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Review

Design of Heterogeneous Catalysts for the Conversion of Furfural to C5 Derivatives: A Brief Review

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Abstract

Technological development made in the field of biomass application allows synthesizing several high-value products, such as furfuraldehyde. Furfural, produced through sequential hydrolysis and dehydration reactions from biomass, is considered a platform molecule and a precursor of several other chemicals and biofuels that are generated following reactions such as hydrogenation, hydrodeoxygenation, and decarboxylation. This review aims to reveal the environmental-friendly mechanisms followed for producing furfural derivatives and the design of catalysts and supports. Redox and acid-base properties of the molecules have been discussed. The stability, the details of the surface area, and the applications of the molecules to reduce the bottlenecks faced in the industrial production of bioproducts have been explored.

Keywords

Chemical Platforms; catalyst design; heterogeneous catalyst; support; active site; selectivity

1. Introduction

Currently, the world economy is primarily based on fossil fuels. Approximately 81% of the energy, fuel, electricity, and chemical products generated worldwide are obtained from fossil fuels [1]. The increase in the consumption of fossil fuels and the increase in the extent of generation of greenhouse gases and waste has prompted researchers to search for renewable raw materials that can be used in the industrial sector and have a lower impact on the environment than fossil fuels [2, 3].

The concept of biorefinery can be potentially used in chemical industries for the production of various environmentally friendly molecules. Lignocellulosic biomass can be used as a source of raw material for the production of fuels and chemicals, as it is readily available, boasts of good chemical composition, exhibits a renewable character, and is cost-effective [4, 5]. This matrix comprises of forestry waste, and industrial, and agricultural residues, such as sugarcane bagasse. This eliminates the possibility of competition between the processes of food and energy production. The complex structure comprises of lignin, hemicellulose, and cellulose, which need to be pretreated for the biomass to be converted into reactive components [6, 7].

Technological advances made in the field of application of biomass as a source of raw material make it possible to produce several high-value products, especially furfural (FF), that belongs to the group of furans. These compounds are extensively used in chemical platforms as they exhibit high reactivity [8]. FF can be produced by conducting sequential hydrolysis and dehydration reactions of xylans that are obtained from biomass. The compound can be used as an organic solvent and a precursor for several products, such as furfuryl alcohol (FA), 2-methylfuran (2-MF), tetrahydrofurfuryl alcohol (THFA), levulinic acid (LA), γ-valerolactone (GVL), and pentanediols (n-PeD) [8, 9].

The conversion of FF into high-value products is directly related to catalytic processes [10]. The composition and method of preparation of the catalysts, as well as the synergy between their redox, acid-base, and hydrothermal properties, dictate the efficiency of the highly selective conversion process. However, developing efficient catalysts for converting chemical products from biomass is still a challenge. The difficulty can be primarily attributed to the complexity in the alignment of catalytic properties and the diversity of products that can be obtained [11]. Thus, this review aims to discuss and expand knowledge on the design of heterogeneous catalysts for the conversion of furfuraldehyde into high-value-added five-carbon compounds.

2. Biorefinery

The concept of a biorefinery is based on the integrated system involving the conversion and recovery of raw materials derived from biomass (such as agricultural, industrial, and forest residues) into energy, fuels, chemicals, and materials. Biorefineries can be classified into three phases according to the type of raw material used, the processes used for the valorization of biomass, and the products generated [12, 13].

Phase I biorefineries operate in a more restricted way, use a single raw material, perform a single process, and generate a single product. Phase II maintains its limitation regarding the use of a single raw material but performs several processes and generates various products. The most advanced biorefinery is the phase III biorefinery, which, in addition to the flexibility of phase II, uses various types of raw materials, including lignocellulosic biomass. This provides a platform for the production of biofuels (bio-oil, bioethanol, and synthesis gas), biomaterials (hydrogels, fibers, and polymers), and chemicals (alcohols, furanic compounds, and flavorings) [2, 14].

2.1 Lignocellulosic biomass

Lignocellulosic biomass is composed of cellulose and hemicellulose (polymeric carbohydrates), and lignin (aromatic polymers). The corresponding percentages are approximately 45%, 25%, and 15% of all dry matter [2].

Cellulose is the primary and most important constituent of lignocellulosic biomass, and approximately 7.5×10^{10} tons is produced yearly. It is formed by homogeneous carbohydrates (D-glucose) linked together through β (1,4)-glycosidic bonds and hydrogen bonds (between polymers) and is widely used as a raw material for the production of biofuels, such as bioethanol [2, 6, 15].

Depending on the source of the raw material, lignin is the second largest constituent (in terms of the mass percentage) of lignocellulosic biomass. It is an aromatic compound with a complex structure formed by hydroxyphenylpropane monomers, namely sinapyl, coniferyl, and p-coumaryl. Although it consists of aromatic compounds of very promising biological origin, its structure, physical and chemical resistance, and insolubility in water make its valorization challenging [15].

Hemicellulose is the second most abundant polysaccharide present in lignocellulosic biomass. It consists of heterogeneous polysaccharides that include hexoses and pentoses, such as mannose, galactose, glucose, xylose, and arabinose. Several chemicals and physical and biological treatment methods are used to treat lignocellulosic fibers to simplify the matrix structure and transform the polysaccharides into smaller sugars for efficient conversion [6]. Hemicellulose, in addition to having an amorphous structure, has a lower degree of polymerization than cellulose. Due to this structure, it is more easily biodegradable and sensitive to pretreatment methods that are used for the conversion of biomass into biofuels and chemicals (such as FF) [12, 16].

2.2 Furfural

FF is a biological organic chemical compound (heterocyclic aldehyde) currently produced following the process of acid hydrolysis of lignocellulosic biomass (Figure 1). At the beginning of the 19th century, FF was obtained as a by-product of formic acid. Its large-scale production began in 1922, and it was produced by the Quaker Oats company. The company used agricultural residues such as sugarcane bagasse and corn cobs as raw materials for FF production [17, 18].

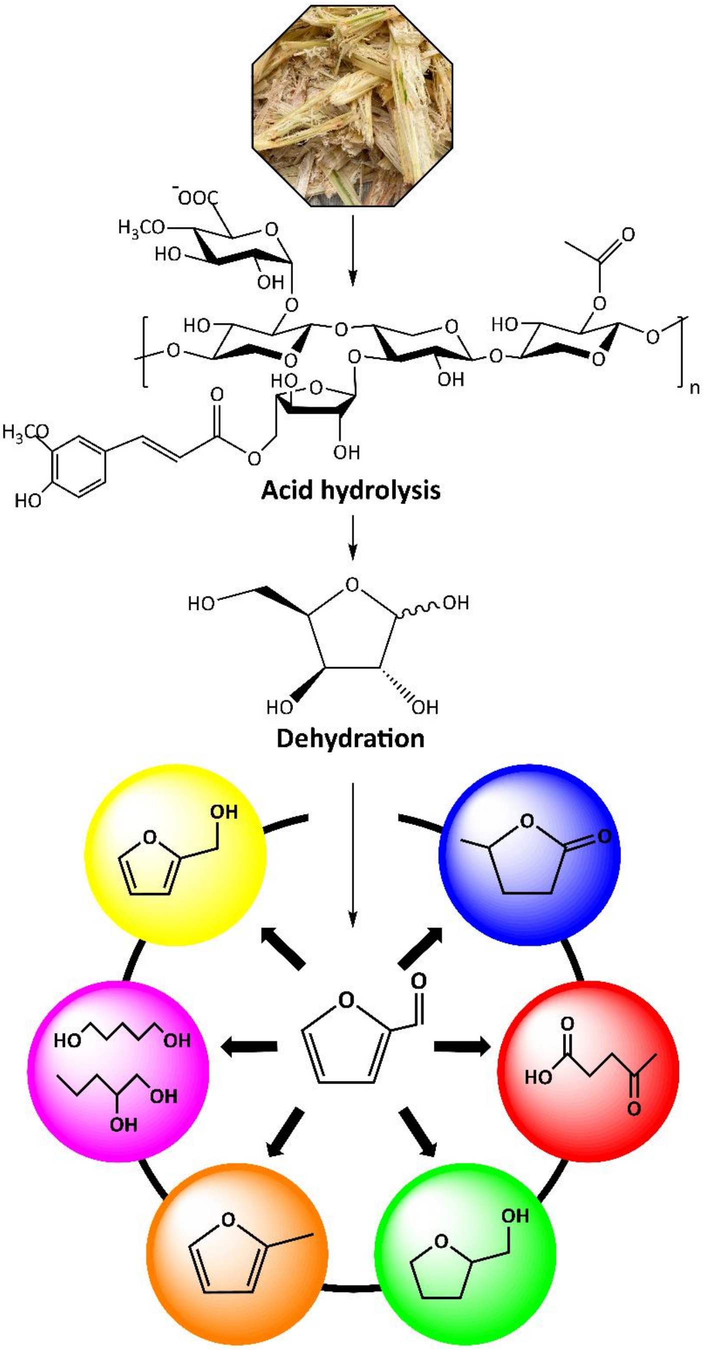

Figure 1 Conversion of biomass to furfural and its derivatives.

