ* produced cellulase into a single step. Gratifyingly, the yield of ethanol reached 70.7% from the fermentation



**Fig. 1.4** Schematic pathway for integrated processing of rice straw with acid-base pretreatment/enzyme catalysis to produce ethanol (Adapted with permission from Ref. [28], Copyright © 2014 Royal Society of Chemistry)

of the whole rice straw slurry after 60 h, which was relatively higher than that (49.7% yield) obtained by simultaneous saccharification and fermentation (SSF) of washed solids of pretreated rice straw (Fig. 1.4) [28]. These results demonstrate both the advantages of an integrated process in the production of ethanol from rice straw.

The activation of hydrotalcite (HT) with  $\text{Ca}(\text{OH})_2$  simultaneously increases its basicity and acidity from 0.42 and 0.21 mmol/g to 1.76 and 1.17 mmol/g, as measured by  $\text{CO}_2$ - and  $\text{NH}_3$ -TPD, respectively [29]. The resulting  $\text{HT-OH}_{\text{Ca}}$  catalyst shows a greatly enhanced glucose yield (39.8%) and selectivity (85.3%) in the hydrolysis of ball-milled cellulose, as compared with pristine HT (11.0% yield and 40.6% selectivity),  $\text{Ca}(\text{OH})_2$  (10.6% yield and 39.8% selectivity) and reference experiments without a catalyst (0.4% yield and 3.5% selectivity) at 150 °C in 24 h (Table 1.1). The  $\text{HT-OH}_{\text{Ca}}$  catalyst was able to be recycled for at least four times (sequentially reused catalysts denoted as  $\text{HT-OH}_{\text{Ca}2}$ ,  $\text{HT-OH}_{\text{Ca}3}$  and  $\text{HT-OH}_{\text{Ca}4}$ ), with glucose yield and selectivity slightly decreasing to 35.0% and 80.5%, respectively (Table 1.1, entries 5–7) [29]. In addition,  $\text{Ba}(\text{OH})_2$ , KOH and NaOH-activated HTs were found to show moderate glucose selectivities and yields (Table 1.1, entries 8–10), further confirming that the catalyst performance was positively correlated with the content of both acid and base sites.

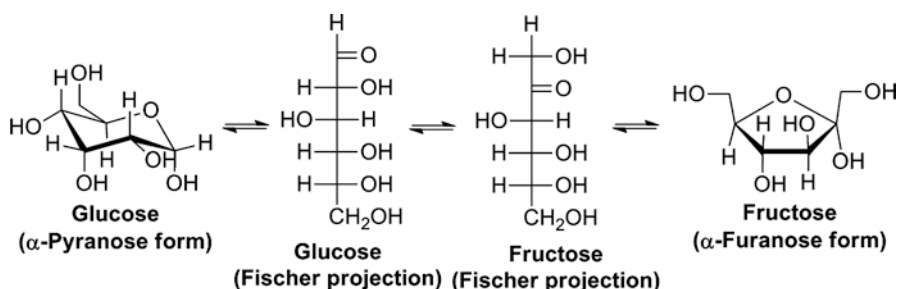
### 1.3 Sugar Isomerization

Enzymes (e.g., glucose isomerase) are commonly active for the isomeric conversion of simple monosaccharides. The stability of an enzyme can be increased by immobilization onto solid supports such as silica or chitosan [30, 31]. Solid basic and acidic chemocatalysts that have comparable reactivity as their homogeneous counterparts and which have favorable reaction times and recycle characteristics have

**Table 1.1** Hydrolysis of cellulose in water with hydrotalcite (HT) and Ca(OH)<sub>2</sub>activated HT (HT-OH<sub>Ca</sub>) or other activated HT forms

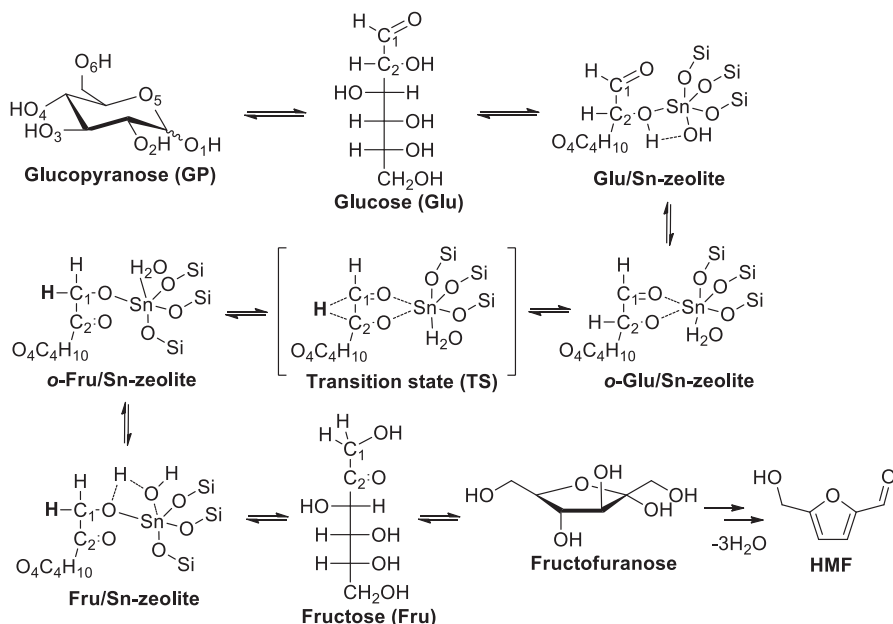
Entry	Catalyst	Glucose (%)		Acid-base content (mmol/g)	
		Selectivity	Yield	Basicity	Acidity
1	None	3.5	0.4	–	–
2	HT	40.6	11.0	0.42	0.21
3	Ca(OH) <sub>2</sub>	39.8	10.6	Solution pH = 12.84	
4	HT-OH <sub>Ca</sub>	85.3	39.8	1.76	1.17
5	HT-OH <sub>Ca2</sub>	83.4	36.6	1.54	1.09
6	HT-OH <sub>Ca3</sub>	82.3	36.0	1.48	1.06
7	HT-OH <sub>Ca4</sub>	80.5	35.0	1.47	1.05
8	HT-OH <sub>Ba</sub>	84.6	38.2	1.57	1.12
9	HT-OH <sub>K</sub>	72.9	29.6	0.87	0.64
10	HT-OH <sub>Na</sub>	69.0	27.2	0.75	0.52

Reaction conditions: 0.45 g ball-milled cellulose, 0.5 g catalyst, 150 mL distilled water, and 150 °C for 24 h reaction time. Values after Ca (2, 3, 4) refer to recycle number  
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**Fig. 1.5** Schematic illustration of the isomerization of glucose to fructose

been proposed for the selective isomerization of sugars [32, 33]. Solid bases such as TiO<sub>2</sub>, ZrO<sub>2</sub> and relevant hybrids normally have low catalytic activity, giving no more than 20% yields of fructose in the case of glucose isomerization [34, 35]. However, Sn-beta, which typically acts as a Lewis acid, is able to isomerize glucose to fructose with high yields of 31% in water at 110 or 140 °C in 30 min or 12 min reaction time, respectively [36]. Glucose in the pyranose form partitions into the zeolite, followed by ring-opening to the acyclic form over the Lewis acid center and isomerizes into fructose in the acyclic form, which finally proceeds to ring closure to give the furanose form of fructose (Fig. 1.5) [37].

