



## Review Article

# Chemocatalytic Production of Lactates from Biomass-Derived Sugars

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In recent decades, a great deal of attention has been paid to the exploration of alternative and sustainable resources to produce biofuels and valuable chemicals, with aims of reducing the reliance on depleting confined fossil resources and alleviating serious economic and environmental issues. In line with this, lignocellulosic biomass-derived lactic acid (LA, 2-hydroxypropanoic acid), to be identified as an important biomass-derived commodity chemical, has found wide applications in food, pharmaceuticals, and cosmetics. In spite of the current fermentation of saccharides to produce lactic acid, sustainability issues such as environmental impact and high cost derived from the relative separation and purification process will be growing with the increasing demands of necessary orders. Alternatively, chemocatalytic approaches to manufacture LA from biomass (i.e., inedible cellulose) have attracted extensive attention, which may give rise to higher productivity and lower costs related to product work-up. This work presents a review of the state-of-the-art for the production of LA using homogeneous, heterogeneous acid, and base catalysts, from sugars and real biomass like rice straw, respectively. Furthermore, the corresponding bio-based esters lactate which could serve as green solvents, produced from biomass with chemocatalysis, is also discussed. Advantages of heterogeneous catalytic reaction systems are emphasized. Guidance is suggested to improve the catalytic performance of heterogeneous catalysts for the production of LA.

## 1. Introduction

Due to the burgeoning world population, demands for energy and chemicals are sharply increasing. Therefore, traditional nonrenewable fossil resources, particularly coal and petroleum, are going to be run out, and their concomitantly environmental and climatological impacts are also urgently needed to be addressed in the meantime [1–4]. With regards to this, alternatively manners to transform renewable, sustainable, and carbon-neutral biomass resources from plants into potential biofuels, polymer building blocks, and value-added chemicals are widely researched. Carbohydrates, the largest fraction of biomass, are being deemed as the main feedstocks in the biorefineries that will

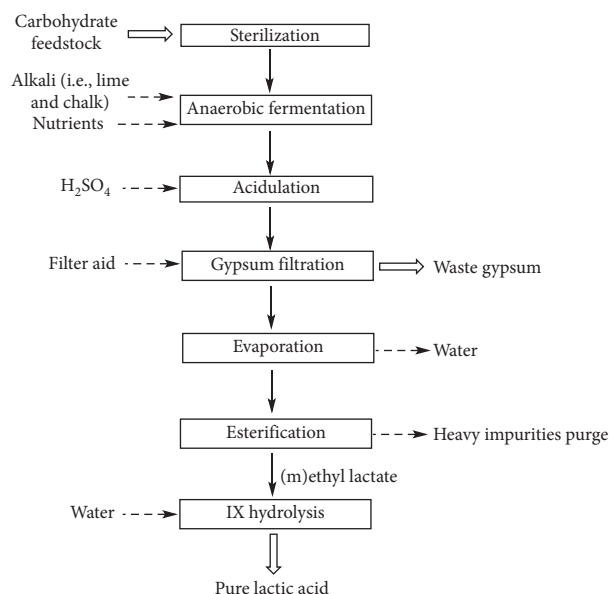
derive platform molecules to be served as precursors to the chemical industry [5–8]. In addition, cellulose, composed of glucose units, is recognized as the single most abundant organic compound on Earth, which can be upgraded to glucose and subsequently converted into value-added chemical molecules [9]. Taking the predicted energy demands (30–60 TW in 2050) into account, cellulosic biomass shows the large potential (supply approximately 30 TW) towards satisfying the energy demand of mankind [10]. Consequently, efficiently selective conversion of cellulosic biomass into valuable chemicals as well as biofuels and materials is highly preferable [11–13].

Lactic acid (LA, 2-hydroxypropanoic acid), one of the great appeals among carbohydrate-derived platform

molecules, is an important feedstock for the production of alkyl lactates, biodegradable plastics such as polylactic acid (PLA), and other valuable chemicals under suitable reaction conditions in the assistance of catalytic functionalities. Specially, PLA polymer bearing the advantages of biodegradability, compostability, and biocompatibility could be utilized in a wide range of applications such as eco-friendly packages. In addition, carbon neutral balance is accepted when PLA is disposed to release  $\text{CO}_2$  and water. LA was firstly found in 1780 by the Swedish chemist Scheele in acid milk [14, 15]. In spite of its late discovery, LA has found widespread applications in the food industry, and the commercialization of LA-based biopolymers is also of high interest currently [16]. In addition, alkyl lactates (methyl lactate (ML), and ethyl lactate (EL)), important versatile platform chemicals, have also attracted much attention because of their extensive applications including that in nontoxic and biodegradable green solvents, that in plasticizers for cellulose plastics and vinyl resins [17], and being environmental, recyclable, noncorrosive, and economic [18].

It is estimated that LA demand in 2020 will be above 600000 tons [7]. Currently, commercial LA production is manufactured through anaerobic fermentation method (over 90%), showing some merits such as low production temperature, low energy consumption, and high purity via an appropriate strain [19, 20], as illustrated in Scheme 1. Typically, 4 main steps should be processed for the production of LA by traditional fermentation when starting from cellulosic biomass, including (1) pretreatment of feedstocks, (2) anaerobic fermentation, (3) acidulation, and (4) separation and purification of LA. However, the low productivity, need for high price enzymes (strict pH and temperature), and complicated separation along with purification requirements are always accompanied, accordingly. As a consequence, sustainability issues regarding the up-scaling of the present fermentation process are highly required to be disposed via a promising alternative method, chemocatalysis, which could be regarded as the research hotspot in the state-of-the-art development of lactic acid research.

Chemical catalysis (homogeneous or heterogeneous), being considered to be the formidable strategy to transform cellulosic biomass into value-added chemicals with acceptable selectivity, is rising progressively [21]. In particular, in a platform approach, chemocatalysts are playing a vital role in the fundamental and novel production routes of lactic acid (or lactates), using sugars even real lignocellulosic biomass (i.e., cornstalk). However, the chemical production of lactic acid (or esters) generally leads to racemic mixtures, which is not an issue when compounds such as acrylic acid, 2,3-pentanedione, etc. are target compounds to be produced. However, chirality control is very important if lactide (industrial building block of PLA) production is the target as this will determine the properties of the polymer. Chromatographic methods [22, 23], chemical resolution [24] and the combination of the chemo- and biocatalysis [25] are regarded as the means for chiral resolution of racemic lactic acid. Nonetheless, enantioselective chemoproduction of lactic acid from sugars directly has not been reported.



SCHEME 1: Conventional fermentative method for producing LA.

Currently, many research groups are employing the chemocatalysts to synthesize lactic acid (in water) or lactates (alcoholic solvents). The main emphasis of this review is to depict the state-of-the-art development of LA or lactates production from sugars and real lignocellulosic biomass resources, with chemocatalysis especially heterogeneously catalysts which have tremendous advantages (i.e., recyclable, reusable, and environmentally benign). Furthermore, structure-function relationships, reaction mechanisms, and guidance on designing heterogeneous acid catalysts for LA or lactates production are also discussed, accordingly.

## 2. Chemocatalytic Production of LA

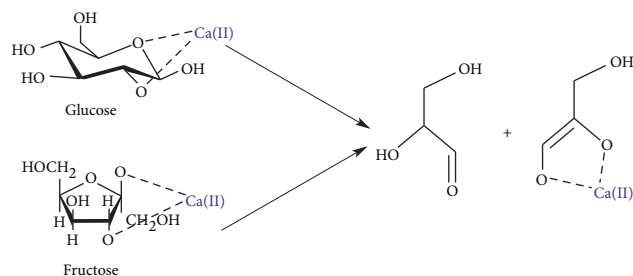
**2.1. Alkaline Catalytic Manners for LA.** The hydrothermal process, one of the most potential approaches, is used in the conversion of biomass into valuable resources, since water can serve as a reaction medium bearing special properties when treated in the high temperature and pressure [26]. With respect to the issue of catalytic transformation of biomass into LA with the hydrothermal process using alkaline catalysts, Jin research group made many valuable contributions to this research theme [26–34]. Initially, they demonstrated that glycolaldehyde, an aldose with two carbon atoms, usually produced via reverse aldol condensation of  $\text{C}_6$  sugars, can also generate LA with 28% yield using 0.75 M-NaOH basic catalyst (300°C, 10 min) [26]. After then, they employed glucose as the substrate to produce LA with moderate yield employing NaOH and  $\text{Ca}(\text{OH})_2$  as the alkaline catalyst, respectively (Table 1, Entry 2). It is worth noting that, on the basis of the viewpoint of economy,  $\text{Ca}(\text{OH})_2$  was regarded to be more suitable than NaOH [27]. Interestingly, in order to enhance the market values of glycerin, biodiesel byproduct, Jin et al. attempted to convert glycerin into LA under alkali-catalyzed hydrothermal conditions and some valuable results were obtained [28]. After

TABLE 1: Catalytic transformation of lactic acid from different feedstocks by alkaline.

