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Review

Carbon-Based Heterogeneous Catalysis for Biomass Conversion to Levulinic Acid: A Special Focus on the Catalyst

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Abstract

The conversion of cellulosic biomass into renewable chemicals can serve as a sustainable resource for levulinic acid (LA) production. LA yield is significantly influenced by reaction temperature, reaction time, substrate concentration, active sites, catalyst amount, catalyst porosity, and durability. Beyond the features of the catalyst, such as acidity, porosity, functional groups, and catalytic efficiency, the contact between the solid acid catalyst and the solid substrate is of vital importance. Solid-based catalysts show remarkable catalytic activity for cellulose-derived LA production, thanks to the incorporation of functional groups. For a solid carbon-based catalyst to be effective, a synergistic interaction between the binding domain (functional groups capable of anchoring cellulose to the catalyst surface, such as chloride groups, COOH, or OH) and the hydrolysis domain (due to their ability to cleave glycosidic bonds, such as in SO_3H) is essential. As a relatively new market niche, carbon-based catalyst supports are projected to reach a market value of nearly USD 125 million by 2030. This review aims to highlight the advantages and limitations of carbon-based materials compared to conventional catalysts (including metal oxides or supported noble metals, among others) in features like catalytic activity, thermal stability, and cost, examine recent advancements in catalyst development, and identify key challenges and future research directions to enable more efficient, sustainable, and scalable processes for LA production. The novelty of this review lies in its focus on carbon-based catalysts for LA production, emphasizing their physical and chemical characteristics.

Keywords: carbon-based catalysts; levulinic acid; biomass conversion; heterogeneous catalysis; biorefinery integration

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1. Introduction

The conversion of cellulosic biomass into renewable chemicals can serve as a sustainable resource for the production of platform chemicals [1–3]. For the production of levulinic acid (LA), the use of fructose as a raw material is preferable since glucose is less reactive than fructose because of its stable glucopyranose form [4]. However, the production of glucose from cellulose is preferred over fructose as a raw material due to its greater abundance and lower cost [5], since cellulose is a naturally occurring polymer [3]. The hydrolysis and depolymerization of cellulose into glucose represent an essential first step [6]. Cellulose degradation is restricted due to its crystallinity, the degree of polymerization, the availability of chain ends, and the fraction of accessible bonds [7]. Subsequently, glucose is further catalytically converted into intermediates, chemicals, and fuels [6].

Figure 1 shows the production mechanism of LA from cellulose [8–13].

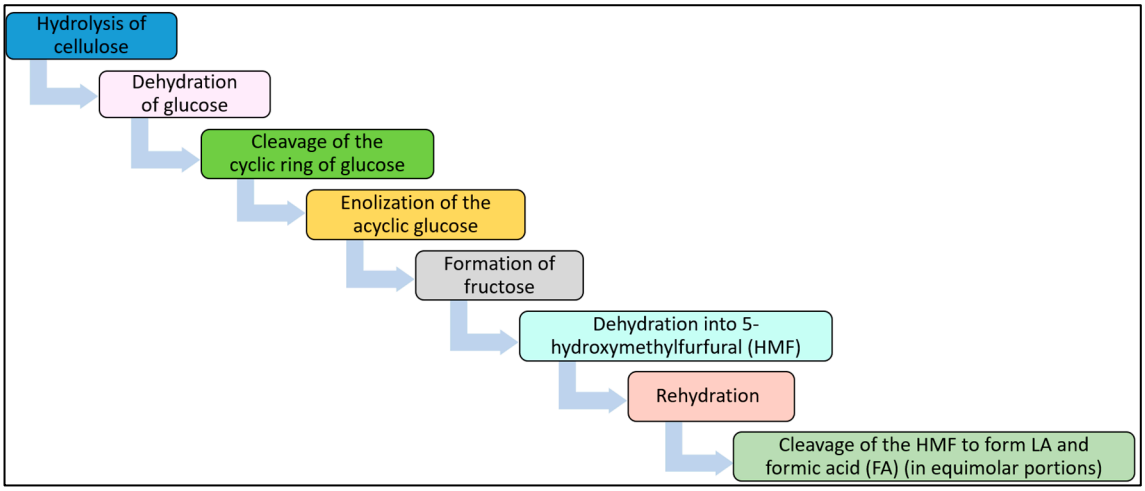

Figure 1. Production mechanism of LA from cellulose.

The sequence in Figure 1 depicts the integration of glucose isomerization to fructose and its subsequent dehydration–rehydration, which requires the presence of both Lewis [14] and Brönsted [15] acid sites. Recent reviews [16,17] explain the biosynthesis of LA from lignocellulosic biomass.

To initiate the hydrolysis of cellulose, acid catalysts are required [18,19]. Typically, H_2SO_4, HNO_3, $HClO_4$, H_3PO_4, HCl, HF, and FA are used as homogeneous acid catalysts [20]. In contrast, the use of solid acid catalysts for cellulose conversion that can be recovered and reused is a highly appealing alternative [21]. Solid acid catalysts are environmentally friendly in terms of safety, waste generation, corrosiveness, separation, and recovery [22]. Unlike homogeneous catalysts, solid heterogeneous acid catalysts can be easily separated from the reaction mixture through centrifugation or filtration, which facilitates their recovery, reduces equipment corrosion, and simplifies handling [23]. Some of them are even magnetic, which further enhances the separation process [24] from the reaction medium. Furthermore, these solid catalysts can be easily applied to a continuous-flow fixed-bed reactor [6]. The parameters of interest when studying heterogeneous catalysts that determine their catalytic activity and selectivity toward the desired intermediates and products are detailed in Ref. [25]; namely, the active species, the active sites, the pore dimensions, and the surface area.

The conversion of cellulose through heterogeneous catalysis is a solid-to-solid reaction. The rate of this reaction is primarily limited by mass transfer and surface reactions [26] as cellulose is insoluble in water and most common solvents [3], due to its supramolecular structure [27]. Then, the accessibility and reactivity of cellulose are determined by the hydrogen bond-breaking activation steps of OH groups [28], the breaking of β-O-4 glycosidic bonds, achieved by attacking the oxygen atom of the linkage [29] (in turn, related to the *p*ka of the catalyst acid [30,31]), and by its interaction with the reaction media [27] (e.g., swelling, which usually precedes dissolution [32]).

Carbon-based heterogeneous catalysts have recently attracted considerable attention due to their low cost, ease of preparation, high thermal stability, elevated acid density, and versatile functionalization potential [33] (see references [34,35] for other applications of carbon-based materials). To be effective in various reactions, these catalysts typically require surface functionalization. For cellulose hydrolysis, the presence of SO_3H groups is necessary, in addition to COOH and OH groups [36]. Cellulose hydrolysis is an essential initial step for many chemical reactions, but it can only occur after cellulose is adsorbed

onto the surface of a solid acid. In contrast, hydrolysis products are more hydrophilic and are easily desorbed [37].

This review aims to highlight the advantages and limitations of carbon-based materials compared to conventional catalysts, including a discussion of the practical applications of carbon-based catalysts in real biomass systems, examine recent advancements in catalyst development, and identify key challenges and future research directions to enable more efficient, sustainable, and scalable processes for LA production. The novelty of this review lies in its focus on carbon-based catalysts for LA production, emphasizing their physical and chemical characteristics. The literature reviewed to date does not summarize the production of LA from the perspective of carbon-based catalysts but instead focuses on the reaction conditions of the catalytic system.

2. Reaction Conditions and General Considerations

High cellulose conversion rates and LA yields are typically achieved at elevated temperatures, with low biomass concentrations and extended reaction times [38] (see Table 1 for the reaction conditions). The catalytic conversion of cellulose increases from 6.33% to 20.32% when the temperature rises from 140 °C to 170 °C (1 g of cellulose and 0.3 g of sulfonated carbon in 10 mL of water over 6 h) [39]. The reaction rate increases with temperature (since atoms then donate or receive electrons more easily [40]), which boosts the production of LA [41,42]. Additionally, the time needed to achieve the maximum product yield decreases considerably with increasing temperature [43]. The increased conversion of LA likely relates to the enhanced solubility of cellulose at elevated temperatures, i.e., approximately 190 °C for 24 h [44]. In one study [45], the authors found that the reaction time for glucose conversion to LA decreased from 210 min to 150 min when the reaction temperature increased from 160 °C to 200 °C in 50 mL of distilled water. At 180 °C for 180 min, the highest LA yield (64.4 mol%) was achieved using 0.75 g of an 8% Cr/HZSM-5 catalyst because, at very high temperatures, side reactions are also accelerated [29], favoring the formation of humins from glucose [46,47]. Temperatures exceeding 200 °C generally led to the formation of humins, whereas lower temperatures facilitated the production of LA. Moreover, humins were more easily formed from HMF than from glucose [43], due to aldol addition and the condensation reactions of HMF [48,49] (humins are not produced from LA [50,51]).

Another disadvantage of working at high temperatures is that LA becomes unstable above 230 °C, where it undergoes dehydration to form unsaturated lactones [52].

Although FA is theoretically produced in equimolar amounts with LA, several studies have reported significantly lower concentrations of FA [53], suggesting that it decomposes into CO_2, H_2, CO, and H_2O under acidic and heated conditions [54] at temperatures exceeding 180 °C [55]. Conversely, there are reactions in which the ratio of LA to FA is low, due to glucose reactions that do not correspond to HMF production, but rather to alternative pathways to produce furfural from hexoses via a pentose unit, with FA as a by-product [56,57].

Water is the most commonly used solvent for producing LA [52,58]. At temperatures higher than 160 °C [59], water is also a by-product of the reaction [60]. The use of water as a solvent is attractive from both an economic and environmental perspective because it is a cheap, non-toxic, and non-flammable solvent [61]. Properties such as the partition coefficient, boiling point, thermal stability, and recyclability are also important [25].

However, the choice of a solvent that can solubilize cellulose (such as GVL [62], 2-sec-butylphenol [63], ionic liquids [64], dioxane [65], tetrahydrofuran (THF) [66], and butanol [67]) increases the possibilities of cellulose–catalyst interaction, so that maximizing LA production [68] is sometimes preferred. The use of biphasic systems, typically consisting

of polar aprotic solvents and water, stabilizes the acidic proton and reduces the activation free energy of the catalytic process, resulting in accelerated reaction rates [69,70]. For example, under identical reaction conditions (160 °C, 120 min), the use of GVL as a solvent instead of water enhanced the yield of LA from glucose by a factor of five when catalyzed by CH_3-SBA-15-SO_3H [71]. The polar phase of biphasic systems dissolves and converts the substrate, while the less polar phase extracts the products [72]. As a consequence, LA is extracted into an organic phase [9].

The recommendation has been made to use biphasic systems to prevent the subsequent reaction of products into humins [9] since their formation is favored at high water contents [73]. Therefore, controlling the water content is a strategy for managing the formation of humins [60,74]. With a water ratio greater than 0.5 concerning an organic solvent, the hydration of HMF to LA is beneficial, due to its water-like properties [75].

Table 1. Yields of LA with various solid acid catalysts.

Raw Material	Reaction Conditions	Yield	Ref.
Cellulose	2 g of cellulose, 2 g of zirconium dioxide, 100 mL of water, 180 °C, 3 h	53.90 mol%	[48]
Cellulose	2 wt.% of cellulose, 0.2 g of Amberlyst 70, 3 mL of solvent (90 wt.% GVL/10 wt.% water), 180 °C, 16 h	69.00%	[76]
Cellulose	2 wt.% of cellulose, 0.2 g of C–SO_3H, 3 mL of solvent (90 wt.% GVL/10 wt.% water), 180 °C, 16 h	56.00%	[76]
Cellulose	0.05 g cellulose, 0.1 g of C–SO_3H, 5 mL of water, 180 °C, 12 h	51.50%	[77]
Cellulose	1 g of cellulose, 1.5 g of Al-doped mesoporous niobium phosphate, 15 mL of water, at 150 °C, 3 h, total acid density: 1.09 mmol H^+/g	52.90%	[78]
Cellulose	0.5 g of cellulose, 0.4 g of H-ZSM-5 (Al/Si = 1/25), 10 mL of water, 180 °C, 24 h	27.00%	[79]
Cellobiose	100 mg of cellobiose, 200 mg of CP-SO_3H, 2 mL of water, 180 °C, 5 h, total acid density: 1.69 mmol H^+/g	40.00%	[68]
Glucose	30 g of glucose, 0.5 g of graphene oxide, 200 mL of water, 200 °C, 2 h, total acid density: 2.70 mmol H^+/g	78%	[28]
Glucose	30 g of glucose, 0.5 g of sulfonated graphene (GO–SO_3H), 200 mL of water, 200 °C, 2 h, total acid density: 2.70 mmol H^+/g	78.00%	[28]
Glucose	1 g of glucose, 1 g of 10%Fe/HY zeolite, in 50 mL of water, 180 °C, 180 min, total acid density: 2.68 mmol H^+/g	62%	[40]
Glucose	1 g of glucose, 1 g of 10% Fe/HY, 50 mL of water, 180 min, total acid density: 2.30 mmol H^+/g	62.00%	[40]
Glucose	Catalyst/glucose ratio: 1:1, $CrCl_3$/HY zeolite (2:1), water 180 °C, 160 min, total acid density: 2.94 mmol H^+/g	44.00%	[53]
Glucose	1.5 mL of glucose, 0.3 g of CH_3-SBA-15-SO_3H, 13.5 mL of GVL/water, 180 °C, 150 min	60.00%	[71]
Glucose	0.05 g glucose, 0.1 g of C–SO_3H, 5 mL of water, 180 °C, 12 h	61.05%	[77]
Glucose	100 mg of glucose, 0.05 g of Fe-NbP, 10 mL of water, 180 °C, 3 h, total acid density: 3.59 mmol H^+/g, Brønsted/Lewis ratio: 1:2	64.20%	[80]
Glucose	11.9 g of glucose, 18.1 g of Amberlyst 70, 85 mL of water, 180 °C, 120 min	55.00%	[81]
Fructose	1 g of fructose, 1 g of LZY zeolite, 140 °C, 15 h	43.20%	[82]
Fructose	9 wt.%, 0.28 mmol of fructose, Fructose: Amberlyst 15 (1:1), 0.5 mL of water, 120 °C, 24 h	55.00 mol%	[83]

