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Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: A critical review

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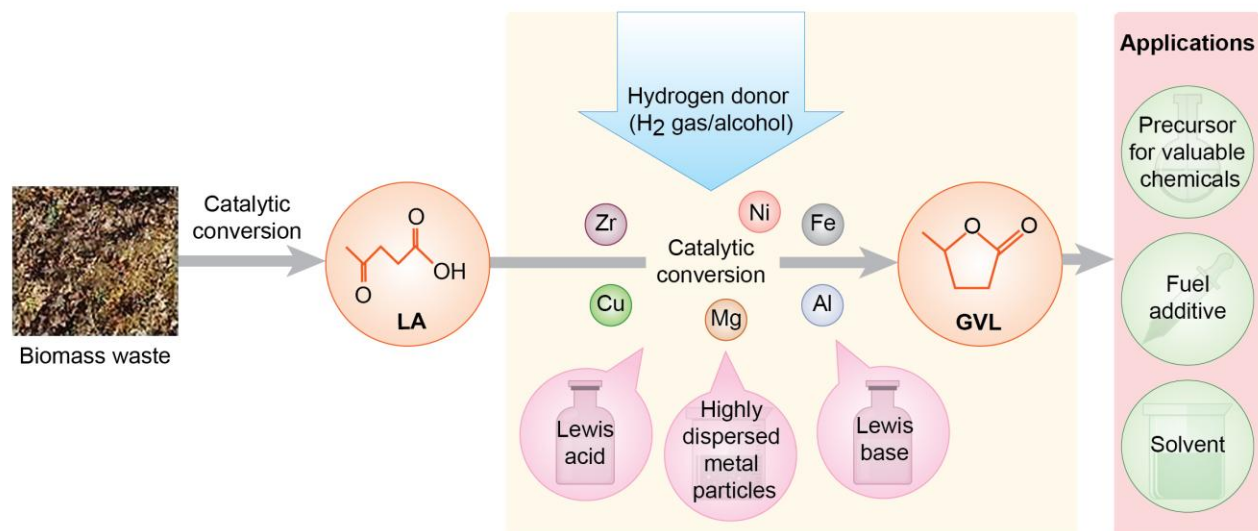
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Graphical Abstract



Highlights

- Gamma-valerolactone is a precursor for valuable chemicals and potential fuel additive
- Non-noble metals can be used in catalytic transfer hydrogenation (CTH) to produce GVL
- Dispersion of metal particles on catalysts influences hydrogenation efficiency
- Lewis acid and base sites are needed for obtaining high GVL yield and selectivity
- Metal leaching from catalysts is significant in aqueous conditions

Abstract

The distinct physicochemical properties and renewable origin of gamma-valerolactone (GVL) has provided opportunities for diversifying its applications, particularly as a green solvent, excellent fuel additive, and precursor to valuable chemicals. Among the related publications found in the SCOPUS database (≈ 172 in the last 10 years), we focused our effort to review the conversion of levulinic acid (LA) to GVL over non-noble metal catalysts and the corresponding mechanisms (≈ 30 publications) as well as the applications of GVL as a solvent, fuel additive, and platform chemical (≈ 30 publications) mostly in the last five years (some preceding publications have also been included due to their relevance and importance in the field). The use of non-noble metals (*e.g.*, Cu and Zr) presents a greener route of GVL synthesis than the conventional practice employing noble metals (*e.g.*, Pd and Ru), in view of their higher abundance and milder reaction conditions needed (*e.g.*, low pressure and temperature without H_2 involved). The significance of the catalyst characteristics in promoting catalytic transfer hydrogenation of LA to GVL is critically discussed. Structural features and acid–base properties are found to influence the activity and selectivity of catalysts. Furthermore, metal leaching in the presence of water in catalytic systems is an important issue, resulting in catalyst deactivation. Various endeavors for developing catalysts using well-dispersed metal particles along with a combination of Lewis acid and base sites are suggested for efficiently synthesizing GVL from LA.

Keywords: Sustainable biorefinery; Green solvent; Catalytic Transfer Hydrogenation; Lewis acid; Waste valorization/recycling.

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1. Introduction

The production of chemicals and fuels from renewable materials is perceived as an attractive concept by the emerging biorefinery industry [1]. Gamma (γ)-valerolactone (GVL) has drawn considerable attention in the last decade (Figure 1) as a value-added chemical synthesized from renewable feedstock (*e.g.*, biomass waste and food waste) because of its distinct physicochemical properties and potential fuel applications [2,3]. GVL is a naturally existing, safe, biodegradable, and nontoxic chemical which can be utilized as a food additive; it can also be used as a green solvent for processing biomass, and as an efficient fuel additive [2,4]. Furthermore, GVL can be transformed and upgraded to various derivatives such as methyltetrahydrofuran, alkanes, and 1,4-pentandiol [5,6].

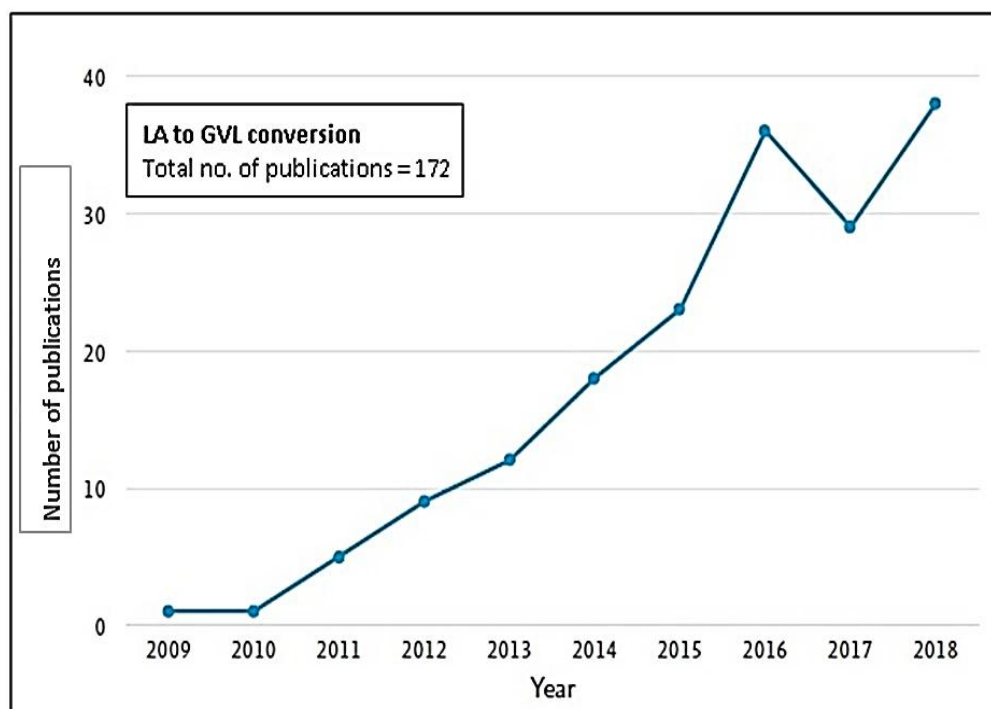


Figure 1. Science Citation Indexed publication on LA to GVL in SCOPUS database.

GVL is a key derivative of levulinic acid (LA) and is synthesized by the hydrogenation of LA [7-9]. LA can be easily generated by the acid catalysis of cellulose or C6 sugars involving the production of hydroxymethylfurfural (HMF) as an intermediate [10,11]. Alternatively, it can form via the acid catalysis of hemicellulose or C5 sugars with furfural as an intermediate [11]. LA can be produced using lignocellulosic biomass [12] and food waste [13], through the hydrolysis of cellulose/starch and hemicellulose following the pathways mentioned above. Researchers have investigated the catalytic hydrogenation of LA to obtain GVL by using various catalysts, solvents, and hydrogen donors, resulting in different reaction pathways and yields of GVL. Noble metal catalysts, such as ruthenium (Ru) [7,14-16], iridium (Ir) [17,18], palladium (Pd) [19,20], and platinum (Pt) [21,22], have been extensively explored owing to their high activity during LA hydrogenation, with carbon-supported Ru catalysts being the most extensively used.

Research interest in the conversion of LA to GVL is growing rapidly particularly in the last five years (Figure 1). Recently, related studies are being published every month while China, USA, and India (according to SCOPUS) are the top three contributors in research related to 'LA to GVL conversion'. Existing review papers have discussed the use of heterogeneous noble and base metal catalysts [23] and reaction pathways along with the applications of GVL [24]. Tang et al. [25] summarized the production of GVL from both biomass-derived and commercial LA using different hydrogen sources, whereas Liguori et al. [26] reviewed the catalytic design of high energy efficiency for the one-pot production of GVL.

Non-noble metal catalysts, such as Cu, Ni, Fe, Al, and Mg, are preferred over precious metal catalysts because of their abundance in nature and economic sustainability. They can accommodate the use of H₂ gas, formic acid (FA), or alcohols as hydrogen donors for efficient

hydrogenation of LA to produce GVL [27-29]. Therefore, using non-noble metal catalysts could possibly eliminate pressurized H₂ conditions, which are needed in conventional catalytic systems raising potential safety concerns. The use of alcohols in place of H₂ gas generally promote catalytic transfer hydrogenation (CTH) of LA to GVL, in which a reaction temperature as low as 110 °C is possible [30]. Alcohols (*e.g.*, iso-propanol, 2-butanol) also act as solvents in the conversion of LA to GVL, which pose lower toxicity to human health and environment compared to common industrial solvents [31]. Due to such mild reaction conditions, non-noble metal-catalyzed CTH can be considered as a greener route for GVL synthesis compared to conventional hydrogenation. While CTH systems were covered in recent reviews summarizing diverse products from LA [32,33], there has not been a critical review that focuses on GVL synthesis over non-noble metal catalysts to the best of our knowledge. In-depth discussion of the roles of different parameters is imperative to assist high-performance design, such as structural and acid-base properties of catalysts and their compatibility with various hydrogen donors. In this review, we summarize the important properties of GVL and its diverse applications. More importantly, recent advances within the last five years in the design of non-noble metal catalysts for high-performance GVL production are discussed (some preceding publications have been included due to their relevance and importance in this field). We highlight the significance of the physicochemical properties of non-noble metal catalysts and reaction conditions (*e.g.*, H₂, non-H₂ hydrogen donors, and solvents) in regulating the conversion efficiency, providing insights into the development of sustainable catalytic systems for biorefineries and circular bio-economy.

2. Properties and applications of GVL

2.1. Physicochemical properties

GVL, which is a C5-cyclic ester (C₅H₈O₂), is a chemical that exists in nature (*e.g.*, fruits). GVL is often used as a food additive and a sustainable precursor chemical in the production of energy and consumer products (*e.g.*, adipic acid as nylon precursor). It is a renewable and biodegradable chemical that can be easily and safely stored as well as transported to distant places. GVL has a low melting point (−31 °C), a high boiling point (207 °C), and a high flash point (96 °C) that minimizes the ignition hazard; further, its vapour pressure is considerably low at high temperatures (3.5 kPa at 80 °C). Because of the pleasant but distinct smell of GVL, its leakage and spills can be detected. Importantly, it does not generate peroxide in air for a considerable period of time, which will enable its extensive usage as a safe chemical [2]. Despite being soluble in water, which is important for its biodegradation, GVL does not react with water at a temperature lower than 60 °C for four weeks; therefore, it can be considered to be a stable chemical. Furthermore, appropriate catalysts are required for its thermal breakdown [34,35].

2.2. GVL as a solvent

GVL has been recognized to be a green and nontoxic solvent because it has useful polarity properties, low toxicity (Lethal Dose 50% (LD₅₀), oral for rat 8800 mg kg^{−1}), and can be derived from biomass feedstock [2,36]. In the CHEM21 solvent selection guide [31], GVL exhibits a better score in terms of safety compared to tetrahydrofuran (THF) which is a popular solvent for chemical conversion. While THF is very prone to peroxide formation, *i.e.*, 160 mg L^{−1} in 20 days at room temperature (> 100 mg L^{−1} as safety limit), it has been reported that GVL does not form peroxides for a month at 60 °C [37].

