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Review

Hydrothermal conversion of fructose to lactic acid and derivatives: Synergies of metal and acid/base catalysts

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ABSTRACT

With increasing strict regulation on single-use plastics, lactic acid (LA) and alkyl lactates, as essential monomers for bio-degradable polylactic acid (PLA) plastic products, have gained worldwide attention in both academia and industry. While LA is still dominantly produced through fermentation processes from start, chemical synthesis from cellulosic biomass remains a grand challenge, owing to poor selectivity in activating C—H and C—C bonds in sugar molecules. To our best knowledge, recent publications have been focused on hydrothermal conversion of glucose to LA, while this review summarizes the highlights on direct thermal conversion of fructose as starting material to LA and derivatives. In particular, the synergies of metal/metal cations and acid/base catalysts will be critically revised on retro-aldol and dehydration reactions. This work will provide insights into rational design of active and selective catalysts for the production of carboxylic acids from biomass feedstocks.

1. Background

With rapidly growing consumption of fossil fuels, researchers are paying increasing attention to renewable energy sources. For this consideration, biomass is believed to provide essential material supplies for the production of transportation fuels and chemicals for human society. The substitution of fossil-derived feedstocks with renewable energy sources has been the major driving force for the evolution of modern chemical industry [1–3]. Fructose, as a common cellulosic biomass feedstock, presents potential of transformation into a variety of commodity products such as 5-hydroxymethylfurfural (5-HMF), propylene, isomerized sugars, and sugar alcohols [4,5]. Among various fructose-derived intermediates, lactic acid (LA) is one of the important platform chemicals, which can be applied in synthesizing many downstream chemicals such as acrylic acids, pyruvic acid, 1,2-propanediol, and 2,3-pentanedione [6]. With global movement striving for manufacture of renewable plastics to address the serious pollution in ocean and on land, worldwide efforts have been put in developing efficient technologies for synthesizing LA and its derivatives (Fig. 1).

Fructose actually occurs naturally in large quantities. Direct conversion of fructose to various value-added renewables can be important alternative for current biomass conversion technologies. Current literature reports often consider fructose as an intermediate during glucose upgrading, it is however true that direct conversion of fructose can be more flexible and potentially leads to formation of specialty products. Fundamental understanding of reaction chemistry and catalysis undoubtedly provides new insights into sugar-based bio-refineries. There has been lack of comprehensive discussion on conversion road map for fructose refining.

Synthesis of LA from fructose has been one of the most popular topics in the past few years, with particular focus on catalyst design and reaction mechanism in alkaline, base-free, metal oxide and metal complex systems [7–12]. However, to our best knowledge, the key role of metal species and Lewis acid/base in homogeneous and heterogeneous catalytic materials, in thermal conversion of fructose to LA, has not been summarized and critically discussed in recent literature [13–17]. Therefore, in this focused review article, the critical role of metal cations, metallic particles, Lewis/Brønsted acidic and basic catalysts in synthesis of LA and derivatives, involving C—C/C—H bond activation and catalyst design will be discussed with details.

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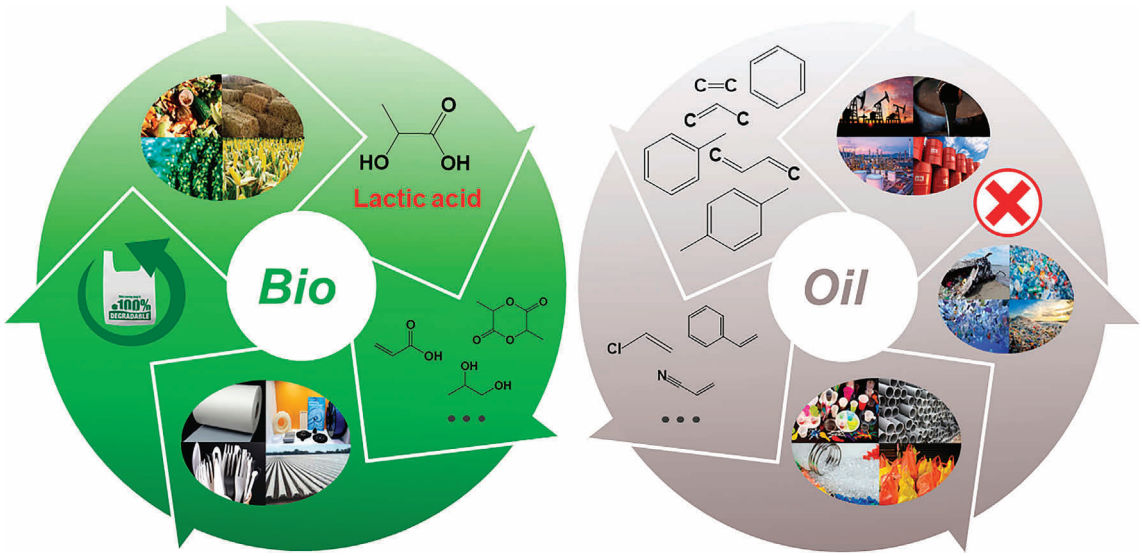

Fig. 1. Renewable PLA and oil-derived plastic products.

1.1. Production of fructose

Fructose is a simple hexose, which is widely found in honey, fruits, flowers, and root vegetables. It is a white, hygroscopic, crystalline solid, known as the sweetest natural sugar. The mixture of a certain concentration of glucose and fructose (42%–55%) as monosaccharides is called high-fructose corn syrup (HFCS), which has replaced sucrose as the main sweetener in the food industry [18]. Although humans have discovered fructose from plants since ancient times, it was not produced at industrial scale until 1970s. For a long time, the commercial competitiveness of fructose could not match some other sweeteners such as sucrose [19]. Due to the functional advantages of HFCS in sweetness, taste, solubility, consistency, transportation and humidity stability, *etc.* [20], consumption of HFCS increased ten folds between 1970 and 1999 and represented over 40% of all sweeteners added to foods and beverages [19,21,22]. In addition to the starch route, fructose can be produced from inulin [22,23]. This route has a richer source of raw materials than the starch route, the overall productivity is however still not comparable to the latter.

The conventional industrial production of HFCS is one of the largest biocatalytic processes, which basically involves three processes (Fig. 2): (i) liquefaction, which incompletely hydrolyzes the starch to dextrins and maltodextrins with hydrochloric acid and/or α-amylase (EC 3.2.1.1); (ii) saccharification, which hydrolyzes the oligomers to glucose with amyloglucosidase (AMG) (EC 3.2.1.3, glucoamylase); and (iii) isomerization, which isomerizes glucose to fructose with glucose isomerase (GI) (EC 5.3.1.5, xylose isomerase) [24,25]. Research advances in isomerization, refining and separation technologies like corn wet-milling, immobilized glucose isomerase, simulated moving bed, ion-exchange resin, *etc.*, increased the yield and quality of HFCS [20].

Besides, obtaining fructose from lignocellulose or glucose with chemical catalysis method is a research hotspot as the enzyme system has some drawbacks, such as easy deactivation and high price [26–31]. The key point of those works is generally designing a proper acid or base catalyst. For example, the hydrolysis of lignocellulose could be catalyzed by the Brønsted acid, and the formation of fructose were proved to be promoted by Lewis acid in the isomerization step. Those studies of acid-base catalytic system pave the way for the production of LA from fructose even glucose or lignocellulose (Fig. 3).

The manufacture of crystalline fructose has additional requirements for processing. Finnish Sugar Company developed ion-exchange methods first in early 1980s for hydrolyzing sucrose and separating the hydrolysate into fructose and glucose and then commercial crystalline fructose became available. Up to now, a number of methods for fructose separation have been established including the differential crystallization method [32], calcium compound method [33,34], ionic liquid [35,36], and chromatographic method [37]. Aqueous crystallization [38–40], organic crystallization [41,42], and drying crystallization are the three main crystallization methods of fructose separation [43]. With the advent of those techniques, the production of crystalline fructose grew to nearly 0.3 million tons, while the production of HFCS is about 8.3 million tons at the end of the twentieth century, according to the U.S. Department of Agriculture [44]. According to the latest data (2012–2020), global HFCS production is currently 13–14 million tons per year [45]. The U.S. accounted for about 51% of the world production, while China accounted for about 23%.

1.2. Conversion of fructose to LA and other renewable chemicals

With the saturation of the demand for HFCS in the food processing industry and the exploration of advanced sweeteners, consumption of HFCS has stopped growing in the last 20 years [46]. The extensive sources, sufficient capacity, and considerable economy of fructose (around 450 USD·t^{-1}) have promoted investigators to explore its transformation into other high value-added chemicals (Fig. 4). It can be transformed into furanic products including 5-HMF, 2,5-diformylfuran (2,5-DFF), 2,5-furandicarboxylic acid (2,5-FDCA), 2,5-bis(hydroxymethyl)-furan (2,5-BHF), and 2,5-dimethylfuran (2,5-DMF), through dehydration, reduction and oxidation reactions [47–51].

It is reported that fructose can also cleave to xylose or arabinose for further transformation into furfural and derivatives [5,52]. These furanic derivatives are widely applied in polymer production, solvents, biofuels, pharmaceuticals, and textile. Fructose can also be transferred into D-mannose by isomerization [53]; tagatose and D-psicose by epimerization [4,54]; and D-hamamelose by stereospecific isomerization [55,56].

Erythritol can be obtained from fructose [57]. Hexitols, such as sorbitol and mannitol can be obtained from hydrogenation of fructose [58]. Fructose can also be selectively oxidized into 5-ketofructose [59], gluconic acid, and glucaric acid [60,61]. In addition, fructose molecules can be used as the basic material to

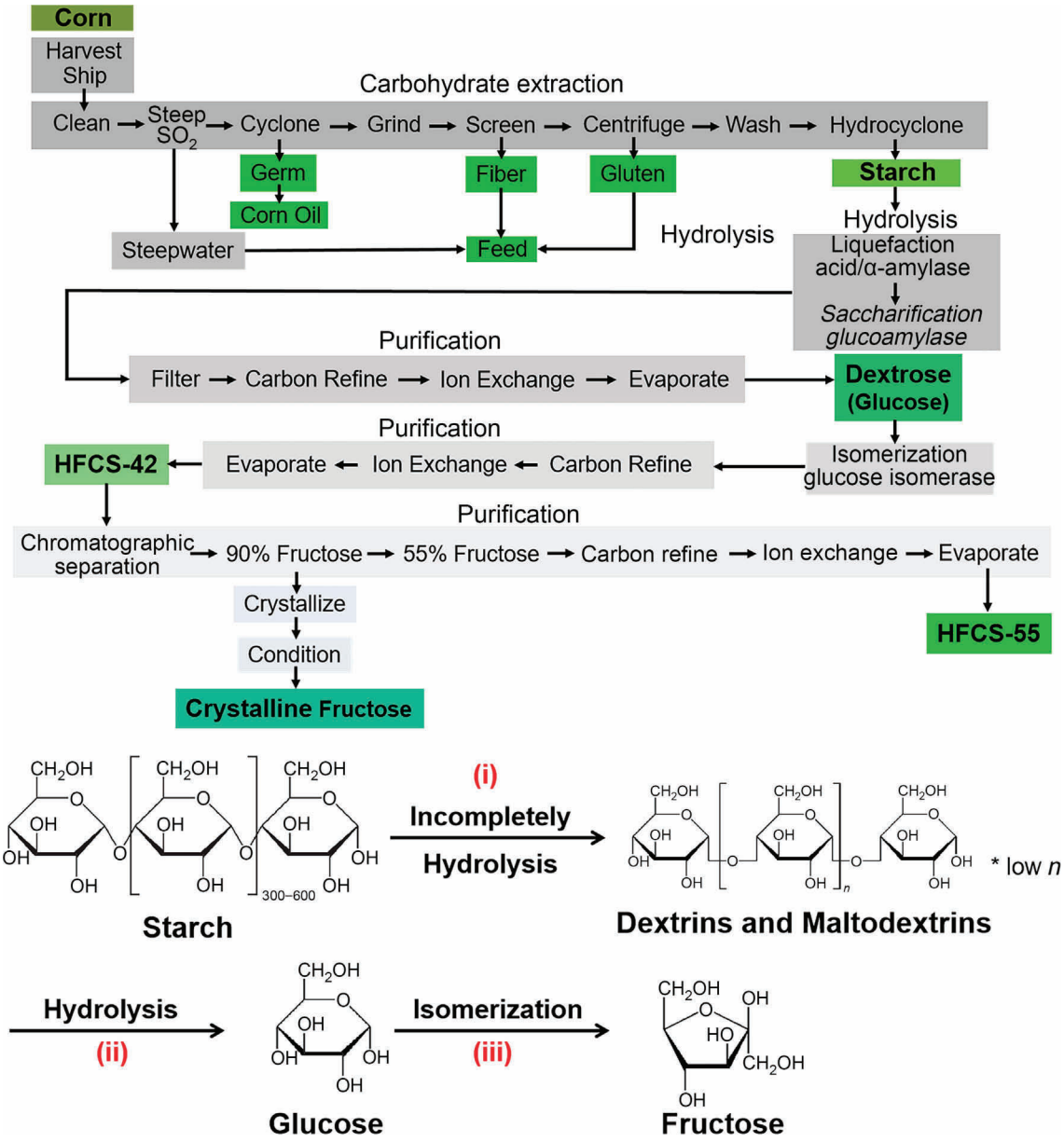

Fig. 2. Fructose production process (reproduced from Ref.[18] with permission of Springer).

synthesize complex compounds like 5,5′-[oxybis (methylene)]bis [2-furancarboxylic acid] (OBFA) [62], tri-orthogonally protected polyhydroxylated pyrrolidine alkaloids (PDPA) [63], amino- and thio-sugars [64], diacetone-β-fructose [65], and topiramate [66]. Many of those compounds are potential precursors for functionalized polymers in bio-medical applications [67]. The low carbon number compounds such as glycolic acid, glyceric acid, 1,2-propanediol, LA and glycerol can also be produced from fructose [68,69]. Among those, LA is a high-profile platform chemical with total production capacity over 600000 tons globally, of which China provides about 250000 tons [70]. We will introduce the production of fructose to LA detailly in this work.

