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Review

Some Insights into the Use of Heterogeneous Copper Catalysts in the Hydroprocessing of Levulinic Acid

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Abstract: Levulinic acid and its esters are close to being extensively produced through consolidated industrial processes, thus playing a central role in biobased industries producing commodities within the principles of the circular economy. One of the main pathways of levulinic acid and ester valorization is their transformation with hydrogen to obtain γ-valerolactone, valeric esters, 1,4-pentanediol and 2-methyl tetrahydrofuran. These reactions are catalyzed by noble and non-noble metal-based heterogeneous catalysts. The use of an abundant and non-toxic element, such as copper, is advantageous with respect to expensive or harmful metals, such as Rh, Ru, Pt or Ni. In this critical review, we wish to give a deeper insight into research advancements in the last ten years regarding the processing of levulinic acid and its esters with hydrogen using heterogeneous copper catalysts.

Keywords: levulinic acid; heterogeneous copper catalysts; γ-valerolactone; valeric esters; 1,4-pentanediol; 2-methyl tetrahydrofuran

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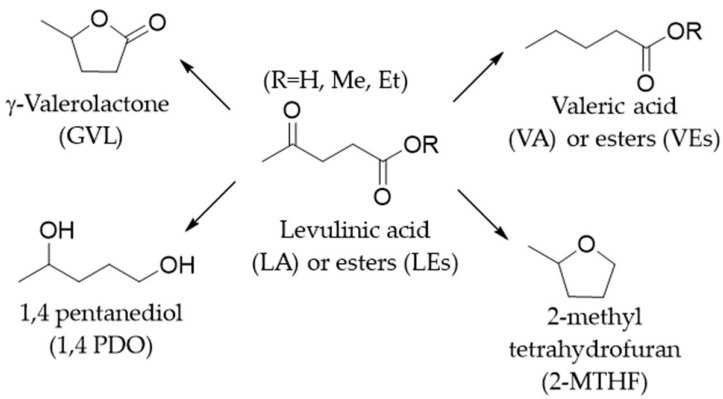
1. Introduction

1.1. Importance of LA/LEs and Scope of the Review

Levulinic acid (LA) is likely the most attractive platform molecule derived from lignocellulose, as it can be produced in relatively high yields from this renewable source. Indeed, it has been identified by the United States Department of Energy as one of the top 12 promising bio-based building blocks [1,2]. LA is typically produced using mineral acids (i.e., HCl or H_2SO_4) at around 200 °C, in a process in which C-6 sugars are converted into LA and formic acid, while C-5 sugars yield furfural. Biofine (by Biofine Renewables) is one of the most celebrated technologies in the production of this chemical, even if the first attempt at a conversion plant based on this process, which was developed in Caserta (Italy) by GFBiochemicals, has not gone into operation thus far. An improved process was recently designed, and a joint venture between GFBiochemicals and Towell Engineering group (named NXTLEVVEL) is currently working on a new production plant [1–3]. Levulinic esters (levulinates, LEs), especially methyl and ethyl levulinates, are also convenient platform chemicals, instead of LA, because of their specific physicochemical properties. LEs can be directly obtained from lignocellulose in the presence of an alcohol, in particular from the cellulose stream through the transformation of glucose [4–6], or from the hemicellulose stream, via a domino reaction from furfural [7–10]. Compared to LA, LEs show easier product separation [4] and they limit the metal leaching when a reaction is carried out in the presence of a metal-based heterogeneous catalyst [5,11].

As already pointed out, the synthetic routes of LA and LEs commonly involve the use of mineral acids that result in equipment corrosion, difficult separation and purification and potential environmental pollution, thus limiting the sustainability of the process. For these reasons, research is also oriented towards heterogeneous catalysts (i.e., Brønsted acid-based ones, such as zeolites, or ion exchange resins), but they result in lower LA/LE yields and easy deactivation [2,6,12].

LA and LEs are near to being extensively produced through consolidated and sustainable processes, and therefore they could play a central role in biobased industries producing commodities within the principles of the circular economy. Indeed, they can be transformed into different chemicals, such as γ-valerolactone (GVL), succinic acid, diphenolic acid, 1,4-pentanediol (1,4-PDO), valeric esters, 2-methyl tetrahydrofuran (2-MTHF), aminolevulinic acid, ketals and others [1,13–15], by different catalyzed processes (e.g., hydrogenation, oxidation, amination, condensation). In this critical review, we wish to give a deeper insight into recent research advancements (over the last ten years) related to the transformation of LA/LEs with hydrogen using heterogeneous copper-based catalysts. Thus, we will focus our attention on the following products: GVL, valeric esters, 1,4-PDO, and 2-MTHF (Scheme 1). The processes of catalytic transfer hydrogenation (CTH), as an alternative to the use of molecular hydrogen, will also be examined, although copper-based materials find a limited diffusion compared to others (e.g., Zr-catalysts).



Scheme 1. Main hydrogenation products derived from LA/LEs.

1.2. General Considerations about Copper Catalysts

Heterogeneous Cu-based catalysts are materials used in a wide range of chemical transformations, especially those linked to the methanol economy, but also in organic chemistry (i.e., C=O and C=C hydrogenation, coupling reactions and click chemistry, dehydrogenations, deoxygenation) [16], environmental remediation and deNO_x activity [17–21]. Copper is a non-noble metal, with a very low toxicity, compared to other metals such as Ni [22,23].

Moving to the objective of this review, several copper-based catalysts have been designed for the hydrogenation of LA/LEs in the last ten years. The dominant controlling factors are Cu-support interactions, morphology and dispersion of the Cu phase and the use of a second metal (e.g., Ni, Ag). The preparation method is the key, but the combination and the rationalization of all these parameters to obtain a highly performant catalyst is not an easy task and, at the same time, not always linear. One of the main issues preventing their large-scale application is deactivation, which mainly occurs through copper leaching, metal sintering or carbon deposition [24–28]. Catalyst stability and durability represent priorities in the scaling-up of the process at an industrial level. It is worth noting that sintering phenomena are in strong correlation with temperature. In particular, copper Hüttig temperature (that is, the semi-empirical value at which atoms at the surface start to exhibit mobility) is only 134 °C, while the reactions of LA/LE hydrogenation are normally carried out over 200 °C [29,30], thus limiting the lifetime (and the applicability) of copper catalysts. Traditionally, Adkins-type catalysts, namely copper chromites, have been used for hydrogenation of carboxylic acids and esters to alcohols due to their effectiveness and inexpensiveness [31,32]. Because of these reasons, since the 1950s, they have been applied in the production of biomass-derived chemicals, in particular in the hydrogenation of LA and LEs to GVL [33]; some examples can also be found in the recent literature [34,35]. However, despite copper chromites being simple and cheap catalysts, they suffer from toxicity and recyclability problems and could rapidly undergo deactivation, especially

when free carboxylic acids are used. In particular, the presence of free acids or short-chain alcohols slows down the hydrogenation reaction rate [31,36].

2. LA/LE Hydrogenation to GVL and Valerates

There is a growing interest in the production of GVL under environmentally friendly conditions because it is a safe, non-toxic, biodegradable and renewable-based added-value chemical, with many applications [37–39]. GVL can be (i) used as a biofuel additive, with combustion properties comparable to ethanol when blended with gasoline [40–43], (ii) converted to alkyl valerates, which are used as fuel components for gasoline and diesel engines [24,39,44], (iii) an environmentally safe solvent [25,40] hydrogenated to form 1,4-PDO, which undergoes dehydration to form 2-MTHF [45,46], and (iv) employed as a renewable monomer to produce polyesters [47,48]. In addition, it can be used as cutting oil, brake fluid and as a coupling agent in dye baths [26], converted to methyl pentenoate, which can be further transformed into nylon intermediates, such as adipic acid, dimethyl adipate or caprolactam [27], or even used as a food additive [49]. Several noble metals, such as supported Ru, Rh, Pt and Ir, have also been recently employed [41,50–59] for the heterogeneous catalyzed selective hydrocyclization of LA/LEs to GVL, in high yield. However, noble metals are expensive, and their supply is a limitation for large-scale plant applications. On the contrary, the use of abundant elements, such as Cu and Zr, offers more environmentally friendly routes because of their higher abundance and lower price.