Currently, the FF market and the production of FF are dominated by three countries. China is the largest producer, followed by South Africa and the Dominican Republic. Together, these countries produce approximately 90% of the FF produced worldwide. In addition to being the largest producer, China is responsible for the largest consumer of FF. In 2013, the world demand for FF was 300 thousand tons, with a projected increase of 117% for 2020. In Brazil, FF import in 2016 was 28.6 thousand tons, with the United States being the largest supplier (satisfying 95% of all national demand). Though biomass is widely used for low-efficiency energy generation, Brazil exhibits great potential to produce high-value products from the waste generated from sugar biorefineries [19, 20].

FF is produced from agricultural residues, and although it can be obtained from petroleum derivatives following the catalytic oxidation of 1,3-butadiene, this process is not economically viable. This reinforces the need to develop production processes in biorefineries. There are several production routes for FF (from xylose), but the traditional way is associated with a pretreatment process that involves the acid hydrolysis of lignocellulosic biomass (Figure 1). The process uses mineral acids under the conditions of heating to release the pentoses. This is followed by the dehydration of carbohydrates [8, 21].

FF is used as a raw material for producing more than 80 types of five-and four-carbon fuels and chemicals. The chemicals are obtained following different reaction mechanisms such as oxidation, decarboxylation, hydrodeoxygenation, and hydrogenation. [18].

3. Design of catalysts for the conversion of FF and its derivatives

The development of heterogeneous catalysis was a major milestone for scholars seeking to improve preparation methods and increase reaction yields. The development of these catalysts also provided a platform for the reduction of expenses incurred during chemical production. New catalysts and unit operations for product purification were developed. Although the heterogeneous catalysts are highly interesting (as these catalysts can be potentially reused and ease the separation processes), the development of active and stable material is still challenging. This is especially true for biomass valorization reactions that demand a set of properties. The process also demands the use of various catalysts, compounds, and raw materials [22, 23]. Thus, it is challenging to design heterogeneous catalysts for the valorization of compounds from biomass. Table 1 presents various heterogeneous catalysts for the production of high-value-added compounds from FF.

Table 1 List of catalysts and products associated with FF valorization reactions.

Product	**Support**	**Active site**	**Synthesis method**	**Reaction conditions**	**C (%)**	**Y (%)**	**Ref.**
FA	CuFe oxide	Cu-Fe	Citric acid complexation	IPA[a]; 200 °C; 2 h; N_2 10 bar; ct[b] 0.2 g	96.1	89.6	[24]
	$CoFe_2O_4$	Zr	Precipitation	IPA; 160 °C; 4 h; ct 0.1 g	93.9	97.3	[25]
	Al_2O_3	Al	Precipitation	IPA; 150 °C; 1 h; N_2 8 bar; ct 0.05 g	96.5	95.5	[26]
	oxide-nitrogen-doped carbon	Al	Hydrothermal	IPA; 120 °C; 6 h; ct 0.05 g	99.3	96.6	[27]
	Hydrotalcite	Pt	Incipient wetness impregnation	H_2O; 30 °C; H_2 15 bar; ct 0.05 g	99.9	99.0	[28]
	SBA-15	Zr	Hydrothermal	IPA:H_2O 1:1; 130 °C; 6 h; N_2	18.0	45.0	[29]

				30 bar; ct 0.0312 g			
	TS-1 zeolite	Na-Cu	Cu encapsulation followed by Na ion-exchange	IPA; 110 °C; H_2 10 bar; ct 0.3 g	93.0	98.1	[30]
	ZrO_2-Al_2O_3	Zr-Al	Co-precipitation	IPA; 2 h; 10 bar N_2; 110 °C; ct 0.1 g	95.0	90.0	[31]
THFA	Al_2O_3	Ni-Cu	Co-precipitation	Ethanol; 190 °C; 4 h; H_2 50 bar; ct 2.85 g/h	100	63.0	[32]
	MgO-Al_2O_3	Ni	Co-precipitation	Ethanol; 170 °C; 3 h; H_2 40 bar; ct 0.04 g	100	90.1	[33]
	Al_2O_3	Ni-Cu	Co-precipitation	2-butanol; 140 °C; 4 h; H_2 30 bar; ct 0.1 g	100	98.0	[34]
	UiO-66	Pd	Wet impregnation	H_2O; 60 °C; 4 h; 10 bar; ct 0.05 g	100	100	[35]
	Mesoporous clay	Ni-MgO	Hydrothermal	$H_2$0; 140 °C; 4 h; H_2 40 bar; ct 0.6 g	100	100	[36]
	Hectorite	Ni-Cu	Hydrothermal	Ethanol; 140 °C; 4 h; H_2 40 bar; ct 0.6 g	100	95.0	[37]
	SBA-15	Ni-Co	Incipient wetness impregnation	Ethanol; 130 °C; 3 h; H_2 45 bar; ct 0.8 g	100	99.1	[38]
n-PeD^c	PVP + HDA	Ru	Stabilization of colloidal particles in situ	1-propanol; 125 °C; 48 h; H_2 20 bar; ct 0.02 mmol	100	36.0	[39]
	C-SBA-15	Ru	Hydrothermal	H_2O; 140 °C; 4 h; H_2 15 bar; ct 0.02 g	100	87.0	[40]
	ZnO	Ru_3Sn_7	Co-precipitation	IPA; 140 °C; 6 h; 35 bar; ct 0.1 g	100	96.9	[41]
	MgO	Ru	Impregnation	H_2O; 190 °C; 1 h; 30 bar; ct 0.06 g	100	47.7	[42]
	$La(OH)_3$	Ni	Co-precipitation	IPA; 150 °C; H_2 30 bar; ct 0.025 g	97.6	87.9	[43]
	CuMgAl	Cu	Co-precipitation	150 °C; 6 h; H_2 60 bar	84.1	83.7	[44]

2-MT	γ-Al_2O_3	Cu-Re	Sequential wetness impregnation	IPA; 200 °C; 6 h; H_2 20 bar; ct 20% wt	100	86.4	[45]
	γ-Al_2O_3	Co-Cu	Impregnation	IPA; 220 °C; 2 h; N_2 5 bar	100	54.1	[46]
	Norit_S (activated carbon)	Cu-Ni	Wet impregnation	IPA; 230 °C; 2 h; H_2 40 bar; ct 0.2 g	96.0	61.0	[47]
	N-RGO	Cu	Ammonia evaporation	4-dioxane; 240 °C, 4 h; H_2 15 bar; ct 10% wt	100	95.5	[48]
	Carbon	Ir	Wet impregnation	IPA; 220 °C; 5 h; H_2 6,9 bar; ct 10% wt	99.0	95.0	[49]
	$CuFe_2O_4$	Cu	Liquid-phase routes	IPA; 200 °C; 1.5 h; ct 0.1 g	99.4	97.6	[50]
	SiO_2	Cu	Ammonia evaporation	fixed-bed reactor; 200 °C; molar ratio H_2:FF = 10:1; ct 1 g.	100	94.5	[51]
LA	SiO_2	$H_3PW_{12}O_{40}$	Incipient wetness impregnation	IPA; 170 °C; 10 h; ct 50% wt	-	51.0	[52]
	SiNF	-SO_3H	Soft template	GVL:H_2O = 4.5:0.5; 120 °C; 2.5 h; ct 0.05 g	100	90.0	[53]
	SAPO-18	Si-Al	Hydrothermal with template	GVL:H_2O; 190 °C; 1.33 h; ct 20 g/L	-	70.2	[54]
	Dowex@Na	Ru	Ru complex treated with Dowex@Na via ion exchange	H_2O/Formic acid; 80 °C; 19 h; ct 1 mol%	100	100	[55]
GVL	NbP	Nb-Cu	Impregnation	H_2O/Formic acid; 160 °C; 3 h; ct 1.5% wt	92.7	67.0	[56]
	Hf-Al-USY	Al	Dealumination and solid-state ion-exchange	IPA; 140 °C; 12 h; N_2 10 bar; ct 0.05 g	100	64.9	[57]
	SAPO-34	Zr	Wet impregnation	IPA; 150 °C; 10 h; N_2 ~1 bar; ct 0.192 g	100	80.0	[58]
	Beta Zeolite	Zr-HPA	Dealumination and solid-state	IPA; 160 °C; 24 h; ct 0.34 mol/L	90.0	68.0	[59]

		ion-exchange				
VPA	Hf	Solvothermal	IPA; 180 °C; 14 h; ct 0.2 g;	100	81.0	[60]
MCM-41	Fe-Zr	Impregnation and calcination	IPA; 150 °C; 24 h; N_2 1 atm; ct 0.04 g	99.3	80.8	[61]
SBA-15	Zr-HPA	Hydrothermal	IPA; 170 °C; 11 h; ct 2.5 g/L;	100	81.0	[62]
KIT-5	Zr	Hydrothermal	IPA; 180 °C; 4 h; ct 0.1 g	94.0	40.1	[63]
SiSPH	Zr	Wet impregnation	IPA; 5 h; 180 °C; ct 0.2 g	98.0	64.0	[64]

a – 2-propanol; b – catalyst; c – the yield shown refers to all pentanediols formed.