2. Key Points for Fructose Conversion to LA

2.1. Biological and chemical synthesis of LA

LA is one of the oldest known organic acids, widely found in nature and used as acidifier, emulsifier, flavoring agent, antibacterial agent, and protective agent in food industry [71,72], tanning and dyeing agent in leather textile industry [73], peritoneal dialysis and calcium lactate for calcium deficiency in medical applications [6,74], as well as moisturizing agents for the skin in cosmetic industry [15,75]. Other manufacturing applications include replacing ethylene glycol as a coolant, adjusting pH in adhesive production and being used in lithography as a stop agent [6,76]. Popular applications of LA include synthesizing polylactic acid, acrylic acid, pyruvic acid, 1,2-propanediol, 2,3-pentanedione, acetaldehyde, and alkyl lactates (Fig. 5) [6]. They have a variety of different applications including coatings, adhesives, thickeners, fiber cleaners, electrolytes, absorbers, dispersants drugs, pesticides, skin care products and food additives, *etc.* [16,77–96].

Fossil fuel route. Conventional chemical synthesis of LA and alkyl lactates mainly relies on the side reaction of acrylonitrile technology. Its costs are high, and it is easily limited by other petroleum industry by-products. Therefore, this method was gradually eliminated [72,97,98].

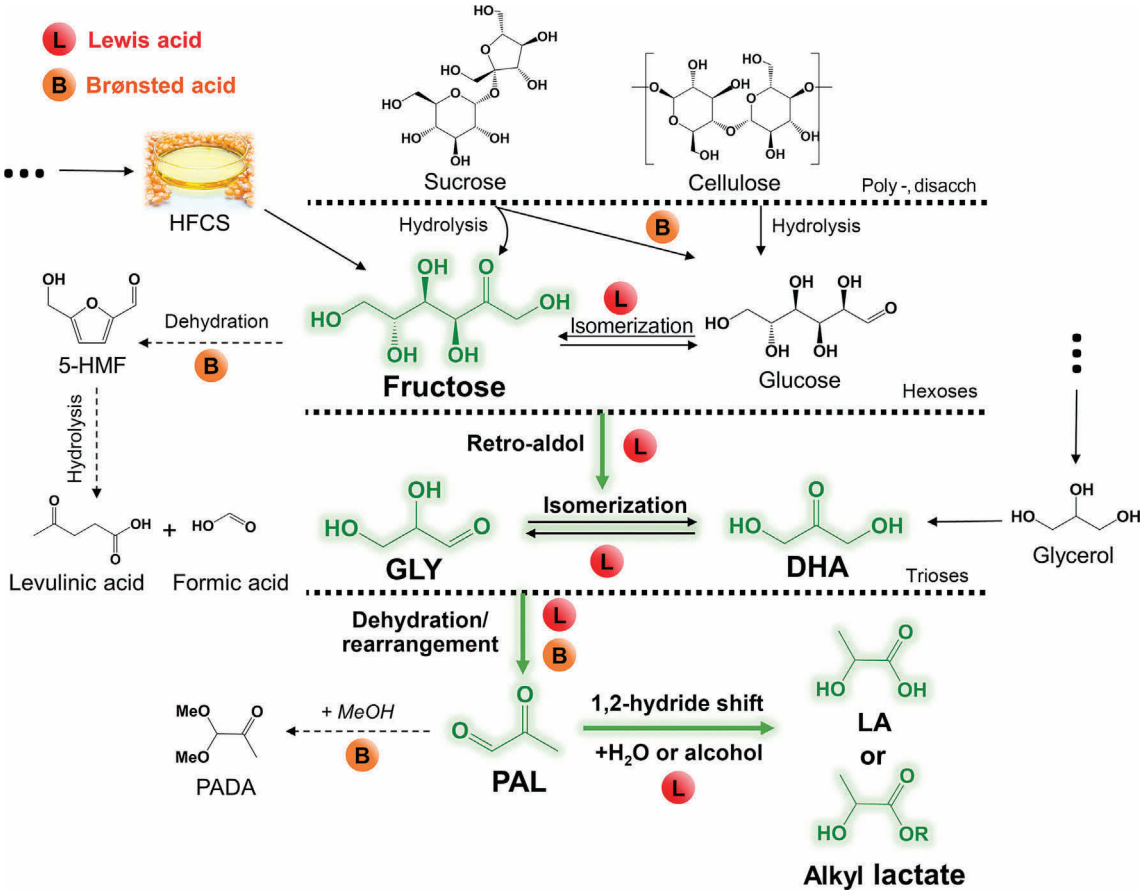

Fig. 3. Conversion route of carbohydrates to LA/alkyl lactate over Lewis and Brønsted acidic catalysts.

Fermentation. Worldwide LA production from microbial fermentation accounts for around 90% of the total [99]. The key of LA fermentation is the selection of prominent microorganism and the types and sources of fermentation substrates [73]. Approximately 90% of the commercially available LA is produced by submerged fermentation of corn [100]. Cellulosic substrates [101], microalgae [102–105], whey [106], and food waste were also reported to have the potential to produce LA [107]. Typically, four main steps are involved for the production of LA by fermentation, including: (i) pretreatment of feedstocks, (ii) anaerobic fermentation, (iii) acidulation, and (iv) separation and purification [108].

Hydrothermal/Catalytic synthesis. Recently, a series of investigations have been conducted on the hydrothermal conversion of biomass derivatives into LA. Glycerol, as a by-product of the biodiesel production, has been studied to produce LA and alkyl lactates [109–121]. Cellulosic substrates can also be applied in the chemical synthesis into LA [122]. As demonstrated above, fructose is one of the considerable cellulosic biomass feedstocks to produce LA, which will be canvassed in this article. And the investigation of this is a bridge between the long-chain carbohydrates or disaccharide, hexoses, and trioses to LA, playing a key role in the whole system [6]. The general steps of product LA or alkyl lactates from fructose are shown in Fig. 3: (i) retro-aldol condensation of fructose to dihydroxyacetone (DHA) and glyceraldehyde (GLY), (ii) dehydration or tautomerization of the trioses to produce pyruvic aldehyde (PAL), and (iii) PAL further undergoes hydration with the solvent to produce LA or alkyl lactate [122].

2.2. Synergistic Lewis and Brønsted acidic/basic catalysts

Lewis and Brønsted acidic sites play a key role in the thermal conversion path of fructose to LA (Fig. 3). In general, Lewis acidic sites facilitate (i) the retro-aldol of fructose into DHA and GLY, (ii) the isomerization between DHA and GLY, (iii) the dehydration and rearrangement of trioses into pyruvic PAL, and (iv) the 1,2-intramolecular hydride shift of PAL to form the LA type structure [109,111,123]. Brønsted acidic sites were reported to catalyze the transformation of trioses to PAL, but they would as well promote side reactions like dehydration of fructose into 5-HMF, rehydration of 5-HMF to levulinic acid and formic acid, and the formation of pyruvic aldehyde dialkyl acetal (PADA) from PAL with methanol solvent [11,124].

Obviously, an appropriative balance of acidic sites is critical to obtain a higher yield of LA. In most of the works, the contributions were aimed at improving the density of Lewis acidic sites and decreasing that of Brønsted acid, but it is also reported that over-reduction of the number of Brønsted acidic sites could suppress the dehydration of trioses to PAL while the amount of LA formed would decrease [124].

Researchers have established numerous methods to controllably adjust the balance of acidic sites. For example, in many reports, methanol and ethanol were used, instead of water thus forming methyl lactate (MLA) and ethyl lactate (ELA), respectively, rather than free carboxylic acids to diminish the catalytic effect of those Brønsted acids [9]. In homogeneous catalytic system, inorganic strong bases were used to neutralize Brønsted acids and various metal cations could provide Lewis acids [125–127]. In the studies of heterogenous catalysts, preparation and modification of catalysts are the main methodologies to adjust the acidic sites. The methods to control the balance of acidic sites generally include utilizing different skeleton structures of solid catalysts, selecting appropriate precursors, and adjusting the conditions for chemical modification [11,128–130]. Introducing metal species could promote facile formation of acidic sites and basic

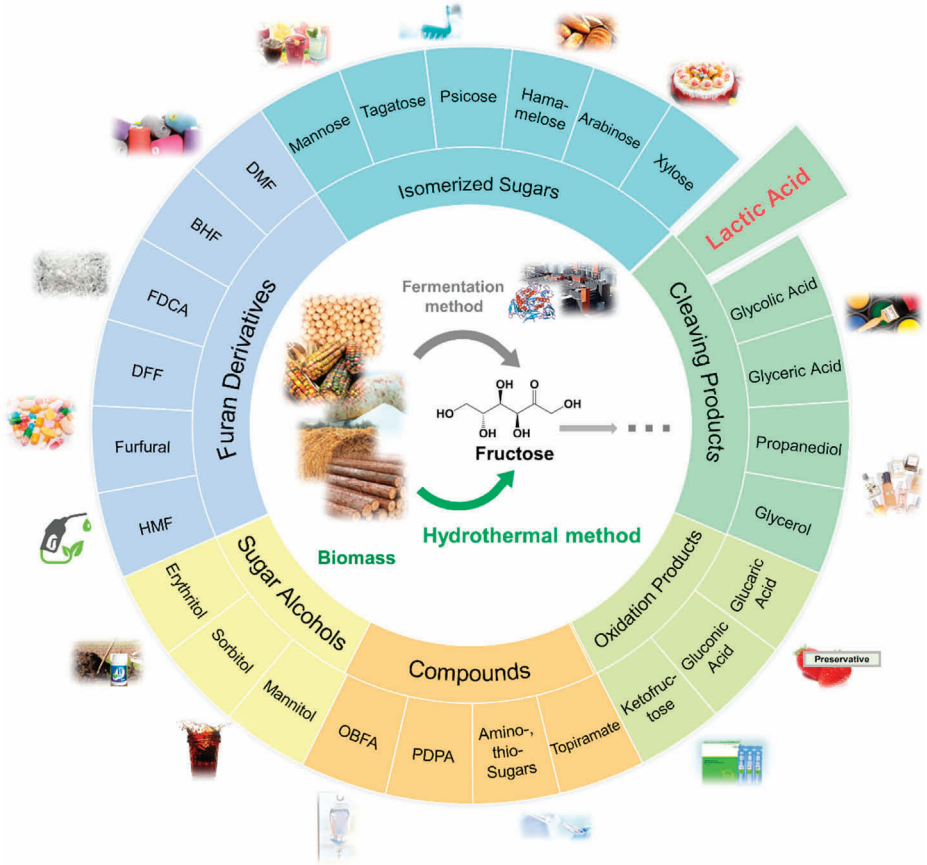

Fig. 4. Fructose resources and applications.

sites such as NH_2- were also introduced to balance the acidity in some works [131].

2.3. Effects of metal species

Fundamental understanding on the structure-property features of metal species is also critical for the conversion of fructose into LA or alkyl lactates in both homogeneous and heterogeneous systems.

In homogeneous catalytic medium. Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} from the added strong bases are the common metal cations in homogeneous alkaline catalytic systems. Those metal cations would affect the ionization of OH^- in aqueous solution, thus affecting the catalytic activity of those bases [132]. Besides, some metal cations such as Ba^{2+} was considered to form a complex with intermediate product PAL thus further promoting the conversion of fructose to LA [7].

A series of metal salts were studied in the conversion of fructose to LA in homogeneous Lewis acidic systems. Metal cations like Pb^{2+} act as Lewis acid, shifting the main reaction route to LA by reducing the activation Gibbs energy for the retro-aldol fragmentation and the isomerization of PAL to LA [133]. Not only Lewis acidic strength, but the formation of intermediate complexes play a key role, as demonstrated by the comparison of a series metal cations (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) [134]. Relations between cationic radius and conversion performances have also been studied, where different metal cations would follow different trends [135,136]. For example, smaller metallic cationic radius of lanthanide triflates leads to stronger binding ability of metallic ions with the hydroxyl groups of fructose, facilitating C—C cleavage to form LA. From hydrolysis point of view, the effects of protons or special species like $[Y(OH)_2(H_2O)_2]^+$ have been discussed in literature as well [125,137]. Dual-cation combinations have been studied, confirming that different metal cations show varied mechanisms during the conversion of fructose to LA [8,126,138]. Conclusions should thus be discussed on a case-by-case basis. In general, the types of metal cations should be noted in the conversion of fructose to LA and alkyl lactates in homogeneous Lewis acidic systems.

