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# Heterogeneous Ru catalysts as the emerging potential superior catalysts in the selective hydrogenation of bio-derived levulinic acid to γ-valerolactone: Effect of Particles Size, Solvent, and Support on activity, stability, and Selectivity

Mulisa Maumela[a*], Sanette Marx[b] and Reinout Meijboom[c*]

[a]*Department of Mathematics, Science, and Technology Education, University of Limpopo, Private Bag x1106, Sovenga, 0727*

[b]*DST/NRF Research Chair in Biofuels and Other Clean Alternative Fuels Centre of Excellence in Carbon-based Fuels Faculty of Engineering North-West University Potchefstroom South Africa*

[c]*Department of Chemical Sciences, University of Johannesburg, P.O. Box 524, South Africa, Johannesburg, Auckland park 2006*. South Africa.

**Abstract:** Catalytic hydrogenation of a biomass-derived molecule, levulinic acid (LA) to γ-valerolactone (GVL) has been getting a lot of attention from researchers across the globe recently. This is because GVL has been identified as one of the potential molecules for the replacement of fossil fuels. For instance, GVL can be catalytically converted into liquid alkenes in the molecular weight range close to that found in transportation fuels via a process that does not require an external hydrogen source. Noble and non-noble metals have been used as catalysts for the selective hydrogenation of LA to GVL. Of these, Ru has been reported to be the most active metal for this reaction. The type of metal supports and solvents has been proved to affect the activity, selectivity, and yields of GVL. Water has been identified as a potential, effective "green" solvent for the hydrogenation of LA to GVL. The use of different sources of $H_2$ other than molecular hydrogen (such as formic acid) has also been explored. In a few instances, the product, GVL, is hydrogenated further to other useful products such as 1,4-pentanediol (PD) and methyl tetrahydrofuran (MTHF). This review selectively focuses on the potential of immobilized Ru catalysts as a potential superior catalyst for selective hydrogenation of LA to GVL.

Keywords: **Ruthenium, Heterogeneous, Levulinic acid, hydrogenation, γ-valerolactone**.

## Introduction

One of the biggest challenges facing the world recently is the production of sufficient energy as per world population demand. For example, one-third of the energy produced throughout the world is utilized in the transportation industry. Most of this energy is solely derived from fossil resources, *i.e*, crude oil. Because these fossil resources can deplete some time, there is an urgent need to find alternative, renewable sources of energy. Moreover, it is important to develop industrial production processes that are sustainable and environmentally friendly (greener). Presently, the first generation of biofuels can be produced from sugars, starches, and vegetable oil. However, biofuels produced from these biomass sources face direct competition from the food industry. As a consequence, it is unlikely that enough volume of biofuels as per global demand can be produced from them. Lignocellulosic biomass, which can be derived from sugars, grass, wood, and other agricultural waste has been identified as a potential renewable replacement for fossil fuels [1-3].

Cellulose, hemicellulose, and lignin are the three main components constituting lignocellulosic biomass. Of these, cellulose, which accounts for 30 – 50 wt% of lignocellulosic biomass, can be converted into glucose *via* chemical or enzymatic hydrolysis [4, 5]. It is from this formed glucose that some important platform chemicals such as 5-hydroxymethylfurfural (HMF), levulinic acid (LA), and formic acid (FA), ethanol, and liquid fuels can be produced (see Figure 1) [4, 6, 7]. The other two components, hemicellulose, and lignin each, independently, account for 15 – 30 wt% of lignocellulosic biomass [8]. Hemicellulose is an amorphous polymer comprised of $C_5$ and $C_6$ sugars while lignin on the other side, is also an amorphous polymer that is rich in aromatic monomers. Additionally, lignin also has been reported to be a potential source for biofuels and other chemicals of great value [9]. However, the complexity of its structure and non-uniformity of its composition render it less attractive as compared to the other two components in this regard. Additionally, about 170 tons of these biomass materials are produced naturally *via* photosynthesis.

The catalytic conversion of sugars to HMF, LA, and FA has been getting a lot of attention from many scientists in the last few decades [10, 11]. For instance, Qi *et al*. reported the catalytic conversion of sugars (fructose, glucose, and sucrose) into LA, FA, and HMF *via* hydrolysis [12, 13]. The conversion of various sugars was carried out by adding a desired amount of sugars into the mixture containing a diluted acid (dilute $H_2SO_4$) and a solvent. The mixture was then heated at elevated temperatures (130 °C) until the decomposition of the sugar is complete. Decomposition products were analyzed by NMR. Various solvents, such as DMSO, THF, MeCN, acetone, GVL, or DCM were also investigated in the decomposition of fructose. It was found that DMSO and THF showed higher selectivity for the formation of HMF. However, the use of THF has environmental issues due to the formation of peroxides when exposed to air. Using GVL as a solvent showed selectivity towards HMF of about 70%.

The concentration of acid catalyst ($H_2SO_4$) in the GVL solvent was found to affect the selectivity of the products. For instance, no HMF or LA could be detected when the acid concentration is below $10^{-4}$ mol/L. The maximum conversion for HMF and LA (58% and 13%, respectively) was observed when the acid concentration of 0.1 mol/L was used. However, as the concentration of the acid was increased to 0.6 mol/L, a decrease (by 2%) in the formation of HMF was observed with that of LA raising to 62%. This was, therefore, the indication that the product distribution in GVL is sensitive to the acid concentration. Moreover, GVL proved to be a tunable solvent for the conversion of carbohydrates to either HMF, LA, and FA. The HMF can also be converted further into LA or FA in the presence of acid $H_2SO_4$ and the GVL solvent at 130 °C. Likewise, the LA yield was observed to rapidly increase as the concentration of the acid is increased. The conversion of carbohydrates into LA or FA has been reported elsewhere [13]. The discussion of this review will however put the focus on the supported Ru-catalyzed conversion of LA to GVL *via* hydrogenation reaction.

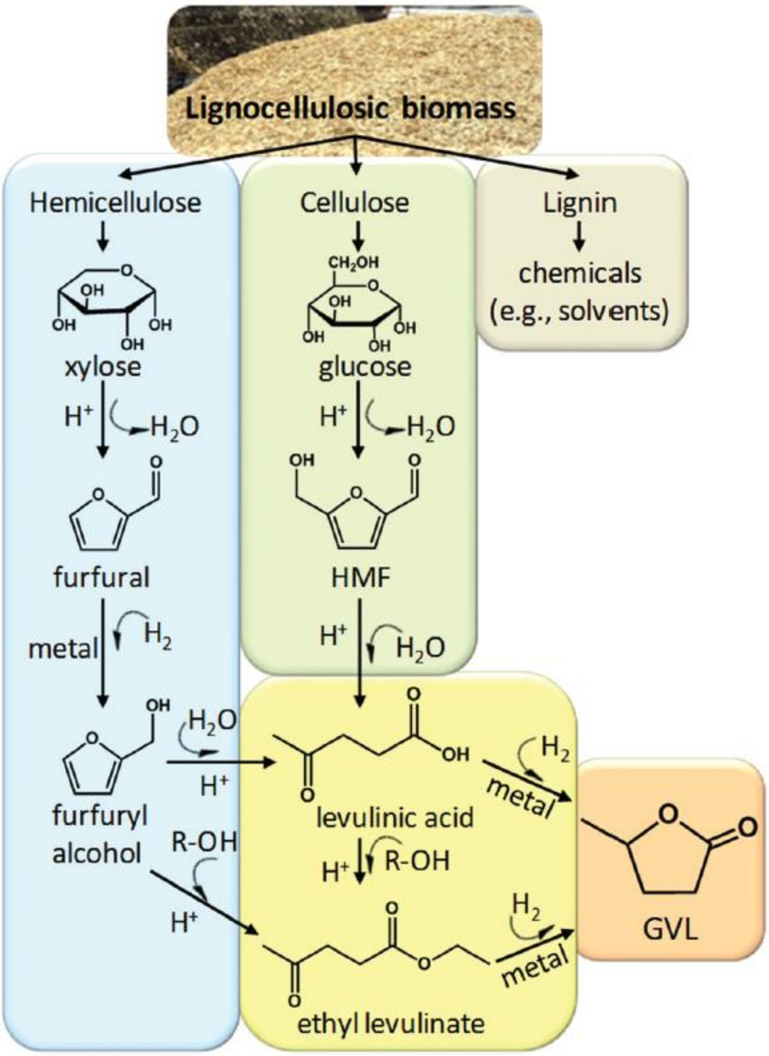


**Figure 1**: Fractionation of lignocellulosic biomass and the reaction pathway to produce GVL from hemicellulose and cellulose. Reproduced from ref [14] with permission from The Royal Society of Chemistry.

One of these important platform chemicals, LA, can undergo catalytic hydrogenation to produce γ-valerolactone (GVL) [15]. However, the development of suitable economical production technology for large-scale production of GVL direct from carbohydrates remains an ongoing challenge. The four consecutive steps o the reaction process (conversion of carbohydrates to GVL) involves the acid-catalyzed dehydration of carbohydrates to HMF [13, 16-20], the acid-catalyzed hydration of HMF to LA and FA [12, 21], and catalytic hydrogenation of LA to 4-hydroxyvaleric acid (4-HVA) and a subsequent ring closure via dehydration to form GVL [1]. It is noteworthy to mention that other valuable chemicals can be obtained by direct catalytic conversion of LA [1, 22, 23].

For example, Luo *et al*. reported selective, one-pot conversion of LA to pentanoic acid (PA) using bifunctional zeolite supported Ru catalysts (Ru/H-ZSM5) [23]. In their study, a series of Ru/H-ZSM5 catalysts were prepared by varying metal precursors, Si/Al ratio *via* wet impregnation method. The average sizes of the particles of the Ru/H-ZSM5 catalysts were determined by TEM to be in the range of 1.7- 4.9 nm. The Ru/H-ZSM5 catalyst was prepared using the $Ru(NH_3)_6Cl_3$ and $NH_4^+$-ZSM5 (Ru/H-ZSM5($NH_3$, A, 11.5)) was found to have the smallest particle size (1.7 nm) compared to other Ru/H-ZSM5 catalysts. A higher PA yield (91.3%) was achieved when this catalyst was used under standard conditions (200 °C, $H_2$ = 40 bar, 10 hrs). The improved activity of the Ru/H-ZSM5($NH_3$, A, 11.5) catalyst in the direct conversion of LA to PA was attributed to improved dispersion of small Ru particles and the presence of accessible acidic sites required for this type of reaction. The discussion in this review, however, will be limited to the supported Ru-based catalytic conversion of LA to GVL.

The versatile molecule GVL has been identified as a potential sustainable liquid for renewable energy production [24, 25]. Interestingly, GVL can further be converted via catalytic hydrogenation to produce other important chemicals such as 1,4-pentanediol (PD), methyl tetrahydrofuran (MTHF), and pentanoic acid [3, 13, 26] (see Figure 2). Alternatively, GVL can be used directly as a fuel additive with similar or even better properties than those of ethanol or liquid alkenes in biofuels [2, 25, 27, 28]. This is because water can easily be separated from GVL as compared to ethanol. Most importantly, GVL has been identified as a petrol additive [24] that can potentially greatly reduce the emission of carbon monoxide [29], a sustainability issue faced by large cities around the globe. Additionally, it is also used as a green solvent, food additives, or perfume [30, 31]. For instance, Al-Shaal *et al.* reported the solvent-free hydrogenation of GVL to 2-MTHF in the presence of a Ru/C catalyst, achieving an MTHF yield of 43%. The conversion of GVL into liquid alkenes with an appropriate molecular weight range to be used for transportation fuel in the presence of zeolite catalysts (HZSM-5, Amberlyst-70) [2].

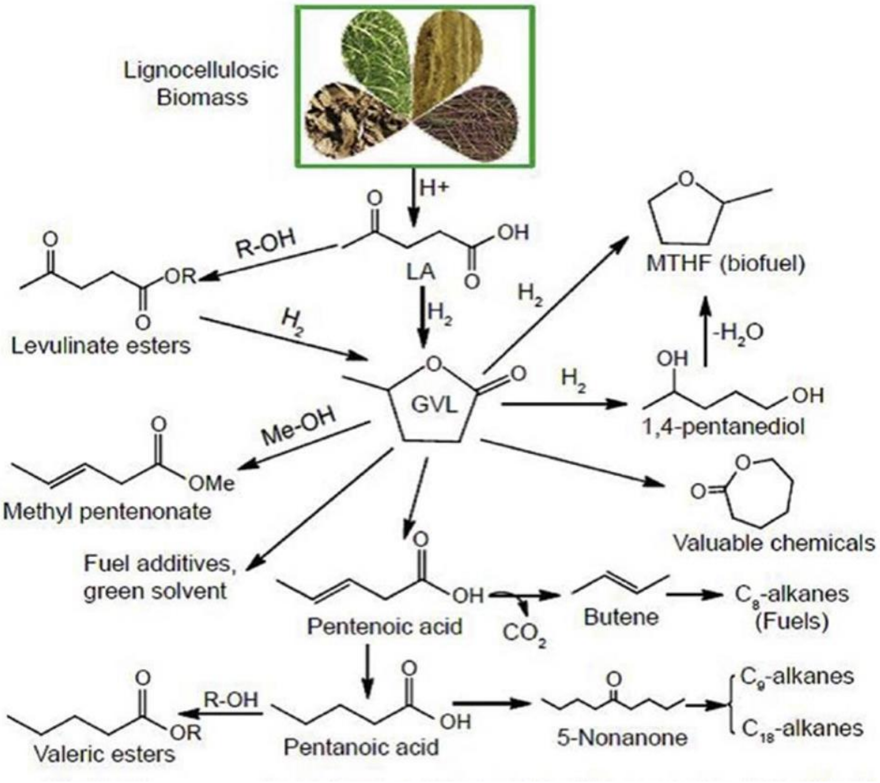


**Figure 2**: Schematic illustration of different important products that can be derived from GVL. Reproduced from ref [32] with permission from Elsevier.