GVL has been used as an efficient solvent for synthesizing biomass-derived chemicals [24]. Wettstein et al. [38] developed a biphasic system that comprised GVL and an aqueous solution of HCl for cellulose deconstruction to form LA and FA, which eventually produced GVL in a high yield (70% from LA/FA). In their experiment, cellulose was completely solubilized, and the usage of GVL as a solvent eased the separation and extraction of the final product. Meanwhile, Luterbacher et al. [39] reported a high yield of carbohydrates (70% to 90%) based on corn stover, hardwood, and softwood using bio-derived GVL, water as the solvent, and dilute H₂SO₄ as the catalyst. Qi et al. [40] demonstrated the acid-catalyzed transformation of carbohydrates to LA and FA in GVL solvent. Song et al. [41] utilized bio-derived GVL as a solvent and catalyst for efficiently converting CO₂ to amines (98% selectivity and 84% yield), which could be attributed to the lactone structure of GVL. In another experiment conducted by Lê and co-workers, a GVL/water mixture was used for the fractionation of *Eucalyptus globulus*, resulting in 80% total recovery of cellulose, hemicellulose, and lignin [42]. A GVL-containing medium was reported to maintain the activity of the Sn catalyst in bread waste conversion to HMF (yield of 20 mol%) [43]. The applications of GVL as a solvent are summarized in Table 1, highlighting its versatility in serving a wide variety of biorefinery reactions involving bio-based chemicals and feedstocks.

Table 1. Representative reactions conducted using GVL as the solvent

Experiment	Catalyst	Yield	Reference
Cellulose to LA and FA	HCl (aq)	70%	[38]
Carbohydrates from corn stover, hardwood, and softwood	H ₂ SO ₄	70% to 90%	[39]
Fructose, glucose, and sucrose to HMF	H ₂ SO ₄	75%	[40]
Fructose, glucose, and sucrose to LA and FA		50% to 70%	[40]
CO ₂ to amines	GVL	84%	[41]
Fractionation of <i>Eucalyptus globulus</i> wood in GVL/water		80% of the starting materials were converted to cellulose, hemicellulose, and lignin	[42]
Bread waste to HMF	SnCl ₄	20 mol%	[43]
Corn Stover to LA and furfural	PtSn/SiO ₂ , Amberlyts 70	70% for LA	[11]
Glucose to HMF	Amberlyst 70, Sn-beta	59%	[44]
Hemicellulose to furfural	H-Modernite	80%	[45]
Xylose to furfural	H ₂ SO ₄	75% (selectivity)	[46]
Fructose to GVL	H ₂ SO ₄ , Shvo catalyst	55%	[47]
Corncob, xylan and xylose to furfural	FeCl ₃ •6H ₂ O	66.8%, 68.6%, 86.5% respectively	[48]
Xylose and cornstalk to furfural	Sulphonated carbon	78.5%, 60.6%	[49]

2.3. Fuel characteristics and derivatives

GVL retains 97% of the energy content of glucose [50], and its combustion energy is similar to that of ethanol (29.7 MJ/kg) [24]. By utilizing a low-cost feedstock, GVL can be produced at prices ranging from 2 to 3 USD/gallon, which renders it to be a quite cheap and practical potential biofuel [51]. However, in comparison to fossil fuels, GVL has lower energy density and cetane number and higher water solubility, which limit its direct application in transportation fuel production [25].

Horváth et al. [2] suggested that the performance of GVL as a fuel additive was very similar to that of ethanol. In comparison to oxygenates, such as methanol, ethanol, methyl t-butyl ether, and ethyl t-butyl ether, GVL has the lowest vapour pressure (3.5 kPa at 80 °C). The latter is a significant parameter of fuel in terms of controlling the emission of volatile organic compounds

(VOCs). GVL can be mixed with gasoline and diesel fuels [52]. Bereczky et al. [4] reported that the addition of GVL (7.1% in fossil diesel-biodiesel mixture) led to only a slight decrease in engine performance when compared with that using 100% fossil diesel and a blend of fossil diesel and biodiesel. However, by blending with GVL, the emissions (CO, total hydrocarbon, and smoke) were significantly reduced (*e.g.*, 47% reduction in particulate matter emission as compared to that for 100% fossil diesel), highlighting the opportunity of GVL in combating air pollution and abating global warming. Fabos et al. [53] recommended the usage of GVL as a lighter fluid and as an illuminating liquid for burning charcoal that does not create smoke or odour and that produces low VOC emissions.

Furthermore, GVL is a potential precursor for producing other chemicals, including methyltetrahydrofuran (Me-THF) and 1,4-pentandiol [5,6], alkyl 4-alkoxy and tetraalkyl ammonium 4-hydroxyvalerates [54,55], mixtures of alkanes [5], isomers of butenes [50], alkyl valerates [56], 4-hydroxypentane alkylamides [57], and adipic acid (precursor for nylon) via pentenoic acids [58].

3. Reaction mechanisms during the synthesis of GVL

In general, GVL can be synthesized by the hydrogenation of LA using one of the following two reaction mechanisms (Figure 2): (1) hydrogenation of the ketone group of LA, leading to the formation of an unstable intermediate 4-hydroxypentanoic acid, and subsequent dehydration followed by an intramolecular esterification that results in ring closure yielding GVL (Pathway 1 in Fig. 2), and (2) dehydration of LA to α -angelica lactone followed by its hydrogenation to GVL (Pathway 2 in Fig. 2) [15,16]. In both pathways, the hydrogenation step depends on the activity

of the metal catalyst, and the dehydration and ring closure steps are influenced by the acidic condition of the system [59-61].

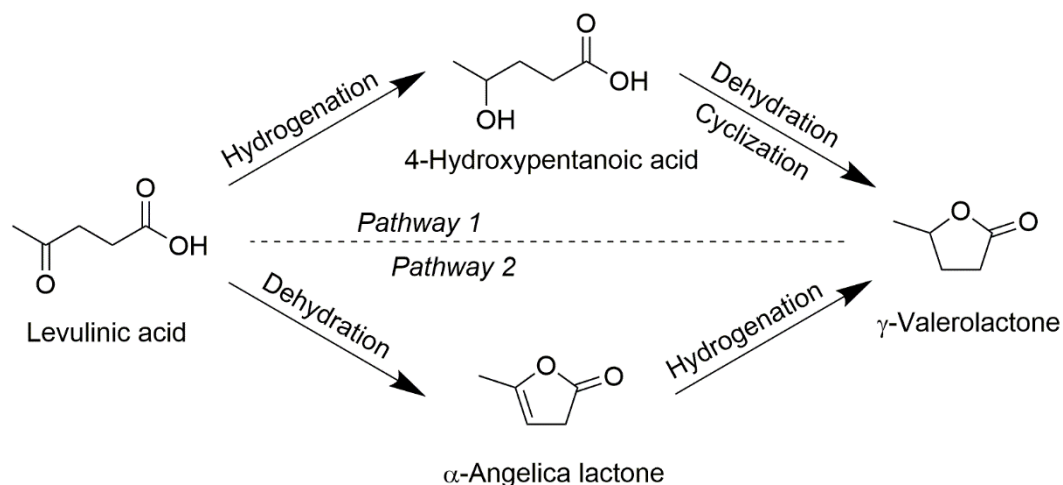


Figure 2. Probable reaction mechanisms of LA hydrogenation to GVL (Pathway 1: hydrogenation followed by dehydration and ring closure; Pathway 2: dehydration followed by hydrogenation) (adapted from literature [15,16,59-61]).

The former pathway of GVL synthesis is thermodynamically preferred and has been proven to kinetically dominate at a low temperature [16]. In an experiment performed by Piskun et al. [62], 4-hydroxypentanoic acid, and not α -angelica lactone, was detected during the hydrogenation reaction, which was indicative of the dominance of the first reaction pathway. In addition, the reaction of LA is reported to proceed through 4-hydroxypentanoic acid as an intermediate in liquid-phase hydrogenation [15,16], whereas α -angelica lactone is formed when hydrogenation occurs in the vapour phase [21,63]. Grilic and Likozar [64] reported the presence of α -angelica lactones in trivial concentration for LA-to-GVL conversion in a solvent-free condition.

Different hydrogen donors can be used during the hydrogenation process to produce GVL from LA. Conventional hydrogenation is conducted using external molecular hydrogen gas (H_2),

which is the most popular source for reducing unsaturated organic compounds and produces a quantitative yield of GVL [65,27]. Although atom economic is favourable with no necessary by-products, hydrogenation by H₂ gas is inconvenient in terms of environmental sustainability because the gas is usually obtained from fossil fuel. Meanwhile, CTH is performed using FA or alcohol as hydrogen donors [30,66]. Because FA is produced as a by-product in an equimolar concentration during LA production from carbon-based substrates [67], it is preferred for the CTH of LA. However, the utilization of FA entails some drawbacks such as the requirement of precious metal catalysts, homogeneous catalysts, and/or harsh reaction conditions such as high temperature [68,28].

In this context, CTH using the Meerwein–Ponndorf–Verley (MPV) reaction constitutes an effective approach to produce GVL from LA, which can be carried out over heterogeneous non-noble metal catalysts, using alcohol as a greener hydrogen donor in place of H₂ gas. In addition, mild reaction conditions enable liquid-phase MPV reduction at the boiling point of alcohol and under an ambient pressure, which makes the process environment-friendly and cost-effective. The MPV reaction is highly chemo-selective for the reduction of carbonyl compounds and the presence of C=C functional groups is favourable for the process [28]. The alcohol donates the hydrogen to LA that forms 4-hydroxypentanoic acid or undergoes transesterification which ultimately leads to the formation of GVL; the alcohol utilized during the reaction is transformed into the corresponding ketone (*e.g.*, 2-propanol is transformed into acetone), which can also be recycled as a valuable chemical [28,66,69-71].

A probable reaction pathway for conducting the CTH of LA to synthesize GVL is illustrated in Figure 3. Recently, several research studies have focused on the CTH of LA and its esters to

GVL using alcohols as H donors. The performance of non-noble metal catalysts utilizing different hydrogen donors, particularly alcohols, is discussed in section 6.1.

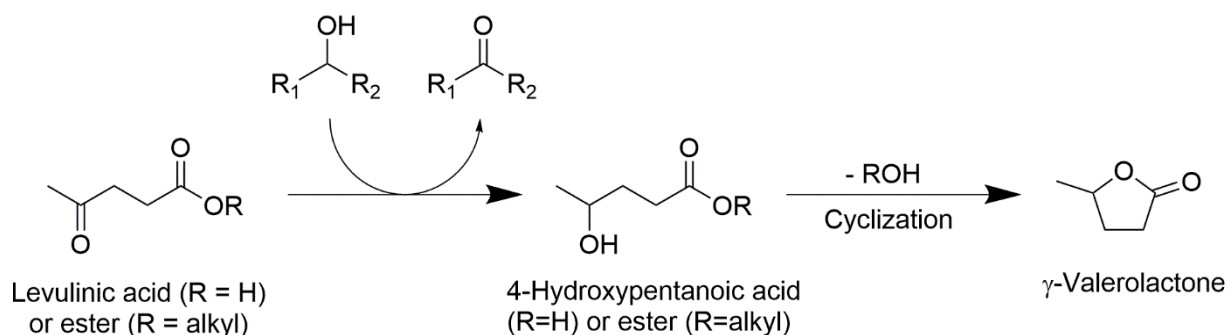


Figure 3. Probable reaction pathway for the CTH of LA to synthesize GVL

(adapted from literature [28,66,69-71]).

4. Non-noble metal catalysts for efficient conversion of LA to GVL

Heterogeneous non-noble metal catalysts have attracted the interest of researchers for GVL synthesis because they provide easy catalyst separation and recycling and are beneficial in terms of economic viability and environmental sustainability. In this section, the performance of such non-noble metal catalysts, including nickel-, copper-, zirconium-based catalysts and combined metal catalysts, in the conversion of LA to GVL is discussed. The summary of the corresponding experimental conditions and results are summarized in Tables 2-5, respectively.