2.1. Hydrogenation of LA/LEs to GVL with Molecular Hydrogen

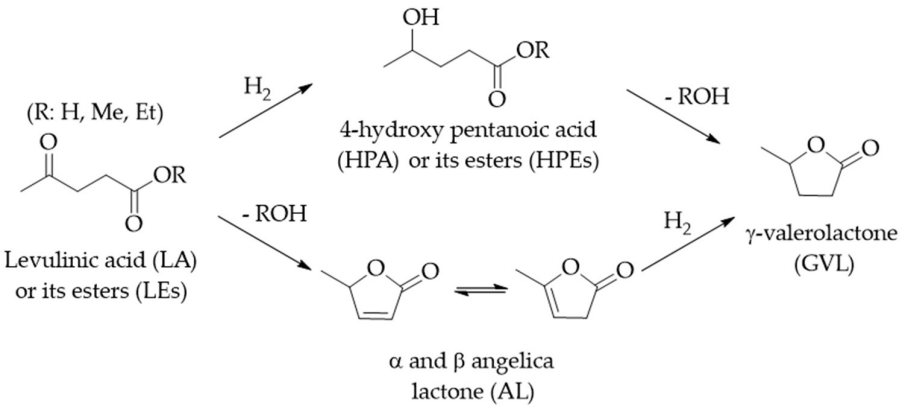
In Table 1, the main results obtained in the last ten years in the hydrogenation of LA/LEs to GVL with copper-based heterogeneous catalysts are summarized. The reactions are performed by using water, alcohols (primary or secondary) or, rarely, organic solvents such as THF [11], dioxane [60] or even *n*-hexane [61]. However, some of these compounds are toxic or harmful, thus their replacement is a priority to improve the sustainability of the process. This is the case with *n*-hexane, which is neurotoxic [62,63], and of THF, which is suspected to be carcinogenic [64]. 2-MTHF, which is less toxic and which can be derived from LA/LEs via GVL (*vide infra*), can be proposed instead of THF [46,65,66]. The solvent has a strong impact on the reaction, and from this point of view, water is considered a green solvent and LA is highly soluble in this medium. However, easier copper leaching is observed in water, thus reducing the lifetime of the catalyst [5,67]. Therefore, the use of organic solvents and/or LEs can have a positive effect on the phenomenon. It is worth noting that a reaction under no solvent conditions is reported [68], following the principles that "the best solvent is no solvent" [69]. The vapor phase hydrogenation of LA was indeed performed in a fixed-bed down-flow gas reactor, over a bimetallic Cu-Ni/SiO_2 catalyst, and provided a conversion (C) and GVL selectivity (S) of 98% and 97%, respectively [68].

The temperature range is generally between 180 and 250 °C. Remarkably, in some cases, it has been possible to reduce the temperature to 110, 120 or 140 °C [70–72]. This was achieved using, respectively, Cu–Ni bimetallic NPs supported on functionalized SiO_2 nanosphere (C = 99% and S = 97% in 13 h), CuMgAl mixed oxides derived from calcined hydrotalcites (C = 100% and S = 95%) or Cu/Al_2O_3-SiO_2 (C = 79% and S = 96%) in continuous plants.

Usually, the reactions are performed using high-pressure batch reactors at a H_2 pressure >25 atm. On the other hand, the literature on continuous-flow systems is still scarce [41–43,72], despite their role as a step ahead towards industrial scale-up [30,68,73–75].

As summarized in Scheme 2, GVL can be synthesized from LA/LEs via two reaction pathways, both containing hydrogenation and dehydration steps. The first one involves the hydrogenation of the carbonyl functionality of LA, thereby forming the unstable intermediate 4-hydroxypentanoic acid (4-HPA), and the subsequent dehydration followed by an intramolecular esterification (ring closure) to yield GVL. The other one is promoted by an acid catalyzed dehydration of LA to form angelica lactone (AL), followed by its hydrogenation to GVL [24,39,44]. Starting from LEs, the reaction was found to preferentially

proceed via the first pathway, in which the levulinate hydrogenation forms the 4-hydroxy pentanoic ester (HPE), which undergoes a rapid lactonization to yield GVL [25,45].



Scheme 2. Two possible reaction pathways for the hydrocyclization of LA/LEs to GVL.

As already stated, the use of LEs instead of LA has a positive effect on catalyst stability, since it can limit copper leaching [5,11]. Regardless of the reaction pathway, a well-balanced amount of metal sites and of acidic ones for the hydrogenation and the dehydration, respectively, is a prerequisite to obtain an efficient catalyst [44–46].

Metallic copper is indeed required for the hydrocyclization of LA/LEs to give GVL, as well highlighted in the literature [76–78]. Interestingly, some publications have pointed out that a balanced Cu(0) and Cu(I) surface distribution can promote the hydrogenation of ester, acyl and ketone groups [30,79–81]. In particular, Cu(0) facilitates the H_2 adsorption and dissociation, while Cu(I) can activate LA/LEs C=O groups [30]. Small Cu nanoparticles (NPs) and a highly dispersed copper phase are reported to be crucial factors to achieve good catalytic performances [76,82] on a high surface area support [83], although they would easily sinter and deactivate during the reaction (we already pointed out the low Cu Hüttig temperature, namely 134 °C) [30]. Therefore, the catalyst preparation method and support are precious tools helping to overcome this issue.

Copper-based catalysts for the hydrogenation of LA/LEs to GVL were prepared over different oxides or mixed oxides such as SiO_2, TiO_2, ZrO_2, Al_2O_3, Cr_2O_3, BaO, SiO_2-ZrO_2, Al_2O_3-ZrO_2, WO_3–ZrO_2 and others [76,77,82]. The ZrO_2-based ones are the most widespread [5,30,61,73,76,77,82,84]. Indeed, the fruitful combination between copper and zirconia has been demonstrated to be a winning strategy in the design of active catalysts with tunable properties for many applications (e.g., methanol economy) [85]. High surface area [30,76] and strong Cu-support interactions [30,61,75,77,82] enhance the dispersion of the metal phase, especially at high Cu loading, and reduce the sintering. Despite this, many papers (among these the majority of those related to Zr-based materials) report catalysts with very low surface area (i.e., <100 m^2/g, but also <50 m^2/g) [5,61,71,73,77,82,84] and this usually results in either reduced copper dispersion or metal loading, thus leaving space for further improvements. Some oxides (e.g., Al_2O_3) [11,74,86,87] more commonly lead to high surface area materials, while for other systems, the use of an amorphous phase [88], instead of crystalline ones, or their dispersion into a high surface area matrix (e.g., SiO_2) would be preferable [89,90]. This is the case, for example, with ZrO_2.

The support not only affects the metal dispersion, but it also plays a direct role in the activation of the reactants. The presence of acid sites, both Lewis and Brønsted ones, for instance, favors C=O polarization or the dehydration reaction [5,71,74]. It is curious that this aspect is often neglected in many papers that focus their attention mainly on hydrogenation activity. Balla et al. [73] compared a series of Cu-supported catalysts prepared on different oxides (ZrO_2, Al_2O_3, SiO_2, TiO_2). They found that the most acidic material, namely Cu/Al_2O_3, was the most active one, resulting in conversion and selectivity even higher than the Cu/ZrO_2 (C = 98% and S = 87%, respectively, vs. C = 81% and S = 83%).

Previously, Hengne et al. also showed that supports not exhibiting acid sites (e.g., BaO) have a considerably low activity when compared to ZrO_2- and Al_2O_3-based catalysts, which both provided C = 100% and S > 90% [5]. Unfortunately, these papers do not discuss in depth the role of the acid sites and, in particular, their nature (Lewis vs. Brønsted) and strength. In 2019, a more in-depth analysis of the acid–base properties of the catalyst was performed, through pyridine-adsorbed FT-IR, and NH_3 and CO_2 TPD measurements on a series of CuMgAl catalysts with different Mg/Al ratios [71]. In this case, moderately strong Brønsted acidity appears to be the most suitable feature to obtain GVL from LA, while the introduction of basic sites promotes the formation of 1,4-PDO through ring opening. In this paper, the authors present the Brønsted acid sites' role in suppressing the ring-opening reaction. This contrasts with what was reported one year earlier in another work, where this side reaction was ascribed to the strong Brønsted acidity [70]. In this view, we agree that the control of the acid strength is critical to promote/inhibit the ring-opening reaction, analogous to what we reported on furfural and HMF [91].

