







Article

Catalytic Valorisation of Biomass-Derived Levulinic Acid to Biofuel Additive γ -Valerolactone: Influence of Copper Loading on Silica Support

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Abstract: γ -valerolactone (GVL) is a crucial chemical feedstock used in the production of fuel additives, renewable fuels, and fine chemicals alternative to petroleum-based solvents and chemicals, supporting the transition to sustainable energy solutions. It is promptly acquired by hydrogenating levulinic acid (LA) in a gaseous or liquid phase with a homogeneous or heterogeneous catalyst using a variety of recognized catalytic processes. Herein, this work focuses on the use of silica-supported copper (Cu/SiO₂) catalysts for the gas-phase hydrogenation of LA to GVL under mild reaction conditions. The study analyzes how copper loading can affect the catalytic activity of the Cu/SiO₂, while the flow rate of LA, time-on-stream, reaction temperature, and LA concentration affect the catalytic efficiency. The SiO₂ support's various Cu loadings are crucial for adjusting the catalytic hydrogenation activity. One of the studied catalysts, a 5 wt% Cu/SiO₂ catalyst, demonstrated ~81% GVL selectivity with ~78% LA conversion and demonstrated stability for ~8 h while operating at atmospheric pressure and temperature (265 °C) and 0.5 mL/h of LA flow rate. The ability to activate hydrogen, high amount of acidic sites, and surface area were all discovered to be advantageous for increased GVL selectivity.

Keywords: biomass; γ -valerolactone; biofuel additive; green solvent; vapour-phase hydrogenation; selectivity

1. Introduction

In recent years, the search for sustainable alternatives to fossil fuels and petrochemical-based products has gained significant momentum. Biomass, an abundant and renewable resource, has emerged as a promising feedstock for the production of various chemicals and fuels [1–5]. Among the many biomass-derived compounds, levulinic acid (LA) has garnered attention due to its versatile nature and potential applications [6]. LA is a platform chemical derived from biomass, primarily agricultural and forestry residues, such as corn

stover, wheat straw, and wood chips. It can also be obtained from cellulose, hemicellulose, and other carbohydrate-rich materials through various conversion processes. LA possesses several desirable properties that make it an attractive starting material for chemical synthesis [6–8]. It is water-soluble, stable under mild reaction conditions, and exhibits a high degree of functional group compatibility.

One particularly exciting development is the conversion of LA into γ -valerolactone (GVL), a cyclic ester derived from LA and a valuable chemical with a wide range of applications in the chemical industry, including as a solvent, reaction medium, and precursor for the synthesis of various chemicals and materials such as 2-methyl tetrahydrofuran, polyesters, and bioplastic industries [9–11]. GVL is highly valued for its favorable physical and chemical properties, such as low vapor pressure, high boiling point, and good solubility in water and common organic solvents. One of the key advantages of biomass-derived LA conversion into GVL is the utilization of a renewable feedstock. By leveraging biomass resources, this process reduces dependence on fossil fuels and mitigates greenhouse gas emissions. Moreover, the production of GVL from LA offers an alternative to petroleum-based solvents and chemicals, contributing to the transition towards a more sustainable and environmentally friendly chemical industry. The versatility of GVL opens up various possibilities for its applications. As a green solvent, it can be employed in a range of industrial processes, including coatings, adhesives, and pharmaceutical formulations. GVL's potential as a fuel additive or precursor for the production of renewable fuels further highlights its significance in the quest for sustainable energy solutions. Additionally, GVL can serve as a building block for the synthesis of polymers, resins, and other high-value chemicals, thereby expanding its potential applications across multiple industries [11].

The conversion of LA into GVL involves a catalytic process known as hydrogenation. Several processes exist today for hydrogenating LA in the presence of molecular hydrogen, alcohol, or formic acid, plus a catalyst to produce GVL. The choice of catalyst significantly impacts the yield and selectivity of GVL production. Catalysts commonly used include metal catalysts (e.g., iridium (Ir) [12–14], palladium (Pd) [15], platinum (Pt) [16], and ruthenium (Ru) [17–19], Raney nickel (Ni) [20], etc.) supported on appropriate substrates (alumina, zirconia, alumina titania, niobia, etc.) (Table 1) [17,21–23]. Heterogeneous catalysts are more frequently utilized in biomass valorization compared to homogeneous catalysts (Table 1) [11]. When comparing Cu-based catalysts with other catalysts for the conversion of biomass-derived LA into GVL, several factors come into play, including catalytic activity, selectivity, stability, and cost-effectiveness (Table 1). For example, noble metal catalysts, such as Pt, Pd, Ir, and Ru, exhibit high catalytic activity for the hydrogenation of LA derivatives (Table 1). Non-noble metal catalysts generally offer comparable or slightly lower selectivity towards GVL production compared to supported noble metal catalysts (Table 1) [24–26]. Supported noble metal catalysts are known for their excellent stability and can withstand harsh reaction conditions. Noble metal catalysts, including Pt and Ru, are more expensive than Cu/SiO₂ catalysts, making the latter more cost-effective for large-scale applications.

