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

Carmen Moreno-Marrodan and Pierluigi Barbaro*

A bifunctional heterogeneous catalyst based on sulfonated cation exchange resin and embedded Ru nanoparticles shows complete conversion and selectivity at low temperatures and H_2 pressure in the direct, one-pot conversion of levulinic acid to GVL under continuous flow conditions, with excellent durability and no need for additives.

 γ -Valerolactone (GVL) is a safe, renewable material widely used as a food additive, a solvent, an intermediate in fine chemicals synthesis¹ and as a progenitor of a platform for liquid fuels, commonly referred to as "valeric biofuels"² that can be obtained from the degradation products of plant biomass, particularly levulinic acid (LA).³ The conversion of LA into GVL was extensively studied and several homogeneous⁴ and heterogeneous catalysts^{5,6} were proposed. The process involves a twostep reaction sequence: a metal-catalysed hydrogenation and an acid-catalysed lactonization (Scheme 1).^{2c,6a,d} Although the heterogeneous catalysts would be clearly preferred by industry,⁷ they usually require drastic reaction conditions, organic solvents and/or the presence of strong soluble acids.⁸ Bifunctional solid catalysts enabling both steps in a single reactor unit may provide significant benefits in terms of efficiency, safety and waste emission,9 whereby the achievement of high selectivity requires the combination of well-defined supported acid and metal sites acting under the same reaction con-



Scheme 1 Proposed mechanism for the selective catalytic conversion of levulinic acid to γ -valerolactone.

ditions.¹⁰ Compared to conventional batch setups, additional advantages in terms of space-to-time yield productivity, purification, environmental impact, automation and energy consumption may be brought about by the engineering of continuous flow reactor systems.¹¹ However, efficient flow processes for the continuous conversion of LA to GVL at low energy expenses have not been implemented yet.¹²

Herein we describe a novel bifunctional metal/acid heterogeneous catalyst for use in the direct conversion of LA to GVL in the liquid phase under continuous flow in one pot. The catalytic system consists of ruthenium nanoparticles (RuNP) immobilized onto a commercial, sulfonic acid ion-exchange resin (Fig. 1). Benefits of ion-exchange polymers as supports for MNP-based catalysts are multiple, including low cost, a large choice of available materials, easy handling, satisfactory chemical, mechanical and thermal resistance, electrostatic and steric stabilization of MNP.¹³

Thus, a DOWEX 50WX2-100 gel-type resin was metallated by treatment with an aqueous solution of RuCl₃, followed by conventional reduction with NaBH₄, to give brownish beads (Ru@DOWEX) with a typical bulk 0.87% (w/w) metal loading (ICP-OES), corresponding to *ca.* 60% ruthenium uptake, and embedded RuNP of 2.8 \pm 0.8 nm diameter (TEM) (Fig. 1).¹⁴ ESEM experiments showed that the beads were not damaged by metal incorporation, while EDS analysis indicated an eggshell-type metal distribution within the solid support, as shown in Fig. 2 where sulphur and Ru maps are reported for comparison.^{15,16}



Fig. 1 Sketch of the microstructure (left), representative TEM image (center) and RuNPs size distribution (right) of Ru@DOWEX catalyst.

Istituto di Chimica dei Composti Organo Metallici (ICCOM), Consiglio Nazionale delle Ricerche (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy. E-mail: pierluigi.barbaro@iccom.cnr.it

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Fig. 2 ESEM image (left, backscattered electrons) and EDS sulphur (center, S K α 1) and ruthenium (right, Ru L α 1) maps of a Ru@DOWEX bead section (25 keV, 650 magnifications).

