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Published in:
ACS Sustainable Chemistry & Engineering

DOI:
[10.1021/acssuschemeng.5b00774](https://doi.org/10.1021/acssuschemeng.5b00774)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Piskun, A. S., de Haan, J. E., Wilbers, E., de Bovenkamp, H. H. V., Tang, Z., & Heeres, H. (2016). Hydrogenation of Levulinic Acid to gamma-Valerolactone in Water Using Millimeter Sized Supported Ru Catalysts in a Packed Bed Reactor. *ACS Sustainable Chemistry & Engineering*, 4(6), 2939-2950. <https://doi.org/10.1021/acssuschemeng.5b00774>

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Hydrogenation of Levulinic Acid to γ -Valerolactone in Water Using Millimeter Sized Supported Ru Catalysts in a Packed Bed Reactor

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Supporting Information

ABSTRACT: γ -Valerolactone (GVL) has been identified as a sustainable platform chemical for the production of carbon-based chemicals. We here report an experimental study on the catalytic hydrogenation of levulinic acid (LA) in water to GVL in a packed bed reactor using supported Ru catalysts (carbon, alumina, and titania) with particle sizes in the millimeter range ($C_{LA,0} = 1.2$ mol/L, LA feed = 1 mL/min, H_2 feed = 30 mL/min, 90 °C, 45 bar, and WHSV = 30 $g_{feed}/g_{cat} \cdot h$). Intraparticle diffusion limitations for hydrogen and LA were confirmed by performing LA hydrogenation experiments with different catalyst particle sizes (0.5 wt % Ru/C) and supported by calculations. The best performance was obtained with Ru/C, showing high LA conversion during 6 h on stream with negligible deactivation. Ru/ Al_2O_3 was found to be less active, and stability was also considerably reduced due to the reactivity of the support. Ru/ TiO_2 was considerably less reactive, though stability was better than that for the alumina based counterpart. A long duration test (52 h) for Ru/C (0.5 wt % of Ru) showed a small though significant reduction in LA conversion (from 95 to 82 mol %). Catalyst characterization studies showed a significant decrease in the specific surface area of the catalyst (from 1110 m^2/g to 390 m^2/g) and sintering of the Ru particles (TEM-HAADF).

KEYWORDS: Levulinic acid hydrogenation, γ -Valerolactone, Ru-catalyst, Packed bed reactor, Flow chemistry

INTRODUCTION

The conversion of biomass into platform molecules with a broad application range has attracted a great deal of attention in the last 15 years.¹ γ -Valerolactone (GVL) is an example of a platform molecule and has large potential to serve as a feed for renewable chemicals like solvents, for bulk chemicals like methylpentenoates and adipic acid, as an intermediate in fine chemicals synthesis and for fuel (additives), commonly referred to as “valeric biofuels”.^{2–5}

The catalytic hydrogenation of levulinic acid (LA) is an effective synthetic methodology for the synthesis of GVL. The former can be obtained by the dehydration of C6-sugars in acidic media.^{6,7} The catalytic hydrogenation of LA involves a two-step sequence: a metal-catalyzed hydrogenation of LA to 4-hydroxypentanoic acid (4-HPA) followed by an acid-catalyzed intramolecular esterification to GVL (Scheme 1).

Extensive research has been performed on the hydrogenation of LA to GVL using homogeneous^{8–11} and heterogeneous^{12–27} catalysts. Especially, supported metal catalysts have received great attention. Manzer¹⁷ screened the catalytic activity of Ir,

Rh, Pd, Ru, Pt, Re, and Ni supported on activated carbon (5 wt %) and showed that Ru was the most active and selective for GVL formation. An overview of the performance of Ru catalysts on various supports in batch setups is given in Table S1 (Supporting Information). Most studies involve the use of Ru on a carbon support in various solvents (among others water, dioxane, alcohols, DMSO, and various solvent combinations), and excellent yields of GVL have been reported (>99%). The addition of a solid acid (e.g., amberlyst, sulfated zirconia) was shown to be beneficial in some cases. Other supports have been tested as well, and examples include silica, alumina, niobia, titania, ZSM-5, and hydroxyapatite. Significant support effects were observed, though a proper comparison is difficult as most studies are focused on one support only, and systematic studies are generally lacking.

Received: July 30, 2015

Revised: February 28, 2016

Published: April 11, 2016

Scheme 1. Proposed Reaction Scheme for the Catalytic Hydrogenation of LA to GVL

Table 1. Literature Overview on LA Hydrogenation in Continuous Setups Using Heterogeneous Catalysts