Table 1. *Cont.*

Raw Material	Reaction Conditions	Yield	Ref.
Mixture of pentoses	Pentoses: 1.56 g/100 g biomass, Y zeolite treated with 0.25 M NaOH, 190 °C, 180 min	4.71 g/100 g of biomass	[47]
Xylose	0.9 g of xylose and 0.5 g of catalyst, Y zeolite treated with 0.25 M NaOH, 170 °C, 3 h, N_2 at 15 bar, total acid density: 1.409 mmol H^+/g	30.40%	[84]

3. Catalyst Design and Characterization

The yield of LA is significantly influenced by factors such as reaction temperature, reaction time, substrate concentration, the availability of active sites, the amount and porosity of the catalyst, and its durability [48,85]. Beyond the features of the catalyst, the contact between the solid acid catalyst and the solid substrate is of vital importance [81]. To enhance mass transfer between the solid acid catalyst and the substrate, sodium chloride (NaCl) can be added to the reaction medium, which improves the yield of LA. The addition of NaCl disrupts the hydrogen bonds in cellulose, leading to increased solubility under hydrothermal conditions [86].

The activity of solid catalysts is correlated with their functionalization, surface area, and porous structure [87]. They must be water-resistant [88], since the hydrolysis activity of a solid acid catalyst decreases with increasing amounts of water due to the hydration of the acid sites [89]. Both the final yield and the product distributions during the reaction depend on the catalyst's characteristics [53]. A small amount of by-products, such as fructose, suggests that the isomerization process is highly efficient and selective [90]. That is to say, fructose dehydration occurs rapidly as the catalyst provides adequate acidity for its transformation [91]. Additionally, any fructose derived from glucose is likely converted into HMF [50]. Figure 2a presents the main features of the catalyst used for producing LA, and Figure 2b shows the main characterization techniques for solid catalysts.

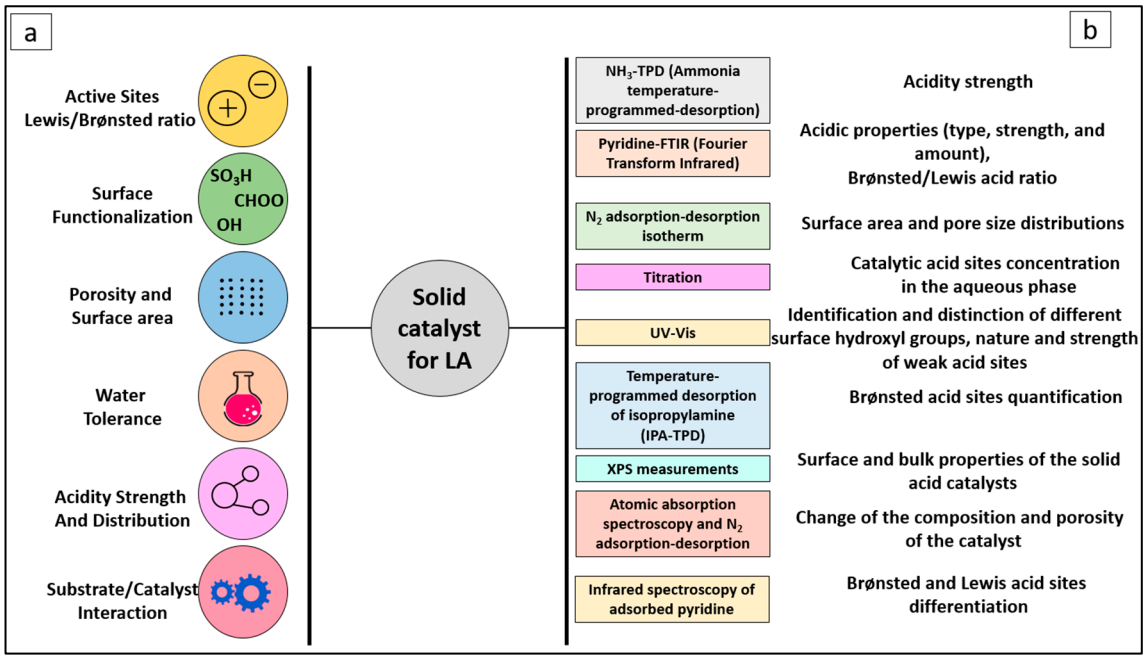

Figure 2. (**a**) Main features of a solid catalyst for producing LA. (**b**) Main characterization techniques for solid catalyst characterization, as related to their acid sites (adapted from [45,53,58,91–93]).

Acid strength precisely indicates the amount of energy needed to detach a proton from a solid acid. This energy, known as deprotonation energy (DPE), is an intrinsic characteristic of the acid itself and does not depend on the probe used to measure it [94]. For the NH_3-TPD profiles, the higher the desorption temperature, the stronger the acid strength of the catalyst [95]. In the case of the sulfonated carbon catalyst, its temperature falls within the range of 500 °C to 600 °C, corresponding to an acid strength of 6.28 mmol/g [96].

In the case of the functionalized catalyst with Lewis acid, like Fe/HY catalysts for the production of LA [40], the strength of the acid sites increased when Fe was impregnated into the HY-zeolite (the impregnation of Fe induced new acid sites). According to infrared spectroscopy analyses of adsorbed pyridine, Brønsted acid sites are observed at a band around 1545 cm^{-1}, while the band at 1450 cm^{-1} is associated with Lewis acid sites. In the case of FTIR vibration bands, the identification of Brønsted acid sites is at 1400 cm^{-1}, which corresponds to O=S=O stretching in SO_3H, and the bands at 1035 cm^{-1} correspond to SO_3 stretching [97].

3.1. Active Sites on the Catalyst

Solid-based catalysts show remarkable catalytic activity for LA production from cellulose, thanks to the incorporation of functional groups [98]. These can be grouped into Lewis (e.g., $AlCl_3$, $CrCl_3$, $SnCl_4$, zeolites, Zirconia, γ-Al_2O_3 [58,99–101]) and Brønsted (e.g., HCl, H_2SO_4, HNO_3, lactic acid, formic acid, acetic acid, Amberlys, Heteropolyacids [25,102–105]) acid types. Lewis acid sites are considered to be strong acid sites, while Brønsted acid sites are classified as medium acid sites [28,106].

The acid sites on the solid surfaces are highly polarized groups "acting as H^+ donor (Brønsted acid), or coordinatively unsaturated cationic sites, which leave M^+ exposed to interact with guest molecules as an acceptor of an electron-pair (Lewis acid)" [107]. In addition, it is necessary to optimize their strength and Lewis/Brønsted ratio in cascade reactions to maximize the production of the desired product [108]. The selectivity of LA increases as the ratio of Lewis to Brønsted acids decreases [58]. For example, the yield of LA rose from 21% to 51% when glucose was reacted in water at 180 °C for 4 h; this was achieved by lowering the Lewis/Brønsted ratio from 0.3 to 0.06 [109]. For the production of HMF from glucose, a yield of 42% was obtained at 195 °C for 30 min, using H-ZSM-5 as the catalyst, at a Lewis/Brønsted ratio of 0.25 [5].

The formation of humin species during the reaction is higher at higher Lewis/Brønsted ratios [58,80]. High Lewis acidity can lead to rapid, undesired side reactions of fructose after glucose isomerization [110] due to cross-oligomerization between glucose and HMF [45]. Lewis acid sites may be deactivated in water [111] by coordinating with them [112], leading to the formation of Brønsted acidic protons [92,113,114].

For a solid carbon-based catalyst to be considered efficient, it is essential to verify a synergistic effect between the binding domain and the hydrolysis domain [20,115]. Therefore, the presence of functional groups capable of anchoring cellulose to the catalyst surface is crucial [116], including chloride groups [68], COOH [36], OH [28], and sulfonated groups that convert cellulose into glucose [117], due to their ability to cleave glycosidic bonds [20]. SO_3H is not an adsorption site [36]. Therefore, this synergistic effect may explain the excellent catalytic activities observed in carbonaceous solid acid catalysts, which also exhibit low activation energy. The contents of -SO_3H, -OH, and -COOH groups on carbon-based materials typically range from 0.1 to 4.9 mmol/g, 0 to 0.9 mmol/g, and 0 to 7.8 mmol/g, respectively [118].

Carbon-based catalysts attack both the chain ends and the random interchain components of cellulose [37], which is an advantage.

3.2. Sulfonation of Carbon-Based Catalyst

A wide variety of carbon-based materials can serve as catalyst supports [119]. Their properties notably influence the performance of the catalyst [120]. The most important are activated carbons [121], nanotubes and nanofibers [122], and graphene [123]. They all have one thing in common: for the conversion of cellulose, the presence of sulfonic groups is necessary [124]. Carbon-based catalysts offer high sustainability, abundant raw material sources, excellent chemical stability, and adaptable surface modifications to enhance their catalytic activity [125].

Regarding surface modification, as said, sulfonated materials are the best candidates for the hydrolysis of cellulose to glucose [88]. The sulfonation process consists of the covalent attachment of SO_3H groups to the carbon framework through the substitution of hydrogen [126]. These sulfonated carbon-based materials are typically characterized by an increase in surface acidic strength and hydrophilicity [127]. The sulfonation procedure results in the reordering of the catalyst structure [28]. There are some studies [33] where sulfonation with H_2SO_4 decreases the surface area and pore structure of the catalyst [128]; the pores also become smaller [129] because a reduction in total pore volume can be attributed to partial oxidation, condensation, carbonization, and partial pore structure destruction during sulfonation [130]. Although sulfonation introduces sulfonic acid groups and oxygen atoms [131], it also results in acid-catalyzed dehydration reactions, causing slight decreases in the O/C and H/C ratios of the solid material [132].

The zeta potential of carbonaceous materials increases with a higher sulfonation degree and surface charge, which contributes to electrostatic attraction forces [133]. The sulfonation temperature, reaction time, and sulfonating agent load determine the degree of sulfonation achieved [134]. The sulfonation temperature significantly affects acid density [88] and the specific surface area of the solid catalyst, with higher temperatures yielding greater total acid density [124]. As the sulfonation temperature increases, the hydrophilicity of the solid material also increases [135]. That is, sulfonation increases the water dispersibility of materials [131]. The former provides better access to the reactants in solution to the sulfonic groups, which gives rise to the high catalytic performance of the solid catalyst [104].

A higher acid content for the solid catalyst is obtained with a longer sulfonation time [128]. Using the same catalyst, the acid amount increased from 0.7 to 1.1 mmol H^+/g for sulfonation times of 6 h and 15 h, respectively [128]. In the sulfonation of ordered mesoporous carbon materials, the density of SO_3H groups increased from 2.02 to 2.33 mmol SO_3H/g throughout 2 to 6 h [136].

The sulfonation degree could be controlled with different sulfonating agents [137]. The most commonly used sulfonating agents are sulfuric acid [132], 3-mercaptopropyltrimethoxysilane [138], thiourea [68], ammonium sulfate [139], and 4-benzene-diazonium sulfonate [118]. However, the most widely used reagent is sulfuric acid, although separating the excess material is a difficult task. While fuming sulfuric acid exhibits higher catalytic activity, concentrated sulfuric acid is preferred due to handling issues. The use of 4-benzene-diazonium sulfonate is recommended as an alternative to sulfuric acid, due to the possibility of working at lower sulfonation temperatures [118]. Table 2 shows the various sulfonation strategies.

Table 2. Carbon-based catalyst sulfonation strategies.