Catalytic conversion of LA to GVL using supported noble (Ru, Pt, Pd, Au) [30, 33-37] and non-noble (Ni, Mo) [38] metal catalysts have been reported in the past two decades. For example, Jiang *et al*. reported MgO-$Al_2O_3$ supported Ni catalyzed hydrogenation of LA to GVL [37]. Other studies on supported Ni catalyzed hydrogenation of LA to GVL have been reported by other authors [26, 39, 40]. Of these reports, it has been previously shown that Ru catalysts are more active than other noble and non-noble metals in the aqueous phase hydrogenation of LA [30, 41]. However, in the gas phase hydrogenation of ketones, Ru catalysts were observed to be less active than other noble metals [42]. Some explanation on why Ru based catalysts have tend to display excellent activity for the aqueous phase hydrogenation of carbonyl compounds has been reported by other authors [43]. Although there are several reports on the Ru based homogeneous catalyzed hydrogenation of LA to GVL [3, 13, 44-46], the discussion in this review will solely be devoted to supported Ru (including Ru containing bimetallic catalysts) catalyzed hydrogenation of LA to GVL. This is primarily because heterogeneous catalysts can easily be separated from reaction products and be re-used, making them ideal “green catalysts” as compared to their homogeneous counterparts. Other factors such as catalyst support ($TiO_2$, $SiO_2$, $Al_2O_3$, C, *etc*.) and the effect of solvent on the activity, selectivity, and product yield will also be discussed.

### 1.2. Carbon-supported Ru catalyzed hydrogenation of LA

As briefly highlighted in the introduction section, carbon-supported Ru catalysts have been perceived as the most active catalysts reported in the hydrogenation of LA to GVL thus far. However, some of the limitations of Ru/C catalysts have been that they are not stable because they easily aggregate or leach out of the carbon support materials during catalytic reactions. For example, Yan and Liu published a study on the hydrogenation of LA to GVL over Ru/C (5% metal loading) catalysts [47]. For comparison purposes, Pd/C, Raney nickel, and Urushibara nickel catalysts with the same metal loading as that of Ru were also screened for the same reaction. The Ru/C catalyst was found to show higher activity as compared to other catalysts. This higher activity of Ru/C was attributed to small particle size as well as good metal dispersion on the carbon support. After roughly 2.5 hours, the conversion of LA as well the selectivity to GVL was observed to have reached a plateau. Similarly, at the pressure of 1.2 MPa, maximum conversion and selectivity were reached. Both LA conversion and selectivity towards GVL decreased by 50% after the fourth catalyst recycle. This was ascribed to significant leaching of Ru nanoparticles out of the carbon support during catalytic runs of the recyclability study as determined by X-ray photoelectron spectroscopy (XPS) analysis.

On the contrary, Galletti *et al.* demonstrated that Ru/C can remain stable even after 5 reaction cycles when used with a heterogeneous acid co-catalyst (such as niobium, phosphate, or ion exchange resins Amberlyst) [48]. In their study, they used commercial Ru catalysts (5%) supported on carbon and alumina. The Ru/C (without co-catalyst) was generally observed to show higher activity compared to other studied catalysts with 100% LA conversion and activity of 569.6 $h^{-1}$. Heterogeneous acidic co-catalysts were found to enhance the performance of the Ru/C supported catalyst (see Figure 3). The ion exchange resin Amberlyst as co-catalyst showed the highest activity (555.2 $h^{-1}$) as compared to all other co-catalysts used. Two reaction mechanisms leading to the formation of GVL were proposed in this study. One path involves the formation of intermediate γ-hydroxyvaleric acid followed by the removal of water (esterification) to form GVL. The other second path entails the formation of the thermodynamically unstable enol form of levulinic acid which undergoes esterification to form angelica lactone (AL) which is subsequently hydrogenated to give GVL (see Scheme 1). Manzer screened several carbon-supported catalysts (Ir, Rh, Pd, Ru, Pt, Re, Ni) in the hydrogenation of LA to GVL [49]. The Ru/C catalyst was found to be more active and gave higher selectivity towards GVL relative to other screened catalysts.

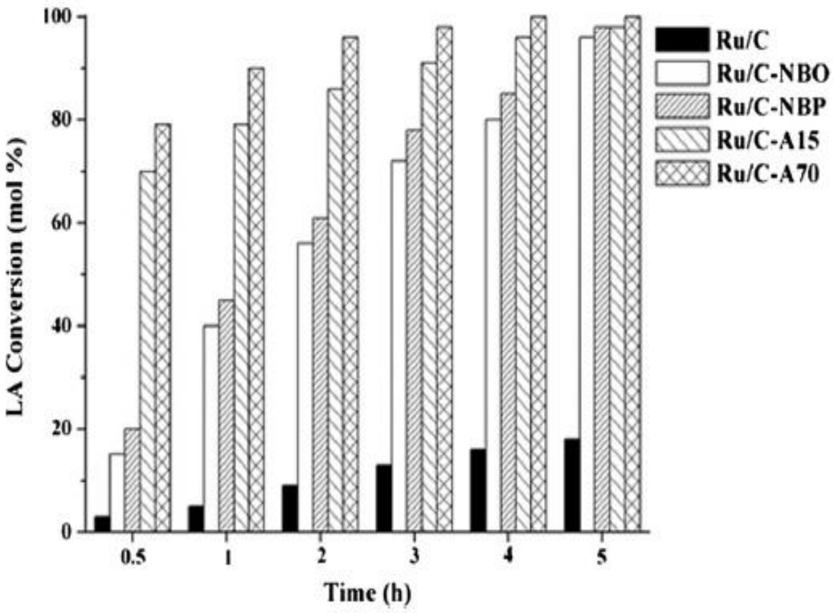
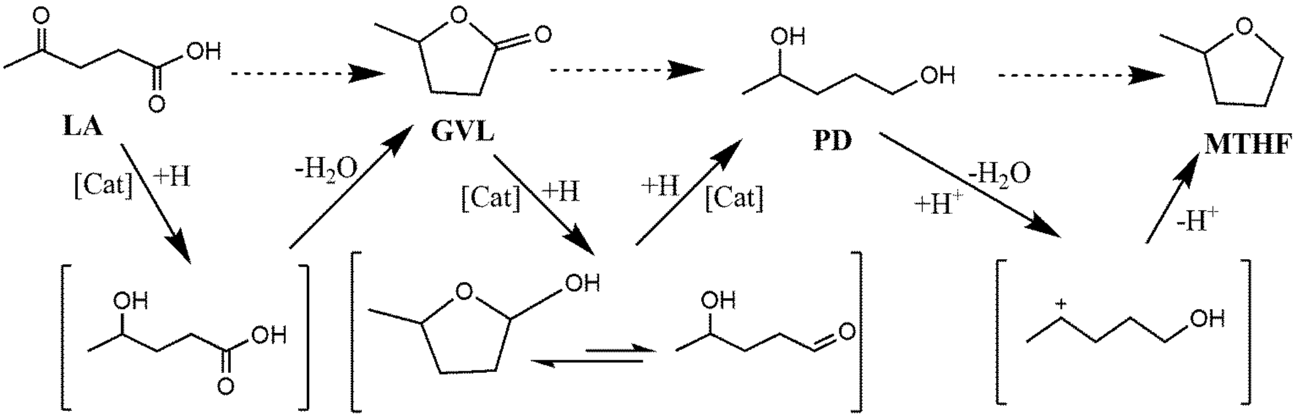


**Figure 3:** Effect of different heterogeneous acid co-catalysts on LA conversion (mol%) vs. time (hrs), employing 5% Ru/C under mild conditions. Reproduced from ref [48] with permission from The Royal Society of Chemistry.



**Scheme 1:** Proposed mechanism for the catalytic selective hydrogenation of LA to GVL, PD, and MTHF [3].

Al-Shaal *et al.* studied the influence of the solvents (methanol, ethanol, 1-butanol, 1,4 dioxane, methanol-$H_2O$, ethanol-$H_2O$, butanol-$H_2O$, and $H_2O$) in the Ru-C catalyzed hydrogenation of LA [50]. Other inorganic supports such as $TiO_2$, $Al_2O_3$, and $SiO_2$ were also investigated for comparison purposes. Among used alcohol solvents, methanol was found to show the highest LA conversion and GVL yields. This observation was attributed to the high solubility of $H_2$ in the solvent as compared to others used in this study. The lowest LA conversion (48.6%) was obtained when 1-butanol was used.

A significant increase in the conversion of LA was observed when the $H_2$ pressure was increased from 12 bar to 20 bar for 1-butanol. However, the selectivity for 1-butanol was still comparable to what was observed for other solvents.

A significant enhancement in the conversion of LA was observed when a mixture of 1-butanol-water (90/10% by volume) was used as a solvent. This observation further confirmed that $H_2$ has a higher solubility in water than other used alcohol solvents. The highest LA conversion (99.5%) was generally obtained using water as a solvent. Surprisingly, no change in terms of LA conversion was observed when the methanol-water solvent was used. In an attempt to optimize reaction conditions, solvent free-reactions were also carried out. However, in this case, prolonged reaction time (50 hrs) was required to achieve 100% LA conversion under mild reaction conditions (25 °C). A complete conversion of LA was obtained within 40 minutes of reaction time albeit at elevated temperature (190 °C). In some instances, the intermediate (AL) that forms before GVL tends to polymerize over the acidic catalyst's surface. This phenomenon leads to the loss of carbon or complete deactivation of the catalyst.

In the same year, the cascade method for the conversion of cellulose to GVL was reported by Dumesic's group [1]. Their method involves the decomposition of cellulose *via* hydrolysis followed by subsequent dehydration of the resulting glucose over sulphuric acid as a catalyst to produce equimolar amounts of LA and FA in a batch reactor. The LA was then hydrogenated to GVL using FA as a source of $H_2$ in the presence of commercially obtained Ru/C catalyst. After 3 hrs of reaction time, both the LA conversion and GVL yields were observed to be above 90%. The produced GVL then separated from the aqueous sulfuric acid catalyst and was subsequently hydrogenated further to give other useful products such as pentanoic acid (PA) as an intermediate. The PA was then converted to 5-nonanone (a precursor to hydrocarbon fuels) using a niobium oxide-supported Pd catalyst.

Dumesic's group later reported an alternative method to avoid the deactivation of the catalyst for the conversion of LA to GVL, which was subsequently converted to 5-nonanone using Ru/C catalyst [22]. In this way, the LA hydrogenation formed, GVL, was subsequently hydrogenated further to give 5-nonanone at a lower temperature (150 °C). The used method and reaction conditions allowed for the reaction to favor the formation of 5-hydroxypentanoic acid (HAP), instead of AL, before the formation of GVL. The Ru/C catalyst showed more activity and selectivity for GVL as compared to other catalysts ($Pd/Nb_2O_5$, $CeZr_{0.5}O_2$) for the same reaction under similar reaction conditions. A full LA conversion and a selectivity towards GVL of 96% was obtained for Ru/C at ambient temperature.

The catalytic hydrogenation of LA to GVL over Ru/C and bimetallic RuRe/C catalysts has been reported by the same group as well [51]. They observed that both mono- and bimetallic catalysts showed more stability in the presence of sulfuric acid, a common catalyst used in the conversion of cellulose to LA. In this case, they started with the conversion of cellulose to LA and formic acid using $H_2SO_4$ as a catalyst in a batch reactor (see Figure 4). Both monometallic Ru/C and RuRe/C catalysts were prepared using the conventional incipient wetness impregnation method. Formic acid was used as a source of hydrogen in a flow reactor. The initial rates of the reaction were observed to be high at the beginning of the reaction for the Ru/C catalyst and started decreasing over time. After 50 hrs, sulphuric acid was introduced into the reaction feed and the catalyst started to show more stability. However, after the introduction of sulphuric acid, the selectivity towards GVL was observed to decrease from >98% to 60-70%. This decrease in selectivity was attributed to the formation of LA-sulfuric acid anhydride species that formed upon the addition of sulphuric acid. The formation of this anhydride has been reported to be reversible and catalyst independent [52]. On the contrary, however, no effect on the selectivity for GVL in the presence or the absence of the sulphuric acid in the case of RuRe/C catalyst was observed. Instead, an increase in the activity by a factor of two was observed in the presence of sulphuric acid as compared to the Ru/C catalyst. This was due to the enhanced activity of the bimetallic RuRe/C catalyst relative to Ru/C counterpart.

