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Highly Selective Hydrogenation of Levulinic Acid to γ-Valerolactone Over Ru/ZrO₂ Catalysts

Bilge Coşkuner Filiz · Edwin S. Gnanakumar · Arturo Martínez-Arias · Régis Gengler · Petra Rudolf · Gadi Rothenberg · N. Raveendran Shiju

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Abstract We studied the catalytic hydrogenation of levulinic acid over zirconia supported ruthenium catalysts. Four different Ru/ZrO₂ catalysts were prepared by different pre-treatments and using different zirconium supports (ZrOₓ(OH)₄₋₂ₓ and ZrO₂). Although the final compositions of the catalysts are the same, the pre-treatments strongly affect catalytic activity. Remarkably, one of the catalysts gave >99% yield of γ-valerolactone under mild conditions. This catalyst was also robust, and could be recycled at least four times without any loss in activity or selectivity. The activity is attributed to the presence of small ruthenium particles together with acidic sites on the catalyst.

Graphical Abstract Pre-treatment changes the performance for ruthenium nanoparticles on zirconia supports, giving TONs over 3500 in the hydrogenation of levulinic acid to γ-valerolactone with over 99% yield.

Electronic supplementary material The online version of this article (doi:10.1007/s10562-017-2049-x) contains supplementary material, which is available to authorized users.

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Keywords  γ-Valerolactone · Zirconia · Hydrogenation · Levulinic acid · Biomass conversion · Ruthenium

1 Introduction

Converting lignocellulosic biomass to high-value-added chemicals is a ‘hot topic’, and rightly so. Biomass is our only practical source of renewable carbon,[1] yet there is enough of it to meet the worldwide demand for polymers, agrochemicals and fine chemicals. But notwithstanding the advantages of its rich chemical variety, practical applications of biomass must focus on a few simple and common building blocks [2–4]. These so-called ‘platform molecules’ can then be incorporated into existing processes or form the basis for new processes using current unit operations [5–9].

Levulinic acid (LA, 1) is one of the most promising candidates. It is produced easily and economically from biomass, [10–15] and can be converted into many valuable chemicals. These include γ-valerolactone (GVL, 2), 1,4-pentanediol, methyltetrahydrofuran, and valeric acid and esters [16, 17]. Of these, the stable and non-toxic GVL has already several applications: it can be used directly as a fuel additive or as a precursor for fuels and chemicals and as a renewable solvent [10, 18–21]. Various companies such as Green Future SRL, DuPont, Segetis and Biofine have developed processes for the manufacturing of levulinic acid through bio-based routes. These processes are expected to reduce the price of levulinic acid from its current US$ 5–8/kg to less than US$ 1/kg [22].

Although the hydrogenation of levulinic acid to GVL was also reported using homogeneous catalysts, any large-scale process is much more likely to use heterogeneous catalysis, owing to the ease of catalyst separation and the simpler product workup [22–24]. The separation costs are often the deciding factor, because any remaining catalyst will often react further with the product and by-products. Supported ruthenium catalysts are known to perform well in LA hydrogenation [10, 19, 25–29]. The problem is that small changes in any number of parameters often cause large variance in catalyst performance. Using different supports and even using different phases of the same compound [30–32] alters conversion and yield [17]. Another parameter that influences catalyst performance is the metal dispersion on the surface. In general, smaller Ru particles are more active, but the catalyst is less robust [17, 19, 31, 33]. Also, it is reported in literature that mixing acid catalysts with Ru metal catalysts promoted hydrogenation and bifunctional catalysts are active and recyclable in aqueous solution [18, 34]. The nature of the support and the synthesis method influence the catalytic activity significantly in hydrogenation reactions [35]. Considering the relatively high cost and low availability of ruthenium, catalyst robustness is a key issue for any practical application [36].