Table 1. Various catalytic systems for hydrogenation of LA to GVL transformation.

| S. No. | Catalyst | Reaction Conditions | | | LA Conversion (%) | GVL Selectivity (%) | Ref. |
|--------|---|---------------------|----------------|----------|-------------------|---------------------|-----------|
| | | Temperature (°C) | Pressure (MPa) | Time (h) | | | |
| 1 | [Cp*Ir(dpa)(OSO ₃)] ^{a,b} | 100 | 0.5 | 72 | 92 | - | [14] |
| 2 | Ir complex (6) ^{a,b,c} | 120 | 1.01 | 36 | - | 78 | [27] |
| 3 | [Ir(COE) ₂ Cl] ₂ ^{a,b} | 100 | 5 | 17 | 100 | 99 | [28] |
| 4 | [Ru(acac) ₃]/TPP ^{a,b} | 140 | 8 | 168 | >99 | 95 | [29] |
| 5 | [Ru(acac) ₃] + TPPTS ^{a,b} | 140 | 5 | 5 | 99 | 97 | [30] |
| 6 | [Ru(acac) ₃]/DPPB ^{a,b} | 140 | 10 | 1.8 | 99.9 | 99.9 | [31] |
| 7 | Pt/ZrO ₂ ^{b,c} | 240 | 4 | 24 | 97 | 90 | [32] |
| 8 | Ru/C ^{b,c} | 190 | 1 | 5 | 81 | 57 | [33] |
| 9 | Ru/C ^{b,c} | 150 | - | 5 | 100 | 97 | [34] |
| 10 | Ru/C + A70 ^b | 70 | 3 | 3 | 100 | 99 | [35] |
| 11 | Pd/C ^{b,c} | 150 | - | 5 | 9 | 17 | [34] |
| 12 | Pt/C ^{b,c} | 150 | - | 5 | 13 | 13 | [34] |
| 13 | Ru/ZrO ₂ ^{b,c} | 150 | - | 5 | 11 | 18 | [34] |
| 14 | Ru/ZrO ₂ ^{b,c} | 150 | 1 | 12 | 73 | >99 | [36] |
| 15 | Ru/SBA-15 ^{b,c} | 150 | - | 5 | 31 | 71 | [34] |
| 16 | Ru/HAP ^b | 70 | 0.5 | 4 | 99 | 99 | [37] |
| 17 | Au/ZrO ₂ -VS ^{b,c} | 150 | 0.5 | 6 | 95 | 99 | [38] |
| 18 | Co ₈ Pd ₂ @N-C ^{b,c} | 150 | - | 9 | ~100 | 99.3 | [39] |
| 19 | Ru _{0.18} /Al ₂ O ₃ /NC ^b | 150 | 4 | 3 | - | 99.7 | [40] |
| 20 | Ni ₁ -Zn ₁ @OMC ^b | 180 | 2 | 1.5 | 100 | 93 | [41] |
| 21 | Raney Ni ^b | 100 | 1.5 | 4 | 99.3 | 98.1 | [42] |
| 22 | Co-LA@SiO ₂ -800 ^{b,d} | 120 | 3 | 24 | >99 | 97 | [43] |
| 23 | Co@NC-700 ^{b,d} | 190 | 1.9 | 2 | 100 | 100 | [44] |
| 24 | 4Co/Al ₂ O ₃ ^{b,d} | 180 | 5 | 3 | 100 | >99 | [45] |
| 25 | Sn/Al-SBA-15 ^{b,e} | 200 | 0.1 | 3 | 99 | 100 | [46] |
| 26 | Cu/Ni hydrotalcite ^{b,d} | 140 | 3 | 3 | 100 | 100 | [47] |
| 27 | CuAl ^{b,e} | 110 | 3 | 2 | 100 | 95.3 | [48] |
| 28 | Cu/MCM-41 ^f | 265 | 0.1 | 5 | 85 | 77 | [22] |
| 29 | Cu/MCM-48 ^f | 265 | 0.1 | 5 | 92 | 92 | [22] |
| 30 | Cu/KIT-6 ^f | 265 | 0.1 | 5 | 78 | 69 | [22] |
| 31 | Cu/SBA-15 ^f | 265 | 0.1 | 5 | 100 | 98 | [22] |
| 32 | Cu/Al ₂ O ₃ ^f | 265 | 0.1 | 1 | 98 | 87 | [23] |
| 33 | Cu/ZrO ₂ ^f | 200 | 2.7 | 4 | - | 75 | [49] |
| 34 | Cu/ZrO ₂ ^f | 265 | 0.1 | - | 81 | 83 | [21] |
| 35 | Cu/SiO ₂ -Q6 ^{f,c} | 250 | - | - | 66 | 81 | [50] |
| 36 | Cu/Zr _{0.8} -Ce _{0.2} ^{f,c} | 260 | 0.5 | 2 | 88.5 | 94.2 | [51] |
| 37 | Cu-hydrotalcite ^f | 265 | 0.1 | 2–3 | 87.5 | 95 | [52] |
| 38 | Cu/ZrO ₂ -Al ₂ O ₃ ^b | 130 | 3 | 5 | 100 | 100 | [53] |
| 39 | Cu/Al ₂ O ₃ -ZrO ₂ ^b | 200 | 3 | 2 | 100 | 100 | [54] |
| 40 | Cu/Al ₂ O ₃ ^f | 240 | 3 | 1–5 | 93.7 | 91.5 | [55] |
| 41 | CuCo-Al ₂ O ₃ ^f | 250 | 0.1 | 24 | 100 | 99 | [56] |
| 42 | Cu/SiO ₂ ^f | 265 | 0.1 | 1 | 78 | 81 | This work |

