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Review

# Homogeneous and Heterogeneous Catalysis of Glucose to Lactic Acid and Lactates: A Review

Thomas Saulnier-Bellemare and Gregory S. Patience*

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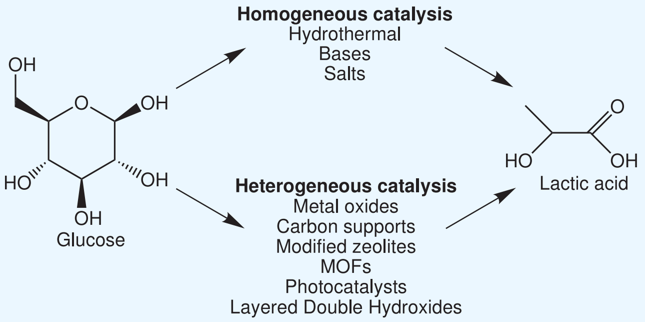
**ABSTRACT:** The current societal demand to replace polymers derived from petroleum with sustainable bioplastics such as polylactic acid (PLA) has motivated industry to commercialize ever-larger facilities for biobased monomers like lactic acid. Even though most of the lactic acid is produced by fermentation, long reaction times and high capital costs compromise the economics and thus limit the appeal of biotechnological processes. Catalytic conversion of hexose from biomass is a burgeoning alternative to fermentation. Here we identify catalysts to convert glucose to lactic acid, along with their proposed mechanisms. High Lewis acidity makes erbium salts among the most active homogeneous catalysts, while solvent coordination with the metal species polarize the substrate, increasing the catalytic activity. For heterogeneous catalysts, Sn-containing bimetallic systems combine the high Lewis acidity of Sn while moderating it with another metal, thus decreasing byproducts. Hierarchical bimetallic Sn-Beta zeolites combine a high number of open sites catalyzing glucose isomerization in the mesoporous regions and the confinement effect assisting fructose retro-aldol in microporous regions, yielding up to 67% lactic acid from glucose. Loss of activity is still an issue for heterogeneous catalysts, mostly due to solvent adsorption on the active sites, coke formation, and metal leaching, which impedes its large scale adoption.



## ■ INTRODUCTION

To reduce societies' dependence on fossil resources, alternative carbon sources must be adopted. Biomass is the most abundant carbon source in nature, making it a promising low-cost feedstock for the chemical industry. The global biobased plastics market is expected to quadruple by 2030, reaching 43 billion USD,[1] of which polylactic acid (PLA) is a compelling alternative for packaging due to its favorable mechanical and optical properties.[2]

Biotechnological process plants have been built with capacities up to 140 kta to produce lactic acid (LA), a monomer that condenses directly to PLA and a feedstock for lactide (also for PLA) from biomass.[3] However, the high cost and long reaction times of enzymes engender prohibitive investment and operating costs that reach $1,200/t of LA, dragging down operating margins.[3] Chemocatalytic processes potentially improve margins with lower investment costs due to shorter reaction times and the ability to operate over a wider range of reaction conditions. Biomass monosaccharides such as glucose rapidly degrade under hydrothermal conditions to multiple products, of which LA is produced in small yields.[4,5] A large range of homogeneous and heterogeneous catalysts have been tested to convert glucose to LA over the last 20 years. Among them, rare metal salts have been identified as the most efficient homogeneous catalysts due to their high Lewis acidities, achieving LA yields over 85%.[6−8] Such a performance has yet to be achieved in heteregeneous catalytic systems due to leaching of the rare metal species.[9,10] Other metal salt combinations that tune the Lewis acidity improve LA yield. Hierarchical bimetallic Sn-Beta zeolite is the most promising heterogeneous catalyst due to its pore system and Lewis acidity leading to LA yields over 65%.[11−14] Other bifunctionalized aluminosilicates attain LA yields over 60% due to their well-tuned Lewis acidities accelerating the rate-determining retro-aldol decomposition of fructose. Reusability is still an issue with Lewis acidic aluminosilicates primarily due to solvent adsorption on the active sites, decreasing accessibility. Coke formation and metal leaching are other important causes of deactivation. More advanced catalysts, such as photocatalysts and layered double hydroxides, reach LA yields over 70%, but their technological development stage is much lower than that of other catalysts.[15−18] More research to build a catalyst that is

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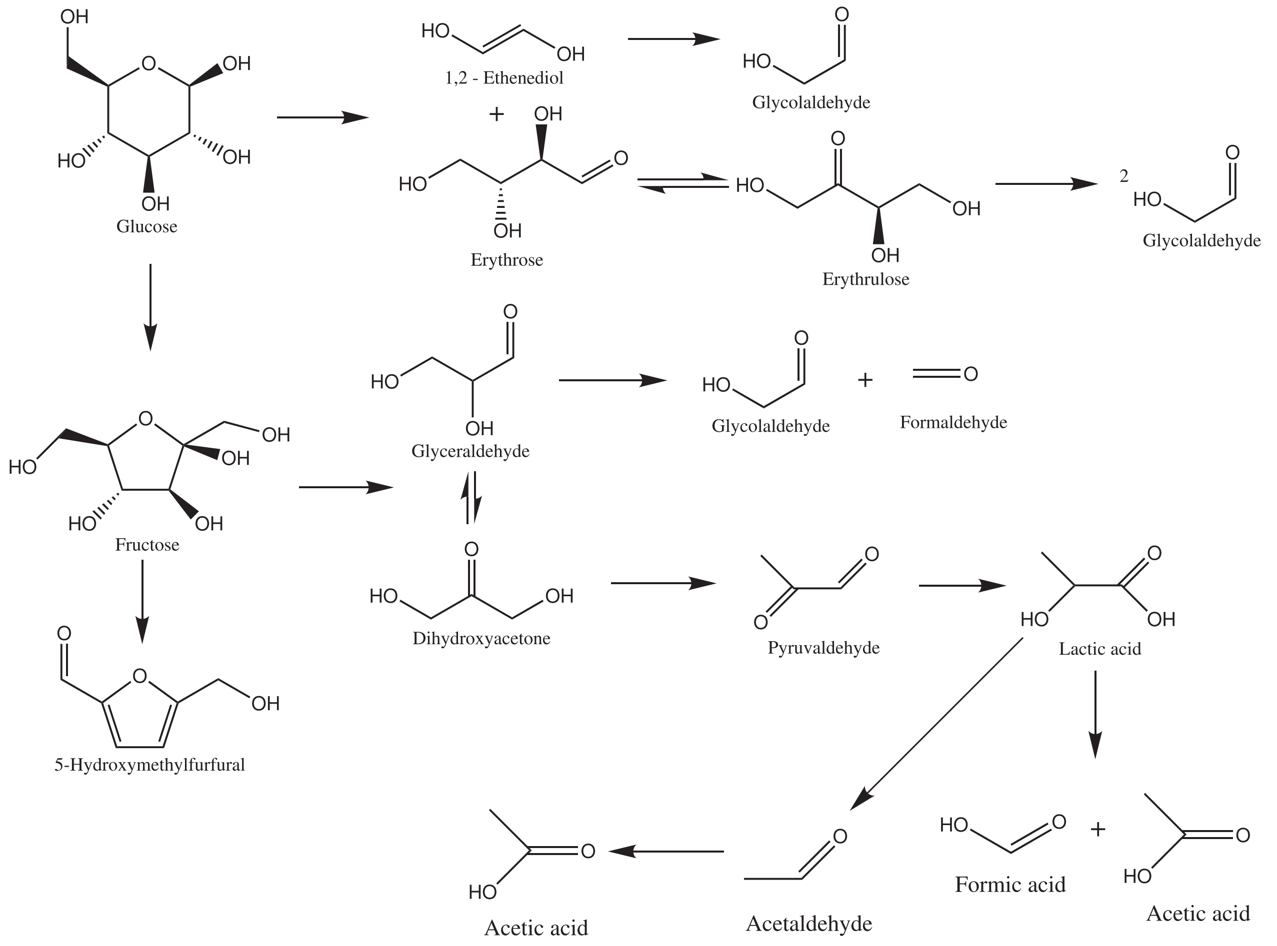

**Figure 1.** Proposed glucose reaction mechanism to LA.

both highly efficient and stable is required to develop a profitable biobased lactic acid process. This review article aims to highlight the characteristics of the most promising catalysts and identify the key research pathways to investigate.

## ■ HOMOGENEOUS CATALYSIS

**Hydrothermal Conditions.** Water in hydrothermal conditions undergoes autoprotolysis, generating Brønsted basicity and acidity able to catalyze sugar reactions.[19] The dissociation constant, $K_W$, depends on the difference of chemical potential between pure water and its ions, controlled both by density and by the internal energy of the medium.