Addressing these challenges, we synthesised several zirconia-supported Ru catalysts and tested these in the liquid phase hydrogenation of LA. We chose zirconia as the support because previous works showed that, for other reactions, its interaction with the active phase enhances activity and selectivity [37, 38]. Moreover, it is more robust than Al2O3 and SiO2, a crucial practical criterion of special importance for biomass derivatives, which are generally reacted under aqueous-phase conditions. Thus the support should withstand the hydrolytic attack and not lose surface area. The surface parameters of zirconia can be tuned by appropriate pre-treatment. For example, the acidity in tungstated zirconia changes significantly depending on whether the calcination is done before or after the impregnation with tungstate groups [39]. Doping zirconium oxide (or hydroxide) can change its surface area, conductivity and crystal structure, affecting the catalytic performance. Again, these parameters depend on the treatment conditions. Here, we found that the pre-treatment strongly influences the hydrogenation results. The best catalyst achieved a turnover number (TON) of 3500, better than any of the values reported so far under similar conditions. This catalyst retained 100% of its activity in four consecutive runs.

2 Experimental Section

2.1 Materials and Instrumentation

Ruthenium chloride (RuCl3), zirconyl chloride octahydrate (ZrOCl2·8H2O, 98%; used as the source of zirconia for preparing the homemade zirconia samples) and DMSO were purchased from Aldrich. Commercial zirconia (TOSOH TZ-3Y) was purchased from Tosoh. Ammonium hydroxide (NH3·OH) and ethyl lactate (98%) were purchased from Fluka. Levulinic acid (LA, 98+%) and ammonium nitrate (NH4NO3) were purchased from Acros Organics and Merck, respectively.

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Mini Flex II diffractometer operating at 15 mA and 30 kV, using Ni-filtered CuKα radiation (λ = 1.5406 Å) with a step size of 0.05°. Temperature programmed reduction (TPR) analyses were carried out on a Thermo Electron TPDRO series 1100 instrument. Samples were pre-treated in N2 (40 cm3 min−1) at 200°C for 5 min with 5°C min−1 heating rate before H2-TPR analyses. Analyses were carried out at a heating rate of 10°C min−1 in 5% H2/N2 at a constant flow rate of 20 cm3 min−1. The N2 adsorption isotherms were measured at 77 K on a Thermo Scientific Surfer instrument after evacuation at 473 K for 16 h. Surface areas were calculated using the BET method. High
resolution transmission electron microscopy images were acquired with a TEM/STEM JEOL 2100F microscopy operating at 200 kV and with a field emission gun, able to achieve point resolution of 0.19 nm. The microscope is coupled with an EDX detector (INCA x-sight from Oxford Instruments), which allows semi-quantitative chemical analysis of the samples. Specimens were prepared by were prepared by depositing them from ethanol dispersion onto a nickel grid supporting a perforated carbon film. X-ray Photoelectron spectroscopy was performed using a SSX-100 surface science instrument equipped with a monochromatic Al Kα X-ray source (1486.3 eV) with a spot size on the sample of 600 µm. The base pressure during the measurements was 5 × 10^{-10} mbar. The samples were prepared by drop casting an ethanol dispersion onto gold on mica and dried under vacuum before introduction into the spectrometer. An electron flood gun in combination with an EDT detector and a 30 m RTX-1701 column (0.25 mm ID, 1 µm df). Products were identified using standard solutions, and quantified using ethyl lactate as standard. The catalytic tests were carried out in a 35 ml cylindrical stainless steel autoclave, equipped with a PTFE insert and a thermocouple. NH3-TPD experiments were measured on a Micromeritics AutoChem II 2920 instrument. Approximately 100 mg of sample was initially pretreated at 250 °C under 10% H2/He (samples A, B and D) or He (sample C) for 30 min and subsequently saturated with 50 ml/min 5% NH3/He at 40 °C for 60 min. Loosely bound ammonia was hereafter removed by purging with 50 ml/min He for 60 min, before performing temperature programmed desorption (TPD) at a heating rate of 10 °C/min in the range 40–900 °C in a He flow of 25 ml/min.

### 2.2 Procedure for Preparing Zirconia-supported Ruthenium Catalysts

Zirconium oxohydroxide was prepared by controlled addition of an aqueous zirconium oxychloride (ZrOCl2·8H2O) solution to an NH4OH (0.1 M)/NH4NO3 (0.1 M) buffer solution, keeping a constant pH 10. The precipitate was filtered under vacuum and washed with deionized water until the filtrate reached pH 7. The solid (zirconium oxohydroxide, ZrO2(OH)4−2x; denoted hereafter as ZrOH) was filtered and dried at 120°C for 12 h. ZrO2 was obtained from this ZrOH after calcination in static air at 500°C for 4 h.