In heterogeneous catalytic systems. Different types of metals could provide completely different acidity. For example, Sn-β presents Lewis acidity, H-Al-β presents Brønsted acidity, and Si-β presents nonacidity [9]. The same metallic element could exist and react in different forms of metal species due to complicated surrounding environments. For example, Ni could catalyze fructose to MLA as NiOOH species on the surface of NiO metal oxide [139], while as β-$Ni(OH)_2$ and γ-NiOOH in the Ni-2-methylimidazole organometallic complex catalyst [140]. In dual-metal combinations, different metal species generally play distinct roles in different steps of the conversion of fructose. For example, in Zhang and colleagues' work on Pb-Sn-β catalysts, Sn species promote the dehydration of DHA, hydration of PAL and isomerization of PAL hydrates. Meanwhile, Pb species promote the retro-aldol reactions from fructose to DHA and GLY and inhibit the formation of by-products [141]. More details are given in the following chapters.

3. Synthesis of Lactates in Alkaline Medium

Alkali-catalyzed conversion of cellulose and its related carbohydrates into LA has been extensively studied in the past decade

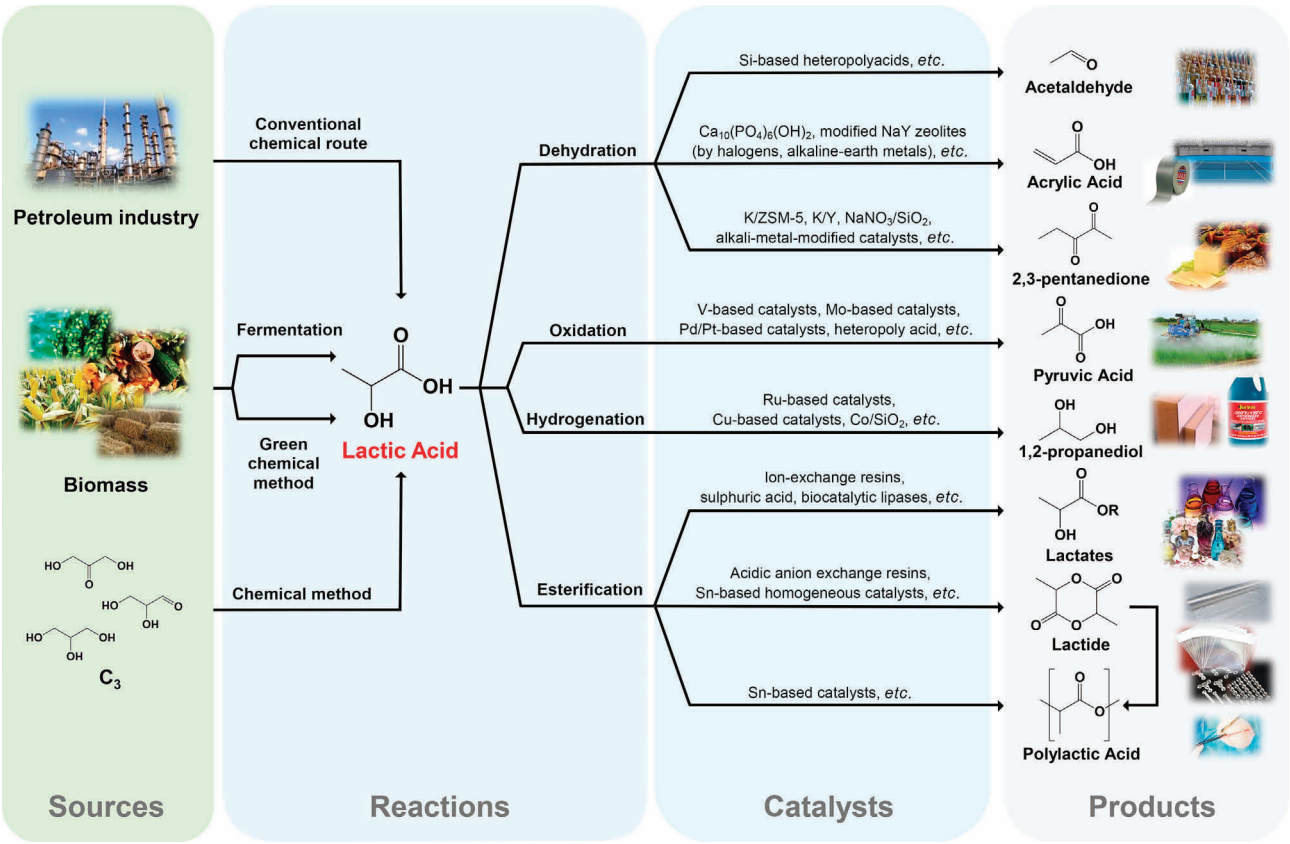

Fig. 5. LA and downstream products.

[142–145]. Hydrothermal conversion is not a new chemistry in organic synthesis, but it is very effective. In this medium, OH^- was identified as the reactive component, in particular for the promotion of isomerization and C—C bond cleavage reactions during the reactions [146,147]. All of the works could achieve almost complete conversion of fructose under certain reaction conditions; hence we list the yields of target products in tables for comparison (Table 1).

Another research effort in this area is primarily focused on conversion of cellulosic biomass to LA under subcritical and supercritical conditions [134,149,150]. Subcritical or supercritical water could catalyze the reaction in the absence of other additional catalytic species, showing a pathway similar to that in alkaline medium. The source of H^+ and OH^- was supposed to the strong tendency to ionize solvent molecules under subcritical or supercritical condition [10].

Furthermore, the types of metal cations are studied to influence the formation of LA. Jin *et al.* showed that the formation of LA in a hydrothermal reaction of fructose could be promoted by using NaOH, KOH, and $Ca(OH)_2$ [132]. LA yields of 43.5% with NaOH and 46% with KOH, respectively were obtained at the temperature of 300 °C (entries #1, #2 in Table 1). The types of cations were observed to influence ionization of OH^- in the solution, by which $Ca(OH)_2$ showed low solubility and catalytic activity.

A similar discussion about the poor performance of $Mg(OH)_2$ has also been reported by Qi *et al.* [7]. Qi *et al.* tested $Mg(OH)_2$, KOH, NaOH, and $Ba(OH)_2$ in this conversion and achieved LA yield up to 83.5% at room temperature (25 °C) in 48 h with $Ba(OH)_2$ (entries #3 in Table 1). It is worth noting that, as in most works the reaction conditions are above 160 °C, this result displays strong environmental and technological advantages. The promotional effect by Ba^{2+} is believed to follow a divalent mechanism, as the coordinated species bind strongly with Ba^{2+} to ensure C_3—C_4 cleavage to formulate precursors for LA. Ba^{2+} was considered to form a complex with PAL immediately after dehydration of DHA. The complex is then transformed into lactate *via* 1,2-hydride shift in basic conditions, after which the resulting barium lactate is transformed into lactic acid by addition of H_2SO_4 aqueous solution (Fig. 6).

Wang *et al.* [148] incorporated $Ba(OH)_2$ and $Ca(OH)_2$, utilizing the characteristics of each metal cation. $Ca(OH)_2$, with limited solubility, acts as a controlled-release alkali to sustainably supply OH^-, considering the generation of LA continuously consumes OH^-. The released Ca^{2+} cations have smaller size and stronger

Table 1
Product yield in alkaline medium

No.	Catalyst	Substrate amount	Catalyst amount	T/℃	t/h	Yield/%	Product	Ref
1	NaOH	70 mg	2.5 mol·L^{-1}	300	0.025	43.5	LA	[132]
2	KOH	70 mg	2 mol·L^{-1}	300	0.025	46.0	LA	
3	$Ba(OH)_2$	0.1 mol·L^{-1}	2.5 mol·L^{-1}	25	48	83.5	LA	[7]
4	$Ba(OH)_2$ + $Ca(OH)_2$	0.5 mol·L^{-1}	0.25 mol·L^{-1} + 0.5 mol·L^{-1}	60	4	42.4	LA	[148]

eletrophilicity, which bonds tighter with lactate to form calcium lactate, leaving Ba^{2+} freely in the solution to promote PAL to LA. Calcium lactate is the main product in this step (also found in fermentative production). The separation and purification of LA can be accomplished by using traditional methods.

In the catalytic system with strong alkaline aqueous solution as the medium, the corrosion of reactor is inevitable. To obtain high lactate yields, high concentration of sodium hydroxide or potassium hydroxide are required because of the acid-base reaction between LA and hydroxide [151]. In addition, the final products were produced in the form of lactates, corresponding to the plied alkali. The lactates in turn needs to be acidified to produce LA and by-product corresponding inorganic salt in downstream industrial production, which obviously raises the processing cost.

4. Synthesis of LA with Homogeneous Lewis Acids

Since metal cationic species are found to play a crucial role for the conversion of fructose to LA in alkaline medium, homogeneous Lewis acid catalysts with varied metal cationic species have also raised extensive interests in this area. This is mainly because that, the use of metal cationic species with tunable Lewis acidity in alkali-free solution avoid the formation of lactate salts and consequent acidification and purification involved in LA production. And their yields are comparable with the results obtained in alkaline catalytic systems (Table 1, Table 2). In addition, solvation effects have also been studied in the conversion of fructose [156–160].

Like Ca^{2+}, Mg^{2+}, and Ba^{2+} in alkaline medium, various divalent metal cationic species have also been studied as homogeneous Lewis acids. Wang *et al.* [133] demonstrated that simple Pb^{2+} cation which combines with water molecule, can accomplish complicated cascade reactions for the transformation of cellulose to LA. The reaction using fructose as substrate showed 74% yield of LA at 190 °C within 2 h (entries #1 in Table 2). The dehydration of fructose to 5-HMF would preferentially proceed due to the relatively lower energy barrier in the absence of Pb^{2+} (Fig. 5). According to computation, the presence of Pb^{2+} significantly reduces the activation Gibbs energy for the retro-aldol fragmentation and the isomerization of PAL to LA, thus shifting the main reaction route to the formation of LA. The species of the Pb-fructose complex and the fragment formed *via* the C_3—C_4 cleavage of fructose coordinated to Pb^{2+} were observed in the mass (MS) and the tandem mass (MS/MS) spectra, while only the fragments from the dehydration of fructose were detected in the absence of Pb^{2+}. Those results indicated that Pb^{2+} optimizes each key step of fructose to LA. Fig. 7 (a) shows the isomerization of trioses *via* Pb^{2+} model, while Fig. 7 (b) presents Pb^{2+}-OH model.

Wang *et al.* [152] then compared a series of V compounds ($VOSO_4$, $VOHPO_4$, VOC_2O_4, NH_4VO_3, and V_2O_5) in this conversion. $VOSO_4$ showed 58% yield of LA at 160 °C (entries #2 in Table 2) with VO^{2+} species playing a key role. Same with Pb^{2+}, VO^{2+} cationic species accelerate the retro-aldol fragmentation and subsequent isomerization of the trioses as a less toxic Lewis acid. Moreover, atmosphere was demonstrated having a significant influence on the reaction pathways and product selectivity. The presence of O_2 in the atmosphere would increase the yield of formic acid and decrease that of LA, possibly due to the oxidative cleavage of C—C bonds of intermediates catalyzed by VO_2^+/VO^{2+} with strong redox properties.

Bicker *et al.* [134] tested the catalytic performances of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} cations in the conversion of fructose to LA in subcritical water. A optimal 51% yield of LA was obtained at 200 °C, 25 MPa (entries #3 in Table 2) with $ZnSO_4$ as the catalyst in this work. Cu^{2+} is even more Lewis-acidic than Zn^{2+} but the main product was 5-HMF in this conversion. This suggested that not only Lewis acidic strength, but the formation of complexes affects the catalytic conversion of fructose to LA with metal cations in homogeneous systems (Fig. 7(c)).

Jin *et al.* [135] used ethanol as solvent and try to find the connection between the yield of ethyl lactate (ELA) and cationic radius. But they only found that the best one among the tested metal cations (arranged by radius from small to large is: Al^{3+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+}, Er^{3+}, and Pd^{2+}) is Zn^{2+} and the last three cations restrict the yield of ELA. The conversion with $ZnCl_2$ as homogeneous catalyst showed 51.7% yield of ELA at 200 °C for 3 h (entries #4 in Table 2) and the inhibiting effect from the last three cations weakened with the increase of cationic radius. In the comparison of Zn^{2+} salts with different anions, the effect on solubility was particularly obvious. $ZnCl_2$ performed best with its relative high solubility in ethanol. In this work, the benefits of adding a small amount of water (around 3%) has also been investi-

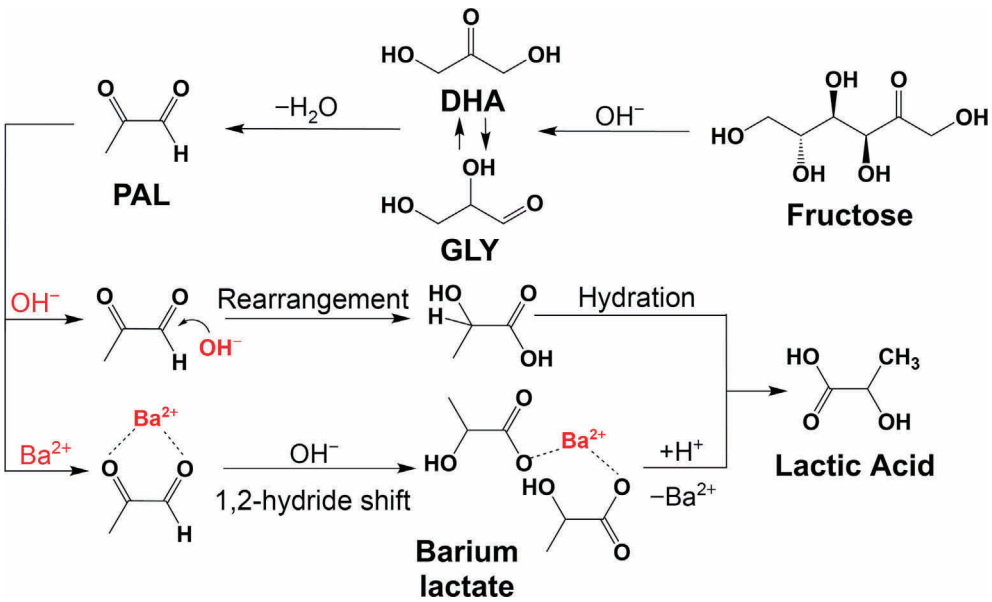

Fig. 6. Conversion of fructose to LA in aqueous alkaline medium (reproduced from Ref.[7] with permission of Royal Society of Chemistry).