catalyst	solvent	reaction conditions	WHSV (g _{feed} /g _{cat} ·h)	LA conversion (%)	GVL selectivity (%)	ref
Catalyst Powder ($d_p \leq 100 \mu\text{m}$)						
Ru/C (5 wt % Ru)	H ₂ O	packed-bed (upflow), 150 °C, H ₂ (35 bar)	32	start: 90 106 h: 68	start: 96 106 h: -	28
Ru/C (5 wt % Ru)	H ₂ O	packed-bed (downflow), 150 °C, FA + H ₂ (35 bar)		35	>98	29
5% Ru/C ($d_p = 45\text{--}90 \mu\text{m}$)	H ₂ O	packed-bed (upflow), 50–150 °C, H ₂ (4–41 bar)	50 °C–5 150 °C–1500	50 °C–99 150 °C–3	50 °C–4 150 °C–81	30
Ru/C (5 wt % Ru)	1-butanol/ H ₂ O	packed-bed (downflow), 180 °C, H ₂ (35 bar)	0.9	91	97.8	31
Ru/C (5 wt % Ru)	1,4-dioxane	packed-bed (downflow), 265 °C, H ₂ (1–25 bar)	0.5	100	>96	32
Ru/C (5 wt % Ru)	2-sec- butylphenol	fixed-bed (upflow), 180 °C, H ₂ (35 bar)	3.6		77	33
RuRe(3:4)/C (15 wt % RuRe)	H ₂ O	packed-bed (downflow), 150 °C, FA + H ₂ (35 bar)		15–40	>95	29
Ru–Sn(1:4)/C	GVL	packed-bed (upflow), 180–260 °C, FA	0.36–2.4			34
RuSn (3,6:1)/C (5 wt % RuSn)	2-sec- butylphenol	packed-bed (upflow), 220 °C, H ₂ (35 bar)	2.2 1.5	98 46	95.8 93.4	35
Ru _x Sn _y /C	2-sec- butylphenol	fixed-bed (upflow), 180 °C, H ₂ (35 bar)	1.2		73–100	33
Ru/DOWEX (0.87 wt % Ru) ($d_p = 84 \mu\text{m}$)	H ₂ O	fixed-bed (concurrent flow), 70 °C, H ₂ (5 bar)	0.52	100	99	36
Pd/C (10 wt % Pd) (Ru/C, 5 wt % Ru)		packed-bed (downflow), 180 °C, FA + butylformate + H ₂ (35 bar)	0.9	96	99	31
Zr/beta-100	sec-alcohols	fixed-bed (downflow), 118 °C, 2-pentanol		100	>96	37
Rh/SiO ₂ (4 wt % Rh)	H ₂ O	tubular-flow reactor, 80 °C, H ₂ (60 bar)		100	77	38
Rh–MoOx/SiO ₂ (4 wt % Rh)				100	35	
Mo ₂ C/CNT (20 wt % Mo)	H ₂ O	trickle-bed reactor, 200 °C, H ₂ (30 bar)	LHSV = 3 h ^{−1}	100	>90	39
Catalyst Particles ($d_p \geq 100 \mu\text{m}$)						
Ru/DOWEX (0.87 wt % Ru) ($d_p = 276 \mu\text{m}$)	H ₂ O	fixed-bed (concurrent flow), 70 °C, H ₂ (5 bar)	0.47	90	99	36
Pt/SiO ₂ (0.8 wt % Pt) ($d_p = 1.6 \text{ mm}$)	H ₂ O/GVL	packed-bed (upflow), 200 °C, H ₂ (40 bar)	2	15 h: 85 460 h: 22	15 h: 92 460 h: 83	40
Pt/TiO ₂ (1 wt % Pt) ($d_p = 1.6 \text{ mm}$)	GVL	packed-bed, 200 °C, H ₂ (40 bar)	9	start: 98 100 h: 85	>95	41

Besides batch studies, the catalytic hydrogenation of LA to GVL using supported catalysts has also been reported in continuous setups, and an overview is given in Table 1. In the Table, not only the performance of the Ru catalyst is provided but also the data for bimetallic Ru catalysts (with Re, Sn) and monometallic Rh, Pd, and Pt are given as well. A wide variety of supports, solvents, and reaction conditions were tested. Most of the reactions were performed in water, and typical reaction conditions are between 50 and 265 °C with hydrogen pressures ranging from 4–60 bar, though in some cases formic acid was used as the hydrogen source. WHSV's are between 0.5 and 1500 g_{feed}/g_{cat}·h, typically between 0.5 and 5, and both upflow and downflow reactor configurations have been applied. LA conversions were in general excellent (>90%), with GVL selectivities between 4 and 99%.

However, most studies describe the use of heterogeneous catalysts with small particle sizes ($d_p \leq 100 \mu\text{m}$). Typical particle sizes for packed-bed reactors in commercial operation are normally in the millimeter range to avoid excessive pressure

drops. Only a few studies were performed with particles sizes >100 μm ; see Table 1 for details. Lange and co-workers, used 1% Pt/TiO₂ extrudates (1.6 mm)⁴¹ for the hydrogenation of LA with GVL as the solvent (200 °C and 40 bar of H₂). High LA conversion (>85%), high selectivity to GVL (>95%), and a low level of deactivation for 100 h on stream (conversion of LA decreased from 98 to 85%) were observed. In a very recent paper, Moreno-Marrodan reported the catalytic activity of a bifunctional Ru on DOWEX (gel-type resin) in water at mild conditions (70 °C, 5 bar H₂).³⁶ Catalysts with two different bead sizes (84 ± 8 and 276 ± 2 μm) were prepared and tested. The catalyst with smaller particle diameters resulted in ca. 10% higher LA conversion under otherwise similar conditions. This indicates that intraparticle mass transfer limitations play a role for larger catalyst particles, suggesting that the time scale of the intrinsic kinetics are similar or faster than intraparticle mass transfer rates. This is an important finding as optimization strategies for hydrogenations performed in the kinetic regime are different for those in the mass transfer limited regime.

We here report an experimental study on the catalytic hydrogenation of LA with Ru based catalysts on various supports with particle sizes in the millimeter range in a continuous packed-bed reactor. Such systematic studies on representative Ru catalyst particles in the millimeter range have not been reported in the literature (Table 1). Initial experiments in the packed-bed reactor were carried out using Ru/C, the benchmark catalyst of this study. Process conditions like temperature and initial concentration of LA were varied, and the effects on the LA conversion and GVL selectivity were determined. Effects of mass-transfer on catalyst performance and particularly intraparticle hydrogen and LA mass transfer were assessed experimentally by performing experiments with different particle sizes. The findings are supported by the determination of relevant mass transfer limitation criteria. Finally, support effects and Ru loading (Ru/Al₂O₃, 0.3 and 0.5 wt % Ru; Ru/TiO₂, 1 wt % Ru; and Ru/C, 0.5, 2, and 5 wt % of Ru) were probed at benchmark conditions. Catalyst performance at longer runtimes was investigated, and the catalysts were analyzed in detail (TEM-HAADF, BET) after reaction to gain insight into possible deactivation pathways.

EXPERIMENTAL SECTION

Materials. Levulinic acid (purity >98%, less than 1 wt % H₂O) and 1,4-dioxane (purity >99%) were purchased from Acros Organics. Deuterium oxide (purity 99.9%) and RuCl₃·xH₂O (35–40% Ru) were purchased from Sigma-Aldrich. Hydrogen and nitrogen gas were from Linde Gas (purity 99.9%). All chemicals were used without purification.