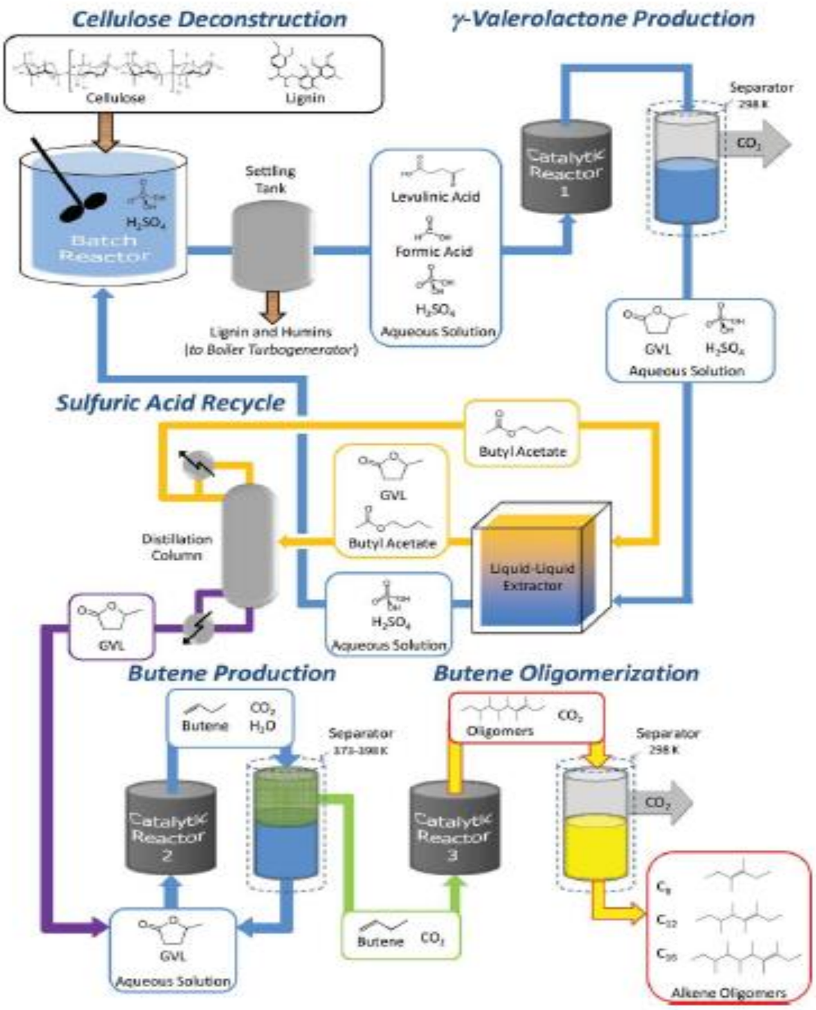


**Figure 4**. Schematic flowsheet for the cascade conversion of cellulose to liquid alkene oligomers. Reproduced from ref [51] with permission from The Royal Society of Chemistry.

In another study, Domesic's group reported a comparative study between the monometallic Ru/C and the bimetallic RuSn/C catalysts in the selective hydrogenation of LA to GVL [53]. Commercial monometallic 5 wt% Ru/C was used and bimetallic ($Ru_xSn_y/C$) catalysts were prepared via incipient wetness impregnation. The catalytic hydrogenation was carried using 2-*sec*-butyl-phenol (SBP) as a solvent. Surprisingly, the Ru/C catalyst was found to exhibit more activity than the bimetallic RuSn/C catalyst. However, the Ru/C showed less stability overtime on stream compared to the RuSn/C, which maintained its initial activity even after 300 hrs of time on stream. Of the various RuSn/C catalysts with different metal ratios, the highest stability was displayed by the catalyst with higher Sn concentration. The choice for this solvent (SBP) was based on its ability to easily extract LA from sulphuric acid which is used as a catalyst during LA production from cellulose. This was after a previous study from the same group showed that alkylphenol solvents can successfully extract LA from aqueous solutions of sulphuric acid [54]. This method, however, has limitations in that: i) it requires final purification of the product by distillation, which can be costly, ii) the partition coefficient fo LA extraction is relatively low and iii) the partition coefficient of the extracted FA was less than 0.2, making it not possible to use it as an internal source of $H_2$ for hydrogenation reaction.

In trying to overcome such limitations, the same research group published some work in which GVL was used as a solvent to extract both LA and FA from aqueous solutions [55]. The use of GVL as a solvent during the production of LA and FA from cellulose materials enables for easy separation/extraction of LA and FA into the organic phase. In the case where the targeted product is GVL for the hydrogenation of LA, the need to separate the product from the solvent was eliminated. Additional advantages of using GVL as a solvent in the cellulose decomposition process to produce LA and FA is that GVL solubilizes humin formed during the process. The conversion of LA to GVL was carried out in the presence of commercially obtained Ru-Sn/C (5% wt) catalyst. They found that the conversion rate of cellulosic LA was lower as compared to that of the commercial LA under similar reaction conditions. This was attributed to the impurities generated during the decomposition of cellulose materials to produce LA and FA. The catalyst was, however, observed to show stability even after 40 hrs in the reaction feed. This indicated that the “assumed” impurities do not necessarily deactivate the Ru-Sn/C catalyst. It is also noteworthy to mention that the LA conversion was found to increase as the temperature is elevated without hydrogenation products of the GVL solvent forming.

Yang *et al.* also recently reported a comparative study on the use of monometallic Ru and bimetallic Ru-Ni nanoparticles supported on ordered mesoporous carbon (OMC) as catalysts in the hydrogenation of LA to GVL [56]. The synthesis of OMC-supported Ru or Ru-Ni nanoparticles was carried out using a novel procedure depicted in Figure 5 Firstly, the metal precursors were coordinated with the modified chitosan to form the precursor composite materials by CTAB-directed self-assembly. The nanoparticles were formed during pyrolysis at high temperature (750 °C) without any additional reductant and the silica was removed by etching with an aqueous solution of concentrated NaOH (3.0 M). All OMC-supported Ru and Ru-Ni catalysts showed excellent activity for the hydrogenation of LA and showed high selectivity towards GVL. The bimetallic OMC-supported Ru-Ni catalyst exhibited more active sites than the monometallic Ru counterparts under similar reaction conditions. For instance, a turn over frequency for the Ru-OMC catalyst was calculated to be 1716 $h^{-1}$ as compared to 870 $h^{-1}$ determined for commercial Ru/C catalyst. The Ru-Ni-C catalyst prepared via direct pyrolysis of chitosan-Ru-Ni coordination showed the lowest activity, giving LA conversion and GVL yield of 34 and 15%, respectively. This suggested that the textural properties of the support material play a crucial role in the overall performance of the catalyst. Similarly, the catalyst with unetched silica (Ru-Ni-OMSC) showed appreciable activity, however, lower than that observed for silica-free Ru-Ni-OMC catalysts. Generally, the bimetallic Ru-Ni-OMC catalyst showed higher activity compared to the Ru-OMC catalyst when subjected to similar reaction conditions. The bimetallic catalyst with the highest Ru content ($Ru_{0.9}Ni_{0.1}$-OMC) was found to exhibit more activity and stability than all monometallic and bimetallic catalysts. This catalyst was also chosen as a representative catalyst for the investigation of water as a potential solvent. Under similar reaction conditions as in the absence of a solvent, similar LA conversions were observed, however, the GVL yield was found to have slightly decreased to 84% from 97%. The $Ru_{0.9}Ni_{0.1}$-OMC catalyst was observed to maintain its activity after being used in 15 reaction cycles. This was attributed to higher pore volume, high surface area, and high Ru dispersity on the mesoporous carbon support.

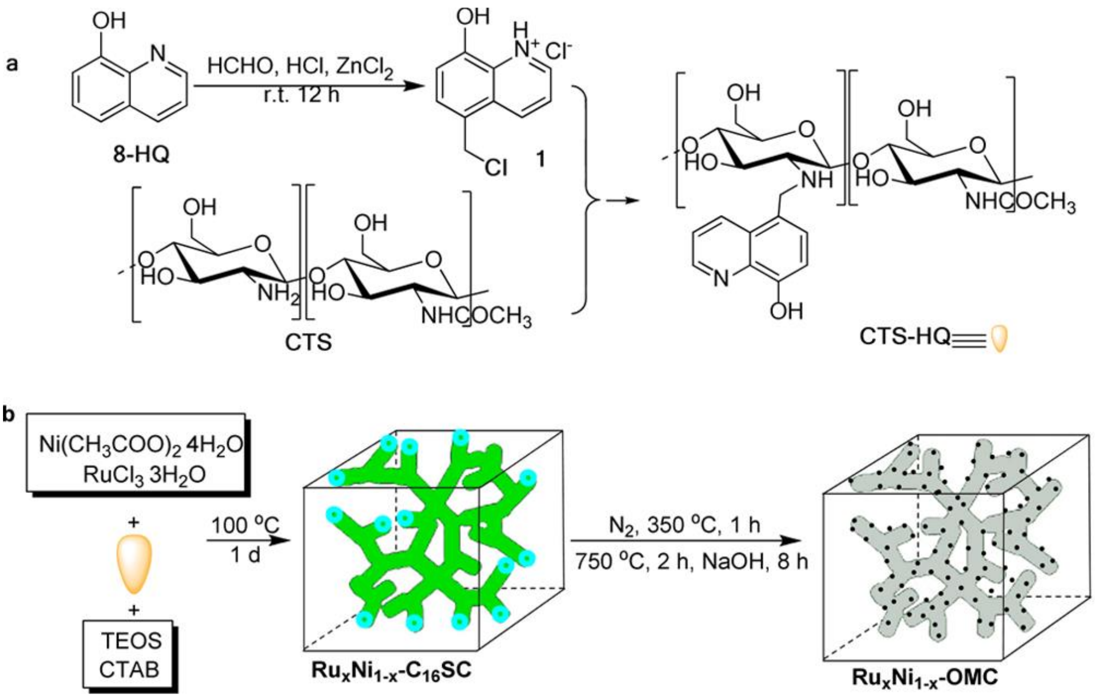


**Figure 5**. Synthesis of $Ru_xNi_{x-1}$-OMC catalysts. Reproduced from ref [56] with permission from American Chemical Society.

Rhenium has also been used to promote the activity of carbon-supported Ru catalysts for the hydrogenation of LA [57]. Monometallic and Re promoted carbon-supported Pt and Pd were also evaluated under similar reaction conditions as those applied for Ru-based catalysts. The monometallic 2.1%Ru/C was observed to show superior activity for the conversion of LA to GVL. About 100% LA conversion was achieved for 2.1%Ru/C within just 10 minutes of reaction time, while under similar conditions, 70% and 53% LA conversion were observed for 2.7%Pd/C and 4.1%Pt/C catalysts after 2 hours, respectively. The bimetallic ReRu/C catalyst also showed similar if not slightly higher activity compared to the monometallic Ru catalyst counterpart. It is noteworthy to mention that, in the case of Re promoted Pd and Pt, a significant improvement in activity was observed. For instance, complete LA conversion was achieved for Pd−Re/C and Pt−Re/C catalysts after 2 and 7 hours, respectively. However, the bimetallic 2.8%Ru−3.9%Re/C catalyst gave the highest GVL yield (85%). The formed product, GVL, was further hydrogenated to PD. For example, in the case of the 2.8%Ru−3.9%Re/C, complete GVL conversion was achieved after 24 hrs with 55% selectivity towards PD.

Upare *et al*. published a study on the production of GVL from LA under vapor phase conditions using commercially purchased carbon-supported Ru catalyst (5 wt%) [58]. The reactions were run on a continuous-flow fixed-bed reactor system. For comparison, other carbon supported metal catalysts (5 wt% Pd or Pt) were also studied for the same reaction conditions. All studied catalysts gave 100% LA conversion. However, the highest selectivity for GVL was observed for the Ru/C catalyst (98.6%), while 90% and 30% GVL selectivity were obtained for Pd and Pt catalysts, respectively. The effect of pressure (from 1-25 bars) on the activity and selectivity was also investigated in this study. It was found that the activity and selectivity were not affected when the pressure was varied from 1-5 bar for Ru/C catalyst. A further increase to the pressure led to an increase in the selectivity of other side products such as MTHF and AL while the selectivity for GVL marginally decreased. Generally, the Ru/C showed no lowered activity for 10 days in the continuous flow reactor.