Sulfonating Agent	Sulfonation Conditions	Total Acid Density	Ref.
H_2SO_4	1 g of carbonized lignin, 10 mL of H_2SO_4, 200 °C, 5 h	1.34 mmol H^+/g	[26]
H_2SO_4	1 g of char, 10 mL of H_2SO_4, 150 °C, 14 h, N_2	0.02 S/C ratio	[33]
H_2SO_4	150 °C, 24 h, 60 mmol H_2SO_4/g carbon	0.90 mmol H^+/g	[37]

Table 2. *Cont.*

Sulfonating Agent	Sulfonation Conditions	Total Acid Density	Ref.
H_2SO_4	fast pyrolysis biochar (7 g) and 150 mL of H_2SO_4, 80 °C, 10 h, N_2	-	[96]
H_2SO_4	2.6 g of sucrose, 0.25 g of H_2SO_4 and 4.2 g of distilled water, 160 °C, 15 h	0.90 mmol H^+/g	[128]
H_2SO_4	1 g of alkaline lignin, 10 mL of H_2SO_4, 150 °C, 10 h, N_2	6.21 mmol H^+/g	[134]
H_2SO_4	20 g sample of D-glucose powder, 200 cm^3 of concentrated H_2SO_4 (> 96%), 150 °C, 15 h, N_2	0.75 mmol/g [a]	[140]
H_2SO_4	50 mg of reduced graphene oxide, 20 mL of H_2SO_4, 150 °C, 15 h	-	[141]
H_2SO_4	12.5 g of biochar, 12 mL of H_2SO_4, 100 °C, 15 h	0.65 mmol H^+/g	[142]
H_2SO_4	1 g of ordered mesoporous carbon, 15 mL of H_2SO_4, 200 °C, N_2 (30 mL/min), 16 h	1.82 mmol H^+/g	[143]
H_2SO_4	1 g of polyethylene pellets, 35 g of H_2SO_4, 120 °C, 3 h	85% [b]	[144]
H_2SO_4	1:10 carbon: H_2SO_4, 100 °C, 5 h	1.15 mmol H^+/g	[145]
H_2SO_4	1 g of carbon, 20 mL of H_2SO_4, 150 °C, 13 h, N_2	0.64 mmol H^+/g	[146]
H_2SO_4	300 mg of lignin-based carbon, 10 mL H_2SO_4, 150 °C, 8 h	1.58 mmol H^+/g	[147]
H_2SO_4	20 mL of H_2SO_4/g of glucose-based carbon, 150 °C, 15 h Ar	5.43 mmol H^+/g	[148]
H_2SO_4	0.2 g of carbon, 10 mL of H_2SO_4, 80 °C, 8 h under reflux	1.12 mmol H^+/g	[149]
H_2SO_4	1 g of lignin-based carbon, 20 mL of H_2SO_4, 180 °C, 12 h, N_2	1.46 mmol H^+/g	[150]
H_2SO_4	carbonized cellulose, 15 wt.% of H_2SO_4, 80 °C, 10 h	0.92 mmol/g [a]	[151]
H_2SO_4	cup-stack carbon nanotubes, plasma- 100 mL of 1 M H_2SO_4, 30 min	1.60 wt.% [c]	[152]
4-benzene diazonium sulfonate	Fe_3O_4-reduced graphene oxide, 50 °C, 1.5 h	1.06 mmol/g [a]	[153]
4-benzene-diazonium sulfonate	100 mL of water, 12 g of 4-benzene-diazonium sulfonate, 2 g of activated carbon, 30 min	1.01 mmol H^+/g	[154]
$Fe(SO_4)_3/H_2SO_4$	1 g of carbon material, 10 mL of the sulfonating mixture, 190 °C, 10 h	1.15 wt.% of sulfur	[155]
Sulfanilic acid	373 mg of graphene, 789 g of sulfanilic acid, 25 °C, 24 h	1.75 mmol/g [a]	[156]
5-sulfosalicylic acid dihydrate	32 g of cellulose, 50 mL of aqueous solution of 20 g of 5-sulfosalicylic acid dihydrate; stainless-steel autoclave for 4 h at 180 °C, with stirring	3.54 mmol H^+/g	[157]
Na_2SO_3	0.4 ratio of Na_2SO_3 to lignin in weight, 90 °C, 5 h	1.55 mmol/g [a]	[133]
SO_3/H_2SO_4	0.3 g of mesoporous carbon, 5 mL 50 wt% SO_3/H_2SO_4, Teflon-lined autoclave at 60 °C, 48 h	1.30 mmol H^+/g	[158]
Ferrous sulfide	1 g of carbonized lignin, 25 g/L of ferrous sulfide solution, 105 °C, 10 h, N_2	1.79 wt.% [c]	[159]
Chlorosulfonic acid	1 g of graphene oxide, 0.5 g of chlorosulfonic acid, 50 mL of Chloroform, 1 h, 70 °C, 4 h ultrasound	2.70 mmol H^+/g	[28]

Note: [a] mmol SO_3H/g, [b] crosslink percentage was used to indicate the sulfonation degree, and [c] elemental S content.

3.3. Catalyst Porosity

Porosity is one of the most important properties of solid materials. In addition to active sites, the high selectivity of LA results from an ordered porous structure, which allows reactants to enter the pores quickly and proceed with the reaction [108]. It is recommended to use catalysts with high relative mesoporousness and low relative microporosity [40]. When using solid catalysts and water, cellulose hydrolysis occurs at the interface, due to the low solubility of cellulose in water. Therefore, a large pore diameter and a high surface area favor hydrolysis using solid materials as catalysts [138].

The pore systems are essential for creating high surface areas, which are crucial for increased activity [107], and also determine the selectivity of the products through steric effects [160] and shape selectivity [53]. The molecular dimensions of the reactants, products, or transition states influence the selectivity of the reaction. Reactant selectivity arises when only one type of reactant can diffuse into the pores of the catalyst. Product selectivity occurs when several products can be formed, but only those with molecular dimensions that are compatible with the pore size can diffuse out and be recovered as final products. Transition state selectivity occurs when restricted space within the porous system limits the formation of certain transition states that require more space than is available, thereby preventing the generation of several products [107].

The dimensions of the reactants primarily determine the selectivity of the process [107]. The molecular dimensions of 0.86 nm [161], 0.86 nm [101], and 0.82 nm [53] are suitable for glucose, fructose, and HMF, respectively. For effective reactions with cellulose and glucose materials, the pores of the catalyst must be at least 1 nm in size to allow the substrate to enter [42]. In heterogeneous catalytic systems, the active sites are mainly located within the pores of the catalyst [108]. Therefore, the shape, size, and volume of these pores play a significant role in determining the catalyst's activity during cellulose hydrolysis [20,138].

3.4. Substrate/Catalyst Ratio

The amount of catalyst significantly influences the substrate's conversion to LA, necessitating optimization to maximize selectivity for the desired product (see Figure 3) [48]. The optimal substrate-to-catalyst ratio is essential for efficiently using cellulose and maximizing lactic acid yield [52]. Excessive amounts of catalyst can lead to the subsequent formation of humins [162], but for glucose conversion, a low substrate-to-catalyst ratio is necessary [163]. For reactions with cellulose, a substrate-to-catalyst ratio of less than 1 is generally used [88]. In one study, when the substrate-to-catalyst ratio decreased from 0.5 to 0.2, the final yield increased from 40.0% to 58.2% at 150 °C over 6 h [39].

Increasing the substrate concentration while fixing the catalyst dosage could enhance the amount of cellulose available for conversion to LA. However, product feedback inhibition can occur, leading to decreased reactivity or insufficient catalyst dosage for additional cellulose [52].

Starting with fructose at 160 °C with 20 mL of water and 30 mL of 2-butanol, it was found that catalyst ratios exceeding 1:1.2 (substrate to catalyst) promoted the rehydration of HMF into LA because of the increased availability of acidic sites within the system [59]. By increasing the catalyst loading from 0.5 to 10 wt.% (with 2 g of cellulose and 2 wt.% of catalyst in 100 mL of water at 180 °C for 3 h), the yield of LA increased from 30 to 54 mol% [48]. Conversely, when using substrate/catalyst ratios of 9:1 with cellulose as a substrate, yields of less than 6% of LA were obtained (at 190 °C) [55].

The concentration of the substrate also determines the time required for glucose dehydration, increasing along with it [164]. Yields of 13% and 66% of LA were obtained for 15 min and 120 min of reaction time, respectively, using 0.125 g of cellulose, 0.250 g of catalyst, and 10 mL of methanol [96].

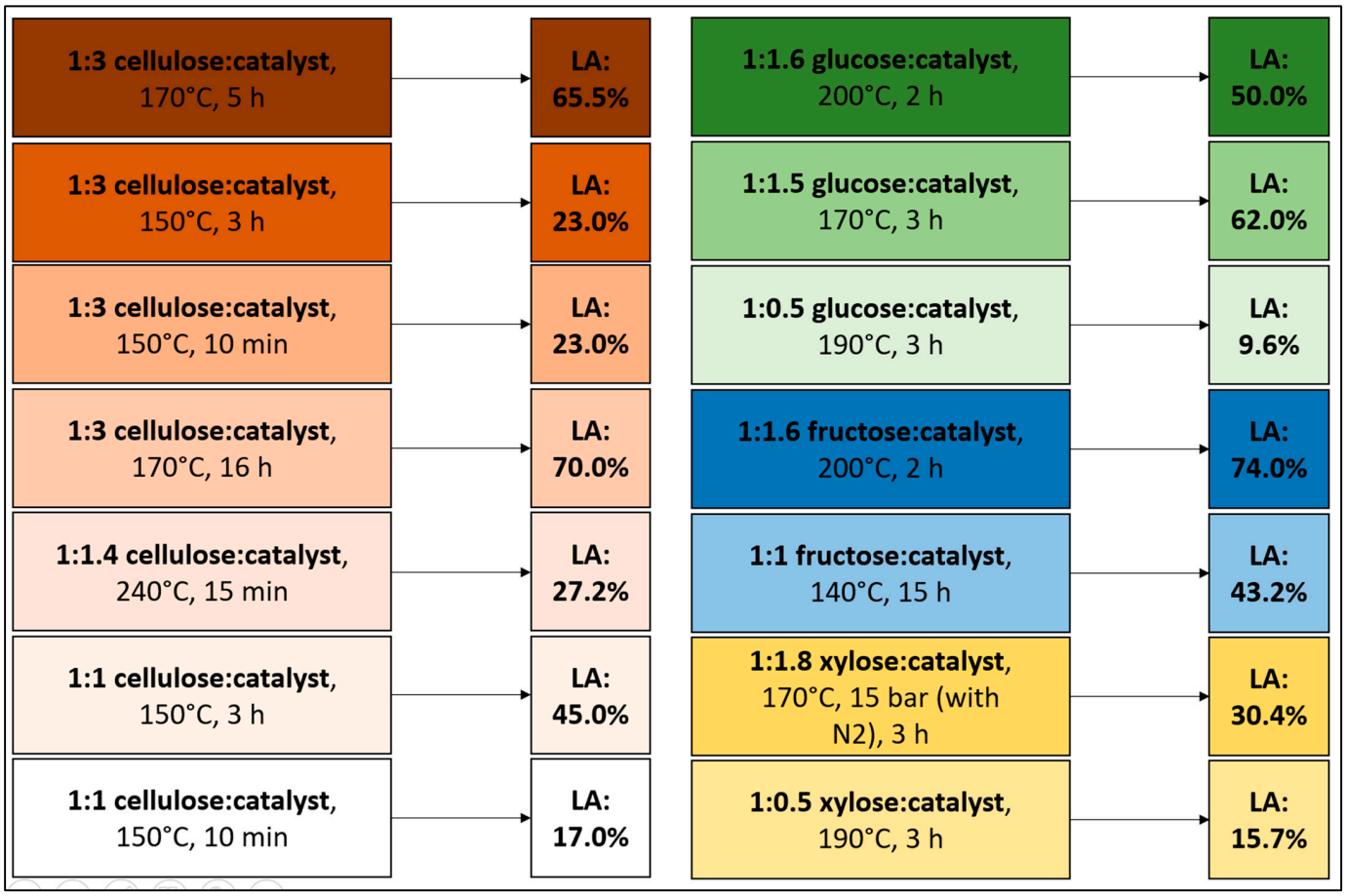

Figure 3. Different LA yields (%) from different feedstock:catalyst ratios. Adapted from [28,47,76,78,84,165–167].

4. Challenges and Perspectives

4.1. Catalyst Deactivation

The recovery and reusability of the solid catalyst for the production of LA are some of the most relevant factors from gan economic point of view [48]. There are cases where the catalyst maintains its catalytic activity through successive runs [70]. However, the catalyst could decrease its catalytic activity [48,68]. Although there are many causes of catalyst deactivation [168], in catalytic systems for producing LA, two chief causes are generally verified [169]: the deposition of insoluble humins on the catalyst surface or the leaching of the active species, which translates into the loss of catalytic activity and/or the selectivity of the catalyst over time [170]. For example, in the case of the conversion of sucrose to LA with Amberlyst-36 as a catalyst at 130 °C, the catalyst surface became covered by the humins generated during the reaction. The activity recorded in successive reactions was 85%, 62%, and 28% after 2, 5, and 10 cycles, respectively. During these cycles, 1 mg of humins was deposited on 150 mg of catalyst, resulting in an activity loss of approximately 3.4% [171]. This reduction in catalytic activity due to humin deposition occurs because it physically obstructs the catalyst, potentially deactivating it by blocking pores or covering active sites.