All catalysts/supports were provided in the millimeter range and, when required, were crushed and sieved to particle diameters between 1.25 and 2.5 mm. Ru/C (0.5 wt % Ru, 3.98 wt % H₂O, and 2 wt % Ru and 1.3 wt % H₂O) and Ru/γ-Al₂O₃ (0.5 wt % Ru and 2.2 wt % H₂O) were obtained from Johnson Matthey, Ru/C (5 wt % Ru and 43.6 wt % H₂O) from Evonik and Ru/γ-Al₂O₃ (0.3 wt % Ru and <5 wt % H₂O) from BASF. The TiO₂ support (Ti 1100E, anatase phase) was obtained from BASF.

Ru/TiO₂ (1 wt % Ru) was prepared by a wet impregnation procedure in water using RuCl₃·xH₂O as the precursor (50 °C for 24 h). The catalyst was reduced at 450 °C for 4 h in a H₂/N₂ flow (10% H₂).

Catalyst Characterization. TEM images were recorded using an electron microscope CM12 (Philips, Eindhoven, The Netherlands) operating at 120 keV. Samples were made by ultrasonication in ethanol and dropping the suspension onto carbon coated 400 mesh copper grids. Images were taken using a slow scanning CCD camera. At least 100 nanoparticles were measured to determine the average diameter of the Ru nanoparticles.

Nitrogen physisorption experiments were carried out in a Micromeritics ASAP 2020 at −196.2 °C. The samples were degassed in vacuum at 200 °C for 10 h. The surface area was calculated using the standard BET method (*S*_{BET}). The single point gas adsorption pore volume (*V*_T) was calculated from the amount of gas adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distributions (PSD) were obtained from the BJH method using the adsorption branch of the isotherms. The mean pore size (Φ_{BJH}) is given by the position of the PSD maximum. The t-plot method was employed to quantify the micropore volume (*V*_m).

Description of the Hydrogenation Setup. The hydrogenation setup is schematically depicted in Figure 1 and is constructed from stainless steel 316L. The setup consists of a feeding section, a preheating section (ID = 0.6 cm; L = 13.5 cm), a reaction section (ID = 0.6 cm; L = 13.5 cm), and a gas–liquid separator. The liquid feed is fed to the setup using a piston pump (Williams P250 V225), the hydrogen is fed from a cylinder, and the pressure and flow rate are controlled by a Brooks 5866 pressure controller and Bronkhorst F-211-C-FA-11-V flow controller. The reactor and preheater are heated

Figure 1. Schematic representation of the continuous reactor setup.

electrically. After the reactor, a back pressure valve (Tescom 26-1726-24) is installed to reduce the pressure to atmospheric values. Subsequently, the liquid and gas phases are separated in a gas–liquid separator. The gas, mainly hydrogen, is mixed with nitrogen and vented. The liquid phase is collected and weighed. Temperature and pressure are monitored at various locations; viz. at the entrance and exit of the reactor (temperature) and before the preheating section and after the reactor section (pressure).

Experimental Procedure for the Packed-Bed Setup. All experiments were carried out in the hydrogenation setup as described in the previous section. The following ranges of process conditions were tested: reactor temperatures between 90 and 150 °C, a LA feed concentration in water between 0.1 and 11.2 M, and catalyst intakes between 2 and 5 g.

The aqueous LA feed solution of the desired concentration was prepared by diluting pure LA with deionized water (Milli-Q water). All catalysts were used without a preliminary reduction/activation step, and a fresh catalyst was used for each experiment. Typically, 2 g of catalyst was charged into the reactor. Subsequently, the aqueous LA solution was fed to the reactor, and the pressure was increased to 45 bar. The reactor was heated to the predetermined temperature (between 90 and 150 °C), and the hydrogen flow was started. After the temperature of the liquid reactor exit reached 85 °C, the outlet valve of the gas–liquid separator was closed, and this moment was set as the beginning of the reaction (*t* = 0 min). Liquid samples were taken every 15 min by emptying the content of the gas–liquid separator.

Analytical Procedures. The composition of a reaction mixture (LA, 4-HPA, and GVL) was determined quantitatively by ¹H NMR. A sample (approximately 200 μL) was weighed and dissolved in D₂O, and 1,4-dioxane (internal standard, IS, 10 μL) was added. All spectra were integrated using MestReNova software. The number of moles of a component in a sample was calculated using eq 1.

$$N_a = N_{IS} \times \frac{I_a}{I_{IS}} \times \frac{H_{IS}}{H_a} \quad (1)$$

where *N*_a is the number of moles of compound A in the sample, *N*_{IS} the known amount of moles of the internal standard in the sample, *I*_a is the peak area of the methyl group of component A (δ 2.1 ppm for LA, δ 1.03 ppm for 4-HPA, and δ 1.3 ppm for GVL), *I*_{IS} peak area of the CH₂ groups in 1,4-dioxane at δ 3.6 ppm, and *H*_{IS} and *H*_a are the

number of H atoms corresponding with the relevant NMR peak (3 for H_a and 8 for H_{IS}). The concentrations of LA, GVL, and 4-HPA in the samples were calculated using eq 2.

$$C_a = \frac{N_a}{V_t} \times D_f \quad (2)$$

where V_t is the liquid volume in the NMR tube and D_f the dilution factor, which was calculated using eq 3.

$$D_f = \frac{\text{volume of the sample} + \text{volume of D}_2\text{O} + \text{volume of internal standard}}{\text{volume of the sample}} \quad (3)$$

Mole Balance Closure. The mole balance closure for the continuous runs was evaluated by comparing the sum of the amounts of products (4-HPA and GVL) and unconverted LA with the initial intake of LA. Mole balance closure at the steady state operation of the setup was very good and >97%.