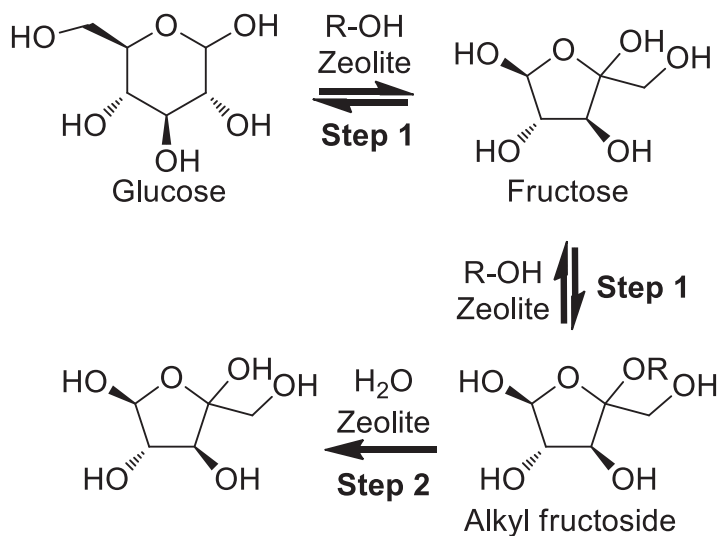
Besides the Lewis acid center of Sn species being located in the framework of BEA zeolite, the adjacent silanol group synergistically promotes the hydride transfer in the glucose-to-fructose isomerization, and allows the single-step reaction to proceed with a low activation energy barrier while the epimerization of glucose to mannose via a Bilik-type rearrangement is impeded [38]. The proximate hydroxyl group is possibly derived from either co-adsorbed water or intrinsic silanol, and the



**Fig. 1.6** Possible reaction mechanism for the catalytic isomerization of glucose (Glu) to fructose (Fru) with partially hydrolyzed (SiO)<sub>3</sub>Sn-OH site in a BEA-type zeolite framework [39, 40]

cooperative effect of the Sn center and -OH group compensates the negative charge more effectively on the O1 atom of glucose during the rate-controlling step of a hydride shift from the C2 carbon to the C1 carbon (transition state (TS) in Fig. 1.6) [39, 40]. In the isomerization of glucose to fructose over tungstite (WO<sub>3</sub>·H<sub>2</sub>O), cooperative action of tungsten species (Lewis acid site) with a neighboring proton donor occurs [41]. The conversion of glucose increases when methanol is used as solvent instead of water, probably due to the differences in the solvation of the hydrophobic pores [42]. However, the epimerization of glucose to mannose as the dominant side reaction may take place by either two subsequent 1,2-intramolecular hydride transfer steps over Sn-Beta or one 1,2 intramolecular carbon shift step on Na-exchanged Sn-Beta in methanol [42]. Gao et al. conducted a series of glucose isomerization reactions in subcritical aqueous straight- and branched-chain alcohols, and found that primary and secondary alcohols could promote glucose conversion to fructose in high selectivity, while the increase of *t*-butyl alcohol concentration resulted in a decrease of both glucose conversion and fructose yield [43, 44]. In addition, the ordered mesoporosity of the Sn-containing zeolite was favorable for the isomerization of C5 and C6 sugars (e.g., xylose and glucose) because it improved mass transfer and increased reaction rate [45]. Further, even the aldose component in the disaccharide could be isomerized to ketose (e.g., lactose-lactulose and cellobiose-cellobiulose) over Sn-beta zeolites in water or subcritical aqueous ethanol [46, 47]. Unexpectedly, the beta zeolite containing Ti<sup>4+</sup>centers (Ti-beta) were





**Fig. 1.7** Reaction pathway for converting glucose to fructose in a two-step process (Step 1, in R-OH; Step 2, water addition) (Adapted with permission from Ref. [49], Copyright © 2013, American Chemical Society)

found to preferentially catalyze the isomerization of glucose to sorbose through an intramolecular C5-C1 rather than C2-C1 hydride-shift [48].

By using commercially available zeolites as Brønsted-Lewis acidic catalysts, efficient isomerization of glucose to fructose is possible with remarkable yields (up to 55%) via a two-step methanol-water process that uses methanol in the initial reaction for the isomerization and etherification of glucose to a mixture of fructose and methyl fructoside at 120 °C for 1 h (step 1), and that is followed by water addition in the second step proceeding hydrolysis to regenerate fructose from methyl fructoside (step 2) as shown in Fig. 1.7 [49]. In this catalytic process, the isomerization of glucose to fructose and trapping of fructose as fructoside in the alcohol are catalyzed by Lewis and Brønsted acid sites, respectively [50]. It is found that the H-form zeolite (e.g., H-USY) promotes the glucose-to-fructose isomerization via an intramolecular hydride-shift rather than through solvent exchange [51]. Likewise, catalytic isomerization of xylose to xylulose (up to 47% yield) via the two-step methanol-water process, and erythrose to erythrulose (45% yield) in water can be realized over the commercial large-pore zeolites such as H-USY-6 (Si/Al = 6) and H-beta (Si/Al = 12.5) [52, 53]. In the presence of a single-unit-cell Sn-MFI with both Brønsted and Lewis acid sites, a maximum fructose yield of 65% is obtained from glucose via an identical two-step process in ethanol and water [54]. The coupling of Lewis and Brønsted acidity with newly developed catalytic routes allows an increase in reaction efficiency.

## 1.4 Synthesis of Biofuranic Compounds

In the past decade, a large number of catalytic systems and functional materials have been reported that are selective for the transformation of biomass-derived hexoses and pentoses into furans such as 5-hydroxymethylfurfural (HMF), furfural, 2,5-dimethylfuran,  $\gamma$ -valerolactone, 5-ethoxymethylfurfural, 2,5-diformylfuran, 2,5-furandicarboxylic acid and maleic anhydride via cascade reactions such as hydrolysis, dehydration, etherification, hydrogenation and oxidation (Fig. 1.8) [55]. These biofuranic compounds have high potential for use in industrial applications. In this section, catalytic strategies used for production of furanic products from bio-based compounds are briefly discussed.