Entry	Substrate	Catalyst	Reaction conditions	Yield of LA (%)	Reference
1	Glycolaldehyde	NaOH	300°C, 10 min	28.1	[26]
2	Glucose	NaOH	300°C, 1 min	27	[27]
3	Glycerin	Ca(OH) <sub>2</sub>	300°C, 1 min	20	[27]
4	Glucose	KOH	300°C, 80 min	90	[28]
5	Glucose	NaOH	300°C, 1 min	27	
6	Glucose	Ca(OH) <sub>2</sub>	300°C, 1 min	20	[29]
7	Cellulose	Ca(OH) <sub>2</sub>	300°C, 90 s	19.2	
8	Starch	Ca(OH) <sub>2</sub>	300°C, 90 s	18.7	
9	Cellulose	NaOH + Ni	300°C, 1 min	34.1	[30]
10	Glucose	NaOH + CuO	188°C, 0.15 min	59	[31]
11	Cellulose	NaOH + Zn/Ni/C	300°C, 5 min	42	[32]
12	Glucose	NaOH + NiCl <sub>2</sub>	300°C, 1 min	25	[33]
13	Glucose	Na <sub>2</sub> SiO <sub>3</sub>	300°C, 1 min	30	[34]
14	D-Glucose	Hydrotalcite	50°C, 8 h	20.3	[35]
15	D-Glucose			75	
16	D-Mannose			41	
17	D-Fructose	KOH/Al <sub>2</sub> O <sub>3</sub>	180°C, microwave 3.1 W·g <sup>-1</sup> , 40 min	36	[36]
18	D-Ribose	Microwave		43	
19	D-Arabinose			35	
20	D-Sucrose			23	
21	Hydroxyacetone	Pt/MgO-Al <sub>2</sub> O <sub>3</sub> -800	40°C, 6 h	100 (selectivity)	[37]
22	Glucose	[IMEP]Cl, NaOH	100°C, 30 min, N <sub>2</sub>	63	[38]
23	Glucose	[IMEP]Cl, KOH		65.5	[38]
24	Glucose	Ba(OH) <sub>2</sub>	250°C, 3 min	57	[39]
25	Glucose	Ba(OH) <sub>2</sub>	Ball milling (solvent-free)	35.6	[40]
26	Glucose			95.4	
27	Fructose	Ba(OH) <sub>2</sub>	25°C, 48 h	83.5	[41]
28	Corn cobs	Ca(OH) <sub>2</sub>	300°C, 30 min	44.76	[42]
29	Bread residues	Ca(OH) <sub>2</sub>	300°C, 30 min	73	[43]
30	Rice straw	NaOH, NiO nanoplates	260°C, 2 h	58.81	[44]
31	Alginate	CaO	200°C, 6 h	14.66	[45]

screening the alkali-metal hydroxides and alkaline-earth-metal hydroxides, they presented that KOH exhibited the best activity with 90% yield, using the lower concentration or a shorter reaction time (Table 1, Entry 3). Generally, to clearly present the reaction mechanism is very important to understand the targeted reaction process, to some extent. To our satisfaction, Jin et al. conjectured the mechanism (Figure 1) with regard to converting glucose into LA under alkaline hydrothermal reaction with more economic catalyst Ca(OH)<sub>2</sub>. To be specific, Ca<sup>2+</sup> is a divalent cation, whose radius is determined to be larger than that of Na<sup>+</sup>. Consequently, Ca<sup>2+</sup> was believed to be easier to combine with two O atoms, to form complexes than Na<sup>+</sup>. These complexes are likely to facilitate the C<sub>3</sub>-C<sub>4</sub> bond breaking via reverse aldol condensation. In addition, they also proposed the reaction pathway of glucose transformation to LA under alkaline hydrothermal reaction conditions (Figure 2). Notably, nearly 20% yield of LA could be also obtained using cellulose and starch substrates, respectively [29].

To keep up Jin group's works concerning the conversion of carbohydrates biomass into LA, they added Ni as co-catalyst in the LA production started from cellulose under hydrothermal conditions with NaOH [30]. However, the reaction mechanism was not clearly presented. After then, they conducted a detailed study with respect to converting glucose into LA using 0.01 M·Ni<sup>2+</sup>, 0.01 M·NaOH as

FIGURE 1: Proposed retro-aldol of glucose and fructose by complexation with Ca<sup>2+</sup>.

cocatalysts, with 35% water filling at 300°C for 1 min, generating 25% LA yield, accordingly [33]. Most importantly, the detailed reaction mechanism was also clearly demonstrated. To be specific, (1) coordination with Ni<sup>2+</sup>, (2) nucleophilic attack by OH<sup>-</sup>, (3) retro-aldolization, (4) Lobry de Bruyn Alberda van Ekenstein (LBAE) to form double bond, (5) elimination of water, and (6) benzoic acid rearrangement were determined as the main 6 steps during this process. Accordingly, glyceraldehyde was demonstrated to be the key intermediate. Some other interesting works of Jin group regarding the production of LA from biomass are also demonstrated here in Table 1 [31, 32, 34]. It is noteworthy that the low-cost and highly active basic catalyst Na<sub>2</sub>SiO<sub>3</sub>,

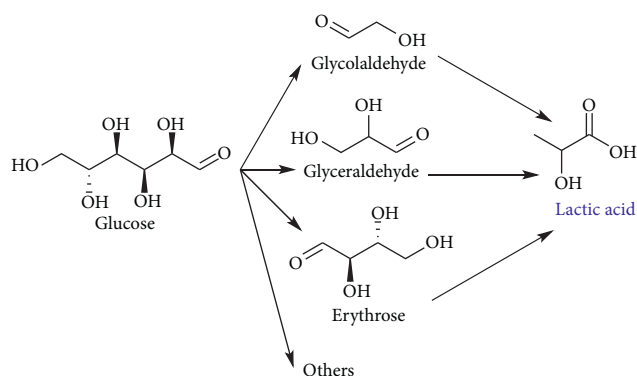


FIGURE 2: Proposed pathway of formation of LA from glucose by alkaline hydrothermal reaction.

acted as a mild catalyst to address the corrosion issue was researched in detail, giving 30% LA yield [34].

As mentioned above, solid alkaline catalyst bearing low corrosiveness seems to be a better choice, when employed in the production of LA under hydrothermal process. In this regard, versatile activated hydrotalcites were utilized as alkaline catalysts to convert glucose in a flow reactor into LA, giving 20.3% LA yield at 50°C [35]. The results indicated that hydrotalcite (Mg/Al = 2) activated at 723 K contained the most Brønsted-base sites, and a linear increase was determined with respect to LA yield and accessible Brønsted-base sites. Similarly, with slight modifications, Albuquerque et al. employed dual metal/base catalyst systems (Pt-Mg-Al hydrotalcite) to converting hydroxyacetone to LA, under oxidative aqueous-phase reaction conditions [37]. The highly remarkable 100% selectivity to LA with the bi-functional catalysts was determined, which was believed to be based on the proximity of metal and basic centers along with hindering the side reaction of LA to pyruvic acid. Surprisingly, Epane et al. found that microwave as an effective and environmentally friendly means could also make a contribution to the production of LA from saccharides, under solvent-free conditions which was deemed to be within the green chemistry concept [36]. On the basis of the presence of KOH/Al<sub>2</sub>O<sub>3</sub> and microwave, high 75% LA yield could be obtained from glucose without solvent, as presented in Table 1, Entry 11.

Unfortunately, the aforementioned hydrothermal process almost adopted relatively high reaction temperatures (i.e., 300°C), thus limiting their promising industrial applications to some extent. For the sake of overcoming this challenge, Wang et al. used the polymeric catalyst (polymerization of imidazole and epichlorohydrin, [IMEP]Cl) as weak Lewis acid along with NaOH/KOH to transform glucose into LA [38]. Several parameters including the base, [IMEP]Cl loading, reaction temperature, and atmosphere were investigated in detail to determine the best reaction conditions. A high 63% LA yield could be obtained from glucose along with a low 62.66 kJ·mol<sup>-1</sup> activation energy, even only at 100°C for 30 min under N<sub>2</sub>. The key reaction mechanism was also studied, and the rate determining step was also determined to be dihydroxyacetone (DHA) to pyruvic aldehyde (PAL), accordingly. The detailed mechanism

regarding DHA to PAL involved the coordination of active hydrogens of [IMEP]Cl with the electronegative oxygens on trioses, followed by keto-enol tautomerism through a 1,2-hydride shift to produce LA.

In spite of the LA production using Ba(OH)<sub>2</sub> investigated by Jin group before, Esposito and Antonietti also researched the LA manufactured from glucose with Ba(OH)<sub>2</sub> in detail [39]. Interestingly, differing from Jin et al.'s results, LA yields up to 57% could be gained within 3 min at 250°C. In connection with the interesting work employing Ba(OH)<sub>2</sub> as the basic catalyst in the production of LA from biomass, Qi research group presented two interesting and valuable results (Table 1, Entry 15 and 16). Without harsh conditions is the key innovation point regarding their research works to transform biomass to LA. The first attempt is to use a mechanochemical ball milling method, employing glucose feedstock and Ba(OH)<sub>2</sub>, giving 35.6% LA yield after 6 h [40]. Valuably, Li et al. reported an effective method to quantitatively converting sugars into LA only at room temperature under a N<sub>2</sub> atmosphere, wherein 95.4% LA yield could be determined from glucose at room temperature for 48 h under 1 bar N<sub>2</sub> [41]. In addition, based on their experimental results, they also proposed the reaction mechanism (Figure 3). To be specific, in addition to the common isomerization and retro-aldol fragmentation, Ba(OH)<sub>2</sub> may form the important barium lactate complex via Path II, followed by converting to lactic acid with the addition of H<sub>2</sub>SO<sub>4</sub> aqueous solution. The anaerobic environment was determined to play the vital role in hindering the oxidation of glyceraldehyde (GLY) and DHA or other intermediates, into side products according to the detailed results.