The as prepared material was preliminary tested in the onepot, catalytic hydrogenation reaction of concentrated LA in neat water, under batch conditions and various temperatures and H₂ pressures. Representative results are reported in Table 1 in terms of conversion and productivity, both turnover frequency (TOF) and space-to-time yield (STY).¹⁷ The catalyst showed to be active under very mild conditions ($T \ge 50$ °C, H₂ ≥ 5 bar; Table 1, entries 2–4) with moderate and poor efficiency dependence on temperature and pressure, respectively. In the benchmark experiment at 70 °C and 5 bar H₂ (Table 1, entry 2), 79.5% conversion was achieved after 4 h, corresponding to 82.7 h⁻¹ TOF and 0.0017 kg l⁻¹ h⁻¹ STY,

Table 1 Catalytic conversion of LA to GVL by Ru@DOWEX under batch conditions a

Entry	$T(^{\circ}C)$	H ₂ (bar)	Time (h)	Conv. ^b (%)	$\begin{array}{c} {\rm TOF}^c \\ \left({{{\rm{h}}^{ - 1}}} \right) \end{array}$	${ {STY} \atop {({\rm kg} \ {\rm L}^{-1} \ {\rm h}^{-1})} } }$
1	70	5	7.0	99.8	59.4	0.0012
2	70	5	4.0	79.5	82.7	0.0017
3	50	5	4.0	29.3	30.5	0.0006
4	70	10	4.0	98.3	102.3	0.0021
5^d	70	5	4.0	16.2	16.9	0.0002

 a Reaction conditions: LA 0.43 M in water, Ru@DOWEX (particle size 276 $\mu m)$ 60 mg (0.87% w/w Ru), substrate/catalyst molar ratio 420, reactor volume 25 mL. b Data from GC analysis. c Calculated on bulk Ru loading and overall conversion. d Using the lithiated Ru@DOWEX catalyst.

without use of any additive. Full conversion could be achieved after 7 h (Table 1, entry 1). Selectivity to GVL was >99% in any case (GC-Ms, NMR, HPLC). The catalyst reuse was possible showing >98% activity retention over three consecutive runs under benchmark conditions.^{18,19} Ru leaching in solution was negligible (ICP-OES), nor catalytic activity was shown by the recovered solution, thus indicating that the metal is firmly anchored on the support under the conditions of catalysis.²⁰ In order to ascertain the role of the solid acid catalyst, experiments were carried out using the corresponding non-acidic support in which all mobile protons were substituted for lithium ions.²¹ A conversion of 16.2% was obtained in that case (Table 1, entry 5 vs. entry 2), demonstrating the positive contribution of the acidic resin to the catalyst activity. A similar effect was previously reported using a physical mixture of 5% Ru/C and Amberlyst-type polymer cocatalysts.^{22,23}

Prompted by the above favourable results, we decided to explore the catalytic hydrogenation of LA by Ru@DOWEX under continuous flow conditions. To this purpose, the solid catalyst was packed into a commercial glass column resistant up to 1200 psi pressure, and connected to a home-made reactor system allowing for a concurrent flow of substrate solution and H₂ gas.^{18,24} Reaction conditions similar to those of batch operations were adopted. Representative results are reported in Table 2. The catalyst was tested under a variety of flow rates showing >99% selectivity to GVL at conversions higher than 90% (Table 2, entry 1).²⁵ Conversion could be easily adjusted to 100%, with no selectivity drop, either by decreasing the solution flow rate (i.e. by increasing the residence time, Table 2, entry 2) or by increasing the hydrogen flow rate (i.e. by increasing the H2/substrate molar ratio, Table 2, entry 3), while keeping constant the other experimental parameters.¹⁸ In no case ruthenium leached in solution was above the detection limit of ICP-OES. Catalytic reactions under fixed flow conditions were typically monitored for 8 h time-on-stream, followed by overnight switch off (due to safety reasons), and restart the day after for an analogous period. No significant decay of conversion nor selectivity was observed over 4 days under these conditions (Fig. 3).²⁶ Based

Table 2 Representative experiments for the catalytic conversion of LA to GVL by Ru@DOWEX under continuous flow conditions^a

		Reactio	on conditions						
			Solution ^b		H ₂ ^c				
Entry	Beads ϕ (µm)	$T(^{\circ}C)$	Flow rate (mL min ^{-1})	τ (s)	Flow rate (mL min ^{-1})	Pressure (bar)	$\operatorname{Conv.}^{d}(\%)$	$\operatorname{TOF}^{e}\left(h^{-1}\right)$	$STY \left(kg \; l^{-1} \; h^{-1} \right)$
1	276	70	0.15	70	1.0	5.0	95 ± 2.7	49.5	0.10
2	276	70	0.10	106	0.7	4.8	100.0	$n.d.^{f}$	n.d.
3	276	70	0.15	70	1.5	5.3	100.0	$n.d.^{f}$	n.d.
4^g	276	70	0.05	211	1.5	5.0	89 ± 2.0	77.7	0.16
5	84^h	70	0.15	70	1.0	6.0	100.0	$n.d.^{f}$	n.d.
6	$84^{h,i}$	70	0.17	62	0.35	7.0	97 ± 1.2	117.4	0.12