Definitions. The conversion of LA, the yield, and the selectivity of 4-HPA and GVL were calculated according to eqs 4–7.

$$X_{LA} = \frac{C_{LA,0} - C_{LA}}{C_{LA,0}} \times 100\% \quad (4)$$

$$Y_{GVL} = \frac{C_{LA,0} - C_{LA} - C_{4-HPA}}{C_{LA,0}} \times 100\% \quad (5)$$

$$Y_{4-HPA} = \frac{C_{LA,0} - C_{LA} - C_{GVL}}{C_{LA,0}} \times 100\% \quad (6)$$

$$S_i = \frac{Y_i}{X_{LA}} \times 100\% \quad (7)$$

where X_{LA} is the conversion of LA (mol %); $C_{LA,0}$ the inlet concentration of LA (mol/L); C_{LA} the concentration of LA in the exit stream (mol/L); Y_{GVL} the yield of GVL (mol %); Y_{4-HPA} the yield of 4-HPA (mol %), and S_i the selectivity to GVL or 4-HPA (mol %).

The space time yield (STY $g_{LA}/g_{Ru} \cdot h$) was calculated using eq 8.

$$STY = \frac{(C_{LA,0} - C_{LA}) \times \phi \times M_{LA}}{m_{Ru}} \quad (8)$$

where ϕ is the volumetric flow rate of the feed (l/h); M_{LA} the molar mass of LA (g/mol); and m_{Ru} the mass of ruthenium in the catalyst in the packed-bed reactor (g).

RESULTS AND DISCUSSION

Catalyst Characterization. The catalysts were characterized using nitrogen physisorption (BET surface area) and TEM. The latter was used to determine the average metal nanoparticle size distribution, which is an important characteristic for catalyst performance. An overview of the data is given in Table 2, and representative TEM images are given in Figure 2.

Table 2. Overview of Catalyst Characterization Studies

catalyst	Ru loading (wt %)	BET surface area (m ² /g)	average diameter of Ru nanoparticles (nm)
Ru/C	0.5	1110	8.4 ^a
Ru/C	2	950	6.5
Ru/C	5	1030	9.2
Ru/ γ -Al ₂ O ₃	0.3	180	1.9
Ru/ γ -Al ₂ O ₃	0.5	102	5.8
Ru/TiO ₂	1	96	2.0

^aStrongly agglomerated nanoparticles.

Figure 2. Representative TEM images for Ru/C (5 wt %) (left) and Ru/TiO₂ (1 wt %) (right).

Considerable differences in the average Ru nanoparticle sizes were observed (between 1.9 and 9.2 nm). The ruthenium particle sizes for the C based catalysts are at the high end of the range and all above 6.5 nm. However, the particles for the Ru/C (0.5 wt %) are strongly agglomerated, and the individual particles are by far smaller. The particles sizes for the two alumina based catalysts differ considerably (5.8 and 1.9 nm).

The highest catalyst surface area was detected for the Ru/C catalysts and varied in range 950–1110 m²/g; the exact value depends on ruthenium loading. The smallest surface areas (around 100 m²/g) were found for the Ru/ γ -Al₂O₃ (0.5 wt % Ru) and Ru/TiO₂ (1 wt % Ru) catalysts.

Initial Screening Studies with a Millimeter Sized Ru/C Catalyst. Initial experiments were performed using a mm sized Ru/C (0.5 wt % Ru) catalyst (average particle diameter of 1.88 mm) for a 6 h runtime. Benchmark reaction conditions are given in Table 3.

Table 3. Benchmark Conditions for a Continuous Experiment

LA inlet concentration	1.1–1.2	mol/L
LA feed rate	1	mL/min
H ₂ feed rate	30	mL/min (STP)
temperature	90	°C
hydrogen pressure	45	bar
WHSV	30	g _{feed} /g _{cat} ·h
time on stream	6	h

The concentrations versus runtime profiles for the three main components (LA, 4-HPA, and GVL) for a representative run are given in Figure 3. The experiment was carried out in triplicate, and the average value as well as the error bars are given. Clearly, the experiments are reproducible, with relatively low errors in the LA and GVL concentrations. The error in the 4-HPA concentration is slightly higher, likely due to analytical issues related to the thermal sensitivity of 4-HPA and its conversion to GVL upon storage.

It is evident that steady state is achieved after about 1–2 h on stream. In the steady state regime, the LA conversion was high (92%), and negligible deactivation was observed after 6 h on stream. The selectivity toward GVL was about 77%, the remainder being 4-HPA. Other byproducts like hydrogenation products of GVL (methyl-tetrahydrofuran and pentanoic acid) were not observed, and the selectivity toward the sum of 4-HPA and GVL was close to quantitative. The ratio GVL/4-HPA after the 6 h runtime is 8.0, which is far from the equilibrium constant for the intramolecular esterification reaction of 4-HPA to GVL in water at 90 °C (17–19⁴²).

Figure 3. Exit concentrations versus runtime profiles for a continuous LA hydrogenation experiment using the Ru/C (0.5 wt % Ru) catalyst. Conditions: see Table 3.

This suggests that equilibrium is not attained under the prevailing experimental conditions.

Effect of Prereduction of the Catalyst. The catalytic hydrogenation described above was carried out using a catalyst as received, i.e., without a prereduction step before reaction. To determine the effect of a prereduction step with hydrogen, an experiment was carried out using the Ru/C catalyst (0.5 wt %) at conditions given in Table 3, with prereduction of the catalyst in the reactor at 350 °C for 4 h (250 mL/min gas flow consisting of 10 vol % H₂ in 90 vol % N₂ at 20 bar pressure). The results of the experiment are given in Figure 4 and reveal

Figure 4. Conversion of LA with as received and prereduced Ru/C catalysts (0.5 wt % Ru). Conditions: see Table 3.

that the preactivation step has a negative effect on catalyst performance. LA conversion (average value in the steady state) dropped from 95% to 75% after the activation step. A possible explanation involves an increase in the average Ru-nanoparticle size by the reduction step, which is known to affect the rate of the hydrogenation reaction.^{43,44} As such, the catalysts after reaction were analyzed using TEM, and the results are given in Figure 5.

Figure 5. TEM images of a Ru/C catalyst (0.5 wt %) after a hydrogenation reaction without (left) and with prior catalyst activation (right). Reaction conditions: see Table 3.