The choice of the support is not the only way to tune the acid–base properties, but also the metal phase can have an important role. Ravasio and co-workers [92] showed the possibility of preparing very small copper nanoparticles with a Lewis acid character (Figure 1) with a peculiar, but easy, preparation method (namely, chemisorption–hydrolysis—CH). A similar effect can be obtained by stabilizing Cu^+ species on the catalyst surface using a support such as Al_2O_3 or ZrO_2. Indeed, as discussed above, it has been shown that Cu^+ possesses an acidic character [61,93]. Alternatively, the acidity of the catalyst can be tuned by introducing a second metal (e.g., Ni) [86] or by catalyst doping strategies [30]. This is the case of Li et al., who used boron oxides to modulate the distribution of Cu^0 and Cu^+ on a Cu/ZrO_2. This resulted in a double effect: on one side, the co-presence of Cu^0 and Cu^+ species facilitates the H_2 adsorption and the activation of LA C=O groups; on the other side, the presence of boron oxide retarded the Cu sintering. This led to a total conversion and a selectivity above 90% in a long-term experiment (up to 100 h) in a fixed-bed reactor at a low temperature of 140 °C [30].

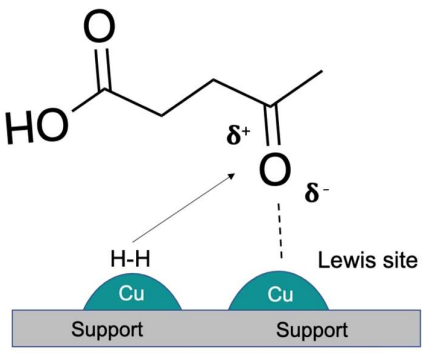


Figure 1. C=O activation over a copper catalyst prepared by CH.

One of the most common strategies to obtain more stable materials is the introduction of another metal (e.g., Ni or Ag) to obtain bimetallic catalysts. Monometallic Ni-based supported materials show high activity, but low selectivity due to the formation of side products and a significant amount of deposited carbon [87]. On the other hand, the intrinsic synergy between Cu and Ni particles in supported bimetallic Cu-Ni catalysts was proposed to be responsible for the higher activity, stability and recyclability. Indeed, the presence of Cu in bimetallic catalysts enhances the reducibility of NiO, behaving as an activation site for H_2 molecules [86]. In the meantime, the reduced Ni species act as a co-active site, able to accelerate the H_2 adsorption and activation, thus lowering the reduction temperature of bimetallic samples [70]. Compared to monometallic systems, the promotion effects of Ni allowed the achieving of full LA conversion after 2 h, while Cu sites were responsible for selectivity improvements (S = 96%) [87]. Moreover, Ni was found to prevent copper leaching [60] and sintering [94], while Cu was capable of suppressing coke formation [87].

Nevertheless, nickel has been classified as a toxic metal and its use should be avoided for a more environmentally friendly process [95,96].

A remarkable attempt to improve Cu catalysts using a different doping metal, namely Ag, was carried out by Zhang et al. [11]. The authors proposed that Ag promotes the CuO in situ reduction during the reaction with less severe sintering. In addition, Ag prevents Cu leaching by maintaining it at metallic state. This improved the catalyst stability, allowing nine catalyst recycles under mild reaction conditions, and providing complete conversion and selectivity in only 1 h at 180 °C.

In Table 1, we summarized the catalytic behavior of the supported Cu or Cu-Ni catalysts for the hydrocyclization of LA/LEs to GVL in the presence of molecular H_2.

Table 1. Catalysts for the selective hydrogenation of LA/LE to GVL.

Batch				
Catalyst	**Preparation Procedure**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
Cu/ZrO_2	CP	LA/LEs, H_2O or MeOH, mol_{LA}/g_{cat} = 0.086 mol g^{-1} in H_2O, mol_{LE}/g_{cat} = 0.069 mol g^{-1} in MeOH, mol_{LA}/g_{cat} = 0.086 mol g^{-1} in MeOH, 200 °C, 5 h, $P(H_2)$ = 35 bar, batch	C = 100 S > 90	[5]
$Cu\text{-}Ni/\gamma Al_2O_3$	WI SG	LA, H_2O, mol_{LA}/g_{cat} = 0.086 mol g^{-1}, 250 °C, 6 h, $P(H_2)$ = 65 bar, batch	C = 100 S = 96	[87]
(1) $Cu\text{-}WO_3/ZrO_2$ (2) Cu/ZrO_2	CP OG	LA, (1) EtOH or (2) H_2O, mol_{LA}/g_{cat} = 0.022 mol g^{-1}, 200 °C, 6 h, $P(H_2)$ = 50 bar, batch	C = 100 (1) S = 94 (2) S = 99	[84]
Cu/ZrO_2	CP	LA, H_2O, mol_{LA}/g_{cat} = 0.086 mol g^{-1}, 200 °C, 2 h, $P(H_2)$ = 35 bar, batch.	C = 100 S = 80	[76]
Cu/ZrO_2	OG DP MT	LA, H_2O, mol_{LA}/g_{cat} = 0.086 mol g^{-1}, 200 °C, 1 h, $P(H_2)$ = 35 bar, batch	C = 90 S = 100	[77]
$Cu\text{-}Ag/Al_2O_3$	WI	LA, THF, mol_{LA}/g_{cat} = 0.017 mol g^{-1}, 180 °C, 1 h, $P(H_2)$ = 14 bar, batch	C = 100 S = 100	[11]
Cu-Ni organosilica nanospheres	ST WI CP	LA, 2-PrOH, mol_{LA}/g_{cat} = 0.031 mol g^{-1}, 120 °C, 13 h, $P(H_2)$ = 40 bar, batch	C = 99 S = 97	[70]
$Cu\text{-}Al_2O_3$	CP	LA, EtOH, mol_{LA}/g_{cat} = 0.0086 mol g^{-1}, 110 °C, 2 h, $P(H_2)$ = 30 bar, batch	C = 100 S = 95	[71]
$Al_2O_3\text{-}Cu/ZrO_2$	CP	LA, H_2O, mol_{LA}/g_{cat} = 0.086 mol g^{-1}, 200 °C, 2 h, $P(H_2)$ = 30 bar, batch	C = 100 S = 100	[82]
$Cu\text{-}Ni/\gamma\text{-}Al_2O_3$	WI	LA, solvent-free, mol_{LA}/g_{cat} = 0.196 mol g^{-1}, 220 °C, 6 h, $P(H_2)$ = 30 bar, batch	C = 100 S = 99	[86]
$Cu\text{-}Ni/Al_2O_3$	CI	LEs, n-HEX, mol_{LE}/g_{cat} = 0.069 mol g^{-1}, 180 °C, 6 h, $P(H_2)$ = 25 bar, batch	C = 100 S = 98	[61]
$B_2O_3\text{-}Cu/ZrO_2$	CP for Cu/ZrO_2, then boric acid	LA, H_2O, mol_{LA}/g_{cat} = 0.069 mol g^{-1}, 150 °C, 5 h, $P(H_2)$ = 30 bar, batch	C = 100 S = 100	[30]
Flow				
Catalyst	**Preparation Procedure**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
$Cu/\gamma Al_2O_3$	WI	LA, H_2O, 265 °C, $P(H_2)$ = 1 bar, H_2 = 30 mL min^{-1}, WHSV = 0.169 h^{-1}, H_2/LA molar ratio = 201, flow	C = 98 S = 87	[74]