^{*a*} Reaction conditions: 70 °C, Ru@DOWEX 40.1 mg (0.87% w/w Ru), reactor volume 176 μ L, LA 0.02 M in water. ^{*b*} τ = residence time. ^{*c*} Pressure at the reactor inlet. ^{*d*} Data from GC analysis. Start time: attainment of steady state conditions, *ca.* 1 h. Average value over 10 h time-on-stream. Selectivity to GVL >99%. ^{*e*} Calculated from conversion average value. ^{*f*} Not determined due to overhydrogenation conditions. ^{*g*} LA 0.10 M in water. ^{*h*} Ru@DOWEX 0.85% w/w Ru. ^{*i*} Ru@DOWEX 20.0 mg.



Fig. 3 Continuous flow conversion of LA to GVL over Ru@DOWEX catalyst. Reaction conditions: LA 0.02 M in water 0.15 mL min⁻¹, H₂ 1.00 mL min⁻¹, temperature 70 °C, Ru@DOWEX 40.1 mg (0.87% w/w Ru), particle size 276 μ m. Line breaks represent overnight switch-offs.

on the pretty nice constant activity of the catalyst, efficiency values comparable with those of batch operations in terms of TOF and 10^2 times higher in terms of STY (Table 2, entry 1 *vs*. Table 1, entry 1) were estimated at similar conversion. Viability to higher LA concentrations was also tested under continuous flow, showing analogous catalyst long term resistance at comparable conversion levels (Table 2, entry 4).

Finally, since it is known that gel-type ion-exchange resins are affected by internal (diffusive) mass-transfer limitations,²⁷ we investigated the efficiency of Ru@DOWEX using smaller size beads.²⁸ Thus, compared to 276 \pm 2 µm pellets, use of 84 \pm 8 µm diameter catalysts resulted in ca. 10% higher conversion under the same flow conditions (Table 2, entry 5 vs. entry 1, and Fig. 4).²⁹ Having established a reliable flow catalyst, we then turned our attention to tune the reaction parameters aimed at reducing the amount of catalyst and the excess of hydrogen used, *i.e.* the overall energy cost of the process. In the optimized experiment a productivity of $117 h^{-1}$ TOF, corresponding to 1.16 ${\rm mol}_{\rm GVL} \; {g_{Ru}}^{-1} \; h^{-1},$ was obtained using 20 mg of the catalyst and a 0.35 mL min $^{-1}$ H₂ flow rate (Table 2, entry 6).¹⁹ Compared to reported flow processes for LA to GVL conversion, productivity in terms of $mol_{GVL} g_{Ru}^{-1}$ h^{-1} was *ca.* 100% higher with respect to 5% Ru/C (a) 10 bar H₂ and 140 °C^{12d} or 5% Ru/C (a) 35 bar H₂ and 150 °C,^{12b} and ca. 1 order magnitude higher compared to 0.8% Pt/SiO₂ (a) 40 bar H₂ and 200 °C.^{12a} Productivity was ca. 10 times higher compared to 1% Pt/TiO2 (a) 40 bar H2 and 200 °C.12c

The excellent performance of Ru@DOWEX may be attributed to the favourable combination of well-defined acid and RuNP hydrogenation sites on the support, with the optimal resistance and swelling of the resin in water. Indeed, this allows for the full site accessibility to all soluble reactants



Fig. 4 Continuous flow conversion of LA to GVL over Ru@DOWEX catalyst: beads size dependence. Reaction conditions: LA 0.02 M in water 0.15 mL min⁻¹, H_2 1.00 mL min⁻¹, temperature 70 °C, Ru@DOWEX 40.1 mg.

under the conditions of catalysis,³⁰ while improving the catalyst's activity at low temperatures due to the acceleration effect by the acid sites on both the dehydration and hydrogenation steps.²² In addition, avoidance of harsh conditions allows to prevent catalyst deactivation by potential coke build up,⁹ degradation of the polymeric support,³¹ NP sintering.³² Site inhibition due to by-products accumulation is further minimized under flow conditions.