Table 2
Product yield in homogeneous Lewis acid systems

No.	Catalyst	Substrate amount	Catalyst amount	T/℃	t/h	Yield/%	Product	Ref
1	$Pb(NO_3)_2$	0.56 mmol	0.14 mmol	190	2	74.0	LA	[133]
2	$VOSO_4$	6 mmol	0.1 mmol	160	1.5	58.0	LA	[152]
3	$ZnSO_4$	0.01 g·g^{-1}	0.0004 g·g^{-1}	200	0.05	51.0	LA	[134]
4	$ZnCl_2$	100 mg	0.004 mol·L^{-1}	200	3	51.7	ELA	[135]
5	$Sn(OTf)_2$	1000 mg	100 mg	200	2	43.0	MLA	[153]
6	$Er(OTf)_3$	300 mg	50 mg	240	0.5	55.0	LA	[136]
7	$ErCl_3$	100 mg	50 mg	240	0.5	84.8	LA	[154]
8	$SnCl_4$	340 mg	0.68 mmol	160	2.5	57.0	MLA	[125]
9	YCl_3	200 mg	200 mg	200	1.5	69.3	LA	[137]
10	$Al_2(SO_4)_3$ + $SnSO_4$	0.56 mmol	0.10 mmol	190	2	90.0	LA	[126]
11	$InCl_3$ + $SnCl_2$	2.5 mmol	0.06 mmol	160	10	72.0	MLA	[138]
12	$InCl_3$ + Bu_2SnCl_2	2.5 mmol	0.035 mmol	200	10	49.0	MLA	[8]
13	Sn(salen)/IL	300 mg	50 mg	160	2	68.9	MLA	[155]

gated. It was taken into consideration that the generation of alkyl lactates would accompany with the formation of water. The increase of the yield of alkyl lactate could explain by higher solubilities of sugars in water and the suppression of side reactions like the hydrolysis of 5-HMF to levulinic acid [9,135,161].

Dusselier *et al.* [153] investigated metal-triflate catalysts in methanol medium and obtained a yield of MLA over 40% at 200 °C (entries #5 in Table 2) from fructose with $Sn(OTf)_2$. Sn triflate catalysts possess both Brønsted and Lewis acidic character, respectively assigned to the triflate and metal group. By tuning the Sn/OTf ratio, the selectivity of esters like MLA, methyl levulinate, and methyl vinyl glycolate can be easily controlled through steering the network towards more or less retro-aldol. In the screening of catalysts, triflates with other metal cationic species (Cu^{2+}, Ag^{+}, Al^{3+}, In^{3+}, Lu^{3+}, Er^{3+}) tended to lead the reaction to form methyl levulinate in methanol solution. And other Sn salts ($SnSO_4$, $SnCl_2{\cdot}2H_2O$) showed no activity when cellulose was substrate, which indicated the Brønsted acidity of OTf. The importance of the choice of metal cationic species and the balance of Brønsted and Lewis acids has been distinctly exhibition.

There have been some studies of higher valent metal cationic species in the above works to be a comparison for the best divalent metal cationic species. And there are also some works with higher valent cations showing better performances under certain conditions. For example, lanthanide triflates are recognized stable Lewis acid catalysts. Dong *et al.* [136] demonstrated those salts can effectively catalyze the hydrothermal conversion of cellulose and its derivatives like fructose into LA. Experimental studies revealed that $Er(OTf)_3$ showed a best yield of LA, compared with other lanthanide triflates. And the total yields of products generally increased with decreasing metallic cationic radius of lanthanide triflates. It was explained that rare earth metallic cations have a higher affinity for oxidized groups to coordinate with the soluble monosaccharides. And the smaller metallic cationic radius of the lanthanide triflates, the stronger the binding ability of metallic ions with the hydroxyl groups of fructose, facilitating its cleavage. Compared with Dusselier's work in which the main product catalyzed by $Er(OTf)_3$ in methanol solution was methyl levulinate, the high yield of LA (>50% within only 0.5 h) in water points to a speculation that the role of metal cations in methanol is more limited than in water, or, that triflic acid is released through methanolysis of the complex [153]. Dong group also reported $ErCl_3$ as a homogeneous Lewis acid catalyst for this conversion [154]. This result supports their speculation that the type of metal cationic species plays a decisive role in the conversion of fructose to LA in water.

Zhou *et al.* [125] discussed the hydrolysis/methanolysis of the metal salts in solution. The methanol solution of $SnCl_4$ (0.68 mmol $SnCl_4$, 15 ml methanol) is fairly acidic (pH = 0.40), which indicated that the hydrolysis/methanolysis of $SnCl_4$ generated a large number of protons. As Brønsted acid is considered disadvantageous for the formation of MLA, base was used to neutralize the protons. When the molar ratio of NaOH/$SnCl_4$ was 1.0, this catalytic system got a best result. 57% yield of MLA was obtained at 160 °C in 2.5 h (entries #8 in Table 2) with fructose as substrate.

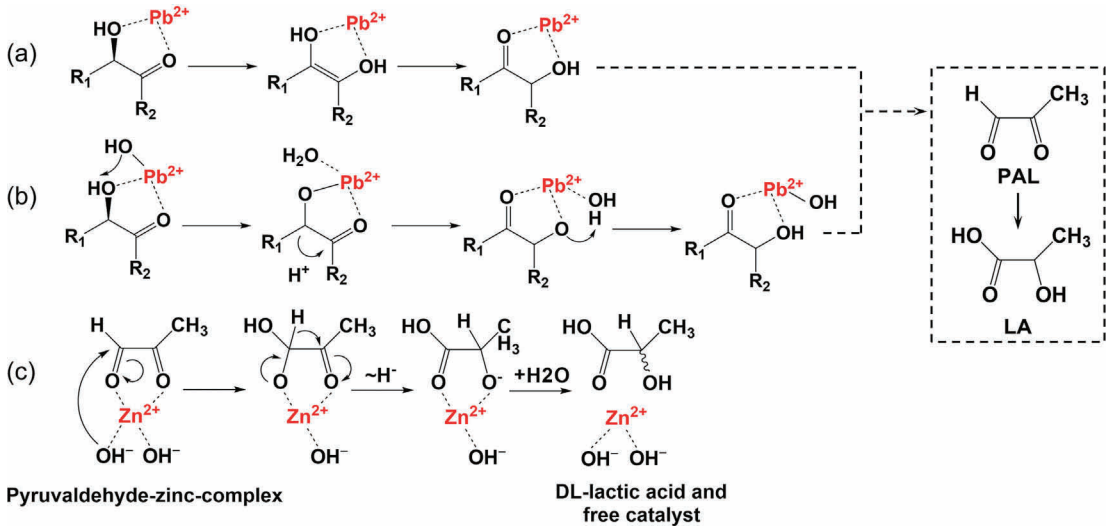

Fig. 7. Isomerization of trioses, (a) *via* Pb^{2+} model(reproduced from Ref.[133] with permission of Nature Publishing Group); (b) *via* Pb^{2+}-OH model; (c) possible model of action of Zn^{2+} in the formation of LA from PAL(reproduced from Ref.[134] with permission of Elsevier).

Xu *et al.*[137] used YCl_3 for the selectively simultaneous conversion of hemicellulose and cellulose components. LA in 69.3% yield from fructose at 200 °C (entries #9 in Table 2) was observed. $[Y(OH)_2(H_2O)_2]^+$ species which were derived from Y^{3+} hydrolysis was proved to favor the electron outflow from C_3 to C_4—O of fructose and lead to the accumulation of electronic density on O atom in C_4—O, thereby significantly weakening C_3—C_4 bond and directing the selective cleavage in fructose. This result was obtained by designed experiments and rigorous DFT calculation.

To utilize the features of different metal cationic species for different steps of the conversion, dual-cation combinations have been studied. Wang *et al.* [126] found Al^{3+} and Sn^{2+} combination showed a 90% yield of LA at 190 °C within 2 h (entries #10 in Table 2) in the experiment that used fructose as substrate. Nemoto and Tominaga *et al.* [8,138] reported the synergistic performance of In^{3+} and Sn^{2+}. The dual combination of $InCl_3$ and $SnCl_2$ directed the conversion of fructose to MLA with 72% yield of MLA at 160 °C within 10 h (entries #11 in Table 2) and $InCl_3$ and Bu_2SnCl_2 gained a 49% yield of MLA at 200 °C (entries #12 in Table 2). It is worth noting that, Sn^{2+} species are confirmed to catalyze the retro-aldol fragmentation of fructose into trioses while Al^{3+} species plays a dominating role in the isomerization of C_3 intermediates to LA in Wang's work (Fig. 8(a)). But in the combination of In^{3+} and Sn^{2+}, Sn^{2+} species are experimentally validated to act in the isomerization of C_3 intermediates and In^{3+} species contribute to the retro-aldol reaction (Fig. 8(b)). This difference may be due to the solvent and other reaction parameters. And it prompts us that the different roles of metal cationic species in different combinations should be noted.

Wang *et al.* reported an ionic liquid functionalized catalyst, consisting of Sn^{4+} salen complex and imidazolium-based ionic liquid [OMIm]Br(IL). Sn(salen)/IL shown better performance than Al (salen)/IL, Zn(salen)/IL, and Sn (salen) catalyst systems. Its outstanding performance (a 68.9% yield of MLA, entries#13 in Table 2) in the conversion of fructose to MLA was ascribed to an intramolecular synergistic effect from the electrophilic Sn^{4+} and the nucleophilic Br^- as well as the imidazolium cation.

In this section, LA production with homogeneous Lewis acids has been fully discussed, which set the tone of subsequent researches. Some basic scientific problems and laws in this conversion have been clarified, such as the effect and mechanism of different metal cations, function of small amount of water in alcohol system, coordination of dual-cation combinations, and

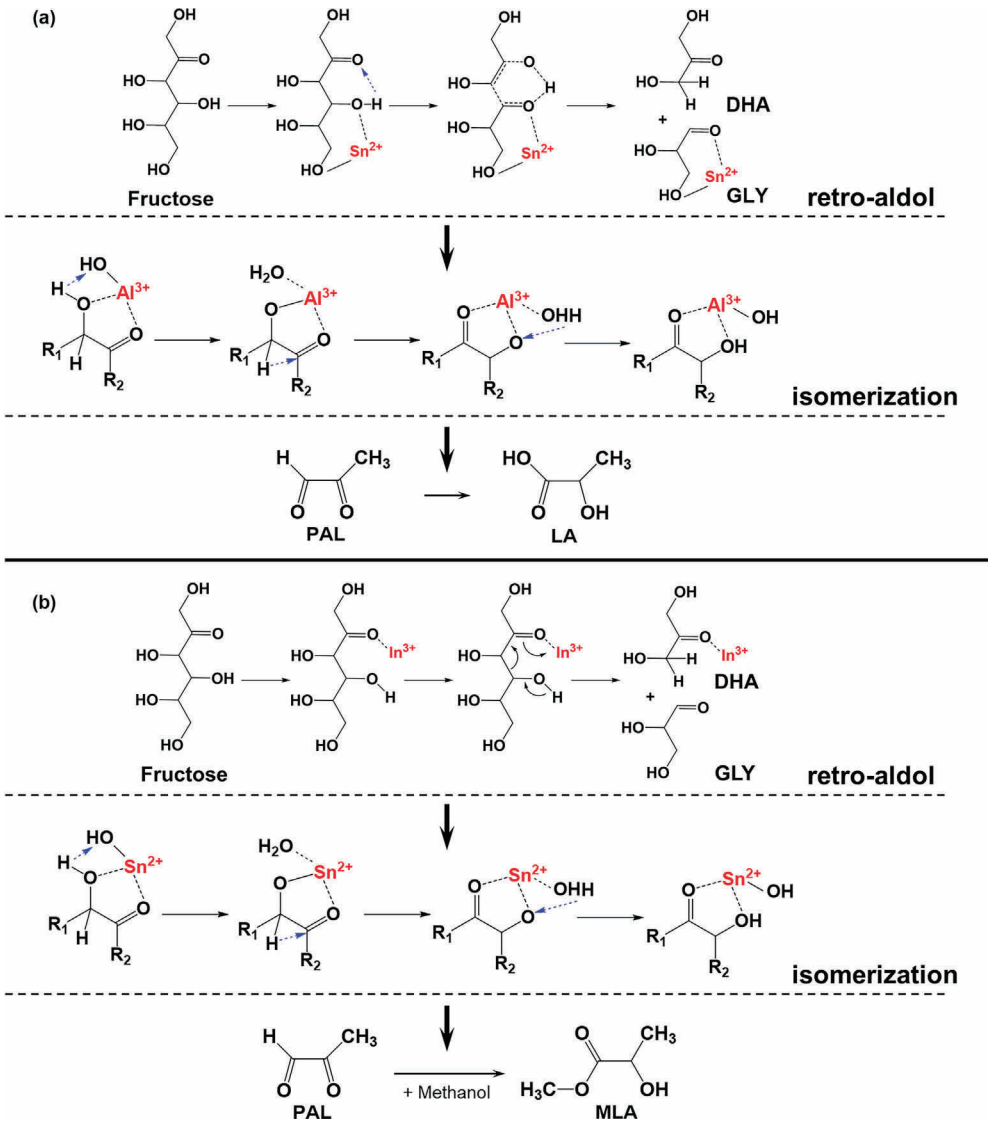

Fig. 8. The effect of binary cations (a) Sn^{2+}, Al^{3+}; (b) Sn^{2+}, In^{3+} on the formation of LA and MLA from fructose (reproduced from Ref. [126] with permission of Royal Society of Chemistry and Ref. [8,138] with permission of Elsevier).

the solvation effects. The most effective metals like Sn, Er also provide ideas for the design of heterogeneous catalysts. On the other hand, the difficulties of the recovery of homogeneous catalysts and the controlled regulation of acidic sites prompt people for new solutions.

