Supporting information for

Energy efficient continuous production of γ-valerolactone by bifunctional metal / acid catalysis in one-pot

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General information

All reaction and manipulations were performed under nitrogen by using standard Schlenk techniques, unless otherwise stated. DOWEX 50WX2 – 100 (50–100 mesh bead size) and DOWEX 50WX2 – 400 (200–400 mesh bead size) strong cation-exchange resins (H^+ form, 2% cross-linked, gel-type, 4.8 meq g^{-1} exchange capacity) were obtained from Aldrich. The commercial resins were washed prior of use to remove all incidental impurities. Thus, 20 g of cation exchange resin ($R\text{-}SO_3^-H^+$) were washed with refluxing deionised water for 2 h and with refluxing methanol for 1 h using a Soxhlet apparatus. After cooling down to room temperature, the resin was washed sequentially with dichloromethane (3 x 100 ml), methanol (3 x 100 ml) and diethyl ether (3 x 100 ml). Then, it was dried in a stream of nitrogen and stored under nitrogen. The lithiated resin ($R\text{-}SO_3^-Li^+$) was prepared by adding 5 g of the purified $R\text{-}SO_3^-H^+$ resin to a 1 M solution of lithium hydroxide (150 ml) in air atmosphere. The mixture was stirred at 150 rpm at room temperature for 24 h using an orbital stirrer. The resin obtained was placed in a glass filter and washed repeatedly with deionised water (5 x 100 ml) until neutral pH of the washings. Then, it was washed with methanol (3 x 100 ml) and diethyl ether (3 x 100 ml) and dried in a stream of nitrogen. The $R\text{-}SO_3^-H^+$ resin obtained as white beads was stored under nitrogen. Levulinic acid, natural 99 % was obtained from Aldrich. All other reagents were commercial products and were used as received without further purifications.

ESEM (Environmental Scanning Electron Microscopy) measurements were performed on a FEI Quanta 200 microscope operating at 25 KeV accelerating voltage in the low-vacuum mode (1 torr) and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). X-ray maps were acquired on the same instrument using a 512 x 400 matrix, 100 μs dwell time and 25 KeV accelerating voltage. TEM (Transmission Electron Microscopy) analyses were performed using a M12 PHILIPS instrument at 120 KeV accelerating voltage. The sample preparation was carried out by dispersing the grinded resin into about 1 ml of ethanol and treating the solution in an ultrasonic bath for 30 min. Successively, a drop of solution was deposited onto a carbon coated Cu TEM grid and the solvent left to evaporate. Statistical nanoparticle size distribution analysis was typically carried out on 300-400 particles. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded at 400.13 and 100.613 MHz, respectively, on a Bruker Avance DRX-400 spectrometer, using a coaxial insert filled with D_2O and pulse sequences suitable for water resonance suppression. Chemical shift in ppm are relative to tetramethylsilane as external reference. The metal content in the supported catalysts was determined by Atomic Absorption Spectrometry (AAS) using a AANALYST200 spectrometer. Each sample (50-100 mg) was treated in a microwave-heated digestion bomb (Milestone, MLS-200, 20 min.@ 220 °C) with concentrated HNO_3 (1.5 mL), 98% H_2SO_4 (2 mL), and 0.5 mL of H_2O_2 30%. After filtration, the solutions were analysed. The content of metal leached in the solutions recovered after catalysis was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument. The detection limit for Ru was 0.006 ppm. The solutions were analysed directly after 1:5 dilution in 0.1 M hydrochloric acid. GC-analyses were performed on a Shimadzu GC 2010 gas chromatograph equipped with flame ionization detector and a 30 m (0.25 mm ID, 0.25 µm FT) VF-WAXms fused silica capillary column. GC-MS analyses were performed on a Shimadzu QP5000 apparatus equipped with the same capillary column. HPLC analyses were performed on a UFLC-Shimadzu apparatus equipped with a refraction index detector (RID) and a Grace Alltech