Conclusions

The present work describes an effective, *truly bifunctional*, *heterogeneous catalytic system* for the one-pot conversion of levulinic acid to γ -valerolactone *under flow conditions*, showing several striking features:

(1) it can be produced by a very simple strategy using commercial, cheap materials,

(2) it does not require high loading of expensive metal,

(3) it shows very good productivity and selectivity under unconventional *low temperatures and* H_2 *pressures*,

(4) it is usable in water, preventing the use of organic solvents,

(5) *any (acidic) additive can be avoided* due to the synergetic effect of acid and metal sites on the same support,

(6) it features excellent STY and durability under continuous flow for long times, with no need of catalyst regeneration,

(7) ruthenium leaching in solution is negligible.

The system addresses the need of a rational design of optimal catalyst for GVL synthesis, showing that a proper combination of supported bifunctional materials and reaction conditions afford stable catalysts, while satisfying both efficiency and low energy consumption criteria, thereby being able to bring considerable benefits to the sustainable production of GVL.³³

Experimental

ESEM (Environmental Scanning Electron Microscopy) experiments were performed on a FEI Quanta 200 microscope operating at 25 keV accelerating voltage and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). TEM (Transmission Electron Microscopy) analyses were performed on a M12 PHILIPS instrument at 120 keV. The metal loading in the catalysts was determined by Atomic Absorption Spectrometry using an AANALYST200 spectrometer. The amount of Ru leached in solution was obtained by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) using a Varian 720ES instrument. GC-analyses were performed on a Shimadzu GC 2010 chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm ID, 0.25 µm FT) VF-WAXms column. GC-MS analyses were performed on a Shimadzu QP5000 apparatus equipped with the same column. Reactions under batch conditions were carried out using an inert autoclave constructed at ICCOM-CNR and equipped with

a magnetic stirrer, a Teflon® inset and a pressure controller. Reactions under continuous flow were carried out using an inert reactor system constructed at ICCOM.¹⁸ The catalyst was packed into a commercial Omnifit Glass Column (3.0 i.d. \times 25 length mm).

Synthesis of the catalyst

In a typical procedure, 0.600 g of dry DOWEX 50WX2 cationexchange resin (H⁺ form, gel-type, 4.8 meq g⁻¹ exchange capacity) were added to RuCl₃ (18.1 mg, 0.087 mmol) in water (34 mL) The mixture was stirred at room temperature for 4 days. The resin was washed with deionized water and treated with an aqueous solution of NaBH₄ (98.6 mg, 2.62 mmol) at 0 °C. The suspension was then stirred at room temperature for 1 h. The resulting black resin was washed with deionized water (5 × 50 mL), methanol (3 × 50 mL) and diethyl ether (3 × 50 mL), and was dried in a stream of N₂ overnight.

Catalytic conversion of LA to GVL under batch conditions

In a typical experiment, a degassed solution of LA in water (2.15 mmol, 5 mL) was transferred under nitrogen in an autoclave containing the supported catalyst (60 mg, 0.005 mmol Ru). N_2 was then replaced with H_2 and the autoclave was charged with the desired pressure of H_2 , stirred at 150 rpm and heated to the selected temperature. After the desired time, the reactor was cooled down and depressurized. The solution was removed and analysed by GC, HPLC, GC-MS, NMR and ICP-OES. The reaction products were unequivocally identified by GC, GC-MS and NMR spectra of authentic specimens.

Catalytic conversion of LA to GVL under continuous flow conditions

In a typical experiment, a degassed solution of LA in water was flowed through the dry packed catalyst (40 mg) at a constant rate of 0.15 mL min⁻¹ until the catalyst was completely wet. H₂ was then simultaneously flowed at a constant rate of 1 mL min⁻¹ and room temperature. The column was heated at 70 °C, and attainment of steady state conditions, *ca.* 1 h, was then taken as the reaction start time. The product solution was periodically analysed by GC, HPLC and ICP-OES.

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