4.1. Nickel-based catalysts

Nickel has been extensively used as a non-noble metal catalyst by various researchers owing to its high activity during LA conversion and high selectivity toward GVL (Table 2). Nickel embedded N-doped multi-chambered mesoporous carbon microspheres (Ni@NCMs) has been fabricated by Liu et al. [72] that exhibited excellent activity (99% conversion and selectivity) and

outperformed the activated carbon-supported nickel (Ni/AC), owing to the promising hierarchical porous structure. Song and co-workers [73] developed a nickel-based (Ni/NiO) catalyst by partially reducing nickel oxide to metallic nickel in hydrogen at 200–300 °C. It exhibited high activity in the hydrogenation of LA (100% conversion after 24 h reaction time) and generated a high yield of GVL (99.9%) using dioxane as a solvent, 20 bar H₂, and a reaction temperature of 120 °C. The productivity of Ni/NiO was 14.1 mmol GVL g⁻¹ h⁻¹ at 120 °C, which was 10-18 times higher than that of metallic Ni and NiO (1.3 and 0.8 mmol GVL g⁻¹ h⁻¹, respectively). Such high activity was attributed to the formation of Ni/NiO heterojunctions in the developed catalyst (significance of heterojunctions in Section 5.1). The authors further highlighted the good stability and recyclability of the catalyst even on its tenth use. Aside from the peroxide forming petrochemical solvent, this represents a potentially scalable process. Continuous processes are able to increase productivity with less waste and lower energy demand. In this respect, Hengst et al. [74] prepared different nickel catalysts (Ni/Al₂O₃) through wet impregnation, urea precipitation, NaOH precipitation, and flame spray pyrolysis. Ni/Al₂O₃ prepared via wet impregnation was the most active probably because of the presence of small nickel particles (an average particle size of 6 nm). The optimal catalytic performance (90% LA conversion and 75% GVL yield) was achieved using 5 wt% Ni/Al₂O₃ after 5 h of reaction at 200 °C in water at 50 bar H₂. The support of catalyst plays a role in controlling the catalytic performance. Hengne and co-workers [59] demonstrated that the montmorillonite (MMT)-supported nickel catalyst exhibited the best performance compared to its Al₂O₃-, ZnO-, and SiO₂-supported counterparts, achieving > 99% LA conversion and GVL selectivity in 1 h with iso-propanol as the H donor at 200 °C. It was suggested that the high acidic strength of MMT facilitated the esterification of LA as well as the cyclization to GVL. Jiang et al. [75] prepared

nickel catalysts that were supported using MgO–Al₂O₃ at different Mg/Al ratios, and Ni/MgAlO_{2.5} gave the optimal yield of GVL of 99.7% (160 °C, 30 bar H₂, 1 h). The larger surface area and higher nickel dispersion over the MgO–Al₂O₃ support may account for the high activity and selectivity toward GVL formation when compared to Ni/MgO and Ni/Al₂O₃. Nevertheless, Lv et al. [76] obtained the optimal results (100% LA conversion and 93.3% GVL selectivity) using Ni/MgO among the prepared catalysts (Ni/SiO₂, Ni/Al₂O₃, Ni/TiO₂, Ni/ZrO₂, and Ni/ZnO), with 2-propanol as both the solvent and H donor at 150 °C for 2 h.

In solvent-free condition, Ni/Al₂O₃ was reported to achieve 92% LA conversion with 100% GVL selectivity (4 h, 200 °C, 50 bar H₂) [77], while in water, Obregon et al. [29] reported 100% LA conversion with 91% GVL selectivity at 250 °C at 65 bar H₂ for 2 h. Fu et al. [78] achieved 100% LA conversion and 99.2% GVL selectivity using Ni/Al₂O₃ catalyst using dioxane as a solvent under relatively mild reaction conditions (180 °C, 2 h, 30 bar H₂).

During the vapour-phase hydrogenation of LA, Mohan and his group [79] reported that Ni/Al₂O₃ and Ni/SiO₂ presented very high activity for LA conversion (98-99%) and a GVL yield of 80%, in comparison to Ni supported on MgO, TiO₂, ZnO, and ZrO₂. However, Kumar et al. [80] could not achieve good LA conversion over Ni/SiO₂, Ni/ZrO₂, or Ni/Al₂O₃ catalysts in the vapour phase. The contrasting results may derive from the higher H₂ flow rate in the former study (30 vs. 20 mL/min in the latter), as higher availability of H₂ might accelerate hydrogenation. Another study conducted by Kumar and co-workers [81] showed that 20 wt% Ni/TiO₂ was considerably efficient for performing vapour-phase hydrogenation, achieving 100% LA conversion and 99% GVL yield.

Despite comparable metal loading (~50%), alumina-supported Ni catalysts showed distinct performances across different studies, *e.g.*, 99% conversion and 90% selectivity according to

Hengne et al. [59], which was superior to that reported by Lv et al. (37.2% conversion and 85.8% selectivity) [76]. This can be attributed to the higher temperature (200 vs 150 °C) and larger amount of catalysts (8.8 vs 4.3 wt/wt% with respect to LA) employed in the former, underscoring the significance of thermal energy input and active site availability. Jiang et al. [75] investigated the effect of variable metal (Ni) loading on catalytic performance and suggested that increasing metal loading (10 to 40%) significantly influences LA conversion (50 to 100%) but it has a minor influence on GVL selectivity (93.4 to 99.7%). These findings can also be supported by a previous study of vapour-phase hydrogenation using Ni/TiO₂ catalyst [81].

Table 2. Nickel-based catalysts for the hydrogenation of LA to GVL

Catalysts (metal loading)	LA Conversion (%)	GVL yield (%)	GVL selectivity (%)	Productivity (mmol GVL g catalyst ⁻¹ h ⁻¹)	TOF (GVL s ⁻¹)	Solvent	H donor	Temp, time	LA loading	Catalyst quantity	Surface area (BET) m ² /g	Active metal species	Catalyst Recyclability (no. of times)	Reference
Ni@NCMs-700 Ni/AC (6.3% Ni)	99 80	-	99	-	-	Dioxane	30 bar H ₂	200 °C, 4 h	1 mmol	0.025 g	508	Metallic Ni	6 0	[72]
Ni/NiO	100	99.9	-	14.1	-	Dioxane 100 mL	20 bar H ₂	120 °C, 24 h	10 mmol	0.2 g	20	NiO, Ni	10	[73]
Ni/Al ₂ O ₃ (5 wt% Ni)	100	82	-	-	0.002 (at 24% LA conversion)	Water 50 mL/min	50 bar H ₂	200 °C, continuous, 100% LA conversion after 4 h	LA/H ₂ O 5 g/h	0.5 g	108	NiAl ₂ O ₄ , NiO	Activity decreased after 4h on stream	[74]
Ni-MMT Ni/Al ₂ O ₃ Ni/SiO ₂ Ni-ZnO (50 wt% Ni)	99 99 95 92	-	99 90 40 35	-	-	2-Propanol 95 mL	2-Propanol	200 °C, 1 h	5 mL	0.5 g	34 18 60 20	Crystalline metallic Ni	5	[59]
Ni/MgO- Al ₂ O ₃ (Ni/MgAlO _{2.5}) (40 wt% Ni)	23.3 45.2 64.6 100	23.0 43.8 62.2 99.7	98.7 96.8 96.3 99.7	-	-	Dioxane 40 mL		130 °C, 1 h 140 °C, 1 h 150 °C, 1 h 160 °C, 1 h	1 g	0.1 g	153	Metallic Ni particles	4	[75]
Ni/SiO ₂ Ni/ZrO ₂ Ni/ γ-Al ₂ O ₃ (20 wt% Ni)	15.7 3.5 10.7		90.9 60.2 71.9	-	1.82 0.52 1.32	Water	H ₂ gas 20 mL/min	270 °C (Vapour phase hydrogenation)	10 wt% in H ₂ O	0.05 g	155.5 108.8 23.5	-	-	[80]
Ni/TiO ₂ (5 wt% Ni) Ni/TiO ₂ (10 wt% Ni) Ni/TiO ₂ (15 wt%) Ni/TiO ₂ (20 wt%) Ni/TiO ₂ (30 wt%) Ni/SiO ₂ (47.89% Ni) Ni/Al ₂ O ₃ (45.95% Ni) Ni/TiO ₂ (43.63% Ni) Ni/ZrO ₂ (39.03% Ni) Ni/ZnO (48.19% Ni) Ni/MgO (31.80 wt%)	26.3 54.8 79.7 99.9 92.1 19.7 37.2 25.7 19.5 41.3 100	-	87.6 90.4 92.9 99.1 96.8 58.9 85.8 76.3 73.8 57.6 93.3	-	-	Water	H ₂ gas 20 mL/min	270 °C (Vapour phase hydrogenation)	10 wt% in H ₂ O	-	49.1 42.2 39.8 33.6 31.4	-	-	[81]
Ni/Al ₂ O ₃ (15 wt% Ni)	92	92	100	-	0.187 (at 20% LA conversion)	Solvent-free	50 bar H ₂	200 °C, 4 h	n _{Ni} /n _{LA} : 0.03,	1 g	96	Metallic Ni particles	2	[77]
Ni/γ-Al ₂ O ₃ (40 wt% Ni)	98.2 100	93.4 99.2	95.1 99.2	-	-	Water Dioxane 40 mL	30 bar H ₂	200 °C, 3 h 180 °C, 2 h	1 g	0.1 g	133.7	Metallic Ni particles	1 4	[78]
Ni/Al ₂ O ₃ (36.11 wt% Ni)	100	91	-	-	-	Water 190 mL	65 bar H ₂	250 °C, 2 h	10 mL (5 wt% aq. solution) 1 mL h ⁻¹	1 g	146.9	-	-	[29]
Ni/Al ₂ O ₃ Ni/MgO Ni/SiO ₂ Ni/TiO ₂ Ni/ZnO Ni/ZrO ₂	98 80 99 20 15 5	80 75 80 20 10 5	-	8.1 8.0 8.5	-		H ₂ gas 30 mL/min	250 °C (Vapour phase hydrogenation)	1 mL h ⁻¹	1 g	134 15 135 7 6 87	Metallic Ni, NiO	Ni/SiO ₂ was stable up to 25 h on stream	[79]

4.2. *Copper-based catalysts*

Several researchers have developed copper-based catalysts for the hydrogenation of LA to GVL as summarized in Table 3. Hengne and Rode [82] developed copper-based catalysts supported on ZrO_2 , Al_2O_3 , Cr_2O_3 , or BaO . Complete LA conversion was achieved in 5 h using Cu/ZrO_2 and $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts in both water and methanol as solvents (200 °C, 35 bar H_2). While both were 100% selective toward GVL in water, Cu/ZrO_2 achieved a higher GVL selectivity (90%) than $\text{Cu}/\text{Al}_2\text{O}_3$ (86%) in methanol. Under similar conditions (200 °C, 5 h, in water), Yuan et al. [83] achieved 100% LA conversion with 100% GVL selectivity but with FA as the hydrogen source. Utilizing a $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst, Obregon et al. [29] obtained 75% LA conversion with 66% GVL selectivity in water at 250 °C and 65 bar H_2 for 6 h. Changing water to THF as the solvent allowed 100% LA conversion to be achieved with 99% GVL selectivity under milder reaction conditions (180 °C, 4 h and 14 bar H_2) [84]. In a vapour-phase hydrogenation experiment, Lomate et al. [61] tested copper catalysts supported on SiO_2 , TiO_2 , ZSM-5, Al_2O_3 , or SiO_2 - Al_2O_3 , with the Cu/SiO_2 catalyst giving the optimal performance (48% LA conversion and 80% GVL selectivity) in CTH using FA at 250 °C. Xu et al. [85] prepared a Cu/WO_3 - ZrO_2 catalyst, which achieved the maximum GVL yield of 94% and 99% in ethanol and water, respectively (200 °C, 6 h, 50 bar H_2).

Table 3. Copper-based catalysts for the hydrogenation of LA to GVL

Catalysts	LA conversion (%)	GVL yield (%)	GVL selectivity (%)	Productivity (mmol GVL g catalyst ⁻¹ h ⁻¹)	TOF (GVL s ⁻¹)	Solvent	H donor	Temp, time	LA loading	Catalyst quantity	Surface area (BET) m ² /g	Active metal species	Catalyst Recyclability (no. of times)	Reference
Cu/Al ₂ O ₃ (0.8 mmol Cu)	100	-	99	-	-	Tetrahydrofuran	14 bar H ₂	180 °C, 4 h	0.3 g	0.15 g	-	Cu(s)	3	[84]
Cu/SiO ₂	48	-	80	-	-	Water	Formic acid	250 °C, 10 h	LA:FA 28:22 wt%	0.5 g	309	CuO, Metallic Cu	Cu/SiO ₂ showed good stability for 10 h	[61]
Cu/TiO ₂	8		25			(50 wt%)		(Vapour phase hydrogenation)			51			
Cu/ZSM-5	38		4								369			
Cu/Al ₂ O ₃	24		77								220			
Cu/SiO ₂ -Al ₂ O ₃ (6 wt% Cu)	48		2								485			
Cu-WO ₃ /ZrO ₂	100	94				Ethanol	50 bar H ₂	200 °C, 6 h	0.25 g	0.1 g	7.4	-	5	[85]
Cu/ZSM-5 (30 wt% Cu)	100	99				Water					92.0			
Cu/Al ₂ O ₃ (30 wt% Cu)	100	3				Ethanol								
Cu/Al ₂ O ₃ (30 wt% Cu)	75	66				Water	65 bar H ₂	250 °C, 6 h	10 mL (5 wt% aq. solution)	1 g	152.9	-	-	[29]
Cu/ZrO ₂ (20 wt% Cu)	60	-	100	94.5 (g Cu ⁻¹ h ⁻¹) (on the 30% LA conversion)	0.023 (at 30% LA conversion)	Water	Formic acid	180 °C, 5 h	18 mmol	0.24 g	40	-	-	[83]
	65		100			40 mL		180 °C, 8 h						
	66		100					180 °C, 10 h						
	67		100					180 °C, 12 h						
	100		100					200 °C, 5 h						
	100		100					200 °C, 2 h						
Cu/ZrO ₂	100	-	100			Water	40 bar H ₂	200 °C, 5 h	5 mL	0.5 g	22.1	Metallic copper, Cu ₂ O	4	[82]
Cu/Al ₂ O ₃	100		100			95 mL	35 bar H ₂				-			
Cu/Cr ₂ O ₃	9		100											
Cu/BaO	12		100											
Cu/ZrO ₂	100		90											
Cu/Al ₂ O ₃	100		86			Methanol								
Cu/Cr ₂ O ₃	72		45			95 mL								
Cu/BaO	78		41											

4.3. Zirconium-based catalysts

Zirconium-based catalysts were reported to show good results in terms of high LA conversion and selectivity toward GVL as summarized in Table 4. It should be noted they were often used in CTH with different secondary alcohols instead of H₂ gas as hydrogen donor.