To remove humins from the used catalyst, two methods are generally used: calcination at high temperatures (around 550 °C) [170,172] and washing the catalyst with organic solvents [85] such as ethanol [173], methanol [174], and acetone [175]. The use of an H_2O_2 solution is also an alternative to regenerating the used catalyst since it can effectively remove humins from solid acids [176].

In particular, the use of heterogeneous catalysts for cellulose hydrolysis requires the presence of SO_3H groups [124]. However, working with this type of material has the effect of leaching away these groups (the active phase) during the reaction. The decomposition temperature of the -SO_3H ranged from 280 to 300 °C [177], although the most widely reported temperature is 250 °C [142]. Cellulose hydrolysis at 120 °C for 60 min was 61% with a catalyst bearing –SO_3H, COOH, and phenolic OH groups, and it maintained its activity for 5 runs without the loss of the active phase [97]. There are also cases where leaching occurs at lower temperatures than 250 °C. For example, at 170 °C, losses of SO_3H density were 31.6% after 1 run [178], but in this case, the leaching of SO_3H species was not caused by the cleavage of C-S bonds but by the exfoliation of the catalyst.

4.2. Conventional Catalysts vs. Biobased Catalysts

Conventional heterogeneous catalysts involve metal oxides, supported noble metals (such as Pd and Ru), and acid-functionalized materials, like sulfonated resins and zeolites. These last ones and mesoporous silicas are commonly studied, due to their high surface area and tunable acidity. Considering LA conversion, microporous zeolites demonstrated thermal stability and strong acid sites, facilitating the conversion of hexoses to LA [179].

The conversion of LA into value-added products such as GVL has been extensively studied using catalysts like beta zeolite and titania supported with ruthenium (Ru), which exhibit high activity and selectivity, highlighting their potential for industrial applications. However, conventional catalytic processes in the chemical industry often face significant challenges, including high energy demands and reliance on scarce and expensive metals such as Ru [180].

Conversion yield and catalyst reusability are key performance indicators of catalytic processes. In the case of LA production from cellulose, a study reported a yield of approximately 61% using a carbon-based catalyst [181], which remains lower than the yields of 80% or higher that are typically achieved with conventional catalytic systems [182]. Besides this, carbon-based catalysts have demonstrated the potential for reuse for up to five cycles, with a 17% decrease in conversion yield from the 1st and 5th cycle [181]. For biodiesel production, these catalysts have shown even greater durability, maintaining activity across nine reuse cycles [183].

Carbon-based catalysts can overcome several challenges similar to those faced by conventional catalysts. Recent advances in heterogeneous catalysts demonstrate that catalysts derived from biomass can achieve similar LA yields with lower environmental impact. Table 3 shows some of the benefits of carbon-based catalysts and conventional catalysts.

Table 3. Key distinctions of biobased and conventional catalysts. Adapted from [181,182,184–187].

Aspect	Conventional Catalysts	Biobased Catalysts
Source	Synthetic and inorganic materials.	Renewable materials (lignin).
Sustainability	Energy-intensive. Use of rare materials.	Biomass-derived, reduced waste.
Reusability	Moderate (in some cases higher than biobased); 14 cycles for biodiesel.	Reported values between 5 (for LA) and 9 cycles (for biodiesel).
Performance	Up to 80% LA yield from cellulose.	61% of LA yield from cellulose.
Status	Commercial availability.	Under development.

4.3. Technological Challenges of Carbon-Based Catalysts and Integration Opportunities

The current market size of heterogeneous catalysts is estimated to exceed USD 22 billion and is projected to surpass USD 30 billion by 2030, driven by a compound

annual growth rate (CAGR) of 4–6% [188,189]. Within this sector, carbon-based catalyst supports represent an emerging niche. One assessment estimates that this segment could reach a market value of approximately USD 125 million by 2030 [190]. Given the growing demand for more sustainable processes, carbon-based catalysts offer an attractive opportunity. As for the global market for biobased products, although precise figures are difficult to determine, some sources estimate its current value at around USD 50 billion [191], with projected CAGRs ranging from 10% to 25% over the coming years [191,192]. Although there is no well-established biobased catalyst available on the market, the market size and trends show a promising future for these emerging materials.

Carbon-based catalysis is a major field of engineering. The use of carbon-based support materials shows several potential advantages compared to other support materials. Their surfaces are inert, and the size distribution and the chemical properties on the surface can be tailored according to the envisaged application [121].

In addition to these promising features, several challenges must be addressed before commercial-scale implementation (see Figure 4).

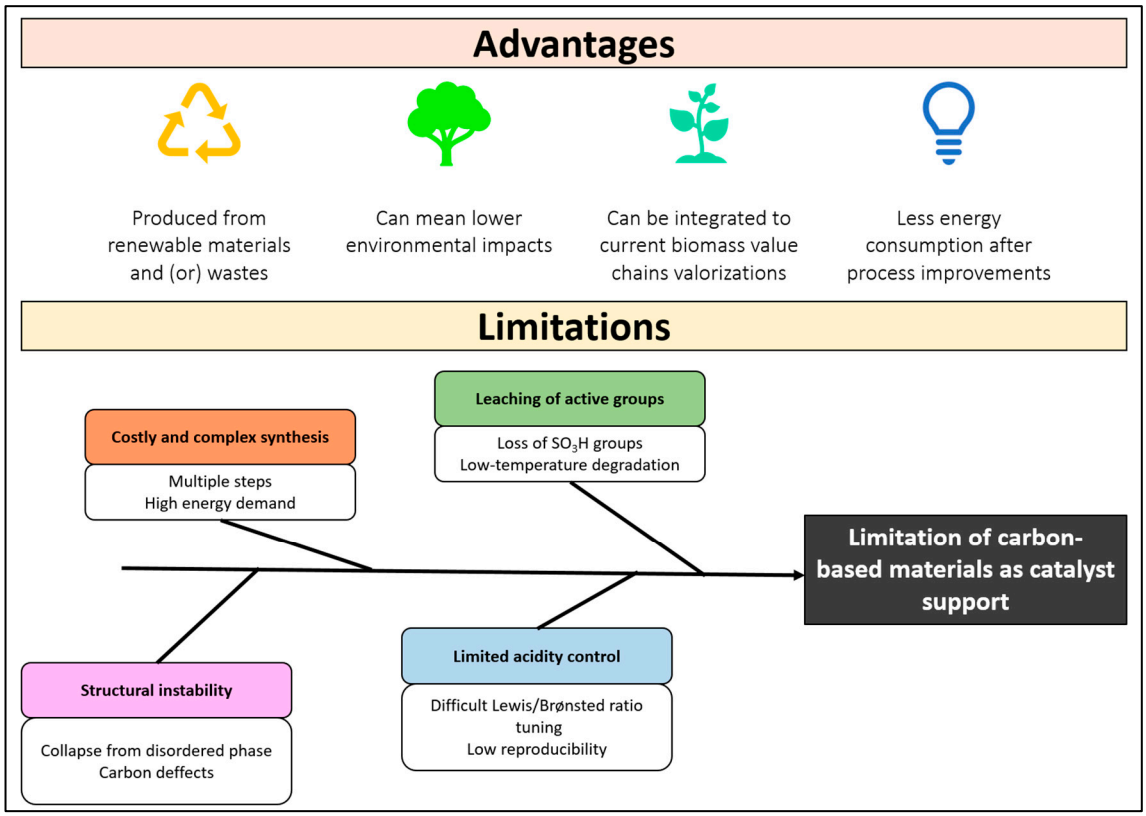

Figure 4. Advantages and limitations of using carbon materials as a catalyst support. Adapted from [193].

The synthesis process typically involves multiple steps, increasing both production costs and complexity [181,194]: stability limitations arise from carbon defects and the risk of structural collapse during reuse, due to the disordered phase in the carbon structure [195,196]; acidity control remains a challenge, as tuning the Brønsted–Lewis acid site ratio is necessary to enhance LA yield through a balanced distribution [181]; co-catalyst dependency often requires acidic deep eutectic solvents, adding complexity to both the reaction system and catalyst handling [189,197]; and pore morphology plays a crucial role, as uniform and stable distribution can significantly improve catalytic activity [181].

The integration of carbon-based heterogeneous catalysts into biorefinery processes can support circular economy strategies by enabling the valorization of biomass waste streams. These catalysts also contribute to the concept of process intensification, particularly through one-pot or cascade reaction systems that enhance overall efficiency [198]. The use of carbon-based materials for biomass valorization aligns with sustainability and green chemistry principles, offering reduced toxicity and lower environmental impact compared to conventional metal-based catalysts [181].

To further demonstrate their potential, several value-added products have been explored in conjunction with LA production. These include biomass-derived pellets [199], biogas [200], furfural [201], and carbon-based electrodes [202]. When integrated into LA production using heterogeneous catalysts, these strategies can significantly enhance the overall performance and resource efficiency of the process.

5. Conclusions

The catalytic conversion of lignocellulosic biomass to levulinic acid supports a sustainable, circular bioeconomy. Integrating carbon-based catalysts into biorefineries promotes process intensification, waste valorization, and the co-production of value-added products, enhancing the overall efficiency and sustainability of biomass conversion.

The market for carbon-based catalyst supports is projected to reach USD 125 million by 2030, reflecting growing scientific interest. More broadly, the expanding biobased products sector, valued at nearly USD 50 billion and with 10–25% annual growth, signals strong potential for scaling up carbon-based catalytic systems.

Among the various catalytic approaches, carbon-based heterogeneous catalysts have emerged as a promising alternative to conventional metal-based systems, offering advantages such as high thermal and chemical stability, abundant feedstock availability, and tunable surface properties. These catalysts can be functionalized with acid groups (e.g., SO_3H, COOH, and OH) to enhance their activity and selectivity for cellulose hydrolysis and LA production.

The performance of carbon-based catalysts is highly dependent on several factors, including the nature and distribution of active sites, porosity, surface area, substrate/catalyst ratio, and reaction medium. A synergistic interaction between binding and hydrolysis domains is essential for efficient biomass conversion. Choosing the right solvent, along with optimizing reaction conditions, such as temperature and time, is key for maximizing levulinic acid yields while minimizing the formation of by-products like humins.

Despite their promise, carbon-based catalysts face challenges regarding commercial-scale use, such as complex synthesis, structural instability, limited acidity control, the potential leaching of active sites, and lower catalytic yields compared to some conventional catalysts.

Nonetheless, their superior reusability, reduced toxicity, and alignment with green chemistry principles position them as strong candidates for future biorefinery applications.

Currently, the use of conventional catalysts remains the most attractive option, due to their overall performance and commercial availability. Considering the progress made in recent years in the design and development of renewable-based processes and products, including carbon-based catalysts, advances in green conversion processes, new regulations related to the development and commercialization of environmentally friendly products, and investments in the research and development of greener processes, the outlook for carbon-based catalysts is an attractive field in the new era of bioeconomy.

As stated, the most relevant carbon-based catalysts are activated carbons, nanotubes, nanofibers, and graphene; more specific studies are needed to analyze the advantages and disadvantages of using each of them.