Glucose undergoes retro-aldol decomposition when exposed to ionized water in hydrothermal conditions. This concerted reaction is a base-assisted proton transfer from C3−OH to C1═O, cleaving the C2−C3 bond and producing both erythrose (4C) and 1,2-ethenediol (2C)[20] (Figure 1). 1,2-Ethenediol rapidly isomerizes to glycolaldehyde.[21] Erythrose reacts to its erythrulose isomer, which is more thermodynamically stable. In supercritical conditions, erythrulose may undergo a second retro-aldol reaction, yielding two glycolaldehyde molecules[22] (Figure 1). In subcritical conditions, most of the erythrulose is formed in equilibrium with erythrose in the presence of some glycolaldehyde. Moreover, glycolaldehyde might react to LA in a base-catalyzed mechanism, yielding 28% LA at 300 °C, 0.75 M NaOH, and 10 min. As the C3 intermediates are reactive species, the low LA yields are due to the prevalence of secondary reactions, notably forming methanol, formic acid, or dimers by aldol condensation.[4]

Glucose isomerizes at high temperature to fructose in the presence of Brønsted bases following the Lobry de Bruyn−van Ekenstein transformation.[23] Matsuoka et al. (2012) observed that fructose yields start to rise in hydrothermal conditions starting at 220 °C, while most of the glucose reacts forming glycolaldehyde. At 250 °C, fructose yield peaks after 20 min to decrease afterward due to retro-aldol or dehydration reactions.[20] Cantero et al. (2015) achieved 20% LA yield, along with 15% glyceraldehyde within 5 s in a continuous reactor operating at 300 °C and 10 MPa.[5] Sasaki et al. (2002) observed that the isomerization product yields peak at 400 °C and 25 MPa due to the lower $K_W$ at higher temperature caused by the transition from subcritical to supercritical conditions. Meanwhile, low temperatures enhance dehydration product yields such as 5-(hydroxymethyl)furfural (5-HMF) and 1,6-anhydro-D-glucose.[22] This highlights the fact that dehydration products are thermodynamic products, while retro-aldol product yields, such as LA, are controlled kinetically. Moreover, dehydration reactions are catalyzed by strong Brønsted acidity, less present in hydrothermal conditions.

Kinetic studies have demonstrated that, in subcritical water, glyceraldehyde decomposes to glycolaldehyde and formaldehyde by a water ion-assisted reaction. In supercritical water, radical decomposition of glyceraldehyde is the domninant reaction pathway, resulting in the formation of glycolaldehyde, formaldehyde, formic acid, and acetaldehyde.

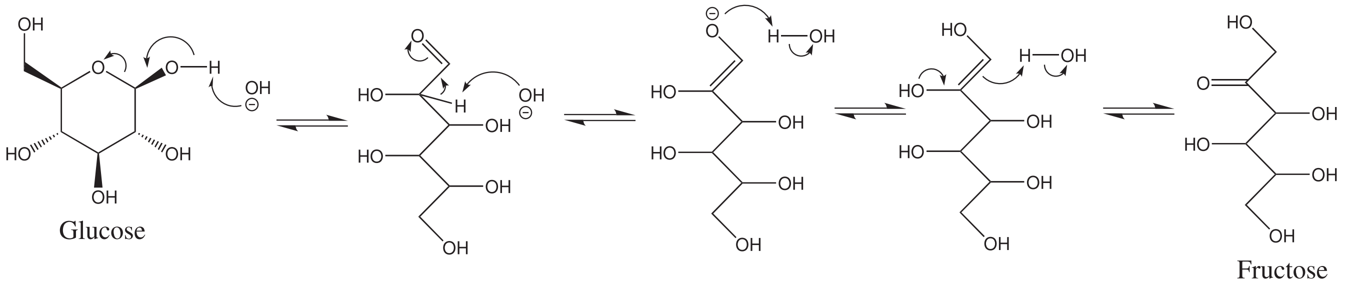

**Figure 2.** Base-catalyzed glucose isomerization mechanism.

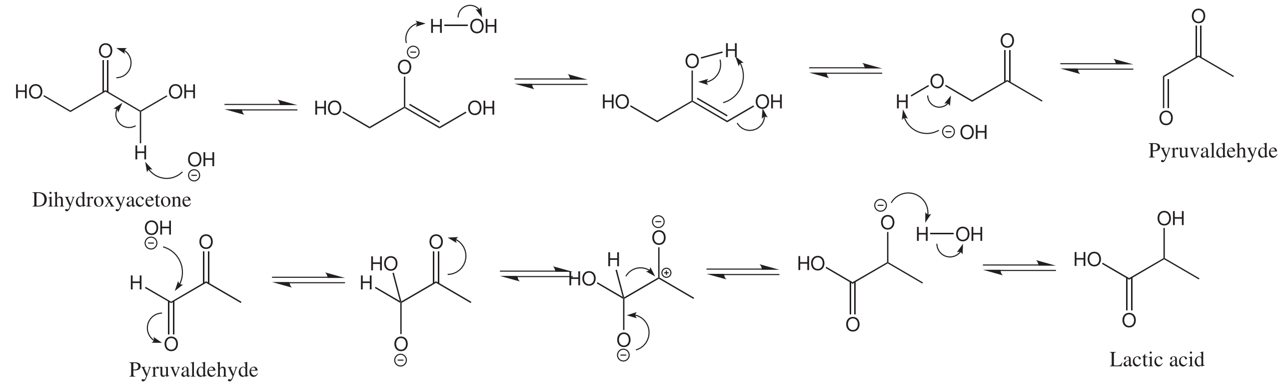

**Figure 3.** Cannizzaro-type reaction mechanism from DHA to LA.

Long reaction times favor gasification to $CO_2$ in subcritical conditions and to CO and $H_2$ in supercritical conditions.[24] Various other compounds also form at 500 °C due to pyrolysis.[25] Thus, to form LA, it is best to maintain subcritical conditions as it avoids radical-driven reactions leading to undesired products.

Glucose reacts in hydrothermal conditions to fructose, but fructose retro-aldol product yields (glyceraldehyde, dihydroxyacetone (DHA), pyruvaldehyde (PA)) are higher, implying that fructose is highly reactive when exposed to Brønsted basicity. Cantero et al. (2015) measured a 67% PA yield from fructose at 330 °C, at a conversion of 90%.[26] Reaction time influences the composition of the retro-aldol product mixture, as glyceraldehyde slowly isomerizes to DHA and DHA dehydrates to PA. The conversion of PA to LA is a Cannizzaro-type benzilic acid rearrangement followed by a facile dehydration reaction. Benzilic acid rearrangement is catalyzed by both acid and base sites.[27] Water autoprotolysis generating both hydroxyl and hydronium ions, the lactic acid formation rate thus depends solely on $K_W$.

At 450 °C and <80 MPa, LA dehydrates to acrylic acid as the pressure increases. The acrylic acid then decarboxylates to acetaldehyde, $CO_2$, and $H_2$ or decarbonylizes to acetaldehyde, CO, and $H_2O$. Acetaldehyde partially oxidizes to acetic acid. At higher pressure, the intramolecular dehydration reaction pathway is preferred at a ratio $k_{hp}/k_{lp} = 0.76$, producing mostly acrylic and propionic acids. Nevertheless, the LA conversion remained below 35% at 450 °C at maximum reaction time for all pressures, showing that LA is a relatively stable compound under hydrothermal conditions.[28]

Water in hydrothermal conditions is thus able to promote various glucose reactions due to autoprotolysis, but it fails to achieve a high LA yield due to the prevalence of secondary reactions, such as glucose retro-aldol degradation, fructose dehydration, and LA decomposition.

**Soluble Bases.** Soluble bases as homogeneous catalysts produce Brønsted basicity assisting LA production from sugar for all reaction steps. Indeed, glucose isomerization to fructose is catalyzed by Brønsted base sites, as fructose undergoes a base-assisted proton transfer from C2 to C1 after ring opening (Figure 2). $OH^-$ ions are also involved for fructose retro-aldol to C3 intermediates and subsequent Cannizzaro-type reactions to form LA (Figure 3).

To produce the Brønsted base sites needed for glucose catalysis to LA, the solid bases have to dissociate. Hence, reaction yields are heavily influenced by the solubility of the bases. Accordingly, Shen et al. (2009) transformed glycerin in 1.25 M KOH, NaOH, or LiOH, yielding respectively 90, 87, and 81% LA at 300 °C for 90 min. Solubilities for these bases are 122 g $L^{-1}$ for KOH, 109 g $L^{-1}$ for NaOH, and 13 g $L^{-1}$ for LiOH at 294 K, matching the same sequence for solubility as for LA yields.[29] Ma et al. (2010) reported the same trend, producing 45% LA from fructose at 300 °C for 60 s with KOH and 40% LA from NaOH at the same conditions (Table 1).[30] A similar trend has been noted by Yan et al. (2008), who reported LA yields of 14% using 0.8 M KOH on glucose in hydrothermal conditions for 660 s and 12% LA yield in 0.8 M NaOH.[31] Sánchez et al. (2014), however, found no significant difference between 0.5 M KOH and 0.5 M NaOH assisting bread residue transformation to LA at 300 °C in 30 min, both yielding 37(2)% LA.[32] This could be due to polysaccharide hydrolysis to monosaccharides undermining solubility effects, as polysaccharides' slow degradation is promoted by Brønsted acidity arising from water autoprotolysis.