On the contrary, Bond and co-workers observed different product selectivity for the Ru/C (commercial, 5% wt) catalyzed hydrogenation of LA at low temperatures [59]. In their work, two possible reaction pathways were proposed leading to the formation of GVL. One path involves the hydrogenation of LA 4-hydroxypentanoic acid, which subsequently undergoes esterification to form GVL. The other path entails the formation of AL via dehydration of LA before the formation of preferred GVL. This is in agreement with what was proposed by other researchers [48]. It was observed that when the reaction temperature is near ambient (50 °C), the selectivity for GVL was very poor (around 5%) as compared to that of HAP (< 95%). However, in the absence of $H_2$ under an inert atmosphere ($N_2$), the formation of AL was found to dominate over HAP. It was concluded from these observations that in the absence of $H_2$, LA is solely consumed by dehydration. Secondly, the GVL is formed through the formation of HAP during the Ru/C catalyzed hydrogenation of LA. Furthermore, the following conclusions were drawn after carrying out a thorough kinetics study: i) at a lower temperature, the esterification of the intermediate (HAP) tends to control the rate of GVL formation, ii) at elevated temperature, mass transfer limits the rate of LA hydrogenation, iii) the production of GVL can potentially be enhanced by using a combination of a strong acidic catalyst and hydrogenation metal catalysts, iv) a deactivation of Ru/C overtime on stream was observed and the causes could not be established at the time of the publication. Recently, Piskun *et al.* reported the hydrogenation of LA using carbon-supported Ru particles as catalysts [41]. Unlike in other studies where the sizes of the Ru particles are usually in the nanometer range, the Ru particles used for this study were in the millimeter range. Ru particles in the range of 1.25 – 2.5 mm were supported (0.5 – 2 wt%) on other inorganic supports such as $TiO_2$ and $Al_2O_3$. However, only the carbon-supported Ru catalyst will be discussed in this section.

The carbon-supported Ru catalyst was observed to exhibit excellent activity compared to those supported on different oxide supports. After 6 hrs of time on stream, about 92% of LA conversion was observed. The selectivity towards GVL was found to be 77% under reaction conditions employed (T = 90 °C, Pressure = 45 bar). The effect of the pre-reduced catalyst on the activity was also investigated using the same catalyst. In that way, the Ru/C catalyst was pre-reduced inside the reactor at 350 °C for 4 hrs under the flow of a mixture of $H_2$ and $N_2$ gas. It was found that this pre-reduction step of the catalyst results in a decrease in the activity. For instance, the conversion of LA observed for a reduced catalyst was 75% compared to 95% for unreduced catalyst under similar reaction conditions. This observation was attributed to an increase in the size of Ru particles during the catalyst activation process. The stability of the Ru/C was also probed at 130 and 150 °C, respectively. A notable decrease in the catalyst's activity with time was observed for a reaction run at 150 °C as opposed to the one run at 130 °C. Very recently, We *et al.* reported the synthesis and catalytic investigation of N-doped hierarchically porous carbon-supported Ru catalyst (Ru/NHPC) in the hydrogenation of LA to GVL [60]. The N atom was doped to the hierarchically porous carbon (NHPC) to improve the interaction between carbon and Ru nanoparticles and subsequently enhance the catalyst stability. This was to try to circumvent the deactivation of the traditional Ru/C catalysts that often suffer from loss of activity during the reaction, even under mild reaction conditions. Moreover, activated porous carbon is believed to depress the mass transport of molecules, which may result in the blocking of pores [61]. The average size of the NHPC supported Ru nanoparticles synthesized via the ultrasonic-assisted deposition method was determined to be 2.1 nm.

The different parameters such as temperature, solvent, and pressure were investigated in the catalytic hydrogenation of LA to GVL. Of all the solvents (cyclohexane, 1,4-dioxane, DMF, ethanol, ethanol, and water) investigated, water gave the highest LA conversion (>99%) even at the lowest temperature (25 °C). Although 1,4-dioxane and DMF gave almost 100% LA conversion, their selectivity towards the anticipated product, GVL, was very poor (1%). The effect of temperature on the activity and selectivity towards GVL was investigated employing water as a solvent. It was observed that no significant change occurred on the conversion of LA. However, the selectivity towards GVL was observed to increase as the temperature is elevated. For instance, GVL selectivity increased from 77%

to >99% when the temperature is raised from 25 to 50 °C. The Ru/NHPC was also compared with a commercial Ru/AC (AC=activated carbon) as well as other commercial catalysts such as Ru/C, Pd/C, and Pt/C. Surprisingly, the Ru/NHPC was found to show excellent activity compared to all other catalysts studied, including Ru/AC, under similar reaction conditions. This was attributed to the presence of N atoms which improved the hydrophilic nature of the Ru/NHPC catalyst. As a result, the Ru/NHPC catalyst was found to have a good dispersion in water as compared to Ru/AC, thereby enhancing the activity. Interestingly, the Ru/NHPC was found to retain its activity even after being aged in the air for 1 year. Moreover, the catalyst maintained its activity even after 13 reaction cycles without significant loss of activity.

In some instances, commercial Ru/C catalysts often suffer from deactivation in the hydrogenation of LA to GVL in either batch or continuous systems. For example, some authors have reported deactivation of Ru/C in MeOH solvent just after the first catalyst recycle run, even at moderate temperature (130 °C). In trying to circumvent such limitations for Ru/C, Cao *et al*. recently prepared Ru/ZrO2@C catalyst with excellent stability [62]. The Ru/$ZrO_2$@C was prepared via wet impregnation and well-dispersed Ru particles with an average size of 3.3 nm were obtained.

### 1.3. Titania-supported Ru catalyzed hydrogenation of LA

Primo *et al.* have reported the study on the synergetic effect between the supports and the nanoparticles in the hydrogenation of LA [63]. They reported that $TiO_2$ supported Ru nanoparticle catalyst is 3 times more active for hydrogenation reactions (LA hydrogenation included) compared to the conventional carbon-supported Ru counterparts. Besides LA, other substrates such as succinic acid and itaconic acid were screened to evaluate the effect of support on the hydrogenation rate. To arrive at their conclusion, they normalized Ru nanoparticles sizes on other supports such as C and $CeO_2$ for comparison purposes and found that the TOF for the $TiO_2$ supported catalyst was much higher than for Ru supported on other supports, for a Ru loading of less than 2%. This enhanced activity was attributed to the good dispersion of Ru nanoparticles on the titania support. Moreover, this enhanced activity for titania supported Ru catalysts was attributed to the synergetic effect between the titania support and Ru nanoparticles which subsequently activate the carbonyl group on the $TiO_2$.

The role of water in the metal-catalyzed hydrogenation of ketones (including LA) was also further investigated using both experimental and theoretical studies by Michel *et al.* [33]. In their study, titania supported Ru, Pd, and Pt catalysts were evaluated in the hydrogenation of LA to GVL under two different environments (water and THF) and mild conditions (70 °C, 50 bar of $H_2$). The catalysts for all metals are prepared in such a way that reproducible average sizes can be obtained to minimize the effect of particle sizes on the catalyst's performance. The average sizes of these metal particles were determined by TEM analysis in the range of 2.1 – 3.2 nm. Additionally, the active metal sites were observed to be homogeneously well-dispersed on the titania support. Because these metal catalysts were all supported on the same support (titania), it was possible to conduct a comparative study on the effect of two solvents in the hydrogenation of LA to GVL under identical reaction conditions.

Both density functional theory (DFT) and experimental data were used to study the role of these two solvents. Both experimental and theoretical results revealed that Ru has a better activity for LA hydrogenation, with the highest activity observed in the $H_2O$ solvent. However, the same was not the case when the Ru catalyst was used in the THF solvent as no activity was observed. This enhanced activity of Ru in the $H_2O$ solvent was attributed to the hydrogen bond effect of water, which reduces the reaction's energetic span.

A related study on this enhancement in the activity of the Ru supported catalysts in aqueous medium was also reported by Tan *et al.* [64]. In their study, $TiO_2$, $SiO_2$, and $ZrO_2$ were used as supports for the Ru catalyst and compared in the hydrogenation of LA to GVL. Titanium supported Ru catalysts showed the highest activity compared to other screened catalysts in aqueous media and moderate temperature (70 °C). The $TiO_2$ supported catalysts with low Ru loading were generally observed to exhibit superior activity for LA hydrogenation. Good dispersion of Ru nanoparticles on the $TiO_2$ support was cited as the reason for this excellent activity. The investigation on the effect of solvent on the activity of the titania supported Ru catalyst was also carried out. Of all solvents screened ($H_2O$, ethanol, ethanol, and 1,4-dioxane), water was found to give high activity while maintaining high selectivity for GVL. Because $H_2$ has very low solubility in water, this promotional effect was attributed to the ability of water to promote the distribution of H atoms on the catalyst's surface. Additionally, LA conversion was found to improve as the amount of water solvent was increased. The possibility of water participating in the reaction was suggested for this observation. At higher Ru loading (2 wt%) and elevated temperature (130 °C), all catalysts screened achieved the complete conversion of LA in just 30 minutes. However, when Ru loading is decreased (to 0.5 wt%) the conversion of LA decreased by almost 20% even after a reaction time of 3 hours. Surprisingly, at moderate loading (1 wt%) and temperature (70 °C), the activity of the catalysts improved significantly with $TiO_2$/Ru giving 100% conversion after 6 hours. This enhanced activity of the $TiO_2$/Ru catalyst with low metal loading was also attributed to the good dispersion of the Ru particles on the $TiO_2$ surface. It is noteworthy to mention that some authors have reported a kinetic and mechanistic study on the Ni/$TiO_2$ catalyzed hydrogenation of LA. They found that Lewis acid sites on the $TiO_2$ surface contribute towards enhancing the selectivity for the formation of GVL [40].

Luo *et al.* also reported a study on the enhanced activity of titanium supported bimetallic Ru based catalysts in the catalyzed hydrogenation of LA to GVL when alloyed with Pd nanoparticles [34]. These catalysts were synthesized using a modified impregnation method for controlled particle sizes with a narrow size distribution. It should be noted that this modified impregnation method involves the addition of excess chlorine (in the form of dilute HCl) to achieve particles with smaller sizes. Encouraged by an observed tremendous improvement in the activity of the Au-Pd/$TiO_2$ in the hydrogenation of LA to GVL, they prepared an alloy of Ru-Pd/$TiO_2$ and compared (catalytic activity) it with the monometallic Ru/$TiO_2$ counterpart. It was found that the bimetallic Ru-Pd/$TiO_2$ gave almost complete conversion of LA after 30 minutes, while a full LA conversion was observed after 40 minutes for the monometallic Ru/$TiO_2$ catalyst. At longer reaction times (>2 hours), the selectivity for GVL was observed to decrease for Ru/$TiO_2$, while the bimetallic Ru-Pd/$TiO_2$ remained stable. This stability observed for the bimetallic Ru-Pd/TiO2 catalyst was attributed to the presence of the Pd species that diluted and isolated Ru sites during the reaction. To understand the effect of excess HCl on the performance of the catalyst, monometallic Ru/$TiO_2$ was prepared (without adding excess HCl). This catalyst was observed to be superior to both the monometallic Ru/$TiO_2$ and bimetallic Ru/$TiO_2$ prepared in the presence of dilute HCl. However, less sintering was observed for monometallic Ru/$TiO_2$ as compared to the bimetallic Ru-Pd/$TiO_2$ catalyst.

The influence of support and solvent on the catalyst selectivity and stability in the hydrogenation of LA to GVL has also been reported by Lu *et al*. [65]. $TiO_2$, $Nb_2O_5$, H-β, and H-ZSM5 were all used as supports for Ru nanocatalysts (1 wt% loading) via wetness impregnation. The influence of the solvent on the hydrogenation of LA was investigated using 2-ethyl hexanoic acid (EHA) and dioxane solvents. The zeolites supported catalysts (Ru/ZSM5 and Ru/H-β were found to be more acidic than the Ru/$TiO_2$ and $Nb_2O_5$ catalysts, with Ru/$Nb_2O_5$ being the least acidic. Consequently, hydrogenation products of GVL (pentanoic acid and ester derivatives were observed in a significant amount when the more acidic catalysts were used in dioxane as the solvent. The formation of ester derivatives was attributed to the esterification of pentanoic acid with dioxane decomposition products. The decomposition of dioxane was caused by its instability in the presence of acidic catalysts under the reaction conditions employed. Indeed, this observation proved that LA can potentially be directly converted to PA in a one-pot reaction. However, it is worth mentioning that the metal/zeolite catalyzed hydrogenation of GVL to PA has already been patented by a petrochemical company, Shell [66].

The extent of catalyst stability in the dioxane solvent was also investigated during the course of the reaction. After 4 hours, the Ru/H-ZSM5 catalyst was observed to have lost about 2.4% of Ru metal. The Ru nanoparticles size increased from 3.5 nm to 4 nm before and after the reaction, respectively.

Post-characterization by powder XRD revealed that the support materials did not undergo any structural/textural change during the reaction. However, $N_2$-physisorption for spent catalysts showed that there was a decrease in surface area and pore volume for $Nb_2O_5$ and zeolite supported catalysts. To try and circumvent problems encountered when dioxane was used as a solvent, EHA was used as an alternative solvent as it is stable under hydrogenation reaction conditions. A significant difference in terms of activity and selectivity was observed when the EHA solvent was used under similar conditions as applied for dioxane. For instance, the selectivity for GVL significantly improved for Ru/$TiO_2$ and Ru/$Nb_2O_5$ catalysts. Full LA conversion was observed for the Ru/$TiO_2$ catalyst after 4 hrs, while only 2.4 mol% of LA was still unconverted for the Ru/$Nb_2O_5$ after 5 hrs. Similarly, the Ru/H-β catalyst also gave a full LA conversion after 4 hrs, whereas 100% conversion of LA was observed after 3 hrs for the Ru-ZSM5 catalyst. Only GVL was observed as the product for Ru/$TiO_2$ and Ru/$Nb_2O_5$ catalysts. This was mainly because these catalysts were rendered to be weakly acidic catalysts and as a consequence, the ring-opening of GVL was not possible under conditions employed. As expected with more acidic catalysts, a significant amount of PA was observed after a reaction time of 10 hrs. The amount of PA observed in the EHA solvent was lower than that produced in the dioxane solvent. This was attributed to the competition that exists among LA, GVL, and solvent for the adsorption or interaction with the catalyst.