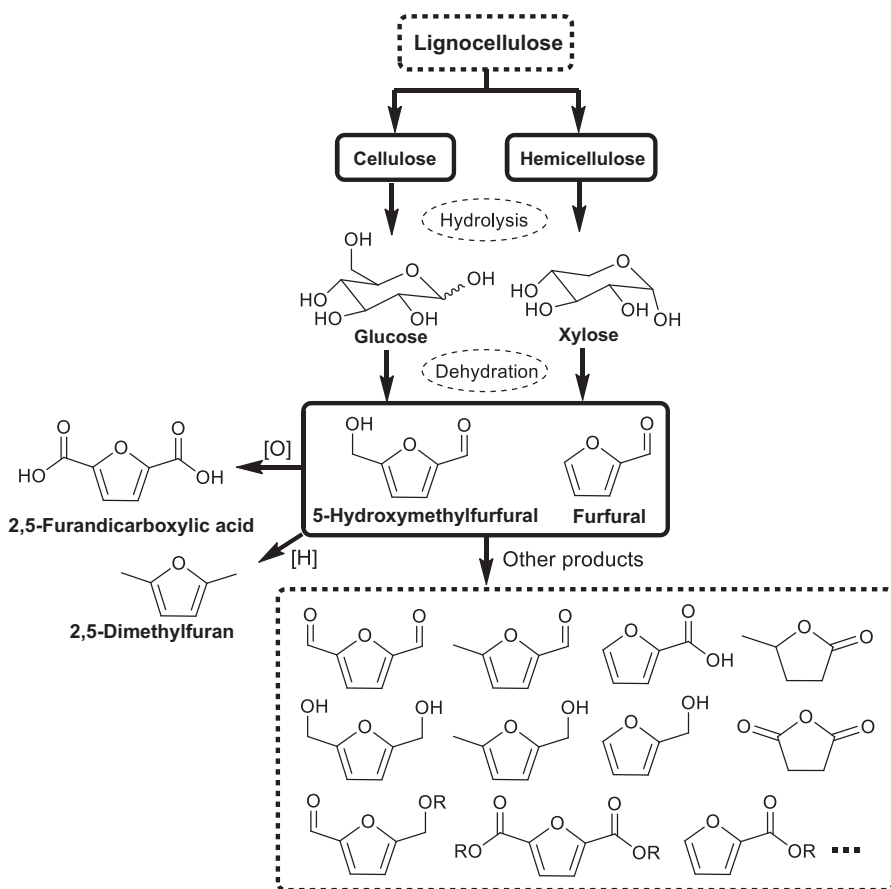
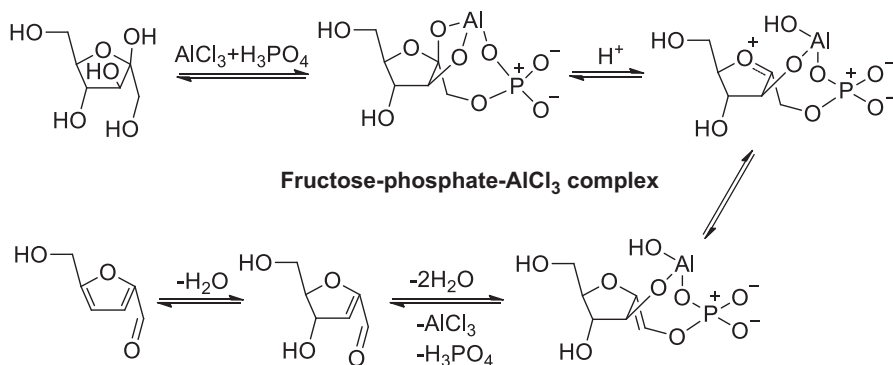


Fig. 1.8 Schematic routes for producing biofuranic compounds from lignocellulose



**Fig. 1.9** Reaction pathway for producing HMF from fructose stabilized by a fructose-phosphate- $\text{AlCl}_3$  complex (Adapted with permission from Ref. [56], Copyright © 2014 Royal Society of Chemistry)

### 1.4.1 Brønsted-Lewis Acid Bifunctional Catalysis

In the dehydration of fructose, either Lewis acid (e.g.,  $\text{AlCl}_3$ ) or Brønsted acid (e.g.,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ ) alone promote formation of HMF with high efficiency (20 min), but in only fair yields (< 60%) at moderate reaction conditions (120 °C). However, a mixture of Lewis and Brønsted acids (e.g.,  $\text{AlCl}_3$  and  $\text{H}_3\text{PO}_4$ ) in a single catalytic system is able to achieve HMF from fructose in yields as high as 92.6% under identical reaction conditions [56]. The *in situ* formed fructose-phosphate- $\text{AlCl}_3$  complex is proposed as the reason for the enhanced stability of the fructofuranose during the reaction through its shifting of the balance from fructopyranose to fructose-phosphate- $\text{AlCl}_3$  complex (Fig. 1.9), followed by dehydration over the protonic acid to give HMF. Binder and Raines showed that glucose, cellulose and even untreated corn stover could also be converted into HMF (48–81% yields) at temperatures of 100–140 °C in a single step with  $\text{CrCl}_3$  and  $\text{HCl}$  catalysts [57].

For producing HMF from glucose in cascade reactions using  $\text{CrCl}_3$  together with  $\text{HCl}$  in aqueous media, Lewis acidic catalysts are active for the isomerization of glucose to fructose, while Brønsted acid catalysts are favorable for subsequently promoting the dehydration reaction to give HMF (Fig. 1.10) [58]. The glucose-to-fructose isomerization is inhibited by  $\text{HCl}$  which decreases the equilibrium  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  concentration, while the overall consumption rate of fructose and HMF over Lewis acid species most likely promotes side reactions. Several other studies show that both the fructose dehydration rate and HMF selectivity (up to 62% yield) are enhanced in a mixed solvent of water and tetrahydrofuran or 2-*sec*-butylphenol at 160–170 °C by introducing a certain amount of  $\text{HCl}$  into the Lewis acidic  $\text{Al}^{3+}$  aqua/hydroxo complexes [59, 60]. In a similar manner, the combined use of  $\text{Sn}$ -beta with  $\text{HCl}$  [61], or metal salts (e.g.,  $\text{CrCl}_3$ ,  $\text{InCl}_3$ ,  $\text{CoSO}_4$ ,  $\text{FeCl}_2$  and  $\text{MnCl}_2$ ) with  $\text{SO}_3$  H-functionalized ionic liquids [62–66] is able to catalyze glucose and glucose-containing saccharides (e.g., cellulose) to obtain HMF in good yields