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References

1. Guleria, A.; Kumari, G.; Saravanamurugan, S. Chapter 17. Cellulose valorization to potential platform chemicals. *Biomass Biofuels Biochem. Recent Adv. Dev. Platf. Chem.* **2019**, 433–457. [CrossRef]
2. FitzPatrick, M.; Champagne, P.; Cunningham, M.F.; Whitney, R.A. A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresour. Technol.* **2010**, *101*, 8915–8922. [CrossRef]
3. Shrotri, A.; Kobayashi, H.; Fukuoka, A. Cellulose Depolymerization over Heterogeneous Catalysts. *Accunts Chem. Res.* **2018**, *51*, 761–768. [CrossRef] [PubMed]
4. Atanda, L.; Silahua, A.; Mukundan, S.; Shrotri, A.; Torres-Torres, G.; Beltramini, J. Catalytic behaviour of TiO_2-ZrO_2 binary oxide synthesized by sol-gel process for glucose conversion to 5-hydroxymethylfurfural. *RSC Adv.* **2015**, *5*, 80346–80352. [CrossRef]
5. Moreno-Recio, M.; Santamaría-González, J.; Maireles-Torres, P. Brönsted and Lewis acid ZSM-5 zeolites for the catalytic dehydration of glucose into 5-hydroxymethylfurfural. *Chem. Eng. J.* **2016**, *303*, 22–30. [CrossRef]
6. Zhou, C.H.; Xia, X.; Lin, C.X.; Tong, D.S.; Beltramini, J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. Rev.* **2011**, *40*, 5588–5617. [CrossRef]
7. Fukuoka, A.; Dhepe, P.L. Catalytic conversion of cellulose into sugar alcohols. *Angew. Chem. Int. Ed.* **2006**, *45*, 5161–5163. [CrossRef]
8. Ya'aini, N.; Amin, N.A.S. Catalytic performance of hybrid nanocatalyst for levulinic acid production from glucose. *AIP Conf. Proc.* **2012**, *1502*, 442–453. [CrossRef]
9. Deng, W.; Zhang, Q.; Wang, Y. Catalytic transformations of cellulose and cellulose-derived carbohydrates into organic acids. *Catal. Today* **2014**, *234*, 31–41. [CrossRef]
10. Chambon, F.; Rataboul, F.; Pinel, C.; Cabiac, A.; Guillon, E.; Essayem, N. Cellulose hydrothermal conversion promoted by heterogeneous Brønsted and Lewis acids: Remarkable efficiency of solid Lewis acids to produce lactic acid. *Appl. Catal B Environ.* **2011**, *105*, 171–181. [CrossRef]
11. Choudhary, V.; Pinar, A.B.; Lobo, R.F.; Vlachos, D.G.; Sandler, S.I. Comparison of homogeneous and heterogeneous catalysts for glucose-to-fructose isomerization in aqueous media. *ChemSusChem* **2013**, *6*, 2369–2376. [CrossRef]
12. Wang, T.; Nolte, M.W.; Shanks, B.H. Catalytic dehydration of C6carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green Chem.* **2014**, *16*, 548–572. [CrossRef]
13. Yan, K.; Jarvis, C.; Gu, J.; Yan, Y. Production and catalytic transformation of levulinic acid: A platform for speciality chemicals and fuels. *Renew. Sustain. Energy Rev.* **2015**, *51*, 986–997. [CrossRef]
14. Delidovich, I.; Palkovits, R. Catalytic Isomerization of Biomass-Derived Aldoses: A Review. *ChemSusChem* **2016**, *9*, 547–561. [CrossRef]
15. Caratzoulas, S.; Davis, M.E.; Gorte, R.J.; Gounder, R.; Lobo, R.F.; Nikolakis, V.; Caratzoulas, S.; Davis, M.E.; Gorte, R.J.; Gounder, R.; et al. Challenges of and Insights into Acid-Catalyzed Transformations of Sugars. *J. Phys. Chem. C* **2014**, *118*, 22815–22833. [CrossRef]
16. Khan, M.A.; Dharmalingam, B.; Chuetor, S.; Cheng, Y.S.; Sriariyanun, M. Comprehensive review on effective conversion of lignocellulosic biomass to levulinic acid. *Biomass Convers. Biorefinery* **2023**, 1–16. [CrossRef]
17. Azlan, N.S.M.; Yap, C.L.; Gan, S.; Rahman, M.B.A. Recent advances in the conversion of lignocellulosic biomass and its degraded products to levulinic acid: A synergy of Brønsted-Lowry acid and Lewis acid. *Ind. Crops Prod.* **2022**, *181*, 114778. [CrossRef]

18. Girisuta, B.; Janssen, L.P.B.M.; Heeres, H.J. Kinetic Study on the Acid-Catalyzed Hydrolysis of Cellulose to Levulinic Acid. *Ind. Eng. Chem. Res.* **2007**, *46*, 1696–1708. [CrossRef]
19. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502. [CrossRef]
20. Hu, L.; Lin, L.; Wu, Z.; Zhou, S.; Liu, S. Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. *Appl. Catal. B Environ.* **2015**, *174–175*, 225–243. [CrossRef]
21. Kobayashi, H.; Kaiki, H.; Shrotri, A.; Techikawara, K.; Fukuoka, A. Hydrolysis of woody biomass by a biomass-derived reusable heterogeneous catalyst. *Chem. Sci.* **2015**, *7*, 692–696. [CrossRef] [PubMed]
22. Kamiya, Y.; Sakata, S.; Yoshinaga, Y.; Ohnishi, R.; Okuhara, T. Zirconium Phosphate with a High Surface Area as a Water-Tolerant Solid Acid. *Catal. Lett.* **2004**, *94*, 45–47. [CrossRef]
23. Ilgen, F.; Ott, D.; Kralisch, D.; Reil, C.; Palmberger, A.; König, B. Conversion of carbohydrates into 5-hydroxymethylfurfural in highly concentrated low melting mixtures. *Green Chem.* **2009**, *11*, 1948–1954. [CrossRef]
24. Lai, D.M.; Deng, L.; Li, J.; Liao, B.; Guo, Q.X.; Fu, Y. Hydrolysis of cellulose into glucose by magnetic solid acid. *ChemSusChem* **2011**, *4*, 55–58. [CrossRef]
25. Yu, I.K.M.; Tsang, D.C.W. Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms. *Bioresour. Technol.* **2017**, *238*, 716–732. [CrossRef]
26. Guo, F.; Fang, Z.; Zhou, T.J. Conversion of fructose and glucose into 5-hydroxymethylfurfural with lignin-derived carbonaceous catalyst under microwave irradiation in dimethyl sulfoxide-ionic liquid mixtures. *Bioresour. Technol.* **2012**, *112*, 313–318. [CrossRef]
27. Klemm, D.; Heublein, B.; Fink, H.P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem. Int. Ed.* **2005**, *44*, 3358–3393. [CrossRef] [PubMed]
28. Upare, P.P.; Yoon, J.W.; Kim, M.Y.; Kang, H.Y.; Hwang, D.W.; Hwang, Y.K.; Upare, P.P.; Kung, H.H.; Chang, J.S. Chemical conversion of biomass-derived hexose sugars to levulinic acid over sulfonic acid-functionalized graphene oxide catalysts. *Green Chem.* **2013**, *15*, 2935–2943. [CrossRef]
29. Zhou, L.; Liang, R.; Ma, Z.; Wu, T.; Wu, Y. Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids. *Bioresour. Technol.* **2013**, *129*, 450–455. [CrossRef]
30. Mosier, N.S.; Ladisch, C.M.; Ladisch, M.R. Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation. *Biotechnol. Bioeng.* **2002**, *79*, 610–618. [CrossRef] [PubMed]
31. Mosier, N.S.; Sarikaya, A.; Ladisch, C.M.; Ladisch, M.R. Characterization of dicarboxylic acids for cellulose hydrolysis. *Biotechnol. Prog.* **2001**, *17*, 474–480. [CrossRef] [PubMed]
32. Medronho, B.; Lindman, B. Competing forces during cellulose dissolution: From solvents to mechanisms. *Curr. Opin. Colloid Interface Sci.* **2014**, *19*, 32–40. [CrossRef]
33. Sangsiri, P.; Laosiripojana, N.; Daorattanachai, P. Synthesis of sulfonated carbon-based catalysts from organosolv lignin and methanesulfonic acid: Its activity toward esterification of stearic acid. *Renew. Energy* **2022**, *193*, 113–127. [CrossRef]
34. Pandey, S.; Karakoti, M.; Bhardwaj, D.; Tatrari, G.; Sharma, R.; Pandey, L.; Lee, M.J.; Sahoo, N.G. Recent advances in carbon-based materials for high-performance perovskite solar cells: Gaps, challenges and fulfillment. *Nanoscale Adv.* **2023**, *5*, 1492–1526. [CrossRef]
35. Shellaiah, M.; Sun, K.W. Review on Carbon Dot-Based Fluorescent Detection of Biothiols. *Biosensors* **2023**, *13*, 335. [CrossRef] [PubMed]
36. Yamaguchi, D.; Hayashi, S.; Suganuma, S.; Kato, H.; Kitano, M.; Nakajima, K.; Hara, M. Adsorption-Enhanced Hydrolysis of β-1,4-Glucan on Graphene-Based Amorphous Carbon Bearing SO_3H, COOH, and OH Groups. *Langmuir* **2009**, *25*, 5068–5075. [CrossRef]
37. Li, S.; Gu, Z.; Bjornson, B.E.; Muthukumarappan, A. Biochar based solid acid catalyst hydrolyze biomass. *J. Environ. Chem. Eng.* **2013**, *1*, 1174–1181. [CrossRef]
38. Park, M.R.; Kim, S.K.; Jeong, G.T. Production of levulinic acid from glucosamine using zirconium oxychloride. *J. Ind. Eng. Chem.* **2018**, *61*, 119–123. [CrossRef]
39. Gong, R.; Ma, Z.; Wang, X.; Han, Y.; Guo, Y.; Sun, G.; Li, Y.; Zhou, J. Sulfonic-acid-functionalized carbon fiber from waste newspaper as a recyclable carbon based solid acid catalyst for the hydrolysis of cellulose. *RSC Adv.* **2019**, *9*, 28902–28907. [CrossRef]
40. Ramli, N.A.S.; Amin, N.A.S. Fe/HY zeolite as an effective catalyst for levulinic acid production from glucose: Characterization and catalytic performance. *Appl. Catal. B Environ.* **2015**, *163*, 487–498. [CrossRef]
41. Garces, D.; Faba, L.; Díaz, E.; Ordóñez, S. Aqueous-Phase Transformation of Glucose into Hydroxymethylfurfural and Levulinic Acid by Homogeneous and Heterogeneous Catalysis. *ChemSusChem* **2019**, *12*, 924–934. [CrossRef] [PubMed]
42. Lourvanij, K.; Rorrer, G.L. Dehydration of glucose to organic acids in microporous pillared clay catalysts. *Appl. Catal. A Gen.* **1994**, *109*, 147–165. [CrossRef]

43. Wei, Q.; Wu, S. Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids. *Chem. Eng. J.* **2017**, *307*, 389–398. [CrossRef]
44. Potvin, J.; Sorlien, E.; Hegner, J.; DeBoef, B.; Lucht, B.L. Effect of NaCl on the Conversion of cellulose to glucose and levulinic acid via solid supported acid catalysis. *Tetrahedron Lett.* **2011**, *52*, 5891–5893. [CrossRef]
45. Wei, W.; Wu, S. Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst. *Fuel* **2018**, *225*, 311–321. [CrossRef]
46. Agirrezabal-Telleria, I.; Gandarias, I.; Arias, P.L. Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review. *Catal. Today* **2014**, *234*, 42–58. [CrossRef]
47. Jeong, H.; Park, S.-Y.; Ryu, G.-H.; Choi, J.-H.; Kim, J.-H.; Choi, W.-S.; Lee, S.M.; Choi, J.W.; Choi, I.-G. Catalytic conversion of hemicellulosic sugars derived from biomass to levulinic acid. *Catal. Commun.* **2018**, *117*, 19–25. [CrossRef]
48. Joshi, S.S.; Zodge, A.D.; Pandare, K.V.; Kulkarni, B.D. Efficient Conversion of Cellulose to Levulinic Acid by Hydrothermal Treatment Using Zirconium Dioxide as a Recyclable Solid Acid Catalyst. *Ind. Eng. Chem. Res.* **2014**, *53*, 18796–18805. [CrossRef]
49. Ordomsky, V.V.; Van Der Schaaf, J.; Schouten, J.C.; Nijhuis, T.A. Fructose dehydration to 5-hydroxymethylfurfural over solid acid catalysts in a biphasic system. *ChemSusChem* **2012**, *5*, 1812–1819. [CrossRef]
50. Girisuta, B.; Janssen, L.P.B.M.; Heeres, H.J. Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. *Chem. Eng. Res. Des.* **2006**, *84*, 339–349. [CrossRef]
51. Patil, S.K.R.; Lund, C.R.F. Formation and growth of humins via aldol addition and condensation during acid-catalyzed conversion of 5-hydroxymethylfurfural. *Energy Fuels* **2011**, *25*, 4745–4755. [CrossRef]
52. Peng, L.; Lin, L.; Zhang, J.; Zhuang, J.; Zhang, B.; Gong, Y. Catalytic conversion of cellulose to levulinic acid by metal chlorides. *Molecules* **2010**, *15*, 5258–5272. [CrossRef]
53. Ya'Aini, N.; Amin, N.A.S.; Endud, S. Characterization and performance of hybrid catalysts for levulinic acid production from glucose. *Microporous Mesoporous Mater.* **2013**, *171*, 14–23. [CrossRef]
54. Saunders, G.J.; Kendall, K. Reactions of hydrocarbons in small tubular SOFCs. *J. Power Sources* **2002**, *106*, 258–263. [CrossRef]
55. Ahlkvist, J.; Wärnå, J.; Salmi, T.; Mikkola, J.P. Heterogeneously catalyzed conversion of nordic pulp to levulinic and formic acids. *React. Kinet. Mech. Catal.* **2016**, *119*, 415–427. [CrossRef]
56. Weingarten, R.; Cho, J.; Xing, R.; Conner, W.C.; Huber, G.W. Kinetics and reaction engineering of levulinic acid production from aqueous glucose solutions. *ChemSusChem* **2012**, *5*, 1280–1290. [CrossRef]
57. Rackemann, D.W.; Doherty, W.O.S. A review on the production of levulinic acid and furanics from sugars. In Proceedings of the 34th Annual Conference of the Australian Society of Sugar Cane Technologists 2012, ASSCT 2012, Palm Cove, Australia, 1–4 May 2012; Volume 34, pp. 605–613.
58. Weingarten, R.; Kim, Y.T.; Tompsett, G.A.; Fernández, A.; Han, K.S.; Hagaman, E.W.; Conner, W.C.; Dumesic, J.A.; Huber, G.W. Conversion of glucose into levulinic acid with solid metal(IV) phosphate catalysts. *J. Catal.* **2013**, *304*, 123–134. [CrossRef]
59. Yang, F.; Liu, Q.; Bai, X.; Du, Y. Conversion of biomass into 5-hydroxymethylfurfural using solid acid catalyst. *Bioresour. Technol.* **2011**, *102*, 3424–3429. [CrossRef]
60. Yuan, Z.; Xu, C.; Cheng, S.; Leitch, M. Catalytic conversion of glucose to 5-hydroxymethyl furfural using inexpensive co-catalysts and solvents. *Carbohydr. Res.* **2011**, *346*, 2019–2023. [CrossRef]
61. Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C.R.; Abou-Shehada, S.; Dunn, P.J. CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.* **2015**, *18*, 288–296. [CrossRef]
62. Wettstein, S.G.; Alonso, D.M.; Chong, Y.; Dumesic, J.A. Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems. *Energy Environ. Sci.* **2012**, *5*, 8199–8203. [CrossRef]
63. Gürbüz, E.I.; Wettstein, S.G.; Dumesic, J.A. Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents. *ChemSusChem* **2012**, *5*, 383–387. [CrossRef] [PubMed]
64. Liu, L.; Li, Z.; Hou, W.; Shen, H. Direct conversion of lignocellulose to levulinic acid catalyzed by ionic liquid. *Carbohydr. Polym.* **2018**, *181*, 778–784. [CrossRef] [PubMed]
65. Jakob, A.; Grilc, M.; Teržan, J.; Likozar, B. Solubility Temperature Dependence of Bio-Based Levulinic. *Processes* **2021**, *9*, 924. [CrossRef]
66. Pileidis, F.D.; Titirici, M.M. Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. *ChemSusChem* **2016**, *9*, 562–582. [CrossRef]
67. Morone, A.; Apte, M.; Pandey, R.A. Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. *Renew. Sustain. Energy Rev.* **2015**, *51*, 548–565. [CrossRef]
68. Zuo, Y.; Zhang, Y.; Fu, Y. Catalytic conversion of cellulose into levulinic acid by a sulfonated chloromethyl polystyrene solid acid catalyst. *ChemCatChem* **2014**, *6*, 753–757. [CrossRef]
69. Mellmer, M.A.; Alonso, D.M.; Luterbacher, J.S.; Gallo, J.M.R.; Dumesic, J.A. Effects of γ-valerolactone in hydrolysis of lignocellulosic biomass to monosaccharides. *Green Chem.* **2014**, *16*, 4659–4662. [CrossRef]