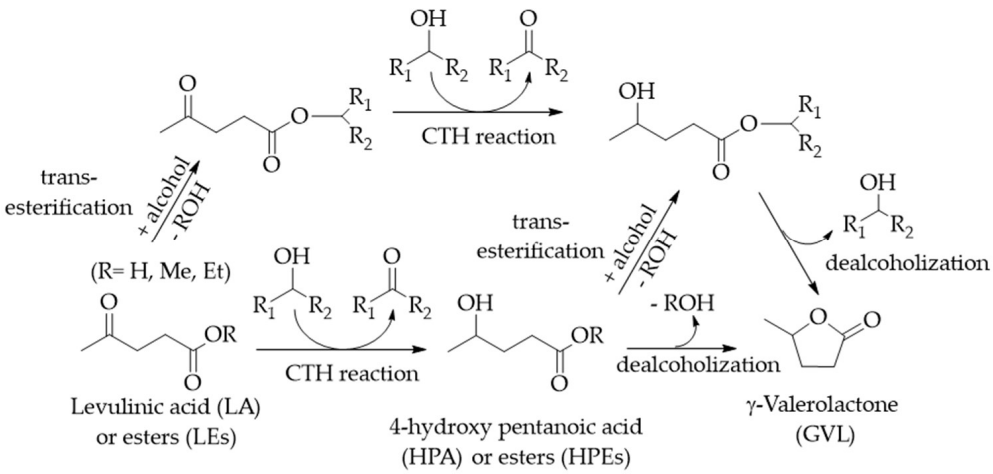
Table 1. *Cont.*

		Batch		
Cu/ZrO_2	WI	LA, H_2O, 265 °C, $P(H_2)$ = 1 bar, H_2 = 30 mL min^{-1}, WHSV = 0.169 h^{-1}, H_2/LA molar ratio = 201, flow	C = 81 S = 83	[73]
Cu/Al_2O_3-SiO_2	CP	LEs, EtOH, 140 °C, 1000 h, $P(H_2)$ = 30 bar, WHSV = 0.6 h^{-1} trH_2/LE molar ratio = 50, flow	C =79 S = 96	[72]
Cu-Ni/SiO_2	WI with citric acid	LA, solvent-free, 250 °C, $P(H_2)$ = 1 bar, H_2 = 30 mL min^{-1}, WHSV = 13.2 h^{-1}, H_2/LA molar ratio = 6, flow	C = 98 S = 98	[68]
Cu-Ni/KIT6/ ZSM-5	WI	LA, 250 °C, $P(H_2)$ = 1 bar, H_2 = 30 mL min^{-1}, time on stream = 24 h, H_2/LA molar ratio = 0.0024, flow	C = 100 S = 80	[75]
B_2O_3-Cu/ZrO_2	CP for Cu/ZrO_2, then boric acid	LA, H_2O, 200 °C, $P(H_2)$ = 30 bar, H_2 = 40 mL min^{-1}, H_2/LA molar ratio = 2711, flow	C = 100 S = 100	[30]

2.2. Catalytic Transfer Hydrogenation (CTH) of LA/LEs to GVL

The use of molecular hydrogen in high-pressure reactors poses several concerns in terms of sustainability, safety and applicability of the process. An alternative strategy is the catalytic transfer hydrogenation (CTH) that exploits an alcohol, both primary or secondary, or formic acid (FA) as hydrogen donor [78,97–102], reducing most of the problems related to the use of high-pressure molecular hydrogen (purchase, transport, safety hazard, expensive high-pressurized industrial plants) [103,104]. Moreover, several hydrogen-donor molecules can be obtained from renewable feedstock, such as lignocellulosic biomass, as in the case of bio-alcohols (obtained from biomass fermentation), and FA (that is a side product in LA/LE production). CTH was performed over Ni-, Zr- and Cu-based systems without the use of precious metal catalysts [105,106]. One of the drawbacks of the CTH process with alcohols is that the primary or secondary alcohol is transformed into the corresponding aldehyde or ketone, respectively, as a side product. Indeed, this may significantly affect the selectivity of the process, opening the path to aldol condensation side reactions [107–109].

The CTH reaction of LA/LEs with alcohols is reported in Scheme 3. First, the alcohol donates the hydrogen to LA/LEs, thus forming 4-hydroxypentanoic acid or its ester, and then GVL is formed by cyclization and ROH elimination.



Scheme 3. Reaction pathway for the CTH of LA to GVL, adapted from ref. [106].

Two mechanisms have been proposed for this reaction in the literature, depending on the catalyst used. When non-noble metals (e.g., Cu, Ni) are used, the reaction proceeds via a hydrogen-borrowing mechanism [94,110,111]. On the other hand, when ZrO_2 is used,

the reaction occurs without the evolution of molecular hydrogen through a concerted Meerwein–Ponndorf–Verley (MPV) mechanism, in which both the reducing alcohol and the carbonyl group are coordinated to the same metal center [91,98,112,113]. In the CTH process of LA/LEs in the presence of alcohols, the transesterification reaction is usually a competitive process. However, the resulting product can, in turn, undergo CTH, thus not usually hindering the GVL formation (Scheme 3).

Several heterogeneous Cu catalysts prepared on different supports, such as ZrO_2, SiO_2, TiO_2, ZnO and γ-Al_2O_3, were proposed for this reaction. Monometallic and bimetallic (i.e., Cu in combination with Ni) materials have been designed by using different preparation methods, such as wet impregnation (WI), deposition–precipitation (DP) or oxalate gel coprecipitation method (OG), and tested, providing high conversion and selectivity to GVL under mild reaction conditions [78,110]. Among these, the best results were obtained when ZrO_2 was employed, thus confirming the importance of Lewis acid-base pairs on the catalyst surface for the CTH reaction. An attempt to improve the catalytic system using bifunctional catalysts with aluminum oxide and hydrogenation sites (Cu-Ni alloy) supported on active carbon (AC) was made by Yu et al. [114]. An adequate Al/Cu-Ni ratio of 1, resulting in the best acidity of the catalyst, was found to promote the esterification reaction step, and thus increase the GVL yield (C = 100% and S = 97%, respectively).

The use of a high surface area support, such as SBA-15, provided high metallic dispersion and a limited diffusion of the metal NPs in the SBA channels, and repressed agglomeration as well as leaching [83]. The introduction of Ni provided benefits also for the CTH reaction, by remarkably enhancing the catalytic activity and stability to poisoning and sintering, thus allowing a better catalyst recyclability [94].

The literature reports the notable work of Yuan et al. [78], in which FA, which is co-produced in an equimolar amount along with LA during the biomass dehydration process [115,116], was employed as an alternative in situ hydrogen source via its selective decomposition. The CTH reaction proceeded in stream and in water on Cu/ZrO_2, providing 100% of C and S, and is an interesting example of an integrated process. In Table 2, the catalytic behavior of the supported Cu or Cu-Ni catalysts for the hydrocyclization of LA/LEs to GVL under CTH conditions is summarized.

Table 2. Catalysts for the CTH of LA/LEs to GVL.

Catalyst	Preparation Procedure	Reaction Conditions	Catalytic Performances (%)	Ref.
Cu/ZrO_2	WI DP OG	LA, FA, H_2O, LA/FA molar ratio = 1, 200 °C, 5 h, flow.	C = 100 S = 100	[78]
Cu-Ni/Al_2O_3	WI	LEs, 2-BuOH, mol_{LE}/g_{cat} = 0.01mol g^{-1}, 150 °C, 12 h, batch.	C = 100 S = 97	[94]
Cu-Ni/SBA15	glycol WI	LEs, 2-PrOH, mol_{LE}/g_{cat} = 0.0048 mol g^{-1}, 140 °C, 3 h, batch.	C = 91 S = 90	[83]
Cu/ZrO_2	OG	LEs, MeOH, mol_{LE}/g_{cat} = 0.019 mol g^{-1}, 220 °C, 1 h, batch.	C = 99 S = 88	[110]
Cu-Ni-Al_2O_3/AC	WI	LA, 2-PrOH, mol_{LA}/g_{cat} = 0.086 mol g^{-1}, 220 °C, 2 h, batch.	C = 100 S = 97	[114]

It is worth noting that bare ZrO_2 is a very active and selective material for CTH processes, including the transformation of LA/LEs to GVL [91,97]. It is our opinion that although the addition of Cu or other metals deserves to be explored to optimize the catalytic performance, the bare ZrO_2 behaves as an effective system by itself [10,67,104,106,117–121].

Table 3 highlights the main milestones in the comprehension of supported Cu and Cu-bimetallic catalysts for the hydrocyclization of LA/LEs to GVL under molecular H_2 or under CTH conditions. Metallic Cu was found to be the active phase, and highly dispersed

Cu NPs are crucial to provide an active catalytic surface. The preparation method, together with high surface area and/or 2D–3D supports, are key factors guaranteeing a highly dispersed metal phase. Despite supported Cu catalysts being highly efficient and selective, both for conventional hydrogenation using molecular H_2 and for CTH, they suffer some drawbacks, such as Cu leaching, especially when LA instead of LEs is used, or when the reaction occurs in water. As many reactions work at temperatures higher than the Cu Hüttig one, sintering occurs and catalysts deactivate. To overcome this, the use of an additive, such as B_2O_3 or Al_2O_3 during catalyst preparation, helps prevent sintering. Moreover, the addition of a second metal, namely Ni or Ag, improves the catalytic lifetime because of synergic effects between the two metals: Ni or Ag prevent metal leaching, while Cu prevents coking and facilitates Ni or Ag reduction. Lewis or Brønsted acid-base pairs are crucial to the promotion of the dehydration step and thus the cyclization to GVL.

