Continuous flow nanocatalysis: reaction pathways in the conversion of levulinic acid to valuable chemicals

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Experimental

TEM images of the various supported metal nanoparticle catalysts utilised in this work

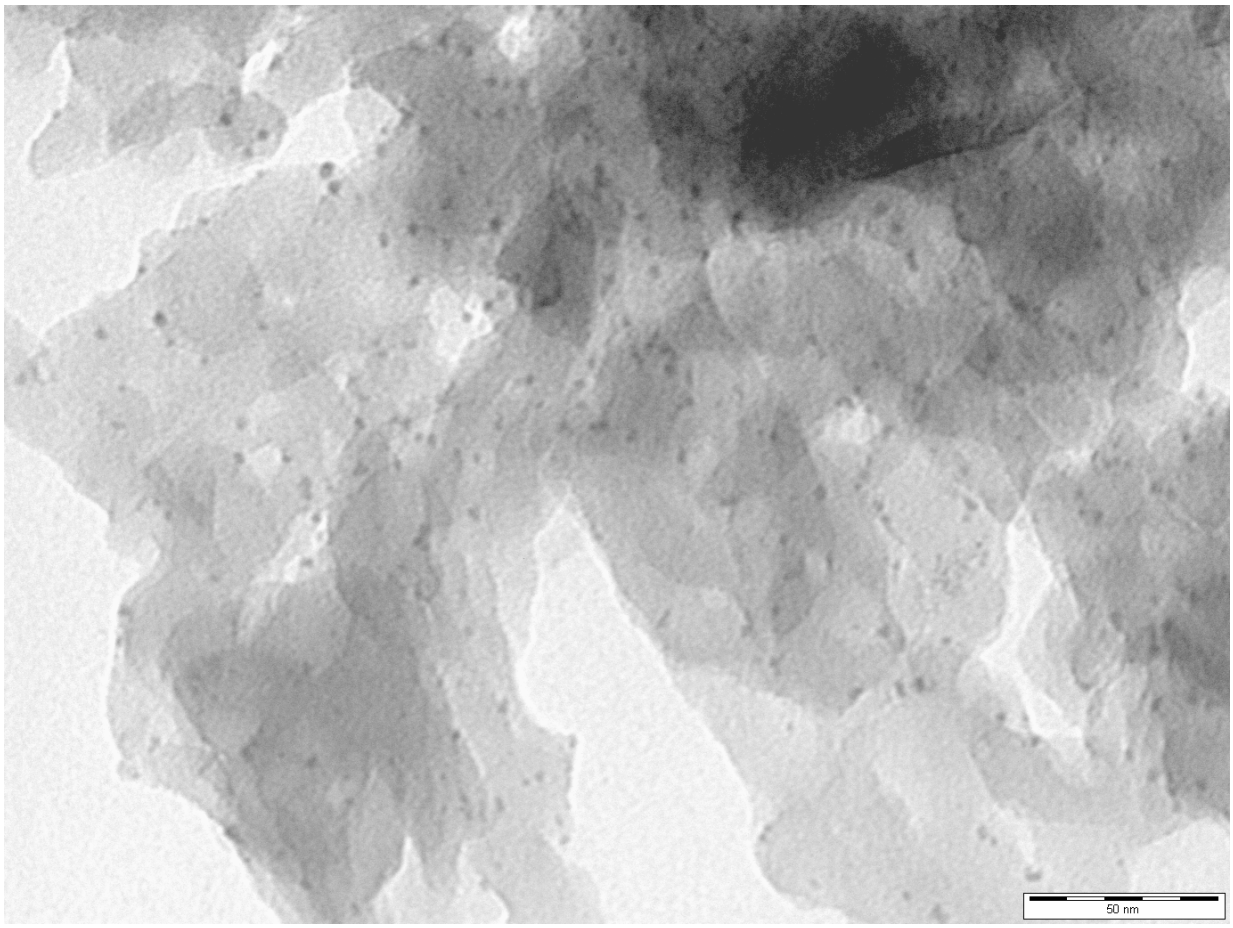

Figure 1S. 5%Ru-Starbon; scale bar 50 nm

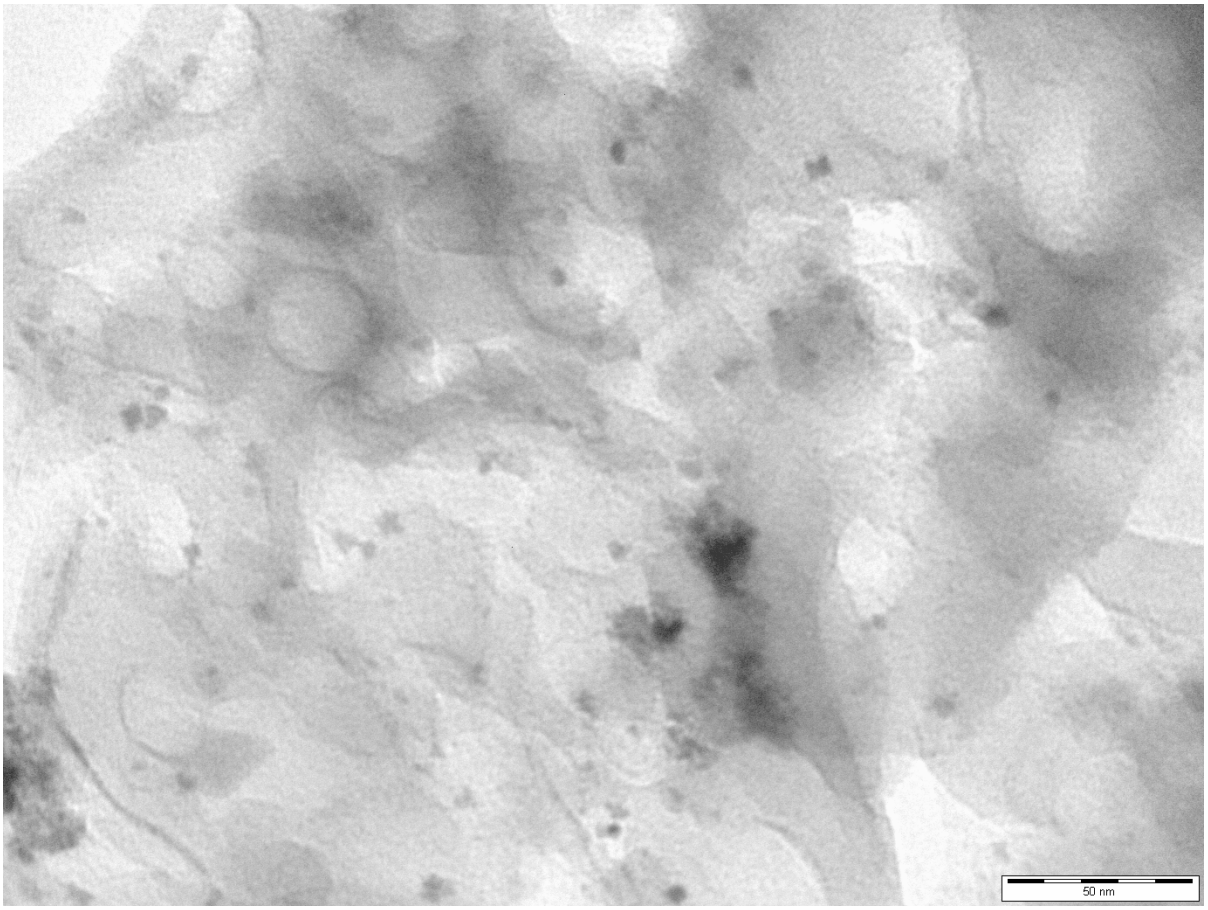

Figure 2S. 5%Rh-Starbon; scale bar 50 nm

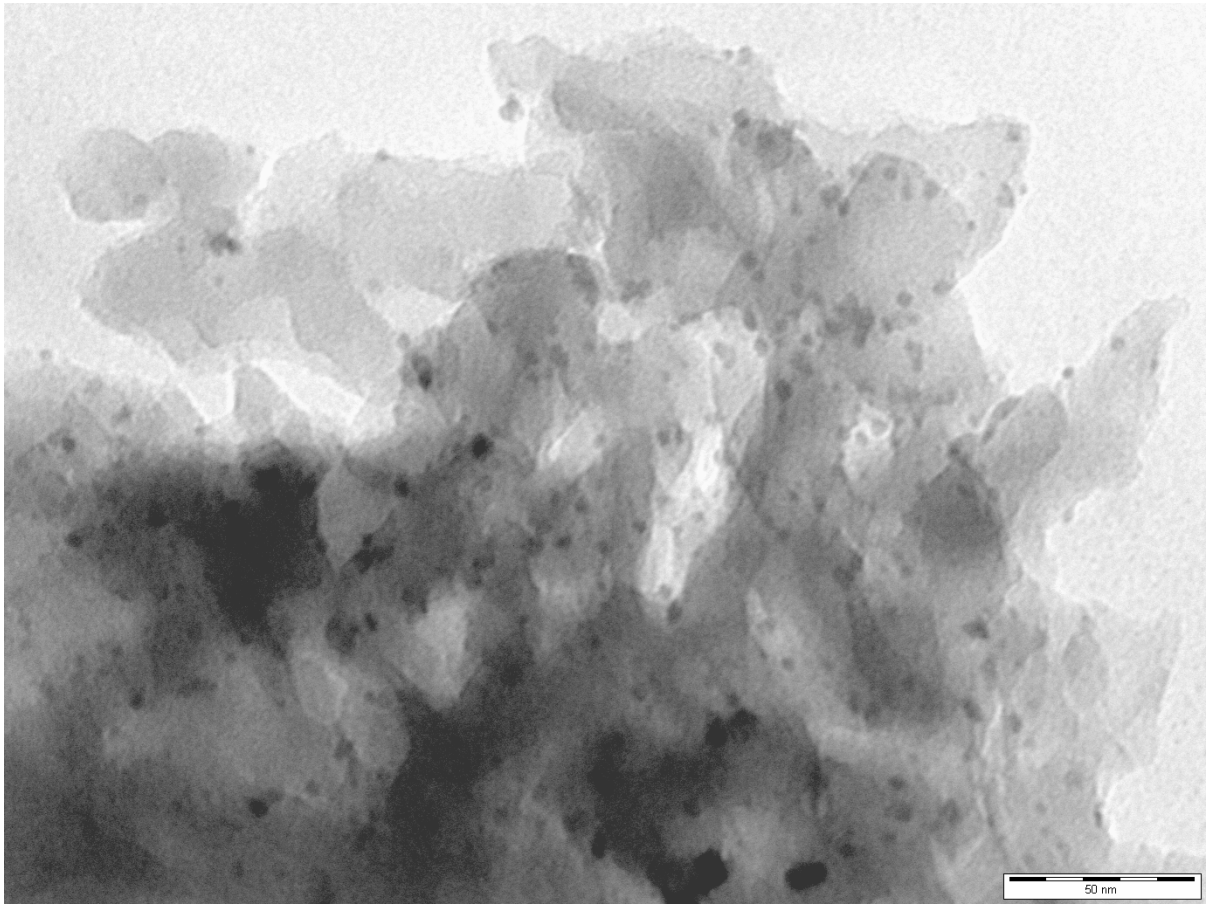

Figure 3S. 5%Pd-Starbon ; scale bar 50 nm

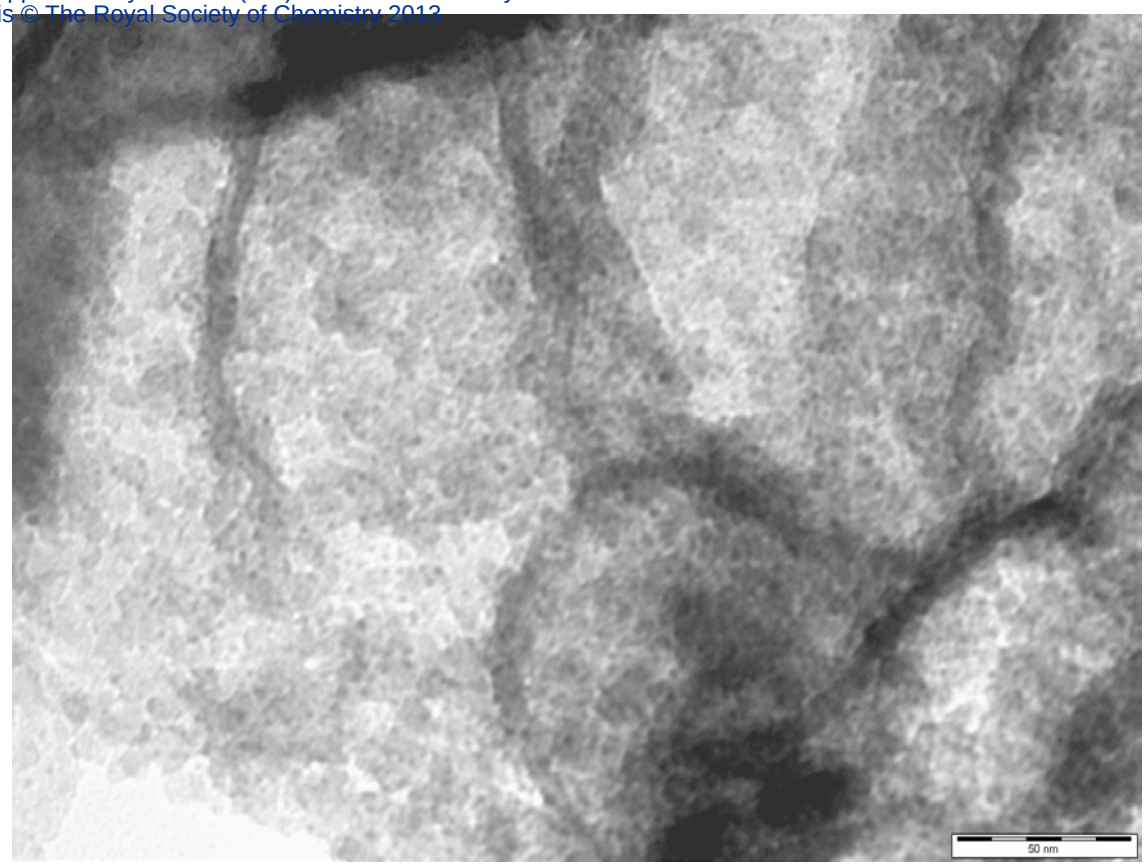

Figure 4S. 0.51%Cu-MINT ; scale bar 50 nm

Table 1S. XPS metallic bands of the different supported metal nanoparticles on Starbon®-300 materials.

Metal[a]	XPS main lines (eV)	
Pd^0	334.6 (Pd $3d_{5/2}$)	339.9 (Pd $3d_{3/2,}$)
Rh^0	306.8 (Rh $3d_{5/2}$)	311.7 (Rh $3d_{3/2,}$)
Ru^0	277.3 (Ru $3d_{5/2}$)	279.1 (Ru $3d_{3/2}$)

Figure 5S. Photograph of supported nanoparticles Ru-Starbon® material

Table 2S**.** Textural properties, metal content and nanoparticle (NP) sizes of investigated supported nanoparticle systems in this work.