The four zirconia-supported Ru catalysts A–D (5 wt% Ru in all cases) were prepared using different zirconia supports and thermal treatment procedures (see Table 1 for details). The RuCl3 precursor (2.6 mmol) was dissolved in deionized water (50 ml) and heated to 80°C. Then, 5.0 g of zirconia support (ZrOH or ZrO2) was added under stirring. The water was evaporated and the cake was dried at 120°C for 12 h. Thereafter, each sample was subjected to different thermal treatments: Catalyst A, prepared using a commercial ZrO2 support, was calcined in static air at 450 °C for 3 h and then reduced at 250 °C for 2 h (for comparison, a control sample of A was reduced at 350 °C, to check the effect of the reduction temperature on the ruthenium). Catalyst B, prepared using a ZrOH support, was calcined in static air at 450 °C for 3 h and then reduced at 250 °C for 2 h. Catalyst C was prepared from ZrOH, but first reduced at 250 °C for 2 h and only then calcined (in static air) at 450 °C for 3 h. Finally, catalyst D was prepared using the homemade ZrO2 support, and directly reduced at 250 °C for 2 h. All reduction treatments were carried out under 25 ml/min of H2:N2 (1:3 volume ratio) flow in tubular furnace.

### 2.3 Procedure for Liquid-phase Hydrogenation of Levulinic Acid Over Zirconia-supported Ruthenium Catalyst

In a typical reaction (see Scheme 1, top), the autoclave was loaded with reactant (4.28 mmol), solvent (10 ml), catalyst (either 12.5 or 25 mg) and a stirring bar. It was then purged thrice with N2 at 296 K, and subsequently pressurized with H2 (12–27 bar), heated up to the chosen temperature (100, 130 or 170 °C) and kept for desired reaction time (30 min–7 h) while stirring at 750 rpm. The reaction was then quenched by cooling the autoclave rapidly to 25 °C using an ice bath. Then the reaction mixture was centrifuged (3000 rpm; 10 min) and the supernatant was analysed using a GC. The conversion was calculated from the amount of levulinic acid consumed in the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Description of catalysts used in this work</th>
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<tbody>
<tr>
<td>Catalyst</td>
<td>Zr source</td>
</tr>
<tr>
<td>A</td>
<td>Tosoh zirconia</td>
</tr>
<tr>
<td>B</td>
<td>ZrOCl2·8H2O</td>
</tr>
<tr>
<td>C</td>
<td>ZrOCl2·8H2O</td>
</tr>
<tr>
<td>D</td>
<td>ZrOCl2·8H2O</td>
</tr>
</tbody>
</table>
Highly Selective Hydrogenation of Levulinic Acid to γ-Valerolactone Over Ru/ZrO₂ Catalysts

The selectivity was calculated by dividing the amount of GVL formed by the amount of levulinic acid consumed, expressed as percentage. The yield is defined as the product of selectivity and conversion; duplicate analyses confirmed the results, with mass balance >95%. We did not observe any hydrogenation products of GVL by GC. For recycling tests, the catalyst was filtered, washed with acetone, dried at 120 °C for 12 h in air and reduced in 25 ml/min of H₂:N₂ (1:3 volume ratio) flow at 250 °C before the next cycle.

3 Results and Discussion

Converting LA to GVL is not a simple hydrogenation. We must ensure that we hydrogenate only the keto group, enabling the cyclisation to the lactone product. Previous studies have shown that both the size and the dispersion of the ruthenium sites are crucial, as well as the properties of the support [17, 21, 32, 33]. This is because the hydrogenation of keto group is catalysed by a combined effort of both the ruthenium active site and the support. The support activates carbonyl group of LA, while ruthenium efficiently dissociates H₂ [31, 33, 34]. Ruthenium is an excellent hydrogenation catalyst, and ZrO₂ is a known support for hydrogenation, [40–42] dehydration, [43] esterification [38], and isomerization reactions [44–47]. The mechanical, thermal and chemical properties of ZrO₂ are favourable for these reactions. It is stable under coking conditions and remains active even after a week’s exposure to hot carboxylic acid [21]. Thus, we chose zirconia as support (ZrOH and ZrO₂) and prepared Ru/ZrO₂ catalysts using different pre-treatments. Such thermal treatments may modify the support properties as well as the ruthenium-support interactions and consequently the catalytic performance.