Table 3. Selected key catalytic aspects of the comprehension of Cu and bimetallic catalysts.

Focus	Key Catalytic Aspects	[Ref.]
Bimetallic Cu-Ni	• Balanced amount of acid and metallic sites • NP synergistic effects • Cu inhibits coke, Ni enhances activity and prevents sintering	[87]
Cu-γAl_2O_3	• Importance of catalytic acidity for the C-O bond cleavage	[74]
Cu-MOx	• Effect of the support on acidity • Catalytic performances: Cu-γAl_2O_3 > Cu-ZrO_2 > Cu/SiO_2 > Cu/TiO_2 • Effect of Cu loading on acid site concentration	[73]
Cu/SiO_2 vs. Cu/Al_2O_3-SiO_2	• Importance of the support acidity • Tuning product selectivity with activation temperature • Particle size matters	[72]
Cu/t-ZrO_2	• Identification of Cu^0 as the catalytically active site • Importance of Cu NP dispersion	[77]
Bimetallic Cu-Ag/Al_2O_3	Effect of Ag: • limitation of Cu leaching • facilitated in situ CuO reduction • maintenance of Cu in metallic state	[11]
Cu-Ni organosilica nanospheres	• Organosilica as innovative support allows lowering of the reaction T • Synergic effect of Cu-Ni is responsible for high reactivity and stability	[70]

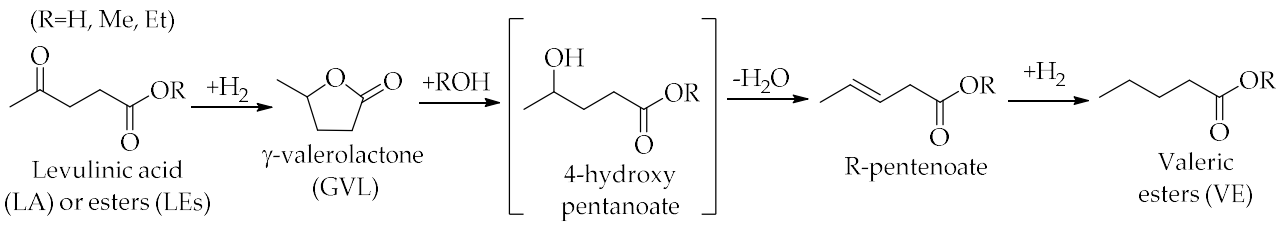
Table 3. *Cont.*

Focus	Key Catalytic Aspects	[Ref.]
Cu-Ni on KIT-6 ZSM-5 doped	• Confinement effect of the support on metal nanoparticles: high dispersed Cu-Ni and limited sintering • Hydrogenation at ambient P due to highly dispersed and active particles • Importance of Lewis–Brønsted acid sites for the ring opening	[75]
B_2O_3-Cu/ZrO_2	Effect of B: • favored Cu dispersion • retarded Cu sintering • inhibited ZrO_2 phase change • tuning of Cu^0/Cu^+ surface distribution • improved surface acidity	[30]
Al_2O_3-Cu/ZrO_2	• enhanced electronic interaction between Cu and ZrO_2 due to the dilution of Cu by Al_2O_3	[114]
Cu-Ni on mesoporous high surface SBA-15	• Low reaction temperature (140 °C), stable Cu-Ni into SBA-15 mesopores	[83]

2.3. Transformation of LA/LEs and GVL to VE

Valeric esters (VE) have been identified as a new class of cellulosic-derived potential biofuels, suitable both for gasoline and diesel engines, as they provide fully compatible components with transportation fuels [39,44]. VE, depending on the alcoholic residue, have shown better fuel blending properties than GVL because of energy density, appropriate polarity and volatility–ignition properties [24,53,122].

The reaction occurs under H_2 either from LA/LEs or GVL through nucleophilic addition of the alcohol to the carboxylic group, followed by dehydration to pentenoate and hydrogenation to valeric ester (Scheme 4).



Scheme 4. Reaction mechanism for the conversion of EL into valeric esters, adapted from refs. [92,122].

Lange et al. [24] were pioneers in developing a process to convert GVL into valerates, in continuous high-pressure tubular reactor units, using a Pt/ZSM-5 bound with a SiO_2 catalyst with balanced acidic and hydrogenation properties, or Pt supported on ZrO_2 or TiO_2. Although Pt-based catalysts tend to convert GVL, providing a high PV/VA ratio, they produce a large amount of undesired light hydrocarbons and are expensive, as already discussed above. Some investigations [123] were reported of GVL conversion or one-pot conversion of LA over Ni- [124], Ru- [125,126], Re-Ru- [127], Co- [128], Pd- [129], Rh- [130] or Pt-based catalysts [131,132], whereas Cu-supported catalysts, although advantageous, are still scarcely studied.

In an attempt to switch from noble to non-noble metal-based catalysts, and to develop a bifunctional system for a one-pot cascade process, some of us [122] successfully com-

bined the acidic properties of several solid supports with the hydrogenation activity of pre-reduced CuO catalysts prepared by CH for the one-pot ring opening and hydrogenation of GVL to valerate esters in a batch reactor. The best performances were obtained with Cu/SiO_2-ZrO_2 (4.7 wt.% ZrO_2) in the presence of ethanol or 1-pentanol to form ethyl valerate (C = 69%; S = 59%) or pentyl pentanoate (C = 90%; S = 83%). The significant hydrogenation activity of finely dispersed supported Cu, together with relevant Lewis acidity exhibited by very small Cu particles, allowed us to design a new Cu/SiO_2 bifunctional catalyst [92], without the need of an acidic support, converting 91% of GVL and improving the selectivity to 1-pentyl valerate up to 92%.

Liu et al. [93] claimed a novel separate nucleation and aging steps assistant reduction–oxidation strategy, developed to synthesize CuO/ZrO_2 with homogeneously distributed Cu and Zr components, which were reduced to obtain highly dispersed Cu/ZrO_2 catalysts and used for the transformation of GVL to valerate esters under H_2 pressure, exhibiting excellent catalytic performances with several alcohols (e.g., with 1-pentanol C = 85%, S = 98%).

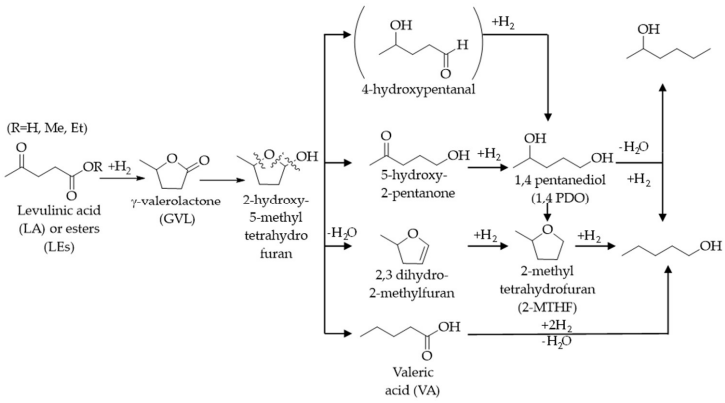
3. Hydrogenation of LA/LEs and GVL to Give 1,4-PDO

As shown in the previous section, LA/LEs can be converted into GVL through a combination of hydrogenation and dehydration reactions. However, GVL can be further hydrogenated to produce other interesting and useful compounds, such as 1,4-PDO and 2-MTHF (Scheme 5). Biomass-derived diols can be utilized not only as bio-monomers to synthetize bioderived polyesters [133,134] and polyurethanes [135,136] but also as solvents [137,138]. The reaction pathways of LA/LEs to give GVL and 1,4-PDO diverts depending on dehydration or hydrogenation sequences, as already reported. In particular, it involves the formation of the 4-HPA intermediate if the hydrogenation occurs first; on the other hand, if dehydration is the first step, angelica lactone (AL) is formed instead. GVL can be subsequently hydrogenated to 1,4-PDO, which can be further dehydrated to give 2-MTHF [139].