3.1 Furfuryl Alcohol

FA is an organic compound that belongs to the furan family. It is one of the most important chemicals produced in biorefineries. It is primarily obtained during the production of resins [65]. It is classified as primary alcohol that contains a heteroaromatic furan ring. It is formed during the direct hydrogenation of FF [65, 66]. FA is primarily used during the production of foundry resins, alkanes, fuels, and food additives. It is also used as a precursor of fine chemicals during the production of ascorbic acid, levulinic acid, and lysine. It also finds its application in the field of the manufacture of lubricants [65-68].

Currently, the industrial production of FA proceeds through the selective hydrogenation of FF. The process proceeds in the vapor or liquid phase in the presence of copper chromite (Cr–Cu) as a catalyst [65, 69]. However, Cr–Cu-based catalysts undergo considerable deactivation during the process, both in the gaseous and liquid media. Immense attention should be paid to the disposal of the highly toxic Cr species. In addition, the use of H_2 gas as a hydrogen source increases the risks of FA production. The transport and storage methods should be taken care of as high pressures are employed during the reaction. These add to the complexity of the production process. Hence, new FA production routes have been proposed using chromium-free catalysts and alternative sources of hydrogen to make the production process safer and more sustainable [65-67].

It has been proposed that the hydrogenation of FF using copper-based catalysts involves the participation of the carbonyl oxygen on the metal surface through the formation of the η^1(O)-aldehyde bond (Figure 2). The furan ring is perpendicular to the metallic surface, and this orientation can be attributed to the repulsion between the aromatic rings and the superposition of the three-dimensional copper bands. Thus, hydrogenation can occur through two different routes, resulting in the formation of two types of intermediates. An alkoxide is formed when hydrogen attacks the carbonyl carbon, and a hydroxyalkyl unit is formed when hydrogen attacks the carbonyl oxygen. The second compound is more stable than the first [67, 70, 71].

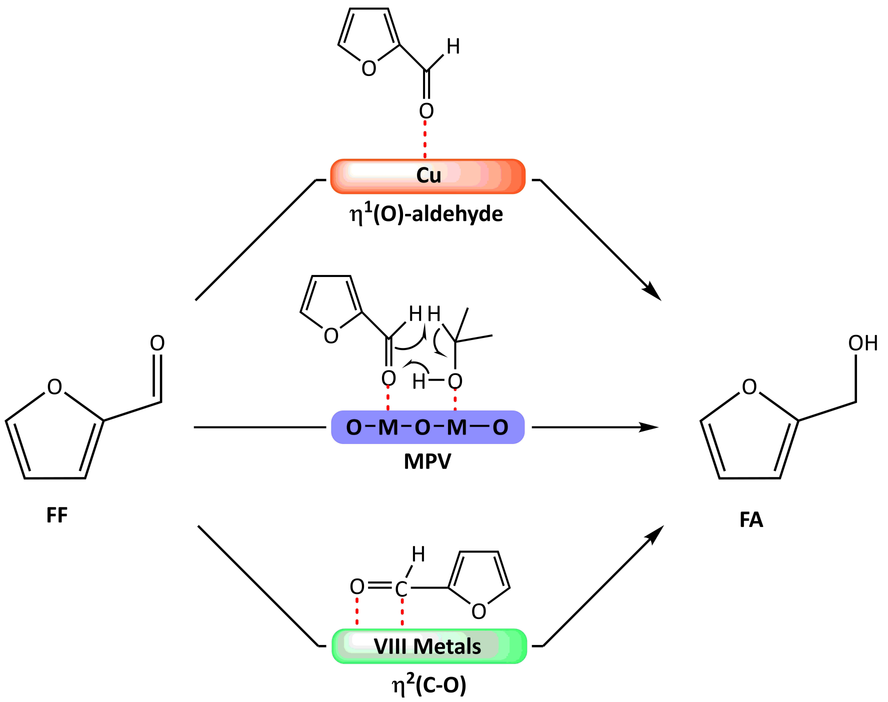

Figure 2 Hydrogenation of furfural (FF) to furfuryl alcohol (FA).

For metals belonging to group VIII (Ni, Pd, and Pt), adsorption between FF and the metallic surface occurs through a flat η^2(C-O)-type bond. The process can be used for the generation of various other products in addition to FA [67]. Hydrogenation can occur through the production of the hydroxyalkyl intermediate when these catalysts are used. This route followed for the formation of FA is analogous to the route followed in the presence of Cu. However, FF can be converted to furan following a decarbonylation reaction involving the formation of an η^2(C)-acyl bond as an intermediate. The production of 2-methyl furan via the hydrogenation of the alkoxide intermediate is followed by the deoxygenation and hydrogenation reactions of methylfuran [70].

Considering the low selectivity and stability of metals involved in the hydrogenation of FF to FA, various synthetic routes have been explored using bifunctional acid–base materials as catalysts. Alcohols function as hydrogen donors in the Meerwein–Pondorf–Verley (MPV) reaction. The MPV reaction is an alternative and sustainable method for the selective hydrogenation of ketones and aldehydes in the presence of various other functional groups [67, 70, 72].

The method is based on the transfer of a hydride and a proton from a donor (usually alcohols) to an acceptor (ketones and aldehydes) [73, 74]. The reaction proceeds through the formation of a six-membered ring between the hydrogen donor and its acceptor. Lewis acid sites interact with the C = O bond, activating the carbonyl carbon and the oxygen unit present in the hydroxyl group in alcohols. The basic Lewis sites interact with the hydrogen unit present in the donor compound, weakening the O-H bond and favoring the release of hydrogen. However, it is still challenging to reduce FF to FA and maintain the strength between acidic and basic sites [67, 70, 72]. Hence, researchers have sought to develop catalysts with metallic and acid–base sites that are stable and active.

CuFe-based catalysts were prepared by Kalong et al. [24] following a citric acid complexation method. The process of complexation was followed by heat treatment at different temperatures. Following the in-situ activation of the catalysts, active Cu_2O, Fe_3O_4, and metallic Cu phases were generated. The extent of conversion achieved for the catalysts treated at 600 and 700 °C was greater than the extent of conversion achieved using the catalyst treated at 800 °C. This can be attributed to the formation of large aggregates of particles at this temperature. The results obtained by conducting reuse tests revealed considerable deactivation of both catalysts from the third run. The extent of deactivation was the least for the catalyst heated at 700 °C. This reveals a stable structure.

Hou et al. [25] studied the conversion of FF to FA using acid–base catalysts. The magnetic structures (Co_2FeO_4, core; $Zr(OH)_4$, shell) with different molar ratios were synthesized following the hydrothermal treatment and precipitation methods. The core–shell structure that presented the best result was Zr@Co-2. This material could be used to achieve 87.1% conversion and 97.1% selectivity. The high conversion rate can be attributed to the high percentage of Zr in the structures. Consequently, it can be inferred that a large number of acidic and basic sites are responsible for the activation of FF and 2-propanol for catalytic hydrogen transfer. A study using pyridine-poisoned catalysts revealed that the conversion rate dropped from 87.1 to 44.3%, reinforcing the importance of acidic sites. Liu et al. [26] synthesized metallic oxides (MgO, ZrO_2, Fe_2O_3, and Al_2O_3) containing acidic and basic sites following the precipitation method to realize the hydrogenation of FF to FA following the catalytic hydrogen transfer method using different alcohols as the hydrogen source. The maximum extent of FF conversion and FA yield was achieved using 2-propanol, and this could be attributed to the low reduction potential and the low steric effect recorded for 2-propanol (compared to the other alcohols with a higher carbon chain). The maximum FF conversion rate and the highest selectivity for FA production under mild reaction conditions were achieved using Al_2O_3 as the catalyst, and this can be attributed to the high surface area and high density of sites.

More than twenty catalysts have been developed by Xu et al. [27] following the hydrothermal method. They used various metallic precursors and chitosan as carbon precursors. The catalysts were tested using alkali metals, alkaline earth metals, and transition metals such as Zr, Ti, Fe, and Zn, in addition to Al, Si, and Sn, among others. The maximum product yield was obtained using AlOx-NC. This effect is explained by the properties presented by the materials. A large amount of weak and medium acidic sites and the high basicity of the compounds compared to other transition metals can explain the observations. Furthermore, the addition of aluminum resulted in an increase in the surface area of the NC matrix from 0.96 to 154 m^2/g, increasing the availability of the active sites on the surface of the material. The catalyst was filtered hot, indicating its heterogeneity. It was also revealed that solubilized complexes did not drive the reaction.