70. Victor, A.; Sharma, P.; Pulidindi, I.N.; Gedanken, A. Levulinic Acid Is a Key Strategic Chemical from Biomass. *Catalysts* **2022**, *12*, 909. [CrossRef]
71. Cheng, X.; Feng, Q.; Ma, D.; Xing, F.; Zeng, X.; Huang, X.; Teng, J.; Feng, L. Kinetics for glucose conversion to levulinic acid over solid acid catalyst in γ-valerolactone solution. *Biochem. Eng. J.* **2022**, *180*, 108360. [CrossRef]
72. Zhang, J.; Zhuang, J.; Lin, L.; Liu, S.; Zhang, Z. Conversion of D-xylose into furfural with mesoporous molecular sieve MCM-41 as catalyst and butanol as the extraction phase. *Biomass Bioenergy* **2012**, *39*, 73–77. [CrossRef]
73. Yang, Y.; Hu, C.; Abu-Omar, M.M. Conversion of glucose into furans in the presence of $AlCl_3$ in an ethanol-water solvent system. *Bioresour. Technol.* **2012**, *116*, 190–194. [CrossRef]
74. Mahmoud, E. Glucose Conversion to Furans in Alcohols Catalyzed by Lewis Acidic Beta Zeolites and Brønsted Acidic Resins. *ChemistrySelect* **2017**, *2*, 10336–10339. [CrossRef]
75. Jia, S.; Xu, Z.; Zhang, Z.C. Catalytic conversion of glucose in dimethylsulfoxide/water binary mix with chromium trichloride: Role of water on the product distribution. *Chem. Eng. J.* **2014**, *254*, 333–339. [CrossRef]
76. Alonso, D.M.; Gallo, J.M.R.; Mellmer, M.A.; Wettstein, S.G.; Dumesic, J.A. Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catal. Sci. Technol.* **2013**, *3*, 927–931. [CrossRef]
77. Shen, F.; Smith, R.L.; Li, L.; Yan, L.; Qi, X. Eco-friendly Method for Efficient Conversion of Cellulose into Levulinic Acid in Pure Water with Cellulase-Mimetic Solid Acid Catalyst. *ACS Sustain. Chem. Eng.* **2017**, *5*, 2421–2427. [CrossRef]
78. Lai, D.M.; Deng, L.; Guo, Q.X.; Fu, Y. Hydrolysis of biomass by magnetic solid acid. *Energy Environ. Sci.* **2011**, *4*, 3552–3557. [CrossRef]
79. Ding, D.; Wang, J.; Xi, J.; Liu, X.; Lu, G.; Wang, Y. High-yield production of levulinic acid from cellulose and its upgrading to γ-valerolactone. *Green Chem.* **2014**, *16*, 3846–3853. [CrossRef]
80. Liu, Y.; Li, H.; He, J.; Zhao, W.; Yang, T.; Yang, S. Catalytic conversion of carbohydrates to levulinic acid with mesoporous niobium-containing oxides. *Catal. Commun.* **2017**, *93*, 20–24. [CrossRef]
81. Hu, X.; Wang, S.; Westerhof, R.J.M.; Wu, L.; Song, Y.; Dong, D.; Li, C.Z. Acid-catalyzed conversion of C6 sugar monomer/oligomers to levulinic acid in water, tetrahydrofuran and toluene: Importance of the solvent polarity. *Fuel* **2015**, *141*, 56–63. [CrossRef]
82. Jow, J.; Rorrer, G.L.; Hawley, M.C.; Lamport, D.T.A. Dehydration of d-fructose to levulinic acid over LZY zeolite catalyst. *Biomass* **1987**, *14*, 185–194. [CrossRef]
83. Thapa, I.; Mullen, B.; Saleem, A.; Leibig, C.; Baker, R.T.; Giorgi, J.B. Efficient green catalysis for the conversion of fructose to levulinic acid. *Appl. Catal. A Gen.* **2017**, *539*, 70–79. [CrossRef]
84. Chamnankid, B.; Ratanatawanate, C.; Faungnawakij, K. Conversion of xylose to levulinic acid over modified acid functions of alkaline-treated zeolite Y in hot-compressed water. *Chem. Eng. J.* **2014**, *258*, 341–347. [CrossRef]
85. Kang, S.; Fu, J.; Zhang, G. From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. *Renew. Sustain. Energy Rev.* **2018**, *94*, 340–362. [CrossRef]
86. Jiménez-Morales, I.; Santamaría-González, J.; Jiménez-López, A.; Maireles-Torres, P. Glucose dehydration to 5-hydroxymethylfurfural on zirconium containing mesoporous MCM-41 silica catalysts. *Fuel* **2014**, *118*, 265–271. [CrossRef]
87. Vilcocq, L.; Castilho, P.C.; Carvalheiro, F.; Duarte, L.C. Hydrolysis of oligosaccharides over solid acid catalysts: A review. *ChemSusChem* **2014**, *7*, 1010–1019. [CrossRef]
88. Van de Vyver, S.; Geboers, J.; Jacobs, P.A.; Sels, B.F. Recent Advances in the Catalytic Conversion of Cellulose. *ChemCatChem* **2011**, *3*, 82–94. [CrossRef]
89. Chen, D.; Liang, F.; Feng, D.; Xian, M.; Zhang, H.; Liu, H.; Du, F. An efficient route from reproducible glucose to 5-hydroxymethylfurfural catalyzed by porous coordination polymer heterogeneous catalysts. *Chem. Eng. J.* **2016**, *300*, 177–184. [CrossRef]
90. Zhang, Y.; Wang, J.; Li, X.; Liu, X.; Xia, Y.; Hu, B.; Lu, G.; Wang, Y. Direct conversion of biomass-derived carbohydrates to 5-hydroxymethylfurural over water-tolerant niobium-based catalysts. *Fuel* **2015**, *139*, 301–307. [CrossRef]
91. Peng, K.; Li, X.; Liu, X.; Wang, Y. Hydrothermally stable Nb-SBA-15 catalysts applied in carbohydrate conversion to 5-hydroxymethyl furfural. *Mol. Catal.* **2017**, *441*, 72–80. [CrossRef]
92. Weingarten, R.; Tompsett, G.A.; Conner, W.C.; Huber, G.W. Design of solid acid catalysts for aqueous-phase dehydration of carbohydrates: The role of Lewis and Brønsted acid sites. *J. Catal.* **2011**, *279*, 174–182. [CrossRef]
93. Velthoen, M.E.Z.; Nab, S.; Weckhuysen, B.M. Probing acid sites in solid catalysts with pyridine UV-Vis spectroscopy. *Phys. Chem. Chem. Phys.* **2018**, *20*, 21647–21659. [CrossRef] [PubMed]
94. Macht, J.; Carr, R.T.; Iglesia, E. Functional assessment of the strength of solid acid catalysts. *J. Catal.* **2009**, *264*, 54–66. [CrossRef]
95. Wang, H.; Zhang, C.; He, H.; Wang, L. Glucose production from hydrolysis of cellulose over a novel silica catalyst under hydrothermal conditions. *J. Environ. Sci.* **2011**, *23*, 601–606. [CrossRef] [PubMed]
96. Dora, S.; Bhaskar, T.; Singh, R.; Naik, D.V.; Adhikari, D.K. Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. *Bioresour. Technol.* **2012**, *120*, 318–321. [CrossRef]