Note: ^a = homogeneous; ^b = liquid phase; ^c = formic acid as hydrogen donor; ^d = 1,4-dioxane as hydrogen donor; ^e = 2-propanol; ^f = vapour phase.

Cu catalysts generally offer higher selectivity towards GVL production compared to Ni, which may show side reactions leading to the formation of undesired by-products [11]. Moreover, Raney nickel is relatively expensive due to the complex and energy-intensive production process, while Cu-based catalysts can be more cost-effective. It is important to note that the choice of catalyst depends on specific process requirements, such as desired selectivity, reaction conditions, and economic considerations. The performance and

suitability of different catalysts can vary depending on the specific reaction system and optimization efforts. Introducing promoter elements or modifying the support material can improve the catalyst's efficiency. Cu/SiO₂ catalysts are typically prepared by impregnating copper (Cu) precursors onto high-surface-area silica (SiO₂) support. The catalyst's structure depends on factors such as copper loading, method of synthesis, and calcination conditions. Cu/SiO₂ catalysts exhibit excellent catalytic activity for various reactions, including hydrogenation, dehydrogenation, oxidation, and coupling reactions [10,57–60]. The presence of Cu nanoparticles on the SiO₂ support enhances the catalyst's performance due to its high surface area and dispersion of active sites. The selectivity of Cu/SiO₂ catalysts can be tuned by controlling the copper loading, reaction conditions, and support characteristics. These catalysts often demonstrate good selectivity towards specific products, making them valuable tools for fine-tuning chemical processes. The stability of Cu/SiO₂ catalysts is crucial for continuous and large-scale applications. Careful design of the catalyst composition and support properties can enhance stability and reduce catalyst deactivation. Therefore, Cu/SiO₂ catalysts find application in several industries, including petrochemicals, fine chemicals, pharmaceuticals, and renewable energy. They are particularly useful in biomass conversion processes and green chemistry applications due to their ability to promote sustainable and eco-friendly transformations. Ongoing research focuses on optimizing the performance of Cu/SiO₂ catalysts through the development of new synthesis methods, understanding catalytic mechanisms, and exploring novel support materials to enhance their activity, selectivity, and stability.

While the conversion of biomass-derived LA into GVL holds immense promise, there are still challenges to address. The development of efficient and selective catalysts capable of operating under mild conditions remains a focal point of research. This article explores the process of biomass-derived LA conversion into GVL over silica-supported copper catalysts and its significance for sustainable chemical production. The previous study provided descriptions of the measurements conducted on the Cu/SiO₂ catalysts, including X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), UV-Vis diffused reflectance spectra (UV-DRS), hydrogen temperature-programmed reduction (H₂-TPR), temperature-programmed desorption of NH₃ (NH₃-TPD), N₂O decomposition, Brunauer–Emmett–Teller (BET) surface area, and pore size distribution [10]. In this study, the parameters/variables (activity, conversion, selectivity, and stability) tuning their LA catalytic performance to GVL were examined herein.