Chia and Dumesic [28] pioneered the use of non-noble metal catalysts for the CTH of LA; they achieved 99.9% LA conversion with 71% GVL selectivity using 2-butanol as both the solvent and hydrogen donor at 220 °C for 16-h reaction. This result was improved in a recent study by Kuwahara et al. [66] in which ZrO₂/SBA-15 was employed for LA hydrogenation in 2-propanol (99.9% LA conversion with 90% selectivity) under mild reaction conditions (150 °C, 3 h). The reaction rate obtained using ZrO₂/SBA-15 was 1.7 times higher than that using the conventional bulk ZrO₂ catalyst. Enumula and co-workers [71] also tested ZrO₂/SBA-15 catalysts in three different secondary alcohols for continuous hydrogenation and obtained excellent results; 2-butanol gave the optimal result (100% LA conversion with 96% GVL selectivity) at 250 °C. The use of zeolite as support (Zr–beta zeolite) also showed excellent performance in LA hydrogenation (98-100% LA conversion with 96-99% GVL selectivity) [69,70].

Song et al. [86] reported the preparation of organic–inorganic hybrid catalysts using natural phytic acid obtained from seeds and grains as building blocks for the first time. They synthesized zirconium phosphonate (Zr–PhyA) from phytic acid and ZrCl₄, which efficiently catalyzed LA hydrogenation (100% conversion) to GVL of high selectivity (98.7%) using 2-propanol (130 °C, 2 h). The researchers attributed the excellent performance of Zr–PhyA to both Zr and phosphate groups (detailed mechanism in Section 5.2). Tang et al. [87] prepared HCl/ZrO(OH)₂ catalysts by *in situ* autonomous decomposition of ZrOCl₂·8H₂O in LA solution. The researchers proposed a mechanism by which the esterification of LA occurred in tandem with the hydrocyclization of

GVL through MPV reaction using 2-butanol as the H donor. The highest GVL yield was 92.4% from LA (99.9% conversion). The researchers achieved very good productivity of 65.5 mmol GVL g catalyst⁻¹ h⁻¹ (240 °C, 2 h), and even higher productivity was attained for a shorter reaction time (119.8 mmol GVL g catalyst⁻¹ h⁻¹ at 240 °C, 1 h).

Table 4. Zirconium-based catalysts for the hydrogenation of LA to GVL

Catalysts	LA conversion (%)	GVL yield (%)	GVL selectivity (%)	Productivity (mmol GVL g catalyst ⁻¹ h ⁻¹)	TOF (GVL s ⁻¹)	Solvent	H donor	Temp, time	LA loading	Catalyst quantity	Amount of alcohol	LA: Alcohol	Surface area (BET) m ² /g	Active metal species	Catalyst Recyclability (no. of times)	Reference
ZrO ₂ /SBA-15 (9.8 wt% ZrO ₂)	99.9	90	90	-	-	2-Propanol	2-Propanol	150 °C, 3 h	2 mmol	0.04 mg	10 mL (7.86 g, 130.70 mmol)	1:50 (V: V) 1:65.35 (molar ratio) ^a	810	Zr ⁴⁺ -O ²⁻ , Zr-OH	5	[66]
ZrO ₂ /SBA-15 (23.1 wt% ZrO ₂)	99 100 100	-	93 96 91	-	-	2-Propanol 2-Butanol Cyclohexanol	2-Propanol 2-Butanol Cyclohexanol	250 °C, continuous	1 mL h ⁻¹	0.5 g	-	1:7 (molar ratio)	446	Zr ⁴⁺ , ZrO ₂	Constant activity (100% LA conversion) for 20 h on stream	[71]
HCl/ZrO(OH) ₂ from ZrOCl ₂ ·8H ₂ O	99.9 99.9	92.4 84.5	-	65.5 119.8	-	2-Butanol	2-Butanol	240 °C, 2 h 240 °C, 1 h	43 mmol	5 mol% relative to LA	95 g (1.28 mol)	1:17 (V: V) 1:29.80 (molar ratio) ^a	351	HCl/ZrO(OH) ₂	-	[87]
Zr-PhyA	100	98.7	-	-	-	2-Propanol	2-Propanol	130 °C, 2 h	1 mmol	0.2 g	4 mL (3.14 g)	1:40 (V: V) 1:52.3 (molar ratio) ^a	215	Zr ⁴⁺	5	[86]
Zr-Beta zeolite (Si/Zr 107)	100	96	96	30 (g Zr ⁻¹ h ⁻¹) (after first 2h)	-	2-pentanol	2-pentanol	118 °C, 10 h	1 mmol	0.2 g	5 mL	1:50 (V: V) 1:46 (molar ratio) ^a	474	-	Stable for 10 h in continuous flow reactor	[70]
Zr-Beta zeolite	98	-	99	2.5 (mmol Zr ⁻¹ h ⁻¹)	-	2-Butanol	2-Butanol	120 °C, 11 h	0.34 mmol	1 mol% relative to LA	0.75 mL (0.60 g, 8.15 mmol)	1:24 (molar ratio) ^a	-	-	4	[69]
ZrO ₂	52 99.9	-	22 71	0.234 -	-	2-Butanol	2-Butanol	150 °C, 16 h 220 °C, 16 h	5 wt%	1:2 1:2	-	1:7 (molar ratio)	-	ZrO ₂	ZrO ₂ Deactivated for the first 100 h on stream and stabilized afterwards	[28]
ZrO ₂ +MgO (1:1)	99.9 99.9	-	39 92	1.002 -	-	-	-	-	-	2:1 (catalyst:L A)	-	-	-	-	-	-

^a Molar ratio is calculated based on the mass/volume of LA and alcohol given in the respective paper

4.4. Combined metal catalysts

Catalysts combining different non-noble metals have been investigated for the hydrogenation of LA to GVL (Table 5). The synergistic effects of combined metals have been suggested for enhanced catalytic performance.

Gupta and Kantam [27] developed a hydrotalcite-derived catalyst (Cu/Ni/Mg/Al catalyst (molar ratio 0.75/0.5/1/1)) and achieved complete conversion of LA with 100% selectivity toward GVL at 30 bar H₂ in dioxane (140 °C, 3 h). The LA conversion increased with the copper content, whereas the GVL selectivity increased with the nickel content. The excellent catalytic activity was ascribed to the synergistic effect between copper, nickel, and MgO. In addition, the presence of nickel-copper alloys might be important for preventing sintering and metal leaching in the developed catalysts [27]. Similarly, a low-cost and magnetic hydrotalcite-derived catalyst (Ni/Cu/Mg/Al/Fe) was developed by Zhang et al. [88], achieving complete LA conversion with 98% GVL selectivity in methanol (142 °C, 3 h). Meanwhile, Gundekari and Srinivasan [89] combined Ni and Al and reported the *in situ* generation of Ni(0)@boehmite from NiAl-layered double hydroxide (LDH) under moderate reaction conditions (water as solvent, 30 bar H₂, 200 °C, 6 h). The developed catalyst exhibited superior catalytic performance to that of homogeneous and heterogeneous Ni catalysts, achieving complete LA conversion with 100% GVL selectivity. The hydrotalcite-derived Cu–Fe catalyst resulted in 90.1% GVL yield and 98.7% LA conversion in relatively harsh reaction conditions (water as the solvent, 70 bar H₂, 200 °C, 10 h) [90]. Obregon et al. [29] investigated the monometallic Ni and Cu catalysts and a combined Ni–Cu catalyst supported on Al₂O₃. The bimetallic Ni–Cu/Al₂O₃ catalysts presented similar activity to that of monometallic Ni/Al₂O₃ and suppressed by-product formation and carbon deposition, indicating the important synergistic effects between metals. Complete LA conversion to 96%

GVL yield at 65 bar H₂ was reported (250 °C, 2 h). Zhong et al. [91] recently reported the hydrogenation of LA to GVL using zerovalent non-noble metals and water splitting at high temperature (250 °C). They combined Zn with Fe, Cu, Ni, Cr, or Mo, and the highest LA conversion was achieved over Ni–Zn (99.7%), while the maximum GVL yield (96.5%) was obtained over a Fe–Zn catalyst.

Table 5. Combined metal catalysts for the hydrogenation of LA to GVL

Catalysts	LA conversion (%)	GVL yield (%)	GVL selectivity (%)	Productivity (mmol GVL g catalyst ⁻¹ h ⁻¹)	TOF (GVL s ⁻¹)	Solvent	H donor	Temp, time	LA loading	Catalyst quantity (with respect to LA)	Metal ratio	Surface area (BET) m ² /g	Active metal species	Catalyst Recyclability (no. of times)	Reference
Cu/Ni/Mg/Al (hydrotalcite-derived)	100	100	-	-	4.5	Dioxane, 30 mL	30 bar H ₂	140 °C, 3 h	0.5 g, 4.31 mmol	0.1 g, 20 wt%	0.75:0.5:1:1 (molar ratio)	65	Cu ⁰ , Cu ²⁺ , CuO, Ni ⁰ , NiO, MgO	4	[27]
Ni/Al (LDH, hydrotalcite)	100	100	-	-	-	Water, 40 mL	30 bar H ₂	200 °C, 6 h	1 g, 2.5 wt%, 8.6 mmol	0.161 g, 7 wt%	3:1 (atomic ratio)	-	Ni (0) @boehmite	4	[89]
Fe & Zn	98.8	96.5	97.7	-	-	Water	Water splitting in high temp.	250 °C, 2.5 h	86 mmol/L	21 mmol of Zn and 0.5g of other metal	-	-	Zn/ZnO	4	[91]
Ni & Zn	99.7	93.0	93.3	-	-										
Cu & Zn	93.9	92.0	98.0	-	-										
Cr & Zn	56.2	42.7	76.0	-	-										
Mo & Zn (zero valent metal)	84.2	59.2	70.3	-	-										
Fe–Ni/MMT (25 wt% Fe+ 25 wt% Ni)	99	-	98	-	-	2-propanol 95 mL	35 bar H ₂	200 °C, 1 h	5 wt%	0.5 g	1:1 (w/w)	75	-	6	[92]
Ni/Cu/Mg/Al/Fe	100	98.1	-	-	-	Methanol/water 20 mL/0.5 g	20 bar H ₂	150 °C, 3 h	0.5 g, 0.2155 mol/L	0.125 g	-	-	-	5	[88]
Ni–Cu/Al ₂ O ₃	100	96	-	-	-	Water 190 mL	65 bar H ₂	250 °C, 2 h	10 mL (5 wt% aq. solution)	1 g	1.56, 8.56:5.5 (wt%)	132.4	Cu ⁰ , Ni ⁰	-	[29]
Cu/Fe (hydrotalcite-derived)	98.7	90.1	-	-	-	Water 5 mL	70 bar H ₂	200 °C, 10 h	1.02 g	0.1 g	1.0	-	CuFe ₂ O ₄ , CuO	3	[90]

5. Significance of catalyst properties influencing hydrogenation performance

5.1. Structural characteristics of catalysts

Catalyst loading and metal dispersion over a solid support were suggested to influence the catalytic activity and selectivity toward GVL [92,75]. Enumula et al. [71] (Table 4) reported that GVL selectivity increased from 59% to 93% with the increasing zirconia loading on SBA-15 from 10% to 25%, whereas pure zirconia exhibited only 7% GVL selectivity. This highlighted the significance of metal dispersion over a support for accessible active sites. It was observed that catalysts containing Ni particles with sizes of smaller than 10 nm showed the highest activity for LA conversion, due to high nickel surface area [77,74]. The formation of small particles was favoured at a low nickel loading. Integration of macropores and mesopores along with homogeneous dispersion of nickel nano-particles on porous carbon microsphere significantly improved LA hydrogenation (99% conversion and selectivity) [72].