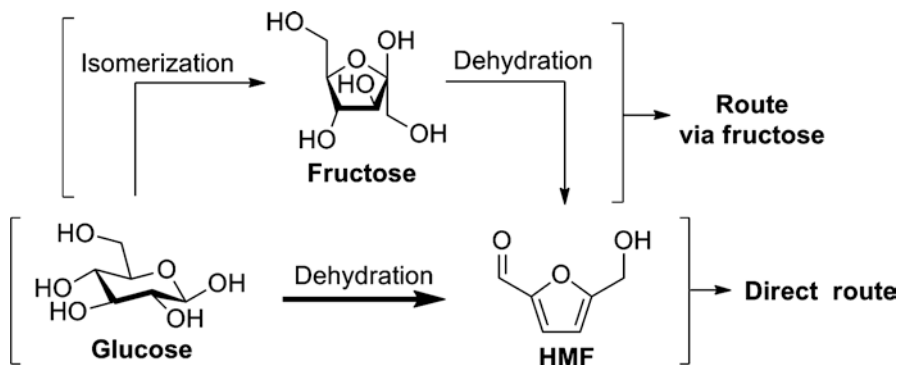


Fig. 1.10 Reaction pathway for the synthesis of HMF from glucose via fructose

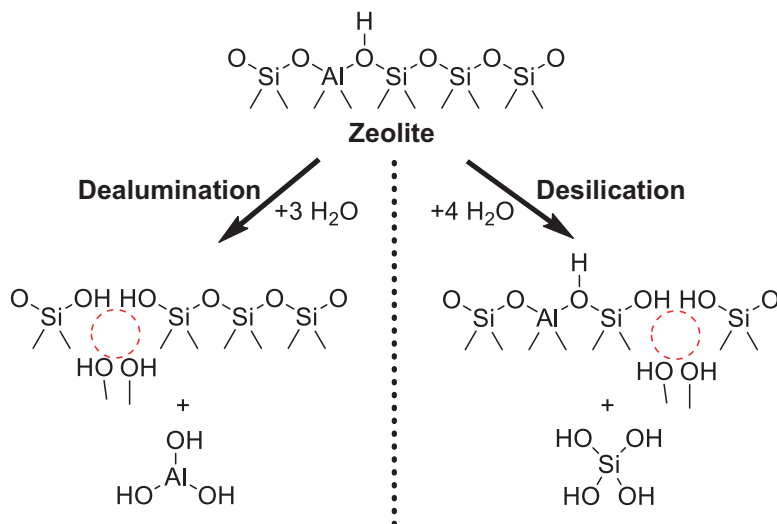


Fig. 1.11 Schematic route for synthesis of Lewis-Brønsted bifunctional SBA-Sn-OH (Adapted with permission from Ref. [77], Copyright © 2014 Royal Society of Chemistry)

(up to >80%). The recyclability of the acidic ionic liquids coupled with metal salts can be improved by immobilizing both active species into a solid polymer that retains catalytic activity [67].

Metal oxides are typically Lewis acid catalysts, and they rarely exhibit high selectivity and reactivity in the conversion of glucose to HMF [68]. However, the introduction of Brønsted acid sites into metal oxides by treatment with mineral acids (e.g., phosphoric acid and sulfuric acid) or acidic metal species (e.g., tungsten), and the resulting Brønsted-Lewis acid bifunctional hybrids (e.g., zirconium, aluminum, titanium, tantalum and niobium phosphates, sulfated zirconia, and W-Zr or W-Sn oxide) increase the efficiency of the direct conversion of glucose to HMF as compared with pristine metal oxides [69–76]. Some other neoteric strategies have been explored for the introduction of Brønsted acid sites into metal oxides. For example, the SBA-Sn-OH Lewis and Brønsted bifunctional catalyst can be prepared by grafting of dimethyldichlorostannane onto the SBA-15 surface (SBA-Sn-Me) that is followed by calcination to transform the  $-\text{CH}_3$  into  $-\text{OH}$  groups (Fig. 1.11) [77].

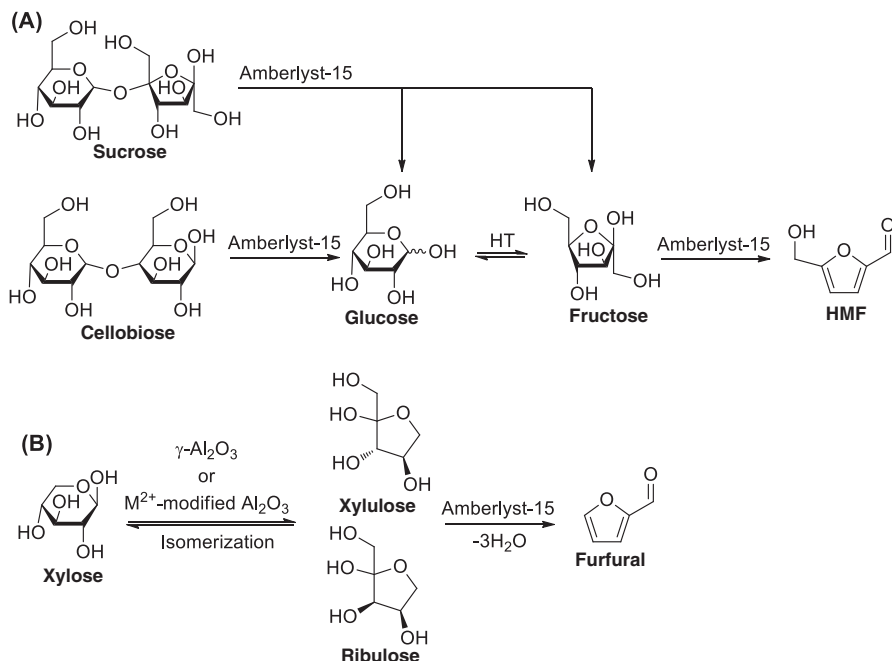
The synthesis of heteropolyacid salts via exchange with metal ions ( $\text{Cs}^+$ ,  $\text{Ag}^+$  and  $\text{Cr}^{3+}$ ) is an efficient way to solidify homogeneous heteropolyacids such as 12-tungstophosphoric acid and silicotungstic acid for obtaining Lewis-Brønsted dual sites and porous structure [78–80]. Notably, the replacement of W in 12-tungstophosphoric acid with Cr makes the resulting acid  $\text{H}_3\text{PW}_{11}\text{CrO}_{39}$  simulta-



**Fig. 1.12** Schematic representation for the framework dealumination (left) under steaming or acidic aqueous conditions, and desilication (right) under neutral or basic aqueous conditions

neously bear strong Brønsted and Lewis acid centers, while the further introduction of hexadecyltrimethylammonium bromide (CTAB) forms a highly water-tolerant salt [81]. Due to the dual acidity and hydrophobicity of the catalyst, more than 90% hexose conversion has been reported for the production of HMF [81]. The framework dealumination and desilication of H-form zeolites are efficient for the extension of pore diameters and for the adjustment of Lewis-Brønsted acid sites distribution [82]. The resulting desilicated H-ZSM-5 and dealuminated H-beta zeolites display pronounced performance in the transformation of either cellulose or glucose (67–81% conversion) into HMF (up to ca. 50% yield) in water or ionic liquids [83–85] (Fig. 1.12).