Gao et al. [28] prepared a platinum-based catalyst supported on commercial hydrotalcite following the incipient wetness impregnation method using 3 wt.% of Pt. Although the use of non-precious metals has been the focus of catalyst design, the high catalytic activity of Pt is still the subject of many studies. The dispersion of the metal on the supports and the interaction of the metal with the support are the foci of interest. The experiment was carried out at 30 °C under a pressure of 15 bar of H_2. Water was used as the solvent. High degrees of conversion and excellent selectivity were achieved, and the activation energy (E_a) was 12.8 kJ/mol. Other catalysts were also prepared using Al_2O_3, MgO, and MgO-Al_2O_3. The best conversion was achieved using the hydrotalcite support. Such observations were linked to the typical structure of hydrotalcite, and the results revealed the excellent dispersion of Pt on the support.

Perez et al. [29] studied the direct conversion of xylose to FA using ZrSBA-15 catalysts prepared following the process of direct synthesis. They used 2-propanol as the hydrogen source. It was verified that the acidity of the material increased as the Zr content increased. The pyridine adsorption property was studied, and the predominance of Lewis acidic sites was revealed. For the sample characterized by a Si/Zr ratio of 195, it was observed that the isomerization of xylose to xylulose drove the process. 60% selectivity was achieved in xylulose. For the sample characterized by the Si/Zr ratio of 77, the direct conversion of xylose into FA could be achieved with a selectivity of 45%. FF and xylulose were the primary co-products. The effects of inhibition of catalytic activity, the drop in selectivity due to the presence of water, and the effect of different concentrations of 2-propanol were also discussed. Cao et al. [30] studied how alkaline species improved the catalytic performance of Cu nanoparticles encapsulated in TS-1 zeolites. The sample Na-Cu@TS-1, prepared following the in situ encapsulation method, presented excellent catalytic performance. The performance of this sample was better than the performance of non-encapsulated samples. The FF conversion rate achieved was 93%, and the FF selectivity was 98.1%. The addition of Na helped reduce the extent of leaching of the Cu species, and this was revealed by conducting recycling tests. The researchers reported that the Na species influenced the acid/base properties of the zeolite and acted as electron donors for the encapsulated Cu nanoparticles. This facilitated the activation of hydrogen during the selective hydrogenation of FF to FA.

Garca-Sancho et al. [31] studied mixed oxides (Al_2O_3 and ZrO_2) synthesized following the co-precipitation method in a basic medium. The oxides were used for the catalytic transfer hydrogenation of FF to obtain FA. 2-propanol was used as the source of hydrogen in the liquid phase. The best performance was obtained for the sample characterized by the Zr/Al ratio of 1. The FF conversion rate was >95%, and the FA yield was >90%. The researchers reported that the coexistence of the ZrO_2 and Al_2O_3 phases exerted a synergistic effect that maximized the number of acidic sites in this sample. This showed high selectivity toward FA and only promoted the reaction of interest.

3.2 Tetrahydrofurfuryl alcohol

THFA is obtained following sequential hydrogenation reactions involving furfural, as shown in Figure 3. THFA is an important intermediate obtained in the green form, and it can be used to produce several compounds. The biofuel tetrahydrofuran and the alcohols 1,2-pentanediol and 1,5-pentanediol are the most important products obtained from THFA [75, 76].

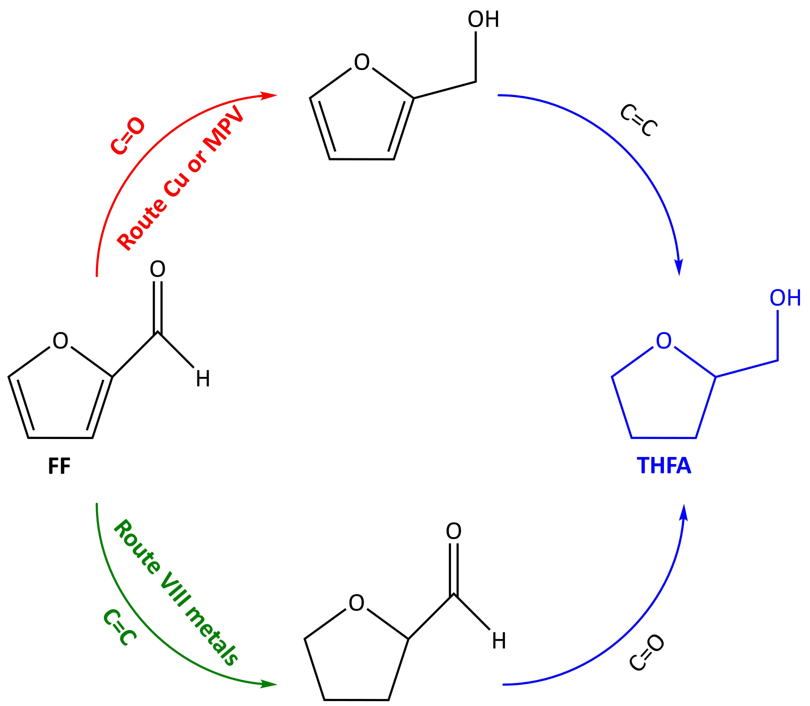

Figure 3 Hydrogenation of FF to tetrahydrofurfuryl alcohol (THFA).

The hydrogenation of FF to THFA occurs following two parallel routes. The first route involves the hydrogenation of the carbonyl atom, and the second route involves the hydrogenation of the ring. In both processes, the catalyst used dictates the viability of the routes. FA is produced following the process of carbonyl hydrogenation in the presence of acid–base catalysts or copper sites, as seen in the previous section. The group VIII metals can be used for hydrogenation. The second route involves the hydrogenation of the furan ring, and the group VIII metals (Ni, Pd, and Pt) are used as catalysts as the planar adsorption of the ring on the metals can be achieved using these metals [76].

Hydrotalcites are widely used as precursors for the development of mixed oxide catalysts. The applicability of these catalysts can be attributed to their properties. The ion exchange capacity, moderately high surface area, good pore distribution, and low production cost increase the applicability of the catalysts. Hydrotalcite-based Cu and Ni catalysts were prepared by Aldureid et al. [32] following the co-precipitation method. The catalysts were fabricated at a constant pH. The catalysts were tested under conditions of two different catalytic processes in the PFR reactor and the batch reactor. In the liquid phase, THFA was produced as the primary product with a Cu/Ni ratio of 1. In the PBR reactor, FA was the primary product with a selectivity of 61%. The sequential hydrogenation of FA and THFA was reported to be the primary route, and the product was selected based on the composition of the catalyst and the reactor used. Thus, it is possible to conclude that the degree of conversion and selectivity are not only influenced by the composition of the catalyst and the reaction conditions (such as temperature and concentration) but also by the type of processing and reactants.

Shao et al. [33] developed hydrotalcite-based catalysts following the co-precipitation method. The use of the Mg–Al hydrotalcite support with a mesoporous structure favored the dispersion of metallic Ni sites. This helped achieve a high FF to THFA conversion rate, and the high extent of conversion can be attributed to the strong adsorption of the C =C bond of the furan ring on the metallic Ni sites on the catalyst surface. As Fe is introduced into the mixture, the Ni–Fe catalyst starts to interact with the oxygen unit of the furan ring. This can be explained by the oxophilic character of the Fe species. The conversion to diols is evidenced by the hydrogenolysis reaction of FA, which results in a drop in the yield of THFA. Another Ni–Cu–Al hydrotalcite-based catalyst was fabricated by Rao et al. [34]. The Ni species participated in the reduction of the C =C bond of the ring and the C =O of the carbonyl group, while the Cu species participated only in the reduction of the carbonyl group. When the monometallic Ni–Al catalyst was used, 7% FF was converted to 50% FA and 35% THFA. Although the catalyst was efficient, the low selectivity for THFA and the high concentration of FA indicate that the active sites of the catalyst were completely involved in the reactions. This resulted in incomplete hydrogenation. The bimetallic catalyst (Ni1Cu1-Al1) presented a satisfactory performance for the reduction of FF to THFA, and this could be attributed to the presence of developed pores and a high degree of dispersion of the Ni and Cu species on the Al surface. The release of the Ni sites for the hydrogenation of the C =C bond also contributed to the process. It was observed that the Cu sites promoted the reduction of FF to FA.

Pd supported on UiO-66 was fabricated by Wang et al. [35] following the impregnation method. They used ethanol as the solvent during catalyst fabrication. Pd/SiO_2 and Pd/γ-alumina were also synthesized for comparison. The good extent of conversion achieved using the Pd/UiO-66 catalyst was explained by the greater degree of dispersion of the metal and the high extent of interaction between FF and UiO-66 (achieved via the adsorption between the C =O unit and the coordinately unsaturated sites present on the support). The results from the leaching test revealed that the catalyst was stable over four cycles, and a significant loss in yield was not recorded.