At low LA conversion, the Ru/H-β catalyst was found to produce a significant amount of PA. This was attributed to more available acidic sites accessible (responsible for the formation for GVL ring-opening) by GVL in the Ru/H-β catalyst as compared to the Ru/ZSM5 counterpart. However, after a lengthy reaction rime (10 hrs), the selectivity of PA for the Ru/H-β catalyst was found to be lower as compared to that for Ru/ZSM5. This suggested that the Ru/H-β catalyst is more prone to deactivation than Ru/ZSM5 catalyst. The catalyst stability study in the EHA solvent showed comparable results to what was observed in the dioxane solvent except for the Ru/ZSM5 catalyst, that suffered severe sintering and particle agglomeration (confirmed by TEM and EDX).

Solvent-free reactions were also performed to investigate the influence of acidity of the support on the activity and selectivity. For this, only Ru/H-β and Ru/$TiO_2$ catalysts were chosen. It was found that the catalysts showed more activity as compared when reactions are run in EHA solvent. For instance, the turn over frequency calculated for Ru/$TiO_2$ was 0.239 $s^{-1}$ compared to 0.164 $s^{-1}$ for Ru/H-β determined in the EAH solvent. Similarly, TOF for Ru/H-β increased from 0.131 to 0.403 $s^{-1}$ for reactions run in EAH and neat LA, respectively. Indeed, this observation further confirms the completion between LA and EAH solvent for adsorption on the catalyst's surface. The stability of catalysts was also studied using neat LA with no solvent. It was observed that the Ru metal loss and sintering were relatively limited for Ru/$TiO_2$ compared to when there is solvent involved in the reaction. More coke formation was observed for the Ru/H-β catalyst than when the EHA solvent was used. Generally, more coke formation was observed for all catalysts compared to in EHA solvent, hinting that this coke formation is not induced by the presence of EHA solvent but rather by LA derivatives.

The influence of titania support on the GVL yield during Ru catalyzed LA hydrogenation was investigated by Ruppert and co-workers [67]. In their study, titania supports (high and low surface area) with different crystalline phases (anatase and rutile) were used as supports for Ru nanoparticles. To explore further, a catalyst consisting of a mixture of both rutile and anatase phase was also evaluated in the same reaction. These Ru based, titania supported, catalysts were prepared by either incipient wet impregnation or liquid phase direct chemical reduction. The average particle sizes of Ru were determined by TEM to range between 2.1 nm to 4.5 nm. For all systems studied, all Ru-based catalysts were observed to exhibit superior activity in the hydrogenation of LA to GVL in terms of both conversion and GVL selectivity as compared to Pt-based catalysts screened for the same reaction. More interesting to note was that these titania supported Ru catalysts were found to give higher GVL yields than their carbon-supported counterparts.

For both reaction temperatures studied (30 °C and 70 °C), the anatase-rutile mixed-phase supported Ru catalysts showed the highest activity as well as high GVL yields. For instance, Ru/$TiO_2$ (rutile: anatase = 10:80%) gave 100% for LA conversion as well as GVL yield. On the other hand, with rutile: anatase ratio of 20:80% gave LA conversion of 99% and GVL yield of 95%. It should be mentioned, however, that even the Ru catalyst supported on pure rutile phase also gave appreciable results, giving 95% and 83% for LA conversion and GVL yield, respectively. The Ru catalysts supported on high surface area pure anatase phase showed relatively low activity. For example, the highest LA conversion and GVL yield obtained for these pure anatase phases supported Ru catalysts was 38% and 31%, respectively. The presence of micropores on the anatase phase support was cited as the reason for this reduction in activity as compared to either pure rutile or rutile-anatase mixed-phase supported Ru catalyst. Additionally, these micropores were observed to induce the formation of Ru agglomerates on the support's surface, thereby compromising the catalyst activity. To improve the activity of this pure anatase supported Ru catalysts, further calcination was performed (at 500 °C for 3 hrs). Indeed, a significant improvement in the activity was observed with the calcined catalysts, giving LA conversion and GVL yield of 99% and 93%, respectively. These values were comparable to those obtained for pure rutile supported or mixed phases supported Ru catalysts under similar reaction conditions. Two important key factors were cited for the difference in the activity of these different supports with different physicochemical properties: i) electronic properties which facilitate the dispersion of particles on the oxide surface and ii) the morphology of the oxide support which in turn affects the surface area and porosity and consequently the overall catalyst's activity. For instance, HRTEM analysis revealed that mixed oxide supported Ru nanoparticles prefers to grow on the rutile grains than on the anatase phase of the mixed-phase support. As a result, Ru catalyst supported on pure rutile phase showed significantly higher activity than those supported on pure anatase phase.

We have recently published work on the use of dendrimer-derived supported Ru nanoparticles in the hydrogenation of LA to GVL [68]. The dendrimer-derived Ru nanoparticles were immobilized on mesoporous $TiO_2$ support via wet impregnation and were denoted as $Ru_{40}$@Meso-$TiO_2$. The dendrimer template was removed by calcination at high temperature (550 °C) before catalytic evaluation of the supported Ru catalysts. The average sizes of the mesoporous titania were determined by HRTEM to be 1.4 ± 0.2 nm (see Figure 6).

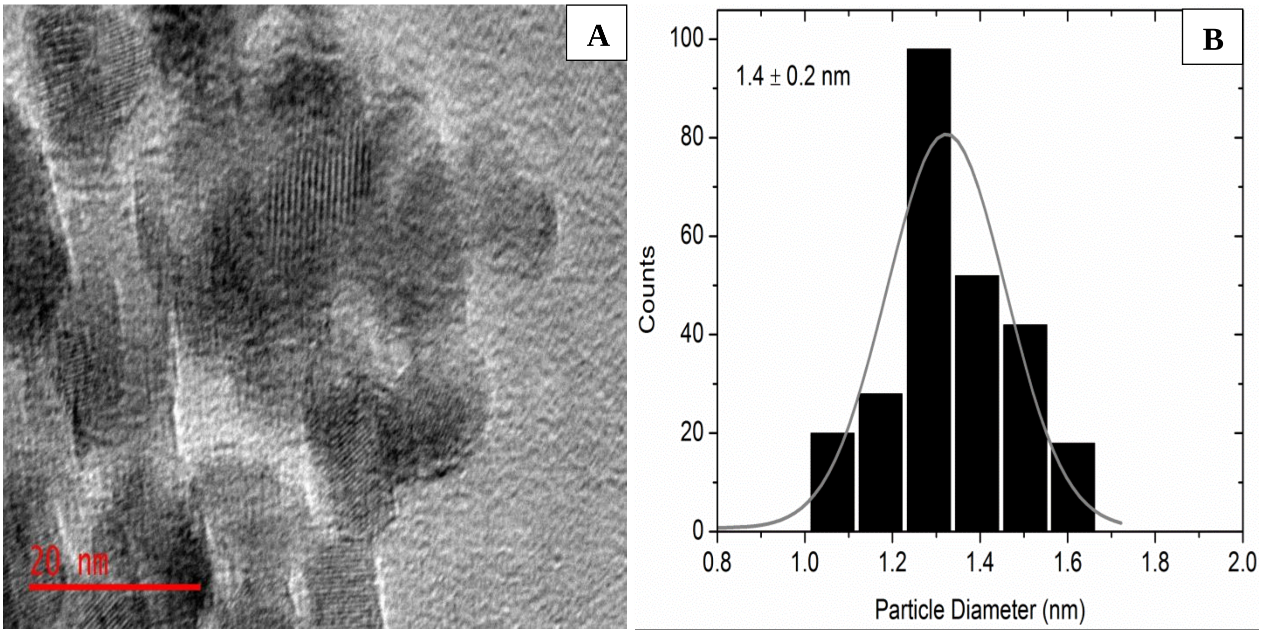


**Figure 6:** A) HRTEM images of mesoporous titania supported Ru particles ($Ru_{40}$@Meso-$TiO_2$) and B) the corresponding particle size distribution histogram for $Ru_{40}$@Meso-$TiO_2$. Reproduced from ref [68] with permission from Elsevier.

At a temperature of 150 °C, $H_2$ pressure of 10 bar, and reaction time of 5 hrs, both these catalysts were found to perform at their optimum level for the hydrogenation of LA to GVL. For instance, 98% LA conversion was observed for $Ru_{40}$@Meso-$TiO_2$. The $Ru_{40}$@Meso-$TiO_2$ catalyst showed higher selectivity towards the formation of GVL under conditions employed. Higher selectivity for GVL was attributed to the presence of Lewis acid sites on the titania support. The effect of solvent on the activity and selectivity of these mesoporous supported Ru catalysts was investigated using 1,4-dioxane and $H_2O$ as solvents. In our case, both solvents produced comparable results. However, some authors have reported an enhanced activity for $H_2O$ as compared to other solvents [64]. The $Ru_{40}$@Meso-$TiO_2$ catalyst proved to be robust even after 3 reaction cycles, thereby indicating that there was no severe leaching under reaction conditions employed.

Anatase $TiO_2$ supported ultrasmall $Ru(OH)_x$ nano-clusters have been reported to show excellent catalytic activity in the hydrogenation of levulinic acid as well as its levulinate esters (ML) [69]. Another oxide support such as $Al_2O_3$, MgO, $CeO_2$, $ZrO_2$, HT (Mg-Al hydrotalcite) was also used to support $Ru(OH)_x$ nanocatalysts for comparison purpose. The catalysts were evaluated via catalytic transfer hydrogen (CTH) using 2-propanol (2-PrOH) as a source of hydrogen under mild conditions (90 °C) for a reaction time of 24 hrs. Unsupported $Ru(OH)_x$ was found to achieve ML conversion and GVL yields of 52% and 47%, respectively. When the same amount of $Ru(OH)_x$ is supported on high surface area anatase $TiO_2$, higher ML conversion was observed. Among all catalysts screened for these reactions, $TiO_2$ supported Ru (0.8 mol%) catalysts gave the highest ML conversions.

Titanium containing pure anatase or anatase/rutile phase catalysts gave the highest GVL yields as compared to their pure rutile phase counterparts. For instance, pure anatase containing catalyst gave a GVL yield of 76% as compared to that obtained for pure rutile supported Ru catalysts of 49%. The effect of Ru loading on the performance of the catalysts was also investigated using pure anatase and anatase/rutile titanium supports. It was found that the catalyst activity decreases as the Ru loading is increased (from 0.8 wt% to 4.2 wt%) on the anatase/rutile titania support. However, the opposite was observed for the pure anatase titania support. For example, 4% $Ru(OH)_x/TiO_2(A)$ gave the highest ML conversion of 99% and GVL yield of 89%. Using the optimum catalyst (4% $Ru(OH)_x/TiO_2(A)$), various alcohols (MeOH, EtOH, 2-BuOH, 1-PrOH, and CyOH) were also evaluated as a source of $H_2$ for CTH reactions. It was found that primary alcohols such as MeOH, EtOH, and 1-PrOH did not act as effective $H_2$ donors for the CTH reactions. This was attributed to the difficulty of β-H elimination from primary alcohols [70]. About 80% LA conversion and 64% GVL yield were obtained when the 4 mol% Ru catalyst was used.

Recently, another work describing the catalytic hydrogen transfer (CHT) for the $TiO_2$ supported Ru catalyzed hydrogenation of LA and its derivative, methyl levulinate (ML) to GVL has been reported [71]. The average particle sizes of these $Ru/TiO_2$ catalysts with different metal loading (2-5 wt%) were determined by TEM to be around 5 nm. 2-Propanol was used as both solvent and source of hydrogen for this CHT hydrogenation of ML. Their solvent choice was inspired by previous reports that showed that 2-propanol acts as a good $H_2$ donor with higher conversion and product selectivity [70]. Optimization of the reaction conditions was performed using the 5% Ru/$TiO_2$ catalyst. A good ML conversion (98%) and GVL selectivity (71%) was observed at 150 °C and an ML concentration of 0.3 mol/L. When the temperature was raised to 200 °C, ML conversion and GVL selectivity increased to 99% and 98%, respectively. Product selectivity decreased drastically with an increased inlet flow-rate. When the inlet flow-rate was increased from 0.3 to 0.5 mL/min, the ML conversion and GVL selectivity decreased to 90% and 41%, respectively. Instead of GVL formation dominance, the product intermediate, 4-hydroxypentanoate was observed as the main product. Commercial 5%Ru/C and 5%Ru/$Al_2O_3$ catalysts were also evaluated for the same reaction for comparison purposes. It was found that these commercial catalysts gave lower activity and selectivity as compared to the as-synthesized 5%Ru/$TiO_2$ under similar reaction conditions. For instance, 5%Ru/C gave ML conversion and GVL selectivity of 83% and 52%, respectively. Likewise, 5%Ru/$Al_2O_3$ also showed a dramatic decrease in both ML conversion (31%) and GVL selectivity (97%).