With alkaline earth bases, the larger cations are able to conjugate with two oxygens in a bidentate mode. This coordination mode was first mentioned by Okuyama et al. (1982), who reported a kinetic effect from the addition of divalent ionic salts for hydride shifts in Cannizzaro-type reactions, such as the DHA-to-LA reaction steps. This is due to

Table 1. Soluble Base Catalytic Performances

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| cellulose | 1.75 M NaOH | 200 °C, 60 min | N/A | 17 | 36 |
| glucose | 2.5 M NaOH | 300 °C, 1 min | N/A | 27 | 31 |
| glucose | 2.5 M NaOH | 300 °C, 1.5 min | N/A | 43 | 30 |
| glycerin | 1.25 M KOH | 300 °C, 90 min | 100 | 90 | 29 |
| corncobs | 0.7 M $Ca(OH)_2$ | 300 °C, 30 min | N/A | 45 | 40 |
| DHA | 1.1 M $Ca(OH)_2$ | 25 °C, 300 min | 100 | 59 | 38 |
| glucose | 0.1 M $Ba(OH)_2$ | 250 °C, 3 min | N/A | 57 | 34 |
| glucose | 0.15 M $Ba(OH)_2$,<br>0.5 M $Ca(OH)_2$ | 60 °C, 12 h | 100 | 43 | 41 |

the stabilization of the transition state (TS) during the hydride shift by chelation.[33] Esposito et al. (2013) identified the role of divalent cations by assessing the LA yields from glucose at 220 °C during 12 h with NaOH (17% LA yield), $Ba(OH)_2$ (53% LA yield), and a combination of NaOH/$BaCl_2$ (40% LA yield).[34] This yield enhancement with the presence of divalent cations is attributable to the coordination of $Ba^{2+}$ to the two double-bonded oxygens in PA, stabilizing the TS during the hydride shift reaction to LA. Such a yield enhancement was also observed for $Ca(OH)_2$ (49% LA) and $Sr(OH)_2$ (40% LA), implying that an analogous mechanism is encountered for other alkaline earth bases.[34] Li et al. (2017) found a similar effect by switching from monovalent to divalent cations at room temperature during 48 h in a nitrogen atmosphere with DHA, achieving 87% LA yield in $Ba(OH)_2$ at optimal conditions.[35] They also highlighted the importance of the alkaline earth base solubility, as no catalytic effect was observed over the insoluble $Mg(OH)_2$. When $O_2$ was introduced in the reactor's atmosphere, the LA yield dropped quickly and byproducts such as malonic acid, formic acid, and $CO_2$ appeared.[35] Yan and Qi (2014) described the formation of malonic and formic acids from cellulose hydrothermal degradation in the presence of 2.5 M NaOH, identifying that DHA hydrates to malonic acid, while glyceraldehyde decarboxylates to formic acid and $CO_2$.[36]

DHA dimerizes by aldol condensation at high base concentration and high temperature (Figure 4). These dimers either react back to DHA or polymerize to form humins.[37−39]

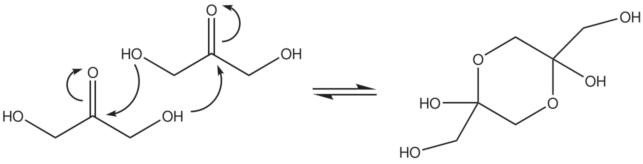

Figure 4. DHA dimerization by aldol condensation mechanism.

After 1 h at room temperature, $Ba(OH)_2$ reached 30% LA for $Ca(OH)_2$ from DHA, which follows the solubilities of both bases.[38,42] However, after 6 h, the LA yield with $Ca(OH)_2$ increases to 58% LA while $Ba(OH)_2$ produces only 50% LA (Table 1).[38] This is likely due to barium complexation with lactates in a monodentate mode, inducing a C1−C2 bond cleavage by polarizing the substrate. Indeed, the degradation product concentrations pattern match those associated with lactic acid degradation.[29] The nucleophilic attack of $OH^-$ on the lactate complex completes the LA decomposition to formic and acetic acids (Figure 5).[29,41] Cations with larger ionic radii complex more with lactate and thus cause more product degradation by stabilizing the TSs to the undesired products. Moreover, $Ca^{2+}$ degrades less LA than $Ba^{2+}$ due to the lower alkalinity and lower solubility of $Ca(OH)_2$. Combining $Ca(OH)_2$ and $Ba(OH)_2$ respectively at 0.5 and 0.15 M yielded a maximal LA yield at 43% from glucose at 60 °C in 12 h in nitrogen (Table 1).[41] In that dual-catalyst system, $Ba(OH)_2$ provides alkalinity and divalent cations to promote the glucose-to-LA reaction. In the meantime, the total alkalinity is controlled by $Ca(OH)_2$ dissociation and replenishment, inducing a controlled-release catalytic system. Furthermore, $Ca^{2+}$ has a stronger binding ability with lactate than $Ba^{2+}$ and calcium lactate is more stable than LA, inhibiting LA degradation.[41]

The most complete study on the mechanism of alkaline earth bases on glucose to LA was published by Zhao et al. (2022), who used diffusion ordered spectroscopy nuclear magnetic resonance (DOSY NMR) and isotopic labels to identify the coordination states.[43] In basic conditions, $Ba^{2+}$ complexes with water, giving $[Ba(OH)(H_2O)_2]^+$. The presence of $OH^-$ groups in the solution coupled with the weak acidity of glucose enables pyranose coordination with $[Ba(OH)(H_2O)_2]^+$, opening the ring and faciliting the isomerization to fructose through a C2−C1 hydride shift. Subsequent retro-aldol with aqueous $Ba(OH)_2$ happens instantly after glucose isomerization to generate glyceraldehyde and DHA. DHA, assisted by barium complexation, dehydrates to PA, releasing the Ba complex. The two double-bonded oxygens on PA may then coordinate again with the Ba complex to get barium lactate through rehydration and benzilic acid rearrangement.[43]

Hence, $Ba(OH)_2$ is the most effective soluble base for glucose catalysis to LA with a maximum observed LA yield from glucose in water of 57% (Table 1).[34] To counter Ba-assisted LA degradation, $Ca(OH)_2$ can be used in combination with $Ba(OH)_2$, thus increasing LA yields. However, the use of soluble bases comes with safety issues and high cost due to the high alkalinity of the system and the low reusability of the catalysts,[44] decreasing their attractiveness for industry.

**Salts.** Homogeneous catalysis has been tested not only with bases but also with salts, highlighting the activities of the different metal cations. The type of metal species has an effect on the coordination mode, while the LA yield is affected not only by the Lewis acid character of the cation but also by its hydration capability, its oxidation state, and the anion composing the salt.

Lewis acidity is the parameter having the most effect on LA yields when salts are used.[45] Bicker et al. (2005) first tested several metal sulfates on sucrose and DHA, finding that the LA yield follows the sequence of the Lewis acidity of the tested salts, with $ZnSO_4$ being the most efficient catalyst with a LA yield of 39%, compared to $NiSO_4$ and $CoSO_4$, respectively achieving 36 and 31% LA yields (Table 2).[45] Their kinetic study shows that the glucose isomerization reaction has the highest activation energy (102 kJ $mol^{-1}$), while fructose retro-aldol has a slightly lower activation energy (96 kJ $mol^{-1}$), and the PA transformation to LA activation energy is much lower (58 kJ $mol^{-1}$) for the $ZnSO_4$-catalyzed reaction.[45] $Zn^{2+}$ polarizes the products in a bidentate coordination mode,

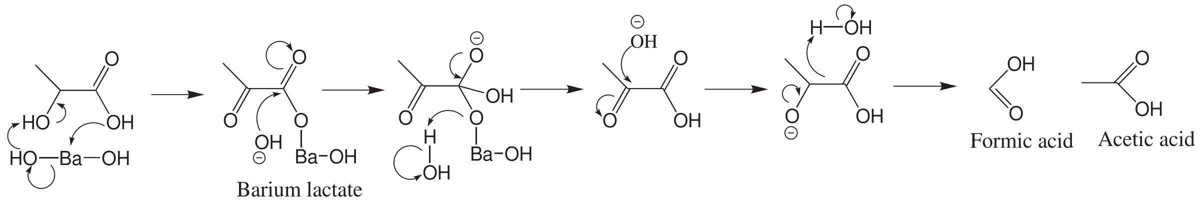

**Figure 5.** Barium complexation followed by lactate degradation to acetic and formic acid.

**Table 2. Salt Catalytic Performances**

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| DHA | 0.005 M $AlCl_3$ | 140 °C, 90 min | 100 | 98 | 46 |
| glucose | 0.005 M $AlCl_3$, 0.005 M $SnCl_2$ | 180 °C, 3 MPa, 120 min, pH 2.8 | 100 | 81 | 47 |
| glucose | 0.045 M $SnCl_4$, 0.045 M $Ba(OH)_2$ | 160 °C, 150 min | 100 | 48 ML | 50 |
| glucose | 0.004 M $ZnCl_2$ | 200 °C, 180 min, 3% water, 97% $CH_3OH$ | N/A | 51 ML | 9 |
| glucose | 400 ppm $ZnSO_4$ | 300 °C, 3 MPa | N/A | 42 | 45 |
| cellulose | 0.007 M $Pb(NO_3)_2$ | 190 °C, 3 MPa, 240 min | 100 | 62 | 49 |
| cellulose | 0.0066 M $YCl_3$ | 220 °C, 2 MPa, 30 min | 100 | 57 | 53 |
| rice straw | 0.0066 M $YCl_3$ | 240 °C, 2 MPa, 90 min | N/A | 66 | 52 |
| cellulose | 0.012 M $ErCl_3$ | 240 °C, 2 MPa, 30 min | 100 | 91 | 7 |
| glucose | 0.14% mol $La(OTf)_3$ | 250 °C, 60 min | N/A | 74 | 56 |
| treated hardwood chips | 0.0017 M $Er(OTf)_3$ | 250 °C, 60 min | N/A | 72 | 58 |
| cellulose | 0.0027 M $Er(OTf)_3$ | 240 °C, 2 MPa, 30 min | 100 | 89.6 | 6 |

promoting the Cannizzaro-type reaction to LA. Rasrendra et al. (2010) proposed a similar way of action of the metal cation for $Al^{3+}$ and $Cr^{2+}$.[46] As proposed by Wang et al. (2017), Zn(II) cations coordinate with two fructose molecules, polarizing the electron cloud of C3 or C4, inducing the C3−C4 bond cleavage to produce both DHA and glyceraldeyde.[9] Deng et al. (2018) came to a high 81% LA yield from glucose by combining Sn(II) and Al(III), with the former exhibiting strong Lewis acidity and the latter showing moderate Lewis acidity (Table 2).[47] In this system, Al(III) catalyzes glucose isomerization and DHA transformation to LA better than Sn(II), due to its binding with a solvent molecule in addition to the bidentate coordination to the substrate, which decreases the Gibbs free energy of activation for glucose isomerization to fructose from 88 to 54 kJ $mol^{-1}$, based on DFT calculations.[47] Sn(II) catalyzes the retro-aldol reaction, due to its large ionic radius and its closed shell configuration giving it the ability to specifically increase fructose C4−OH group acidity. Its strong Lewis acidity arises primarily from its empty d-orbitals readily interacting with $s^2$ lone pairs. Sn(II) has a similar electronic configuration as Pb(II), which also efficiently catalyzes glucose to LA (Table 2).[48,49] The estimated $\Delta G$ values by density functional theory (DFT) for glucose isomerization are positive for $Pb^{2+}$ but negative for Pb(II)−OH, identifying the promoting effect of solvent coordination on the reaction mechanism. The calculated $\Delta G$ is highest for the fructose retro-aldol step, confirming it as the rate-determining reaction step when Lewis acidic salts are used.[49] This solvent promoting effect arises from the added substrate polarization induced by the presence of a vicinal −OH group. Catalyst−solvent interaction was also noted by Zhou et al. (2014), who tested the $SnCl_4$ catalysis of glucose in methanol. In this system, methanol deprotonates due to interaction with $SnCl_4$, which generates Brønsted acidity, thus decreasing the LA yield. Adding NaOH at a molar ratio of 1:1 with the Sn salt to neutralize Brønsted acidity resulted in a methyl lactate (ML) yield increase from 28 to 47%, while dehydration product (5-HMF, methyl levulinate) yields were cut by more than half (Table 2).[50]