Catalyst	Surface area (m^2 g^{-1})	Pore diameter (nm)	Pore volume (mL g^{-1})	Metal content (wt.%)	NP size (nm)[b]
Starbon®	293	17.2	0.53	-	-
Ru-Starbon®	240	16.9	0.49	4.11	2.7
Rh- Starbon®	256	17.0	0.52	4.32	8.5
Pd- Starbon®	201	16.7	0.49	4.87	8.9
Cu-MINT	586	<1.5	0.25	0.51	2.5

[a] Starbon®-300 materials were selected as supports due to their water tolerant properties [b] Nanoparticle sizes were worked out from TEM of the materials (as an average of particle size after counting >20 nanoparticles)

Flow experiments

Upon optimisation of reaction conditions under batch microwave experiments, optimised conditions and catalysts were translated into a continuous liquid flow process performed using a commercially available stainless-steel flow reactor-system (X-Cube, Thales Nanotechnology Inc.) equipped with changeable catalyst cartridges and an external gas-module with mass-flow controller (1-98 mL min^{-1}) interfaced with the reactor software (Scheme 1).[24] Reaction mixtures are delivered by an HPLC pump (0.1-1 mL min^{-1}) and gas-liquid mixing ratio and bubble generation (if any) can be monitored with a bubble detector followed by a gas-mixing-valve. The gas-liquid mixing ratio is automatically controlled and stabilized by the software. All reactor parameters and valves are controlled via a touchscreen-operated user-interface.

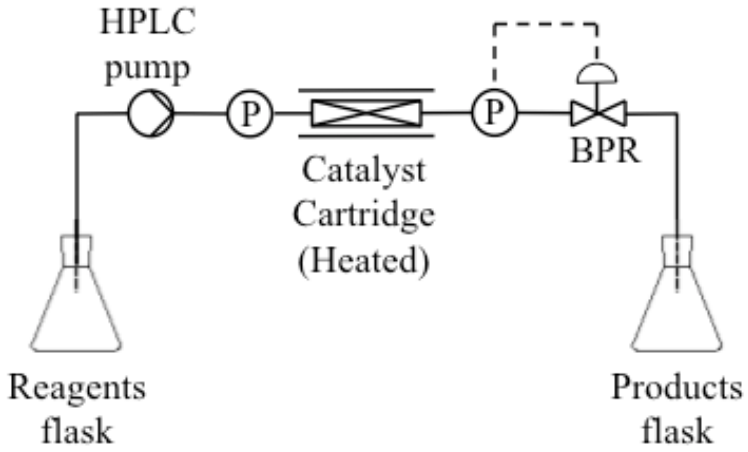

Figure 6S. Simplified representation of the flow chemistry experimental (X-cube, Thalesnano Inc.). P: Pressure sensors; BPR: Back-pressure regulator.

The installed thermostatable (20-150 °C) catalyst cartridge is 70 mm long (4 mm i.d.) and contains ~ 250 mg packed catalyst (similar quantities for commercial materials and Cu-MINT). Together with the void volume inside the cartridge of ~ 100 µL, the total internal volume of the reactor with all pipe connections is ~4 mL. A motor-controlled variable backpressure-regulator allows conducting reactions at pressures up to 100 bar to mimick the relatively high autogenous pressures (>15 bar) present in microwave batch experiments. The product mixture can either be directly collected for rapid screenings, or continuously recirculated to reach higher conversions.

In a typical flow reaction, a solution containing 0.1 mL levulinic acid in 0.3 mL FA (containing <5% water) was pumped through a thermostated fixed bed (150ºC) containing the catalyst at 0.1 mL min^{-1} flow rate. The contact time between feed and catalyst under the investigated conditions is of ca. 60 seconds and the reaction mixture takes about 40 min to go through the system. Samples were collected every10 minutes and subsequently analysed by GC and GC/MS Agilent 6890N fitted with a capillary column HP-5 (30 m × 0.32 mm × 0.25 µm) and a flame ionisation detector (FID). Products were identified and quantified in a similar way to that described before for microwave-assisted experiments.