5. Synthesis of LA over Heterogeneous Catalysts

As mentioned in previous section, metal cationic species are found to be efficient for the transformation of fructose to LA in homogeneous Lewis acids. Immobilization of metal species on solid supports has raised extensive attention owing to the promising features of catalyst separation in downstream processes and the multiple prepared methods and performances of tunable solid structures.

5.1. Sn-β catalysts

Considering the remarkable promotional role of Sn species in homogeneous Lewis acid catalysts, heterogeneous Sn-β catalysts have been extensively studied for the conversion of fructose to LA in the past few years. Developed mesopores are also a key feature of Sn-β catalysts, which contribute the dispersion of active sites and are sufficiently large to accommodate acyclic monosaccharides [9]. As one of common zeolites, the Lewis acidic sites of Sn-β are generally thought to be provided by introducing Sn, while Brønsted acidic sites originate from the small amount of residual framework Al [162]. The characteristic ratio and distribution of Lewis acidic sites and Brønsted acidic sites of Sn-β catalysts contribute to their impressive performance in the conversion of fructose to LA and alkyl lactates.

Early in 2010, Holm *et al.* [9] have synthesized highly crystalline β zeolites and zeotypes which differ in the type of metal that is incorporated into the framework and tested them in the conversion of fructose into MLA. The prepared catalysts can be divided into Lewis acidic (Ti-, Sn-, and Zr-β), Brønsted acidic (H-Al-β), and nonacidic (Si-β) classes. In accordance with the previous rules, the Lewis acidic zeotype catalysts lead to retro-aldol reaction of fructose and finally induced MLA. Of the three Lewis acidic catalysts, Sn-β has the strongest Lewis acidic sites, which leads to highest yield of MLA (44%, entries #1 in Table 3). The Brønsted acidic zeolite H-Al-β was found to catalyze the dehydration, leading to 5-HMF derivatives. And the nonacidic Si-β did not improve the yield of MLA. Those results indicate that the catalytic performance is related to the acidity of the metals incorporated into the zeolite structure.

Zeolites with hierarchical porous structures containing both mesopores and micropores are denoted as hierarchical zeolites. Researchers have developed various methods to prepare hierarchical Sn-β zeolite catalysts and applied in the conversion of fructose to LA or MLA (Fig. 9(a)) [27,128,162]. The developed hierarchical porosity is confirmed to be favorable for the enrichment of sugar and the fast formation of complex intermediates with bulky diameter, followed by fast transformation to cleavage the C—C bonds [128]. A widely used methodology for one-pot synthesis of hierarchical zeolites was developed by Xiao group using cationic polymers (polydiallyldimethylammonium chloride) as template [165]. They then synthesized hierarchical Sn-β catalysts with three-dimensionally interconnected mesopores in this way and gained a 51% yield of MLA at 160 °C (entries #4 in Table 3) from fructose (Fig. 10(a), (c)) [128].

Li *et al.* [27] developed hierarchical Sn-β zeolite *via* alkali-induced degradation of Si-β and self-assembly of the resultant Si-β fragments with $SnCl_2{\cdot}2H_2O$ in the hydrothermal condition templated with tetraethyl ammonium hydroxide (TEAOH) and polydiallydimethylammonium chloride (PDADMAC, Fig. 10(e)). The Lewis acidity related to isolated tetrahedrally coordinated Sn species in the hierarchical porous β framework was revealed. And the partially hydrolyzed Sn species had a higher acidity strength than the framework integrated species. The effect of hydrophilicity/hydrophobicity of Sn-β zeolite has also been discussed. Defect silanol groups are hydrophilic, which are usually created in the dealumination/desilication procedures of some post-synthesis strategy (Fig. 9(b)). The hydrophilic defect silanol groups are fatal to the cleavage of fructose to trioses [162,163]. Taking mesoporosity, existing states of Sn species, hydrophilicity/hydrophobicity, and

Table 3
Sn-β catalysts for the conversion of fructose into LA/alkyl lactates

No.	Catalyst	Substrate amount	Catalyst amount	*T*/℃	*t*/h	Yield/%	Product	Ref
1	Sn-β	225 mg	160 mg	160	2	44.0	MLA	[9]
2	Sn-β	124 mg	80 mg	160	10	47.0	MLA	[163]
3	Sn-β	124 mg	80 mg	160	10	55.0	MLA	[162]
4	Sn-β	225 mg	160 mg	160	20	51.0	MLA	[128]
5	Sn-β	124 mg	80 mg	160	6	58.0	MLA	[27]
6	Pb-Sn-β	225 mg	200 mg	190	2	54.6	LA	[141]
7	Zn-Sn-β	225 mg	160 mg	190	2	52.0	LA	[164]
8		225 mg	160 mg	160	20	29.0	MLA	
9	Mg-Sn-β	370 mg	200 mg	140	1	37.0	MLA	[129]
10	Sn-β-NH_2	225 mg	140 mg	190	2	50.0	LA	[131]

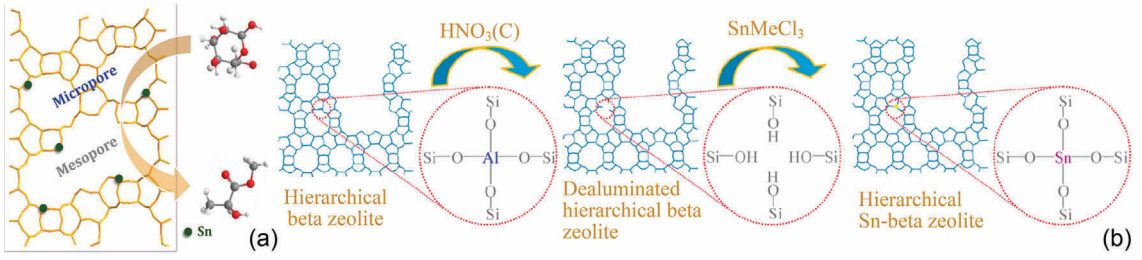

Fig. 9. Schematic description for Sn-β zeolite, a) structure and function diagram of hierarchical Sn-β zeolite (reproduced from Ref.[137] with the permission of Nature Publishing Group); (b) proposed procedures for preparation of the Sn-β (reproduced from Ref.[128] with the permission of American Chemical Society).

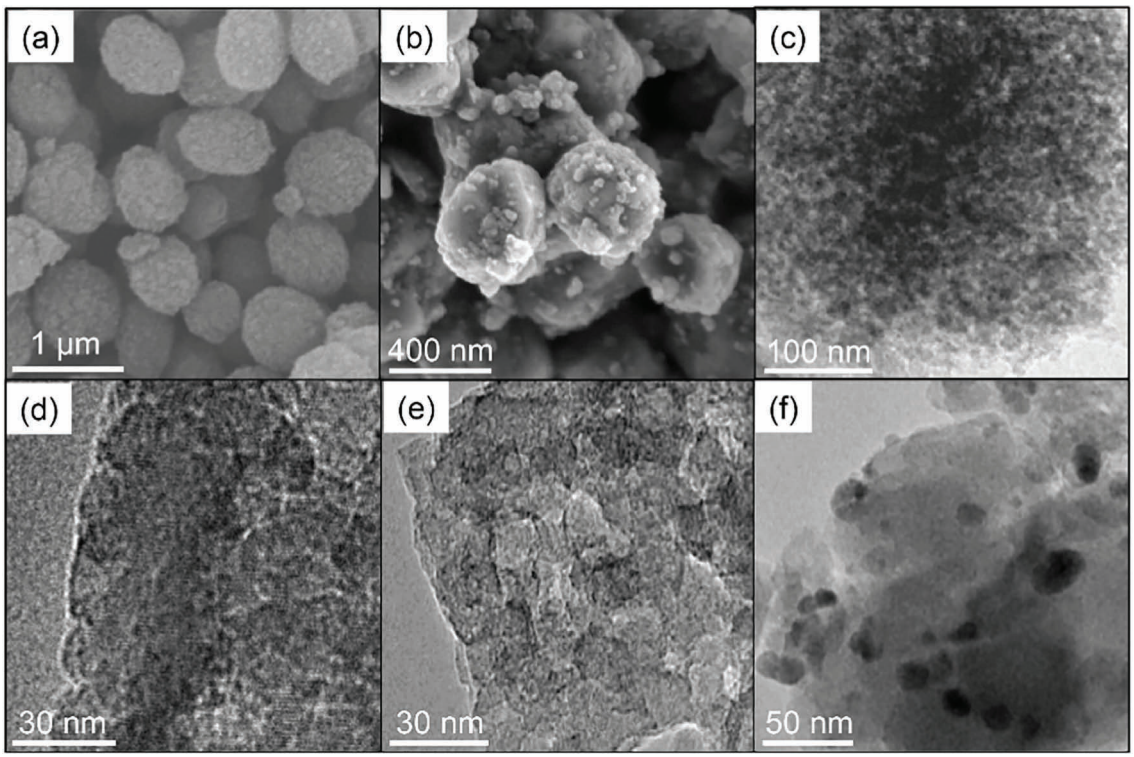

Fig. 10. SEM images of (a) Sn-β (reproduced from Ref.[128] with the permission of American Chemical Society); (b) Sn-β (reproduced from Ref.[163] with the permission of American Chemical Society) and TEM images of (c) Sn-β (reproduced from Ref.[128] with the permission of American Chemical Society); (d) Sn-β (reproduced from Ref.[162] with the permission of Royal Society of Chemistry); (e) Sn-β (reproduced from Ref.[27] with the permission of American Chemical Society); (f) Sn-β-NH2 ((reproduced from Ref.[131] with the permission of American Chemical Society).

Lewis acidity into consideration, the best sample of synthesized hierarchical Sn-β catalyst obtained 58% yield of MLA at 160 °C (entries #5 in Table 3).

Yang *et al.* [162] developed a grinding method with no fluoride and a small amount of TEAOH to synthesize hierarchical Sn-β zeolite (Fig. 10(d)). They suggested that recrystallization of Sn-β in the presence of low concentration of TEAOH can heal silanol defects and generate hierarchical porosity at the same time, both of which benefit the main reaction, supported by the conclusions we obtained above. In this work, the experimental and computational results indicated that the hierarchical structure of Sn-β pronouncedly facilitates the retro-aldol reaction of fructose. It is attributed to reducing steric hindrance of the hydromethyl group of the transition states for the retro-aldol reaction, and making it proceed smoothly.

Yang *et al.* [163] also developed a rapid synthesis method employing Si-β as parent, which was crystallized in several hours by the hydrothermal method. The characterizations revealed that the successful incorporation of Sn^{4+} strongly depends on the crystallinity of the parent Si-β. Si-β with lower crystallinity (<90%) had a considerable amount of silanols which provided sites for Sn^{4+} incorporation into the framework sites. For Si-β with higher crystallinity and less silanols, desilication was used to generate more silanols for the incorporation of Sn^{4+} sites. The obtained Sn-β with nano size and fewer defects catalyzed efficient transformation of fructose to MLA (Fig. 10(b)).

In addition to morphological effect, tandem catalysis induced by incorporating two active species leads to synergistic performances. The dual metal combination is promising because each of the metallic components shows distinct functionality in the key steps of the transformation of fructose to LA or MLA. For example, Zhang *et al.* modified Sn-zeolite with Pb^{2+} [141]. Sn species in this catalyst were demonstrated to have a superior catalytic performance in dehydration of DHA, hydration of PAL and isomerization of PAL hydrates. Meanwhile, Pb species were revealed to promote the retro-aldol reactions from fructose to DHA and GLY and have a positive effect on inhibition primary by-product, 5-HMF. Xia introduced In to Sn-β in the form of In_2O_3 species to suppress the yield of humins and soluble side compounds [166].

Yang *et al.* [129] also synthesized Mg-Sn-β zeolite with different Mg/Sn molar ratios prepared from deAl-β by co-impregnation method. This bimetallic incorporated catalyst has higher Lewis acidity and less silanol defects than Sn-β. Both Mg^{2+} and Sn^{4+} can be incorporated into the framework sites of β zeolite and generate Lewis acid sites, but the Lewis acidity of framework Mg^{2+} is weaker than framework Sn^{4+}. Introduction of Mg^{2+} species was proved to eliminate the proximal silanol of Sn sites and lower the activation energy for the formation of MLA (Fig. 11).