Lanthanide salts interact with water to induce autohydrolysis, resulting in the generation of octahedral complexes.[51−53] Xu et al. (2020) found that these complexes bond more rapidly to the substrate than $H_3O^+$, undermining the Brønsted acidity effect.[51] They also found that these complexes assist the specific $C_3$−$C_4$ cleavage during fructose retro-aldol, as it was calculated that the $C_2$−$C_3$ and $C_4$−$C_5$ bond lengths decrease by 0.009−0.019 Å when fructose complexes with Y(III), while the $C_3$−$C_4$ bond length increases by 0.012 Å during the complexation.[51] Such complexes have also been observed with Zr oxide, creating hydrogen bonds with carbohydrates (Figure 6), stabilizing the TS of the Lewis acid catalyzed reactions.[54]

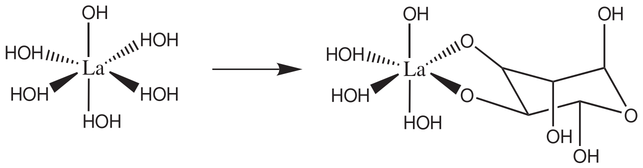

**Figure 6.** Bidentate coordination of lanthanide octahedral complex with glucose.

LA yields as high as 91% from cellulose and 97% from glucose were observed with $ErCl_3$, which are the highest yields observed to our knowledge (Table 2).[7,55]

Lanthanide triflates have very high Lewis acidities and solubilities and achieve LA yields from glucose in water exceeding 70% (Table 2). LA yield over $La(OTf)_3$ reaches 74% at 180 °C (Table 2). However, when the temperature was raised, humin formation was more prominent due to the autoprotolysis of water in hydrothermal conditions resulting in an increase of Brønsted acidity, decreasing yields.[56] $H_3O^+$ in the medium, arising from water autoprotolysis, accelerates the hydrolysis of polysaccharides, increasing the overall LA yields from those molecules. LA yields from cellulose are inversely proportional to the lanthanide ionic radius, due to an increase in binding ability between the lanthanide and the glucose hydroxyl groups as the radius gets smaller.[6,57] Hence, Er(OTf)$_3$ is the most active catalyst, as erbium possesses the smallest ionic radius of all lanthanides.[6,58] The triflate groups on the lanthanide are stable in water, and the catalyst is reusable, which has not been found with other rare metal salts, where interaction with solvent predomines. In an attempt to make these catalysts heterogeneous, Kim et al. (2020) impregnated La(OTf)$_3$ on $SiO_2$, but metal leaching and coke were detected, leading to poor reusability.[10]

As for transition metal salts, oxidation state is a determining parameter for catalytic activity. Although a significant product distribution difference was observed between $SnCl_2$ (33% LA yield) and $SnCl_4$ (24% LA yield), it is unclear how the degree of oxidation of Sn affects the reaction mechanism.[59] This is probably due to the $SnCl_2$ species displaying higher Lewis acidity than $SnCl_4$. $SnCl_4$, in turn, would interact more with the solvent, generating more Brønsted acidity, favoring a fructose dehydration mechanism. More work has to be pursued to decipher the mechanistic differences between Sn(II) and Sn(IV) catalyses.

The anion effect on the reaction performance remains controversial. Hayashi et al. (2005) observed a high anion effect on Sn(II) activity, as the ML yield from DHA decreased between $SnCl_2$ (89% ML yield), $SnBr_2$ (83% ML yield), and $SnI_2$ (71% ML yield), while no ML formation was observed with $SnSO_4$.[60] On the other hand, Rasrendra et al. (2010) tested both chlorine and sulfate salts for a variety of metals without finding a correlation between the anion identity and the catalytic activity.[46] However, Wang et al. (2017) noted a high anion effect on $ZnX_2$, correlating salt solubility with its catalytic activity. Solubility was insufficient to explain the fact that no EL is formed when $ZnSO_4$ was used, while EL yields up to 30% were observed at 200 °C at 3 h $Zn(NO_3)_2$, 48% with $ZnBr_2$, and 52% with $ZnCl_2$.[9] Zhang et al. (2021) also correlated catalytic performance with solubility for Yb(III) salts.[61] Interestingly, placing $Yb_2(SO_4)_3$ in water decreased the pH of the medium to 3.0. This generation of Brønsted acidity using sulfate could explain the decrease in LA yields, as Brønsted acidity favors fructose dehydration instead of the retro-aldol reaction pathway.[61] Elliot et al. (2018) reported that the catalytic performances of salts of strong acids increase with the salt concentration until it reaches a plateau.[62] Indeed, a low concentration of strong salt is sufficient to get to total conversion, while higher salt concentrations do not affect the reaction. With salts of weak acids, ML yield increases rapidly to form a peak and then decreases slowly with the concentration of salt. This is explained by the fact that, at a certain concentration, Brønsted acidity starts to be generated by the interaction between the cation and the solvent, which favors other products than LA to be formed.[62] However, this does not fully explain the anion effect within the strong acid salt category identified by Hayashi et al. (2005) or the much different performance from an anion to another observed by Rasrendra et al. (2010).[46,60] Hence, an anion effect has been identified by most of the studies on the subject, but the exact way of action of the anion is still to be fully elucidated.

## HETEROGENEOUS CATALYSIS

**Metal Oxides.** Metal oxides present the advantage of being heterogeneous catalysts that are easy to synthesize and study in a large set of conditions. Metal oxides as catalysts are in the form of metallic crystalline frameworks. A few mechanisms have been proposed to explain their catalytic activity. A first mechanism proposes the hydrogenation of the surface oxygens of the framework by the dissociation of water molecules, generating free $OH^-$ ions acting as Brønsted bases (Figure 7).[63,64] The whole reaction mechanism is then the same as for soluble bases.

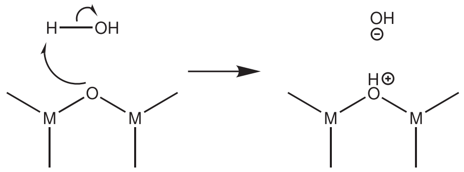

**Figure 7.** Surface oxide hydrogenation generating Brønsted basicity.

Udomcharoensab et al. (2019) grafted Cu, Co, Ni, and Zn oxides on MgO to generate surface hydroxylated oxygen groups and unsaturated cations, forming Brønsted basic and Lewis acid surface sites.[65] Lewis acidity may also arise from surface oxygens forming M═O groups during calcination.[66,67] When the available surface area decreases, either by structural modifications or particle agglomeration, catalytic activity decreases too, supporting the proposition that the active sites are on the surface of the framework (Figure 8).[68,69]

The activity of both the Lewis acidic metal and the basic surface oxygen were identified on numerous metal oxides, notably by FTIR and $CO_2$ temperature programmed desorption (TPD).[44,70,71] These vicinal active sites readily coordinate with the substrates, forming two partial bonds with two substrate oxygenated groups. This conjugation polarizes the substrates, promoting the different reaction steps from glucose to LA.[72−74]

The hydroxyl and carbonyl groups in the reaction intermediates (glucose, fructose, PA) coordinate with the surface active sites, promoting every step of the mechanism, except DHA dehydration to PA. This fast reaction step is promoted by the Brønsted acidity arising from water autoprotolysis at high temperature.[71] As for the retro-aldol step, fructose conversion is closely related to Lewis acidity, when comparing the activities of the lowly acidic $SnO_2$ (83% conversion) and the highly acidic $MoO_3$ (93% conversion). $SnO_2$ impregnated with $MoO_3$ formed a nanostructured dual catalyst, increasing the number of open Sn sites, thus increasing the Lewis acid site density.[75] Other oxides with higher Lewis acidities ($Y_2O_3$, ZnO, $Al_2O_3$, $TiO_2$, $ZrO_2$) exhibited higher conversions.[76] However, a too high density of Lewis acid sites, as found in $Al_2O_3$, promoted secondary reactions, decreasing the LA yield. By grafting In on $Al_2O_3$, Xiao et al. (2021) increased the ML yield until reaching an optimum at 0.12 g $g^{-1}$ (Table 3), as In's weak Lewis acidity moderates $Al_2O_3$'s strong Lewis acid sites.[69] Similarly, by grafting Cr(III) on $Al_2O_3$ by incipient wetness impregnation, Kosri et al. (2021) achieved 74% LA from glucose, confirming the promoting effect of well-tuned bimetallic Lewis acidic metal systems on glucose reactions.[77]