Sunyol et al. [36] impregnated Ni and MgO species into different mesoporous clays prepared following the hydrothermal treatment method for the hydrogenation of FF. The catalysts characterized by high acidity and containing low amounts of metallic centers favored deactivation and high selectivity, while the catalysts containing MgO contained a low percentage of metallic nickel. The addition of MgO neutralized the acidity of the support and favored the conversion and selectivity in THFA. The catalyst MK-10, containing 30 wt.% of MgO and 8.8 wt.% of metallic Ni, could be used to achieve excellent conversion and selectivity.

Sánchez et al. [37] studied mesoporous hectorites synthesized following the hydrothermal treatment method. The catalysts contained supported Ni, Cu, and Ni-Cu species for the hydrogenation of commercial FF to THFA. The use of the pure material resulted in low FF conversion (<33%) and zero selectivity toward THFA, and this could be attributed to the absence of the metallic phase. The use of the Ni–Cu catalyst characterized by a ratio of 1:1 resulted in 95% of selectivity in THFA. This could be explained by the formation of the Ni–Cu alloy, as low selectivities were obtained for the Ni:Cu ratios of 6:1 and 1:6. This was true under conditions of low NiCu alloy percentages. Among the monometallic catalysts, Cu–DH presented higher conversion and higher selectivity than Ni-DH. This could be attributed to the presence of large amounts of metallic phases in the material containing copper. This can be attributed to the fact that Ni was not completely reduced in the Ni–DH catalyst. Li et al. [38] also fabricated Ni-containing catalysts for THFA production. A series of monometallic and bimetallic Ni–Co catalysts characterized by different molar ratios were synthesized using the incipient wetness impregnation technique in SBA-15. The maximum extent of conversion and selectivity were obtained for the Ni-CoSBA-15 catalysts. The maximum value was recorded for the sample characterized by the Ni/Co ratio of 0.67. 100% FF conversion and 99.1% selectivity in THFA were achieved. The results could be attributed to the low extent of blockages and large pore sizes in $NiCo_2O_4$ that favored a uniform distribution of the Ni^0 and Co^0 species (active sites). These properties also promoted the inhibition of crystallite growth.

3.3 Pentanediol

Alcohols are among the most important products obtained from biomass. The five-carbon alcohols 1,2-pentanediol and 1,5-pentanediol are two of the most important compounds obtained from biomass. Currently, the industrial production of these alcohols involves redox reactions carried out in the presence of fossil fuels. These are produced from nonrenewable raw materials, and the process of producing pentanediols from petroleum is complex. Low selectivity is achieved. Therefore, FF is a potential raw material for the large-scale production of these alcohols, and this can be attributed to the wide availability of lignocellulosic biomass and the relatively simple production process [77].

The hydrogenolysis reaction is the simplest reaction that can be conducted to obtain pentanediols from biomass. In addition to the adsorption and hydrogenation of FF to FA on metallic catalysts, acid–base sites affect the bond cleavage position and the selectivity of the reaction (Figure 4).

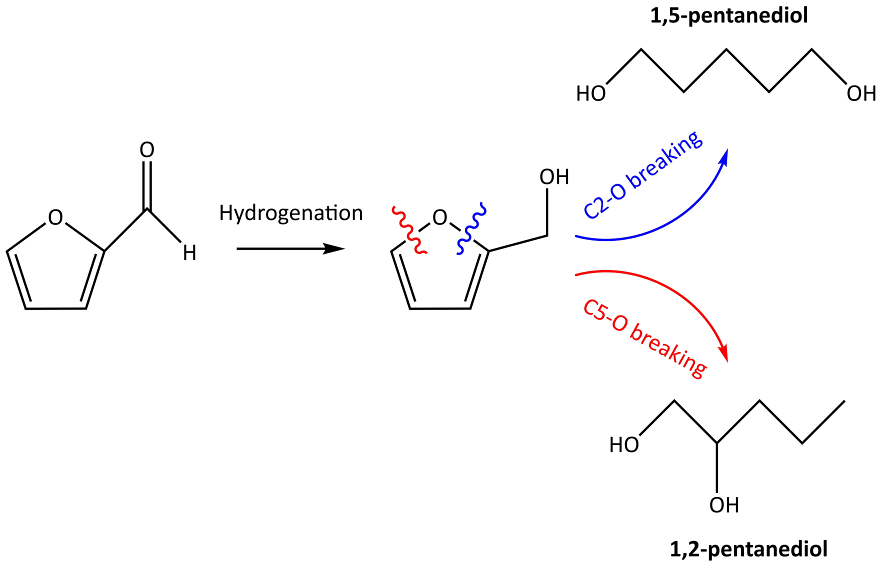

Figure 4 Hydrogenolysis of FA to pentanediol.

Bruna et al. [39] prepared colloidal Ru particles with polyvinylpyrrolidone modified with different organic compounds to produce 1,2-PeD and 1,5-PeD from FF, FA, and THFA. The amine-modified Ru/PVP catalyst could be efficiently used for the production of n-PeD directly from FF. The yield was recorded to be 36%, and the yield could be attributed to the efficiency in the hydrogenation of the C =O bond in FF. After 5 h, the hydrogenation of the C =C bonds of the ring was initiated. Although an efficient hydrogenation process could be conducted using Ru, the formation of acetal limits the selectivity of the process. This can be attributed to the low extent of the formation of acetal in the presence of a basic ligand. The authors highlighted that although the catalyst was not suitable for industrial applications, given its low activity and reusability, the process of amine modification could be used to modulate the selectivity of the system. Cui et al.

[40] prepared Ru-based catalysts by impregnating metal nanoparticles into a sulfonated carbon layer coated with SBA-15 for the selective hydrogenation of FF to n-PeD. The Ru/C-SBA-15 catalyst showed the best catalytic activity, with a total conversion of FF and 87% yield in 1,4-PeD. This was attributed to the coordination interaction between the sulfonic acid groups and the adjacent Ru sites. The synergy between these species endowed the Ru sites with high electron density, which in turn promoted better H_2 dissociation. This helped promote the sequential hydrogenation of the intermediates. In addition, the catalyst also exhibited good durability. Appreciable changes in its properties were not observed over six cycles.

Ru, Sn, and Zn-based catalysts were developed by Upare et al. [41] following a co-precipitation method. The Ru_3Sn_7/ZnO catalyst showed high activity for the hydrogenolysis of FF in 1,2-PeD. The yields of 84% and 12% for 1,5-PeD were achieved. The Sn2 + and Sn4 + species played an important role in the adsorption of FF on the catalyst surface. The species promoted the activation of the carbonyl group for further hydrogenolysis. ZnO helped achieve strong interaction and dispersion of the active phase. The DFT technique was used to study the mechanism of formation of 1,2-PeD, and it was verified that the scission of the α-C−O bond was favored for this compound. This helps achieve high selectivity in Ru and Sn species in the alloys (Ru_3Sn_7). Yamaguchi et al. [42] studied several Ru catalysts supported by different materials fabricated following the process of impregnation. Supports such as Al_2O_3, ZSM-5, CeO_2, TiO_2, graphite, ZrO_2, and MgO were tested, and the best yield was achieved when Ru/MgO was used and water was the solvent. The dispersion of the active Ru sites and the basic sites from the support were responsible for the greater selectivity of 1,2-PeD in water. It was also observed that 1,2-PeD was not obtained when the reactions were catalyzed by PD/C.

Al-Yusufi et al. [43] prepared Ni-based catalysts for the conversion of bio-based THFA to 1,5-PeD. The lanthanide catalysts, La, Sm and Pr, and Ni, were prepared following a simple co-precipitation method. Only the catalysts reduced with Ni0 were active for the reaction, and the basicity of the support dictated the deprotonation of the raw material. It also played a major role in the initiation of the hydrogenolysis process.

Lamellar double oxides derived from CuMgAl hydrotalcite were synthesized by Fu et al. [44] following the co-precipitation method. Urea was used as a precipitating agent, and the oxides were generated under conditions of heat treatment under conditions of varying calcination temperatures. The CuMgAlO-S3 catalyst heat-treated at 500 °C showed the best result, and 4.1% FF conversion and selectivity were achieved for 1,2-PeD. The corresponding values were 55.2 and 2.5% for 1,5-PeD. The Cu^+ species were responsible for the adsorption of FF, while the acid–base sites influenced the selectivity of the diols and the process of ring opening. The catalyst was reused over five cycles, and the conversion efficiency was maintained.

3.4 2-Methylfuran

2-MT is one of the most important products produced from FA. It is primarily used as a solvent and in the fuel industry as it is an excellent gasoline additive characterized by a high-octane number. It is derived from a renewable matrix, and the performance of 2-MT is significantly better than the performance of other biofuels. It can also be used directly to drive internal combustion engines [78, 79].

FF can be adsorbed in different ways on metallic catalysts or their oxides. The method of adsorption depends on the nature of the active sites. Results from DFT studies reveal that 2-MT can be produced following several competing routes: (i) through the direct dissociation of the C =O and C-H bond or (ii) through the hydrogenation of the carbon of the C =O bond, generating an alkoxy intermediate [80]. A mechanism involving the use of catalysts with acid–base and metallic sites is also proposed (Figure 5) [78].