The average ruthenium nanoparticle size after reaction differs slightly for both samples and is 1.5 nm at standard conditions and 1.9 nm when using a reduction step. As such, the observed reduced activity after the reduction step may be due to a slightly higher Ru-nanoparticle size. This increase could be due to some sintering of the Ru-nanoparticles during the activation step. However, other factors may play a role as well, for example, differences in the extent of Ru leaching during a run (*vide infra*).

Effect of LA Feed Concentration. When considering process economics, the use of an external solvent should be avoided to reduce workup and solvent recycle costs. DSM recently reported¹⁴ the hydrogenation of LA with molecular hydrogen and Ru/C (5 wt % Ru) in batch setups using highly concentrated LA solutions (130 °C, 20.6 bar of hydrogen pressure). This shows that operation at high LA concentrations is possible. Al-Shaal et al. also reported experiments in neat LA, and quantitative LA conversion was observed within 40 min in a batch setup.²⁰ In this study, considerably higher temperatures (190 °C) and Ru/C with a small average particle size (<100 nm) were used.

We have performed a number of experiments at benchmark conditions (Table 3), using a Ru/C catalyst (0.5 wt % Ru) with different inlet LA concentrations (0.1 to 11.2 mol/L) to determine the effect of initial LA concentration on the conversion and selectivity and to assess whether operation with an undiluted LA feed is feasible in a continuous setup. A summary of the average steady state conversion for 6 h on stream experiments with different inlet LA concentrations is shown in Table 4.

Table 4. Overview of LA Hydrogenation Experiments with Different LA Inlet Concentrations^a

#	inlet LA concentration (mol/L)	X _{LA} (mol %) ^b	STY (g _{LA} /g _{Ru} ·h)
1	0.1	100	80
2	0.5	100	370
3	1.2	92	770
4	5.8	20	1030
5	11.2	5	365

^aReaction conditions: see Table 3. ^bAverage conversion for a 6 h run.

The inlet LA concentration has a remarkable effect on the LA conversion (Table 4). Quantitative LA conversion is possible only at low initial LA concentrations (0.1 and 0.5 mol/L). With increasing inlet LA concentration, the LA conversion decreases and is 5% at 11.2 mol/L (pure LA).

The STY versus the inlet LA concentration is given in Figure 6 and shows an optimum at a LA concentration of about 6

Figure 6. Effect of inlet LA concentration on the STY for 6 h experiments with the Ru/C (0.5 wt % Ru) catalyst. Conditions: see Table 3.

mol/L. Possible explanations for the observed reduction in activity at high LA concentration are medium effects (solvent properties of water and LA differ considerably), which will affect both the intrinsic catalyst activity as well as the rate of mass transfer, which plays a major role in the packed-bed reactors with larger catalyst particles (*vide infra*).

To enhance the LA conversion at high LA inlet concentrations, two additional experiments were performed. The first was carried out at a higher reaction temperature (150 °C instead of 90 °C), higher hydrogen flow rate (120 mL/min instead of 30 mL/min), and higher catalyst intake (5 g instead of 2 g); see Table 5 for details. The LA conversion increased to 54% (compared to 5% at standard condition; Table 4, entry 3).

Table 5. Catalyst Performance for LA Hydrogenation in the Continuous Setup at Different Temperatures Using Ru/C^a

#	T (°C)	H ₂ feed (mL/min)	m _{cat} (g)	inlet LA concentration (mol/L)	X _{LA} ^b (mol %)	WHSV (g _{feed} /g _{cat} ·h)	STY (g _{LA} /g _{Ru} ·h)
1	90	30	2	1.2	92	30	770
2	130	30	2	1.2	99	30	830
3	130	30	1.4	1.3	75	48	990
4	150	30	1.4	1.4	84	48	1240
5	150	120	5	11.2	54	12	1685

^aAll experiments were performed using Ru/C (0.5 wt % Ru), 45 bar hydrogen pressure, and a LA feed rate of 1 mL/min. ^bAverage LA conversion for the 6 h run.

The second experiment was performed at a higher catalyst intake (4.75 g instead of 2 g) and hydrogen flow rate (200 mL/min instead of 30 mL/min) at 90 °C. During this experiment, the feed mass flow rate was slowly reduced, and the results are given in Figure 7. The LA conversion increased from 30% at the highest flow rate to 70% at the lowest. Higher LA conversion could not be attained as the flow rate could not be reduced below 0.2 g/min (lower limit of the pump). Thus, higher LA conversions when using concentrated LA feeds are

Figure 7. LA hydrogenation using a concentrated LA feed versus runtime and feed mass flow rate for a Ru/C catalyst (0.5 wt % Ru, $C_{LA,0} = 8.9$ mol/L, LA feed = 1–0.2 g/min, H₂ feed = 200 mL/min, 90 °C, 45 bar, and $m_{cat} = 4.75$ g).

possible by tuning reaction conditions, though quantitative LA conversion for a high LA inlet concentration was not possible at the experimental window of operation.

Catalyst Performance of the Ru/C Catalyst (0.5 wt % Ru) at Elevated Temperatures. The performance and particularly the stability of the Ru/C catalyst at elevated temperature was determined by performing additional experiments with the Ru/C catalyst at 130 and 150 °C (Table 5, entries 3 and 4). The results are provided in Figure 8. Catalyst

Figure 8. Conversion of LA with the Ru/C (0.5 wt % Ru) catalyst for reactions at 130 and 150 °C. Conditions: see Table 5, entries 3 and 4.

activity at the start of the run is higher at 150 °C (84%) than at 130 °C (75%). This difference is relatively small, rationalized by considering that the overall reaction rate is also affected by mass transfer effects (*vide infra*), which are by far less temperature sensitive than intrinsic kinetics. The LA conversion is a function of the runtime, indicative for some catalyst deactivation at these temperatures. The stability at 150 °C is lower than that at 130 °C, which is evident from the slope of the conversion versus time profiles. Thus, it appears that some

Table 6. Catalyst Performance and Product Distribution for the Various Catalysts in the Packed Bed Reactor^a

#	catalyst	Ru loading wt %	LA conversion ^b (mol %)	GVL selectivity (%)	4-HPA selectivity (%)	STY (g _{LA} /g _{Ru} ·h)
1	Ru/C	0.5	92	78	22	770
2	Ru/C	2	96	63	36	195
3	Ru/C	5	98	83	15	80
4	Ru/ γ -Al ₂ O ₃	0.3	31	31	69	420
5	Ru/ γ -Al ₂ O ₃	0.5	26	62	38	195
6	Ru/TiO ₂	1	26	54	47	105

^aSee Table 3 for reaction conditions. Concentration versus runtime profiles are given in Figures S1–S5 (see Supporting Information). ^bAverage steady state conversion.

catalyst deactivation occurs for runs at elevated temperature for runtimes of 6 h.