Hata et al. (2021) tested glucose conversion to LA using $TiO_2$, $Al_2O_3$, $Nb_2O_5$, MgO, ZnO, and $Y_2O_3$, confirming that both intrinsic Lewis acidity and Brønsted basicity have a considerable effect on the product distribution.[80] XRD detected $Y(OH)_3$ groups at the surface of $Y_2O_3$ and 0.30 g $g^{-1}$ $Y_2O_3/SiO_2$ frameworks, which are Brønsted bases and

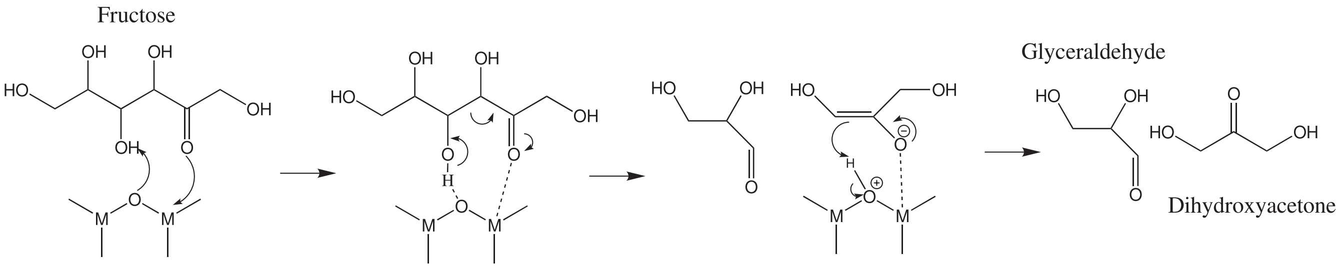

**Figure 8.** Lewis acid/Brønsted base metal oxide catalyzed fructose retro-aldol to glyceraldehyde and DHA.

**Table 3. Metal Oxide Catalytic Performances**

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| glucose | ZnO | 200 °C, 120 min | N/A | 42 | 71 |
| xylose | ZnO | 180 °C, 3 MPa, 30 min | 92 | 43 | 76 |
| glucose | ZnCTAB/MgO | 140 °C, 0.4 MPa, 60 min | 100 | 12 | 65 |
| cellulose | $ZrO_2$ | 200 °C, 360 min | 87 | 21 | 72 |
| DHA | $ZrO_2$− $TiO_2$ | 130 °C, 120 min | 100 | 33 EL | 74 |
| glucose | $Al_2O_3$ | 160 °C, 0.5 MPa, 360 min | N/A | 34 ML | 68 |
| glucose | In/$Al_2O_3$, 0.01 g/L $K_2CO_3$, 7% water, 93% methanol | 180 °C, 2 MPa, 600 min | N/A | 49 ML | 69 |
| DHA | Sn/$Al_2O_3$ | 100 °C, 420 min | 95 | 68 | 78 |
| fructose | $SnO_2$/$Al_2O_3$, 0.3 g/L $K_2CO_3$ | 160 °C, 180 min, 98% ethanol | 100 | 61 EL | 79 |
| DHA | $SnO_2$/$Nb_2O_5$ | 160 °C, 280 min | 100 | 12 | 67 |
| glucose | $Y_2O_3$ | 200 °C, 1 MPa, 30 min | 100 | 30 | 80 |
| glucose | Cr/$Al_2O_3$ | 170 °C, 1.5 MPa $N_2$, 360 min | 100 | 74 | 77 |

assist the retro-aldol reaction and dehydration of DHA to PA. $Y^{3+}$ arising from the oxide dissociation promotes glucose isomerization to fructose as a Lewis acid in a bidentate coordination mode.[80] A catalytic activity enhancement has been noted by Li et al. (2016) when grafting $Y_2O_3$ on $SiO_2$. When grafted, $Y_2O_3$ is more subject to dissociation, forming the highly Lewis acidic surface $Y^{3+}$, increasing the cellulose-to-LA yield from 33 to 45%. All the cellulose reacts above 220 °C and 3 h.[81] As for other rare metal heterogeneous catalysts, deactivation by metal leaching is an issue due to their high affinity with water.

Grafting $SnO_2$ on $Al_2O_3$ increases the acidity of the catalytic system, increasing the ethyl lactate (EL) yield from DHA from 5 to 70%.[78] Indeed, surface Sn forms open Sn−OH sites, which effectively catalyze this reaction. The effect of open Sn sites has been extensively studied with tin-impregnated zeolite frameworks. Incorporating $SnO_2$ on a $Nb_2O_5$ framework also greatly improves the LA yields for both oxides, due to the formation of oxygen vacancies in the framework, increasing Lewis acidity (Table 3).[67] However, Sn has a high concentration of Lewis acid sites, which leads to high lactate yields but also to the formation of more dehydration products.[82] Coupling $SnO_2$ with ZnO on an $Al_2O_3$ support instead of $Nb_2O_5$ addresses this problem by decreasing the Lewis acid site density, avoiding a high 5-HMF yield while keeping a high lactate yield.[79] Hence, the main parameters driving the catalytic reaction are the surface Lewis acid site density and strength.

Apart from catalysis arising from Lewis acidity or basicity, some oxides are involved in the reaction as oxidizing agents in redox reactions. The reduction of the metal species promotes the usual reactions leading to LA production, but they happen at higher temperature and in less time than the usual chemocatalytic reactions. The high temperature slowly degrades LA, yielding a small part of formic acid, while LA is also degraded by electrochemical pathways to acetic acid after 60 s at 300 °C with CuO, the oxide displaying the most electrochemical activity.[83,84] The first step of the electrochemical reaction is the dissociation of the metal oxide to generate cations, which requires alkaline conditions. Indeed, Younas et al. obtained a 9.6% LA yield from rice straws with NiO in water.[85] However, when they added 1 M NaOH, a synergistic effect increased the yield to a high 59% LA, probably due to the base-catalyzed reduction of the oxidized species in the alkaline medium, generating electrochemical activity. They also measured a higher yield using $Ni^{2+}$ over NiO. These results show that the most active sites arise from the dissociation of the metal species generating oxidizing agents, and not from the oxides themselves. The presence of Ni species detected by X-ray diffraction (XRD) after the reaction highlights the electrochemical activity reducing $Ni^{2+}$.[85] The use of surfactants also enhances redox activity by helping the reduction of the metal species, as it stabilizes the TS during the reaction in the aqueous phase.[86] After transforming glucose to LA with CuO in an alkaline medium, Choudhary et al. (2015) noted the presence of $Cu_2O$ as well as $Cu_4O_3$, which clearly shows that a redox reaction happens, modifying the oxidation state of Cu(II).[87] Although it is known that CuO participates in redox reactions transforming glucose in LA, the full reaction mechanism is yet to be elucidated.[88]

The use of metal oxides is useful to rapidly test a large variety of metal catalytic performances and identify the mechanism, but the generally low LA yields decrease their chances of being used on an industrial scale.

**Carbon Supports.** To find a biobased and efficient catalyst support, carbon structures such as graphite, graphite oxide, and graphene oxide are used as catalyst supports. Yu et al. (2019) grafted Al on these three different carbon supports using an air heating method, finding that Al interacts with the oxygen groups of the carbon structure to form active amorphous

Table 4. Carbon-Supported-Catalyst Performances

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| glucose | $SnO_2$/AC | 160 °C, 360 min | 99 | 45 EL | 93 |
| glucose | ZnO/AC | 160 °C, 360 min | 99 | 37 EL | 94 |
| glucose | Sn−Al/AC | 180 °C, 3 MPa, 120 min | 100 | 40 | 94 |
| glucose | $Pb(OH)_2$/reduced graphene oxide | 170 °C, 2.5 MPa, 120 min | 100 | 40 | 92 |

octahedral metallic groups. These groups act as Lewis acid sites, assisting glucose isomerization through adsorption/activation mechanisms. In that way, a maximum 35% fructose yield from glucose using Al−graphene oxide was achieved by microwave heating at 160 °C.[89] However, the catalytic activity of Al−graphene oxide is insufficient to promote fructose retro-aldol at high rates. Graphite is an ineffective support, as its oxygen content is too low to graft a sufficient amount of Al and generate the active sites.[90] Similar conclusions were drawn by Xiong et al. (2020), as they tested Al grafting on graphite oxide and graphene oxide, yielding a 35% fructose yield from glucose for both oxides.[91] On the other hand, a 29% fructose yield was achieved using Al−biochar. This difference in yield is explained not by the difference in Al content but by the Al distribution in the framework. Indeed, graphite and graphene oxides are both more porous than biochar, facilitating the mass transfer to the active sites. The lack of porosity in biochar is partly due to residual lignin and cellulose.[91] Optimization of biochar is yet an interesting path to be investigated, as it is a low-cost, green catalyst support.

$Pb^{2+}$ grafted on graphene oxide nanosheets yielded 59% LA from fructose and 40% from glucose at 160 °C and 2.5 MPa $N_2$ (Table 4).[92] The electrostatic forces of O groups in the graphene oxide framework attract $Pb^{2+}$, forming $Pb(OH)_2$ detected by XRD, thus providing the Brønsted basicity necessary for fructose retro-aldol and other subsequent reactions to produce LA.[92]

Steam and acid treatments generate carbonyl and hydroxyl groups at the surface of activated carbon (AC), producing weak Brønsted acid sites accelerating the reaction. Al and Sn grafted on activated carbon yield 42% LA from glucose in 20 min at 180 °C (Table 4).[93] A ratio of 1/1 Al/Sn content achieves the best yield, which is consistent with the findings of Deng et al. (2018).[47] Grafting metal oxides on the treated activated carbon also shows high LA yields. $SnO_2$ on AC yields 99% EL from DHA due to its strong acidity arising from open Sn sites. Indeed, acid−base titration showed an increase in acid site concentration between parent AC (0.84 mmol $g^{-1}$) and $SnO_2AC$ (1.37 mmol $g^{-1}$). From glucose, this strong acidity increases byproduct formation, resulting in a 42% LA yield. ZnO on AC, displaying a lower acid site concentration (0.73 mmol $g^{-1}$), achieves a lower glucose conversion but a higher selectivity, leading to similar yields as with $SnO_2$ on the carbon support (Table 4).[94] Hence, carbon supports do not offer, for now, LA yields high enough to attract interest in scaling up the process, and more studies have to be done to enhance the catalytic activities of these supports.