As discussed above, sugars can be transformed into LA with acceptable yield under alkaline hydrothermal process. Nonetheless, LA production directly from real biomass is highly more commended without hesitation. As shown in Table 1, corn cobs and bread residues could be treated as the potential feedstocks for the production of LA, giving 44.76% and 73% LA yield using Ca(OH)<sub>2</sub>, respectively [42, 43]. Furthermore, China's most abundant agricultural waste, rice straw, was also converted into LA of 58.81% yield at 260°C for 2 h, using 1 M-NaOH and 0.052 g NiO nanoplates as cocatalysts [44]. It is noteworthy that marine biomass, considered to be the third-generation promising renewable biomass feedstock, could also be transformed into LA with hydrothermal technique [46, 47]. Starting from alginate biomass, 14.66% LA yield was determined at 200°C for 6 h, using CaO as a solid basic catalyst [45]. The detailed reaction mechanism is illustrated in Figure 4. As investigated according to their experimental results, the hydration of CaO to Ca(OH)<sub>2</sub> in an aqueous medium, generating Brønsted bases (OH<sup>-</sup>), is the key point during the reaction. Different from Reference [38], they believed that PAL to LA is the rate-determining step wherein CaO could enhance the LA yield from PAL, by benzylic acid Rearrangement.

**2.2. LA Production via Acid Catalysis.** As discussed above, with the addition of alkaline catalysts especially under hydrothermal reaction conditions, LA could be produced with

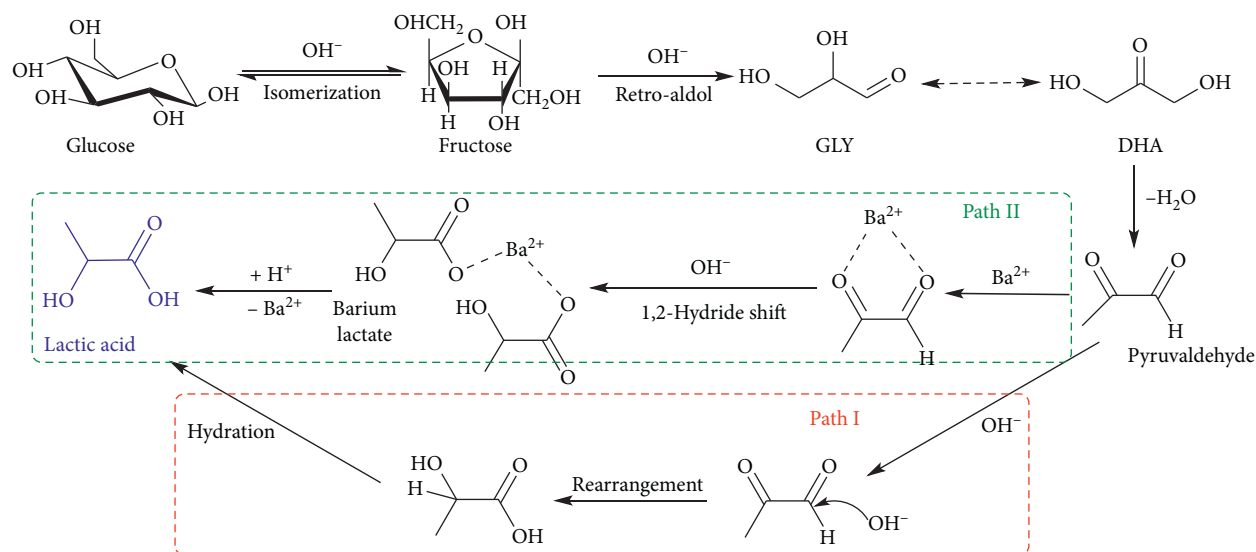


FIGURE 3: Proposed pathway for the conversion of glucose to lactic acid with the base at room temperature under nitrogen (Path I general base catalyst route; Path II:  $\text{Ba}(\text{OH})_2$  catalytic-complex route).

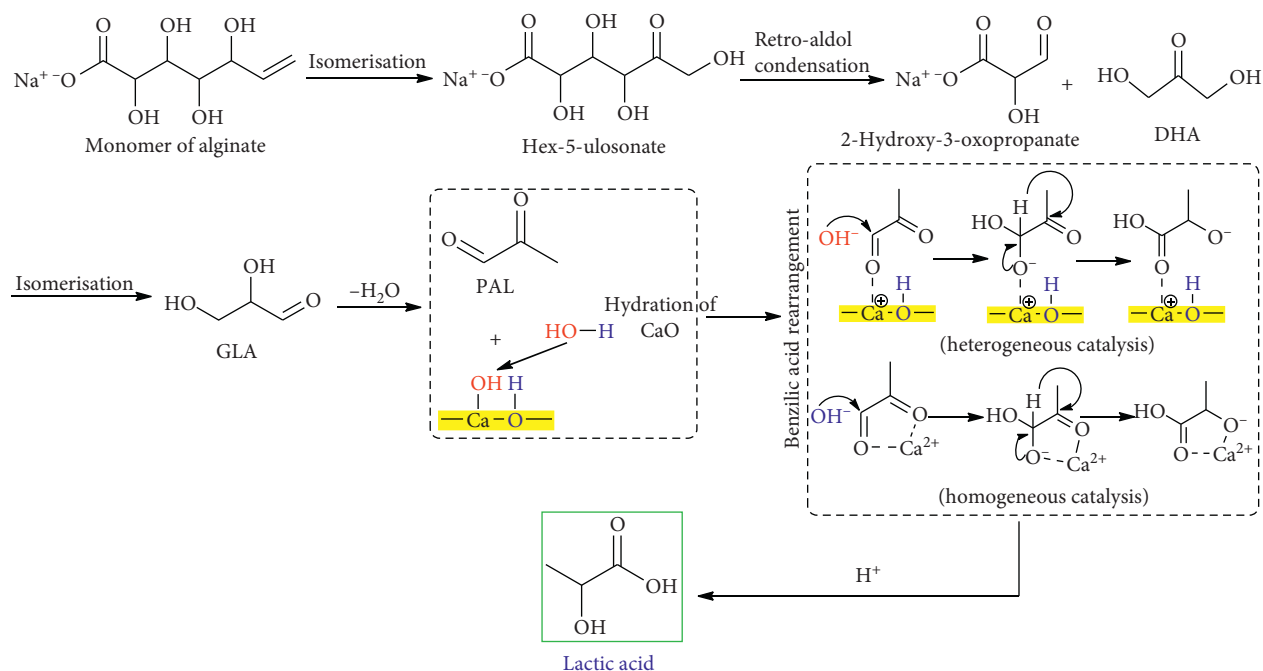


FIGURE 4: Proposed reaction pathway for catalytic hydrothermal conversion of sodium alginate into lactic acid with hydrated  $\text{CaO}$  catalyst.

relatively acceptable yield, to some extent. However, acid solution was always needed to employ to neutralize the base, along with hydrolysis the possible lactates to acquire the final product, pure LA. Therefore, acidic catalysts appear to be a better choice to be used in the production of LA and lactates, starting from different types of feedstocks (i.e.,  $\text{C}_6$ ,  $\text{C}_3$  sugars, and so on), through several specific catalytic reactions. Specifically, Lewis acidic sites are regarded as the key role in the transformation of LA or lactates from different carbohydrates even cellulose. In addition, from the environmental point of view, heterogeneously acidic catalysts which are less corrosive and can be recycled from the

products for reutilization are the main discussed objects regarding the LA preparation in the following two parts, accordingly.

**2.2.1. Trisaccharides to LA.** DHA or GLY is being deemed as the key intermediate with respect to transforming saccharides into LA. As a consequence, illuminating the LA production directly from simply  $\text{C}_3$  sugars is important to further understand the reaction of converting  $\text{C}_6$  and cellulose to LA. Generally, 100 (DHA) and 120 (GLA) kJ/mol are demanded to be energetically favored, in order to be



isomerized to LA [48]. It is widely believed that DHA/GLY to LA include two steps: (1) DHA is transformed into PAL through the successive keto-enol tautomerization and dehydration [26, 49], catalyzed by both Lewis and Brønsted acids [50, 51]; (2) rehydration of PAL followed by 1,2-hydrate shift produces LA wherein Lewis acids are regarded to perform better than Brønsted acids [49, 50, 52]. Some homogeneous catalysts including  $\text{H}_2\text{SO}_4$  [53],  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  [54],  $\text{ZnSO}_4$  [55],  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  [54, 56],  $\text{SnCl}_2$  [54, 57], and  $\text{SnCl}_4 \cdot 6\text{H}_2\text{O}$  [54] have been studied in DHA into LA and its esters. For instance, Rasrendra et al. investigated the 26 metal salts towards LA preparation from DHA in detail, and they found that  $\text{Al}^{\text{III}}$  salts were determined to be the most active, quantitatively with 93% LA yield at  $140^\circ\text{C}$  for 90 min [50]. In addition, the detailed reaction pathway was also proposed based on the experimental results, as shown in Figure 5 which is similar to the 2 steps as discussed above. However, they did not explain why  $\text{Al}^{\text{III}}$  salts performed the best and why other metals were less active. The good news is, to continue the interesting work, Jolimaître et al. [58] investigated the detailed reaction mechanism regarding the best performance of  $\text{Al}^{\text{III}}$  salts for the conversion of DHA into LA, as inspired by the valuable work of commercial OLI Systems (OLI Systems Stream Analyzer Software, OLI Systems, 2012) [59]. According to the thermodynamic analysis and kinetic studies, hydrolysis of aluminium aqua complexes such as  $[\text{Al}(\text{OH}_2)_6]^{3+}$  to form the most active Lewis acids, namely, cationic hydroxyl-aluminium complexes  $[\text{Al}(\text{OH})_n]^{(3-n)+}$ , are believed to be the key active Lewis acidic sites towards PAL into LA.