97. Guo, H.; Qi, X.; Li, L.; Smith, R.L. Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid. *Bioresour. Technol.* **2012**, *116*, 355–359. [CrossRef]
98. Rezayan, A.; Zhang, Y.; Li, B.; Xu, C.C.X. Catalytic Conversion of Cellulose to 5-Hydroxymethylfurfural: Advancements in Heterogeneous Catalysts and Cutting-Edge Hydrolysis Strategies. *ChemCatChem* **2023**, *15*, e202300973. [CrossRef]
99. Gupta, S.; Gambhire, A.B.; Jain, R. Conversion of carbohydrates (glucose and fructose) into 5-HMF over solid acid loaded natural zeolite (PMA/NZ) catalyst. *Mater. Lett. X* **2022**, *13*, 100119. [CrossRef]
100. Yang, Y.; Hu, C.-W.; Abu-Omar, M.M. Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using $AlCl_3 \cdot 6H_2O$ catalyst in a biphasic solvent system. *Green Chem.* **2012**, *14*, 509–513. [CrossRef]
101. Wang, L.; Guo, H.; Xie, Q.; Wang, J.; Hou, B.; Jia, L.; Cui, J.; Li, D. Conversion of fructose into furfural or 5-hydroxymethylfurfural over HY zeolites selectively in Γ-butyrolactone. *Appl. Catal. A Gen.* **2019**, *572*, 51–60. [CrossRef]
102. Tao, X.; Li, H.; Chang, K.; Huang, L.; Wang, L. Regulation of Brønsted-Lewis acid sites by combination of Amberlyst-15 and Cr-MOFs based catalysts for glucose conversion. *J. Phys. Chem. Solids* **2024**, *193*, 112159. [CrossRef]
103. Akiyama, T.; Mori, K. Stronger Brønsted Acids: Recent Progress. *Chem. Rev.* **2015**, *115*, 9277–9306. [CrossRef] [PubMed]
104. Nakajima, K.; Hara, M. Amorphous Carbon with SO_3H Groups as a Solid Brønsted Acid Catalyst. *ACS Catal.* **2018**, *2*, 1296–1304. [CrossRef]
105. Zhang, X.; Zhang, D.; Sun, Z.; Xue, L.; Wang, X.; Jiang, Z. Highly efficient preparation of HMF from cellulose using temperature-responsive heteropolyacid catalysts in cascade reaction. *Appl. Catal. B Environ.* **2016**, *196*, 50–56. [CrossRef]
106. Katada, N.; Tsubaki, T.; Niwa, M. Measurements of number and strength distribution of Brønsted and Lewis acid sites on sulfated zirconia by ammonia IRMS-TPD method. *Appl. Catal. A Gen.* **2008**, *340*, 76–86. [CrossRef]
107. Rinaldi, R.; Schüth, F. Design of solid catalysts for the conversion of biomass. *Energy Environ. Sci.* **2009**, *2*, 610–626. [CrossRef]
108. Zhang, Y.; Wang, J.; Wang, J.; Wang, Y.; Wang, M.; Ciu, H.; Song, F.; Sun, X.; Xie, Y.; Yi, W. Al_2O_3-TiO_2 Modified Sulfonated Carbon with Hierarchically Ordered Pores for Glucose Conversion to 5-HMF. *ChemistrySelect* **2019**, *4*, 5724–5731. [CrossRef]
109. Taghavi, S.; Pizzolitto, C.; Ghedini, E.; Menegazzo, F.; Cruciani, G.; Peurla, M.; Eränen, K.; Heinmaa, I.; Aho, A.; Kumar, N.; et al. Levulinic Acid Production: Comparative Assessment of Al-Rich Ordered Mesoporous Silica and Microporous Zeolite. *Catal. Lett.* **2023**, *153*, 41–53. [CrossRef]
110. Otomo, R.; Yokoi, T.; Kondo, J.N.; Tatsumi, T. Dealuminated Beta zeolite as effective bifunctional catalyst for direct transformation of glucose to 5-hydroxymethylfurfural. *Appl. Catal. A Gen.* **2014**, *470*, 318–326. [CrossRef]
111. Marianou, A.A.; Michailof, C.M.; Pineda, A.; Iliopoulou, E.F.; Triantafyllidis, K.S.; Lappas, A.A. Effect of Lewis and BrØnsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media. *Appl. Catal. A Gen.* **2018**, *555*, 75–87. [CrossRef]
112. Marianou, A.A.; Michailof, C.M.; Pineda, A.; Iliopoulou, E.F.; Triantafyllidis, K.S.; Lappas, A.A. Glucose to Fructose Isomerization in Aqueous Media over Homogeneous and Heterogeneous Catalysts. *ChemCatChem* **2016**, *8*, 1100–1110. [CrossRef]
113. Enslow, K.R.; Bell, A.T. $SnCl_4$-catalyzed isomerization/dehydration of xylose and glucose to furanics in water. *Catal. Sci. Technol.* **2015**, *5*, 2839–2847. [CrossRef]
114. Román-Leshkov, Y.; Davis, M.E. Activation of carbonyl-containing molecules with solid lewis acids in aqueous media. *ACS Catal.* **2011**, *1*, 1566–1580. [CrossRef]
115. Huang, Y.B.; Fu, Y. Hydrolysis of cellulose to glucose by solid acid catalysts. *Green Chem.* **2013**, *15*, 1095–1111. [CrossRef]
116. Rinaldi, R.; Schüth, F. Acid hydrolysis of cellulose as the entry point into biorefinery schemes. *ChemSusChem* **2009**, *2*, 1096–1107. [CrossRef] [PubMed]
117. Cheng, M.; Shi, T.; Guan, H.; Wang, S.; Wang, X.; Jiang, Z. Clean production of glucose from polysaccharides using a micellar heteropolyacid as a heterogeneous catalyst. *Appl. Catal. B Environ.* **2011**, *107*, 104–109. [CrossRef]
118. Kang, S.; Ye, J.; Chang, J. Recent Advances in Carbon-Based Sulfonated Catalyst: Preparation and Application. *Int. Rev. Chem. Eng.* **2013**, *5*, 133–144.
119. Serp, P.; Figueiredo, J.L. *Carbon Materials for Catalysis*; Wiley: Hoboken, NJ, USA, 2009. [CrossRef]
120. Albers, P.W.; Pietsch, J.; Krauter, J.; Parker, S.F. Investigations of activated carbon catalyst supports from different natural sources. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1941–1949. [CrossRef]
121. Iwanow, M.; Gärtner, T.; Sieber, V.; König, B. Activated carbon as catalyst support: Precursors, preparation, modification and characterization. *Beilstein J. Org. Chem.* **2020**, *16*, 1188–1202. [CrossRef]
122. Shao, S.; Yang, Y.; Guo, S.; Hao, S.; Yang, F.; Zhang, S.; Ren, Y.; Ke, Y. Highly active and stable Co nanoparticles embedded in nitrogen-doped mesoporous carbon nanofibers for aqueous-phase levulinic acid hydrogenation. *Green Energy Environ.* **2021**, *6*, 567–577. [CrossRef]
123. Wang, Y.; Rong, Z.; Wang, Y.; Wang, T.; Du, Q.; Wang, Y.; Qu, J. Graphene-based metal/acid bifunctional catalyst for the conversion of levulinic acid to γ-valerolactone. *ACS Sustain. Chem. Eng.* **2017**, *5*, 1538–1548. [CrossRef]
124. Pang, J.; Wang, A.; Zheng, M.; Zhang, T. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. *Chem. Commun.* **2010**, *46*, 6935–6937. [CrossRef]

125. Hassan, A.H.; Zainol, M.M.; Zainuddin, K.R.; Rosmadi, H.A.; Asmadi, M.; Rahman, N.A.; Amin, N.A.S. A Review on Alkyl Levulinates Synthesis from Renewable Levulinic Acid using Various Modified Carbon-Based Catalysts. *Malays. J. Chem.* **2022**, *24*, 264–282. [CrossRef]
126. Zhang, M.; Sun, A.; Meng, Y.; Wang, L.; Jiang, H.; Li, G. Catalytic Performance of Biomass Carbon-Based Solid Acid Catalyst for Esterification of Free Fatty Acids in Waste Cooking Oil. *Catal. Surv. Asia* **2015**, *19*, 61–67. [CrossRef]
127. Konwar, L.J.; Mäki-Arvela, P.; Mikkola, J.P. SO_3H-Containing Functional Carbon Materials: Synthesis, Structure, and Acid Catalysis. *Chem. Rev.* **2019**, *119*, 11576–11630. [CrossRef] [PubMed]
128. Qian, E.W.; Sukma, L.P.P.; Li, S.; Higashi, A. Saccharification of cellulosic biomass using sulfonated mesoporous carbon-based catalysts. *Environ. Prog. Sustain. Energy* **2015**, *35*, 574–581. [CrossRef]
129. Chen, S.S.; Maneerung, T.; Tsang, D.C.W.; Ok, Y.S.; Wang, C.H. Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts. *Chem. Eng. J.* **2017**, *328*, 246–273. [CrossRef]
130. Kitano, M.; Arai, K.; Kodama, A.; Kousaka, T.; Nakajima, K.; Hayashi, S.; Hara, M. Preparation of a sulfonated porous carbon catalyst with high specific surface area. *Catal. Lett.* **2009**, *131*, 242–249. [CrossRef]
131. Jiang, Y.; Li, X.; Cao, Q.; Mu, X. Acid functionalized, highly dispersed carbonaceous spheres: An effective solid acid for hydrolysis of polysaccharides. *J. Nanopart. Res.* **2011**, *13*, 463–469. [CrossRef]
132. Ogino, I.; Suzuki, Y.; Mukai, S.R. Esterification of levulinic acid with ethanol catalyzed by sulfonated carbon catalysts: Promotional effects of additional functional groups. *Catal. Today* **2018**, *314*, 62–69. [CrossRef]
133. Li, J.; Li, H.; Yuan, Z.; Fang, J.; Chang, L.; Zhang, H.; Li, C. Role of sulfonation in lignin-based material for adsorption removal of cationic dyes. *Int. J. Biol. Macromol.* **2019**, *135*, 1171–1181. [CrossRef]
134. Chen, X.; Zhang, Z.; Yuan, B.; Yu, F.; Xie, C.; Yu, S. Lignin-based sulfonated carbon as an efficient biomass catalyst for clean benzylation of benzene ring compounds. *J. Ind. Eng. Chem.* **2022**, *111*, 369–379. [CrossRef]
135. Yu, H.; Jin, Y.; Li, Z.; Peng, F.; Wang, H. Synthesis and characterization of sulfonated single-walled carbon nanotubes and their performance as solid acid catalyst. *J. Solid State Chem.* **2008**, *181*, 432–438. [CrossRef]
136. Na, S.; Minhua, Z.; Xiuqin, D.; Lingtao, W. Preparation of sulfonated ordered mesoporous carbon catalyst and its catalytic performance for esterification of free fatty acids in waste cooking oils. *RSC Adv.* **2019**, *9*, 15941–15948. [CrossRef] [PubMed]
137. Yang, Q.; Liu, J.; Zhang, L.; Li, C. Functionalized periodic mesoporous organosilicas for catalysis. *J. Mater. Chem.* **2009**, *19*, 1945–1955. [CrossRef]
138. Zhou, L.; Liu, Z.; Shi, M.; Du, S.; Su, Y.; Yang, X.; Xu, J. Sulfonated hierarchical H-USY zeolite for efficient hydrolysis of hemicellulose/cellulose. *Carbohydr. Polym.* **2013**, *98*, 146–151. [CrossRef]
139. Du, C.Y.; Zhao, T.S.; Liang, Z.X. Sulfonation of carbon-nanotube supported platinum catalysts for polymer electrolyte fuel cells. *J. Power Sources* **2008**, *176*, 9–15. [CrossRef]
140. Okamura, M.; Takagaki, A.; Toda, M.; Kondo, J.N.; Domen, K.; Tatsumi, T.; Hara, M.; Hayashi, S. Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon. *Chem. Mater.* **2006**, *18*, 3039–3045. [CrossRef]
141. Morales-Acosta, D.; Flores-Oyervides, J.D.; Rodríguez-González, J.A.; Sánchez-Padilla, N.M.; Benavides, R.; Fernán-dez-Tavizón, S.; Mercado-Silva, J.A. Comparative methods for reduction and sulfonation of graphene oxide for fuel cell electrode applications. *Int. J. Hydrogen Energy* **2019**, *44*, 12356–12364. [CrossRef]
142. Kastner, J.R.; Miller, J.; Geller, D.P.; Locklin, J.; Keith, L.H.; Johnson, T. Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catal. Today* **2012**, *190*, 122–132. [CrossRef]
143. Hou, K.; Zhang, A.; Gu, L.; Liu, M.; Guo, X. Efficient synthesis and sulfonation of ordered mesoporous carbon materials. *J. Colloid Interface Sci.* **2012**, *377*, 18–26. [CrossRef]
144. Li, C.; Zhu, H.; Salim, N.V.; Fox, B.L.; Hameed, N. Preparation of microporous carbon materials via in-depth sulfonation and stabilization of polyethylene. *Polym. Degrad. Stab.* **2016**, *134*, 272–283. [CrossRef]
145. Estevez, R.; Aguado-Deblas, L.; Montes, V.; Caballero, A.; Bautista, F.M. Sulfonated carbons from olive stones as catalysts in the microwave-assisted etherification of glycerol with tert-butyl alcohol. *Mol. Catal.* **2020**, *488*, 110921. [CrossRef]
146. Mo, X.; López, D.E.; Suwannakarn, K.; Liu, Y.; Lotero, E.; Goodwin, J.G.; Lu, C. Activation and deactivation characteristics of sulfonated carbon catalysts. *J. Catal.* **2008**, *254*, 332–338. [CrossRef]
147. Li, M.; Zhang, Q.; Luo, B.; Chen, C.; Wang, S.; Min, D. Lignin-based carbon solid acid catalyst prepared for selectively converting fructose to 5-hydroxymethylfurfural. *Ind. Crop. Prod.* **2020**, *145*, 111920. [CrossRef]
148. Roldán, L.; Pires, E.; Fraile, J.M.; García-Bordejé, E. Impact of sulfonated hydrothermal carbon texture and surface chemistry on its catalytic performance in esterification reaction. *Catal. Today* **2015**, *249*, 153–160. [CrossRef]
149. Tamborini, L.H.; Militello, M.P.; Balach, J.; Moyano, J.M.; Barbero, C.A.; Acevedo, D.F. Application of sulfonated nanoporous carbons as acid catalysts for Fischer esterification reactions. *Arab. J. Chem.* **2015**, *12*, 3172–3182. [CrossRef]
150. Zhu, J.; Gan, L.; Li, B.; Yang, X. Synthesis and characteristics of lignin-derived solid acid catalysts for microcrystalline cellulose hydrolysis. *Korean J. Chem. Eng.* **2017**, *34*, 110–117. [CrossRef]