Lewis-Brønsted bifunctional catalysts like cesium salts of 12-tungstophosphoric acid, silicoaluminophosphate, partially hydroxylated magnesium fluoride, Zr-(W,Al) mixed oxides, sulfonated carbonaceous TiO<sub>2</sub>, and H-form zeolites promote formation of furfural in moderate to good yields from pentose sugars (e.g., hemicellulose, xylan, xylose, arabinose and ribose) [21, 86–93]. The catalysts with high molar ratios of Brønsted to Lewis acid sites have selectivity towards furfural as much as 30 times higher than that for relatively higher concentrations of Lewis acid sites [93]. Notably, the transformation of hexoses (e.g., glucose) into furfural (up to 37% yield) is realized by involving a retro-aldol reaction to form pentoses over H-form zeolites (e.g., H-ZSM-5 and H-beta) in  $\gamma$ -valerolactone with 10 wt% water, while the strong Brønsted acid Amberlyst-70 is exclusively selective for the dehydration of glucose and fructose to HMF rather than furfural [94]. These results show that the close interplay of Lewis acid and Brønsted acid centers in the solid catalyst seems to be crucial for achieving good activity in the synthesis of either HMF or furfural from biomass-derived sugars.



**Fig. 1.13** One-pot transformation of glucose- and xylose-containing sugars into HMF and furfural catalyzed by solid base and acid: (a) via fructose and (b) xylulose as key intermediate, respectively

### 1.4.2 Base-Acid Bifunctional Catalysis

Besides the interplay of Lewis-Brønsted dual acidic sites, the reactivity of acids in the catalytic transformation of glucose into HMF is also affected by the presence of a solid base catalyst [95]. Combination of a solid base catalyst with an acidic catalyst allows glucose to be efficiently converted into HMF through glucose-to-fructose isomerization over HT, and the subsequent dehydration is catalyzed by Amberlyst-15 under mild conditions (Fig. 1.13a) [96]. After reaction in *N,N*-dimethylformamide at 80 °C for 9 h, 58% selectivity towards HMF for a glucose conversion of 73% is obtained, while no HMF forms in the presence of either Amberlyst-15 or HT. These results clearly show the synergistic role of solid acid and solid base in the synthesis of HMF from glucose. The mixed catalytic systems can be further extended to disaccharides including sucrose and cellobiose for producing HMF to obtain yields of 54% and 35% at 120 °C in 3 h reaction time, respectively [96]. The formation of anhydroglucose from glucose over an acid (i.e., Amberlyst-15) is evidently limited by HT (base)-catalyzed isomerization of glucose to fructose at relatively low reaction temperatures [97]. By using this solid acid-base mixed catalyst system, xylose can be directly transformed into furfural (up to 41% yield) at 100 °C for 3 h, with the isomer xylulose as a key intermediate (Fig. 1.13b) [98, 99]. Likewise, a mixture

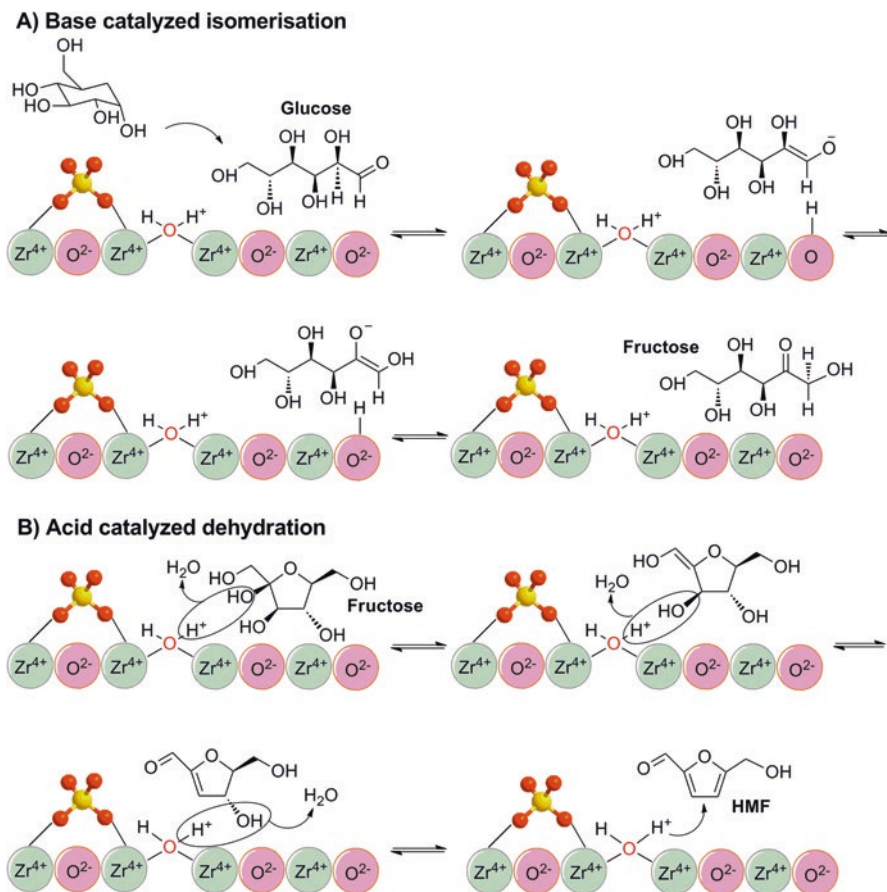
of arabinose, rhamnose and lactose over Amberlyst-15 and HT is selectively converted to yield furfural (30.5%), HMF (29.1%) and 5-methyl-2-furaldehyde (32.2%) at 110 °C after 6 h, respectively [100]. Catalytically upgrading sugar components of crude biomass with solid base and acid mixtures is most likely to be a promising approach for one-pot synthesis of biofuranic compounds especially HMF and furfural.