2. Materials and Methods

Copper nitrate, silica, and levulinic acid were purchased from Sigma–Aldrich, Germany. Wet impregnation is a simple and effective technique for preparing catalysts with SiO₂ support and variable Cu loadings (2–20 wt%) after calcination [10]. In the study, the vapor-phase hydrogenation of LA to GVL was evaluated using a continuous fixed-bed stainless steel tube reactor (length: 32 cm and inner diameter: 9 mm) under 0.1 MPa hydrogen pressure over a temperature range of 250 to 310 °C. Glass wool packed from both ends was placed in the center of the reactor along with the catalyst (0.3 g), which was combined with glass beads. The catalyst was pretreated with a H₂ stream at 350 °C for 3 h before the activity test. After the reduction, the reactor temperature was lowered to 265 °C, and H₂ and a stream of LA aqueous solution (10 wt%) were introduced at WHSV 0.550 h⁻¹. The liquid products were collected every hour in an ice-cold trap and subsequently analyzed using a HP5973 quadruple GC-MSD system with a HP-1MS capillary column. The temperatures of the injector and detector were set to 250 and 260 °C, respectively. The column temperature was programmed to initiate heating at 40 °C, maintain the temperature for 2 min, and then increase the temperature to 250 °C at a heating rate of 10 °C min⁻¹. To calculate the conversion of LA and the selectivity of desired products, the following formulas were utilized.

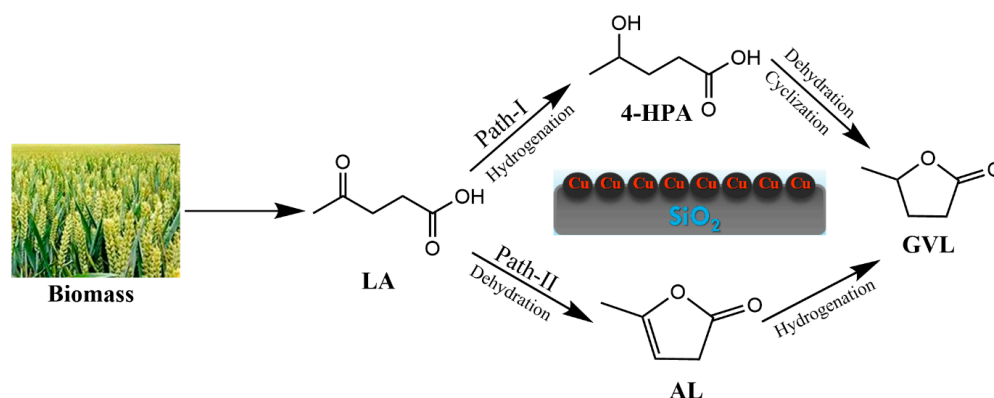
$$\text{LA conversion (\%)} = \frac{\text{mole of LA (in)} - \text{moles of LA (out)}}{\text{Moles of LA in the feed (in)}} \times 100 \quad (1)$$

$$\text{Product selectivity (\%)} = \frac{\text{Moles of one product}}{\text{moles of all products}} \times 100 \quad (2)$$

TOF = rate of reaction/number of active Cu sites (the number of Cu active sites was determined by a N₂O decomposition method) [10].

3. Results and Discussion

During the conversion of LA to GVL production over a Cu/SiO₂ catalyst, molecular hydrogen dissociates into hydrogen atoms, which then migrate from CuO sites. The reduction of CuO into metallic Cu species demonstrates that hydrogen spillover from Cu is crucial for in situ catalyst reduction. Cu nanoparticles may interact strongly with SiO₂ support (Cu-O-Si-O-), leading to a partially electropositive state due to oxygen atoms on the support's surface [57]. There exist various reaction pathways to generate GVL (Scheme 1). During LA hydrogenation, the main and favored product was determined to be GVL. However, by-products such as angelica lactone (AL) and pentanoic acid or valeric acid (VA) were also generated (Scheme 1). One pathway involves hydrogenating LA, which generates 4-hydroxypentanoic acid (4-HPA), an unstable intermediate. Upon ring closure by intramolecular esterification, GVL is produced by the spontaneous loss of a water molecule. Another pathway to producing GVL from LA involves dehydrating LA to form AL, followed by hydrogenation [11].



Scheme 1. Possible reaction mechanisms for GVL production from LA hydrogenation.

The catalyst loading, reaction temperature, reactant flow rate and concentration, effect of turnover frequency (TOF) and catalyst stability are crucial parameters that significantly impact the conversion of biomass-derived LA into GVL. Let us examine the effects of each parameter.