OA Organic Acida column (300 mm x 6.5 mm), using 0.01 N sulphuric acid as eluent (flow 0.8 mL min^{-1} at 35ºC). Reactions under batch conditions were carried out using a H_2 generator Parker H2PEM-260, a stainless steel autoclave (25 mL internal volume) constructed at ICCOM-CNR (Firenze, Italy) and equipped with a magnetic stirrer, a Teflon ® inset and a pressure controller. Reactions under continuous flow were carried out using a reactor system constructed at Istituto di Chimica dei Composti OrganoMetallici, Sesto Fiorentino (Italy). The system was designed to allow for a simultaneous flow of substrate solution and hydrogen gas (up to 40 bar pressure). The reactor was completely inert, as all wet parts were made of PEEK, PFA or PFTE. The flow of the substrate solution was regulated by an Alltech® model 426 HPLC pump in PEEK. A constant flow of hydrogen gas was adjusted, and its pressure monitored, by a BRONKHORST flow controller and pressure meter, respectively. The concurrent flows of gas and liquid were driven through a T-shaped PEEK mixer equipped with a 2μm filter to ensure efficient gas dispersion. The mixed hydrogen-substrate solution stream was introduced in the reactor through a 6-port Rheodyne switching valve in PEEK. The system was equipped with a temperature controller accurate to ± 1.0 °C. The solid catalyst was packed into a commercial Omnifit Labware Glass Column (3.0 i.d. x 25 length mm) resistant up to 1200 psi and equipped with 0.2 µm PE frits at the entrance of the catalyst bed to ensure an optimum flow distribution. An upflow liquid arrangement was adopted. The hydrogen pressure within the reactor was regulated by a back-pressure valve. At the outlet of the reactor, the product solution was collected for GC analysis and the excess amount of the hydrogen gas released to the atmospheric pressure.

Synthesis of the catalyst

In a typical procedure, 0.600 g of dry cation-exchange resin ($R-SO_3^-H^+$ or $R-SO_3$-Li+) were added into a flask containing a degassed solution of ruthenium (III) chloride hydrate (18.1 mg, 0.087 mmol, ratio Ru/sulfonic groups = 1/33) in deionized water (34 ml) The mixture was stirred using an orbital stirrer at 225 rpm and room temperature for 4 days until complete discolouration of the solution. The resulting brown resin was washed with deionized water and then left in ca. 30 ml of deionized water at 0 °C to be subsequently treated with about 4 ml of an aqueous solution of $NaBH_4$ (98.6 mg, 2.62 mmol). The resin became immediately greenish. The suspension was then stirred at 225 rpm and room temperature for 1h. The obtained resin was transferred into a glass filter via a Teflon tube under nitrogen and washed with deionized water (5 x 50 ml), methanol (3 x 50 ml) and diethyl ether (3 x 50 ml), and was dried in a stream of nitrogen overnight. The product, obtained as black beads when dry, was stored under nitrogen in the dark. ICP-OES analysis showed the catalyst Ru@Dowex to contain an average loading of 0.87 wt% Ru, corresponding to ca. 60% ruthenium uptake.

Catalytic conversion of LA to GVL under batch conditions.

In a typical experiment, the supported catalyst precursor, either Ru@Dowex or lithiated Ru@Dowex (60 mg, ca. 0.87 wt % Ru, ca. 0.005 mmol of ruthenium), was placed under nitrogen into a metal-free autoclave. A degassed solution of levulinic acid (2.15 mmol) in deionized water (5 ml) was transferred under nitrogen via a Teflon tube into the autoclave. Nitrogen was replaced by hydrogen with three cycles pressurization/depressurization. The autoclave was finally charged with the desired pressure of hydrogen, stirred at 150 rpm using a mechanical stirrer and heated up to the selected temperature using an oil bath. After the desired time, the reactor was cooled down and depressurized and the solution was completely removed under a stream of hydrogen using a gas-tight syringe. A sample of this solution was used for GC and HPLC (product yield), GC-MS and NMR (product identification) and ICP-OES analysis (metal leaching). For recycling experiments, a fresh solution of levulinic acid was then transferred under hydrogen via a gas-tight syringe into the reactor containing the recovered supported catalyst. The autoclave was again charged with hydrogen, stirred at 150 rpm and heated up, after the desired time, the mixture was treated as described above. The same recycling procedure was used in the subsequent hydrogenation cycles. After use in catalysis, the solid catalyst was washed with deionized water (3 x 10 ml), methanol (3 x 10 ml) and diethyl ether (3 x 10 ml), dried in a stream of nitrogen and stored under nitrogen for later characterization.The reaction products were unequivocally identified by the GC retention times, HPLC analysis, mass and $^{13}C\{^1H\}$ NMR spectra of those of authentic specimens. The only by-product detected was γ-hydroxyvaleric acid. ESEM experiments showed the catalyst beads were not damaged by use in catalysis. Catalyst immobilized onto larger size beads was preferably used under batch set-ups due to the easier handling.

Catalytic conversion of LA to GVL under continuous flow conditions.

Reactions under continuous flow were carried out using the flow reactor system described above and sketched in Figure S1.