3.1 Characterization of Zirconia Supported Ru Catalysts

Figure 1 shows the XRD patterns of the supports and Ru/zirconia catalysts. ZrOH gives rise to two broad peaks at around 30° (monoclinic phase) and 52° (tetragonal phase) respectively. ZrO₂, prepared from ZrOH by calcination at 500 °C has both monoclinic and tetragonal phases. However, the monoclinic phase is predominant. Conversely, the majority phase of the commercial TOSOH ZrO₂ is tetragonal (peaks at 20 ~30°, 35°, 50°, and 60°). For the Ru/ZrO₂ catalysts, the peaks of the ruthenium species could not be observed (expected 2θ values of Ru peaks are 38.3°, 42.1° and 44°, JCPDS No. 06-0663), due to the high dispersion of the particles. Catalyst A, prepared by the impregnation of TOSOH ZrO₂, gives rise to a pattern similar to that of the bare support. Catalysts B and C, despite their different calcination and reductions steps, showed similar crystalline structure (Fig. 1). The monoclinic phase was more dominant in catalyst D, prepared by impregnating ZrO₂ followed by reduction [48–50].

The textural properties of supports and Ru/ZrO₂ catalysts are given in Table 2. The commercial TOSOH zirconia was found to have the smallest surface area, 14 m² g⁻¹. The ZrOH support, prepared by precipitation from ZrOCl₂, has a surface area of 197 m² g⁻¹, which decreases to 57 m² g⁻¹ after calcination to ZrO₂. Nevertheless, catalysts B and C, prepared from ZrOH, have higher surface areas compared to A and D, which were prepared from ZrO₂.

Note that these samples were synthesized by first impregnating the zirconium hydroxide followed by heat treatment. We observed in a previous study that when zirconium hydroxide is first impregnated with WOₓ and then calcined, the decrease in surface area is lower compared to calcination of zirconium hydroxide alone [37]. Our results show a similar behaviour with RuCl₃ impregnation, but the effect is not as dominant as that reported for WOₓ/ZrO₂.

Figure 2 shows the nitrogen adsorption–desorption isotherms of zirconia supports and Ru/ZrO₂ catalysts. The isotherms of the supports are of different types; commercial TOSOH zirconia gives a Type II isotherm with 48 nm average pore diameter (on the border between meso- and macropores), while ZrOH shows a Type I isotherm, mostly microporous, with a 3.7 nm average pore size. The isotherm changes into Type IV and the average pore size nearly doubles (to 6.5 nm) after calcination to ZrO₂.
Impregnating ruthenium on TOSOH zirconia (catalyst A), does not change the isotherm dramatically. Catalysts B, C and D show a classical Type IV (mesoporous) isotherm. The average pore sizes of catalysts B and C, prepared from ZrOH, were similar (5.9 and 6.0 nm, respectively). The average pore size of D almost doubles (14.6 nm) after ruthenium impregnation. Note that the surface area and the pore volume decrease while the average pore size increases. This shows that the impregnation and subsequent reduction of ZrO₂ breaks down the original texture. The inner walls collapse, creating fewer (yet larger) pores.

Table 2  Surface properties of supports and Ru/ZrO₂ catalyst

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Specific pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrOH</td>
<td>197</td>
<td>0.16</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>57</td>
<td>0.16</td>
</tr>
<tr>
<td>TOSOH ZrO₂</td>
<td>14</td>
<td>0.08</td>
</tr>
<tr>
<td>A</td>
<td>20</td>
<td>0.30</td>
</tr>
<tr>
<td>B</td>
<td>65</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>63</td>
<td>0.26</td>
</tr>
<tr>
<td>D</td>
<td>22</td>
<td>0.09</td>
</tr>
</tbody>
</table>
from a detailed analysis of selected representative high resolution images (see Fig. 4). For D, the presence of small ruthenium particles (interplanar distance of ca. 2.06 Å, corresponding to (101) planes of metallic ruthenium) supported on zirconia (interplanar distance of ca. 3.15 Å, related to (111) planes of monoclinic zirconia) in profile as well as front view can be identified. This agrees with the XRD pattern, which also showed the predominant formation of the monoclinic phase. The Ru particles appear as truncated semicuboctahedral shapes. They are of around 3–4 nm long and 1–2 nm high.