3.1. Effect of Copper Loadings on Catalytic Activity

The catalytic performance of LA hydrogenation using Cu/SiO₂ catalysts with varying copper metal loading was examined, and the findings are presented in Table 2. The conversion of LA and the selectivity to GVL for an optimized catalyst (5 wt% Cu/SiO₂) containing 5 wt% Cu loading were ~78% and ~81%, respectively. Increasing the copper loading from 2 to 20 wt% resulted in a decrease in the conversion of LA from 56% to 33% and GVL yields from 61% to 29%. Generally, increasing the catalyst loading can enhance the reaction rate and increase the conversion of LA into GVL. However, there is an optimal catalyst loading beyond which further increases may not lead to substantial improvements. The active site density, dispersion of copper species, and acidity/basicity of the catalyst support can impact the reaction kinetics. The concentration of copper on the catalyst surface affects the availability of active sites for the reaction. An optimal copper loading can lead to higher catalytic activity and selectivity. Higher catalyst loadings may potentially favor side reactions or by-product formation, leading to decreased selectivity towards GVL. The

decline in activity with increasing copper content from 2 to 20 wt% is tentatively attributed to a reduction in copper surface area and surface acidity. Higher catalyst loadings increase the overall cost of the process. Thus, it is important to strike a balance between activity, selectivity, and cost-effectiveness. It is important to note that the support material has a small surface area, so higher copper loading does not necessarily lead to increased activity due to the deposition of active sites in multiple layers on the support. This implies that the conversion of LA and selectivity towards GVL are directly influenced by the acid strength and active copper sites of the catalyst.

Table 2. Comparison between catalytic activity with catalyst properties in different Cu/SiO₂ catalysts.

| Catalyst (% Cu Loading) | Specific Copper Surface Area (m ² g ⁻¹ Cu) ^a | Average Particle Size of Cu (nm) ^b | Conversion of LA (%) ^a | Selectivity (%) ^c | | | |
|-------------------------|---|---|-----------------------------------|------------------------------|----|----|--------|
| | | | | GVL | AL | VA | Others |
| 2 | 120 | 5.55 | 56 | 61 | 27 | 1 | 11 |
| 5 | 132 | 5.11 | 78 | 81 | 11 | 1 | 7 |
| 10 | 76 | 8.97 | 61 | 57 | 29 | - | 14 |
| 15 | 52 | 13.2 | 49 | 41 | 48 | - | 11 |
| 20 | 34 | 20.7 | 33 | 29 | 59 | - | 12 |

^a Reaction conditions: feed rate of LA: 10 wt%; weight of Cu/SiO₂ catalyst 0.3 g; reaction temperature: 265 °C; H₂ pressure: 0.1 MPa; H₂ flow rate: 30 mL min⁻¹. ^b Determined from N₂O decomposition values [10]. ^c AL: angelica lactone; VA: valeric acid.

3.2. Effect of TOF

To determine the relation between catalytic activity and copper loading, the turnover frequency (TOF) values were calculated and are reported in Table 2. The number of Cu active sites was determined by a N₂O decomposition method [10]. The TOFs were calculated from N₂O decomposition data as the number of molecules of LA converted by one surface copper atom per second. The TOF calculation gives insight into the efficiency of a catalyst and allows for the comparison of different catalysts with varying active site densities. It is an essential parameter for understanding catalytic kinetics and optimizing reaction conditions in heterogeneous catalysis. Figure 1, which presents the relationship between turnover frequency (TOF) and copper loading, illustrates the connection between copper dispersion and hydrogenation activity. Conversion of LA decreases as the copper loading increases up to 20 wt% due to the formation of CuO crystallites on the surface of the SiO₂ support. The decline in GVL selectivity, as shown in Table 2, may be attributed to the lower dispersion and larger particle size of copper, which is evident from the N₂O decomposition and XRD studies. The results reported in Table 2 demonstrate a strong correlation between the data from N₂O decomposition and the activity of the catalyst.

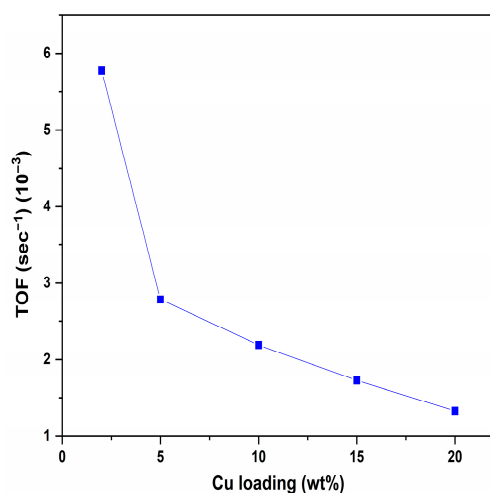


Figure 1. TOF studies of various Cu/SiO₂ catalysts.