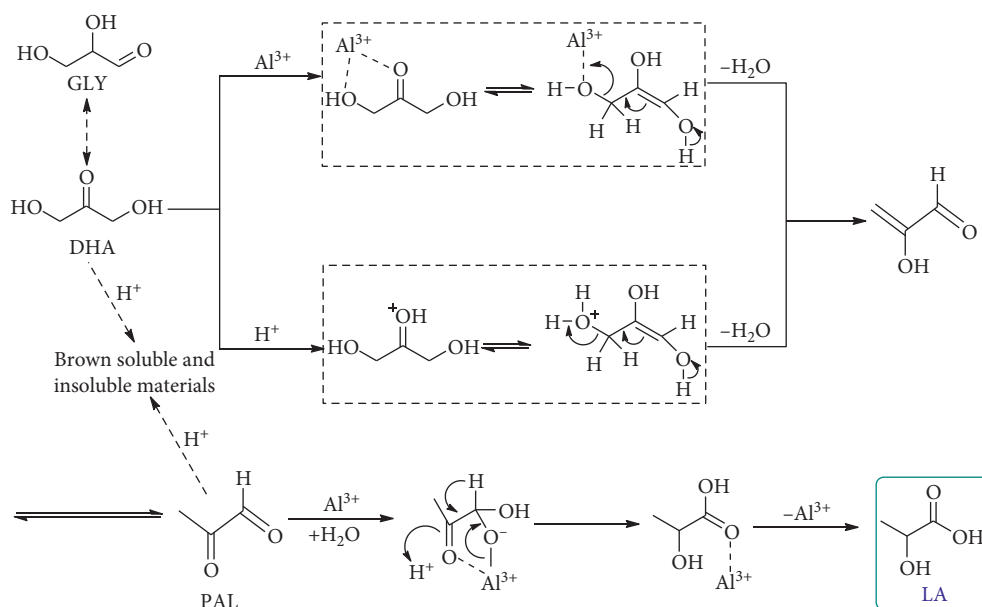
It is worth noting that during the bioprocessing of biomass upgrading, tunable acidic, thermal stable, and shape-selective zeolites materials are considered to be the most promising heterogeneously solid acidic catalysts with superior catalytic performance [60]. With respect to the transformation of DHA to LA, zeolites as efficient catalysts have also been reported [51, 57, 61, 62]. Taarning et al. firstly used several Lewis-acidic zeolites in the production of LA from DHA and Sn-Beta was found to be highly selective for the isomerization of trioses to LA [51]. In addition, based on Corma's research with respect to NMR evidence [63], the real catalytically active site is determined as the partially hydrolyzed framework tin species. On the basis of Taarning's valuable works, some other interesting studies regarding the LA formation from  $\text{C}_3$ -sugars using zeolites, such as the H-USY [57], the MFI [61], and the hierarchical tin zeolite with microporous structure [62] were also proposed and investigated for the production of LA from  $\text{C}_3$  sugars. Lewis acidic sites are believed to be the key role with regards to isomerization of trioses to LA, along with weak Brønsted acids. After then, based on the excellent reactivity of tin, Wang et al. designed the surfactant-modified SnP catalyst for the isomerization of DHA to LA, and poly (ethylene glycol) (PEG) was found to be the most potential, along with 96.1% LA yield at  $140^\circ\text{C}$  for 4 h [63]. Recently, Nakajima et al. presented an interesting study regarding the efficient production of LA from DHA, using  $\text{Nb}_2\text{O}_5$  with an orthorhombic structure and a high surface area ( $208\text{ m}^2/\text{g}$ ) [64]. Thanks to its high water-tolerant Lewis acid sites

( $0.21\text{ mmol/g}$ ) and Brønsted acid sites ( $0.10\text{ mmol/g}$ ), nearly 80% LA yield could be achieved at  $100^\circ\text{C}$  within 3 h. As identified in this research, the high density of water-compatible Lewis acid sites should be believed to play the crucial role in the isomerization of PAL to LA (the rate-determining step for the conversion of DHA to LA).

**2.2.2. Hexose to LA.** As a consensus, effective LA production from hexoses is more preferable compared to  $\text{C}_3$  sugars. In a similar manner, the novel well-aligned  $\text{Nb}_2\text{O}_5$  nanorod owning highly single crystallinity was also designed to produce LA from glucose [65]. A promising LA yield of 39% could be achieved along with a good reusability among the 4 successive processes. However, Sn-based catalysts have been studied and found to exhibit satisfied reactivity for LA production as presented above. Therefore, to find the modified Sn-based catalysts is a good choice with respect to LA production, accordingly. As illustrated in Table 2 (Entry 2–4), Sn(IV)-based organometallic complexes [66], Zn-Sn-Beta Lewis acid-base catalyst [67], and Pb-Sn-Beta catalyst [68] were investigated in detail to prepare LA from fructose, sucrose, and glucose, respectively. Acceptable LA yields could be obtained using the aforementioned catalysts and Sn species bearing the good Lewis acid character was believed to play the key role regarding the formation of LA step. Nonetheless, leaching of metals was found to lead to the poor reusability.

In addition to these functional materials aforementioned for LA transformation from hexoses, Huang et al. employed the solid Lewis acidic material (Table 2, Entry 5), MIL-100 (Fe), a metal-organic frameworks (MOFs) material with outstanding advantages such as large surface area, extrahigh porosity, highly thermal and chemical stability, and so on [69, 86–88]. 32% LA yield could be reached with MIL-100 (Fe), and the catalytic activities were found to be affected by the framework's metal, surface area, and Lewis acid properties, accordingly. In addition, the MIL-100(Fe) could be reused among 4 successive recycles with a simple dispose. Nevertheless, very few studies researched LA production directly from cellulosic biomass, due to the complexity of biomass structures (i.e., cellulose, hemicellulose, and lignin), along with the catalyst deactivation induced by lignin [89]. Interestingly, Liu et al. presented a valuable work regarding LA production directly from lignocellulosic sugars including levoglucosan, glucose, and xylose with good yields [70]. Using a Lewis acid catalyst,  $\text{La}(\text{OTf})_3$  which is stable in both aqueous and organic solvent, 61% LA yield for  $\text{C}_5$  sugars and >70% LA yield from  $\text{C}_6$  sugars could be obtained. On the basis of their studies, two efficient methods including fast pyrolysis combined with retro-aldol condensation of pyrolytic sugars, and ionic liquid pretreatment combined with retro-aldol condensation of the sugar-rich fraction, could be demonstrated to impart significant meaning on biorefinery of lignocellulosic biomass.

**2.2.3. Cellulose to LA.** The direct transformation of cellulose being the main component of lignocellulosic biomass into valuable chemicals such as LA is highly desired in making

FIGURE 5: Proposed reaction pathway for converting C<sub>3</sub> sugars to LA in aqueous with Al<sup>III</sup> salts catalyst.TABLE 2: Catalytic transformation of lactic acid from C<sub>6</sub> sugars and cellulose by acids.

Entry	Substrate	Catalyst	Reaction conditions	Yield of LA (%)	Reference
1	Glucose	Nb <sub>2</sub> O <sub>5</sub> nanorod	250°C, 4 h	39	[65]
2	Fructose	Sn(IV) organometallic complexes	190°C, 0.5 h	63	[66]
3	Sucrose	Zn-Sn-Beta	190°C, 2 h	54	[67]
4	Glucose	Pb-Sn-Beta	190°C, 2 h	52	[68]
5	Fructose	MIL-100 (Fe)	190°C, 2 h	32	[69]
6	Levoglucosan	La(OTf) <sub>3</sub>	250°C, 1 h	75	[70]
	Glucose			74	
7	Xylose	AlW	190°C, 24 h	61	[71]
	Cellulose			28	
8	Cellulose	ZrW	190°C, 24 h	19	[72]
	Pine wood sawdust		190°C, 8 h	3 g/L <sup>-1</sup> 1.2 g/L <sup>-1</sup>	
9	Xylose	ZrO <sub>2</sub>	200°C, 40 min	42	[73]
	Xylan		200°C, 90 min	30	
10	Cellulose	ZrO <sub>2</sub> (monoclinic)	200°C, 6 h	21.2	[74]
11	Cellulose	10%ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	200°C, 6 h	25.3	[75]
12	Cellulose	Er(OTf) <sub>3</sub>	240°C, 30 min	89.6	[76]
13	Cellulose	ErCl <sub>3</sub>	240°C, 30 min	91.1	[77]
14	Cellulose	Er-K10	240°C, 30 min	67.6	[78]
15	Cellulose	Er/deAlβ-zeolite	240°C, 30 min	58	[79]
16	Cellulose	Pb(NO <sub>3</sub> ) <sub>2</sub>	190°C, 2 h	71	[80]
17	Cellulose	VOSO <sub>4</sub>	180°C, 2 h	54	[81]
18	Fructose	AlCl <sub>3</sub> + SnCl <sub>2</sub>	190°C, 2 h	90	[82]
	Glucose		180°C, 2 h	81	
19	Cellulose	NbF <sub>5</sub> -AlF <sub>3</sub>	190°C, 2 h	65	[83]
	Cellulose		180°C, 2 h	27.3	
20	Cellulose	Nb@CaF <sub>2</sub>	180°C, 2 h	15.4	[84]
	Xylose		200°C, 1 h	38	
21	Glucose	LaCoO <sub>3</sub> perovskite	200°C, 1 h	40	[85]
	Cellulose		240°C, 1 h	24	