TiO<sub>2</sub>, ZrO<sub>2</sub> and their mixed oxides possess both basic and acidic sites for the conversion of glucose components to HMF via the key intermediate fructose [101]. Moreover, the use of these single catalysts greatly simplify the separation and recovery process, although hot compressed water (ca. 200–300 °C) is required to transform glucose into HMF (<20% yields) [102, 103]. The relatively low HMF yields can be ascribed to the lack of strong Brønsted acid sites. In connection to this, Qi et al. found that the acidity of ZrO<sub>2</sub> could be significantly enhanced by impregnation with H<sub>2</sub>SO<sub>4</sub>, and the resulting sulfated ZrO<sub>2</sub> exhibited good activity in the dehydration of fructose (93.6% conversion) to HMF (72.8% yields) under microwave heating in acetone/dimethylsulfoxide (DMSO) at 180 °C for 20 min reaction time [104]. Under mild conditions of 100 °C and 6 h, the sulfated ZrO<sub>2</sub> catalyst could also afford HMF (<10% selectivity) but with a large portion of fructose (ca. 80% selectivity) from glucose [105]. It can be speculated that tetragonal ZrO<sub>2</sub> (Lewis base) should be active for the isomerization of glucose to fructose via an enol intermediate, while polydentate surface SO<sub>4</sub><sup>2-</sup> species (Brønsted acid) acts on the subsequent dehydration of fructose to HMF, as illustrated in Fig. 1.14. Moreover, Lewis acidic Zr<sup>4+</sup> might assist the stabilization of the enolate intermediate formed during the isomerization reaction. With the aim of combining both basic and acidic centers into a single catalyst, some other protocols have been examined. For example, the post-grafting of SO<sub>3</sub> H and NH<sub>2</sub> groups onto mesoporous silica nanoparticles via covalent bonds [106], the assembly of lysine with 12-tungstophosphoric acid [107], and the incorporation of heteroatoms (e.g., Sn, Zr, Cr and Ti) into the framework of molecular sieves make the resulting hybrids highly disperse and to have compatible dual active sites [108], which are active for producing HMF in yields of reaching >80% from hexose sugars.

### 1.4.3 Metal-Base Bifunctional Catalysis

Selective oxidation of biomass derivatives to carboxylic acids is an important route to petroleum-based chemicals. In particular, 2,5-furandicarboxylic acid (FDCA) has been regarded as a potential replacement for terephthalic acid to produce polyethyleneterephthalate, which can be attained by the aerobic oxidation of HMF (Fig. 1.15) [109]. In most cases, the addition of a basic additive (e.g., NaOH) is necessary to facilitate the oxidation reaction by desorption of the acid product from the metal (e.g., Pt, Pb and Au) surface, wherein the reactivity of hydroxide is generally superior to that of carbonate [110, 111]. The alcohol oxidation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) into FDCA is found to be the



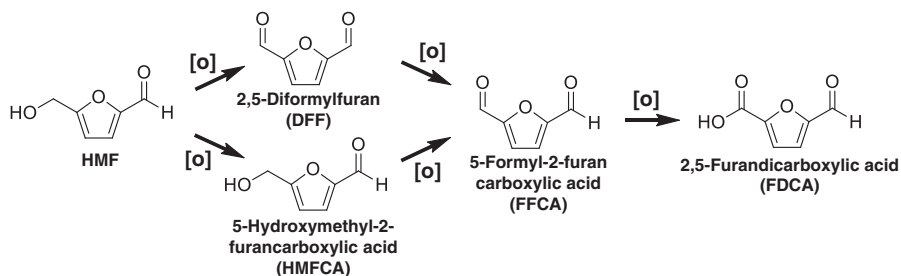


**Fig. 1.14** Sulfated  $\text{ZrO}_2$ -mediated reaction mechanism for (a) glucose-to-fructose isomerisation over basic sites ( $\text{O}^{2-}$ ), and (b) fructose-to-HMF dehydration with Brønsted acid sites ( $-\text{OH}$ ) (Adapted with permission from Ref. [105], Copyright © 2014 Royal Society of Chemistry)

rate-determining step [110, 111]. In the presence of 5 mol% NaOH, 1 wt% Au supported on  $\text{TiO}_2$  catalyzes HMF being fully oxidized to FDCA (71% yield) at 30 °C and 2.0 MPa  $\text{O}_2$  after 18 h [112]. The formation of partially oxidized intermediate HMFCFA is proportional to the base dosage and  $\text{O}_2$  pressure, implying that the reaction occurs mainly through initial oxidation of the  $-\text{CHO}$  moiety to 5-formyl-2-furancarboxylic acid (FFCA) followed by oxidation of the  $-\text{OH}$  group in HMF to yield the final product FDCA (Fig. 1.15). The possible oxygenated intermediate 2,5-diformylfuran (DFF) is hardly observed during the reaction [113–115], which means that the reaction pathway is most likely that shown in Fig. 1.15.

To improve the recyclability of the catalyst system, porous solid base (e.g., HT) can be used as either a co-catalyst or a support [116, 117]. The combination of HT with Au/ $\text{TiO}_2$ , and Au supported on HT both show excellent performance in the



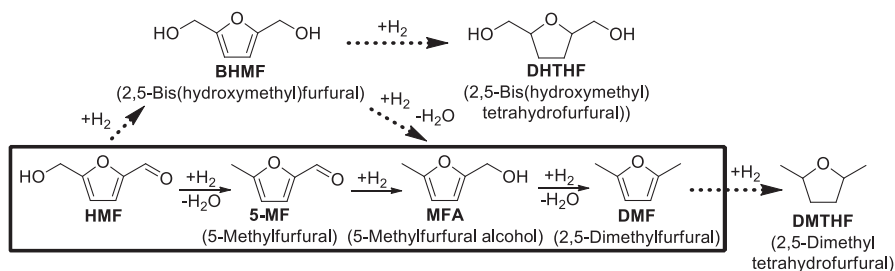


**Fig. 1.15** Probable reaction pathway for the oxidation of HMF to FDCA

aerobic oxidation of HMF [116, 117], giving FDCA in maximum yield of 99% at 95 °C in water under flowing O<sub>2</sub> (50 mL/min). By simple deposition of a relatively low-cost ruthenium salt (e.g., Ru(NO<sub>3</sub>)<sub>3</sub> or RuCl<sub>3</sub>) onto a basic support (e.g., HT, MgO, La<sub>2</sub>O<sub>3</sub> or spinel), supported ruthenium catalysts are active in the oxidation reaction, and Ru(OH)<sub>x</sub> with basic supports as the active center [118–120]. On the other hand, metal ions (e.g., Fe<sup>3+</sup> and Co<sup>2+</sup>) supported on porphyrin-based porous organic polymers exhibit good activity in the oxidation of HMF (>95% conversion) to yield FDCA (up to >90%) at 100 °C after 3–24 h using either oxygen/air or peroxide (e.g., *tert*-butyl hydroperoxide), wherein basic porphyrin subunits and metal ion centers are dual active species [121, 122]. Unlike catalytic systems mediated by zero-valent metal particles (e.g., Pt, Pd and Au), DFF instead of HMFCFA is observed to be the key intermediate for producing FDCA from HMF over supported metal-porphyrin catalysts [122]. The reactivity of metal-base bifunctional catalytic materials is greatly enhanced by their concerted interplay, but the reaction pathways might be affected by the type of active species.