N-Heterocyclic carbenes (NHCs), however, display extraordinary activity when used to self-support iridium complexes. Indeed, used in the presence of a soluble base, these catalysts offer almost quantitative LA yields from sorbitol[95] and 93% yield from glycerol.[96] NHCs are strong $\sigma$-electron donors, which increases the electron density around the iridium complex.[97] They also enhance the steric bulkiness of the complex, while avoiding clustering of iridium.[95] Thus, this catalyst is more active than homogeneous iridium-based catalysts. Wu et al. (2020) also found that adding ethylene glycol and methanol to the mixture inhibits 2−4 retro-aldol reactions in favor of the 3−3 retro-aldol reaction leading to the formation of lactic acid, due to a displacement of the chemical equilibrium.[95] The presence of a soluble base activates the catalyst by replacing the −CO group on the iridium species by an hydroxyl group. This hydroxyl group initiates the reaction by facilitating a hydrogen transfer from the substrate to the iridium complex, initiating the rate-determining reaction step, either for glycerol dehydration to DHA[98] or for 3−3 retro-aldol for sorbitol.[95] Although it has not been tested until now, it is probable that this NHC−Ir catalyst would also be active for fructose retro-aldol to DHA and glyceraldehyde, which further improves lactic acid selectivity.

**Zeolites.** Zeolites are the most studied heterogeneous catalysts for glucose reactions to LA due to their high intrinsic acidities and their channel sizes allowing good diffusion. These aluminosilicates are also relatively easy to functionalize. They come in various topologies exhibiting different pore sizes and structures, while being low-cost and generally showing good stability, making them promising catalytic supports.

Functionalization is typically done postsynthesis, requiring dealumination or desilication in order to generate vacant sites, leaving space for other species to be included in the framework. Dealumination is done in harsh acidic conditions where Al sites, which are weak Brønsted and strong Lewis acid sites, are withdrawn from the zeolitic framework. As Al is the minority species in zeolites, with Si/Al ratios being rarely under 15, the crystalline structure is usually preserved. Vacant sites left after dealumination form silanol nests, which are then filled with metals through incipient wetness impregnation, solid state ion exchange, or other postsynthesis methods (Figure 9). Metals grafted by incipient wetness impregnation only reach the surface vacant sites of the framework, and extraframework metal species are formed.[99] These extraframework metallic species are metal oxide species, cluttering the pores and being generally less active than the same metal grafted on the zeolites. Similarly, solid state ion exchange, which is achieved by grinding solid metal precursors with the dealuminated zeolite, also forms extraframework metal groups. Chemical vapor deposition is able to reach a higher metal fraction in the framework but still generates extraframework metal species, which undermines the LA yields.[100,101] A

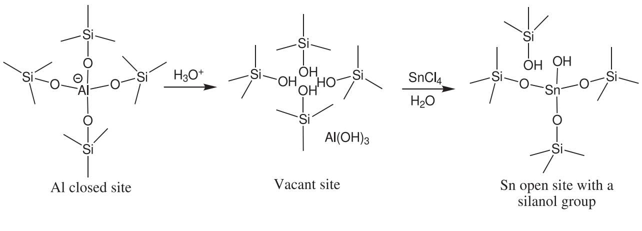

Figure 9. Zeolite postsynthesis functionalization procedure.

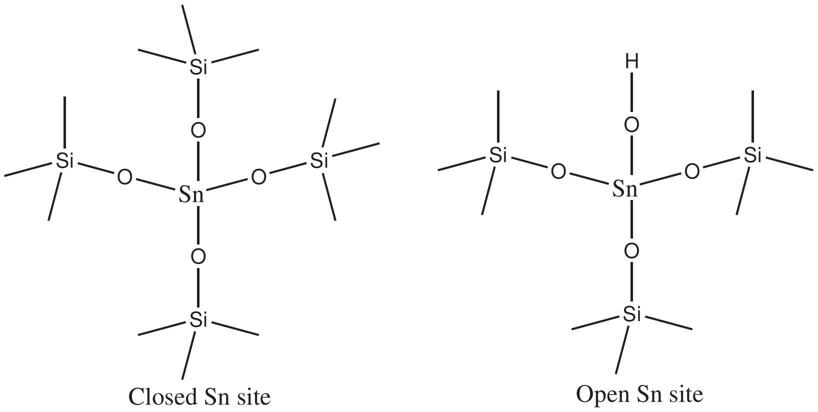

**Figure 10.** Closed and open site conformations in Sn zeolites.

combination of Ga and Zn was notably grafted on nanozeolites Y by Verma et al. (2017) by incipient wetness impregnation to get the high Lewis acidity of Ga, while neutralizing its Brønsted acidity with the intrinsic basicity of Zn. They got a high 58% ML yield from cellulose along with good reusability.[102]

Apart from dealumination, desilication in highly alkaline medium is another method to generate vacant sites in the zeolitic framework. Mesoporosity emerging from the withdrawal of Si groups forms open Al sites, increasing the Lewis acidity. Dapsens et al. (2013) desilicated Al-MFI with NaOH and structure directing agents to replace silica by aluminum. They achieved 90% LA yield from DHA in 6 h. However, Lewis acid site concentration decreased over the runs, caused by Al leaching.[103] This was also observed by Graça et al. (2018), who desilicated on Na−Al-Beta zeolites to graft Mg in the framework. While Mg leaching was also detected by Yang et al. (2020), who grafted Mg after dealumination, this leaching was more important with desilication.[104,105] This might be due to the weakening of the framework caused by the withdrawal of Si−O links.

Hydrothermal zeolite synthesis is also a method used to functionalize the zeolitic framework. It consists of using raw $SiO_2$, metal salts and a structure directing agent to synthesize zeolites containing the desired metal. It results in more closed metal sites and less metal leaching.[106,107] However, this method generally necessitates a fluoride medium, which introduces environmental and safety issues to the procedure. Hydrothermal synthesis also requires long crystallization times, from a couple of days to several weeks to get a high degree of crystallinity.[108] Moreover, the atomic radius of the metal included in the framework is usually higher than that of Al, which creates deformities and defects in the framework, limiting its degree of crystallinity and stability. Hence, even though hydrothermal synthesized zeolites are stable and have a high number of closed sites, they possess some drawbacks that hinder their attractiveness for industrial catalysis.

The metals included in the framework occupy two types of site: closed sites and open sites. Closed sites are fully included in the framework, while open sites possess one hydrolyzed M−OH bond, generally vicinal to a silanol group (Figure 10). In Sn-Beta, the most studied catalyst for glucose to LA, closed Sn sites coordinate with glucose in a bidentate way,[109] while open Sn sites, which are more Lewis acidic, coordinate in a monodentate way, as the substrate also coordinates with a vicinal silanol group.[110] DFT calculations demonstrated that the monodentate coordination open site mechanism for glucose isomerization was energetically favorable compared to the closed site mechanism, as the activation energy when a vicinal silanol group is participating in the transition state is 20 kJ $mol^{-1}$ lower than when it is not participating.[111] Steric interactions between the substrate and the framework are the major reason why monodentate coordination is preferred to bidentate.[112] However, few studies opt for a bidentate coordination mechanism between the open Sn site and the substrate molecule, with the difference of activity between closed and open sites mostly owing to the required geometric distortion for an optimal host−guest interaction being less energetically costly for open sites.[113−115]

The hydrogen atom on the −OH group of the open sites can be replaced by other cations, tuning the catalytic properties of the zeolite. Bermejo-Deval et al. (2014) exchanged $H^+$ with $Na^+$ by adding $NaNO_3$ in the hydrothermal synthesis gel and found that this cation enhances glucose epimerization to mannose via a 1,2 intramolecular carbon shift instead of isomerization to fructose via a 1,2 intramolecular hydride shift due to $Na^+$ strong electrostatic presence stabilizing the epimerization TS.[113,116] Aho et al. (2023) included cations in a Sn−Al-Beta framework to find that Sr/Sn−Al-Beta catalysts produce 53% ML from glucose, highlighting the promoting effect of some Lewis acidic cations on the catalytic activity.[117] On the other hand, surface $H^+$ species add Brønsted acidity to the catalyst, causing more secondary reactions to occur.[118] Exchanging the surface −OH group for a fluoride atom during hydrothermal synthesis makes the pores less hydrophilic, decreasing the solvent adsorption on the active sites, thus making the catalyst more stable.[109] Even though solvent internal diffusion is inhibited in hydrophobic pores, glucose diffuses through the pores by van der Waals attractive interactions.[119]

The presence of a vicinal silanol group inhibits the retro-aldol of fructose. Indeed, silanol groups increase isomerization rates but decrease retro-aldol product yield.[120] Josephson et al. (2018) came to a similar conclusion by studying a Sn-SPP catalyst containing a high density of silanol nests, versus a Sn-Beta catalyst comprising a smaller number of Si−OH groups. They found that fructose in ethanol readily reacts to ethyl fructoside when a silanol group is vicinal to an open Sn center by an $S_N1$ mechanism.[121] Silanol groups also increase the hydrophilicity of the framework, which leads to water adsorption on the active sites. This eventually leads to a decrease in LA yields, as the active sites are less accessible to glucose. LA yield slightly increases over the runs after