Because some of the products (like LA, formic acid, acetic acid and levulinic acid) could exist as Brønsted acids, which are demonstrated leading dehydration route to 5-HMF (Fig. 3). Enhancing or introducing basic sites can also tune the balance of acidic sites and benefit the transformation of fructose to LA. Shen and colleagues [164] tested performances of Zn-Sn-β catalysts in water and methanol with a yield of 52% and 29% for LA and MLA, respectively (entries #7, #8 in Table 3). Surface characterization suggested that the introduction of Zn^{2+} to Sn-β zeolites created basic sites and enhanced the strength of both Lewis acidic and basic sites, facilitating the main reaction to produce LA and MLA. The experiments have also showed that the introduction of Zn^{2+} did not accelerate the formation of LA, but only acted by inhibiting the side reactions, further supporting the previous theory. They further reported a modification approach using 3-aminopropyltrimethoxysilane to directly introduce basic sites NH_2- to the surface of Sn-β Lewis acid catalysts (Fig. 10(f)) [131]. In the experiments to investigate the balance of acids, when

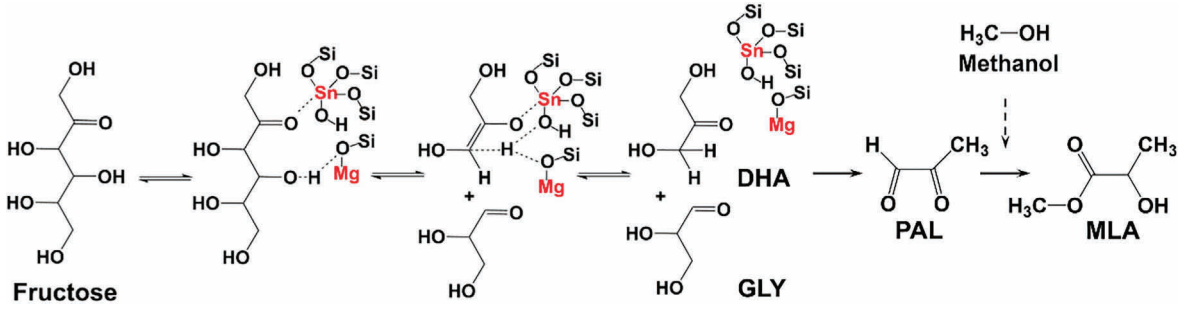

Fig. 11. Proposed mechanism of retro-aldol of fructose to MLA over Mg-Sn-β catalyst (reproduced from Ref.[129] with permission of Royal Society of Chemistry).

the Sn^{2+} salt dosage is below the optimum, the amount of Lewis acidic sites generated from the Sn species is not enough to improve the LA yield. Meanwhile, a high Sn^{2+} salt dosage gave rise to excessive Lewis acid sites, compared to which the number of basic sites was insufficient to suppress the side reaction, decreasing the LA yield as well. It is clear that the utility and balance of acids are of vital importance in this conversion.

In this section, we mainly introduce Sn-β catalysts in the conversion of fructose to LA and MLA. Due to the earlier research, Sn-β catalysts have been widely studied in this conversion as a typical heterogeneous catalyst. Having both Lewis and Brønsted acidic sites allows them more methods to be adjusted for an optimal sample. Their deployable hierarchical porosity is favorable for the enrichment of sugar and the fast formation of complex intermediates with bulky diameter. The research methods like introducing other metals provide reference for the studies using other zeolites in this conversion.

5.2. Other metal incorporated zeolite catalysts

Sn and other commonly known metals such as Zr, Yb, Er and Ga can also be immobilized in zeolitic materials for effective LA synthesis from fructose. Several distinct zeolite materials have shown promising promotional roles for this reaction. The design and utilization of the various zeotype structures with the optimization of cooperative metal species are the crucial parts of those works to tune the balance of acids thus finding the best catalysts for the conversion of fructose to LA or alkyl lactates.

Li *et al.* [167] synthesized Sn-MWW zeolite by deboronating B-MWW zeolite followed by Sn^{4+} incorporation. Subsequent calcination could convert the well-known lamellar structure of MWW precursor to 3D MWW structure (Fig. 12(a)). B-MWW as a typical Brønsted acid catalyst exhibited a high DHA conversion but relatively poor selectivity of LA product due to facilitating acetalization reaction of PAL. Upon exchange of trivalent lattice B sites by tetravalent Sn, pronounced Lewis acidic sites were incorporated into the catalysts and the selectivity of MLA increased. Ti-MWW was also synthesized and showed triple selectivity of MLA than the Brønsted acidic catalyst B-MWW but lower than Sn-MWW. Those results demonstrate that the characteristic structure of the zeotypes and the type of incorporating metal species affect the balance of acid sites and thus the yield of MLA.

Sn-Si-CSM catalysts were Si-MCM-41 introduced with Sn and filled with a porous carbon network like Fig. 12(b), reported by Clippel *et al.* [168]. In this work, Lewis acidic sites were introduced by grafting the silica surface with Sn^{4+}, while the surface functional groups like phenols, anhydrides, and carboxylic acids in the carbon framework delivered weak Brønsted acidic sites. Beside the functions of Lewis acidic sites which have been confirmed in many other works, the abilities of Brønsted acidic sites to catalyze DHA isomerization, GLY dehydration, and rearrangement into PAL (Fig. 3) were also emphasized in this work.

Modified SBA-15 catalysts were used in the conversion of fructose to LA or alkyl lactates as well. SBA-15 is a common mesoporous pure silica material, providing no Lewis acidic sites and weak Brønsted acidic sites. It has some exclusive properties, such as thick wall, high surface area, and large pore size (5–30 nm) [10]. Its limited hydrophobic property of silica framework could stabilize the introduced metallic Lewis acidic sites inside the pores. For example, Sn-SBA-15 was synthesized using a post-synthetic metal implantation method by Zhang and colleagues [169]. Sn species were highly dispersed and isolatedly grafted in the framework of SBA-15, which solely provided a large number of Lewis acidic sites and facilitated the conversion (Fig. 13(a), (b)).

Lin *et al.* [10,170] investigated Zr-SBA-15 to produce MLA and ELA in methanol and ethanol medium. In the comparison of Zr species, Zr incorporated in Zr-SBA-15 has stronger Lewis acidity than in ZrO_2. According to the characterization results, Zr-SBA-15

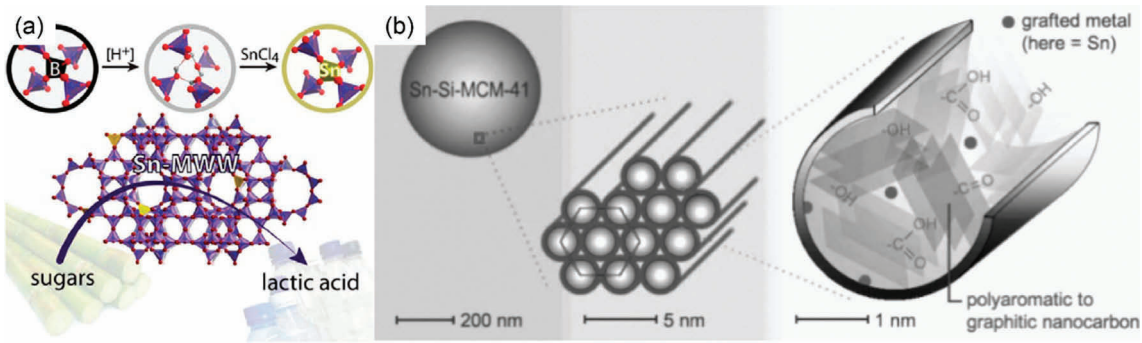

Fig. 12. Schematic diagrams of (a) Sn-MWW catalyst (reproduced from Ref.[167] with permission of Wiley); (b) structure of Sn-Si-CSM catalyst at the various length scales (reproduced from Ref.[168] with permission of American Chemical Society).

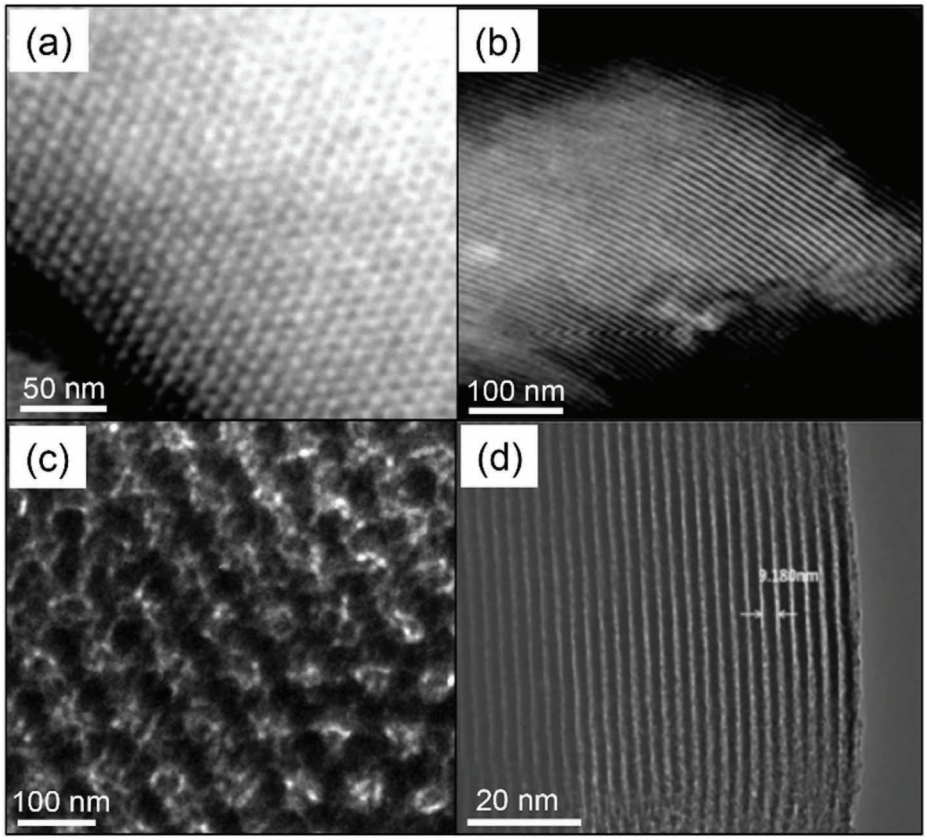

Fig. 13. TEM images of (a, b) Sn-SBA-15 catalysts (reproduced from Ref.[169] with permission of Wiley); (c) Zr-SBA-15 catalyst (reproduced from Ref.[170] with permission of Elsevier); (d) Yb(OTf)2–SO3–SBA-15 catalyst (reproduced from Ref.[171] with permission of Springer).

contained predominantly Lewis acidic sites with weak Brønsted acidic sites, the cooperation and balance of which facilitating the selective transformation. The effect of added water in alcohol mediums has been studied in this work. High proportion of water (>5% (mass)) would lead to the deactivation of Lewis acidic sites, transformed to Brønsted acidic sites. In fact, this is one of the main factors that cause the instability of Lewis acid catalysts in water. In addition, the alcohol medium was also demonstrated in favor of the target transformation through suppressing the repolymerization of the intermediates.

In the aspect of structure-activity, the performance and structure of the Zr-SBA-15 could be controlled by modulating the ratio of Si/Zr. TEM images confirmed that highly ordered mesoporous structure was evident at the Si/Zr ratio of 20 (Fig. 13(c)), while the framework was partially collapsed when the Si/Zr ratio reached 10. The formation of humins at elevated temperature (240 °C) is detrimental for the yield of MLA. Lifting the pore restriction and facilitate the diffusion in and out the stoma channels will suppress the formation of humins, which can be achieved by developing large pores (7.6–10.6 nm) in Zr-SBA-15 catalysts. And the size of the pores can be tuned by optimizing the hydrothermal treatment conditions during the synthesis.

Considering that lanthanide triflates had been utilized in homogenous system to catalyze fructose to LA or MLA [136], Wang *et al.* [171] immobilized Yb triflates on SBA-15 prepared *via* chemical grafting and co-condensation methods to catalyze this conversion. The gained catalysts possessed a 2D-hexagonal space group like Fig. 13(d). The total acidic strength increased with the increasing Yb content in SBA-15 catalysts, selective conversion of fructose into LA correspondingly meliorated.

Oliverio *et al.* [172] discussed the results of $ErCl_3$ grafted MCM-41 for hydrothermal conversion of cellulose and simple sugars into LA with the assistances of microwave and ultrasounds. High yield (78%) (entries #7 in Table 4) towards LA was obtained for the conversion of fructose at 200 °C within a short reaction time (5 min). This work focuses on the experimental method, scale-up, and catalysts recycling. The mechanism of the enhancement from the assistances of microwave and ultrasounds remains to be illustrated. In addition, oxophilicity of the metal centers was also suggested to play an important role in the selective conversion.

Verma *et al.* [122] used fructose as substrate to investigate the pathway of cellulose conversion to MLA over Ga-Zn-HY catalysts, showing a 67.3% MLA yield within 1 h at 270 °C (entries #8 in Table 4). Characterization demonstrated that, while Zn exists in the form of ZnO on the nanozeolite, doping Ga increases the specific surface energy of ZnO nanocrystals, inducing high crystallite solubility. Therefore, the increased solubility can lead to the retardation of crystal growth and a better dispersion of ZnO species. To the role of metal species, doping Ga enhanced the Lewis acidity and facilitated the retro-aldol condensation of sugars, while suppression of Brønsted acidity decreased the formation of levulinic acid, followed by the dehydration of 5-HMF. It has been observed that the introduction of Ga also increased the oxygen vacancies, which can contribute to an enhancement of the active sites for the adsorption of reactants on the surface of Ga-Zn-HY catalysts.

