Exploring the ruthenium catalysed synthesis of γ-valerolactone in alcohols and utilisation of mild solvent-free reaction conditions

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Materials and Analysis

Methanol, ethanol, 1-butanol and 1,4 dioxane, were purchased from Sigma Aldrich in LC-MS grade and were utilised without further purification. Solvent-water mixtures were obtained by diluting 1 mL of deionized water with 9 mL of a given alcohol. The solid catalyst, 5 wt% Ru/C was obtained from Sigma Aldrich and was used as received, while the catalysts Ru/SiO₂ and Ru/TiO₂ (both 5 wt% Ru) were prepared using the incipient wetness method, followed by reduction using a carbotube furnace. The starting materials ruthenium (III) acetyl acetonate, SiO₂ (Cab-O-sil™) were purchased from Sigma Aldrich and Ru/Al₂O₃ (5 wt% Ru) was obtained from Johnson Matthey with all samples used as received. TiO₂ produced by Tronox was purchased from Kerr-McGee Pigments, and the surface area of this material was 6m²/g. Furthermore, X-Ray powder diffraction established that this material consists exclusively of the Rutile phase. TiO₂ obtained from Degussa was of the P25 form, a mixture of both the Anatase and Rutile phases, with a surface area established as being 48m²/g.

Routine ¹H NMR spectra were recorded on aBruker Avance 400 MHz spectrometer, with chemical shifts being referenced to residual protio impurities in the deuterated solvent. Solvent proton shifts (ppm): 7.26 (CDCl₃). Quantification using ¹H NMR was enabled by mixing CDCl₃ with a known mass of mesitylene or cyclooctane, with the singlet presented by the CH₃ or CH₂ moieties of these compound utilised as internal standards. The assignment of ¹H NMR spectra was assisted by the analysis of discrete samples of levulinic acid, γ-valerolactone and methyl-levulinate alongside GC analysis performed using a Sichromat 3 gas chromatograph equipped with a Restek Rtx-1-Pona (100 %) dimethylpolysiloxane capillary column (50m × 250µm × 0.5µm).

General Procedure for Catalyst Screening at 130 °C

All experiments were conducted in a batch reactor with a magnetic stirrer used to provide agitation. LA (500 mg, 4.31 mmol), a given solvent (10 mL) alongside a 5 wt% Ru catalyst (25 mg, 0.012 mmols) were mixed in a glass insert specifically tailored to a Schlesinger B18rb250-01 (50 mL) carousel reactor. This batch reactor was retrofitted in-house to enable measurement of the reaction temperature. After placing the insert into the reactor, the vessel was sealed and placed under an atmosphere of H₂ (12 bar) and was allowed to stir at 25 °C. After 2.6 h, a sample of the reaction mixture was added a catalyst (typically 5 wt% Ru/C, 100 mg, 0.05 mmols), and the mixture was stirred until homogeneous using a magnetic stirrer bar. Next, the vessel was placed under a pressure of H₂ (12 bar) and pressure tested. The vessel was heated to 130 °C for 160 minutes with mixing again provided by the magnetic stirrer bar. After this period, the vessel was cooled, vented and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the reaction solvent was evaporated without further purification. Solvent-water mixtures were obtained by diluting 1 mL of deionized water with 9 mL of a given alcohol. The reaction solution was then charged to an autoclave and stirred at 25 °C for 24 h. After 2.6 h, a sample of the reaction mixture was collected, with samples also obtained at 24, 40, 50 h. These samples were analysed using ¹H NMR spectroscopy. Notably, consumption of H₂ in the hydrogenation reaction resulted in a drastic decrease in the vessel’s pressure. Thus, to maintain a pressure of 12 bar additional H₂ was added after 24 h.

The above procedure was repeated in two separate experiments employing ethanol and 1-butanol as the reaction solvents, but with an increased pressure of 20 bars. For 1-butanol a 100 % conversion was obtained with selectivity for γVI of 98.3 %. In contrast for methanol a 96.4 % conversion and 81.4 % selectivity was achieved.

General Procedure for Catalyst Screening at 25 °C without Additional Solvent

Solid LA (2.0 g, 17.2 mmol) was placed inside the glass insert and warmed to 35 °C to induce melting. To this liquid sample was added a catalyst (typically 5 wt% Ru/C, 100 mg, 0.05 mmols), and the mixture was stirred until homogeneous using a magnetic stirrer bar. Next, the insert was placed inside a carousel reactor retrofitted to enable auto sampling. The vessel was sealed and placed under an atmosphere of H₂ (12 bar) and was allowed to stir at 25 °C. After 2.6 h, a sample of the reaction mixture was collected, with samples also obtained at 24, 50 h. These samples were analysed using ¹H NMR spectroscopy. Notably, consumption of H₂ in the hydrogenation reaction resulted in a drastic decrease in the vessel’s pressure. Thus, to maintain a pressure of 12 bar additional H₂ was added after 24 h.