Table 5. Various Zeolite Catalytic Performances

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| glucose | mesoporous Sn-MCM-41 | 160 °C, 1200 min | 100 | 43 ML | 125 |
| glucose | Zr-SBA-15 | 240 °C, 2.75 MPa, 360 min | 100 | 48 | 127 |
| glucose | Sn-Beta | 160 °C, 1200 min | 99 | 43 ML | 92 |
| glucose | Sn-Beta | 200 °C, 4 MPa, 1200 min, 20% GVL | 100 | 72 | 128 |
| glucose | Sn-Beta | 200 °C, 300 min | N/A | 68 | 129 |
| glucose | Sn-Beta, $WO_3$ | 160 °C, 0.5 MPa, 300 min | N/A | 52 | 120 |
| glucose | Sn-Beta, $CaSO_4$ | 200 °C, 300 min | N/A | 68 | 130 |
| glucose | Sn-Beta, $SiO_2$, SiC | 180 °C, 4 MPa, 30 min | 100 | 68 | 131 |
| glucose | Mg−Sn-Beta | 120 °C, 0.4 MPa, 360 min | 99 | 50 | 120 |
| glucose | In−Sn-Beta | 190 °C, 120 min | 100 | 53 | 132 |
| glucose | Zn−Sn-Beta | 190 °C, 120 min | 100 | 48 | 133 |
| glucose | Fe−Sn-Beta | 210 °C, 120 min | 52 | 34 | 134 |
| glucose | hierarchical Sn-Beta | 160 °C, 0.5 MPa, 360 min | N/A | 52 ML | 13 |
| glucose | hierarchical Zn−Sn-Beta | 220 °C, 2 MPa, 360 min | 100 | 67 | 135 |
| glucose | hierarchical Fe−Sn-Beta | 220 °C, 2 MPa, 360 min | 100 | 67 | 136 |
| cellulose | Er-Beta | 240 °C, 2 MPa, 30 min | 100 | 58 | 124 |
| glucose | Er-ZSM-5 | 200 °C, 2 MPa, 30 min | 100 | 72 | 8 |

calcination, probably due to the transition of open sites to closed sites, more prompt to assist retro-aldol, during calcination.[114] Addition of $WO_3$ particles in the reactor reduces the number of silanol groups, as $WO_3$ species adsorb on the silanol groups, which decreases the activation energy for glucose isomerization from 131 kJ mol$^{-1}$ without $WO_3$ groups to 91 kJ mol$^{-1}$ with the adsorption of the $WO_3$ groups, but it increases the general LA yields (Table 5). Glucose conversion decreases with the adsorption of $WO_3$, as less active silanol groups are available.[120]

Active site hydration happens for extraframework $Sn_xO_y$ species in Sn−zeolitic systems.[122] $SnO_2$ is not a very active catalyst. Tin oxides also agglomerate and clutter the zeolite pores, which undermines the activity of the catalyst. The closed, intraframework species in hydrophobic pores typically have the highest activity for all the reaction steps except glucose isomerization.

The high reactivities of glucose and the intermediates to LA, combined with the high Lewis acidity of Sn zeolites, led to the conclusion that, for Sn-Beta catalyst at more than 120 °C, glucose diffusion in pores and adsorption strength are more determining than the intrinsic reaction rate.[123] As glucose is a relatively bulky molecule, pore size is a determining factor for isomerization to fructose. The 10-membered rings MFI[119] and ZSM-5 zeolites, having too small channels, do not show high activity for glucose reactions. Surprisingly, Er-ZSM-5 achieved 69% LA yield from glucose, for which Xiao et al. (2022) speculated that Er replaces the H in the −OH groups in the zeolitic framework, making it an accessible active group (Table 5).[8] On the other hand, inclusion of Er in the framework in the typical Si−O−M form was observed by Wang et al. (2017) with Beta zeolites, which have bigger channels than ZSM-5 zeolites, resulting in a 58% LA yield.[124] Topologies with larger rings, such as USY, MOR, MCM-41, SBA-15, BEA, and MWW do have channels large enough to enable good glucose diffusion.[99,125,126] Of all the zeolite topologies, the 12-membered BEA ring topology is the topology with the smallest channels able to act as a good host for glucose.

Although it takes a large pore size to get a guest−host interaction between the zeolite and glucose, microporosity assists the retro-aldol reaction by confining the steric interactions arising from the hydroxymethyl group on fructose's C1, stabilizing the TS and, thus, increasing the reaction rate.[137] Mesoporosity arising from desilication and dealumination lowers the LA yield from monosaccharides compared to smaller pore structures, as reaction intermediates are more likely to polymerize in large pores. Large pore systems offer higher LA yields from polysaccharides due to enhanced diffusion in the channels. The phenomenon was measured by Xia et al. (2021), achieving 33% LA yield from microalgae, with the main inhibition coming from lipids poisoning the active sites (Table 5).[136] The addition of formic acid induces controlled-release hydrolysis of microalgae, increasing the LA yield to 83% with a Sn-Beta catalyst (Table 5).[138] As for the Cannizzaro-type reaction from DHA to LA, small pore size does not seem to affect the catalytic performance, due to the small size of the C3 intermediates, in addition to the fact that DHA-to-PA dehydration is a thermal reaction and PA to LA is a fast reaction.[37,139] Moreover, large pore size leaves space for multiple small substrate molecules in a reactive environment, enhancing polymerization and humin formation, affecting the final LA yields.[127] The most suitable pore system to react glucose to LA is thus a combination of mesoporosity for glucose diffusion and microporosity to enhance fructose retro-aldol by confinement. This proposition is supported by the high yields achieved by hierarchical Sn-Beta zeolites possessing both a mesoporous and a microporous region (Table 5).[12−14,127] Bimetal hierarchical zeolites showed even better yields, with both Fe−Sn-Beta and Zn−Sn-Beta yielding 67% ML and displaying good reusability (Table 5).[134,135]

As with other catalysts, the catalyst/reactant ratio has to be high to maintain high reaction rates. For Sn-Beta as for other metal-functionalized zeolites, increasing the glucose concentration reduces the LA yield.[130] Indeed, glucose epimerization to mannose, fructose dehydration to 5-HMF catalyzed, and C3 polymerization to humins are slower reactions than the reaction steps leading to LA formation. For the same reasons, having too strong Lewis acid sites catalyzes faster glucose isomerization than retro-aldol, increasing fructose instantaneous concentration in the medium.[132] This fructose accumulation gives rise to more dehydration products such as 5-HMF and levulinic acid. To overcome fructose accumulation, Zhao et al. (2021) added γ-valerolactone to

Table 6. MOF Catalytic Performances for Sugar Reactions to LA

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| xylose | Zr-UiO-66 | 170 °C, 240 min | 98 | 78 | 151 |
| glucose | Mg-MOF-74 | 200 °C, 180 min | 100 | 27 ML | 152 |
| sucrose | ZIF-8 | 160 °C, 1440 min | N/A | 42 | 153 |

Table 7. Photocatalyst Performances for Glucose Conversion to LA

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| glucose | $Zn_{0.6}Cd_{0.4}S$, 1 M NaOH | 360 min | 90 | 78 | 17 |
| xylose | $CC_1$@mCN, 2 M KOH | 60 °C, 60 min | 100 | 77 | 157 |
| glucose | Ut-OCN, 3 M KOH | 50 °C, 90 min | 97 | 64 | 158 |
| glucose | B@mCN-3, 2 M KOH | 60 °C, 90 min | 100 | 93 | 16 |

the water solvent, introducing competitive adsorption with glucose for the active sites, thus decreasing isomerization rates. This decreased instantaneous fructose concentration, which decreased the side reactions arising from a long fructose residence time (Table 5).[128] Sucrose is typically the sugar giving the highest LA yield, due to its slow degradation to glucose and fructose, keeping both their concentrations low and thus inhibiting side reactions, while being relatively easy to hydrolyze. Liu et al. (2022), using microwaves on the system, affected the isomerization equilibrium toward glucose, lowering glucose conversion, but at the same time increasing LA selectivity, due to low fructose concentration inhibiting side reactions (Table 5).[131] As Sn-Beta readily isomerizes glucose to fructose, but takes more time to proceed to retro-aldol due to its lack of strong acid sites, use of a bimetal catalyst helps to accelerate the reaction and hinder secondary reactions by avoiding fructose accumulation.[133,140,141] Xia et al. (2020) functionalized Beta zeolite with both Sn and In, achieving 53% LA yield from glucose, compared to 31% without the addition of indium.[132] In this system, indium decreased the Lewis acid site strength, slowing down the isomerization reaction from a kinetic constant of 0.0104 $min^{-1}$ to 0.0061 $min^{-1}$, while it almost doubled the retro-aldol kinetic constant. It also had the effect of increasing mannose yields, but in a more modest way than it increased LA yields.[132]

One of the main reasons for the absence, to our knowledge, of large scale application of zeolites in biomass conversion is their fast deactivation. Different mechanisms explain this hardly avoidable fast deactivation. Rajabbeigi et al. (2014) stated that catalyst deactivation does not arise from byproduct presence but arises due to other factors.[142] The main deactivation mechanism is competitive solvent adsorption on active sites. Lewis acidity attracts water molecules, which promptly adsorb to framework and extraframework metal sites, making the active sites unavailable for the substrate.[143] Thus, a high metal content resulting in an increase of extraframework metals increases deactivation by hydration.[144] Although methanol adsorbs to a much smaller extent than water on the active sites, it tends to dehydrate open sites, reducing their catalytic activity. Adding less than 5% water in the methanol solvent improves the catalyst stability by keeping the active sites hydrated while avoiding water adsorption.[145] Brønsted acidity also causes C3 polymerization and other undesirable reactions, forming coke and humins adsorbing on the framework, deactivating the catalyst. Some surface groups, such as $-NH_3$, accelerate coke formation on the zeolite,[146] while water also enhances coke formation due to intrinsic Brønsted acidity at high temperature.[147] Placing the zeolite in harsh hydrothermal conditions can also result in structural collapse, forming amorphous regions in the framework and extraframework metal agglomerates.[148] Although the collapse mechanism is not well described in the literature, it has been found that too harsh acid treatment causes amorphization. A Si/metal ratio smaller than 15 also increases the probability of structural collapse, and large pore size zeolites are more subject to structural change over the reaction runs.[126]