In addition, the use of combined metal particles resulted in high LA conversion and GVL yield with a low by-product content, demonstrating favourable synergistic effects of co-catalysts [27, 29]. The high adsorption of dissociative hydrogen on CuNi alloy was suggested to be beneficial to hydrogenation efficiency [27,93]. The pretreatment of nickel-based catalyst in H₂ gas at 200-300 °C enhanced its catalytic activity (normalized by surface area) [73]. Metallic nickel was produced during the partial reduction of NiO during the pretreatment, which formed heterojunctions with the unreacted NiO. The latter was favourable for the adsorption of LA, whereas metallic nickel was responsible for H₂ adsorption and the subsequent dissociation into hydrogen atoms. Such synergy was suggested to be significant for achieving excellent catalytic performance (100% LA conversion and 99.9% GVL yield). These findings highlight the need for a variety of active sites playing complementary roles for efficient GVL production.

The review of pertinent literature reveals no direct relation between the hydrogenation performance and surface area (BET) of the catalysts. Xu et al. [85] observed that Cu-WO₃/ZrO₂ ($S_{\text{BET}} = 7.4 \text{ m}^2 \text{ g}^{-1}$) gave better performance than Cu/ZSM-5 ($S_{\text{BET}} = 92.0 \text{ m}^2 \text{ g}^{-1}$) under the same reaction condition, despite the smaller surface area for the former. Kuwahara et al. [66] compared the activities of ZrO₂/SBA-15 silica and ZrO₂/SiO₂ having similar zirconium loading (9.6-9.8%) but with considerably different surface areas ($S_{\text{BET}} = 810$ and $250 \text{ m}^2 \text{ g}^{-1}$, respectively). The catalysts exhibited similar activities in terms of ~100% LA conversion with 87-91% GVL yield. In addition, despite the distinctive porous structures ($D_p = 7.7$ and 2.9 nm), ZrO₂/SBA-15 and ZrO₂/MCM-41 catalysts produced similar results of 98-99.5% LA conversion with 89-91% GVL yield. The catalysts had comparable surface areas (783 - $810 \text{ m}^2 \text{ g}^{-1}$) and catalyst loading (9.7-9.8%). The researchers hypothesized that the unique local structure of the Zr atoms that were highly dispersed on the silica support with low coordination geometry may be responsible for the high catalytic activity rather than the textural properties of silica such as topology, pore size, and surface area [66]. Similarly, there was no correlation found between the surface area of the catalysts and LA conversion as well as GVL selectivity in the vapour-phase hydrogenation [61].

While the surface area of prepared catalysts may not directly correlate to their performances, a catalyst support with a high surface area can increase the availability of active sites for reaction by improving metal dispersion [66,71], which is considered an important factor for efficient GVL synthesis. Hydrotalcite-derived catalysts has been reported to achieve uniform distribution of metal cations into the brucite-like layers combining the presence of oxide phase and reduced phase of metals [27].

5.2. Acid–base properties and role of solid support

Besides the obvious significance of metal particles for LA hydrogenation, the acid-base properties and structural characteristics of the solid supports play an important role influencing hydrogenation performance [94]. Metal catalysts are usually supported on silica, Al₂O₃, zeolites, as well as other materials with different acid-base properties as summarized in Table 6. Physical supports allow for the good dispersion of metal nanoparticles providing a high number of active sites [71], as demonstrated in previous studies using noble metal catalysts for GVL production [7,95]. As for non-noble metal catalysts, unsupported porous metals, such as Raney[®] Ni, have been used in some experiments [96,97], and the use of elemental metals (Zn, Fe, Cr, Cu, Ni, and Mo) has been recently reported by Zhong et al. [91].

Mohan et al. [79] explored the effects of solid supports for Ni catalyst, such as Al₂O₃, SiO₂, ZnO, ZrO₂, TiO₂, and MgO, on the catalytic activity of LA hydrocyclization in the vapour phase in the absence of organic additives. The pyridine-adsorbed infrared spectra revealed the presence of both Lewis and Brønsted acid sites, which were responsible for the dehydration of the intermediate 4-hydroxy pentanoic acid to yield GVL. Strong Lewis–Brønsted acidity was also found in the Cu–ZrO₂ [82] and Ni/MMT catalysts [59]. As for the latter, the authors suggested that the strong acid sites of MMT facilitated LA esterification and cyclization, while the metallic Ni sites promoted selective hydrogenation of the LA ester to GVL [59]. Enumula et al. [71] observed that the increased acidity in ZrO₂/SBA-15 catalyst (1.49 mmol NH₃ g⁻¹), owing to the higher ZrO₂ proportion (25 wt%), enhanced the GVL selectivity. However, a further increase in acidity (2.18 mmol NH₃ g⁻¹ for 30 wt% ZrO₂) led to significant generation of dehydration products and ring opening products of GVL, with a concomitant decrease in the GVL selectivity. Similarly, Kumar and co-workers [80] observed that LA conversion was initiated by Lewis acid

sites in Ni-based catalysts, whereas strong Brønsted acidity (*e.g.*, in Ni/ZrO₂, Ni/γ-Al₂O₃, and Ni/TiO₂) resulted in the ring opening products of GVL.

Table 6. Characteristics of commonly used supports for LA to GVL conversion

Support	Acidic/basic	Catalyst	Features	LA conversion (%) / GVL selectivity (%)	Reference
Al ₂ O ₃	Acidic	Ni/ Al ₂ O ₃	-High acidity	100/82	[74]
			-High metal dispersion	99/90	[59]
			-Good support for dehydration	100/99.2	[78]
			-Metal leaching is high in water	100/99	[29]
		Cu/ Al ₂ O ₃	98/80	[79]	
			100/99	[84]	
TiO ₂	Acidic	Ni-Cu/ Al ₂ O ₃		100/100	[82]
		Ni/ TiO ₂	-Moderate Lewis acidity	100/96	[29]
		Cu/ TiO ₂	-Does not provide good yield in liquid phase hydrogenation	99.9/99.1	[81]
				25.7/76.3	[76]
SiO ₂	Acidic	Ni/ SiO ₂		20/20	[79]
ZrO ₂	Acidic	Cu/ SiO ₂	-Good selectivity towards GVL but low LA conversion mostly	15.7/90.9	[80]
			-Good metal dispersion	19.7/58.9	[76]
		Ni/ZrO ₂	-Good stability	99/80	[79]
			-Can be used as support as well as catalyst	48/80	[61]
Cu/ ZrO ₂		19.5/73.8	[76]		
		100/100	[82]		
ZnO	Basic	Ni/ ZnO	-High stability	60/100	[83]
			-Good interaction with Cu		
MgO	Basic	Ni/MgO	-Promotes esterification of hydroxyvaleric acid	92/35	[59]
				41.3/57.6	[76]
Zeolite	Acidic and basic	Zr-Beta	-Promotes esterification of hydroxyvaleric acid	100/93.3	[76]
				80/75	[79]
SBA-15	Acidic And basic	ZrO ₂ /SBA-15	-Moderate Lewis and Bronsted acidity	100/96	[70]
				98/99	[69]
			-Few basic sites		
Montmorillonite (MMT)	Acidic	Ni/MMT	-Mesoporous silica	99.9/90	[66]
			-Highly dispersed metals and acidic sites	100/96	[71]
		Fe-Ni/MMT	-Few basic sites		
			- Strong cation exchange capacity (97 mequi/100 g), -Favors lactonization of GVL, -High metal dispersion -Low metal leaching -High stability and recyclability -Lewis and Bronsted acid sites	99/99	[59]
		99/98	[92]		

The addition of a base (MgO) to the reactant improved the GVL formation rate (16.7 μmol g⁻¹ min⁻¹) compared to the case without base addition (3.9 μmol g⁻¹ min⁻¹), where basic sites have been suggested to work actively for MPV reaction either individually or in support with acid sites improving the efficiency of hydrogen transfer during conversion [28]. In addition, Lewis base sites derived from MgO in a hydrotalcite derived Cu/Ni/Mg/Al catalyst might activate the

carbonyl (C=O) group of LA, leading to efficient LA conversion in conventional hydrogenation [27]. Wang and co-workers [70] reported that Zr-beta zeolite rich in Lewis acid sites (Lewis/Brønsted acid ratio of 8.4) led to good activity (100% LA conversion) and selectivity toward GVL (96%) using 2-pentanol as the H donor. Kuwahara et al. [66] concluded that a combination of acid sites (0.784 mmol g⁻¹) and base sites (0.259 mmol g⁻¹) were responsible for the high activity of ZrO₂/SBA-15. In particular, base sites catalyzed the CTH reaction of methyl levulinate to GVL. The high acidity and basicity of Zr-PhyA catalyst were suggested to be crucial for MPV reaction [86]. The Lewis acid and Lewis base sites were derived from Zr⁴⁺ and from O²⁻ in the phosphate groups, respectively, both of which significantly contributed to the outstanding catalytic performance (complete LA conversion with 98.7% GVL selectivity). The Lewis acid sites (indicated by the high binding energy of Zr and NH₃-TPD measurement) activated the carbonyl groups to accelerate the reaction. Meanwhile, the basicity of Zr-PhyA was higher than that of the other catalysts (*e.g.*, Zr-BTC), which is beneficial for the dissociation of hydroxyl groups in iso-propanol in cooperation with Lewis acid sites (Zr⁴⁺). Utilization of zirconium as a non-noble metal has been highlighted for MPV reaction due to its amphoteric nature, providing necessary acid and base sites to achieve high GVL yield through transfer hydrogenation [28,66,70]. The acid-base properties of catalysts can be tuned through the selection of appropriate support for metal particles.

6. Effects of different reaction parameters

6.1. Hydrogen donor

External hydrogen gas has been widely used in LA hydrogenation to GVL (Tables 2, 3, and 5). A H₂ pressure that was as low as 14 bar resulted in 100% LA conversion and 99% GVL selectivity

over a copper catalyst, under harsh reaction conditions (180 °C, 4 h, 50 wt% catalyst relative to LA, THF as solvent) [84]. With a high H₂ pressure (*e.g.*, 30 bar), comparatively mild conditions (140–160 °C, 1–3 h, 10–20 wt% catalyst relative to LA, dioxane as solvent) can give rise to good LA conversion (100%) and GVL yield (100%) [27,75].

Alternatively, in LA hydrogenation to GVL via CTH process, organic hydrogen donors such as FA and alcohols are utilized. Such practice eliminates the usage of external H₂ and, subsequently, the requirement for a high-pressure reactor [25]. In general, alcohols produce excellent results under mild reaction conditions. When compared to primary alcohols, secondary alcohols, such as 2-propanol, 2-butanol, and cyclohexanol, were more promising H donors resulting in 100% LA conversion and 93%, 96%, and 91% GVL yield, respectively, over the ZrO₂/SBA-15 catalyst [71]. Comparable results were obtained by Kuwahara et al. [66] for the same catalyst using secondary alcohols. In comparison, primary alcohols generally demonstrate a slow breakdown to donate a H atom, thereby hindering transfer hydrogenation [59]. A strong correlation has been established between the reducing capacity of alcohols and MPV reduction, which follows the order MeOH < EtOH < 1-BuOH < 2-BuOH = 2-PrOH [87].

The effect of varying the substrate LA to alcohol molar ratio could be important. We calculated the molar ratio of LA to alcohol employed in different studies, based on the published experimental details (Table 4). It can be observed that the experiments conducted at a low temperature (< 150 °C) utilized a high proportion of alcohol [66,70,86], whereas a low alcohol content was used in the experiments run at high temperature (220 to 250 °C) [28,71].

6.2. *Reaction temperature and time and H₂ pressure*

A wide range of temperatures (118 to 270 °C) and reaction time ranging from 1 to 24 h (2–3 h for the majority of experiments) have been employed for synthesizing GVL from LA in different experiments. Temperatures ranging from 120 to 200 °C are most commonly used for liquid-phase hydrogenation, whereas temperatures of greater than 250 °C are used for vapour-phase hydrogenation (because of the boiling point of LA at 245 °C). Increasing the reaction temperature above 250 °C for CTH increases the dehydration of LA and the formation of α -angelica lactones, thereby decreasing the selectivity to GVL [71]. Xu and co-workers reported that the hydrogenation performance improved at elevated temperatures over a Cu–WO₃/ZrO₂ catalyst at 50 bar H₂. Complete LA conversion with 81% and 94% GVL yields were achieved at 140 and 200 °C, respectively, which was higher than that at 100 °C (35% LA conversion with low GVL selectivity). However, further increase in temperature lowered the GVL yield. On the other hand, H₂ pressure ranging from 14 to 70 bar has been employed during hydrogenation reaction. Although in most experiments 30–40 bar H₂ was adopted, H₂ pressure as low as 14 bar worked efficiently for LA to GVL conversion depending on the choice of catalysts and other operating parameters [84].