3.3. Effect of LA Flow Rates on Catalytic Activity

Generally, increasing the reactant flow rate can potentially enhance the reaction rate by maintaining a higher concentration of reactants near the catalyst surface. Faster flow rates may limit the residence time of reactants, potentially reducing side reactions and improving selectivity. Reactant flow rate can impact the selectivity towards GVL.

The experiment investigated the hydrogenation process of LA using a 5 wt.% Cu/SiO₂ catalyst with varying flow rates of LA, ranging from 0.5 mL/h to 1.5 mL/h (Figure 2). The findings demonstrate that as the flow rate of the LA reactant increases, the conversion of LA and the selectivity of GVL decrease. This phenomenon can be attributed to the longer interaction time between LA molecules and the catalyst when a lower flow rate is employed during the reaction. The reactant flow rate needs to be optimized to ensure efficient mass transfer and reaction kinetics while considering the limitations of the system.

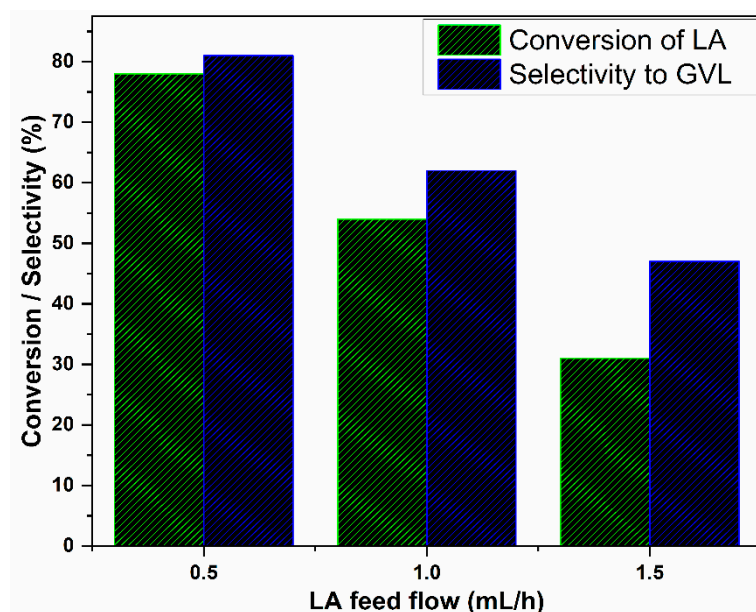


Figure 2. Effect of LA feed flow on the hydrogenation of LA over a 5 wt.% Cu/SiO₂ catalyst.

3.4. Effect of Reaction Temperatures on Catalytic Activity

The reaction temperature can influence the selectivity towards GVL. The reaction pathways leading to GVL formation and competing side reactions may have different temperature dependencies. Certain reactions may have lower activation energies and become more dominant at higher temperatures, leading to the formation of undesired by-products. Understanding the temperature dependence of different reaction pathways is crucial for controlling the selectivity of the reaction. The impact of reaction temperature on the hydrogenation activity of 5 wt% Cu/SiO₂ (5 wt% Cu loading) towards LA was assessed in the 250–310 °C range and documented in Table 3. Results indicate that LA conversion rises with temperature, with low conversion rates at lower temperatures potentially caused by a lack of sufficient energy input for LA dehydration to GVL. Higher temperatures generally increase the reaction rate, but they can also influence the distribution of intermediates and products, affecting selectivity. In some cases, higher temperatures may favor the formation of undesired by-products or lead to thermal degradation of GVL. However, higher reaction temperatures often require increased energy input, impacting the overall process economics and sustainability. As the temperature increases from 250 to 310 °C, GVL selectivity falls from 74% to 54%. However, temperatures above 265 °C are not recommended since the dehydration product of LA becomes predominant.