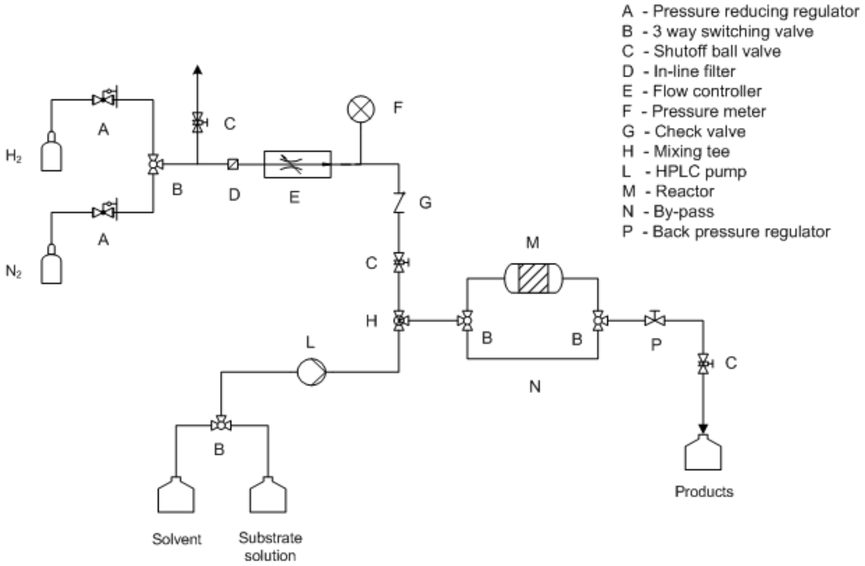

Fig. S1 Schematic view of the continuous-flow, high-pressure reactor system used.

In a typical experiment, the dry catalyst (40 mg of Ru@Dowex-100 or 20 mg of Ru@Dowex-400) was packed into the commercial tubular glass mini-reactor (3 mm diameter x 25 mm length). The system was degassed with N_2 at 3 mL min^{-1} flow rate for 30 minutes, then the N_2 flow was stopped and a degassed solution of levulinic acid in water was allowed to flow through the catalytic bed at a constant 0.15 mL min^{-1} rate until the catalyst was completely wet. After 20-30 minutes and together with the substrate solution, molecular hydrogen was allow to flow through the catalyst at a constant H_2 flow of 1 mL min^{-1} at room temperature. After 15 minutes, the column was introduced into the oven at 70ºC. Attainment of steady state conditions, ca. 1 h, was then taken as the reaction start time. The product solution was periodically analysed for conversion by GC and HPLC, while aliquots were continuously sampled for subsequent Ru leaching analysis by ICP-OES. At the outlet of the reactor, the product solution was collected for GC analysis and the excess amount of the hydrogen gas released to the atmospheric pressure. The reaction was monitored for 8 h time-on-stream, followed by overnight switch off while maintaining an H_2 atmosphere in the reactor, and restart the day after for an analogous period. Typical overall reaction duration was 5 days. The reaction products were unequivocally identified by the GC retention times, HPLC analysis, mass and $^{13}C\{^1H\}$ NMR spectra of those of authentic specimens.

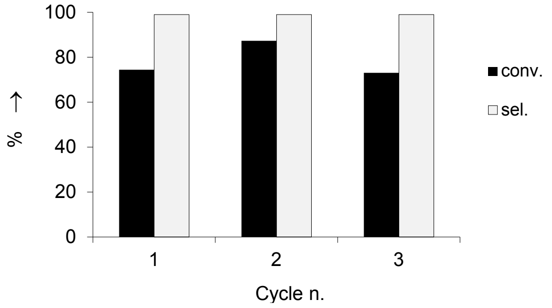

Fig. S2 Recycle of Ru@DOWEX in the batch conversion of LA to GVL. Reaction conditions: LA 0.43 M in water, Ru@DOWEX (particle size 276 μm) 60 mg (0.87 % w/w Ru), substrate / catalyst molar ratio 210, temperature 70 °C, H_2 5 bar, 2 h. Data from GC analysis.