important contributions to biomass-based renewable bio-refinery [90]. To be deemed as a pioneer, Chambon et al. investigated the solid Lewis acids, AlW and ZrW, in the direct transformation of cellulose into LA along with a general yield (Table 2, Entry 7) of 28% and 19%,

respectively [71]. As derived from the research, the positive synergy between water autoprotolysis and solid Lewis acidic catalyst surface were determined as the key role in directly producing LA from crystalline cellulose. The former function was found to depolymerize cellulose to soluble

intermediates, and LA could be produced by the AlW and ZrW Lewis acids from the soluble intermediates. After then, to continue this interesting work, further study was investigated in detail regarding the direct transformation of raw pine-wood sawdust biomass into LA using ZrW Lewis acid [72]. The advantage of the utilization of real raw biomass instead of isolated cellulose for the production of biochemicals is to avoid costly fractionation processes. Interestingly, based on the LA production of kinetic studies of model cellulose and pine-wood sawdust, lignin/hemicellulose present in raw wood biomass was believed to not hinder the function of ZrW for conversion of LA, which is contrary to general expectations. However, solid Lewis ZrW was determined to deactivate among the two reaction kinds. In spite of this, on the basis of their studies, direct transformation of raw cellulosic biomass into biochemicals such as LA comes to be feasible. Hemicellulosic biomass (xylose or xylan) was also investigated to be converted into LA, using a commercial  $\text{ZrO}_2$  catalyst in the pH neutral aqueous solvents [73]. LA yield of 42% and 30% from xylose and xylan, respectively, could be achieved under the optimized reaction conditions, while negligible LA yield was obtained in the absence of  $\text{ZrO}_2$ . A detailed reaction mechanism regarding the formation of LA from xylose was also studied. Acidic-basic bifunctionality of  $\text{ZrO}_2$  was determined to be the key role in LA formation from xylose. To be specific, the carbonyl group of xylose interacts with the  $\text{Zr}^{4+}$  Lewis acidic site, and the  $\text{O}^{2-}$  anion on the  $\text{ZrO}_2$  surface as weak base adsorbs onto the OH group [91–93]. After then,  $\text{Zr}^{4+}$  Lewis acidic site activates the carbonyl group of PAL followed by the nucleophilic attack of  $\text{OH}^-$  from water auto-dissociation. However, an environmental-friendly method for the production of LA from hemicellulosic biomass in the aqueous catalytic process presents a promising way to transform hemicellulosic biomass. In a similar manner, Wattanapaphawong et al. studied the  $\text{ZrO}_2$ -based catalysts (Table 2, Entry 10–11) to produce LA from cellulose directly, giving acceptable yield [74, 75]. However,  $\text{ZrO}_2$ - $\text{Al}_2\text{O}_3$  catalysts bearing more Lewis acid sites and far fewer base sites compared to  $\text{ZrO}_2$  exhibit a higher LA yield. This suggests that Lewis acid sites played a more important role in producing LA than base sites [75].

In fact, the yield of LA is not very high when using the aforementioned catalysts from cellulose. With respect to this regard, Wang et al. designed the erbium- (Er-) based Lewis acid catalyst for the production of LA directly from cellulose, along with high yields (Table 2, Entry 12–15). Initially, they investigated lanthanide triflates catalysts to prepare LA from cellulose, and  $\text{Er}(\text{OTf})_3$  was determined to be the best choice with 89.6% LA yield under optimized reaction conditions [76]. In addition,  $\text{Er}(\text{OTf})_3$  could be recycled and exhibited similar LA yields in up to five consecutive reutilizations. After then, they continued to use  $\text{ErCl}_3$  as an efficient Lewis acidic catalyst for the production of LA from cellulose, and a 91.1% high LA yield could be achieved [77]. Similarly,  $\text{ErCl}_3$  was also determined to be stable among the course of the five catalytic runs. To some extent, this simple and environmental-friendly means is of great importance regarding the economical LA production, from lignocellulosic

biomass in large-scale applications, importantly, inspired by the remarkable reactivity of  $\text{Er}^{3+}$  with regard to LA production from cellulose, and heterogeneous catalysis is playing the more and more role in biomass conversion. Combined with the commercially available and cheap montmorillonite K10 clay bearing many advantages such as significant cation-exchange ability, erbium-exchanged montmorillonite K10 clay catalysts were prepared and investigated in the LA production from cellulose [78]. However, to be served as a heterogeneous catalyst, a high LA yield of 67.6% could be obtained under optimized reaction conditions. Unfortunately, LA yield decreased to some extent during recycling study, and erbium metals leaching along with carbon cokes deposition were believed as the main reasons. Recently,  $\text{Er}/\text{deAl}\beta$ -zeolite prepared by the same group was also examined for LA production from cellulose, and acceptable LA yield could be also obtained. Encouragingly, a better reusability was determined than  $\text{Er}$ -K10 [79].

In addition to Dong group, Wang et al. also researched the LA production from cellulose with a high yield using Lewis metal inorganic salts, and detailed reaction mechanism was also demonstrated (Table 2, Entry 16–18). Their pioneering work regarding the LA preparation with 71% yield by the addition of dilute  $\text{Pb}^{2+}$  ions could be achieved at  $190^\circ\text{C}$  in 2 h [80], which was milder than Dong's studies. More importantly, detailed theoretical (cluster-continuum model) and experimental studies were introduced to determine the reaction pathway, wherein  $\text{Pb}^{2+}$  in combination with water played the key role in isomerization of glucose (cellulose hydrolysis products) to fructose, cleavage of the  $\text{C}_3$ - $\text{C}_4$  bond of fructose into trioses, and the transformation of trioses to LA. Nonetheless, the toxicity of  $\text{Pb}^{2+}$  must be taken into account prior to the practical application on the basis of the interesting study. Furthermore, how to efficiently separate and recover the  $\text{Pb}^{2+}$  without increasing the process cost is also needed to be addressed. After then, to continue their research, a cheaper and less toxic vanadium salt,  $\text{VOSO}_4$ , was found to perform well in both LA or formic acid production from cellulose by simply shifting the reaction atmosphere from  $\text{N}_2$  to  $\text{O}_2$  [81]. They suggested that under anaerobic conditions,  $\text{VO}^{2+}$  could catalyze the isomerization of glucose to fructose, the retro-aldol fragmentation of fructose to  $\text{C}_3$  sugars, and the isomerization of  $\text{C}_3$  sugars into LA. However, to convert cellulose into LA using a more environmental-friendly catalytic system is being highly demanded. With respect to this regard, Wang et al. found that the combination of  $\text{Al}(\text{III})$  and  $\text{Sn}(\text{II})$  cations could be served as an efficient and less-corrosive catalyst for the transformation of LA directly from cellulose [82]. Under the optimized conditions, high LA yields could be achieved, accordingly (Table 2, Entry 18). More importantly, on the basis of experimental and computational studies, the detailed reaction pathway (Figure 6) and mechanism (Figure 7) were proposed. It was found that  $\text{Al}(\text{III})$  was primarily responsible for isomerization of glucose into fructose by 1,2-hydride shift and the conversion of  $\text{C}_3$  intermediates into lactic acid, whereas  $\text{Sn}(\text{II})$  took effect on the retro-aldol fragmentation. On the basis of their valuable studies,



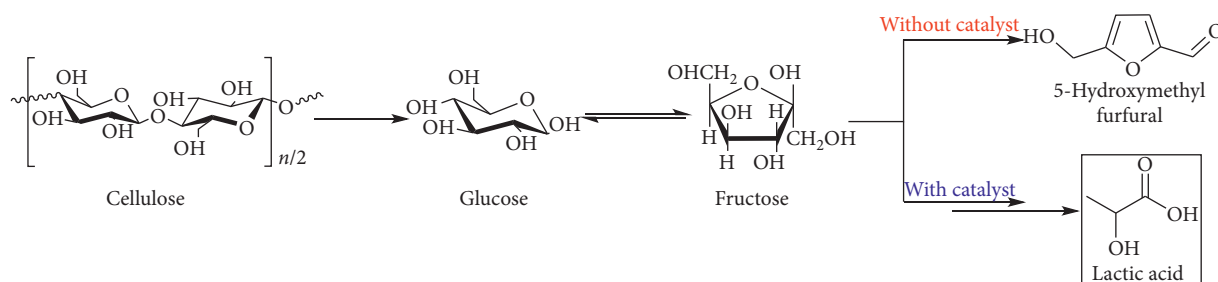


FIGURE 6: Proposed reaction pathways of the transformation of cellulose in the presence and absence of Al(III)-Sn(II) catalyst.