Bi *et al.* [173] synthesized Nb-HUSY catalysts and confirmed that the combination of relatively strong Lewis and weak Brønsted acid sites promote the catalytic activity. This appreciate ratio of Lewis acid/Brønsted acid was provided by introduced metal Nb. As 2% (mass) Nb showed the best performance, the yield of MLA

Table 4
Performances of other metal incorporated zeolite catalysts

No.	Catalyst	Substrate amount	Catalyst amount	T/℃	t/h	Yield/%	Solvent	Product	Ref
1	Sn-MWW	112.5 mg	80 mg	160	20	46.0	Methanol	MLA	[167]
2	Sn-Si-CSM	225 mg	160 mg	155	20	32.0	Methanol	MLA	[168]
3	Sn-SBA-15	200 mg	150 mg	160	20	28.2	Methanol	MLA	[169]
4	Zr-SBA-15	200 mg	100 mg	240	6	44.1	Methanol	MLA	[170]
5	Zr-SBA-15	200 mg	150 mg	220	2	40.0	Ethanol	ELA	[10]
6	$Yb(OTf)_2$-SO_3-SBA-15	550 mg	100 mg	190	1	40.1	Water	LA	[171]
7	Er-MCM-41	100 mg	30 mg	200	0.08	78.0	Water	LA	[172]
8	Ga-Zn-HY	2000 mg	500 mg	270	1	67.3	Methanol	MLA	[122]
9	Nb-HUSY	100 mg	50 mg	140	6	56.1	Methanol	MLA	[173]

had a drop when the amount of Nb increased to 5% (mass). High loadings of Nb caused the collapse of HUSY framework, which noted the proper coordination of loaded metals and supports besides stronger Lewis acid.

In this section, we introduce more types of metal incorporated zeolites catalysts for the conversion of fructose to LA and lactates. Different types of zeolites have their own specific structure, which provide various synthetic methods and sample features for researchers to utilize. The interaction between zeolites and introduced metals and the obtained effect on the acidity generally play a key role in these works. Besides, some studies focus on the assistant enhancement of microwave and ultrasounds for the conversion of fructose to LA have also made progress with metal incorporated zeolite catalysts.

5.3. Metal-oxide catalysts

Generally, metal oxide catalysts do not have sufficient porous structures like zeolite materials. The existing forms of metal species and their interaction with supports were emphasized. Some metal oxide materials like MgO show both acidic and basic properties, providing more approaches to regulate the balance of acidity. Some metal oxide materials like heteropolyacids have their characteristic structure and acidity, not only take effect by the metal species. The combinations of two or more metal species signify that different metal species play different roles in different steps of the conversion and require concrete analysis of concrete catalysts.

Lou *et al.* [151] tested MgO, ZrO_2, and CaO in the conversion of carbohydrates to MLA without homogeneous base. MgO catalysts showed better performance with multiple basic sites associated with the formation of hydrogen carbonates due to surface OH^- groups or Mg^{2+}-O^{2-} pairs with the formation of bridged and bidentate carbonates. MgO samples with three kinds of weakly basic sites showed the best catalytic activity, which implied that weakly basic sites on MgO surface are more active. Under the effect of different metal species, ZrO_2 exhibited a relatively poor yield, most of whose basic sites were weakly and CaO exhibited no activity with its strong basic sites.

Lu *et al.* [139] evaluated NiO catalysts in the conversion of fructose to MLA. The NiOOH species on the surface of NiO gradually decreased with the increase of calcination temperature. Meanwhile, the MLA yield over calcined NiO catalysts also went down. To further detect the effect of NiOOH species, Lu assessed the conversions of intermediate products DHA and GLY. 2.6, 2.2, and 1.4 times more MLA product yield were obtained than that of NiO with no NiOOH in the conversion of fructose, DHA, and GLY, respectively. The results demonstrated that NiOOH is efficient for the conversion of both the fructose and the intermediates to MLA.

Co-catalysts are often introduced into the inorganic strong base catalytic system to promote the conversion of cellulosic species, including Ni [176], CuO [177], Zn/Ni/C [178], $NiCl_2$ [179], [IMEP]-Cl (polymerizate of imidazole and epichlorohydrin) [180], *etc.* Among those, Ebitani *et al.* gained fructose data with hydrothermally loaded CuO species on MgO catalyst using capping agent (cetyltrimethylammonium bromide; CTAB) [174]. Cu-MgO catalyst could dissect fructose to GLY and DHA. Different from Qi's work catalyzed by alkaline-earth cation Ba^{2+}, GLY rather than DHA dominated in this isomer system [7]. The hydrothermally loaded CuO species was found to have strong interaction with support, which prevents the formation of free cationic Cu^{2+} species. The attack of hydroxyl ion of alkali or the bind oxygen atom of Cu—O—Mg from catalyst on the carbonyl carbon may generate the intermediate complexes and be beneficial to the main reaction (Fig. 14).

Wang *et al.* reported a facile preparation of Fe-doped SnO_2 catalysts by replacing Sn^{4+} with Fe^{3+}, which was inserted into SnO_2 crystal lattice thus producing more acidic sites (Fig. 15(a)). The Lewis acidic sites were indicated to locate in the coordinative unsaturated cations, while the Brønsted acidic sites generated from surface hydroxyl groups. The Lewis acidic and Brønsted acidic sites and acidity of the catalysts were adjusted by controlling the Fe doping amounts and calcination temperature [11].

Hu *et al.* [161] developed a series of robust In/γ-Al_2O_3 catalysts with different In loadings. As demonstrated in Yamaguchi's article, lattice oxygen and/or Al-OH groups on the surfaces were regarded as basic sites and Lewis acidic sites were from unsaturated coordination Al and introduced metal species [181]. In this work, In^{3+} doping increased the amount of mid-strong acidic sites on catalysts, which facilitated the selective cleavage of C_3—C_4 bond in hexoses, as well as subsequent esterification reactions. Meanwhile, the amount of weak and mid-strong basic sites of catalysts showed a sharp decrease, inhibiting dehydration reaction of fructose. Based on the results of XRD, XPS, and Raman spectra, the doped In mainly existed as In_2O_3. The binding energies of In_2O_3 in the In/γ-Al_2O_3 catalysts were slight higher than those of commercial In_2O_3, which attributed to the interaction between In species and γ-Al_2O_3 support.

Hu *et al.* [161] also discussed the role of water and additional alkali in reaction medium in the work of In/γ-Al_2O_3 catalysts. A highest MLA yield was up to 42.0% with 7% (vol) of water in methanol solvent, while the MLA yield was only 28.0% when single methanol was used as solvent. One of the contributions of water probably related to the acceleration of the hydrolysis of methyl fructoside (a competing by-product of MLA) and release more fructose [182]. The sharp decrease of MLA yield with excess water could be ascribed to the following reasons. Firstly, high water content might decrease the Lewis acidity of catalyst which instead of affording more Brønsted acidic sites [183]. Secondly, the higher water content could also promote the hydrolysis of MLA. Thirdly, excess water could also lead to the deactivation of catalyst due to the metal leaching [184]. These results could be viewed in conjunction with the discussion in homogeneous systems [135].

Fu *et al.* [175] reported ultrasmall CoO clusters (~1.7 nm) stabilized within silicalite-1 crystals catalyst, exhibiting resistance to sintering in near-critical methanol medium. Blank silicalite-1 had almost no catalytic activity due to the low acidity. Oxidation state

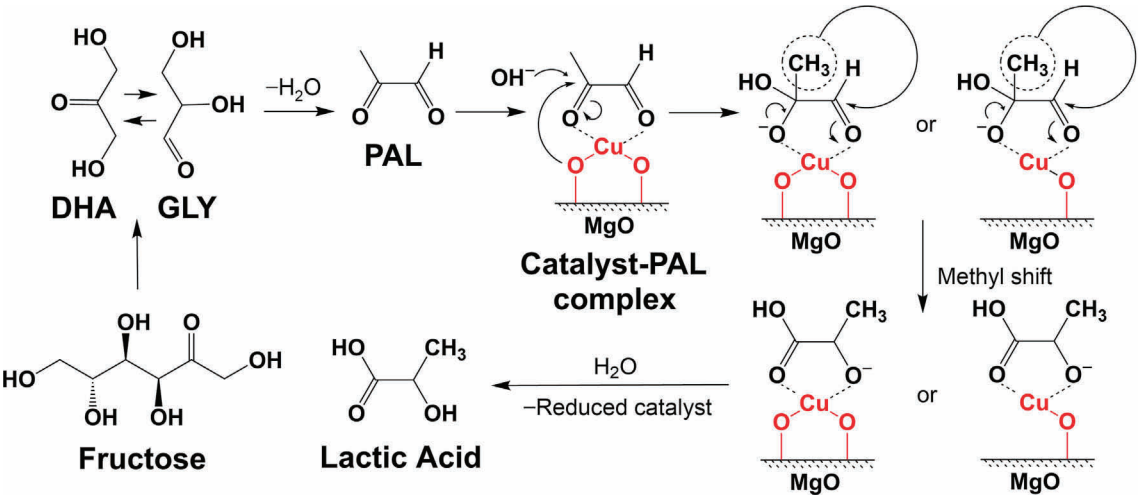

Fig. 14. Conversion of fructose to LA on Cu-MgO catalyst (reproduced from Ref.[174] with permission of Elsevier).

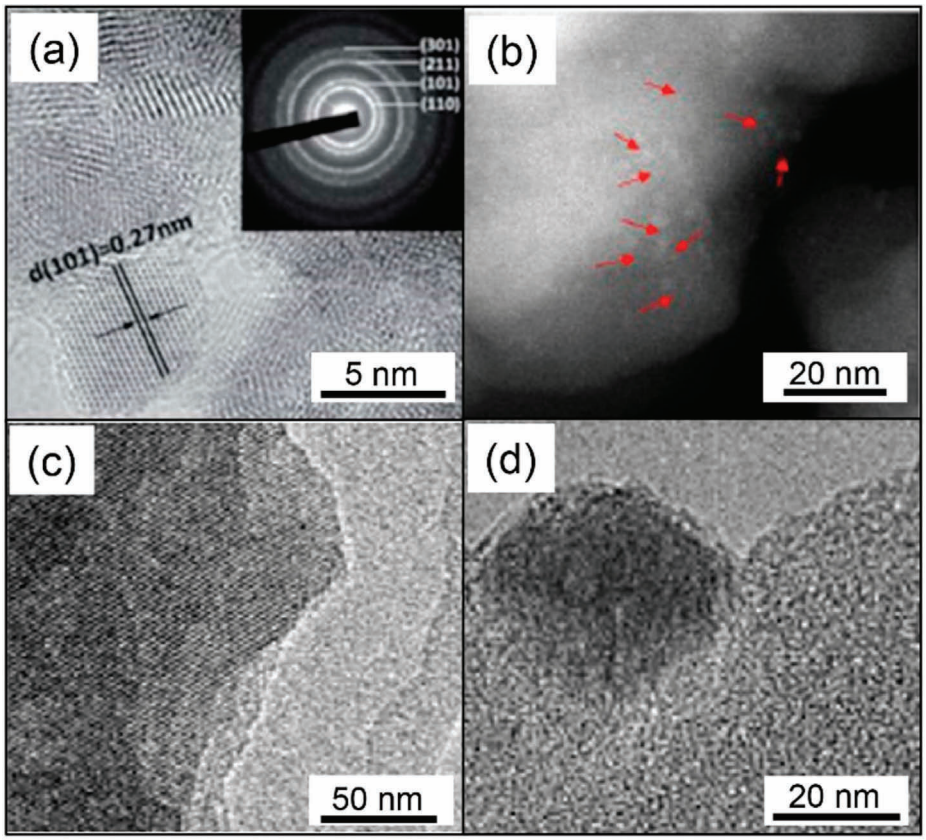

Fig. 15. (a) High resolution TEM (HRTEM) image of Fe-doped SnO_2 catalyst, inset image is the selected area electron diffraction (SAED) pattern (reproduced from Ref.[11] with permission of Royal Society of Chemistry); (b)–(d) TEM images of CoO-silicalite-1 catalysts, CoO clusters are marked by red arrows in Fig. (b) (reproduced from Ref.[175] with permission of American Chemical Society).

of Co was found to be crucial for retro-aldol, dehydration and esterification reactions. CoO clusters were regarded as active sites with their acidity. The covalent interaction between CoO and silicalite-1 was regarded as the reason for the stability and not further oxidation of CoO clusters (Fig. 15(b)–(d)).

Dong *et al.* [124] prepared a series of La-modified phosphomolybdic acid catalysts with different La/Mo atomic ratios by ion exchange method and reach a LA yield of 65% within 1 h (entries #7 in Table 5). The Keggin-type heteropoly acids were characterized by FITR and mainly provided Brønsted acidic sites. The exchange with La^{3+} slightly reduced the amounts of Brønsted acidic sites but significantly increased the concentration of Lewis acidic sites without changing the local structure of the Keggin anion and the secondary structure of the Keggin-type heteropoly acids. Catalytic tests suggested that the selectivity of LA improved with the increase of the Lewis acidic site concentration. However, over-reduction of the Brønsted acidic sites could suppress the dehydration of DHA to PAL, thus formation of LA would also be

Table 5
Performances of metal-oxide catalysts for the conversion of fructose into LA/alkyl lactates

No.	Catalyst	Substrate amount	Catalyst amount	T/℃	t/h	Yield/%	Product	Ref
1	MgO	200 mg	50 mg	200	20	28.0	MLA	[151]
2	NiO	60 mg	30 mg	200	3	40.7	MLA	[139]
3	Cu-MgO	90 mg	60 mg	170	1	52.0	LA	[174]
4	Fe-SnO_2	220 mg	160 mg	160	20	53.0	MLA	[11]
5	In-γ-Al_2O_3	154 mg	75 mg	180	10	54.2	MLA	[161]
6	CoO-silicalite-1	60 mg	30 mg	180	18	52.0	MLA	[175]
7	La-HPMo	100 mg	70 mg	170	1	65.0	LA	[124]
8	Sn-β-WO_3	340 mg	200 mg	160	5	50.0	MLA	[130]

restrained (Fig. 3). This study demonstrated that an appropriate balance of Lewis and Brønsted acidic sites is critical in tandem transformation of fructose to LA.