The Resasco group has given a possible reaction pathway and intermediate formation thanks to a combination of experimental and theoretical studies, considering, in particular, the hydrogenation of GVL in aqueous phase on 5% Ru/C catalysts [140]. The reaction may start with a ring-opening step breaking the bond between the carbonylic carbon and the oxygen, forming the surface intermediate $CH_3CH(O^*)$–$(CH_2)_2$–CO^*. This species can undergo three reversible parallel pathways: (i) decarbonylation to 2-butanol, (ii) hydrogenation to 1,4-PDO and (iii) C-O hydrogenolysis to 2-pentanol [140].

Successively, the same research group had further investigated the reaction profile to shed light on the rate-limiting step. In particular, DFT studies had suggested that the rate-limiting step for the formation of the 1,4-PDO is the hydrogenation one, underlining the need to design hydrogenation-promoting catalysts [141]. Actually, GVL hydrogenation can also result in the formation of valeric acid (VA) or its esters [142].

The fine-tuning of the acid/base and hydrogenation properties of the catalysts allows one to move toward the desired product through a different reaction pathway.



Scheme 5. LA hydrogenation pathways to give GVL and/or 1,4-PDO. Adapted from ref. [65,143].

There are several papers in the literature relying on noble metal catalysts to produce 1,4-PDO [47,48,144]. However, some examples of supported Cu catalysts that are effective in the synthesis of 1,4-PDO from LA/LEs could be found. In these cases, the fine-tuning of acidic and basic sites becomes of crucial importance to modulating the selectivity, having a role in the GVL ring-opening process, has already been highlighted. In particular, basic sites could boost the selectivity towards the diol, enabling the GVL ring opening. The introduction of basic Mg species pushed the selective conversion of GVL to 1,4-PDO, with a yield up to 98% at 140 °C and 60 bar of hydrogen [71]. On the contrary, a high Brønsted acidity, similar to the one found over the CuAl catalyst, suppresses the ring-opening reaction, inhibiting 1,4-PDO formation and thus improving the GVL yield [71]. These results were further confirmed by the same group in a study in which the hydrogenation of ethyl levulinate to give 1,4-PDO with a 99% yield was favored on a CuMg catalyst with abundant basic sites [145].

Due to the complexity of the whole process, the production of 1,4-PDO can be advantageously separated into two different steps: the first one is the synthesis of GVL from LA/LEs, and the second is the transformation of GVL into the diol. In particular, GVL is more prone to be hydrogenated using non-noble metal catalysts, as shown below in this paragraph (see Table 4). Moreover, GVL can be easily obtained from LA/LEs using non-noble metal catalysts, as shown in the previous section.

Table 4. Most relevant copper catalysts used for hydrogenation of GVL to give 1,4-PDO from the literature.

Batch				
Catalyst	**Preparation Method**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
Cu/MgO	CVD	1,4-dioxane, 240 °C, 10 h, $P(H_2)$ = 100 bar, mol_{GVL}/g_{cat} = 0.0125 mol g^{-1}, batch	C = 91 S = 94	[146]
$Cu_{1.5/}Mg_{1.5}AlO$	CP	1,4-dioxane, 160 °C, 12 h, $P(H_2)$ = 50 bar, mol_{GVL}/g_{cat} = 0.0625 mol g^{-1}, batch	C = 93 S = 99	[147]
$Zn_{1.5}Cu/Al_2O_3$	WI	1,4-dioxane, 200 °C, 2 h, $P(H_2)$ = 40 bar, mol_{GVL}/g_{cat} = 0.02 mol g^{-1}, batch	C = 91 S = 97	[148]
Cu/SiO_2	CH	Cyclopentyl-methylether, 160 °C, 22 h, $P(H_2)$ = 50 bar, mol_{GVL}/g_{cat} = 0.05 mol g^{-1}, batch	C = 78 S = 98	[23]
Cu/SiO_2 –10% TEOCS	CH	Cyclopentyl-methylether, 160 °C, 22 h, $P(H_2)$ = 50 bar, mol_{GVL}/g_{cat}= 0.05 mol g^{-1}, batch	C = 80 S = 99	[149]
Flow				
Catalyst	**Preparation Method**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
Cu/ZnO	WI	1,4-dioxane, 140 °C, WHSV = 0.4 h^{-1}, H_2/GVL molar ratio = 810, flow	C = 82 S = 99	[143]
Cu/SiO_2	WI	1-butanol, 130 °C, WHSV = 4.61 h^{-1}, H_2/GVL molar ratio = 2485, flow	C = 32 S = 67	[150]

Most recently, supported copper-based catalysts were shown to be effective in the selective hydrogenation of GVL to give 1,4-PDO. Copper can be supported on a wide fan of metal oxide supports with different properties. A Cu/MgO prepared with a metal–organic chemical vapor deposition method achieved a C = 91% and S = 94% at 100 bar of H_2 for 10 h [146]. The loading of copper was found to be crucial for the catalytic activity and selectivity towards 1,4-PDO. Moving from 6 to 18 copper wt.% loading, conversion increased from 71% to 80%, reaching the maximum selectivity of 86%. On the other hand,

when the copper loading was further increased, a rise in selectivity for 2-MTHF and 1-pentanol was observed [146].

As already cited, it is important to underline the major role of acid/basic sites when considering this hydrogenation reaction. In fact, the major side reaction in the hydrogenation of GVL to 1,4-PDO is the dehydration of the diol to give 2-MTHF, which is a typical acid catalyzed reaction. Thus, it is likely to work with bifunctional basic catalysts or to partially suppress their acidity. For instance, the basic $Cu_{1.5}/Mg_{1.5}AlO$ catalyst derived from layered double hydroxides precursors was found to be particularly efficient, achieving a GVL conversion of 93% and a 1,4-PDO selectivity >99% [147]. These results were mainly ascribed to the cooperative effect between its well-dispersed active Cu nanoparticles and the proper surface basic sites nearby. Notably, when the acidic Cu/HZSM-5 is used, larger amounts of 2-MTHF were obtained due to the acid-assisted diol dehydration. This was observed also when 1,4-PDO was used as the substrate: a C = 69% was found over the Cu/HZSM-5 catalyst when, in contrast, no 1,4-PDO conversion resulted using the basic $Cu_{1.5}/Mg_{1.5}AlO$ catalyst [147]. On the other hand, the addition of Zn on the Cu/Al_2O_3 catalyst significantly improved the selectivity towards the diol, passing from 46% obtained with the bare Cu/Al_2O_3 to 98% in the case of the $ZnCu/Al_2O_3$ catalyst, with a Zn/Cu molar ratio of 1. In fact, Zn reduced the quantity of surface Lewis acid sites and promoted the formation of 1,4-PDO with respect to 2-MTHF [148].

However, it was demonstrated that high yields of 1,4-PDO can be obtained even using mild acidic supports such as SiO_2, both under flow conditions [150] and in batch [23]. Some of us were able to achieve a GVL conversion of 78% with a 1,4-PDO selectivity of 98% using Cu/SiO_2 prepared with the CH on a pyrogenic silica in the green solvent cyclopenthyl methyl ether (T = 160 °C, $P(H_2)$ = 50 bar, t = 22 h) [23]. It was found that the right acid strength is crucial in the activation of the carbonyl group of the lactone, while the formation of 2-MTHF can be avoided, limiting the surface hydrophilicity of the catalyst. In fact, the proper combination of solvent and catalyst hydrophobicity/hydrophilicity allows one to improve the 1,4-PDO yield. In particular, when cyclopentylmethylether and a less hydrophilic SiO_2 are used, the yield in the diol rises from 46% to 78%. It was proposed that a less hydrophilic surface facilitates the desorption of the diol, thus preventing side reactions. On the other hand, the solvent affects the acidic strength [23]. The catalytic system was further optimized by decreasing the hydrophilicity of a Cu/SiO_2 prepared with a silica gel carefully functionalizing the surface with trietoxyoctylsilane, achieving 99% of selectivity of 1,4-PDO, even at 1% loading of the silane under the same conditions as the previous work [149]. The best yield of 80% was achieved with a silane loading of 10%. However, a higher silane loading hinders the GVL from reaching the catalytic active Cu sites on the surface, decreasing the conversion despite keeping the 1,4-PDO selectivity at 99%. This phenomenon was caused by the tendency of the organosilane to reticulate on the surface at higher concentration [149].