Sample A is similar, although the ruthenium particles appear smaller and more difficult to detect in this case. In contrast, supported ruthenium particles could not be identified in the high resolution images of samples B and C, suggesting that they are highly dispersed. Note that the parallel EDX analysis (not shown here) evidences the presence of ruthenium, and the TPR analysis shows Ru reduction peaks for B and C, the areas of which are not very different from those in A and D. The zirconia nanoparticles in B and C have tetragonal phase (based on the interplanar distance of ca. 2.6 Å related to (002) planes observed in most cases where lattice fringes could be resolved). Previously we observed that doping ZrOH with WOx followed by calcination leads to predominant formation of tetragonal ZrO2.17 The present results show that tetragonal phase stabilization by doping is more general.

3.2 Levulinic Acid Hydrogenation

We then tested our Ru/ZrO2 catalysts in the hydrogenation of LA in a batch reactor at 130°C under 12 bar H2. A blank reaction without catalyst showed no conversion. All four catalysts were 100% selective for GVL but we observed large differences in catalytic activity (Fig. 5). Catalyst D, which was prepared from ZrO2 and directly reduced under H2 atmosphere, was the most active, despite its low surface area. Indeed, we found no relation between surface area and activity. Catalyst B, with a threefold higher surface area than A, showed a similar catalytic activity. Moreover, B and C have similar surface areas, yet C is almost twice as active than B. In a separate control experiment, we also pre-reduced catalyst A at 350°C (catalyst A-350) to examine the effect of completely reduced ruthenium sites. As Fig. 5 shows, the reduction temperature affects the conversion of LA, yet the reaction does not depend only on the reduction of all ruthenium species. A direct correlation with the surface areas will not be straightforward also because of the bifunctional character of the reaction, with the metal for the hydrogenation of the carbonyl group and the acid support for the cyclizing esterification.

The XRD and TEM studies show that the crystalline phase of ZrO2 in B and C is different from A and D. This
could affect the environment of Ru particles. The TEM identifies more or less uniform Ru particles of 3–4 nm in sample D, which has the highest catalytic activity. The presence of these well-defined Ru nanoparticles, most of which can be easily reduced as shown by TPR, could account for the high activity of D. The assumption, based on TPR, that samples B and C contain dispersed RuOₓ species also agrees with the fact that TEM could not identify the Ru particles on B and C. Thus the lower activity of B and C might be attributed to absence of crystalline Ru.

Bulk elemental analysis by ICP-AES did not give any major difference between the samples (5 ± 0.4 wt% Ru). We also analysed the samples by XPS (Catalysts B and D are shown in Fig. 6). The surface ratios of Ru to Zr obtained from XPS analysis based on the areas of Ru 3d and Zr 3d peaks (after correcting with the instrument specific sensitivity factor) were similar. This means that the surface concentrations of Ru on these catalysts are similar. This in turn means that the comparative lower activity of B is not due to Ru being buried in the bulk. Previously, we observed that doping zirconium hydroxide with tungstate groups followed by calcination causes the segregation of WO₃ species at the grain boundaries of zirconia. Contrarily, doping tungstate on pre-formed crystalline ZrO₂ showed no such preference, but resulted in bigger tungstate species and lower catalytic activity [39]. Here we did not observe such differences. Thus, the effect of treatment steps on the final structure of the catalyst depends on the nature of the supported species. We also studied the acidity of the catalysts by NH₃ TPD (Fig. 7), and found that all catalysts have some acidity. An intense peak between 450 and 500 °C for sample D shows the presence of strong acid sites, which could be either Brønsted or Lewis in nature. Zirconia is known to possess both Brønsted and Lewis acidites.
1751Highly Selective Hydrogenation of Levulinic Acid to γ-Valerolactone Over Ru/ZrO₂ Catalysts

sites and their density depend on pretreatment temperature. The fact that this peak is strongest for D, which was synthesized by direct reduction of Ru loaded zirconium oxide (see Table 1), shows that further calcination (as applied in the case of the other samples) diminishes these acid sites. The TPD of bare support did not show any major peaks (Figure S3). The strong peak in TPD of sample D may also originate from remaining small amounts of chloride. Overall, we conclude that the well-defined nanoparticles of Ru together with higher concentration of acid sites make catalyst D better than other catalysts.