#### 1.4.4 Metal-Acid Bifunctional Catalysis

Hydrogenation and hydrodeoxygenation (HDO) over metal particles accompanied by acidic species are the frequently used routes to decrease the oxygen contents of biomass components. Much attention has been placed on the selective hydrogenation of HMF to 2,5-dimethylfuran (DMF), which is deemed to be a promising alternative liquid fuel for transportation [123, 124]. A Brønsted acid (e.g., HCl and H<sub>2</sub>SO<sub>4</sub>) can be used to cleave the furanic C–O bond, and then PdAu particles stabilized on carbon support (PdAu/C) show good performance for the complete hydrogenation of HMF to DMF (up to 96% yield) at 60 °C after 12 h under an H<sub>2</sub> atmosphere [125]. The 2-methylfurfural (5-MF) and 5-methylfurfuryl alcohol (MFA) are both observed while ring-hydrogenated products such as 2,5-dimethyltetrahydrofuran (DMTHF) and 2,5-bis(hydromethyl)tetrahydrofuran (DHTHF) do not seem to form (Fig. 1.16), indicating that the reaction proceeds through intermediates containing alcohol groups. Apart from the promotional role of negatively



**Fig. 1.16** Reaction route toward DMF from HMF hydrogenation

charged Au formed by the co-existence of Pd, HCl with strong acidity ( $\text{pK}_a < -5$ ) and chloride ion are necessary as co-catalyst for effective and selective production of DMF by preventing undesirable ring-hydrogenation and facilitating hydrogenolysis through nucleophilic substitution on the alcohol groups of the reactants to form an active chlorinated intermediate [125].

Bimetallic catalysts containing a Lewis acidic center (e.g.,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$ ) and a hydriding metal component (e.g., Pd and Ru) are more recyclable and have good reactivity for forming DMF from hydrogenation of HMF. For instance, the combination of  $\text{Zn}^{2+}$  in the form of ZnO, with Pd, Ru or Cu particles catalyzes HMF conversion to DMF with yields of >85% under 0.8–1.5 MPa  $\text{H}_2$  at 150–220 °C after 5–8 h, which were more active than  $\text{ZnCl}_2$  (no DMF observed) and a single metallic catalyst such as Pd/C and Ru/C (<30% DMF yield) [126, 127]. Likewise, the introduction of acidic  $\text{CoO}_x$  species into Pt, Ru or Ni nanoparticles promotes the hydrogenation of HMF under mild conditions with reaction temperatures as low as 130 °C and no more than 1 MPa  $\text{H}_2$  pressure, producing DMF in yields of up to 98% [128–130]. The co-added Lewis acidic species seems to be favorable for the substrate absorption and the C–O bond cleavage. Notably, the reusability of these bimetallic hybrids is greatly enhanced by the presence of secondary metal oxides (e.g.,  $\text{Co}_3\text{O}_4$  and ZnO) during hydrogenolysis. On the other hand, the use of acidic solid supports (e.g., zeolite and tungsten carbide) to immobilize and disperse metal particles provides another efficient way to efficiently hydrogenate HMF to produce DMF [131, 132]. Further integration of a strong Brønsted acid (e.g., Amberlyst-15) with a solid catalyst containing metal-acid dual sites allows effective conversion of fructose to yield DMF via the intermediate of HMF in a two-step process involving fructose dehydration and subsequent hydrogenation [133]. The design of metal-acid bifunctional catalytic materials seems to be one of the most promising ways to directly valorize upstream biomass derivatives to desired products having low oxygen content.

## 1.5 Synthesis of Bio-Based Organic Acids

Instead of producing oxygenates (e.g., gluconic acid, glycolic acid, and acetic acid) from biomass-derived sugars under aerobic conditions, the anaerobic oxidation process leads to the formation of either levulinic acid (LA) or lactic acid (LAC), as shown in Fig. 1.17, which is closely dependent on the type of catalysts and reaction conditions. For the synthesis of LA or its ester from hexose sugars, HMF is the key intermediate, while the subsequent rehydration removes one carbon atom as formic acid [134]. However, glucose over a Brønsted acid is not converted to LA or its ester, but yields anhydroglucose in dipolar aprotic solvents (e.g., *N,N*-dimethyl formamide or dimethylsulfoxide) or alkyl glucopyranoside in alcohols (e.g., methanol or ethanol) as the dominant product [135]. This obstacle is overcome by the introduction of Lewis acidic species into Brønsted acid-catalyzed systems [136]. In this regard, the solid zeolitic materials seem to be one of the best options that can be used as bifunctional catalysts. Saravanamurugan and Riisager illustrate that the commercial zeolites especially large-pore H-USY(Si/Al = 6) with both Brønsted and Lewis acid sites produce methyl and ethyl levulinates (ML and EL) with yields of >40% from glucose at 160 °C after 20 h, wherein the cascade reactions including isomerization, dehydration, and rehydration take place in sequence [137]. Further doping of Lewis acidic species (e.g., Cr<sup>3+</sup> and Fe<sup>3+</sup>) onto the surface framework of Y-type faujasite zeolites results in the formation of hybrids (e.g., Cr/HY and Fe/HY) with enhanced Lewis acidity, which exhibit pronounced LA yields (ca. 62%) at 180 °C within 3 h [138, 139]. Similarly, a number of solid Brønsted-Lewis acid bifunctional catalysts such as sulfated Dowex 50 modified by cation exchange with FeCl<sub>3</sub> [140] and sulfated or phosphorylated metal oxides (e.g., SO<sub>4</sub>/ZrO<sub>2</sub>, SO<sub>4</sub>/TiO<sub>2</sub>, and PO<sub>4</sub>/ZrO<sub>2</sub>) [141–143] are active for the conversion of glucose to LA, and the appropriate molar ratio of Brønsted to Lewis acid sites (ca. 1.2–2.0) play a crucial role in the enhancement of glucose conversion and LA yields.