Mass Transfer Effects on Observed Reaction Rates. In a three phase hydrogenation reaction (gas–liquid–solid), the observed rate of reaction depends on the intrinsic reaction rate and the rate of mass transfer of hydrogen and LA to the active sites on the catalyst surface. In the extreme case, mass transfer limitation determines the observed rate, for instance when using large catalyst particles, poorly soluble gases, and inappropriate mixing. In the case of pure hydrogen, mass transfer of soluble hydrogen in the liquid phase to the surface of the catalyst, as well as intraparticle hydrogen transport may be limiting, and the same holds for LA.

The experimental data allow the assessment of possible intraparticle mass transfer limitations using the criteria defined by Weisz and Prater (eq 9).

$$N_{W-P} = \frac{-R_{\text{exp}} \times r_p^2}{C_s \times D_{\text{eff}}} \leq 0.3 \quad (9)$$

Here, R_{exp} = experimentally observed reaction rate (mol/m³ cat · s); r_p = radius of catalyst particle (m); C_s = concentration of the component at the catalyst surface (mol/m³); and D_{eff} = effective diffusion coefficient of the component (m²/s);

The criteria were determined for the experiments reported in Table 5, and the data are provided in Tables S5 and S9 (see Supporting Information). Strong intraparticle mass transfer limitations of both hydrogen and LA, mainly due to the high reaction rates in combination with the relatively large particle sizes, were found. Thus, the experiments with Ru/C were all performed in the regime where the reaction rate is determined by both intrinsic kinetics of the reaction and the rate of mass transfer of particularly hydrogen to the active sites. As such, the experimental reaction rates (in terms of STY) are not the intrinsic reaction rates. Moreover, the catalyst deactivation rates reported later on, not only for Ru/C but also for the other catalysts, are not the intrinsic catalyst deactivation rates but are also biased by mass transfer. Thus, catalyst performance trends cannot be related solely to intrinsic catalyst features (size of the Ru nanoparticles, BET surface area, and so on).

Experimental Verification of Mass Transfer Effects.

First, experimental evidence that mass transfer limitations indeed occur to a significant extent were obtained from experiments with the Ru/C catalyst with different Ru loading at otherwise similar conditions (Table 6, entries 1–3). The conversion of LA was shown to be essentially independent of the Ru loading (0.5, 2, and 5 wt % Ru on the carbon carrier). This confirms that mass transfer limitations play a major role and that the particle effectiveness factor for the catalysts are by far less than 1.

Furthermore, continuous experiments were carried out using the Ru/C catalysts with extremes regarding Ru loading (0.5 and 5 wt % Ru) at variable LA inlet concentrations at standard conditions (Table 3), and the results are given in Figure 9.

Figure 9. Effect of initial LA concentration on average LA conversion over 6 h on stream for two Ru/C catalysts with extremes toward Ru loading. Conditions: see Table 3.

Clearly, the catalytic performance for the Ru/C catalyst with 5 wt % of Ru loading is about similar to that for Ru/C with 0.5 wt % of Ru, again a strong indication for mass transfer limitations. Further support for this statement was obtained by performing a number of experiments with the Ru/C catalyst (0.5 wt % Ru) with different particle sizes. For this purpose, the millimeter sized catalyst was crushed and sieved to obtain a fraction with particle sizes between 0.5 and 0.6 mm. The smaller catalyst particles result in a considerably higher LA conversion (34% higher than for the larger particles; see Figure S6, Supporting Information). As such, the experiments with the millimeter sized catalyst particles were not carried out in the kinetic regime, where the intrinsic kinetics of the reaction determine the overall reaction rate, but in a regime where mass transfer plays a major role. The positive effect of the use of smaller catalyst pellets for LA hydrogenations has already been reported in the literature. For instance, a Ru/DOWEX catalyst showed a 10% higher LA conversion when decreasing the catalyst particle size from 276 to 84 μ m.³⁶

Support Effects on Catalytic Performance for Ru Based Catalysts. Profound support effects on the catalytic performance of Ru based catalysts have been reported when using small particles (<100 μ m). In this study, a number of continuous LA hydrogenation experiments was carried out using millimeter sized Ru particles on various supports (C, γ -Al₂O₃, and TiO₂) and with different Ru loadings. All

Table 7. Overview of STY's for the Hydrogenation of LA to GVL in Continuous Setups