Table S1. Representative experiments for the catalytic conversion of LA to GVL by Ru@DOWEX under continuous flow conditions.[a]

Entry	Beads ϕ (μm)	Reaction conditions					Conv.[d] (%)	TOF_{total} [e] (h^{-1})	$TOF_{surface}$ [f] (h^{-1})	STY ($kg\ l^{-1}\ h^{-1}$)
		Solution [b]		H_2 [c]		H_2/sub. ratio				
		Flow rate ($mL\ min^{-1}$)	τ (s)	Flow rate ($mL\ min^{-1}$)	Pressure (bar)					
1	276	0.15	70	1.0	5.0	58	95 ± 2.7	49.5	130.3	0.10
2	276	0.10	106	0.7	4.8	58	100.0	n.d [g]	n.d.	n.d.
3	276	0.15	70	1.5	5.3	95	100.0	n.d [g]	n.d.	n.d.
4 [h]	276	0.05	211	1.5	5.0	54	89 ± 2.0	77.7	204.5	0.16
5	84 [i]	0.15	70	1.0	6.0	70	100.0	n.d [g]	n.d.	n.d.

[a] Reaction conditions: 70 °C, Ru@DOWEX 40.1 mg (0.87 % w/w Ru), reactor volume 176 μL, LA 0.02 M solution in water. [b] τ = residence time. [c] Pressure measured at the reactor inlet. [d] Data from GC analysis. Start time: attainment of steady state conditions, ca. 1h. Average value over 10 h time-on-stream. [e] Calculated from conversion average value. [f] TOF corrected for surface-exposed Rh atoms, as inferred by TEM. [g] Not determined due to overhydrogenation conditions. [h] LA 0.10 M solution in water. [i] Ru@DOWEX 0.85 % w/w Ru.

Table S2. Representative results for the continuous conversion of LA to GVL by Ru@DOWEX using 84 μm size beads catalyst under optimized conditions.[a]

Entry	Reaction conditions					Conv.[d] (%)	TOF_{total} [e] (h^{-1})	$TOF_{surface}$ [f] (h^{-1})	STY ($kg\ l^{-1}\ h^{-1}$)
	Solution [b]		H_2 [c]		H_2/sub. ratio				
	Flow rate ($mL\ min^{-1}$)	τ (s)	Flow rate ($mL\ min^{-1}$)	Pressure (bar)					
1	0.15	70	0.50	6.8	40	> 99.9	n.d [g]	n.d.	n.d.
2	0.17	62	0.35	7.0	27	97 ± 1.2	117.4	309.0	0.12

[a] Reaction conditions: 70 °C, LA 0.02 M solution in water, Ru@DOWEX 20.0 mg (0.85 % w/w Ru), reactor volume 176 μL. [b] τ = residence time. [c] Pressure measured at the reactor inlet (bar). [d] Data from GC analysis. Start time: attainment of steady state conditions, ca. 1h. Average value over 10 h time-on-stream. [e] Calculated from conversion average value. [f] TOF corrected for surface-exposed Ru atoms, as inferred by TEM. [g] Not determined due to overhydrogenation conditions.

Catalyst characterization before and after use under continuous flow reaction conditions* (experimental*: bead size 276 μm, temperature 70 °C, 35 h time-on-stream, LA 0.02 M in water 0.15 mL min^{-1}, H_2 1.00 mL min^{-1}).

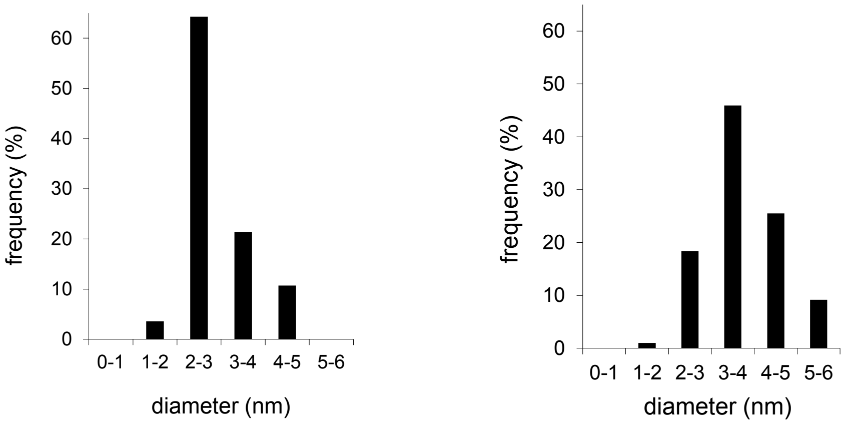

Fig. S3 RuNPs size distribution in Ru@DOWEX before (left, diameter 2.8 ± 0.8 nm) and after (right, diameter 3.7 ± 0.9 nm) use in catalysis, as determined by TEM analysis.

ICP-OES: 0.87 % ± 0.01 (w/w) Ru before, 0.86 % ± 0.03 (w/w) Ru after.