Wojciechowska *et al.* recently published a work on the catalytic evaluation of Ca-modified titania supported Ru catalysts in the hydrogenation of LA to GVL [72]. Their Ru catalysts were prepared by immobilization of the Ru metal on the preformed $TiO_2$, Ca-modified $TiO_2$ (prepared by sol-gel method), or commercial $TiO_2$-P25 support via wet impregnation or photo-deposition. Ru particles prepared via the photo-deposition method were generally observed to be smaller than those prepared using the conventional wet impregnation method. For instance, average sizes of $TiO_2$-P125 supported Ru particles prepared using the photo-deposition method were determined by TEM to be 0.8 nm, while those prepared using wet impregnation were found to have an average size of 2.9 nm. Similarly, the average sizes of Ca-modified-$TiO_2$ supported Ru particles prepared by the photo-deposition method were found to be 1.8 nm while those prepared using wet impregnation were 3.8 nm. The hydrogenation of LA to GVL was run using molecular $H_2$ and formic acid as a source of hydrogenation and $H_2O$ as a solvent at 190 °C.

Catalysts prepared via photo-deposition were observed to give higher GVL yields as compared to those prepared using wet impregnation. Of these catalysts prepared by photo-deposition, the Ca-based catalysts with small Ru particle (1.5 nm) catalysts were found to be the most active in the hydrogenation of LA to GVL. The 5% Ca-based catalysts displayed the highest LA conversion and GVL yield, irrespective of the catalyst preparation method used. However, when the most active catalyst (Ru/5%Ca-T500) is reduced at 200 °C, the average particle size was observed to increase and as a consequence, the GVL yield decreased from 50% to 20%. To investigate the effect of Ca loading on the performance of the catalysts, catalysts with different Ca loading (1% and 5%Ca) albeit with comparable Ru particle sizes (1.4 nm and 1.5 nm) were compared in the LA hydrogenation under similar reaction conditions. It was found that the 5% Ca catalyst displayed superior activity, rendering the concentration of Ca as another important factor influencing the activity of the catalysts. This was attributed to the fact that an increase of Ca resulted in a decrease of the anatase crystallite sizes, enhancing the dispersion of smaller Ru particles on the support surface. Moreover, the addition of $Ca^{2+}$ ions added to the titania support increased the basicity on the catalyst surface as well as metal-support interaction, which subsequently improves the hydrogenation activity of the Ca-based catalysts.

### 1.4. Silica-supported Ru catalyzed hydrogenation of LA

One of the challenges in the hydrogenation of LA to GLV is that the product is in aqueous solution since GVL is miscible with $H_2O$. This necessitates the need for product separation after the reaction, which might be costly. In trying to overcome such costs and time-consuming processes, Poliakoff and co-workers reported the use of supercritical $CO_2$ for easy separation of pure GVL from $H_2O$ and unreacted LA [73]. In their work, 5%Ru supported on commercial $SiO_2$ (Degussa H 3036 XH/D) was used as a catalyst for the conversion of aqueous LA to GVL. This separation technique was inspired by the work reported by Lazzaroni *et al*. who added moderate supercritical $CO_2$ to THF/$H_2O$ which results in liquid/liquid separation into THF-rich and $H_2O$-rich phases [74]. Their reactor allowed them to drain unreacted LA while collecting water-free GVL product in the presence of $ScCO_2$ (see Figure 7). A GVL yield of 99% was obtained under optimum reaction conditions employed. Interestingly, they also claimed that their separation method managed to separate pure GVL even when the reaction is incomplete.

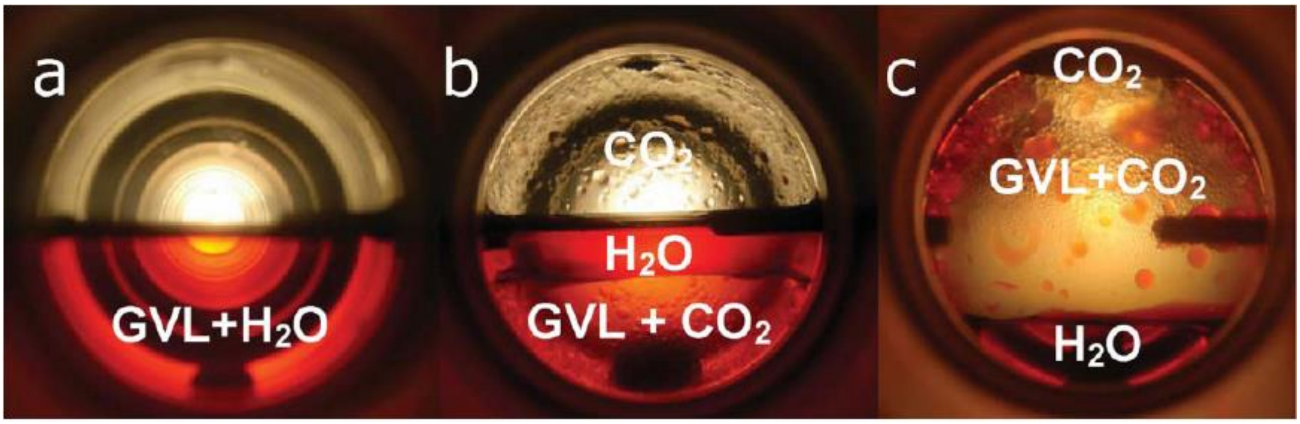


**Figure 7**: Three photographs of different stages of the same experiment demonstrating how the pressure of $CO_2$ induces the phase separation of aqueous GVL (GVL: $H_2O$ = 1:3.15 mol/mol). To void visualization, the mixture has been doped with a dye, Direct Red 23, which partitions preferentially into the water-rich phase. (a) the mixture in the cell without any $CO_2$, (b) the same mixture under a

pressure of 2.7 Mpa $CO_2$ at 21 °C. The system has now split into three phases with $CO_2$ at the top of $H_2O$ plus dye in the middle and GVL and $CO_2$ at the bottom. The reason cited for the organic layer being the bottom is that unusually for a non-halogenated organic compound, pure GVL is denser than $H_2O$. (c) Under a much higher pressure of $CO_2$ 9.3 MPa at 44 °C. There are still three phases but the $H_2O$ phase is at the bottom because the density of the GVL + $CO_2$, is now lower than that of $H_2O$ since, at pressure, liquid/supercritical $CO_2$ is much less dense than either GVL or $H_2O$. Reproduced from ref [73] with permission from The Royal Society of Chemistry.

We have also reported on the use of silica-supported Ru nanoparticles as a catalyst in the hydrogenation of LA to GVL [68]. The silica-supported Ru particles, denoted as $Ru_{40}$@Meso-$SiO_2$, were determined to be well-dispersed and have an average size of 2.0 ± 0.3 nm by HRTEM. A LA conversion of 94% and 100% GVL selectivity was achieved for $Ru_{40}$@Meso-$SiO_2$ when using $H_2O$ as a solvent and optimum temperature and $H_2$ pressure of 150 °C and 10 bar, respectively. However, 100% LA conversion and GVL yield were observed when 1,4 dioxane was used as a solvent under similar conditions as those used for the $H_2O$ solvent. Some authors have reported Ru-$SiO_2$ (5% Ru loading) catalyzed hydrogenation of LA to GVL in ethanol and ethanol-water solvents [50]. In their case, higher LA conversion (98%) was observed for ethanol-water solvent as compared to that of the pure ethanol solvent (82.9%). However, both the selectivity and yield for GVL were observed to increase for reaction run in pure ethanol.

### 1.4. Zeolites and other oxides-supported Ru catalyzed hydrogenation of LA

Another interesting comparison study in the catalysed hydrogenation of LA using Ru/$ZrO_2$, Ru/$TiO_2$ and the commercial Ru/C catalysts was reported by Ftouni *et al.* [75]. The conventional wet impregnation method was applied for the synthesis of Ru/$ZrO_2$ and Ru/$TiO_2$ catalysts (1 wt % Ru). A wide range of analytical techniques such as TGA, BET, STEM, XPS, and XRD was used to characterize the as-synthesized catalysts before the evaluation in the hydrogenation of LA to GVL. The average diameter of Ru particles on fresh Ru/$TiO_2$ was determined by TEM to be 2.7 ± 1.1 nm. However, the average size of Ru particles on the Ru/$ZrO_2$ was not easily determined by TEM analysis.

All reactions were performed for 3 hrs at 150 °C, hydrogen pressure of 30 bar, and a stirring speed of 1250 rpm. Typically, a substrate (LA) to catalyst (bulk Ru) ratio of 1000 was used in the presence of a solvent (1,4-dioxane). Suitable standard reaction conditions for the investigation of the influence of the support on the catalyst performance were established using the commercial Ru/C catalyst. It was observed that the catalytic efficiency is highly sensitive to the reaction temperature and less sensitive to $H_2$ pressure. We, and other authors, have also observed a similar behavior of catalytic efficiency not showing many dependencies on the amount of $H_2$ pressure as opposed to temperature in the hydrogenation of LA to GVL [59, 68]. Similarly, Yan *et al.*, have reported that at a pressure above 12 bar of $H_2$, no increase in GVL yields was observed for reactions run in water [47].

When a reaction temperature of 100 °C was used, a full LA conversion was only observed after 24 hrs. However, at 50 °C, only less than 20% GVL was observed after a similar reaction time interval (24 hrs). A full LA conversion and quantitative GVL yields were observed after a reaction interval of 3 hrs and a temperature of 150 °C. As expected, the change in $H_2$ pressure from 20 to 40 bar at a fixed temperature (150 °C) was not found to show much effect on the overall outcome of the reaction as all different pressures investigated gave almost similar results. For instance, all pressure systems studied were reported to give nearly full GVL yields after 3 hrs reaction interval. Based on these preliminary findings, standard reaction conditions were set to at 150 °C, $P_{H_2}$ = 30 bar, and a fixed molar LA/bulk Ru ratio of 100. Using these reaction conditions, the commercial benchmark catalyst (Ru/C) was compared to that of the as-synthesized $Ru/TiO_2$ and $Ru/ZrO_2$ catalysts.

The amount of GVL produced gradually during the course of the reaction was investigated for all three Ru-based catalysts. A quantitative amount of GVL was observed for all three catalysts after 3 hrs. The TOFs values for Ru/C, $Ru/TiO_2$ and $Ru/ZrO_2$ were determined to be 0.53 $s^{-1}$, 0.29 $s^{-1}$, and 0.24 $s^{-1}$, respectively. Of the three catalysts, $Ru/TiO_2$ was observed to have changed its color from grey to dark black even after just one use. This, of course, signaling a possible deactivation of the $Ru/TiO_2$ catalyst during the reaction. This partial deactivation was confirmed by TEM and TGA post-characterization (for recycled catalyst) as neither as a result of the loss of metallic surface nor as a result of Ru sintering nor deposition of carbonaceous deposits on the catalyst's active sites. This partial deactivation was attributed to the modification of the $TiO_2$ (P125) support, instead. Furthermore, XPS analysis of the fresh and spent $Ru/TiO_2$ showed a significant difference in terms of Ti 2p species core level spectra. The noted change in color for the used $Ru/TiO_2$ catalyst was suspected to indicate the possibility of partial reduction of titania and subsequent formation of $Ti^{3+}$ species [76]. The significant amount of $Ti^{4+}$ that got reduced to $Ti^{3+}$ is said to have been caused by reduction conditions during LA hydrogenation. This reduction has been reported to be induced by Ru via "$H_2$ spillover" [77].

On the contrary, only a small change in terms of physicochemical properties was observed for the $Ru/ZrO_2$ even after five recycling tests. For instance, post-reaction catalyst characterization showed that the BET surface area did not change significantly, even after five reaction cycles. TGA analysis revealed that only 7% weight loss was observed after five reaction cycles. This weight loss was suspected to have caused carbonaceous deposits that resulted in a slight deactivation of the catalyst during recycling tests. Additional SEM analysis showed that both the fresh and the spent catalysts retained the same homogeneous size distribution within a few micrometers range (1 – 3 µm).