Following their works on Sn-β catalysts for the conversion of fructose to LA, Yang *et al.* [130] used WO_3 as co-catalysts. After a series control experiments and calculation, WO_3 was proved to exist in the form of ultra-small WO_3 particles adsorbed on the Sn-β, rather than homogeneous W species. WO_3 alone shows low activity in all steps of fructose to MLA. But compared to Sn-β alone, addition of WO_3 has a significant promotion effect on the retro-aldol step of fructose. Considering those results, WO_3 might take effect by modifying some properties of Sn-β, rather than by its own activity. After characteristics including FT-IR spectra, the modification was explained as the significant decrease of silanols on the surface of Sn-β with the interaction with WO_3 particles. Yang also collated the differences between different types of metal oxides as co-catalysts in this catalytic system. For example, MgO was shown as a typical solid base, unchanging the yield of MLA but restrained other C_3 products. The other metal oxides including NiO, CuO, ZnO, MoO_3 and WO_3 all promoted the formation of MLA, but the yield of other C_3 products is similar with that over sole Sn-β except for MoO_3. In the presence of MoO_3, the formation of other C_3 products was restrained markedly. Those results exhibit the important of selection of the types of metal oxides in this conversion.

In this section, we introduced metal-oxide catalysts in the conversion of fructose to LA and lactates. Compared with zeolite catalysts, metal-oxide catalysts have poor porous structures and the related research mainly focus on the effect of various metal species. Besides, many of the metal-oxide catalysts have both acidic and basic properties, which is difficult for other types of catalysts to realize, allowing them specific approaches to regulate the acidity for a better performance in the conversion of fructose to LA.

5.4. Metal-organic catalysts

Compared with the other solid catalysts, metal-organic catalysts share similar catalytically relevant features but can be synthesized in much greater chemical variety with the contained organic components. The diversified structures means they could be attractive materials in the conversion of fructose into LA/alkyl lactates and other similar processes, with their highly desirable and tunable structural, textural, morphological, and compositional properties. The studies in this area are still preliminary and require further investigation of the way that metal species and organic ligands.

Santos *et al.* [185] tested a series of Sn^{4+} based organometallic complexes in fructose conversion, including butylstannoic acid, di-n-butyl-oxostannane, and dibutyltin dilaurate. The formation of metal oxides or hybrid metal oxides which act as Lewis acidic sites play the key role in C—C cleavage. And the alkyl substituents act to modulate this process. Wang *et al.* [186] explored the performances of MOF materials (Fe, Cr, Al)-MIL-101 and (Zr)-UiO-66 in synthesizing LA. The optimal performance of Fe-MIL-101 (20% yield of MLA within 2 h, entries #2 in Table 6) was attributed to its appropriated acid strength and content. Lu *et al.* [187] tested M-MOF-74s (M = Co, Ni, Mg, Zn) in the conversion of sugars into MLA. This study demonstrated the feasibility of using MOFs for the directed catalytic conversion of sugars to MLA. In Murillo's work, zeolitic imidazolate frameworks (ZIFs) ZIF-8 and ZIF-67 have been tested as catalysts in the conversion of sugars into MLA [12]. ZIF-8 and ZIF-67 have the same sodalite type zeolite structure but behaved differently due to the respective presence of Zn and Co in their structures (Fig. 16). Lu and colleagues, as introduced above who did research on the NiO catalysts in the conversion of fructose into MLA, also synthesized Ni/2-methylimidazole catalysts by a homogeneous precipitation method and tested them in this conversion [140]. It was attested that the obtained Ni species β-$Ni(OH)_2$ and γ-NiOOH on the catalysts availed the conversion. β-$Ni(OH)_2$ can hinder the esterification to the by-products and the γ-NiOOH showed more mesopores in the catalyst, which facilitated the diffusion of reactant and products.

5.5. Photocatalyst

With the progress of photocatalysis, photocatalytic biomass refining has also drawn a lot of attention. Ma synthesized LA from biomass-based monosaccharides including fructose photocatalyzed by ultrathin porous carbon nitride and B doped carbon nitride photocatalysts [188,189]. The yield of LA could reach 69.6% at 50 °C within 1.5 h under visible light irradiation. Completely different with above mechanism based on acidic sites, a series of oxidation active species play roles in photocatalysis. Once the visible light irradiated on the photocatalysts, the h^+ and e^- appeared in pairs. The h^+ reacted with OH^- to produce ·OH, and the e^- reacted with O_2 to produce $\cdot O_2^-$. Meanwhile, the obtained $\cdot O_2^-$ also reacted with h^+ to give $^1O_2$. After a series of catalytic poi-

Table 6
Performances of metal-organic catalysts for synthesis of lactic acid/alkyl lactates

No.	Catalyst	Substrate amount	Catalyst amount	T/℃	t/h	Yield/%	Product	Ref
1	$(C_4H_9)_2SnO$	480 mg	9 mg	210	0.5	63.0	LA	[185]
2	Fe-MIL-101	50 mg	50 mg	190	2	20.0	LA	[186]
3	Mg-MOF-74	60 mg	20 mg	220	6	37.0	MLA	[187]
4	ZIF-8	225 mg	160 mg	160	20	10.5	MLA	[12]
5	Ni-2-methylimidazole	400 mg	200 mg	200	12	45.9	MLA	[140]

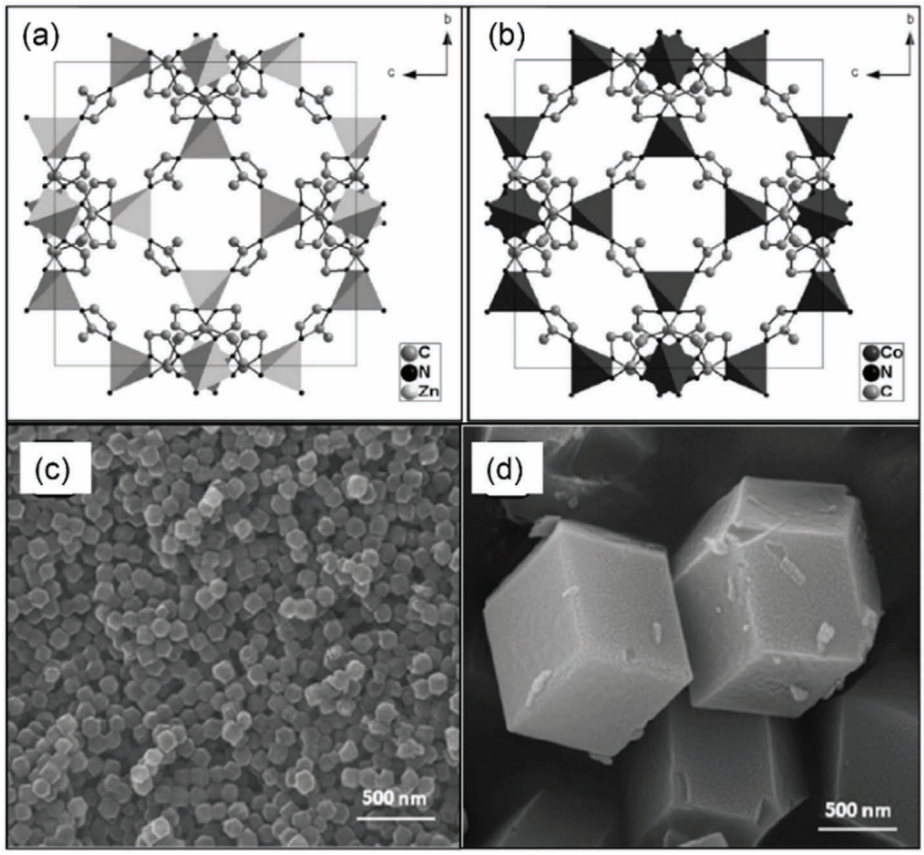

Fig. 16. Representation of (a) ZIF-8 and (b) ZIF-67; SEM images of (c) ZIF-8 and (d) ZIF-67 (reproduced from Ref.[12] with permission of Elsevier).

soning experiments, all the $^1O_2$, h^+, ·OH, and $\cdot O_2^-$ species were certified to be beneficial for the production of LA from fructose. These works pave a way for the LA production *via* photocatalysis, but the details how the different oxidation active species works and in which reaction steps respectively are still to be explored.

6. Conclusions and Outlooks

In this review article, the synergistic roles of metal species and acid/base pairs in conversion of fructose into lactic acid and derivates have been systematically discussed with critical review on mechanism (Fig. 17). Lewis and Brønsted acids play different roles in the reactions. A controlled balance of the Lewis and Brønsted acidity is critical. Metal cations and metallic particles could also act as acidic sites and modulate the catalyst acidity thus promoting the reactions.

(1) For divalent metal cations (M^{2+}), the general promotional effect is believed to follow a divalent mechanism, as the coordinated species bind strongly with M^{2+} to ensure C_3—C_4 cleavage and generate lactic acid precursors. Some alkaline and transition metal cations are believed to follow such mechanism forming a complex with pyruvic aldehyde immediately after dehydration of glyceraldehyde or dihydroxyacetone. The complex is then transformed into lactate *via* 1,2-hydride shift in basic conditions. For M^{2+} type oxide catalysts, some studies have confirmed a better performance with multiple basic sites associated with the formation of hydrogen carbonates due to surface OH^- groups or M^{2+}-

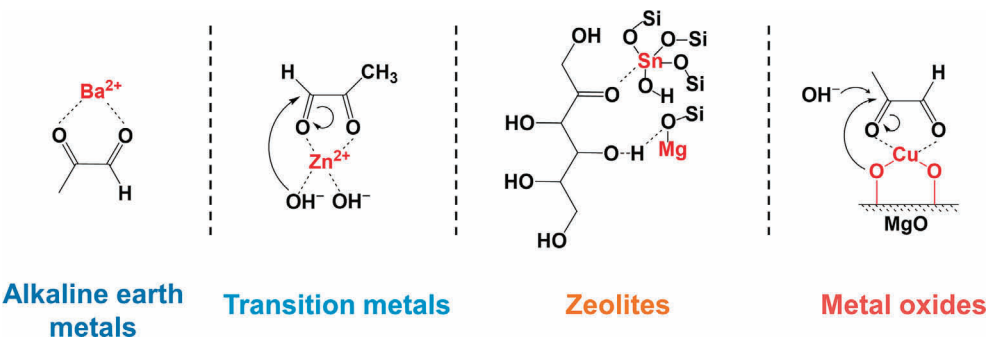

Fig. 17. Summary of synergistic catalysts.

O^{2-} pairs with the formation of bridged and bidentate carbonates. Such system is considered as the most efficient one for fast conversion of fructose to lactate salts.

(2) Limited research efforts have been dedicated to exploring the performances of Er^{3+} and Y^{3+} catalyst. The mechanism for trivalent metal cations such as Er^{3+} and Y^{3+} catalyzed C—C and dehydration reactions is still unclear.

(3) For Sn^{4+} based zeolite catalysts, a six-member ring mechanism is proposed to explain the formation of dihydroxyacetone during C—C cleavage of fructose. This mechanism has been widely established for chemical conversion of glucose to lactic acid, where isomerization of glucose in the presence of Sn^{4+} is a key step to form fructose as the intermediate product. Use of Sn^{4+} based zeolite avoids formation of lactate salts.

The following challenges should be addressed for future implementation of fructose conversion technologies:

(1) More advanced synthetic approaches should be developed to rationally control the balance of acidic/basic sites in solid catalytic materials. With extensive studies of metal cations, immobilizing metal cations on solid support with controllable structures of acidic/basic sites remains to be studied.

(2) The poor structural durability plaguing solid acid/base catalysts remains unsolved in the past decade. Effective passivation and protection methodologies should be developed to improve hydrothermal stability of solid catalyst materials. This is particularly important, as most sugar feedstocks also contains a variety of unknown impurities. Structural decomposition and surface poisoning are still a topic which demand extensive efforts.

(3) Metal/metal cations and acid/base catalyst material have also been found to be effective in other reactions such as hydrogenation, oxidation, dehydrogenation, *etc*. Incoming research efforts should also consider combining synthesis of lactic acid from fructose with those reactions to achieve tandem conversion of sugar molecules to other value-added products, such as propanediols, pyruvic acid, acrylic acid as well as other basic monomers for eco-friendly plastic products.

(4) With the progress of photocatalysis, electric catalysis, and solvation effect, new treatments of cellulosic feedstock to aimed products are rapidly developed. Applying and developing those new methods in the conversion of fructose to LA will be promising paths.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contribution

Tianqi Fang and Mengyuan Liu drafted the manuscript. Zhaozhe Li, Li Xiong, Dongpei Zhang, Kexin Meng, Xiaolei Qu and Guangyu Zhang collected literature information. Xin Jin and Chaohe Yang provided finanical support and comments.

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