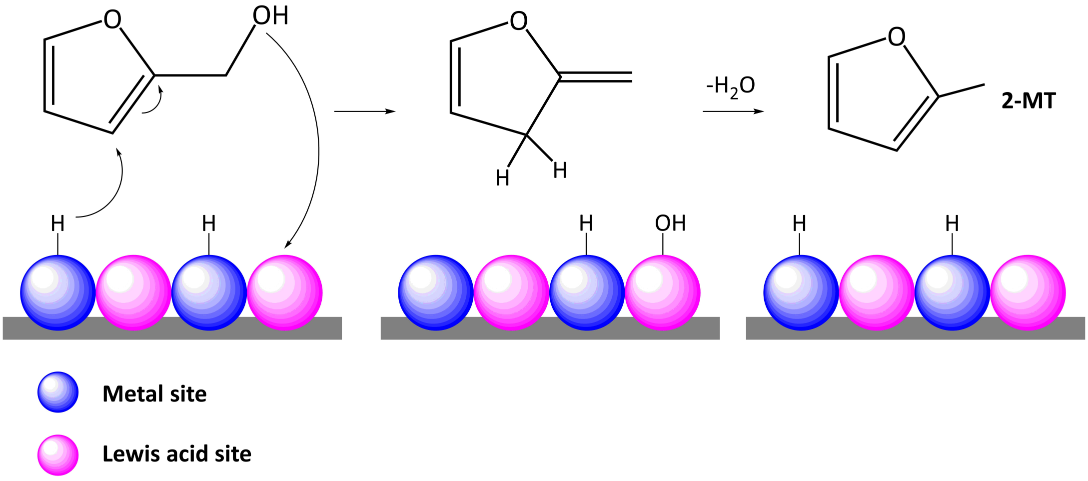

Figure 5 Production of 2-methylfuran (2-MT) from FA using heterogeneous catalyst.

Chuseang et al. [45] investigated catalysts with different proportions of Cu–Re on γ-alumina. The insertion of Re with the Cu:Re molar ratio of 1:0.14 significantly increased the selectivity of 2-MT. The high selectivity could be attributed to the oxophilic property of the material, which could promote the hydrogenolysis of the C-OH bond and the synergistic effect in the presence of copper. Higher concentrations of Re did not result in higher selectivity for 2-MT, and this could be attributed to the low dispersion of the active sites and the process of inhibition by Re species. The catalyst was also subjected to a reuse test, and it was observed that the catalyst remained stable over at least four consecutive cycles. Kalong et al. [46] prepared mono-and bimetallic catalysts based on Ni, Cu, and Co supported on γ-alumina following the impregnation method. The catalysts were tested against the catalytic hydrogen transfer reaction (from FF to FA and 2-MT) using 2-propanol as the hydrogen donor. The CoCuAl catalyst showed the maximum selectivity for 2-MT. A 54.1% selectivity was recorded, which was significantly lower than previously reported values. This can be explained by the presence of a combination of Cu^0 and Cu^+ sites on the surface of the material. These sites preferentially promote the hydrogenation of the C =O bond in the presence of the C =C bond. An increase in temperature resulted in an increase in the selectivity for 2-MT. This indicated the possibility of hydrogenolysis of the C-OH bond in the presence of copper sites. However, the process was inefficient in the absence of H_2. The reuse test without catalyst reactivation showed a considerable reduction in selectivity for 2-MT. The FTIR-Py profiles were analyzed, and the results revealed a reduction in the intensity of the peaks at all positions. This could be attributed to the reduction of the Lewis acidic sites. Results obtained using the TGA technique revealed high extents of weight losses, and this could be attributed to the fact that the carbonaceous compounds were adsorbed on the catalyst surface, resulting in a decrease in the availability of active sites.

In addition to ceramic materials, several organic compounds have been studied as adsorbents, supports, and catalysts. Activated carbons and carbon foams have been widely studied in this regard as they are cost-effective and are characterized by a high surface area. Varila et al. [47] prepared carbon foams from forest residues and tannic acid. They impregnated the system with 5/5% Cu/Ni (dry). The maximum 2-MT yields were achieved using Ni/Cu catalysts supported on carbon foam treated with nitric acid and commercial activated carbon. The yields were 57% and 61%, respectively. The authors reported that the high selectivity could be potentially attributed to the use of a large amount of oxygen in the support. The presence of a large amount of oxygen affects the extent of adsorption of the reactants on the catalyst surface. Although the extent of production of 2-MT in the presence of Ni is lower than the extent of production achieved using noble metals, the existence of the active sites based on Cu (Cu^0, $Cu^{+,}$ and Cu^{2+}) promotes high selectivity. Geng et al. [48] prepared Cu-and carbon-based catalysts using reduced graphene oxide as support. The best yield for 2-MT was achieved using the Cu-Cu_2O/N-RGO catalyst (15 wt.%). The selectivity was attributed to the good dispersion of the Cu species on the carbon structure and the high acidity resulting from the adsorption of NH_3. The material was also subjected to a reuse test, and the results revealed that the extent of conversion and selectivity were maintained for 5 cycles. The results revealed that the system was active and stable under the reaction conditions. The production of 2-MT was also studied by Date et al. [49]. The researchers used an Ir catalyst supported on carbon to fabricate the system following the wet impregnation. Analysis of the XRD pattern did not reveal the presence of a peak corresponding to Ir. This revealed that the metal was well dispersed on the support. The catalyst containing 5% Ir/C could be used to achieve good conversion (99%) and yield (95%) for 2-MT. The high conversion and selectivity were attributed to the Ir^0 species, which resulted in the formation of FA as intermediates through the π bond of the formyl group. The subsequent cleavage of the C-OH bond by the IrO_2 species was also recorded. Another plausible explanation for the formation of 2-MT would be the protonation of FA in the presence of the Bronsted acid sites of the 5% Ir/C catalyst and the subsequent dehydration and hydrogenation of the formed carbocation. In addition, a catalyst leaching test was performed under conditions of hot filtration, and the product was subsequently analyzed using the ICP-OES technique, confirming that the metal was not leached.

Other ceramic materials with naturally occurring structures are also used as catalysts and supports because of their low cost and the versatility in their morphology and composition. Inverted spinels of the type MFe_2O_4 (M = Cu, Ni, and Fe) were prepared by More et al. [50] following a liquid phase route. These were used as catalysts for the production of 2-MT from FF. 99.4% conversion and 97.6% selectivity for 2-MT were achieved when the $CuFe_2O_4$ catalyst was used. The other catalysts, $NiFe_2O_4$ and Fe_3O_4, showed better selectivity for hydrogenation. Results obtained using the DFT technique revealed that the extent of interaction achieved using FF (with Fe) was higher than the extent of interaction achieved using other systems. It was assumed that FF interacted with Fe^{3+}. 2-propanol interacted well with the Cu and Ni sites, and the M^{2+} metals allocated in the octahedral sites of the inverted spinel control the selectivity of the products. Fu et al. [51] synthesized a SiO_2/Cu catalyst using the ammonia evaporation method to produce 2-MT in the vapor phase. Among other synthetic techniques, ammonia evaporation was found to be better than other methods, and this could be attributed to the increase in the $Cu^+/(Cu^0 + Cu^+)$ ratio attributable to the formation of Cu phyllosilicates. The higher concentration of Cu^+ resulted in greater oxophilicity and, consequently, a greater number of weak Lewis acidic sites on the surface of the support. These sites promoted the selective formation of 2-MT through the cleavage of the C-OH bond of the FA intermediate.

3.5 Levulinic acid

LA is an organic acid of formula $C_5H_8O_3$ that can be obtained from biomass [81]. LA is considered a platform chemical due to its reactivity and potential to generate various products under conditions of hydrogenation, oxidation, esterification, etc. Its derivatives have wide applicability in various industries. These compounds can be used for the production of drugs, fungicides, pesticides, fuel additives, etc. [82, 83].

LA was synthesized in the first half of the 19th century using fructose as the raw material and HCl as the catalyst. However, it was not until 1956 that the product was recognized as a potential platform chemical. In 2004, it was designated as one of the most promising five-carbon compounds by the US Department of Energy and the US Department of Agriculture [83-85]. Figure 6 presents a schematic representation of the process of LA production from FA under conditions of hydration and dehydration.