151. Fukuhara, K.; Nakajima, K.; Kitano, M.; Kato, H.; Hayashi, S.; Hara, M. Structure and catalysis of cellulose-derived amorphous carbon bearing SO_3H groups. *ChemSusChem* **2011**, *4*, 778–784. [CrossRef]
152. Li, O.L.; Qin, L.; Takeuchi, N.; Kim, K.; Ishizaki, T. Effect of hydrophilic/hydrophobic properties of carbon materials on plasma-sulfonation process and their catalytic activities in cellulose conversion. *Catal. Today* **2019**, *337*, 155–161. [CrossRef]
153. Yang, Z.; Huang, R.; Qi, W.; Tong, L.; Su, R.; He, Z. Hydrolysis of cellulose by sulfonated magnetic reduced graphene oxide. *Chem. Eng. J.* **2015**, *280*, 90–98. [CrossRef]
154. Liu, X.Y.; Huang, M.; Ma, H.L.; Zhang, Z.Q.; Gao, J.M.; Zhu, Y.L.; Han, X.J.; Guo, X.Y. Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules* **2010**, *15*, 7188–7196. [CrossRef] [PubMed]
155. Koskin, A.P.; Larichev, Y.V.; Mishakov, I.V.; Mel'gunov, M.S.; Vedyagin, A.A. Synthesis and characterization of carbon nanomaterials functionalized by direct treatment with sulfonating agents. *Microporous Mesoporous Mater.* **2020**, *299*, 110130. [CrossRef]
156. Nongbe, M.C.; Ekou, T.; Ekou, L.; Yao, K.B.; Le Grognec, E.; Felpin, F.X. Biodiesel production from palm oil using sulfonated graphene catalyst. *Renew. Energy* **2017**, *106*, 135–141. [CrossRef]
157. Guo, H.; Hirosaki, Y.; Qi, X.; Smith, R.L. Synthesis of ethyl levulinate over amino-sulfonated functional carbon materials. *Renew. Energy* **2020**, *157*, 951–958. [CrossRef]
158. Xing, R.; Liu, Y.; Wang, Y.; Chen, L.; Wu, H.; Jiang, Y.; He, M.; Wu, P. Active solid acid catalysts prepared by sulfonation of carbonization-controlled mesoporous carbon materials. *Microporous Mesoporous Mater.* **2007**, *105*, 41–48. [CrossRef]
159. Han, Y.; Ye, L.; Gu, X.; Zhu, P.; Lu, X. Lignin-based solid acid catalyst for the conversion of cellulose to levulinic acid using γ-valerolactone as solvent. *Ind. Crop. Prod.* **2019**, *127*, 88–93. [CrossRef]
160. Csicsery, S.M. Shape-selective catalysis in zeolites. *Zeolites* **1984**, *4*, 202–203. [CrossRef]
161. Lima, S.; Fernandes, A.; Antunes, M.M.; Pillinger, M.; Ribeiro, F.; Valente, A.A. Dehydration of xylose into furfural in the presence of crystalline microporous silicoaluminophosphates. *Catal. Lett.* **2010**, *135*, 41–47. [CrossRef]
162. Xu, H.; Miao, Z.; Zhao, H.; Yang, J.; Zhao, J.; Song, H.; Liang, N.; Chou, L. Dehydration of fructose into 5-hydroxymethylfurfural by high stable ordered mesoporous zirconium phosphate. *Fuel* **2015**, *145*, 234–240. [CrossRef]
163. Kruger, J.S.; Choudhary, V.; Nikolakis, V.; Vlachos, D.G. Elucidating the roles of zeolite H-BEA in aqueous-phase fructose dehydration and HMF rehydration. *ACS Catal.* **2013**, *3*, 1279–1291. [CrossRef]
164. Nalawade, K.S.; Gogate, P.R. Understanding the effect of reaction parameters on the production of levulinic acid from glucose. *Can. J. Chem. Eng.* **2024**, *102*, 3713–3722. [CrossRef]
165. Wang, P.; Zhan, S.H.; Yu, H.B. Production of Levulinic Acid from Cellulose Catalyzed by Environmental-Friendly Catalyst. *Adv. Mater. Res.* **2010**, *96*, 183–187. [CrossRef]
166. Chen, S.S.; Yu, I.K.M.; Tsang, D.C.W.; Yip, A.C.K.; Khan, E.; Wang, L.; Ok, Y.S.; Poon, C.S. Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous BrØnsted acids: Temperature and solvent effects. *Chem. Eng. J.* **2017**, *327*, 328–335. [CrossRef]
167. Ramli, N.A.S.; Amin, N.A.S. Optimization of renewable levulinic acid production from glucose conversion catalyzed by Fe/HY zeolite catalyst in aqueous medium. *Energy Convers. Manag.* **2015**, *95*, 10–19. [CrossRef]
168. Bartholomew, C.H. Mechanisms of catalyst deactivation. *Appl. Catal. A: Gen.* **2001**, *212*, 17–60. [CrossRef]
169. Boskovic, G.; Baerns, M. Catalyst deactivation. *Springer Ser. Chem. Phys.* **2004**, *75*, 477–503. [CrossRef]
170. Argyle, M.D.; Bartholomew, C.H. Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts* **2015**, *5*, 145–269. [CrossRef]
171. Tang, P.; Yu, J. Kinetic analysis on deactivation of a solid Brønsted acid catalyst in conversion of sucrose to levulinic acid. *Ind. Eng. Chem. Res.* **2014**, *53*, 11629–11637. [CrossRef]
172. Shao, Y.; Sun, K.; Zhang, L.; Xu, Q.; Zhang, Z.; Li, Q.; Hu, X. Balanced distribution of Brønsted acidic sites and Lewis acidic sites for highly selective conversion of xylose into levulinic acid/ester over Zr-beta catalysts. *Green Chem.* **2019**, *21*, 6634–6645. [CrossRef]
173. Bakhtiari, B.; Najafi Chermahini, A.; Babaei, Z. Design of an acidic sulfonated mesoporous carbon catalyst for the synthesis of butyl levulinate from levulinic acid. *Environ. Prog. Sustain. Energy* **2021**, *40*, e13721. [CrossRef]
174. Burmana, A.D.; Tambun, R.; Haryanto, B.; Sarah, M.; Alexander, V. Recycling heterogeneous catalyst waste in biodiesel production using methanol and hydrochloric acid: A case study on the washing effect with lauric acid as raw material. *Case Stud. Chem. Environ. Eng.* **2023**, *8*, 100510. [CrossRef]
175. Cheng, Z.; Everhart, J.L.; Tsilomelekis, G.; Nikolakis, V.; Saha, B.; Vlachos, D.G. Structural analysis of humins formed in the Brønsted acid catalyzed dehydration of fructose. *Green Chem.* **2018**, *20*, 997–1006. [CrossRef]
176. Wu, Y.; Wang, H.; Peng, J.; Ding, M. Advances in catalytic valorization of cellulose into value-added chemicals and fuels over heterogeneous catalysts. *Catal. Today* **2023**, *408*, 92–110. [CrossRef]
177. Oliveira, B.L.; Da Silva, V.T. Sulfonated carbon nanotubes as catalysts for the conversion of levulinic acid into ethyl levulinate. *Catal. Today* **2014**, *234*, 257–263. [CrossRef]

178. Chen, G.; Wang, X.; Jiang, Y.; Mu, X.; Liu, H. Insights into deactivation mechanism of sulfonated carbonaceous solid acids probed by cellulose hydrolysis. *Catal. Today* **2019**, *319*, 25–30. [CrossRef]
179. Pratama, A.P.; Rahayu, D.U.C.; Krisnandi, Y.K. Levulinic acid production from delignified rice husk waste over manganese catalysts: Heterogeneous versus homogeneous. *Catalysts* **2020**, *10*, 327. [CrossRef]
180. Perveen, F.; Farooq, M.; Ramli, A.; Naeem, A.; Khan, I.W.; Saeed, T.; Khan, J. Levulinic Acid Production from Waste Corncob Biomass Using an Environmentally Benign WO_3Grafted $ZnCo_2O_4$@CeO_2 Bifunctional Heterogeneous Catalyst. *ACS Omega* **2023**, *8*, 333–345. [CrossRef] [PubMed]
181. Xu, X.; Liang, B.; Zhu, Y.; Chen, J.; Gan, T.; Hu, H.; Zhang, Y.; Huang, Z.; Qin, Y. Direct and efficient conversion of cellulose to levulinic acid catalyzed by carbon foam-supported heteropolyacid with Brønsted–Lewis dual-acidic sites. *Bioresour. Technol.* **2023**, *387*, 129600. [CrossRef]
182. Covinich, L.G.; Clauser, N.M.; Felissia, F.E.; Vallejos, M.E.; Area, M.C. The challenge of converting biomass polysaccharides into levulinic acid through heterogeneous catalytic processes. *Biofuels Bioprod. Biorefining* **2019**, *14*, 417–445. [CrossRef]
183. Sarangi, P.K.; Singh, A.K.; Ganachari, S.V.; Pengadeth, D.; Mohanakrishna, G.; Aminabhavi, T.M. Biobased heterogeneous renewable catalysts: Production technologies, innovations, biodiesel applications and circular bioeconomy. *Environ. Res.* **2024**, *261*, 119745. [CrossRef]
184. Changmai, B.; Vanlalveni, C.; Ingle, A.P.; Bhagat, R.; Rokhum, L. Widely used catalysts in biodiesel production: A review. *RSC Adv.* **2020**, *10*, 41625–41679. [CrossRef]
185. Appaturi, J.N.; Andas, J.; Ma, Y.K.; Phoon, B.L.; Batagarawa, S.M.; Khoerunnisa, F.; Hazwan Hussin, M.; Ng, E.P. Recent advances in heterogeneous catalysts for the synthesis of alkyl levulinate biofuel additives from renewable levulinic acid: A comprehensive review. *Fuel* **2022**, *323*, 124362. [CrossRef]
186. Chaffey, D.R.; Bere, T.; Davies, T.E.; Apperley, D.C.; Taylor, S.H.; Graham, A.E. Conversion of levulinic acid to levulinate ester biofuels by heterogeneous catalysts in the presence of acetals and ketals. *Appl. Catal. B Environ.* **2021**, *293*, 120219. [CrossRef]
187. Maleki, B.; Talesh, S.S.A.; Mansouri, M. Comparison of catalysts types performance in the generation of sustainable biodiesel via transesterification of various oil sources: A review study. *Mater. Today Sustain.* **2022**, *18*, 100157. [CrossRef]
188. Global Heterogeneous Catalyst Market Size & Outlook. Available online: https://www.grandviewresearch.com/horizon/outlook/heterogeneous-catalyst-market-size/global (accessed on 5 August 2025).
189. Heterogeneous Catalyst Market Report 2025. Available online: https://www.researchandmarkets.com/report/heterogeneous-catalyst (accessed on 5 August 2025).
190. Global Carbon-Based Catalyst Supports Market Insights, Forecast to 2030. Available online: https://reports.valuates.com/market-reports/QYRE-Auto-36A9611/global-carbon-based-catalyst-supports2025:9611 (accessed on 5 August 2025).
191. Offerings, O.; Us, A.; Platform, I.; Trends, M.; Store, R. Bio-Based-Materials-Global-Market-Report 2025. pp. 1–18. Available online: https://www.thebusinessresearchcompany.com/report/bio-based-materials-global-market-report (accessed on 5 August 2025).
192. Wurster, S.; Ladu, L.; Arisaktiwardhana, D. Bio-Based Products. *Int. J. Stand. Res.* **2019**, *17*, 23–39. [CrossRef]
193. Julkapli, N.M.; Bagheri, S. Graphene supported heterogeneous catalysts: An overview. *Int. J. Hydrogen Energy* **2015**, *40*, 948–979. [CrossRef]
194. Saperi, N.Q.; Hassan, A.H.; Zainol, M.M.; Asmadi, M.; Mohamad Daud, A.R.; Yusof, M.Y.; Anggoro, D.D. Catalytic Reaction Study of Levulinic Acid Esterification To Ethyl Levulinate Using Modified Carbon Catalyst and Acidic Des. *Malays. J. Anal. Sci.* **2024**, *28*, 724–736.
195. Jędrzejczyk, M.; Soszka, E.; Goscianska, J.; Kozanecki, M.; Grams, J.; Ruppert, A.M. The Influence of Carbon Nature on the Catalytic Performance of Ru/C in Levulinic Acid Hydrogenation with Internal Hydrogen Source. *Molecules* **2020**, *25*, 5362. [CrossRef]
196. Zhao, Z.; Chen, H.; Zhang, W.; Yi, S.; Chen, H.; Su, Z. Defect engineering in carbon materials for electrochemical energy storage and catalytic conversion. *Mater. Adv.* **2023**, *4*, 835–867. [CrossRef]
197. Signoretto, M.; Taghavi, S.; Ghedini, E.; Menegazzo, F. Catalytic Production of Levulinic Acid (LA) from Actual Biomass. *Molecules* **2019**, *24*, 2760. [CrossRef]
198. Sessa, A.; Prete, P.; Cespi, D.; Scotti, N.; Tabanelli, T.; Antonetti, C.; Russo, V.; Cucciniello, R. Levulinic acid biorefinery in a life cycle perspective. *Curr. Opin. Green Sustain. Chem.* **2024**, *50*, 100963. [CrossRef]
199. Clauser, N.M.; Felissia, F.E.; Area, M.C.; Vallejos, M.E.; Gutiérrez, S. An energy-saving re-use strategy for the treatment of lignocellulosic biomass applied to the production of levulinc acid. *J. Clean. Prod.* **2020**, *257*, 120549. [CrossRef]
200. Hurst, G.; Peeters, M.; Tedesco, S. Integration of Catalytic Biofuel Production and Anaerobic Digestion for Biogas Production. In *Energy and Sustainable Futures, Proceedings of the 3rd International Conference on Energy and Sustainable Futures(ICESF), Coventry University, UK, 7–8 September 2022*; Springer: Berlin/Heidelberg, Germany, 2021; pp. 125–131. [CrossRef]

201. Clauser, N.M.; Gutiérrez, S.; Area, M.C.; Felissia, F.E.; Vallejos, M.E. Techno-economic assessment of carboxylic acids, furfural, and pellet production in a pine sawdust biorefinery. *Biofuels Bioprod. Biorefining* **2018**, *12*, 997–1012. [CrossRef]
202. Thakkar, A.; Shell, K.M.; Bertosin, M.; Rodene, D.D.; Amar, V.; Bertucco, A.; Gupta, R.B.; Shende, R.; Kumar, S. Production of levulinic acid and biocarbon electrode material from corn stover through an integrated biorefinery process. *Fuel Process. Technol.* **2021**, *213*, 106644. [CrossRef]

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