Multiple catalyst recycling tests were performed to assess the stability of the Ru/C, Ru/$TiO_2$, and Ru/$CuZrO_2$ catalysts under applied batch conditions. Catalysts recovery between reaction cycles was achieved by filtering the solid catalyst, washing it with acetone, and leaving to dry overnight at 60 °C before the next reaction cycle. After five reaction cycles, the Ru/C catalyst displayed only a slight drop in GVL yield from 96 to 92% under the batch conditions applied. However, a clear deactivation for the Ru/C catalyst was observed for stability tests carried out at lower LA conversion (3 hrs at 100 °C). For instance, the GVL yield was found to drop from nearly 50% to 20% in the fifth recycling test. However, the selectivity towards GVL was observed not to change. The possibility of sintering causing this catalyst's deactivation was ruled off as TEM analysis for fresh Ru/C and the spent Ru/C (recycled five times) showed no difference in terms of particle sizes. For instance, the size of the average for fresh Ru/C and spent Ru/C (after five recycle) were determined to be 1.7 ± 0.4 and 1.7 ± 0.7 nm, respectively. BET measurements, however, revealed a decrease in surface area from 777 to 674 $m^2/g$ after five reaction cycles. A similar trend was observed with pore volume as it dropped from 0.22 to 0.18 $cm^3/g$.

It only took three recycle runs for the Ru/$TiO_2$ catalyst to show some sign of deactivation with a drop of ~30% in GVL yield. Only a GVL yield of 63% was obtained after five reaction cycles. In the case of the Ru/$ZrO_2$ catalyst, a near qualitative yield of GVL was obtained up to the fourth reaction cycle, thereby proving to be highly stable. A slight drop in GVL yield, similar to that noticed for Ru/C catalyst at high LA conversion, was observed after the fifth recycling run. This slight deactivation was attributed to the carbonaceous deposits that may have built up during the catalyst recycling process. Recycling tests run for Ru/$ZrO_2$ catalyst at lower LA conversion also suggested higher stability for this particular catalyst.

Since dioxane has been deemed convenient when used on a small scale catalysis studies, the effect of other solvents was also investigated using various bio-based γ- and δ-lactones (tetrahydrofuran, γ/δ-hexalactone, γ-octalactone), including GVL itself. High GVL yields were observed with all γ-lactone solvents, including GVL itself. THF and δ-hexalactone proved less idea for the reaction conditions applied and as a consequence, gave lower GVL yield, though with full selectivity towards GVL. This deactivation in THF as a solvent was suspected to be resulting from THF polymerization into polyether polyol [78]. Post-run characterization of the catalyst by TGA analysis revealed that about 8% and 15% weight loss for δ-hexalactone and THF, respectively. Much less carbon deposition (≤5%) was observed for spent catalysts from runs in dioxane, GVL, γ-haxalactone, and γ-octalactone. TOF values for runs in GVL, dioxane, γ-octalactone were calculated to be 0.10, 0.24, and 0.26 $s^{-1}$, respectively. The difference in terms of catalyst performance between the δ- and γ-ketones was attributed to the corresponding enoic acid, which might be more prone to coking.

The influence of water on the performance of the catalyst was also evaluated using the $Ru/ZrO_2$ catalyst. This was simply carried out by adding a different amount of water to act as a co-solvent with the dominant dioxane. The addition of just 1% of water was found to bring an increase in GVL yield by 25% (after 1 hour). When the amount of water was increased to 10%, a near-full LA conversion after 1 hour resulted. However, when a large amount of water (more than 50%) was added, a slight drop in the activity was observed. This observation about the effect of water on the activity of the catalyst in the hydrogenation of LA to GVL correlates well with what other researchers have also reported [33, 64].

Some of the common problems of $Ru/Al_2O_3$ catalysts have been low activity and stability induced by the inhomogeneous dispersion of Ru particles and the unstable nature of $Al_2O_3$ in $H_2O$. Many other support materials including $Al_2O_3$ itself, $TiO_2$, MCM-41, SBA-15, and $CeO_2$ are unstable in an aqueous environment because of the existence of the hydroxyl groups (-OH) on their surfaces [79-85]. Tan *et al*. developed an integrated strategy for the design of highly active and stable $Ru/Al_2O_3$ catalysts [86]. The synthesis of this stable catalyst was achieved by modification of the abundant surface Al-OH groups of γ-$Al_2O_3$ with 3-aminopropyl triethoxysilane (KH550). This resulted in the transformation of the Al-OH groups into a stable Si-O-Si structure (see Figure 8. The amino ligands of KH550 were used to coordinate Ru active centers (with the electron-rich state) with the $Al_2O_3$ surface (r-Ru-$NH_2$-γ-$Al_2O_3$). TEM analysis showed that the prepared r-Ru-$NH_2$-γ-$Al_2O_3$ catalyst has Ru particles with a minimum average size of 1.2 nm, while that of unfunctionalized $Ru/Al_2O_3$ was determined to be 12.3 nm.

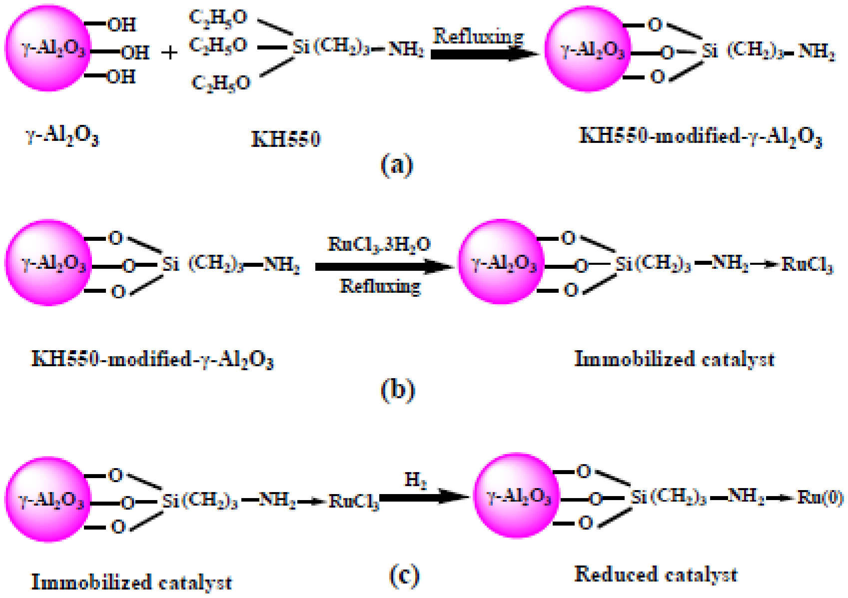


**Figure 8**: (a) Mechanism of surface modification by a silane coupling agent, (b) synthesis of the immobilized Ru-based catalyst, and (c) reduction of the immobilized Ru-based catalyst. Reproduced from ref [86] with permission from The Royal Society of Chemistry.

Both Ru/$Al_2O_3$ and r-Ru-$NH_2$-γ-$Al_2O_3$ catalysts gave the quantitative conversion of LA to GVL at 130 °C, after 30 minutes. For instance, complete LA conversion (100%) and higher selectivity for GVL was observed for both catalysts. However, at a lower temperature (70 °C), the r-Ru-$NH_2$-γ-$Al_2O_3$ catalyst showed superior performance as compared to the Ru/$Al_2O_3$ counterpart. The TOF value for the r-Ru-$NH_2$-γ-$Al_2O_3$ catalyst, for instance, was calculated to 3355 $h^{-1}$, about 8 times the TOF determined for Ru/$Al_2O_3$ catalyst (432 $h^{-1}$). It is noteworthy to mention that the r-Ru-$NH_2$-γ-$Al_2O_3$ catalyst was found to display excellent activity even at low temperatures such as 40 and 25 °C. For instance, LA conversion of 99% and GVL selectivity of 99.8% was achieved at 40 °C after 4 hrs. At room temperature, LA conversion of 99.1% and GVL selectivity of 99.9% was achieved, though after a longer reaction time (13 hrs). This excellent performance displayed by the r-Ru-$NH_2$-γ-$Al_2O_3$ catalyst in the hydrogenation of LA to GVL was attributed to the good dispersion of Ru particles on the KH500 modified $Al_2O_3$ surface. On the other hand, the activity of the Ru/$Al_2O_3$ catalyst was observed to decrease drastically at low temperatures. Only 39.5% LA conversion was recorded after 4 hrs, though the selectivity towards GVL did not change.

Although hydroxyapatite (HAP) supported catalysts (for metals such as Au and Ru) has been reported for other industrial reactions [87-89], the catalytic evaluation of HAP supported catalysts in the hydrogenation of LA to GVL was reported by Sudhakar *et al.* [90]. The HAP support was synthesized using co-precipitation, previously reported elsewhere by the same group [87]. Subsequent immobilization of metal catalysts (Ru, Ni, Pt, Pd) was carried out *via* wet-impregnation. The TEM characterization revealed Ru particles with a size range of 10 – 20 nm, for both unreduced and reduced Ru/HAP catalysts. As expected, the Ru/HAP (pre-reduced at 450 °C, 3 hrs) catalyst was observed to display superior activity in the hydrogenation of LA to GVL (70 °C, $H_2$ = 0.5 MPa, water solvent). LA conversion and GVL selectivity of 99% and 99% were obtained for Ru/HAP catalyst, respectively. However, the unreduced catalyst showed very poor activity with just 20% LA conversion, though with high selectivity towards GVL (99%). This observation, of course, suggests that metallic Ru are responsible for this hydrogenation activity for the reduced Ru/HAP. All other HAP-supported metals (Ni, Pt, Pd) gave LA conversion of less than 50% under identical reaction conditions.

The Ru/HAP catalyst was also used to investigate the influence of the solvent in the hydrogenation of LA to GVL. For this purpose, ethanol, ethanol + water (1:1 ratio), toluene, and water were all evaluated. It was observed that when ethanol (or ethanol: water) is used as a solvent at 70 °C, a significant amount of side products such as ethyl levulinate are formed. This is due to the transesterification of LA with ethanol. For instance, when ethanol and ethanol + water solvents were used, about 22 and 14% of ethyl levulinate was detected, respectively. However, it is noteworthy to highlight that no side products were observed when water was used as a solvent, and as such high LA (99%) and selectivity towards GVL (99%) were obtained. The conversion of LA was found to marginally decline by roughly 20% as the temperature is decreased to 60 °C, although maintaining high selectivity towards GVL. The reaction performed in the toluene solvent showed poor selectivity for GVL and this was attributed to the nonpolar nature of toluene. The recyclability test for Ru/HAP showed that the catalyst can be used for 5 reaction cycles without compromising selectivity for GVL. The conversion of LA was found to decrease by 10% from the first to the fifth reaction cycle.

A few years later, the same research group published an extended investigation of the same catalytic systems (HAP supported Ru, Pt, Pd, Ni, and Cu) in the hydrogenation of LA [91]. Ru/HAP was used to study the influence of temperature (275 – 425 °C) on the conversion of LA and product selectivity. The conversion of LA was found to increase as the temperature is elevated. For example, the conversion of LA increased from 65 to 94% as the temperature is raised from 275 to 425 °C at (GHVS = 3.89 $mL\cdot g_{cat}^{-1}\cdot s^{-1}$). However, the selectivity towards GVL was observed to decrease from 99.8 to 80% due to the formation of both α- and/or β-angelica lactones as side products. The influence of acidic sites on the catalysts' performance and selectivity during vapor phase LA dehydration was also explored by the same research group using the same catalytic systems (Ru/HAP) [91]. It was suggested that at high temperatures, moderate acidic sites are contributing to the conversion of LA to angelica lactones. It was determined during the characterization of the Ru/HAP catalyst that it possesses a high-temperature $NH_3$ desorption peak attributed to strong acidic sites.

The effect of water in the catalytic performance of Ru/HAP was examined by carrying out the reaction using pure LA. As a consequence, only a small amount of LA was converted (4%) at 275 °C although maintaining 100% selectivity towards GVL. Of course, the positive influence of water on the hydrogenation activity has also been reported by others [64, 92]. Interestingly, the selectivity for GVL and angelica lactone was observed to decrease when reactions were run using LA dissolved in other organic solvents such as methanol and ethanol. A significant amount of methyl levulinate formed as a result of the esterification of LA with methanol. It is also noteworthy to mention that role of acid sites on the hydrogenation of LA was investigated. For that purpose, Brønsted acidic sites of Ru were enhanced by the addition of dilute $H_2SO_4$ to the HAP support ($SO_4^{2-}$-HAP). Strong Brønsted acidic sites on the Ru/$SO_4^{2-}$-HAP were found to selectively catalyze dehydration of LA to angelica lactone. Based on these observations, it was, therefore, concluded that weak Brønsted acidic sites together with active metal sites are responsible for simultaneous hydrogenation and dehydration of LA to GVL.

Direct one-pot conversion of LA to GVL via hydrogenation using Ru nanoparticles embedded on sulfonic acid cation resin was reported by Moreno-Marrodan and Barbaro [93]. The as-synthesized Ru nanoparticles were immobilized on commercial sulfonic acid ion-exchange resin *via* wet impregnation yielding Ru particles with an average size of 2.8 ± 0.8 nm. The catalytic evaluation of the prepared resin supported Ru catalyst (Ru@DOWEX) was performed in both batch and continuous flow systems. The Ru@DOWEX was found to exhibit good activity for LA hydrogenation under mild conditions ($T \geq 50$ °C, $H_2 = 50$ bar). For instance, full LA conversion and 99% selectivity towards GVL after 7 hrs.

