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/SiO_2 and Ru/TiO_2 (both 5 wt% Ru) were prepared using the incipient wetness method, followed by reduction using a carbolite tube furnace. The starting materials ruthenium (III) acetyl acetonate, SiO_2 (Cab-O-sil®) were purchased from Sigma Aldrich and Ru/Al_2O_3 (5 wt% Ru) was obtained from Johnson Matthey with all samples used as received. TiO_2 produced by Tronox was purchased from Kerr-McGee Pigments, and the surface area of this material was $6m^2/g$. Furthermore, X-Ray powder diffraction established that this material consists exclusively of the Rutile phase. TiO_2 obtained from Degussa was of the P25 form, a mixture of both the Anatase and Rutile phases, with a surface area established as being $48m^2/g$.[1]

Routine ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, with chemical shifts being referenced to residual *protio* impurities in the deuterated solvent. Solvent proton shifts (ppm): 7.26 ($CDCl_3$). Quantification using ^1H NMR was enabled by mixing $CDCl_3$ with a known mass of mesitylene or cyclooctane, with the singlet presented by the CH_3 or CH_2 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 Sichlomat 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 flushed with H_2. Next, the vessel was placed under a pressure of H_2 (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 using a rotator evaporator. Finally, the mixture was analysed using ^1H NMR spectroscopy, with quantification enabled by addition of mesitylene or cyclooctane standards.

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 γVl 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 H_2 (12 bar) and was allowed to stir at 25 °C. After 2.6 h, a sample of the reaction was collected, with samples also obtained at 24, 40, 50 h. These samples were analysed using ^1H NMR spectroscopy. Notably, consumption of H_2 in the hydrogenation reaction resulted in a drastic decrease in the vessel's pressure. Thus, to maintain a pressure of 12 bar additional H_2 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/SiO_2 and Ru/Al_2O_3 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 H_2 (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 H_2O (1 mL). This mixture was charged to an autoclave and stirred at 130 °C for 1 h under an atmosphere of H_2 (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 catalyst was reused with a constant ratio of LA to catalyst maintained (See Chart S1).

Procedure for the hydrogenation of H_2O/LA and γVl/LA mixtures

To a mixture of H_2O (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

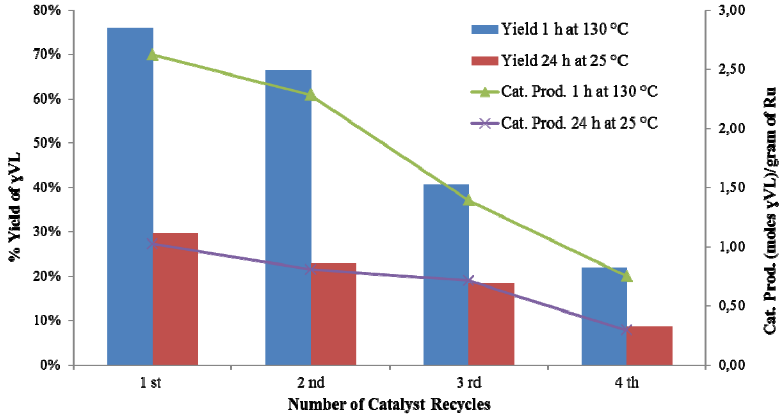

Table S1 Hydrogenation of H_2O/LA and γVl/LA mixtures at 25 °C

Entry	Catalyst	Reaction Composition	Reaction time (h)	% Conver. LA	% Select. for γVl	% Yield of γVl
1	Ru/C (100 mg)	H_2O (1 mL)/LA (2 g)	100	35.6	64.3	22.8
2	Ru/C (157 mg)	H_2O (1 mL)/LA (2 g)	48	95.8	95.4	91.3
3	Ru/C (157 mg)	γVl (1 mL)/LA (2 g)	48	99.6	89.1	88.7

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[1] T. Ohno, K. Sarukawa, M. Matsumura, *J. Phys. Chem. B*, **2001**, 105, 2417-2420.