catalyst	reaction conditions	STY ($\text{g}_{\text{LA}}/\text{g}_{\text{metal}}\cdot\text{h}$)	ref
	$d_p \geq 100 \mu\text{m}$		
Ru/C (0.5 wt % Ru)	90 °C, 45 bar H_2 , H_2O	770	this work
Ru/C (2 wt % Ru)	90 °C, 45 bar H_2 , H_2O	190	this work
Ru/C (5 wt % Ru)	90 °C, 45 bar H_2 , H_2O	80	this work
Ru/ Al_2O_3 (0.3 wt % Ru)	90 °C, 45 bar H_2 , H_2O	420	this work
Ru/ Al_2O_3 (0.5 wt % Ru)	90 °C, 45 bar H_2 , H_2O	195	this work
Ru/ TiO_2 (1 wt % Ru)	90 °C, 45 bar H_2 , H_2O	106	this work
Ru/DOWEX (0.87 wt % Ru) ($d_p = 276 \mu\text{m}$)	70 °C, 7 bar H_2 , H_2O	60	36
Pt/ SiO_2 (0.8 wt % Pt) ($d_p = 1.6 \text{ mm}$)	200 °C, 40 bar H_2 , H_2O	15 h: 210	40
Pt/ TiO_2 (1 wt % Pt) ($d_p = 1.6 \text{ mm}$)	200 °C, 40 bar H_2 , H_2O	Start: 780	41
	$d_p \leq 100 \mu\text{m}$		
Ru/C (5 wt % Ru) ($d_p = 45\text{--}90 \mu\text{m}$)	50–150 °C, 4–41 bar H_2 , H_2O	50 °C–100 150 °C–900	30
RuSn(3.6:1)/C (5 wt % Ru)	220 °C, FA, alkylphenol	55	35
Ru/DOWEX (0.87 wt % Ru) ($d_p = 84 \mu\text{m}$)	70 °C, 7 bar H_2 , H_2O	60	36
$\text{Mo}_2\text{C}/\text{CNT}$ (20 wt % Mo)	150 °C, 30 bar H_2 , H_2O	15	39

Table 8. Ruthenium Leaching Levels, Surface Area, and Pore Volume for Fresh and Spent Catalysts

#	catalyst	$\text{C}_{\text{LA}0}$ (mol/L)	T (°C)	leached Ru (mg) ^a	leached Ru (wt %)	surface area (m^2/g)	pore volume (cm^3/g)
1	Ru/ $\gamma\text{-Al}_2\text{O}_3$ (0.3 wt % Ru)	1.2	90	2.7	45	180 (F) ^b 215 (S)	0.6 (F) 0.67 (S)
2	Ru/ $\gamma\text{-Al}_2\text{O}_3$ (0.5 wt % Ru)	1.2	90	4.2	42	102 (F) 104 (S)	0.22 (F) 0.23 (S)
3	Ru/ TiO_2 (1 wt % Ru)	1.2	90	0.02	0.1	96 (F) 105 (S)	0.28 (F) 0.29 (S)
4	Ru/C (0.5 wt % Ru)	1.2	90	0.08	0.8	1110 (F) 850 (S)	0.48 (F) 0.33 (S)
5	Ru/C (0.5 wt % Ru)	11.8	150	0.3	1.2	1108 (F) 792 (S)	0.48 (F) 0.30 (S)
6	Ru/C (2 wt % Ru)	1.2	90	1.8	4.5	950 (F) 590 (S)	0.34 (F) 0.22 (S)
7	Ru/C (5 wt % Ru)	1.2	90	0.22	0.02	1030 (F) 940 (S)	0.39 (F) 0.35 (S)

^aOn the basis of a liquid sample taken at the end of a run. ^bF: fresh. S: spent.

experiments were performed at benchmark reaction conditions (Table 3), and the results are given in Table 6. The Weisz-Prater criteria for the experiments reported in Table 6 were determined and reveal strong intraparticle mass transfer limitations of both hydrogen and LA, mainly due to the relatively large particle sizes (see Supporting Information, Tables S6 and S10). Thus, we can conclude that the observed support effects on catalyst performance cannot be solely ascribed to differences in intrinsic catalyst features (Ruthenian nanoparticle size, surface area, etc.) but are biased by mass transfer effects. As such, it is not possible to draw sound conclusions regarding catalyst structure–performance relationships.

The LA conversion varied between 25 and 98%, and in all cases, the sole products were GVL and 4-HPA. The Ru/C catalysts showed the highest activity (LA conversion between 92 and 98%) and GVL yield. The LA conversion for the alumina (26–31%) and titania supported catalysts (26%) was significantly lower. However, direct comparison is cumbersome as the metal loadings for each catalyst are different. As such, it is better to compare the STY for the catalyst on a gram Ru basis (Table 6). Again, the Ru/C catalyst with a 0.5 wt % Ru loading is by far more active than all other catalysts (STY: $770 \text{ g}_{\text{LA}}/\text{g}_{\text{Ru}}\cdot\text{h}$), which is in line with literature data^{3,5,20}

An overview of the reported STY's of different ruthenium catalysts in continuous reactors is given in Table 7. The STY's obtained with the millimeter sized Ru catalysts in this study are at the high end when compared to the best results obtained so far ($780 \text{ g}_{\text{LA}}/\text{g}_{\text{Pt}}\cdot\text{h}$ for 1% Pt/ TiO_2 ⁴¹). However, in the latter case, the hydrogenation was performed at 200 °C, which is much higher than our benchmark temperature (90 °C).

The homemade Ru/ TiO_2 millimeter sized catalyst (anatase phase with a BET surface area of around $100 \text{ m}^2/\text{g}$) was the least active of all catalysts. These findings are in contrast to a screening study in our group using smaller catalyst particle sizes in a batch setup. Here, Ru/ TiO_2 (1 wt % Ru) showed comparable results with Ru/C (1 wt % Ru), and full LA conversion was achieved within 4 h with 90% selectivity to GVL.⁴³ Experiments in batch systems by other groups also reported excellent activity for Ru/ TiO_2 in water^{20,43} as well as in organic solvents.²⁵

A possible explanation for the low activity of the Ru/ TiO_2 catalyst in the current study using a continuous setup is the occurrence of significant intraparticle mass transfer effects for the millimeter sized particles used in this study compared to the smaller sized ones in most batch studies (*vide infra*). However, also the support structure and the preparation method of the catalyst may affect catalyst activity and play a role. For instance,

Al-Shaal et al.²⁰ reported support structure effects for LA hydrogenation experiments in ethanol–water mixtures for TiO₂ supports in a batch setup. The use of TiO₂ with a rutile structure resulted in inactive catalysts, whereas TiO₂ containing both rutile and anatase phases gave 81% LA conversion under the same reaction conditions (130 °C, 12 bar H₂, and 160 min).

All catalysts appear to be stable under the prevailing conditions (90 °C) in the continuous reactor (Table 3), and a clear reduction in the LA conversion was not observed after a 6 h runtime. However, catalyst deactivation may occur to some extent, though it will not be clearly visible in the profiles, as the experiments were carried out in the regime where mass transfer limitations play a major role.