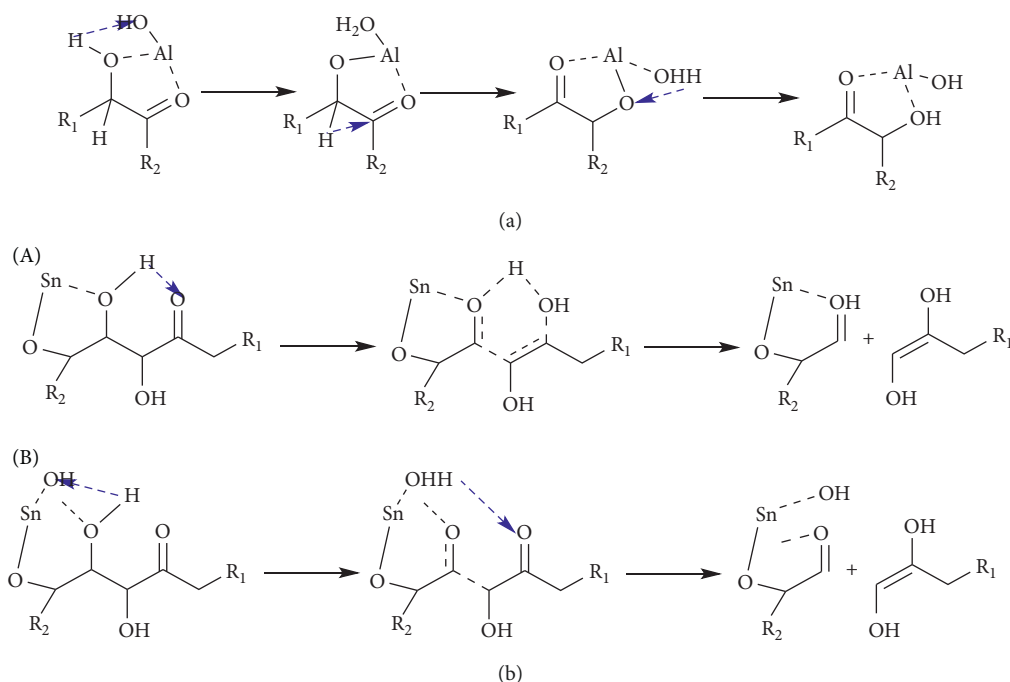


FIGURE 7: Proposed reaction mechanism of the isomerization and retro-aldol fragmentation with Al(III)-Sn(II) catalyst.

designing the suitable catalysts coupling of multifunctional sites for the chemical reactions with high selectivity, especially biomass transformations which contain complex tandem elementary steps may be feasible to some extent.

As shown above, niobium-based catalysts can catalyze  $C_3$  and  $C_6$  sugars into LA (Section 2.2.1). Therefore, employing niobium-based catalysts to convert cellulose into LA may be feasible. Coman et al. fabricated the Nb-based inorganic fluorides catalysts,  $NbF_5-AlF_3$  and  $Nb@CaF_2$  containing both Brønsted and Lewis acid sites, for the effective one-pot conversion of cellulose into LA, in the aqueous reaction phase [83, 84]. Nb(V)/Nb(IV) species were determined as the key active sites with respect to the mainly tandem steps including glucose isomerization into fructose, fructose retro-aldol condensation, and the triose isomerization to LA. However, solid Lewis acids and bases have been proven to be effective for LA preparation from sugars, utilization of the interesting redox catalysts, and relevant reaction mechanism is barely understood. As for this, Yang et al. demonstrated an important work using  $LaCoO_3$  perovskite metal oxides to produce LA, and the detailed reaction mechanism regarding

redox properties of  $LaCoO_3$  was presented clearly (Figure 8) [85]. Unlike traditional Lewis acid or base catalysis, as illustrated in Figure 8, the redox pathway started from the oxidative decarboxylation of aldose sugars and the lattice oxygen atoms participated in the redox cycles. Firstly, glucose was oxidized into gluconic acid; secondly, gluconic acid took oxidative decarboxylation to form xylose; thirdly, xylose repeated the oxidation step to transform into xylonic acid followed by oxidative decarboxylation to produce C4 aldose and which would be oxidized to hydroxybutyric acid; fourthly, dehydration happened at elevated temperatures to form pyruvic acid; fifthly, through the reduced perovskite structure,  $LaCoO_{2.5}$ , pyruvic acid was finally reduced to target product LA.

### 3. Production of Alkyl Lactates

Bio-based methyl/ethyl lactates (ML, EL), nontoxic liquids owning high boiling points, are being served as the potential value-added compounds with a high extent of functionality especially in green alternative solvents [94]. Of particular

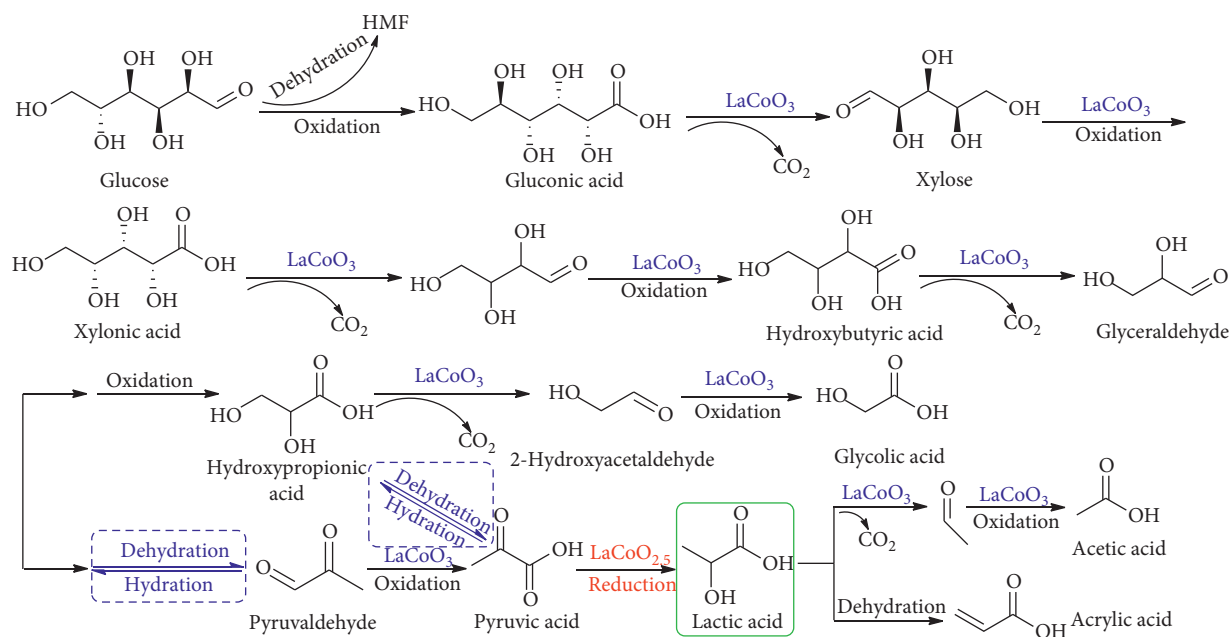


FIGURE 8: Proposed redox reaction pathway of LA production from glucose using  $\text{LaCoO}_3$ .

interest is to employ renewable biomass feedstocks (i.e., cellulose, sugars, and so on) to synthesis alkyl lactates via a chemical process with high yields. Currently, for the industrial production of lactates, esterification of LA with alcohol is the main method using homogeneous acids [95]. However, the use of the highly corrosive acid catalyst which needs costly neutralization and separation steps will cause environmental issues that conflict with the purport of green chemistry. In order to address this, many researchers have presented valuable studies with respect to the efficient preparation of alkyl lactates from sustainable biomass feedstocks.

**3.1.  $\text{C}_3$  Sugars to Lactates.** Generally,  $\text{C}_3$  sugars were usually employed to be the substrates for the production of lactates to serve as the model reaction, with the final aim of using lignocellulose biomass directly. Derived from the relevant studies of mechanism, as illustrated in Figure 9, trioses (DHA or GLA) can be converted into lactates using acids bearing Brønsted/Lewis active sites, wherein Lewis acid is playing the key role in producing lactates. In a similar manner with the production of LA from sugars, zeolites Lewis solid acids showed the most promising application with high reactivity in producing lactates from trioses. Pioneering work was presented by Taarning et al., wherein strong Lewis-acidic Sn-Beta was determined to exhibit the best performance with nearly 100% ML yield at 115°C for 24 h from DHA [51]. In addition, based on their valuable study, during the reaction of trioses in methanol, Lewis acids are believed to be selective towards the ML, whereas Brønsted acids prefer the formation of PADA, accordingly. The reaction pathway involved the Meerwein-Ponndorf-Verley–Oppenauer-type redox reaction of PAL hemiacetal (MeOH), wherein the 1,2-hydride shift takes place in

a concerted fashion to form ML, respectively (Figure 10). Inspired by this important research, starting from  $\text{C}_3$  sugars, zeolites catalysts including USY CBV600 (ML yield of 82% at 110°C for 4 h) [96], Sn-MCM-41 (EL yield of 98% at 90°C for 6 h) [97], Sn-MWW (ML yield of 99% at 120°C for 24 h) [98], GaUSY (EL selectivity of 82% at 85°C) [99], hierarchical tin zeolites (ML yield of 90% at 80°C for 5 h) [62], and hierarchical niobium-containing zeolites (ML yield of 96% at 80°C for 5 h) [100] were investigated in the alkyl lactates preparation. However, the nature of acidic sites was determined to influence products distribution strongly, wherein Lewis acids favor ML/EL formation which is the same conclusion of Christensen's work.

As discussed above, tin-based acids catalysts showed excellent reactivity towards lactates formation. According to these results, tin ion-exchanged montmorillonites [101], and tin-silicate catalyst synthesized by aerosol-assisted sol-gel method [102] were also prepared and used in lactates production with high activities. More importantly, Pighin et al. showed two interesting studies regarding detailed kinetic and mechanistic lactates formation from  $\text{C}_3$  sugars, using  $\text{Sn}/\text{Al}_2\text{O}_3$  catalysts [103–105]. On the basis of the kinetic studies and the proposed pseudohomogeneous mechanism, starting from DHA, ML/EL could be selectively transformed through pyruvic aldehyde hemiacetal intermediates via isomerization by Lewis acids, whereas Brønsted acidic catalysts favored the PADA formation.