6.3. *Solvent*

For CTH, alcohol is used both as the solvent and the H donor. Secondary alcohols such as 2-propanol, 2-butanol, and cyclohexanol have been commonly used to achieve efficient hydrogenation (Table 2 and 4). In the hydrogenation by external H₂, a variety of solvents including water, dioxane, THF, ethanol, and methanol have been employed, with water being the most common. Hydrogen gas solubility does not appear to limit the solvent choice.

Hengst et al. [77] reported significant conversion of LA (75–100%) in different alcohols as solvent in the hydrogenation by external H₂ over a Ni/Al₂O₃ catalyst, which was higher than that in water (only 2% conversion) under identical reaction conditions (150 °C, 10 bar H₂, 6 h). However, the GVL selectivity was low in alcohols, compared to 100% selectivity achieved in water. Therefore, alcohols may assist the activation of LA for conversion, whereas water possibly favoured the pathways for selective GVL production. Interestingly, the optimal result was achieved under solvent-free conditions, *i.e.*, 92% LA conversion with 100% GVL selectivity at 50 bar H₂ (400 °C, 4 h). In another experiment, Fu and co-workers [78] attained higher LA conversion (100%) and GVL selectivity (99.2%) by employing dioxane as the solvent under milder reaction conditions (180 °C, 2 h), compared to that in water (98.2% conversion and 95.1% selectivity at 200 °C, 3 h). Similar results (100% LA conversion and 100% yield) in dioxane as the solvent were reported by Gupta and Kantam [27]. Nevertheless, water is mostly used in vapour-phase hydrogenation, while in liquid-phase hydrogenation, the use of water usually requires a higher reaction temperature (≥ 200 °C) than that in other solvents [29,78,89]. Using a bimetallic catalyst (50 wt% Fe–Ni/MMT), Kadu et al. [92] observed that the leaching of Fe and Ni was considerably higher (732.1 mg L⁻¹ for Fe and 37.5 mg L⁻¹ for Ni) in an aqueous medium because of their hydrophilic nature. Such metal leaching could be suppressed when alcohols were used as solvents. Similar findings were reported by other studies [82,59]. In particular, primary alcohols led to the decrease of GVL selectivity, whereas secondary alcohols were highly selective and suppressed metal leaching [92].

Of the most commonly employed solvents, water is inherently the greenest [31, 98]. The biggest issue is the need of energy-efficient separation and purification of water after its use in chemical processes to avoid pollution. The CHEM21 solvent selection guide ranks solvents according to

the severity of safety (S), health (H) and environmental (E) hazards (Table 7). Alcohols generally bear few hazards, but methanol is acutely toxic. Ethers can form explosive peroxides. It should be discussed that several experiments utilized solvents such as dioxane and THF [27,73,75,78,84], which are not recommended as green solvents due to their high toxicity and potential safety hazards [31] although high GVL yield was achieved. By contrast, secondary alcohols are recommended as green solvents [31] and they have been reported to prevent metal leaching from catalysts during the reaction [59,92]. In addition, alcohols can be bio-derived to substitute their counterparts produced in petrochemical industry [31], and such use of renewable resources can substantially contribute to realizing a green route for GVL production. Solvent-free reaction involving Ni/Al₂O₃ catalyst was reported to achieve 92% LA conversion with 100% GVL selectivity (4 h, 200 °C, 50 bar H₂) [77]. This system represents a potentially green approach for GVL production, i.e., by eliminating the separation step for recovering the organic solvents, there is an economic and environmental advantage when high selectivity is achieved. However, the disadvantage of a solvent-free process is that precise regulation of temperature to avoid runaway reactions and decomposition is more difficult to control in a large-scale operation.

Table 7. CHEM21 solvent selection guide for GVL production solvents [31]

Solvent	S	H	E	Ranking
Water	1	1	1	Recommended
Methanol	4	7	5	Recommended
Ethanol	4	3	3	Recommended
2-Propanol	4	3	3	Recommended
2-Butanol	3	4	3	Recommended
1,4-Dioxane	7	6	3	Hazardous
THF	6	7	5	Problematic

7. Recycling and separation of catalysts

Simple filtration followed by washing with solvent is mostly employed to separate and recover the catalyst from conversion systems. The good recyclability of non-noble metal catalysts has been demonstrated through the reactivation of catalyst at a definite temperature in a H₂ atmosphere, which resulted in promising conversion in successive catalytic runs, although a lowered performance was observed with no catalyst reactivation [27]. Partially reduced Ni-NiO catalyst has been presented as a robust catalyst that was recycled for ten times by simple centrifugation and washing without significant loss in catalytic activity and no leaching detected in the solution. High recyclability was attributed to the stable surface composition of Ni-NiO in the given reaction condition [73]. MMT-supported catalysts (Ni/MMT, Fe-Ni-MMT) have shown high recyclability (99% selectivity and conversion up to 5-6 cycles) [59,92]. The *in-situ* reduction of NiO to Ni⁰ during the reaction increased the Ni⁰ content upon repetitive usage of the catalyst, which maintained its activity in successive runs. Liu et al. [72] reported high stability of Ni@NCMs-700 catalyst that was recycled six times without significant loss in activity (~96% on the 6th run). The unique porous structure, graphitic carbon layer, and synergy between nitrogen and Ni collectively prevented the leaching and aggregation of Ni nanoparticles.

Zhang and co-workers [84] observed that copper leaching (30 mg L⁻¹) from Cu/Al₂O₃ resulted in the loss of catalytic activity after only a few catalytic runs and led to product contamination. By incorporating silver, which is relatively cheap among noble metals, copper leaching was significantly reduced (< 0.1 mg L⁻¹) and the high catalytic activity of CuAg/Al₂O₃ can be maintained even after nine successive runs. Moreover, several studies emphasized that metal leaching can be prevented using alcohol as the reaction solvent instead of water [59,82,92]. The produced GVL can be easily separated from the reaction medium by distillation owing to its high

boiling point compared to those of commonly used solvents such as alcohols, water, and dioxane.

8. Conclusions and prospects

Owing to its renewable origin, biodegradability, and nontoxic nature, GVL is considered a green solvent serving sustainable biorefinery applications such as biomass and chemical conversion.

The use of GVL as fuel additive can reduce emissions and hence combat air pollution.

Furthermore, it is a versatile platform chemical which can be converted to other valuable carbon-based products.

Typically, GVL is synthesized by the hydrogenation of LA over noble metal catalysts (*e.g.*, Ru).

However, non-noble metals, such as Ni, Cu, Fe, Zr, Al, and Mg, have recently attracted

considerable attention owing to their low cost, high abundance in nature, environmental

sustainability, and easy separation and recycling. LA can be hydrogenated by either external H₂

gas or by organic hydrogen donors (such as FA or alcohols) through a CTH process over non-

noble metal catalysts. It was observed that the structural characteristics and acid–base properties

of the catalysts strongly influenced their hydrogenation performance. The well-dispersed metal

particles along with the combination of Lewis acid and base sites could be conducive to high LA

conversion and GVL selectivity. In addition, solvents play an important role in controlling metal

leaching and hence determine the catalyst recyclability.

Despite the extensive research interests in the use of non-noble metal catalysts, a large-scale

demonstration has not been reported. Catalyst stability and recyclability could be the potential

challenges to upscaling GVL production, in view of the metal leaching frequently reported in the

literature. Future research may investigate the interplay between non-noble metals and solid

supports of various physicochemical properties via experimental and computational studies, with

the aim to devise structurally stable catalysts with yield and selectivity improvement. A green route for GVL synthesis necessitates the development of recyclable and high-performance catalysts. The use of carbonaceous supports is a potential research landscape pursuing green synthesis, in which carbon-rich materials are abundant in waste biomass. Green catalysts should be able to accommodate mild reaction conditions (low temperature and pressure, short reaction time), use of non-H₂ hydrogen donors, and solvents with low environmental impacts in CTH. Simple and environmentally benign protocols for green catalyst synthesis are desirable. While most of the previous studies addressed only the LA-to-GVL reaction, future research may incorporate the upstream conversion of biomass to LA, to examine the compatibility between step-wise catalytic systems or even the potential of one-pot catalytic process. Such comprehensive studies can serve as model scenarios for the evaluation of life-cycle environmental and economic feasibility, which are important considerations for sustainable biorefinery and circular bio-economy development.

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References

- [1] F. Cherubini, The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, *Energ. Convers. Manag.* 51 (2010) 1412–1421.
<https://doi.org/10.1016/j.enconman.2010.01.015>.
- [2] I. T. Horváth, H. Mehdi, V. Fábos, L. Boda, L. T. Mika, γ -Valerolactone- A sustainable liquid for energy and carbon-based chemicals, *Green Chem.* 10 (2008) 238–242.
<https://doi.org/10.1039/b712863k>.
- [3] K. Yan, Y. Yang, J. Chai, Y. Lu, Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals, *Appl. Catal. B: Environ.* 179 (2015) 292–304.
<https://doi.org/10.1016/j.apcatb.2015.04.030>.
- [4] Á. Bereczky, K. Lukács, M. Farkas, S. Dóbbé, Effect of γ -Valerolactone blending on engine performance, combustion characteristics and exhaust emissions in a diesel engine, *Nat. Resour.* 05 (2014) 177–191. <https://dx.doi.org/10.4236/nr.2014.55017>.
- [5] H. Mehdi, R. Tuba, L.T. Mika, A. Bodor, K. Torkos, I.T. Horvath, Catalytic conversion of carbohydrates to oxygenates, in: P. Fornasiero, M. Graziani (Eds), *Renewable Resources and Renewable Energy: A Global Challenge*, CRC Press, 2006, pp. 55-60.
- [6] S. Choi, C.W. Song, J.H. Shin, S.Y. Lee, Biorefineries for the production of top building block chemicals and their derivatives, *Metab. Eng.* 28 (2015) 223–239.
<https://doi.org/10.1016/j.ymben.2014.12.007>.
- [7] L.E. Manzer, Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer, *Appl. Catal. A: Gen.* 272 (2004) 249–256.
<https://doi.org/10.1016/j.apcata.2004.05.048>.

- [8] D.M. Alonso, J.M.R. Gallo, M.A. Mellmer, S.G. Wettstein, J.A. Dumesic, Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts, *Catal. Sci. Technol.* 3 (2013) 927–931. <https://doi.org/10.1039/c2cy20689g>.
- [9] S.S. Chen, T. Maneerung, D.C.W. Tsang, Y.S. Ok, C.-H. Wang, Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts, *Chem. Eng. J.* 328 (2017) 246–273. <https://doi.org/10.1016/j.cej.2017.07.020>.
- [10] B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid, *Green Chem.* 8 (2006) 701-709. <https://doi.org/10.1039/b518176c>.
- [11] D.M. Alonso, S.G. Wettstein, M.A. Mellmer, E.I. Gurbuz, J.A. Dumesic, Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass, *Energ. Environ. Sci.* 6 (2013) 76–80. <https://doi.org/10.1039/c2ee23617f>.
- [12] T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Eliot, L. Lasure, S. Jones, Top value added chemicals from biomass. Volume 1-Results of screening for potential candidates from sugars and synthesis gas, Department of Energy Washington DC, 2004. <http://www.osti.gov/bridge>.
- [13] S.S. Chen, I.K.M. Yu, D.C.W. Tsang, A.C. Yip, E. Khan, L. Wang, Y.S. Ok, C.S. Poon, Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Brønsted acids: Temperature and solvent effects, *Chem. Eng. J.* 327 (2017) 328–335. <https://doi.org/10.1016/j.cej.2017.06.108>.
- [14] J. Molleti, M.S. Tiwari, G.D. Yadav, Novel synthesis of Ru/OMS catalyst by solvent-free method: Selective hydrogenation of levulinic acid to γ -valerolactone in aqueous medium

- and kinetic modelling, *Chem. Eng. J.* 334 (2018) 2488–2499.
<https://doi.org/10.1016/j.cej.2017.11.125>.
- [15] Z. Yan, L. Lin, S. Liu, Synthesis of γ -Valerolactone by hydrogenation of biomass-derived levulinic acid over Ru/C catalyst, *Energ. Fuel.* 23 (2009) 3853–3858.
<https://doi.org/10.1021/ef900259h>.
- [16] O.A. Abdelrahman, A. Heyden, J.Q. Bond, Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ -valerolactone over Ru/C, *ACS Catal.* 4 (2014) 1171–1181. <https://doi.org/10.1021/cs401177p>.
- [17] W. Li, J.-H. Xie, H. Lin, Q.-L. Zhou, Highly efficient hydrogenation of biomass-derived levulinic acid to γ -valerolactone catalyzed by iridium pincer complexes, *Green Chem.* 14 (2012) 2388–2390. <https://doi.org/10.1039/c2gc35650c>
- [18] J. Deng, Y. Wang, T. Pan, Q. Xu, Q.-X. Guo, Y. Fu, Conversion of carbohydrate biomass to γ -valerolactone by using water-soluble and reusable iridium complexes in acidic aqueous media, *ChemSusChem.* 6 (2013) 1163–1167. <https://doi.org/10.1002/cssc.201300245>.
- [19] K. Yan, T. Lafleur, C. Jarvis, G. Wu, Clean and selective production of γ -valerolactone from biomass-derived levulinic acid catalyzed by recyclable Pd nanoparticle catalyst, *J. Clean. Prod.* 72 (2014) 230–232. <https://doi.org/10.1016/j.jclepro.2014.02.056>.
- [20] A.S. Amarasekara, M.A. Hasan, Pd/C catalyzed conversion of levulinic acid to γ -valerolactone using alcohol as a hydrogen donor under microwave conditions, *Catal. Commun.* 60 (2015) 5–7. <https://doi.org/10.1016/j.catcom.2014.11.009>.
- [21] P.P. Upare, J.-M. Lee, D.W. Hwang, S.B. Halligudi, Y.K. Hwang, J.-S. Chang, Selective hydrogenation of levulinic acid to γ -valerolactone over carbon-supported noble metal catalysts, *J. Ind. Eng. Chem.* 17 (2011) 287–292. <https://doi.org/10.1016/j.jiec.2011.02.025>.