It is worth noting that there are also few examples relying on heterogeneous copper catalysts for the production of 1,4-PDO from GVL through flow processes. This is the case with a Cu/ZnO prepared with a co-precipitation method using different copper-loading and calcination temperatures. The 40% Cu/ZnO calcined at 500 °C was the best catalyst and gave a C = 82% and S = 99%, at a GVL feed rate of 0.4 g h^{-1}, 140 °C, H_2 pressure of 15 bar and H_2 flow rate of 90 mL min^{-1} [143]. In addition, in this case, the selectivity towards 1,4-PDO increased with the H_2 pressure, while the increase in temperature favored the formation of 2-MTHF [143]. These trends were observed also in the work of Simakova et al., where Cu/SiO_2 was used [150], obtaining a C = 32% and S = 67% in a continuous flow reactor using 1-butanol as the solvent (10% GVL in 1-butanol, GVL flow rate 2.1 g h^{-1} cat = 0.455 g, T = 130 °C, $P(H_2)$ = 13 bar, H_2 flow rate 167 mL min^{-1}, 4 h). Once again, the lower selectivity towards 1,4-PDO compared to that achieved with Cu/ZnO was ascribed to the acidity of the silanol groups, which promotes the dehydration reaction to form 2-MTHF [150].

The analysis of the literature confirms the necessity of having a high hydrogenating system to reach high 1,4-PDO yields, by choosing an appropriate catalyst and/or by increasing the hydrogen pressure. Moreover, strategies to prevent 1,4-PDO dehydration to 2-MTHF should be pursued through an accurate catalyst design. This can be achieved by properly working on the catalyst surface, with the introduction of basic sites and/or with the suppression of the acidic ones, or by playing with the catalyst wettability to promote the diol desorption, thus preventing side reactions. It is worth noting that the wettability is often an underrated parameter in catalyst design [151–153].

4. Hydrogenation of LA/LEs and GVL to Give 2-MTHF

2-MTHF is a very important product of the LA stream due to its role in bioderived gasoline blends. In particular, it represents up to 20% of the "P-series fuels", a family of renewable, non-petroleum liquid fuels, containing about 35% liquid by-products, known as "C5+" or "pentanes-plus", and 45% ethanol, fermented from corn [154]. Moreover, it is considered a sustainable solvent, with a promising environmental footprint (not only biobased, but also easy to degrade) and low toxicity [66,155].

As already pointed out, to produce 2-MTHF from LA/LEs, GVL is initially formed (Scheme 5) and therefore hydrogenated to form 2-hydroxy-5-methyltetrahydrofuran as intermediate. From here, two main routes can take place. The first one involves the formation of 1,4-PDO (via a ring-opening and hydrogenation reaction), followed by intramolecular etherification, as already explained. The second pathway proceeds by dehydration to form 2,3-dihydro-2-methylfuran that, in turn, is hydrogenated to 2-MTHF [65,143].

The literature suggests that the reaction preferentially occurs via the ring opening [84,156,157]. It is worth noting that noble metal-based catalysts also favor the C-O cleavage at the methyl-group side with the formation of valeric acid that can be converted into 1-pentanol, as highlighted by Sun et al. [65,143]. Based on these considerations, the use of non-noble metals, such as copper, for the preparation of 2-MTHF is even more advantageous because they combine low cost and higher availability with superior selectivity, compared to noble-ones, as they exclude the formation of 1-pentanol via valeric acid.

Activity and selectivity are strongly related to both reaction conditions and catalyst features. In particular, H_2 pressure and its availability are critical parameters to obtaining good yields in 2-MTHF, while acid/base properties and stability are the main points to look at for catalyst optimization. Based on the previous considerations, we know that basicity favors the selective formation of 1,4-PDO while acidity pushes towards 2-MTHF.

In Table 5, the main results of 2-MTHF synthesis from LA/LEs and GVL obtained with copper catalysts are reported.

Table 5. Most relevant copper catalysts used for hydrogenation of LA/LEs or GVL to give 2-MTHF from the literature.

Batch				
Catalyst	**Preparation Method**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
Cu-Ni/Al_2O_3–ZrO_2	SG WI	LA, 2-BuOH, 210 °C, 10 h, P (H_2) = 35 bar, mol_{LA}/g_{cat} = 0.043 mol g^{-1}, batch	C = 100 S = 100	[158]
Cu-Ni/Al_2O_3	WI	LEs, n-HEX, 180 °C, 4 h, P (H_2) = 40 bar, mol_{LE}/g_{cat} = 0.0083 mol g^{-1}, batch	C = 100 S = 98	[159]
Ni_2Cu_1/Al_2O_3	CP	GVL, 2-PrOH, 200 °C, 5 h, P (H_2) = 50 bar, mol_{GVL}/g_{cat} = 0.04 mol g^{-1}, batch	C = 100 S = 88	[160]

Table 5. *Cont.*

Batch				
Catalyst	**Preparation Method**	**Reaction Conditions**	**Catalytic Performances (%)**	**Ref.**
		Flow		
Cu/Al_2O_3-SiO_2	CP	LEs, EtOH, 250 °C, 1000 h, P (H_2) = 30 bar, WHSV = 0.6 h^{-1}, H_2/LE molar ratio = 50, flow	C = 100 S = 65	[72]
Ni–Cu/SiO_2	CP	GVL, 1,4 dioxane, 265 °C, P (H_2) = 25 bar, WHSV = 0.5 h^{-1} H_2/LE molar ratio = 80, flow	C = 100 S = 89	[161]
Cu/SiO_2	DP	GVL, H_2O, 300 °C, P (H_2) = 1 bar, H_2 = 50 mL min^{-1}, WHSV = 1.0 h^{-1}, H_2/GVL molar ratio = 24, flow	C = 97 S = 84	[157]

The conversion of LA/LEs into 2-MTHF is usually obtained with high-loading copper catalysts. A Cu/SiO_2 system with 80 wt.% of Cu was found to be selective, allowing one to obtain a 64% yield under 25 bar of H_2 at 265 °C [161]. Interestingly, the results reported show that the selectivity of the reaction can be tuned by changing the Cu loading: low loading favors the selective hydrocyclization of LA to GVL, which, in turn, undergoes a further hydrogenation to 2-MTHF and 1-pentanol in the presence of high-loading catalysts. Other authors proposed the use of a Cu/SiO_2 system doped with Al_2O_3, obtaining a 65% yield in 2-MTHF starting from LEs [72]. The authors underline the important role of alumina in decreasing the particle size of CuO clusters in the co-precipitation process. Smaller Cu particles after reduction and hydrogen spillover from Cu to Lewis acidic sites may account for the much-improved activity of the Cu/Al_2O_3-SiO_2 catalyst. The CuO particles distribute around 20–60 nm in the spent and re-calcined catalyst due to sintering inhibition by anchoring of Cu particles on the Lewis acidic sites and much lower reaction temperature. The stronger Lewis acidic sites also accelerate the dehydration reaction to form GVL as the main product, suppressing the formation of 1,4-PDO and 2-pentanol. The great advantage obtained in the use of a bimetallic catalyst starting from LA/LEs is also claimed in some papers relying on the hydrogenation promoted by Cu-Ni systems. A Cu-Ni/Al_2O_3 obtained 98% of 2-MTHF at 180 °C and 40 bar of H_2 [159]. The excellent catalytic activity observed was ascribed by the authors to both Ni and Cu compositions, where Ni was more readily able to activate the H_2 and hydrogenate EL into GVL, while Cu catalyzed the ring opening of GVL to yield the target molecule 2-MTHF. Moreover, the use of a non-polar solvent, such as n-hexane, significantly reduced the apparent activation energy for the ring opening of GVL. The synergistic effect of Ni and Cu has also been highlighted in another catalytic system, namely a Cu-Ni/ Al_2O_3-ZrO_2 [158], which provided a 100% yield in 2-MTHF starting from LA at 210 °C and 35 bar of H_2, mainly due to the tunable acidic properties of the support.

Some important differences arise when starting from GVL. Thus, while the effect of increased acidity still remains a strong point in selectively obtaining 2-MTHF, the particle size parameter shows a different effect.