The role of the presence of acidic sites of the support on the catalyst's activity was assessed by using corresponding non-acidic supports in which lithium ions substituted all mobile protons. A significant drop in the conversion of LA was observed when this non-acidic resin supported catalyst is used under identical reaction conditions used for acidic supports. The acidic catalyst was also evaluated in a continuous flow system. Preliminary results revealed that LA conversion of 90% with a GVL selectivity of ≥ 90%. Additionally, it was found that the conversion of LA can be improved to 100% either by decreasing the flow rate of the solution or by simply increasing the $H_2$ flow rate. The stability study of this catalyst showed that the catalyst can be reused over 3 consecutive runs without showing signs of deactivation. The excellent catalytic activity displayed by Ru@DOWEX was attributed to a combination of well-defined acid and RuNP active sites on the support.

The synthesis and catalytic evaluation (LA hydrogenation) of cross-linked sulfonated polyethersulfone supported Ru NPs (Ru/SPEP) has been reported [94]. The Ru/SPEP catalyst was prepared *via* wet impregnation using $RuCl_3$ and polyethersulfone as metal and support precursors, respectively. The formed supported Ru NPs were determined to have an average size of ~3.2 nm by TEM analysis. Preliminary catalytic investigation of the synthesized Ru/SPEP catalyst in the LA hydrogenation was carried out using mild conditions (70 °C, $H_2$ = 3MPa, 2 hrs). A conversion of LA of 87.9% and 99% selectivity towards GVL were obtained under those conditions. When $Ru/SiO_2$ and Ru/C were employed for comparison purposes, under similar reaction conditions, LA conversion of 22.2 and 54.5% were achieved, respectively. However, it is important to mention that both Ru/C and $Ru/SiO_2$ showed higher selectivity towards GVL (≥99.9%). It was also found that when the Ru/C or $Ru/SiO_2$ is blended with Amberlyst 15 (acidic), an improved LA conversion of 40.4% and 68.0% was achieved for $Ru/SiO_2$ and Ru/C catalysts, respectively, without compromising their selectivity towards GVL. These observations indeed confirm the role of acidic support in enhancing the performance of supported Ru catalyzed LA hydrogenation.

As a control experiment, the naked catalyst supports, SPES, also showed low conversion of LA, thereby confirming the role of acidic catalysts involving intermolecular lactonization and keto hydrogenation. To further confirm this, the acidic sites of Ru/SPES were neutralized by aqueous NaOH (Ru/SPESNa). The LA conversion was found to drop from 87.9 to 64.6% when the Ru/SPESNa catalyst is used. Blending this Ru/SPESNa catalyst with Amberlyst 15 yielded lower LA conversion (76.8%) as compared to that obtained for Ru/SPES (87.9%). Interestingly, it was found during the catalyst's stability study that the activity was increasing with the number of reaction cycles. For instance, LA conversion was observed to increase from 87.9 to 92.1% after the first hydrogenation cycle. This increase in activity as the number of reaction cycles increases was attributed to the surface RuO species formed when small Ru clusters are exposed to an oxygen-containing environment. These RuO species are said to possibly undergo gradual reduction during the course of the reaction, resulting in increased activity.

Another interesting study on the influence of aluminum coordination in zeolites-supported Ru catalyst was recently reported by Lu *et al.* [95]. This was motivated by other previous reports which suggested that the acidity of the zeolite has a strong dependency on the type of zeolite structure, the amount, and distribution of aluminum within the zeolite framework [96, 97]. It was reported that the removal of aluminum from the zeolites (zeolite dealumination) framework can induce zeolite modification in terms of location, strength, number, and nature (Brønsted acid *vs.* Lewis acid site) of the acidic sites. This in turn can affect the catalytic properties of the zeolite supported catalysts in several ways [98].

The dealumination of the zeolite-supported catalysts (Ru/H-β and Ru/ZSM5) was investigated using a $^{27}$Al triple-quantum magnetic-angle spinning nuclear magnetic resonance spectroscopy (3QMAS NMR). It was observed during the LA hydrogenation that there was an increase in heterogeneity of aluminum speciation for both Ru/H-β and Ru/HZSM5. For the Ru/H-β catalyst, a severe loss of tetrahedral framework aluminum species (FAL) and extra-framework aluminum (EFAL) species into the liquid phase was observed. This consequently results in a significant decrease in strong acid sites as confirmed by FT-IR analysis. On the other hand, the symmetric, FAL was mainly found to be converted into distorted tetrahedral FAL in the case of Ru/ZSM5 catalyst. Based on these observations, it was concluded that this decrease in acidity signal the inferior stability of the strongly acidic Ru/H-β as compared to Ru/ZSM5 counterpart under the applied condition. This was identified as the main reason why these two catalysts will display different catalytic performances as previously observed [65].

The upgrade of LA to GVL using a Ru/C containing liquid triphase catalytic systems made of an aqueous phase, an organic phase, and an ionic liquid (IL) was reported by Selva *et al.* [99] (see Figure 9). Some of the most important benefits of these types of catalytic systems are: (i) easy separation of the product by a simple separation, (ii) preserving of catalyst's activity for *in situ* recycles without any metal loss, (iii) up to quantitative LA conversion with 100% GVL selectivity. In this catalytic system, the catalyst is stabilized inside different liquid phases from the reagents and reaction products and as a result, catalyst recovery becomes an easy process since the metal catalyst is often confined within the IL. The typical confinements of the commercial Ru/C within the IL in the triphase system was achieved by simply mixing Ru/C, $[N_{8,8,8,1}][Cl]$ (**IL1**), $H_2O$, and isooctane (or ethyl acetate/acetone) until all the Ru catalyst was dissolved into the IL phase.

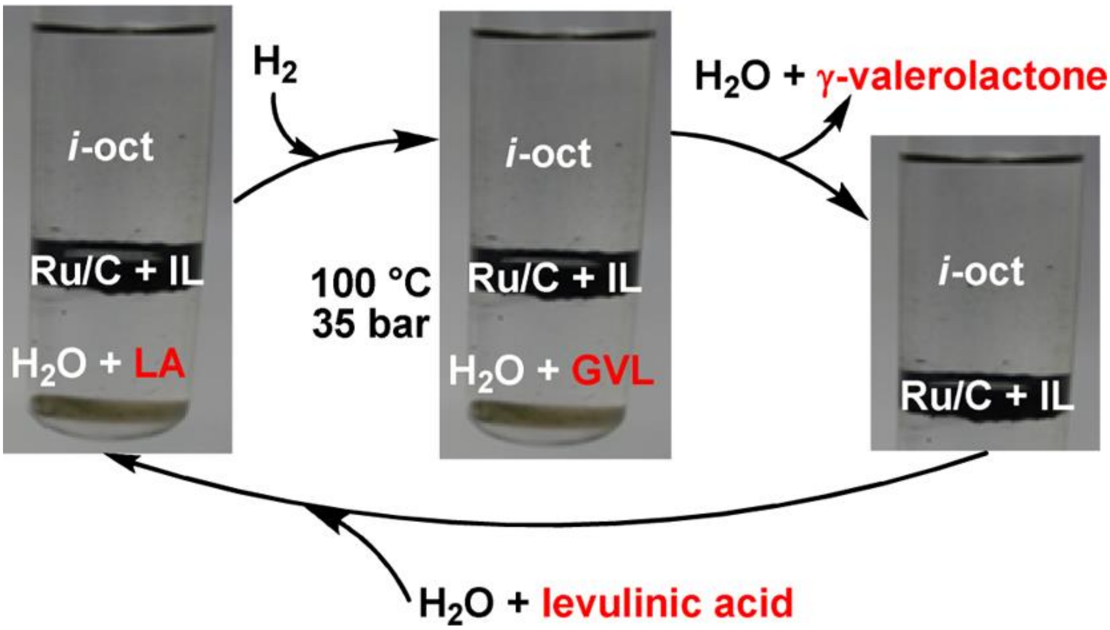


**Figure 9**: Pictures demonstrating the developed triphase catalytic system consisting of an aqueous phase, IL (confined Ru/C), and an organic phase. Reproduced from ref [99] with permission from American Chemical Society.

The preliminary hydrogenation reactions were initiated by adding LA into the tube containing the Ru/C based triphasic catalytic system (ethyl acetate (EA), water and $[N_{8,8,8,1}][Cl]$). The tube was placed into the autoclave at the desired temperature (100 °C) and $H_2$ pressure (35 atm). In the absence of the IL, 100% LA conversion and 91% GVL selectivity were achieved. However, as IL is introduced into the catalytic systems, LA conversion was observed to drop drastically. This decrease in catalyst activity in the hydrogenation reaction was found to be more severe as the amount of IL is increased. For instance, when the IL/catalyst (wt/wt) ratio of 5.7 is used, the conversion of LA and GVL selectivity dropped to 56% and 55%, respectively. A further increase in the IL/catalyst ratio is increased resulted in a significant decrease in LA and GVL selectivity, giving 11% for both LA conversion and GVL selectivity. The separation of product, however, was almost impossible as the GVL was partitioned between EA and water in a 3:1 ratio. In trying to circumvent this separation challenge, a multiphase system consisting of an aqueous solution of LA, isooctane, 5% Ru/C, and $[N_{8,8,8,1}][Cl]$ was established. They referred to this setup as an “inverse multiphase” system because the organic reactant, LA, and the product, GVL remain dissolved in the aqueous phase. The role of isooctane in this setup was to bring good separation as well as catalyst segregation.

During the catalytic hydrogenation testing of this inverse multiphase catalytic systems, the optimum IL/catalyst (wt/wt) ratio was determined to be between the range of 3 and 6. Under the reaction conditions applied (100 °C, $H_2 = 35$ atm, 4 hrs), the conversion of LA in that optimum range was found

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to have improved to 60 – 65%. In all cases, however, GVL was observed as the sole main product. It was discovered, however, that the $[N_{8,8,8,1}][Cl]$ IL did form a distinct three-phase system later, as it was partially soluble in the aqueous phase. About 2-3% was determined to have been lost into the aqueous phase after each hydrogenation test run. In order to avoid that, less soluble IL liquids were prepared; $[N_{8,8,8,1}]$NTf **IL2**, $[P_{8,8,8,1}]$NTf **IL3**, $[N_{8,8,8,1}]$CF3COO **IL4** and $[P_{8,8,8,1}]$NO3 **IL5**. Hydrogenation reactions were performed using triphasic catalytic systems made of different IL (**IL1-IL5**). A complete (100%) conversion of LA was achieved for all four salts IL (**IL2-IL5**), except for **L1**, which gave 32% LA conversion within 4 hrs. However, **IL4** and **IL5** were observed to be very soluble in the aqueous phase and as a consequence, were abandoned. On the other hand, **IL2** and **IL3** were stable enough not to partition into the aqueous phase. Moreover, they both confined the Ru/C catalyst perfectly well without any detectable leaching.

The IL3 catalytic system was chosen for the investigation of the influence of the reaction time and ideal IL/catalyst ratio. For this purpose, three reaction sets were used (0.5, 1, and 2 hrs) were used. For each set of reactions, different IL/catalyst molar ratios, ranging between 6 and 25 to 1, were also used. Data obtained revealed that the amount of IL has very little (if any) effect on the LA conversion. However, an increase in LA conversion was observed as reaction time is increased. Most importantly, the multiphase catalytic system was found to show to remain even after 8 subsequent runs. This was attributed to the fact that the Ru/C remains well-confined even during catalytic reaction under the conditions applied.

### 1.5. Conclusions

GVL is an important molecule that can be obtained from the catalytic hydrogenation of biomass-derived molecule, LA. From the afore-discussed Ru catalysed hydrogenation of LA to GVL systems, it is without any doubt that, indeed heterogeneous Ru catalysts are emerging as superior catalysts for this important reaction. In some instances, the catalyst with more Lewis-acidic sites were found to favour the formation of PA and ring-opening of GVL. Alloying Ru catalysts with other metals such as Sn and Ni seem to significantly improve catalyst's activity, stability and product selectivity. Interestingly, catalytic hydrogen transfer (CHT) using other sources of hydrogen than molecular $H_2$ has been established. For example, alcohols such as isopropanol/isobutanol have successfully being used as alternative hydrogen donor source for this hydrogenation of LA to GVL [69]. Similarly, formic acid has also been used as an internal source of hydrogen. The use of co-catalysts (such as A15 and A70) with the Ru catalyst has been observed to results in enhanced hydrogenation activity.

Of great importance was the potential displayed by water as a potential "green" solvent for the aqueous hydrogenation of LA to GVL. Water was found to enhance the hydrogenation activity when used as an alternative solvent. Modification of support (e.g $Al_2O_3$ with KHOO, C with N, and $TiO_2$ with Ca) improves metal-support interaction, catalyst stability and subsequently the activity. In other cases, it was established that a synergetic effect exists between support and Ru particles. Additionally, textural properties of the support material also play a role in the catalysts activity. $ScCO_2$ can be used to solve problems associated with the separation of GVL from $H_2O$ and other unreacted molecules in the end of the reaction cycle. Confinement of the supported catalyst by ionic liquids proved to greatly preserve the catalyst' activity. Interestingly, $ZrOr_2$ support, though unusually used as catalyst' support for this reaction, has been found to be more robust than catalyst than the benchmark Ru/$TiO_2$ catalyst.

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