Metal leaching is also a cause for metal-functionalized zeolite deactivation, even though it is generally less important than the other causes mentioned above. Metal leaching happens more with postsynthesis functionalization than with hydrothermal synthesis, due to a weaker metal insertion in the framework.[107] As leaching is often more present with water versus methanol, Si−O−M bond hydrolysis might be a cause for this deactivation. Sn deactivates more in methanol due to higher Sn solubility in methanol than in water.[126] Metal leaching becomes a prominent problem when functionalizing the zeolitic framework with erbium as it has a very high affinity to water, which causes it to be more readily solubilized in the medium than to stay in the crystalline structure.[149,150]

Zeolites, and especially Sn-Beta zeolites, are effective catalysts to produce LA from biomass. Their long-term performances and reusability are influenced by the synthesis method and remain the main challenge to overcome to scale up a reactor using this catalyst. More efforts have to be made in using zeolites in continuous flow reactors to reach a higher technology readiness level.

**Metal−Organic Frameworks (MOFs).** Metal−organic frameworks (MOFs) as catalytic supports have recently drawn attention due to their high surface areas, well-defined pore systems, and capabilities for functionalization at their surfaces. Ponchai et al. (2020) grafted Zr on UiO-66, noting that Zr species were only at the surface of the framework, generating open sites.[151] Metal grafting dehydrates MOF surface oxygens, generating Lewis acid sites which readily catalyze glucose to LA.[154] Xylose reaction catalyzed by Zr-UiO-66 yields 78% LA after 4 h at 170 °C due to the presence of these Lewis acid sites (Table 6).[151] Guo et al. (2018) coupled Cr with MIL-101-GLY, leading to the same conclusion that the open sites at the surface of the MOFs brought Lewis acidity to the system, assisting the proton-transfer step in the glucose isomerization reaction. The active sites being on the surface, a higher surface/volume ratio increases catalytic activity.[155] Accordingly, Zn-ZIF-67 yielded more ML with smaller crystals, to reach a maximum at 42% ML from sucrose at 160 °C after 24 h (Table 6).[153] Mg-MOF-74 showed better activity than other MOFs with a higher

Table 8. Layered Double Hydroxide Performances for Glucose Conversion to LA

| reactant | catalyst | conditions | conversion | LA yield | ref |
|---|---|---|---|---|---|
| glucose | MgAl LDH | 150 °C, 600 min | N/A | 38 | 15 |
| glucose | CNT/LDH, 0.15 M NaOH, 2 M KOH | 60 °C, 120 min | 99 | 87 | 18 |

surface area.[152] Six-connectivity MOFs, such as MIL-101 and MOF-808, coordinate easier with their substrates than 8-connectivity MOFs like UiO-66. For 6-connectivity MOFs, the active oxygens at the surface of two different catalytic units coordinate with two carbons to promote the different reaction steps. Meanwhile, for 8-connectivity MOFs, only one catalytic unit coordinates with two carbons, thus forming a less stable reactive complex.[154,156] Hence, even though MOFs offer a stable guest–host interaction between the sugar and the catalyst, relatively low LA yields are achieved, leaving space for more studies on this type of support.

**Photocatalysts.** Almost all tested photocatalysts for the glucose reaction yielded over 75% LA (Table 7). Ma et al. (2020) transformed glucose with photocatalytic carbon nitride over different supports, finding that a graphitic structure doped with boron and oxygen achieved 80% LA yield, the highest reported by this research group.[16,157,158] A similar LA yield is achieved with a $Zn_{0.6}Cd_{0.4}S$ solid solution homojunction photocatalyst with a pseudoperiodic cubic zinc blende. This photocatalyst also coproduces $H_2$ during the glucose reaction, highlighting the possibility of a different reaction mechanism that is yet to be identified.[17] A CuO–chitosan hybrid hydrogel in a weak alkaline medium also displayed photocatalytic activity, reaching LA yields up to 82% from glucose.[159] The photocatalytic glucose reaction also operates at low temperature, as most studies identify 60 °C to be the optimal temperature (Table 7). Reusability is also found for these catalysts, highlighting a good potential for future commercialization. More extensive studies have to be carried to optimize the reaction, as only a very few studies have been published on the topic.

**Layered Double Hydroxides.** Layered double hydroxides (LDHs) are metallic oxygenated sheets held together by anions and water molecules forming a double layer of $OH^-$. These dual metal/base systems readily act as heterogeneous catalysts for glucose reactions, primarily due to their high Brønsted basicity. LDHs typically possess Mg and Al species as metals and $CO_3^{2-}$ and $NO_3^-$ as anions. Although Mg offers Brønsted base sites, it quickly loses activity due to the adsorption of intermediates on the active sites and fast leaching in water.[160−162] Water also adsorbs on hydrophilic sites, deactivating them.[163] These problems are less important in alcohol solvents, giving higher fructose yields at temperatures higher than 120 °C and ML yields at temperatures higher than 140 °C.[15] Ca/Al-hydrotalcites at 90 °C achieve a maximum 87% fructose selectivity from glucose. Strong basicity emerging from Ca complexes controls glucose conversion, while acidity arising from Al regulates fructose selectivity. At Ca/Al ratios greater than 3, EFCa is formed, giving $CaCO_3$. This causes $Ca^{2+}$ cations to complex with the TS during the epimerization reaction, thus increasing mannose yields up to 65% due to high basicity and overall lack of acidity.[164] Ye et al. (2022) built a carbon nanotube/LDH composite catalyst, which develops photothermal activity in the matrix. Carbon nanotubes act as heating centers when exposed to light, increasing the internal temperature, while the LDHs provide Brønsted basicity and Lewis acidity, arising from oxygen vacancies.[18] With the addition of 0.15 M NaOH, the LA yield went up to 86% from glucose, which is one of the highest yields observed to our knowledge (Table 8).

## ■ DISCUSSION

We have identified many of the most promising homogeneous and heterogeneous catalysts along with reaction mechanisms and challenges for scale-up and future research directions. Homogeneous catalysts are relatively simple to test, which accelerates testing and optimization versus heterogeneous systems. Thus, the highest LA yields observed to date from glucose have been produced with erbium salts as catalysts. However, the catalyst stability is poor and the environmental and safety considerations would increase capital and operating expenditures, which compromise any commercial interest. Nevertheless, Ma et al. (2023) performed a techno-economic analysis on a simulated plant producing 52 kt of LA/year working with $ErCl_3$ and calculated a payback period of 7.4 years based on a pessimistic LA selling price of 1250 USD/t.[55] Hence, even though the development stage of such a process is very low, an interest in pushing the research on the high-performance erbium homogeneous catalyst regarding its larger scale is potentially interesting.

The highest LA yields for heterogeneous catalysts have yet to match the maximum LA yields of homogeneous erbium catalysts. However, bifunctional zeolites are promising candidates, as they are relatively easy to synthesize, result in reasonable yields, and are more stable. As most of the deactivation comes from solvent adsorption and coking, coupling a regeneration unit to the catalytic reactor might overcome this challenge. Hence, more work on reactor design, catalyst regeneration, and techno-economic is warranted.

## ■ CONCLUSION

The characteristics of a catalyst able to achieve high LA yields from glucose and other related compounds have been identified, as well as the catalysts possessing these characteristics. For homogeneous catalysts, erbium salts achieve almost quantitative yields from glucose and cellulose due to their high Lewis acidities. However, erbium salts are expensive and suffer from low recyclability. Heterogeneous erbium catalysts suffer from metal leaching due to their high affinity with water, making them impossible to use at a larger scale. Moreover, the anion effect on salt catalysts is still a subject of discussion needing more experimental work. Yields over carbon supports and MOFs are, as of yet, too low for commercial application. The intrinsic acidities of zeolites are sufficient to drive the reaction, and these heterogeneous systems are easy to functionalize with various metals to improve activity. Hierarchical Sn-Beta catalysts are highly active catalysts due to their mesoporous structures with pores large enough to allow glucose diffusion, enabling isomerization to fructose, but they also provide a confinement effect to accelerate the fructose retro-aldol to highly reactive C3 intermediates. Well-tuned bimetallic zeolites have sufficient Lewis acidities to catalyze the reaction steps from glucose to LA while avoiding slow side reactions, making them very promising catalysts.

Zeolite deactivation is a critical issue needing more work in the future. Photocatalysts and LDHs yield more than 80% LA from glucose but need more extensive work for scale-up. As most of the studies tested catalysts in batch reactors, efforts have to be made to transpose these results in continuous flow to consider an industrial application. Some catalysts achieve performances promising enough to consider scale-up, but active site stability and low technological maturity are still major issues to overcome.

The most promising catalysts for industrial transformation of glucose to lactic acid are bimetallic hierarchical Sn-Beta zeolites.

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## ACRONYMS

| | |
|---|---|
| DFT | density functional theory |
| DHA | dihydroxyacetone |
| DOSY NMR | diffusion ordered spectroscopy nuclear magnetic resonance |
| EL | ethyl lactate |
| LA | lactic acid |
| LDH | layered double hydroxide |
| ML | methyl lactate |
| MOF | metal−organic framework |
| PA | pyruvaldehyde |
| PLA | polylactic acid |
| TS | transition state |
| XRD | X-ray diffraction |

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