**3.2.  $\text{C}_6$  Sugars to Lactates.** Compared to trioses, the transformation of hexoses into lactates through chemocatalysis is more preferable. Some relatively typical homogeneous Lewis acidic catalysts were studied with respect to converting  $\text{C}_6$  sugars into lactates, such as  $\text{SnCl}_4$  [106],  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ - $\text{SnCl}_2$  two-component catalyst system [107], and  $\text{ZnCl}_2$  [108] with

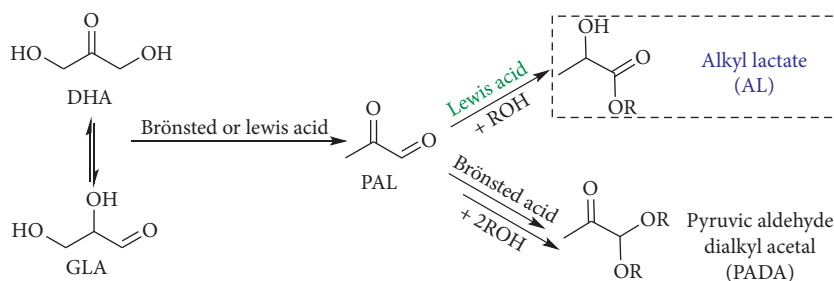


FIGURE 9: Proposed mechanism for the conversion of DHA to ethyl lactate.

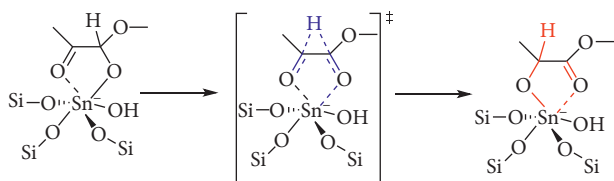


FIGURE 10: Proposed mechanism of ML formation by Sn-Beta.

high yields, respectively. Encouragingly, Yang et al. used  $\text{SnCl}_4$ - $\text{NaOH}$  catalyst system to convert carbohydrates to ML under mild conditions (Table 3, Entry 1). According to the detailed studies, upon neutralizing the protons derived from the methanolysis of  $\text{SnCl}_4$  with  $\text{NaOH}$  base, the side reaction of dehydration of  $\text{C}_6$  sugars to methyl levulinate was restrained, and ML yield could be improved to some extent by this facile and effective method. More importantly, Nemoto et al. revealed a valuable work regarding the role of  $\text{NaBF}_4$  salts in the transformation of ML using  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ - $\text{SnCl}_2$ . Based on hard-soft-acid-base rules [124], Sn species, relative hard acids that could be coordinated with the  $\text{BF}_4^-$  anion (a hard base), while could not be coordinated with the  $\text{Cl}^-$  anion (a borderline base) which would be replaced with  $\text{MeOH}$  (a hard base). As a consequence, by the addition of  $\text{NaBF}_4$ , the  $\text{InCl}_3$  and  $\text{SnCl}_2$  species may exist independent of each other, which would improve about 20% yield of ML, accordingly.

Alternatively, heterogeneously solid Lewis acidic catalysts seem to be a better choice due to their high activity and recyclability. With regard to transformation of lactates from  $\text{C}_6$  sugars, Taarning's work is regarded as the most valuable and pioneering research without hesitation (Table 3, Entry 4). For sucrose to be converted into lactates, the reaction mechanism is wherein Lewis acidic sites are determined to play the key role in the isomerization of PAL to ML via 1,2-hydride shift. A high ML yield of 68% using sucrose as a substrate can be achieved at  $160^\circ\text{C}$  for 20 h. More importantly, the Lewis acidic zeotypes could be simply filtrated and exhibited high stability for multiple recyclings after a simple handling by calcination only, without any substantial change in terms of product selectivity. Similarly, based on the valuable work regarding the excellent reactivity and stability of tin Lewis acidic zeotypes, many studies for the conversion of carbohydrates into ML using modified tin-based zeolites spring up as presented in Table 3 (Entry 5–7, 9–12). Especially, Tolborg et al. revealed that by the addition of alkali salts during the synthesis of tin zeolite, ML yield

could be improved more than two-fold than pure tin beta [112]. They proposed that in the presence of alkali salts, some of the Brønsted acidic sites derived from defects in the framework will be neutralized. As a result, the formation of byproducts could be hindered and the selectivity for ML will be improved, accordingly. Some other modified studies such as hierarchical Sn-Beta zeolites prepared by no fluoride and low concentration tetraethylammonium hydroxide (TEAOH) template [114], hierarchical Sn-Beta zeolites synthesized by the assistant template of polydiallyldimethylammonium chloride (PDADMA) [116], and Sn-Beta zeolites with nano-size and fewer defects [117] were also investigated in detail to clarify the structure-reactivity relationship. In a similar manner, they all revealed that the modified Sn-Beta bearing the promoting effect of mesoporosity performed better than the microporous Sn-Beta zeolite, in terms of yield and turnover frequency values (TOFs). To some extent, this can contribute to the vital and challenging process of the biorefinery when using large molecules such as cellulose.

However, the aforementioned studies investigated the tin-based zeotypes for efficient production of lactates, and little attention was paid to the systematic investigation of kinetic and mechanistic understanding in the Sn-Beta-catalyzed lactates course. With regard to this, Tosi et al. designed the relatively detailed kinetic analysis of fructose, glucose, and sucrose transformation to ML through typical Sn-Beta [125]. Emphasis was focused on the influence of substrate masking and water using 1D and 2D NMR spectroscopy method. They revealed that most ML was not produced from the substrates directly; however, methyl fructosides were determined as the key intermediates. At  $160^\circ\text{C}$ , over 40% of substrate carbon were masked (i.e., reversibly protected in situ) as methyl fructosides within a few minutes when employing hydrothermally synthesized Sn-Beta, while more than 60% methyl fructosides could be formed within a few minutes by post-synthetically treated Sn-Beta. Moreover, the existence of water (to release fructose) could tailor the masking process wherein the addition of small quantities of water was able to accelerate conversion to ML without the decrease of catalyst stability. In addition to tin-based zeolites, another valuable research using bifunctional carbon-silica catalysts (Sn-Si-CSM-773-20.4) bearing both Lewis and weak Brønsted acid sites did make an important contribution to lactates production [118]. Lewis acid sites were introduced through

TABLE 3: Catalytic production of lactates from C<sub>6</sub> sugars and cellulose via acid-catalysis.

Entry	Substrate	Catalyst	Reaction conditions	Yield of lactates (%)	Reference
1	Glucose	SnCl <sub>4</sub> -NaOH	160°C, 2.5 h	47	[106]
	Fructose			57	
	Sucrose			51	
2	Fructose	InCl <sub>3</sub> ·4H <sub>2</sub> O-SnCl <sub>2</sub> , NaBF <sub>4</sub>	160°C, 10 h	72	[107]
	Glucose			47.7	
3	Fructose	ZnCl <sub>2</sub>	200°C, 3 h	51.7	[108]
	Sucrose			47.5	
	Sucrose			68	
4	Glucose	Sn-beta	160°C, 20 h	43	[109]
	Fructose			44	
5	Xylose	Sn-beta	140°C, 20 h	42	[110]
6	Glucose	Sn-MCM-41	160°C, 20 h	43	[111]
7	Sucrose	K-PT-Sn-beta	170°C, 16 h	71	[112]
	Xylose			41	
8	Fructose	Zr-SBA-15	240°C, 6 h	44	[113]
	Glucose			38	
	Sucrose			40	
9	Glucose	Hierarchical Sn-Beta	160°C, 10 h	58	[114]
10	Inulin	Sn-SBA-15	160°C, 20 h	57	[115]
11	Sucrose	Sn-beta-H	160°C, 20 h	72.1	[116]
	Fructose			47	
12	Mannose	Sn-beta-9h	160°C, 10 h	39	[117]
	Sucrose			57	
	Fructose			17	
13	Glucose	Sn-Si-CSM-773-20.4	155°C, 20 h	32	[118]
	Sucrose			45	
14	Sucrose	ZIF-8	160°C, 24 h	42	[119]
15	Glucose	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	160°C, 6 h	34	[120]
	Cellulose		210°C, 4 h	32.1	
16	Sugarcane bagasse	SnCl <sub>2</sub> ·2H <sub>2</sub> O-ZnCl <sub>2</sub>	190°C, 6 h	31.2	[121]
17	Cellulose	Zr-SBA-15	240°C, 10 h	28.1	[113]
18	Cellulose	Zr-SBA-15	260°C, 2 h	~33	[122]
	Cellulose		270°C, 5 h	57.8	
	Glucose		270°C, 1 h	64.0	
19	Fructose	Ga-doped Zn/H-nanozeolite Y	270°C, 1 h	67.3	[123]

grafting Sn (IV) to the silica surface, and important Brønsted acid sites (number and strength) were controlled by tailoring the carbon deposition content, pyrolysis temperature, and thermal posttreatment. With this versatile material, the one-pot transformation of fructose, glucose, and sucrose into ML could be proved, along with 32%, 17%, and 45% yield, respectively (Table 3, Entry 13). However, the complicated and longstanding synthetic procedure should be involved to prepare this material, which would influence its industrial application. Similar to ref. 70, ZIF-8 MOFs were also tested in the conversion of hexoses into ML. Successfully transformation of sucrose to ML with a high yield of 42%, at 160°C in 24 h was achieved [119]. It is worth noting that the latest work regarding hexoses conversion into ML was presented by Yamaguchi et al. using an interesting catalyst  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with acid-base bifunctional characters, showing considerable ML yield [120]. It was found that due to the essential high acid and base densities of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, cascade reactions in glucose to ML consisting isomerization, retro-aldol, and dehydration could be successfully carried out, with 34% yield of ML from glucose at 160°C for 6 h.