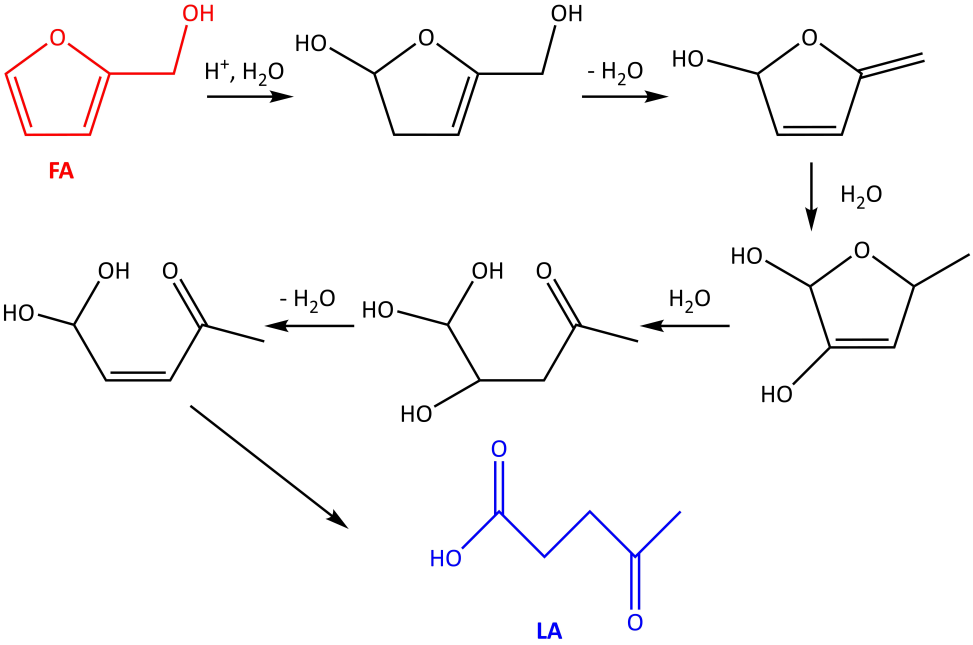

Figure 6 Production of levulinic acid (LA) from FA.

Currently, LA can be obtained from a wide range of raw materials derived from biomass. LA can be obtained following two primary production routes [81]. The first route involves the use of cellulose, which can be converted into 5-hydroxymethyl furfural using an acid catalyst. The second route involves the production of FF via acid hydrolysis and the subsequent dehydration of the five-carbon sugars extracted from hemicellulose [81, 83]. Although the route involving cellulose is the most popular, the use of furfuraldehyde as a raw material for LA production is interesting due to its economic importance [85].

Nandiwale et al. [52] developed silica-supported heteropoly acid catalysts to achieve the one-pot conversion of FF to LA. With the optimized reaction conditions, a yield of 51% was achieved. This could be attributed to the coexistence of the Lewis and Bronsted acidic sites. While Lewis acid–base sites are responsible for the hydrogenation of FF to FA under conditions of catalytic hydrogen transfer, Bronsted acidic sites promote the hydrogenolysis of FA to LA. The catalyst remained stable for three consecutive cycles and lost most of its activity in the fourth cycle. This could be attributed to the decrease in the total acidity and the decrease in the number of Bronsted sites under conditions of leaching of $H_3PW_{12}O_{40}$. The yield reported by Wang et al. [53] was higher than the yield reported previously when a sulfonated silica catalyst was used in a mixed solvent system (GV–-H_2O). The catalyst proved to be highly efficient for converting FA to LA, and the efficiency could be attributed to the high concentration of the Bronsted acid sites (attributable to the SO_3H group) that were necessary for the efficient conduction of the hydrogenolysis reaction. However, after three cycles, the conversion efficiency of the catalyst dropped drastically, and this could be attributed to the deposition of humins on the surface of the catalyst. The deposition of humins prevented access to the active sites. Another silica-based material was developed by Li et al. [54], and this system was used for the direct production of LA from biomass. SAPO-18, characterized by different Bronsted to Lewis site ratios, was prepared following the hydrothermal method using *N*,*N*-diisopropylethylamine as a template. The catalysts have a high surface area of 331.4 m^2/g and variable acidity according to the Si/Al molar ratio. The Bronsted/Lewis acid site density can be represented as SAPO-18–2 > SAPO-18–1 > SAPO-18–0.5. The SAPO-18 system characterized by a B/L ratio of 0.17 provided a better LA yield (70.2%), and this could be attributed to the high content of Bronsted acids that promoted the hydrolysis of the reagents. In addition, the catalyst proved to be stable under the reaction conditions. The yield obtained following the regeneration of the catalyst under conditions of heat treatment was maintained. However, it is worth mentioning that the raw material used during the production process was biomass. The LA yield was influenced by the production routes for the production of FF and 5-hydroxymethyl furfural.

Alshaikh [55] developed Ru-based catalysts following the complexation and ion exchange methods using Dowex@Na resin. The catalyst was tested for catalytic hydrogen transfer reaction using formic acid as a hydrogen donor for the hydrogenation of FF. The catalysts exhibited high catalytic activity and selectivity for LA production. The catalysts were highly stable, and they were tested for four runs. A significant change in yield was not observed. The proposed mechanism for the production of LA was divided into two steps: the first involved the formation of the Ru hydride and the second step involved the dehydration and acid hydrolysis reactions that resulted in the ring opening. Fang et al. [56] proposed another method for LA synthesis, and this method was based on the availability of the Bronsted acid sites on the NbP-supported copper catalysts fabricated following the impregnation method. Other catalysts (Cu/SiO_2 and Cu/Al_2O_3) were also prepared for comparison. The Cu/NbP catalyst was characterized by a higher Bronsted acidity among all the catalysts tested and, and consequently, a higher yield could be achieved. The proposed mechanism is divided into three steps: 1) FA production from the hydrogenation of the C =O bond in the presence of H_2 produced at the Cu^0 sites; 2) the protonation of FA by the Bronsted acid sites of the support, and 3) the hydration of FA to LA. Furthermore, the Cu/NbP catalyst can be used a maximum of four times, with a slight decrease in the LA yield attributable to the leaching of the Cu species.

3.6 γ-Valerolactona

Concerns about environmental health have led to the development of new, sustainable, low-cost, and low-toxicity green solvents [86]. GVL has attracted immense interest due to its ecotoxicity, biodegradability, low melting point, and high boiling point. Moreover, the efficiency of this system is comparable to the efficiency of other common solvents such as acetonitrile and dimethylformamide [86, 87]. Due to its versatility, GVL has also been used as a biofuel and additive in the food industry [87, 88].

GVL can be produced from biomass derivatives following two conventional routes (Figure 7). The most studied route is based on the hydrogenation and dehydration reactions of LA and its esters. This route generates two different intermediates depending on which reaction occurs first [87, 89]. The second route involves the hydrogenation of FF to FA and the subsequent etherification of the product. The ether is transformed into isopropyl levulinate (IPL) following the processes of hydrolysis and furan ring opening. Finally, IPL is reduced under conditions of the MPV reaction and converted to IPVH. Following this, lactonization takes place to form GVL [89, 90]. The conversion of FF to GVL has been less explored, and this can be attributed to the high complexity of the reaction system, the presence of several intermediates, and the need for catalysts containing Lewis/Bronsted acid sites and metallic sites. Further studies should be conducted to understand the necessary properties of the reaction [89-91].