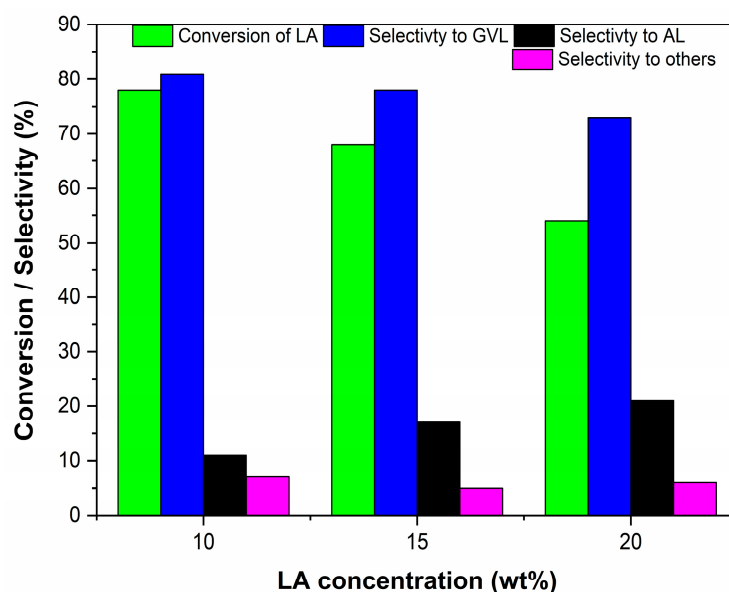
Table 3. LA hydrogenation over 5% Cu/SiO₂ catalysts over various temperatures.

| Reaction Temperature (°C) | Conversion of LA (%) ^a | Selectivity (%) ^b | | | |
|---------------------------|-----------------------------------|------------------------------|----|----|--------|
| | | GVL | AL | VA | Others |
| 250 | 55 | 74 | 20 | 0 | 6 |
| 265 | 78 | 81 | 11 | 1 | 7 |
| 280 | 89 | 69 | 21 | 1 | 9 |
| 295 | 100 | 61 | 27 | 2 | 10 |
| 310 | 100 | 54 | 31 | 5 | 9 |

^a Reaction conditions: feed rate of LA: 10 wt%; weight of Cu/SiO₂ catalyst: 0.3 g; H₂ pressure: 0.1 MPa; H₂ flow rate: 30 mL min⁻¹. ^b AL: angelica lactone; VA: valeric acid.

3.5. Effect of LA Concentrations on Catalytic Activity

The concentration of LA can influence the reaction kinetics. High LA concentrations may favor certain reaction pathways, leading to specific by-products. The effect of LA concentration on the 5 wt.% Cu/SiO₂ catalyst activity was analyzed at 265 °C, and the results are shown in Figure 3. Higher concentrations of LA were discovered to result in a decrease in its conversion. This decline in activity may be attributed to the obstruction of active sites by reactant molecules that are strongly adsorbed, potentially impeding the dehydration process of LA to angelica lactone (AL).

**Figure 3.** Effect of LA concentration on the hydrogenation of LA over a 5 wt.% Cu/SiO₂ catalyst.

3.6. Effect of Time-on-Stream on Catalytic Activity

Catalyst stability is crucial to maintaining consistent catalytic activity throughout the reaction. Catalyst deactivation or degradation can lead to decreased conversion and selectivity. Various factors can influence catalyst stability, including the nature of the catalyst, reaction conditions, presence of impurities, and catalyst preparation methods. To examine the effect of time on stream (TOS) on the conversion of LA and selectivity of GVL, the study observed the 5 wt.% Cu/SiO₂ at 265 °C for 20 h, with findings displayed in Figure 4. The conversion of LA remained stable for up to 8 h on stream before sharply decreasing to 19% at TOS-20 h. The catalyst's decrease in hydrogenation activity can be attributed to its deactivation, which happens when the Cu metal particles clump together and coke forms in the active sites. As a consequence, the surface area of the metal reduces, and the number of active sites decreases.

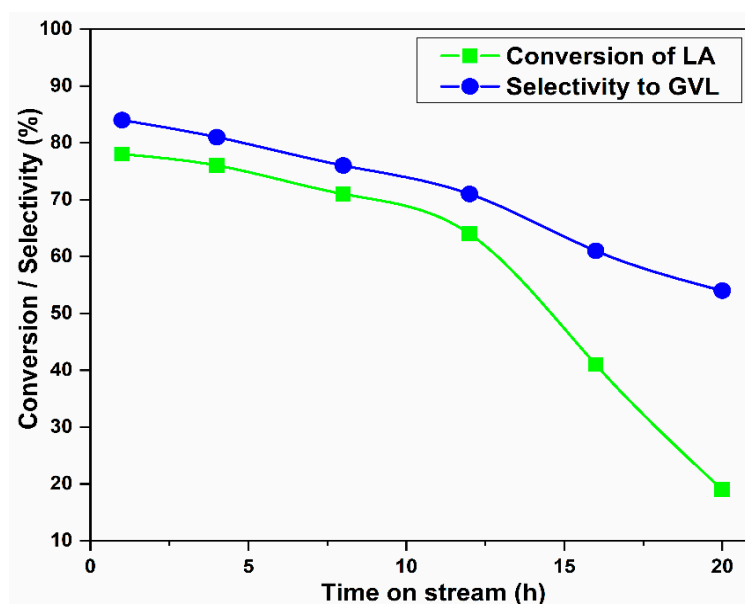


Figure 4. Time on stream study of the 5 wt.% Cu/SiO₂ catalyst.