**3.3. Cellulose to Lactates.** Generally, the direct utilization of cellulose as feedstocks for the production of lactates is being deemed to be a milestone, especially through the versatile chemocatalysis. With respect to this research, limited studies regarding the efficient transformation of lactates from cellulose via chemocatalysis can be presented, because of the very complex reactions and the inherent rigidity of cellulose. For the homogeneous catalyst used in lactates production from cellulose, SnCl<sub>2</sub>·2H<sub>2</sub>O-ZnCl<sub>2</sub> was utilized as an efficient catalyst to ML production with 32.1% yield in methanol, at relatively mild reaction conditions with 210°C for 4 h [121]. In addition, 31.2% ML yield could be also obtained from real biomass sugar cane bagasse at 190°C within 6 h. However, lower yields of ML were achieved from glucose (15.7%) and sucrose (14.7%), may be derived from the strong acidity of SnCl<sub>2</sub>·2H<sub>2</sub>O-ZnCl<sub>2</sub> which would transform many monosaccharides and disaccharides into dark tars. On the other hand, Zr-SBA-15 heterogeneous catalysts developed by Lin group, could not only exhibit good yields of ML from monosaccharides and disaccharides (Table 3, Entry 8) [113], but also perform well from cellulose directly in 95% methanol solvent [113] and in 95% ethanol [122],



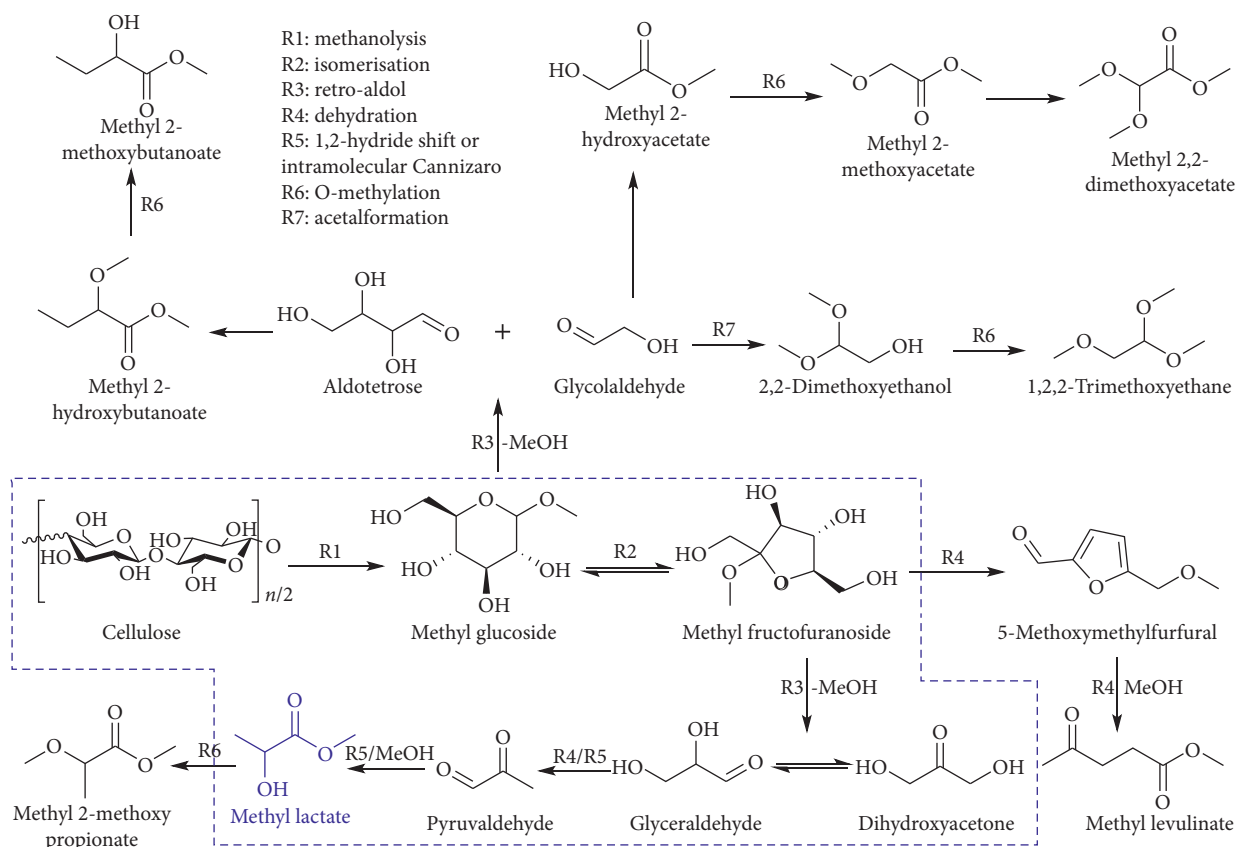


FIGURE 11: Proposed reaction pathway for the conversion of methyl lactate from cellulose using Ga-doped Zn/HNZY.

respectively. The addition of a little amount of water (5 wt%) along with the weak Brønsted acids of Zr-SBA-15, was believed to facilitate the hydrolysis of cellulose. After then, the Lewis acidic sites of Zr-SBA-15 played the key role in a series of reactions such as isomerization, retro-aldol condensation, and so on. However, despite the high cost of the equipment, the “one-pot” process using water as cosolvent in supercritical alcohol conditions can be regarded as an environmental-friendly way to yield lactates directly from cellulosic biomass.

Nonetheless, the aforementioned catalysts not presented high yields of lactates from cellulose directly. With respect to getting a high productivity of lactates from cellulose, Verma et al. designed the Ga-doped Zn/H-nanozeolite Y catalysts, to be served the most efficient materials so far for converting cellulose directly into ML with 57.8% yield at 270°C, 5 h in supercritical methanol [123]. It is believed that due to the enhancement of Lewis acid sites along with the decrease of Brønsted acid sites which derived from doping of Ga on ZnO, together with large external surface areas of HNZY, were determined as the crucial parameters to highly converting cellulose into lactates. More importantly, the catalyst could be reused in four consecutive cycles, with ignorable selectivity towards ML, highlighting its excellent stability. The detailed reaction pathway was proposed accordingly (Figure 11), including several steps such as methanolysis, isomerization, retro-aldol condensation, and so on. Some other side-products could also be formed by tailoring the

reaction parameters; however, Ga-doped Zn/HNZY is determined to be crucial to control the consecutive reaction pathways for the upgrading of cellulose into glucose, retro-aldol condensation into trioses, and intramolecular Cannizzaro reaction into ML.

#### 4. Conclusion and Perspective

Catalytic transformations of valuable organic acids such as lactic acid, levulinic acid, and amino acid from renewable carbon resources including polysaccharides, lignin, and their derivatives is of high interest for a sustainable chemical industry in the future [126, 127]. The development of efficient techniques for commercial lactic acid and alkyl lactates production from lignocellulosic biomass is regarded as an important process of biorefinery, in order to reduce the reliance on petroleum feedstocks. Compared to traditional fermentation methods suffering from waste dispose, costly separation, and the inability to transform cellulosic biomass without costly pretreatments, chemocatalysis is being recognized as an effective formidable strategy to upgrading cellulosic biomass into value-added chemicals with acceptable selectivity. However, the separation of enantiomers is a formidable and tremendous challenge because of the extremely similar physical and chemical properties caused as good as molecular structure. The technical challenge to achieve that is the very low enantiomer selectivity and the limited loss of one of the lactate isomers. Moreover, although

basic catalysts are capable of catalyzing biomass into LA under hydrothermal conditions, the difficulty in acquiring a high LA yield is the main challenge.

From the environmental-friendly point of view, heterogeneously solid acidic catalysts which are less corrosive and can be recycled from the reaction medium for reutilization are considered to be the better choice currently. Sn-based zeotype catalysts bearing strong Lewis acidities have demonstrated excellent performance for the transformation of sugars to lactates. However, long synthesis time especially Sn- $\beta$  with crystallization time up to 10–20 days and the utilization of some toxic tin precursors may hamper the industrial applications, to some extent. Furthermore, the poor stability at elevated temperatures and the narrow channels of Sn-Beta hindering the large biomass molecules (i.e., cellulose) to contact with active sites should also be taken into consideration. It is worth mentioning that the introduction of weak Brønsted acids is believed to be beneficial to LA and lactates transformation. With respect to the catalyst design, some suggestions based on the literature are presented here:

- (i) More attention is recommended to pay on the synthesis of active, selective and durable solid acidic catalysts for the efficient transformation of cellulosic biomass into LA and lactates
- (ii) The design of novel multifunctional (i.e., controllable active sites, strong Lewis acidic functional groups with weak Brønsted acidic sites, and acid-base bifunctional sites) heterogeneous catalysts is highly appreciated
- (iii) It should be reinforced to design the mesoporous nanocatalysts, bearing large surface area along with large pore size, in order to render reactants contact with the active sites easily
- (iv) More studies are demanded to propose a facile method that can prepare the target catalysts in view of large-scale and low-cost
- (v) For lactates production, the recyclability of methanol or ethanol solvent should be taken into consideration, which is likely to affect the whole process economics, in order to intensify the sustainable process
- (vi) It is indispensable to be devoted into an insightful understanding in terms of the reaction mechanism and structure-properties of the catalysts, which is helpful to understand the reaction pathways and the better design of catalysts

## Conflicts of Interest

The authors have no conflicting interests to declare.

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