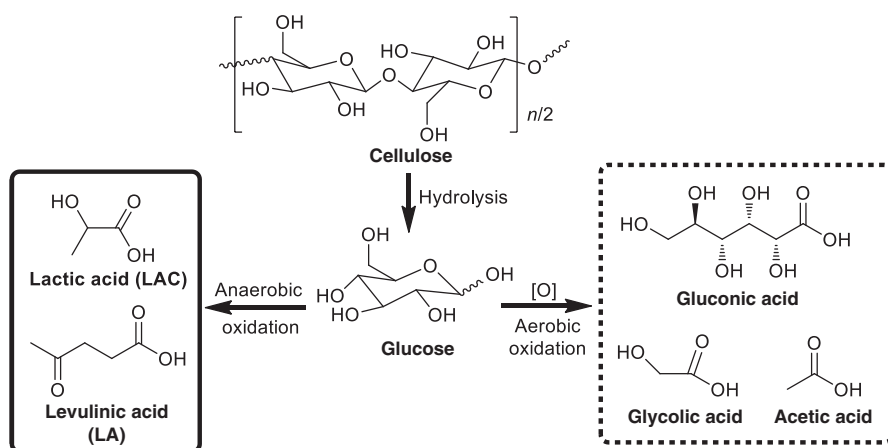
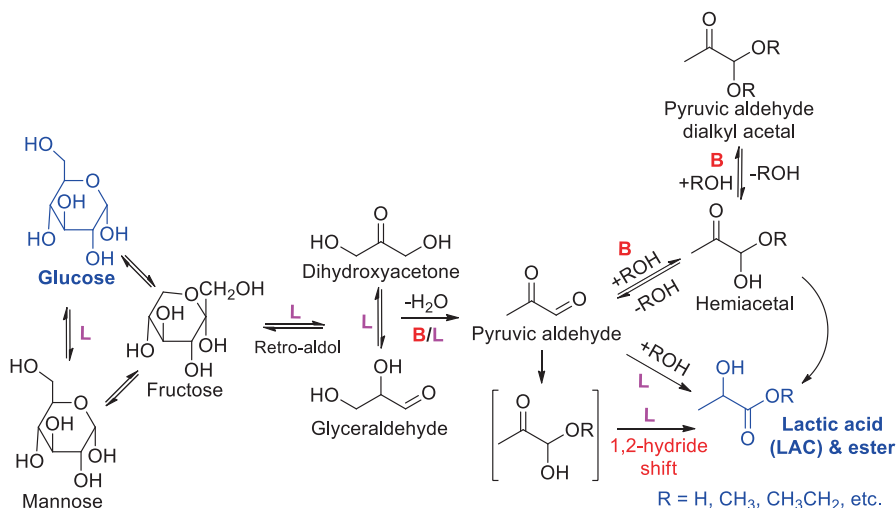


Fig. 1.17 Synthesis of organic acids from sugars via anaerobic and aerobic oxidation



**Fig. 1.18** Reaction pathway for transforming glucose into lactic acid (LAC) and ester; L = Lewis acid, B = Brønsted acid [144]

Besides the occurrence of aldose-ketose isomerization, the presence of excess Lewis acidic sites results in the retro-aldol reaction of hexose sugars (e.g., glucose and fructose) to trioses including glyceraldehyde and dihydroxyacetone, followed by dehydration to pyruvaldehyde over Lewis acid sites, finally giving LAC or its ester via the addition of one molecule water or alcohol and succeeding the 1,2-hydride shift (Fig. 1.18) [144]. The Sn grafted carbon-silica (MCM-41) has both Lewis acidity (Sn<sup>4+</sup>) and Brønsted acidity (e.g., -OH and -COOH derived from carbon part) that can be changed by adjusting the carbon loading amount [145]. The carbon-containing Sn-Si-MCM-41 catalyst with balanced Lewis/Brønsted acidic sites greatly improves the conversion of sucrose in methanol at 155 °C after 20 h to yield methyl lactate (45%), and is superior to SnCl<sub>4</sub>·5H<sub>2</sub>O (26%) and carbon-free Sn-Si-MCM-41 (18%) [145]. Zeolitic materials with both Lewis acidic Sn and Brønsted acidic Al centers exhibit a faster formation of ethyl lactate (>100 h<sup>-1</sup>) from dihydroxyacetone in comparison with Al-free Sn-beta (72 h<sup>-1</sup>), which is possibly due to the dehydration reaction being promoted by Brønsted acid sites [146]. When cellobiose or even cellulose is employed as substrate, the hydrolysis step integrated with retro-aldol, dehydration and hydration reactions is able to be accelerated by the coexistence of strong Brønsted acidity and weak or medium Lewis acidity [16], thus directly giving the desired lactic acid product in moderate yields (e.g., 18–27% over AlW and ZrW) in water under hydrothermal conditions (e.g., at 190 °C for 24 h) via a single-pot process [147]. These results emphasize the significant role that bifunctional catalysts will play in the efficient valorization of low-cost upstream biomass components to value-added products with high selectivity.

## 1.6 Conclusions and Future Outlook

Bifunctional catalytic pathways have been demonstrated to be efficient for multi-step transformations of biomass derivatives into value-added chemicals and biofuels. The combination of Lewis acid or base centers with Brønsted acid sites can selectively promote sequential hydrolysis, isomerization and dehydration of sugars to produce HMF, furfural or organic acids (e.g., LA and LAC) with moderate to good yields, however, the results depend on the sugar type (hexose or pentose) as well as the distribution and characteristics of active sites on solid catalysts. With respect to the oxidation of furanic compounds (e.g., HMF) mediated by metal particles (e.g., Pt, Pb and Au), the catalytic process is greatly accelerated by the presence of basic species that promotes desorption of the acidic product from the metal surface. For the hydrogenation or HDO, the presence of acidic species is able to promote the cleavage of the C-O bond in biomass derivatives, thus facilitating the removal of oxygen content over metal particles.

Some issues regarding the establishment of well-defined reaction systems and solid catalytic materials may be explored for further research on bifunctional catalytic pathways: (1) increasing the incompatibility of different active sites in a single solid catalyst; (2) suppressing the formation of undesirable products or humins; (3) controlling the sequence of cascade reactions as specified; (4) improving the uniformity, stability and recyclability of bifunctional solid catalysts; and (5) employing computational methods to comprehend preferred configurations or arrangements of active species, thus guiding the exploration of suitable approaches for the inclusion of catalytic sites.

A great number of opportunities exist for the development of bifunctional catalytic pathways mediated by well-defined solid materials in both fundamental and applied fields. The examples illustrated in this chapter provide an introduction into some of the ways for practical realization of multi-catalytic processes for biomass valorization.

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