- [22] J.N. Putro, A. Kurniawan, F.E. Soetaredjo, S.-Y. Lin, Y.-H. Ju, S. Ismadji, Production of gamma-valerolactone from sugarcane bagasse over TiO₂-supported platinum and acid-activated bentonite as a co-catalyst, *RSC Adv.* 5 (2015) 41285–41299. <https://doi.org/10.1039/c5ra06180f>
- [23] W.R.H. Wright, R. Palkovits, Development of heterogeneous catalysts for the conversion of levulinic acid to γ -valerolactone, *ChemSusChem.* 5 (2012) 1657–1667. <https://doi.org/10.1002/cssc.201200111>.
- [24] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass, *Green Chem.* 15 (2013) 584-595. <https://doi.org/10.1039/c3gc37065h>.
- [25] X. Tang, X. Zeng, Z. Li, L. Hu, Y. Sun, S. Liu, T. Lei, L. Lin, Production of γ -valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply, *Renew. Sust. Energ. Rev.* 40 (2014) 608–620. <https://doi.org/10.1016/j.rser.2014.07.209>
- [26] F. Liguori, C. Moreno-Marrodan, P. Barbaro, Environmentally friendly synthesis of γ -valerolactone by direct catalytic conversion of renewable sources, *ACS Catal.* 5 (2015) 1882–1894. <https://doi.org/10.1021/cs501922e>.
- [27] S.S.R. Gupta, M.L. Kantam, Selective hydrogenation of levulinic acid into γ -valerolactone over Cu/Ni hydrotalcite-derived catalyst, *Catal. Today.* 309 (2018) 189–194. <https://doi.org/10.1016/j.cattod.2017.08.007>.
- [28] M. Chia, J.A. Dumesic, Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ -valerolactone over metal oxide catalysts, *Chem. Commun.* 47 (2011) 12233-12235. <https://doi.org/10.1039/c1cc14748j>.

- [29] I. Obregón, E. Corro, U. Izquierdo, J. Requies, P.L. Arias, Levulinic acid hydrogenolysis on Al₂O₃-based Ni-Cu bimetallic catalysts, *Chinese J. Catal.* 35 (2014) 656–662.
[https://doi.org/10.1016/s1872-2067\(14\)60051-6](https://doi.org/10.1016/s1872-2067(14)60051-6).
- [30] A. Osatiashtiani, A.F. Lee, K. Wilson, Recent advances in the production of γ -valerolactone from biomass-derived feedstocks via heterogeneous catalytic transfer hydrogenation, *J. Chem. Technol. Biotechnol.* 92 (2017) 1125–1135. <https://doi.org/10.1002/jctb.5213>.
- [31] D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn, CHEM21 selection guide of classical- and less classical-solvents, *Green Chem.* 18 (2016) 288–296. <https://doi.org/10.1039/c5gc01008j>.
- [32] L. Yan, Q. Yao, Y. Fu, Conversion of levulinic acid and alkyl levulinates into biofuels and high-value chemicals, *Green Chem.* 19 (2017) 5527–5547.
<https://doi.org/10.1039/c7gc02503c>.
- [33] Z. Xue, Q. Liu, J. Wang, T. Mu, Valorization of levulinic acid over non-noble metal catalysts: challenges and opportunities, *Green Chem.* 20 (2018) 4391–4408.
<https://doi.org/10.1039/c8gc02001a>.
- [34] I.T. Horváth, Solvents from nature, *Green Chem.* 10 (2008) 1024–1028.
<https://doi.org/10.1039/b812804a>.
- [35] C.Y.Y. Wong, A.W.-T. Choi, M.Y. Lui, B. Fridrich, A.K. Horváth, L.T. Mika, I.T. Horváth, Stability of gamma-valerolactone under neutral, acidic, and basic conditions, *Struct. Chem.* 28 (2017) 423–429. <https://doi.org/10.1007/s11224-016-0887-6>.
- [36] L. Moity, M. Durand, A. Benazzouz, C. Pierlot, V. Molinier, J.-M. Aubry, Panorama of sustainable solvents using the COSMO-RS approach, *Green Chem.* 14 (2012) 1132–1145.
<https://doi.org/10.1039/c2gc16515e>.

- [37] V. Fábos, G. Koczó, H. Mehdi, L. Boda, I.T. Horváth, Bio-oxygenates and the peroxide number: a safety issue alert, *Energ. Environ. Sci.* 2 (2009) 767–769.
<https://doi.org/10.1039/b900229b>.
- [38] S.G. Wettstein, D.M. Alonso, Y. Chong, J.A. Dumesic, Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems, *Energ. Environ. Sci.* 5 (2012) 8199-8203. <https://doi.org/10.1039/c2ee22111j>.
- [39] J.S. Luterbacher, J.M. Rand, D.M. Alonso, J. Han, J.T. Youngquist, C.T. Maravelias, B.F. Pfleger, J.A. Dumesic, Nonenzymatic sugar production from biomass using biomass-derived γ -valerolactone, *Science*. 343 (2014) 277-280.
<https://doi.org/10.1126/science.1246748>
- [40] L. Qi, Y.F. Mui, S.W. Lo, M.Y. Lui, G.R. Akien, I.T. Horváth, Catalytic conversion of fructose, glucose, and sucrose to 5-(hydroxymethyl)furfural and levulinic and formic acids in γ -valerolactone as a green solvent, *ACS Catal.* 4 (2014) 1470–1477.
<https://doi.org/10.1021/cs401160y>.
- [41] J. Song, B. Zhou, H. Liu, C. Xie, Q. Meng, Z. Zhang, B. Han, Biomass-derived γ -valerolactone as an efficient solvent and catalyst for the transformation of CO₂ to formamides, *Green Chem.* 18 (2016) 3956–3961. <https://doi.org/10.1039/c6gc01455k>.
- [42] H.Q. Lê, Y. Ma, M. Borrega, H. Sixta, Wood biorefinery based on γ -valerolactone/water fractionation, *Green Chem.* 18 (2016) 5466–5476. <https://doi.org/10.1039/c6gc01692h>.
- [43] I.K.M. Yu, D.C.W. Tsang, A.C. Yip, A.J. Hunt, J. Sherwood, J. Shang, H. Song, Y.S. Ok, C.S. Poon, Propylene carbonate and γ -valerolactone as green solvents enhance Sn(IV)-catalysed hydroxymethylfurfural (HMF) production from bread waste, *Green Chem.* 20 (2018) 2064–2074. <https://doi.org/10.1039/c8gc00358k>.

- [44] J.M.R. Gallo, D.M. Alonso, M.A. Mellmer, J.A. Dumesic, Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents, *Green Chem.* 15 (2013) 85–90. <https://doi.org/10.1039/c2gc36536g>.
- [45] E.I. Gürbüz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Conversion of hemicellulose into furfural using solid acid catalysts in γ -valerolactone, *Angew. Chem. Int. Edit.* 52 (2013) 1270–1274. <https://doi.org/10.1002/anie.201207334>.
- [46] M.A. Mellmer, C. Sener, J.M.R. Gallo, J.S. Luterbacher, D.M. Alonso, J.A. Dumesic, Solvent effects in acid-catalyzed biomass conversion reactions, *Angew. Chem. Int. Edit.* 53 (2014) 11872–11875. <https://doi.org/10.1002/anie.201408359>.
- [47] L. Qi, I.T. Horváth, Catalytic Conversion of fructose to γ -valerolactone in γ -valerolactone, *ACS Catal.* 2 (2012) 2247–2249. <https://doi.org/10.1021/cs300428f>.
- [48] L. Zhang, H. Yu, P. Wang, Y. Li, Production of furfural from xylose, xylan and corncob in gamma-valerolactone using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst, *Bioresource Technol.* 151 (2014) 355–360. <https://doi.org/10.1016/j.biortech.2013.10.099>.
- [49] T. Zhang, W. Li, Z. Xu, Q. Liu, Q. Ma, H. Jameel, H. Chang, L. Ma, Catalytic conversion of xylose and corn stalk into furfural over carbon solid acid catalyst in γ -valerolactone, *Bioresource Technol.* 209 (2016) 108–114. <https://doi.org/10.1016/j.biortech.2016.02.108>.
- [50] J.Q. Bond, D.M. Alonso, D. Wang, R.M. West, J.A. Dumesic, Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels, *Science.* 327 (2010) 1110–1114. <https://doi.org/10.1126/science.1184362>.
- [51] N. Savage, Fuel options: The ideal biofuel, *Nature.* 474 (2011) S9–S11. <https://doi.org/10.1038/474S09a>.

- [52] K. Yan, Y. Yang, J. Chai, Y. Lu, Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals, *Appl. Catal. B: Environ.* 179 (2015) 292–304.
<https://doi.org/10.1016/j.apcatb.2015.04.030>.
- [53] V. Fábos, M.Y. Lui, Y.F. Mui, Y.Y. Wong, L.T. Mika, L. Qi, E. Cséfalvay, V. Kovács, T. Szűcs, I.T. Horváth, Use of gamma-valerolactone as an illuminating liquid and lighter fluid, *ACS Sust. Chem. Eng.* 3 (2015) 1899–1904.
<https://doi.org/10.1021/acssuschemeng.5b00465>.
- [54] D. Fegyverneki, L. Orha, G. Láng, I.T. Horváth, Gamma-valerolactone-based solvents, *Tetrahedron.* 66 (2010) 1078–1081. <https://doi.org/10.1016/j.tet.2009.11.013>.
- [55] A. Strádi, M. Molnár, M. Óvári, G. Dibó, F.U. Richter, L.T. Mika, Rhodium-catalyzed hydrogenation of olefins in γ -valerolactone-based ionic liquids, *Green Chem.* 15 (2013) 1857–1862. <https://doi.org/10.1039/c3gc40360b>
- [56] J.-P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Valeric biofuels: A platform of cellulosic transportation fuels, *Angew. Chem. Int. Edit.* 49 (2010) 4479–4483. <https://doi.org/10.1002/anie.201000655>.
- [57] M. Chalid, H.J. Heeres, A.A. Broekhuis, Ring-opening of γ -valerolactone with amino compounds, *J. Appl. Polym. Sci.* 123 (2012) 3556–3564. <https://doi.org/10.1002/app.34842>.
- [58] C.O. Tuck, E. Perez, I.T. Horvath, R.A. Sheldon, M. Poliakoff, Valorization of biomass: Deriving more value from waste, *Science.* 337 (2012) 695–699.
<https://doi.org/10.1126/science.1218930>.
- [59] A.M. Hengne, B.S. Kadu, N.S. Biradar, R.C. Chikate, C.V. Rode, Transfer hydrogenation of biomass-derived levulinic acid to γ -valerolactone over supported Ni catalysts, *RSC Advances.* 6 (2016) 59753–59761. <https://doi.org/10.1039/c6ra08637c>.