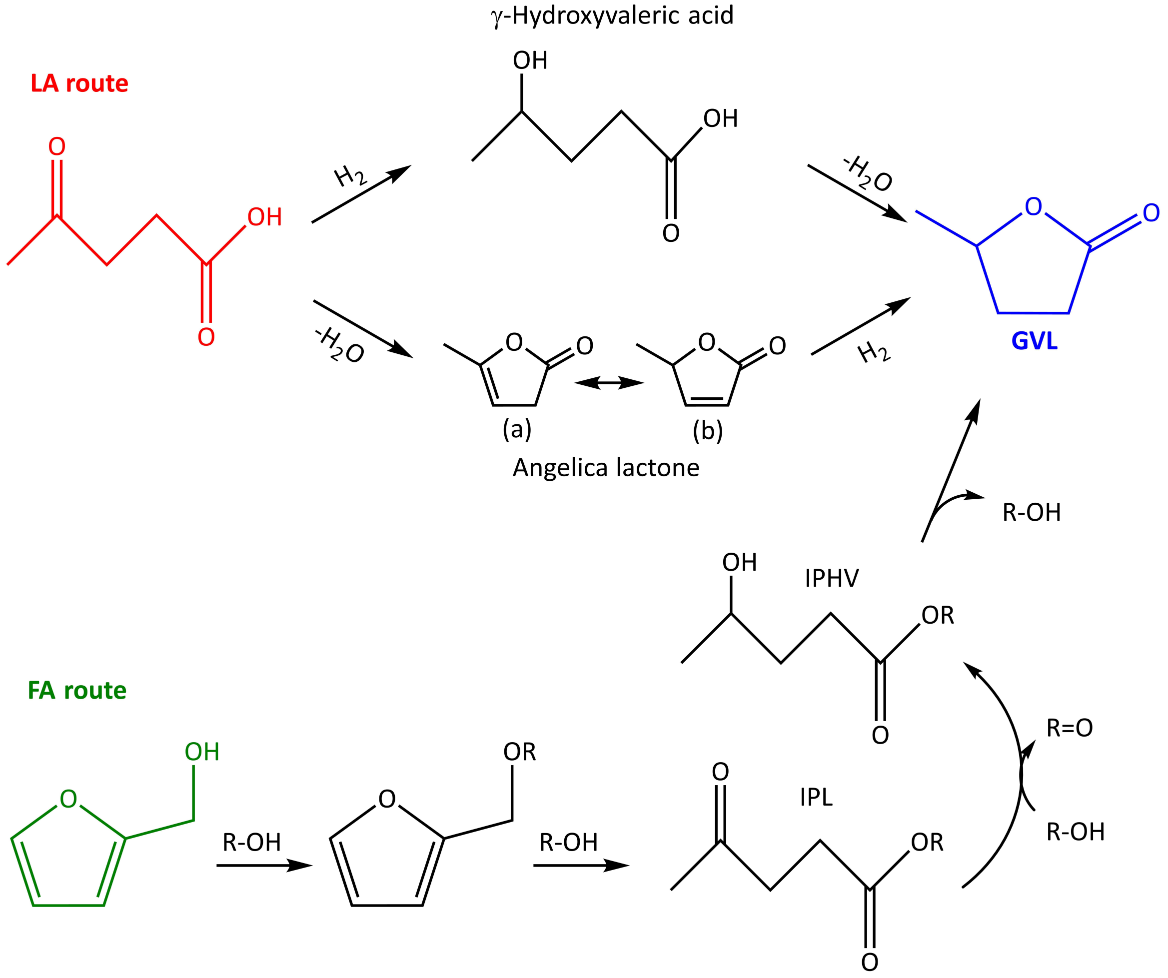

Figure 7 Mechanism of GVL formation from levulinic acid and FA.

Tang et al. [57] developed Hf-Al-USY catalysts using commercial H-USY dealumination and Hf impregnation methods for application in the direct conversion of FF to GVL. The balance between the Bronsted and Lewis acidic sites in the samples (evidenced by pyridine adsorption) and the improvement in the extent of mass transfer explain the efficiency of production of GVL from FF.

The effect of cooperation between the Lewis and Bronsted acidic sites in the cascade reaction promoted the conversion of FF to GVL and the hydrolysis reaction. Consequently, the ring opening process, which occurred in the presence of the Bronsted acidic sites attributable to the presence of the Al species, and the hydrogenation of the system under conditions of catalytic hydrogen transfer (through the Lewis acid sites of Hf) occurred. Good catalytic activity was retained after heat treatment, allowing the reuse of the compound.

Li et al. [58] used zeolites and studied zirconium phosphate-based catalysts supported by SAPO-34 to convert FF to GVL in isopropyl alcohol following a series of cascade reactions. The acidic properties of the material were inferred by analyzing the TPD-NH_3 and Py-FTIR profiles. The results revealed the chemical nature of the acidic sites. It was revealed that the Lewis sites were produced by Zr-O-P or unsaturated Zr bonds, and the Bronsted sites were formed in the presence of Si-(OH)-Al. The success of the FF–GVL conversion reaction was attributed to the equivalent balance between the Bronsted and Lewis sites. the balance was obtained by the fit between the Zr/P species loaded onto the support. The sample characterized by the Zr/P ratio of 1 exhibited the best performance, providing a selectivity of up to 80% for the production of GVL from FF. Leaching/recycling tests revealed that the active species were not leached. The GVL selectivity dropped by 20% over 6 cycles without regeneration. Following catalyst regeneration, the selectivity increased to 75%. Winoto et al. [59] prepared Zr-Beta zeolites following the solid-state ion exchange methods. They impregnated phosphotungstic acid (HPW) and silicotungstic acid (HSiW) into the systems. The study demonstrated that the incorporation of heteropolyacids in the zeolite structure results in an increase in the yields of GVL, and the yields were higher than the yields recorded for Zr-Beta. This was explained by the increased rate of the hydrolytic ring-opening reaction that was promoted by the Bronsted acidic sites of the species that were impregnated and the synergy between the Lewis acidic sites of the Zr species present in the material. The HPW/Zr-Beta sample showed 90% FF conversion and 68% GVL selectivity.

The use of organophosphate polymers has also attracted the attention of researchers because these systems exhibit interesting catalytic characteristics, as reported by Tan et al. [60]. Several Hf-based organophosphate polymers fabricated using vinyl phosphonic acid (VPA) and p-toluenesulfonic acid (p-TSA) were synthesized following a solvothermal method. The quantity and strength of the Lewis and Bronsted acidic sites, as well as the surface area and pore volume, were regulated by adjusting the precursor contents. The optimal VPA:Hf:*p*TSA ratio was (1:1.5:0.5), and the maximum yield recorded was 81%. The catalyst showed good thermal stability and was reused four times without significant yield loss.

Gao et al. [61] prepared MCM-41-based mesoporous silica coated with ZrO_2 and Fe_3O_4 nanoparticles for the conversion of FF to GVL. The incorporation of Fe_3O_4 imparted the catalyst with strong magnetic properties. This also resulted in the adjustment of acidity to promote GVL production. The ZrO_2 species facilitated the catalytic transfer hydrogenation rates from FF to FA and from IPL to GVL and resulted in the selectivity of 85% in GVL. The catalyst could be renewed. It was easily recovered by the application of an external magnetic field. Hence, it was possible to reuse it five times without realizing a significantly high loss of conversion. Srinivasa et al. [62] studied SBA-15 mesoporous silica catalysts, prepared following the hydrothermal method, and containing zirconium species and charged tungstophosphoric acid to realize the conversion of FF to GVL. The complete conversion of FF and the GVL yield of 81% was achieved using the 10%TPA/20%Zr-SBA-15 system. The results could be attributed to the high proportion of Lewis acidic sites. The number of Lewis acidic sites was higher than the number of Bronsted sites, and this could be attributed to the addition of W and the strong interaction between the hydrogen donor alcohol and the active sites of Zr. He et al. [63] investigated the applicability of KIT-5 mesoporous silica, incorporated with zirconium, in the field of producing GVL from biomass, including FF. The Zr-KIT-5 (10) system functioned as a catalyst during the direct conversion of FF to GVL. The GVL yield was recorded to be 40.1%, and isopropyl levulinate was the primary co-product. The yield of the co-product was recorded to be 21.2%. The results could be attributed to the presence of double Bronsted and Lewis acidic sites, which play extremely important roles in cascade reactions. A study of the conversion of FF to GVL using Zr on silica spheres was carried out by García et al. [64]. Silica spheres were prepared using triethanolamine and hexadecyltrimethylammonium bromide as guides and tetraethyl orthosilicate as silica source. Zr was incorporated into the silica matrix following the wet impregnation method using different concentrations of Zr. The process of adsorption of pyridine and ammonia was characterized, and the results confirmed the generation of Lewis and Bronsted acidic sites. Pure silica beads and ZrO_2 were tested, and the conversion of the compound to GVL was not confirmed. The ideal concentration was 7 wt.% of Zr on silica. The efficiency of the system was comparable to the efficiency of the zeolite Y-based catalysts.

4. Conclusions

The need to change the process of producing chemicals using renewable matrices from lignocellulosic biomass to address environmental issues and solve the problem of decreasing fossil fuel reserves has been reported. The use of fossil fuels as currency in the international market results in economic and political instabilities. Under these conditions, FF presents itself as a chemical platform. It can be used as a precursor of a variety of chemicals that can be used directly as biofuels or gasoline additives and indirectly as intermediates for the production of resins, plastics, pharmaceuticals, fertilizers, pesticides, etc.

The importance of the design of catalysts has been reported. The roles of the catalyst properties, synthesis methods, and composition of the catalysts on the yield and selectivity have also been explored. The influence of the balance between active sites (acid–base or metallic), the stability of the supports, and other properties of the catalysts have been studied. Further studies need to be conducted to develop a stable, active, selective, and cost-effective heterogeneous catalyst that can be used in the industry.

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Author Contributions

Gabriel S. Viana – contextualization of the theme, elaboration of the writing, organization of data, elaboration of supplementary material; Rosenira S. da Cruz – orientation, elaboration of the writing, assistance, and literary review; Gabriel P. da Silva – elaboration of the writing and organizing the data; Jorge A. E. L. Bonfim – orientation and organization of data; Miriam S. Tokumoto – orientation and literary assistance; Fernando C. Rangel – orientation and literary assistance; José F. S. de C. Filho – orientation and literary assistance.

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Competing Interests

The authors have declared that no competing interests exist.

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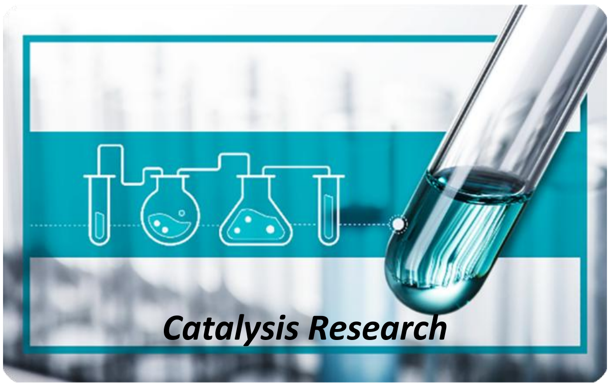
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