Since catalyst D was the most active, we used it for further reaction optimization studies. The conversion changed with reaction conditions, but the catalyst retained its selectivity to GVL. The conversion as a function of reaction time for this catalyst is provided in supplementary information (Fig. S1).

At 12 bar H₂ pressure, the LA conversion was 70%; increasing the pressure to 24 bar gave complete LA conversion (Table 3, entries 1 and 2) due to the saturation of active catalyst sites by H₂. The effect of the reaction temperature on the conversion of LA was also studied (entries 2 and 3). By decreasing the temperature from 130 to 100 °C, the conversion decreased to 96%. The amount of catalyst also affected the conversion, as expected (entries 2 and 4). Decreased conversion was obtained at shorter reaction times (entries 2 and 5, 6). Under these reaction conditions, full conversion of LA to GVL requires 120 min. We then did the reaction with a higher substrate/catalyst ratio of 2100 (entry 7) full conversion was achieved in 7 h at 170 °C retaining the selectivity to GVL. Under the same conditions, we did an experiment with still higher ratio (3500) but this time replacing H₂O by DMSO as solvent (entry 8). This reaction also gave complete conversion, achieving a TOF of 0.07 s⁻¹, which is higher than the reported values under similar conditions. For example, the TOF values reported previously for various catalysts are 0.03 s⁻¹ (5%Ru/C) [17], 0.027 s⁻¹ (5%Ru/TiO₂-P25) [17], 0.0059 s⁻¹ (5%Ru/TiO₂) [33], 0.0137 (0.6%Ru/TiO₂) [33], 0.002 s⁻¹ (5%Pd/C) [32], 0.008 s⁻¹ (RuSn/C) [55], 0.00049 s⁻¹ (15% RuRe/C) [56], 0.004 s⁻¹ (1% Au/TiO₂) [57] and 0.005 s⁻¹ (1% Pd/TiO₂) [57].

3.3 Recycling Tests

We re-used catalyst D four times (Fig. S2) at low conversion; after each reaction, the catalyst was removed and washed with water and acetone and dried at 120 °C in a static oven. The recycling tests were carried out under the same conditions and we did not see any indication for deactivation. Thus, this Ru/ZrO₂ catalyst is reusable and fully selective to GVL.

Two possible pathways are reported for LA hydrogenation in literature [58]. In the first route, an intramolecular esterification of LA leads to angelica lactones (α and β

---

Table 3 Activities of catalyst D under various conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst D (mg)</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>t (min)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>130</td>
<td>12</td>
<td>120</td>
<td>70</td>
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<td>170</td>
<td>27</td>
<td>900</td>
<td>99</td>
<td>99.9</td>
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</table>

Reaction conditions: 4.28 mmol LA, 10 ml water, 5 wt% Ru catalyst: 0.012 mmol Ru
ᵃ25.2 mmol LA, 10 ml water, 5 wt% Ru catalyst: 0.012 mmol Ru
ᵇ42.8 mmol LA, 10 ml DMSO, 5 wt% Ru catalyst: 0.012 mmol Ru
forms) followed by the hydrogenation of the C=C bond. The second pathway involves the hydrogenation of keto groups first, forming 4-hydroxypentanoic acid followed by an intramolecular esterification step. In presence of hydrogen at temperatures higher than 50 °C, the most probable one is the latter [58]. The acidity of the catalyst plays a role in both reaction steps [34]. The second pathway is the more probable one under our conditions (1.2 or 2.4 MPa and 100 or 130 °C).

4 Conclusion

We report here a green catalytic route for producing GVL, an important platform molecule in biomass conversion. Our heterogeneous hydrogenation of levulinic acid can be done in water. The catalytic activity is influenced by the pre-treatment conditions. The best catalyst was obtained by the impregnation of RuCl₃ on pre-calcined ZrO₂ followed by reduction (catalyst D). The Ru particles of 3–4 nm size are uniformly dispersed in this catalyst. This catalyst is highly selective (>99.9%), highly active (>99.9%) and recyclable. The presence of small ruthenium particles together with a higher concentration of acidic sites is responsible for the superior quality of this catalyst.

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