The above procedure was repeated but using a lower loading of Ru/C (1 wt%, 50 mg, 0.025 mmols). No conversion of LA was observed. This procedure was also used to screen the catalytic activities of Ru/SiO₂ and Ru/Al₂O₃ with 100 mg of each catalyst utilised in each instance used to hydrogenate 2 g of LA.

Catalyst Recycling Experiments

1) A reaction solution was prepared by mixing LA (2 g, 0.017 moles) with Ru/C (100 mg, 0.049 mmols). This solution was then charged to an autoclave and stirred at 25 °C for 24 h under an atmosphere of H₂ (12 bar). Through the use of a centrifuge the catalyst was separated from the reaction mixture and washed with ethanol (3×30 ml) before being dried at 50 °C for 16 h. The reaction solution was sampled for ¹H NMR spectroscopy, allowing determination of LA conversion and selectivity. Next, the catalyst was weighed, and reused with a constant ratio of LA to catalyst maintained (See Chart S1).

2) A reaction solution was prepared by mixing LA (1 g, 0.0086 mols) with Ru/C (50 mg, 0.024 mmols), ethanol (9 mL) and H₂O (1 mL). This mixture was charged to an autoclave and stirred at 130 °C for 1 h under an atmosphere of H₂ (12 bar). Again the catalyst was separated from the reaction mixture by using a centrifuge and washed with ethanol before being dried. The volatile components of the reaction mixture were removed in vacuo, allowing analysis of the reaction mixture. The recovered catalyst was washed with ethanol (3×30 ml) before being dried at 50 °C for 16 h. The catalytic solution was reused with a constant ratio of LA to catalyst maintained (See Chart S1).
Procedure for the hydrogenation of H$_2$O/LA and γVl/LA mixtures
To a mixture of H$_2$O (1 mL), LA (2 g, 0.0172 moles) was added Ru/C (100 mg, 0.049 mmols). This solution was charged to an autoclave and stirred at 25 °C under a pressure of H$_2$ (12 bar). After 100 h only 35.5% LA conversion was observed (see Table S1). Thus, this procedure was repeated using higher amounts of Ru/C (157 mg, 0.076 mmols) enabling higher conversions to be obtained within 50 h (see Table S1). Similarly high LA conversions were given from reaction solutions comprised of γVl (1 mL), and LA (2 g, 0.0172 moles) combined with Ru/C (157 mg, 0.076 mmols) (see Table S1).

Procedure for the hydrogenation of LA at 190 °C
LA (2 g, 0.0172 moles) was mixed with Ru/C (100 mg, 0.049 mmols). This solution was charged to an autoclave which was pressurised using H$_2$ (12 bar). Next, the autoclave was placed inside a metal heating block, preheated to 200 °C, enabling rapid heating of the reaction mixture, which reached a temperature of 190 °C after 20 minutes. The reaction vessel was heated for an additional 20 minutes before being cooled and vented. Analysis of the reaction mixture using $^1$H NMR spectroscopy demonstrated that complete conversion of LA to γVl occurred.

Chart S1 Contrasting the recyclability of Ru/C using different reaction conditions

Table S1 Hydrogenation of H$_2$O/LA and γVl/LA mixtures at 25 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Reaction Composition</th>
<th>Reaction time (h)</th>
<th>% Conv. LA</th>
<th>% Select. for γVl</th>
<th>% Yield of γVl</th>
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<tbody>
<tr>
<td>1</td>
<td>Ru/C (100 mg)</td>
<td>H$_2$O (1 mL)/LA (2 g)</td>
<td>100</td>
<td>35.6</td>
<td>64.3</td>
<td>22.8</td>
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<td>2</td>
<td>Ru/C (157 mg)</td>
<td>H$_2$O (1 mL)/LA (2 g)</td>
<td>48</td>
<td>95.8</td>
<td>95.4</td>
<td>91.3</td>
</tr>
<tr>
<td>3</td>
<td>Ru/C (157 mg)</td>
<td>γVl (1 mL)/LA (2 g)</td>
<td>48</td>
<td>99.6</td>
<td>89.1</td>
<td>88.7</td>
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