- [60] J.C. Serrano-Ruiz, D. Wang, J.A. Dumesic, Catalytic upgrading of levulinic acid to 5-nonanone, *Green Chem.* 12 (2010) 574–577. <https://doi.org/10.1039/b923907c>.
- [61] S. Lomate, A. Sultana, T. Fujitani, Vapor phase catalytic transfer hydrogenation (CTH) of levulinic acid to γ -valerolactone over copper supported catalysts using formic acid as hydrogen source, *Catal. Lett.* 148 (2018) 348–358. <https://doi.org/10.1007/s10562-017-2241-z>.
- [62] A.S. Piskun, H.H. van de Bovenkamp, C.B. Rasrendra, J.G.M. Winkelman, H.J. Heeres, Kinetic modeling of levulinic acid hydrogenation to γ -valerolactone in water using a carbon supported Ru catalyst, *Appl. Catal. A: Gen.* 525 (2016) 158–167. <https://doi.org/10.1016/j.apcata.2016.06.033>.
- [63] R. Cao, J. Xin, Z. Zhang, Z. Liu, X. Lu, B. Ren, S. Zhang, Efficient conversion of α -angelica lactone into γ -valerolactone with ionic liquids at room temperature, *ACS Sust. Chem. Eng.* 2 (2014) 902–909. <https://doi.org/10.1021/sc4005185>.
- [64] M. Grilc, B. Likozar, Levulinic acid hydrodeoxygenation, decarboxylation and oligomerization over NiMo/Al₂O₃ catalyst to bio-based value-added chemicals: Modelling of mass transfer, thermodynamics and micro-kinetics, *Chem. Eng. J.* 330 (2017) 383–397. <https://doi.org/10.1016/j.cej.2017.07.145>.
- [65] M. Selva, M. Gottardo, A. Perosa, Upgrade of biomass-derived levulinic acid via Ru/C-catalyzed hydrogenation to γ -valerolactone in aqueous–organic–ionic liquids multiphase systems, *ACS Sust. Chem. Eng.* 1 (2013) 180–189. <https://doi.org/10.1021/sc300088j>.
- [66] Y. Kuwahara, W. Kaburagi, Y. Osada, T. Fujitani, H. Yamashita, Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to γ -valerolactone over ZrO₂

catalyst supported on SBA-15 silica, *Catal. Today*. 281 (2017) 418–428.

<https://doi.org/10.1016/j.cattod.2016.05.016>.

[67] J. Shen, C.E. Wyman, Hydrochloric acid-catalyzed levulinic acid formation from cellulose: data and kinetic model to maximize yields, *AIChE J.* 58 (2012) 236–246.

<https://doi.org/10.1002/aic.12556>.

[68] H. Heeres, R. Handana, D. Chunai, C.B. Rasrendra, B. Girisuta, H.J. Heeres, Combined dehydration/(transfer)-hydrogenation of C6-sugars (D-glucose and D-fructose) to γ -valerolactone using ruthenium catalysts, *Green Chem.* 11 (2009) 1247–1255.

<https://doi.org/10.1039/b904693c>.

[69] L. Bui, H. Luo, W.R. Gunther, Y. Román-Leshkov, Domino reaction catalyzed by zeolites with Brønsted and Lewis acid sites for the production of γ -valerolactone from furfural, *Angew. Chem. Int. Edit.* 52 (2013) 8022–8025. <https://doi.org/10.1002/ange.201302575>.

[70] J. Wang, S. Jaenicke, G.-K. Chuah, Zirconium–Beta zeolite as a robust catalyst for the transformation of levulinic acid to γ -valerolactone via Meerwein–Ponndorf–Verley reduction, *RSC Adv.* 4 (2014) 13481–13489. <https://doi.org/10.1039/c4ra01120a>.

[71] S.S. Enumula, V.R.B. Gurrum, M. Kondeboina, D.R. Burri, S.R.R. Kamaraju, ZrO₂/SBA-15 as an efficient catalyst for the production of γ -valerolactone from biomass-derived levulinic acid in the vapour phase at atmospheric pressure, *RSC Adv.* 6 (2016) 20230–20239. <https://doi.org/10.1039/c5ra27513j>.

[72] D. Liu, L. Zhang, W. Han, M. Tang, L. Zhou, Y. Zhang, X. Li, Z. Qin, H. Yang, One-step fabrication of Ni-embedded hierarchically-porous carbon microspheres for levulinic acid hydrogenation, *Chem. Eng. J.* 369 (2019) 386–393.

<https://doi.org/10.1016/j.cej.2019.03.072>.

- [73] S. Song, S. Yao, J. Cao, L. Di, G. Wu, N. Guan, L. Li, Heterostructured Ni/NiO composite as a robust catalyst for the hydrogenation of levulinic acid to γ -valerolactone, *Appl. Catal B: Environ.* 217 (2017) 115–124. <https://doi.org/10.1016/j.apcatb.2017.05.073>.
- [74] K. Hengst, D.A.J.M. Ligthart, D.E. Doronkin, K.M. Walter, W. Kleist, E.J.M. Hensen, J.-D. Grunwaldt, Continuous synthesis of γ -valerolactone in a trickle-bed reactor over supported nickel catalysts, *Ind. Eng. Chem. Res.* 56 (2017) 2680–2689. <https://doi.org/10.1021/acs.iecr.6b03493>.
- [75] K. Jiang, D. Sheng, Z. Zhang, J. Fu, Z. Hou, X. Lu, Hydrogenation of levulinic acid to γ -valerolactone in dioxane over mixed MgO–Al₂O₃ supported Ni catalyst, *Catal. Today.* 274 (2016) 55–59. <https://doi.org/10.1016/j.cattod.2016.01.056>.
- [76] J. Lv, Z. Rong, Y. Wang, J. Xiu, Y. Wang, J. Qu, Highly efficient conversion of biomass-derived levulinic acid into γ -valerolactone over Ni/MgO catalyst, *RSC Adv.* 5 (2015) 72037–72045. <https://doi.org/10.1039/c5ra12548k>.
- [77] K. Hengst, M. Schubert, H.W.P. Carvalho, C. Lu, W. Kleist, J.-D. Grunwaldt, Synthesis of γ -valerolactone by hydrogenation of levulinic acid over supported nickel catalysts, *Appl Catal A: Gen.* 502 (2015) 18–26. <https://doi.org/10.1016/j.apcata.2015.05.007>.
- [78] J. Fu, D. Sheng, X. Lu, Hydrogenation of Levulinic Acid over Nickel Catalysts Supported on Aluminum Oxide to Prepare γ -Valerolactone, *Catalysts.* 6 (2015) 6. <https://doi.org/10.3390/catal6010006>.
- [79] V. Mohan, V. Venkateshwarlu, C.V. Pramod, B.D. Raju, K.S.R. Rao, Vapour phase hydrocyclisation of levulinic acid to γ -valerolactone over supported Ni catalysts, *Catal. Sci. Technol.* 4 (2014) 1253–1259. <https://doi.org/10.1039/c3cy01072d>.

- [80] V.V. Kumar, G. Naresh, M. Sudhakar, C. Anjaneyulu, S.K. Bhargava, J. Tardio, V.K. Reddy, A.H. Padmasri, A. Venugopal, An investigation on the influence of support type for Ni catalysed vapour phase hydrogenation of aqueous levulinic acid to γ -valerolactone, *RSC Adv.* 6 (2016) 9872–9879. <https://doi.org/10.1039/c5ra24199e>.
- [81] V.V. Kumar, G. Naresh, M. Sudhakar, J. Tardio, S.K. Bhargava, A. Venugopal, Role of Brønsted and Lewis acid sites on Ni/TiO₂ catalyst for vapour phase hydrogenation of levulinic acid: Kinetic and mechanistic study, *Appl. Catal. A: Gen.* 505 (2015) 217–223. <https://doi.org/10.1016/j.apcata.2015.07.031>.
- [82] A.M. Hengne, C.V. Rode, Cu–ZrO₂ nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to γ -valerolactone, *Green Chem.* 14 (2012) 1064–1072. <https://doi.org/10.1039/c2gc16558a>.
- [83] J. Yuan, S.-S. Li, L. Yu, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Copper-based catalysts for the efficient conversion of carbohydrate biomass into γ -valerolactone in the absence of externally added hydrogen, *Energ. Environ. Sci.* 6 (2013) 3308–3313. <https://doi.org/10.1039/c3ee40857d>.
- [84] L. Zhang, J. Mao, S. Li, J. Yin, X. Sun, X. Guo, C. Song, J. Zhou, Hydrogenation of levulinic acid into gamma-valerolactone over in situ reduced CuAg bimetallic catalyst: Strategy and mechanism of preventing Cu leaching, *Appl. Catal. B: Environ.* 232 (2018) 1–10. <https://doi.org/10.1016/j.apcatb.2018.03.033>.
- [85] Q. Xu, X. Li, T. Pan, C. Yu, J. Deng, Q. Guo, Y. Fu, Supported copper catalysts for highly efficient hydrogenation of biomass-derived levulinic acid and γ -valerolactone, *Green Chem.* 18 (2016) 1287–1294. <https://doi.org/10.1039/c5gc01454a>.

- [86] J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Han, Porous zirconium-phytic acid hybrid: A highly efficient catalyst for Meerwein-Ponndorf-Verley Reductions, *Angew. Chem. Int. Edit.* 54 (2015) 9399–9403. <https://doi.org/10.1002/anie.201504001>.
- [87] X. Tang, X. Zeng, Z. Li, W. Li, Y. Jiang, L. Hu, S. Liu, Y. Sun, L. Lin, In Situ generated catalyst system to convert biomass-derived levulinic acid to γ -valerolactone, *ChemCatChem.* 7 (2015) 1372–1379. <https://doi.org/10.1002/cctc.201500115>.
- [88] J. Zhang, J. Chen, Y. Guo, L. Chen, Effective upgrade of levulinic acid into γ -valerolactone over an inexpensive and magnetic catalyst derived from hydrotalcite precursor, *ACS Sust. Chem. Eng.* 3 (2015) 1708–1714. <https://doi.org/10.1021/acssuschemeng.5b00535>.
- [89] S. Gundekari, K. Srinivasan, In situ generated Ni(0)@boehmite from NiAl-LDH: An efficient catalyst for selective hydrogenation of biomass derived levulinic acid to γ -valerolactone, *Catal. Commun.* 102 (2017) 40–43. <https://doi.org/10.1016/j.catcom.2017.08.020>.
- [90] K. Yan, A. Chen, Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu–Fe catalyst, *Fuel.* 115 (2014) 101–108. <https://doi.org/10.1016/j.fuel.2013.06.042>.
- [91] H. Zhong, Q. Li, J. Liu, G. Yao, J. Wang, X. Zeng, Z. Huo, F. Jin, New method for highly efficient conversion of biomass-derived levulinic acid to γ -valerolactone in water without precious metal catalysts, *ACS Sust. Chem. Eng.* 5 (2017) 6517–6523. <https://doi.org/10.1021/acssuschemeng.7b00623>.
- [92] B.S. Kadu, A.M. Hengne, N.S. Biradar, C.V. Rode, R.C. Chikate, Reductive cyclization of levulinic acid to γ -valerolactone over non-noble bimetallic nanocomposite, *Ind. Eng. Chem. Res.* 55 (2016) 13032–13039. <https://doi.org/10.1021/acs.iecr.6b03900>.

- [93] S. Zhang, G. Fan, F. Li, Lewis-base-promoted copper-based catalyst for highly efficient hydrogenation of dimethyl 1, 4-cyclohexane dicarboxylate, *Green Chem.* 15 (2013) 2389–2393. <https://doi.org/10.1039/c3gc40658j>.
- [94] W. Luo, U. Deka, A.M. Beale, E.R.H. van Eck, P.C.A. Bruijninx, B.M. Weckhuysen, Ruthenium-catalyzed hydrogenation of levulinic acid: Influence of the support and solvent on catalyst selectivity and stability, *J. Catal.* 301 (2013) 175–186. <https://doi.org/10.1016/j.jcat.2013.02.003>.
- [95] X.-L. Du, Q.-Y. Bi, Y.-M. Liu, Y. Cao, K.-N. Fan, Conversion of biomass-derived levulinate and formate esters into γ -valerolactone over supported gold catalysts, *ChemSusChem.* 4 (2011) 1838–1843. <https://doi.org/10.1002/cssc.201100483>.
- [96] Z. Yang, Y.-B. Huang, Q.-X. Guo, Y. Fu, RANEY® Ni catalyzed transfer hydrogenation of levulinate esters to γ -valerolactone at room temperature, *Chem. Commun.* 49 (2013) 5328. <https://doi.org/10.1039/c3cc40980e>.
- [97] J. Geboers, X. Wang, A.B. De Carvalho, R. Rinaldi, Densification of biorefinery schemes by H-transfer with Raney Ni and 2-propanol: A case study of a potential avenue for valorization of alkyl levulinates to alkyl γ -hydroxypentanoates and γ -valerolactone, *J. Mol. Catal. A: Chem.* 388 (2014) 106–115. <https://doi.org/10.1016/j.molcata.2013.11.031>.
- [98] I.K.M. Yu, X. Xiong, D.C.W. Tsang, L. Wang, A.J. Hunt, H. Song, J. Shang, Y.S. Ok, C.S. Poon, Aluminium-biochar composite as a sustainable heterogeneous catalyst for glucose isomerization in biorefinery. *Green Chem.* 21 (2019) 1267-1281. <https://doi.org/10.1039/C8GC02466A>.