3.7. Deactivation Study

As shown in Figure 5, the X-ray diffraction (XRD) characterization was performed on a 5 wt.% Cu/SiO₂'s catalyst before (fresh) and after (spent) the stability. A fresh catalyst calcined and reduced Cu/SiO₂, showing high-intensity peaks at the 2θ values of 35.5° and 38.4°, which indexed to the CuO (JCPDS 45–0937). After 20 h stability performance, the spent catalyst examined by XRD shows 2θ values of 44.5° and 50.7° peaks, which indexed to the pristine Cu (JCPDS 04–0836). The spent catalyst revealed that the reduced catalyst showcases two primary diffraction peaks specifically intended for metallic Cu [10,21]. The deactivation was noticed for all the studied catalysts due to the formation of coke as well as an agglomeration of Cu particles.

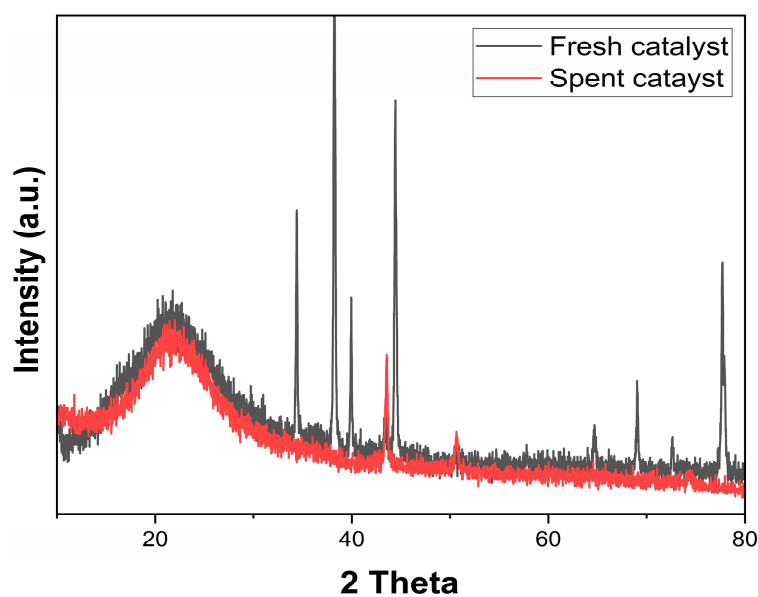


Figure 5. XRD pattern of fresh catalyst before the reaction and spent catalyst after stability performance.

Overall, optimization of catalyst loading, reaction temperature, reactant flow rate, and catalyst stability is essential to achieve high conversion, selectivity, and economic feasibility in the conversion of biomass-derived LA into GVL. Balancing these parameters allows for efficient utilization of catalyst resources, improved product quality, and process

sustainability. The ability to activate hydrogen, a large number of acidic sites, and surface area were all discovered to be advantageous for increased GVL selectivity.

4. Conclusions

The transformation of biomass-derived levulinic acid into γ -valerolactone using a Cu/SiO₂ catalyst represents a significant advancement in sustainable chemical production. The study analyzes the effect of copper loading, flow rate of LA, time-on-stream, reaction temperature, and LA concentration on the catalytic hydrogenation activity of the Cu/SiO₂ catalyst. The findings indicate that as the copper loading increases from 2 to 20 wt%, the conversion of LA and the selectivity to GVL both declines. The analysis further implies that the dispersion of the Cu species corresponds directly to the activity observed during the LA hydrogenation. Moreover, this study demonstrates that as the flow rate of the reactant increases, the conversion of LA and the selectivity of GVL decrease. The catalyst maintains stability for up to 8 h of time-on-stream, beyond which rapid deactivation occurs due to sintering and the formation of coke in the active sites. The conversion of LA rises with a higher reaction temperature ranging from 250 to 310 °C, although the selectivity of GVL decreases above 265 °C. Finally, the study finds that the conversion of LA decreases at higher LA concentrations in the feed. By leveraging renewable feedstocks and employing a highly active and selective catalyst, this process offers a greener alternative to petrochemical-based solvents and chemicals.

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