Sun et al. compared Co, Ni and Cu catalysts in the vapor phase hydrogenation of GVL, observing a marked higher activity of Cu with respect to Ni and Co, particularly in terms of selectivity. Thus, a commercial Cu/Al_2O_3 obtained more than 93% selectivity in 2-MTHF vs. the 75 and 44%, respectively, obtained with Co/Al_2O_3 and Ni/Al_2O_3 [65]. The optimization of the catalyst and of the reaction protocol led to excellent catalytic activity, which means a 2-MTHF selectivity of 99% and a GVL conversion of 98%. Besides acidity, the authors highlighted the importance of particle size as one of the main parameters to work on to maximize 2-MTHF yield. In particular, by increasing the calcination temperature up to 700 °C, the particle size increases with a coherent higher selectivity in 2-MTHF with

respect to 1,4-PDO. A further increase in the calcination temperature leads, on the contrary, to an inversion in product distribution due to the formation of a $CuAl_2O_4$ phase, which reduces the amount of acid sites. This, once again, underlines the effect of acidity/basicity in addressing the formation of 1,4-PDO or 2-MTHF. The optimization of the reaction conditions and of the catalyst textural properties also allowed the obtaining of up to 81% of 2-MTHF at 300 °C under flow conditions with a Cu/SiO_2-impregnated system [157].

Different catalyst properties and reaction conditions for each step would be necessary for these three steps, which would increase the difficulty of the direct production of 2-MTHF from LA. In contrast to the production of 1,4-PDO from LA, which needs precious metal catalysts and high H_2 pressures, the production of 1,4-PDO from GVL can be efficiently catalyzed by Cu-based catalysts under mild reaction conditions [26].

Also, when starting from GVL, some bimetallic systems have been proposed, once again Ni-Cu catalysts. Eighty-eight percent selectivity in 2-MTHF resulted from the use of a Ni_2Cu_1/Al_2O_3 derived from layered double hydroxide (LDH) precursors [160], while the strong beneficial effect of Ni in limiting sintering and leaching of copper was underlined in using a $Ni\text{-}Cu/SiO_2$ system [161].

5. Conclusions and Future Directions

5.1. General Strategies to Selectively Obtain the Desired Product

Copper-based materials are very promising catalysts for the cascade transformation of LA/LEs in the presence of hydrogen. By tuning the experimental conditions (i.e., H_2 pressure, temperature) and the catalyst properties, it is possible to move from one product to another (Figure 2). All these products (GVL, valerates, 1,4-PDO, and 2-MTHF) are obtained through consecutive reaction steps, starting from LA/LEs. A good catalyst is a material with high hydrogenation activity and, depending on the target product, with different acid-base properties. From the analysis of the literature, to draw a clear picture is not an easy task, but some general considerations can be summarized:

- GVL and valerates are preferentially obtained when a catalyst with a pronounced acidic character is used. Clearly, the presence of an alcoholic medium is required for the preparation of valerates.
- By tuning the acid/base properties, the reaction is more prone to proceed through the ring opening, leading to the formation of 1,4-PDO [71]. 1,4-PDO dehydration can be avoided by limiting catalyst acidity or polarity. High H_2 pressure is usually needed to reach high yields.
- The yield in 2-MTHF can be optimized by increasing the acidity of the catalyst and the copper particle size.

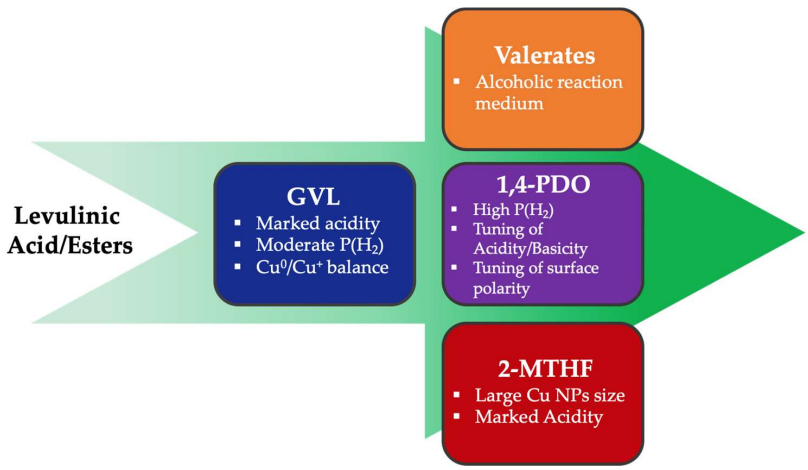


Figure 2. Products obtainable from LA/LEs by varying catalyst properties and reaction conditions.

5.2. Catalyst Deactivation and Stability Considerations

The use of a non-noble, non-toxic metal, such as copper, is a clear advantage for the valorization of LA/LEs, and the literature shows some nice examples in which high conversions and high selectivity are reported. Despite this, catalyst deactivation represents one of the major obstacles to industrial scale-up (Figure 3). Different approaches have been enacted to improve stability, but there is still much to do. Leaching can be limited by using LEs instead of LA and by selecting the most suitable solvent. Water, which is considered a green solvent, favors this phenomenon, but its replacement with an organic solvent could entail sustainability problems. At the same time, leaching can decrease by controlling copper–support or copper–metal (in the case of a bimetallic system) interactions. These strategies are also effective in contrasting sintering, along with the use of high surface area supports, or of materials with a particular 2D/3D structure. Despite its toxicity, the addition of nickel appears to be a good strategy to facilitate H_2 activation and to limit sintering and leaching of copper. It is important to note that the reactions of hydrogenation of LA/LEs usually require temperatures over 200 °C, while copper Hüttig temperature is only 135 °C. It follows that the research should also focus on developing low-temperature processes to improve the catalyst lifetime. Unlike other reactions, the deactivation of copper-based systems due to carbon deposition in LA/LE hydrogenation seems to be less relevant.

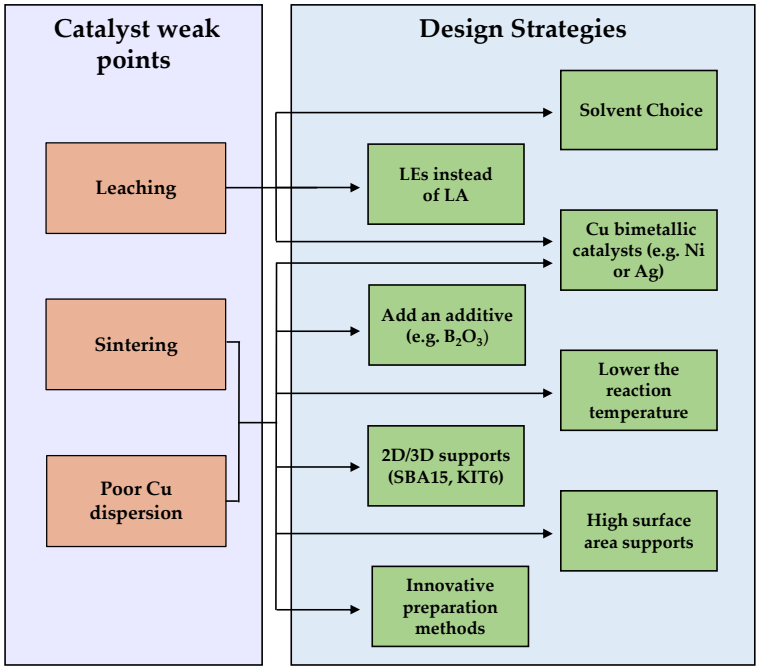


Figure 3. Main factors limiting the catalyst scale-up and the design strategies aimed at optimizing the performance.

5.3. Future Directions

It is our opinion that future papers should put more stress on aspects related to catalyst stability and recyclability, as well as implementation of continuous flow processes. Moreover, there is still a gap in research concerning one-pot, cascade processes that produce 1,4-PDO or 2-MTHF starting from LA/LEs using copper-based catalysts.

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List of Abbreviations

LA = levulinic acid; LEs = levulinic esters; GVL = γ-valerolactone; FA = formic acid; VA = valeric acid; VE = valeric esters; 1,4-PDO = 1,4 pentanediol; 2-MTHF = 2-methyl tetrahydrofuran; OG = oxalate gel; CP = co-precipitation; WI = wet impregnation; CI = co-impregnation; SG = sol-gel; DP = deposition–precipitation; MT = methanothermal; ST = solvothermal method; CVD = chemical vapor deposition; CH = chemisorption hydrolysis; AC = activated carbon.

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