Leaching studies under microwave irradiation

Table 3S**.** ICP-MS results on both filtrate and Cu-MINT catalyst in the microwave-assisted conversion of levulinic acid

Element	Filtrate (after reaction)	Cu-MINT	Cu_MINT (3 uses)
Cu [%]	Not detected (<0.5 ppm)	0.51	0.48
Mn [mg/kg]	-	< 0.005	-
Co [mg/kg]	-	< 0.005	-
Rh [mg/kg]	-	< 0.005	-
Pd [mg/kg]	-	0.02	-
Pt [mg/kg]	-	< 0.005	-
Au [mg/kg]	-	< 0.005	-

Microwave-assisted catalysed hydrogenation of LA

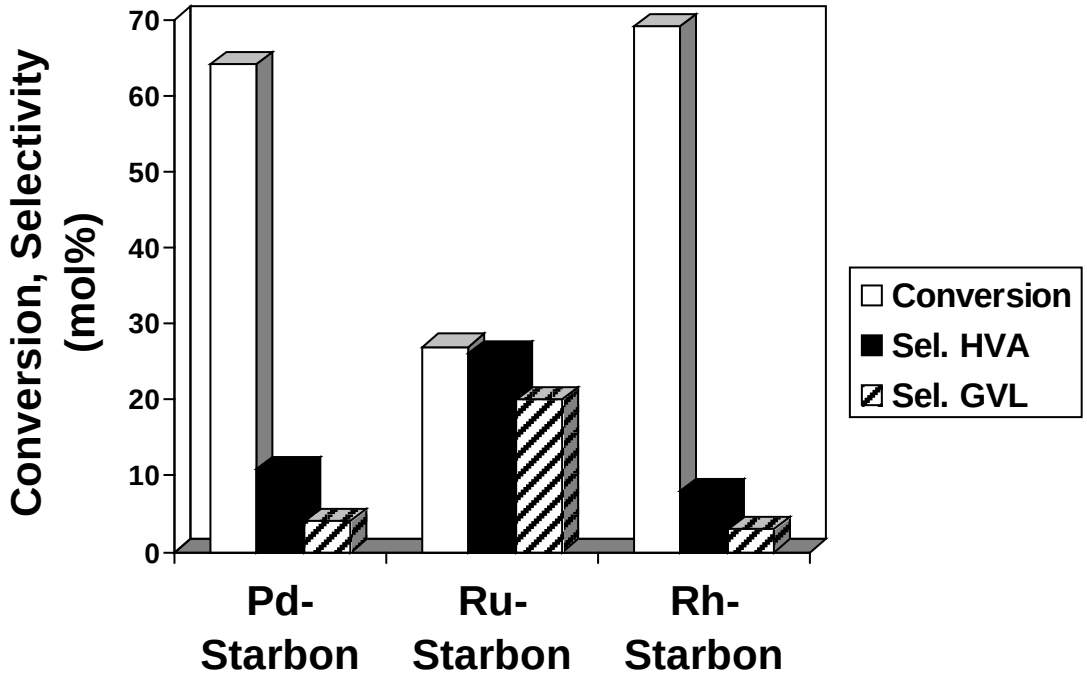

Figure 7S. Microwave-assisted conversion of levulinic acid using supported noble metals on Starbon-300®. Reaction conditions (each run): 0.1 mL LA, 0.3 mL FA, 0.1 g catalyst, 150ºC, 30 min microwave irradiation. Relatively high selectivities to hydroxyvaleric acid (HVA), with some GVL production (max. GVL production 50% after 15 min microwave irradiation) were obtained in the systems.

Leaching studies under flow conditions

Table 4S**.** ICP-MS results on both filtrate and Cu-MINT catalyst in the continuous flow conversion of levulinic acid to valuable chemicals

Element	Filtrate (after reaction)
Cu [%]	62ppm (10 min flow) >90 (20 min flow)

Table 5S**.** ICP-MS results on both filtrate and 5%Pd/C catalyst in the continuous flowconversion of levulinic acid

Element	Filtrate (after reaction)	5%Pd/C
Pd [%]	Not detected (<0.5 ppm)	4.9
Mn [mg/kg]	-	0.2
Co [mg/kg]	-	< 0.05
Rh [mg/kg]	-	< 0.01
Pt [mg/kg]	-	< 0.005
Au [mg/kg]	-	< 0.005

Table 6S**.** ICP-MS results on the final reaction mixture for 13wt%CuO/Al_2O_3 after 80 min reaction in the continuous flow conversion of levulinic acid

Element	Filtrate (after reaction)
Cu [%]	<10 ppm (8.5 ppm)