To gain insights into structural changes in the catalysts during reaction, some of the catalysts were analyzed before and after reaction (XRD and BET surface area). In addition, the level of Ru leaching was determined by analyzing the liquid product phase in the outlet at various stages of the run (5 samples in total, after 15, 30, 75, 195, and 345 min). The results are compiled in Table 8.

The extent of leaching for the Ru/C catalysts with 0.5 and 5 wt % of Ru at benchmark conditions was below 1 wt % after the 6 h run. ICP measurement of samples taken at different runtimes showed that, particularly at the start of the run, some Ru leaching occurred, presumably loosely bound Ru at the outer surface of the particles. An experiment with LA at higher concentrations and temperature (Table 8, entry 5) using Ru/C (0.5 wt % Ru) gave a slightly higher extent of leaching (1.2 versus 0.8 wt %) than an experiment at 90 °C and using a more diluted feed.

Remarkably, higher Ru leaching levels (4.5%) were observed for Ru/C with 2 wt % of Ru, again by far the most at the start of the reaction. Apparently, the catalyst preparation procedure for this particular catalyst was different from that for the two others, which could be related to the type of Ru precursor, the calcination, and reduction procedures.

All Ru/C catalysts showed a significant reduction in the specific surface area and total pore volume after 6 h on stream. Similar observations were made by Chalid et al. for batch experiments with Ru/C.⁴⁵ This reduction in surface area does not have a dramatic effect on the catalytic activity, as no significant deactivation was observed for the 6 h run. This is (partly) due to significant mass transfer limitations of particularly hydrogen which obscure intrinsic catalyst deactivation rates (*vide supra*). However, changes in the texture of the catalyst, e.g., micropore blockage by small amounts of solids (coke), may also play a role.

For both Ru/ γ -Al₂O₃ catalysts, high amounts of ruthenium were found in the liquid samples taken during the continuous catalytic experiments. Almost half of the Ru amount was leached from the catalysts during the first 2 h on stream, even before the reactor achieved steady state (Table 8). The LA conversion versus runtime data (Figure S3 and S4, Supporting Information), however, show that the LA conversion is about constant in the steady state part of the run (2–6 h). Thus, it appears that considerable irreversible loss of Ru occurs at the start of the reaction but that this does not affect the steady state conversion. This effect may be partly due to mass transfer limitations. In this regime, the observed catalyst activity is not the intrinsic activity of the catalyst. However, it also is very possible that the observed steady state LA conversion for Ru/ γ -Al₂O₃ is that of a catalyst with a significant reduced Ru content.

Ru leaching may be associated with irreversible changes in the structure of the alumina support. It is well established that γ -Al₂O₃ may rehydrate in the presence of water to form boehmite (AlOOH),⁴⁶ which is thermodynamically favored at temperatures above 150 °C. For instance, this transformation was observed in the literature for Ru/ γ -Al₂O₃ treated with H₂-saturated water at 200 °C and 40.5 bar over 5 h.⁴⁷ Moreover, a hydrothermal treatment of γ -Al₂O₃ may also lead to (partly) conversion of the support to the α -phase.⁴⁸ To gain insight into changes in the support structure during a run, XRD analysis on fresh and spent catalysts was performed (Supporting Information, Figure S7), and both are remarkably similar and show peaks corresponding to the γ -Al₂O₃ phase.⁴⁸ Clear reflections from boehmite or α -Al₂O₃ were not observed. Thus, the alumina support did not change significantly during the 6 h on stream, presumably due to the relatively low reaction temperature of 90 °C.

Another possible explanation for the loss of Ru is (partly) dissolution of the alumina support in the rather acidic aqueous media with the concomitant dissolution of Ru. This was investigated by determination of the Al content in the liquid phase at various runtimes. The results are shown in Table 9.

Table 9. Aluminum Content of Liquid Samples Taken at Different Runtimes for LA Hydrogenation Experiments with Ru/ γ -Al₂O₃ Catalysts^a

catalyst	time on stream (min)	concentration of Al (mg/L)	total leached Al (wt %)
Ru/ γ -Al ₂ O ₃ (0.3 wt % Ru)	15	320	1.6
	30	255	
	195	120	
	345	105	
Ru/ γ -Al ₂ O ₃ (0.5 wt % Ru)	15	130	0.6
	30	90	
	195	45	
	345	35	

^aFor conditions, see Table 3.

Clearly, a considerable amount of Al is leached from the catalysts. The extent of leaching is a function of the runtime, with higher leaching level at the start of the run. A possible explanation for the observation that only a limited amount of Al (<2 wt %, Table 9) compared to Ru (42–25 wt %, Table 8) is leached is an anisotropic distribution of Ru in the millimeter sized catalyst particles with relatively large amounts of Ru present on the external surface of the catalyst (egg shell catalyst). This is commonly observed for millimeter particles and is related to catalyst preparation procedures. Further studies using TEM-HAADF analysis will be required to confirm this statement.

The BET surface area and the pore volume of both the Ru on alumina catalysts are slightly higher for the spent catalyst than for the fresh one. This may be the results of excessive Ru leaching and/or partly opening/widening of the pores due to partly dissolution of the structure by acids, as observed experimentally (see above).

The Ru/TiO₂ catalyst was also analyzed before and after reaction (Table 8). The specific surface area and total pore volume for this particular catalyst were not reduced after the 6 h run as for the carbon and the alumina support. In addition, no titanium was found in the liquid phase. This observation suggests that the low activity of the Ru/TiO₂ catalyst is not due

to the leaching of active metal from the catalyst particles but more likely due to a poor radial ruthenium distribution on the catalyst pellets. To optimize the catalytic performance of the Ru/TiO₂ catalyst, an alternative synthesis method is required, e.g., preparation of catalyst in powder and subsequent pelletizing, which is beyond the scope of this study.

Experimental Studies with Ru/C at Prolonged Runtimes. As shown in the previous paragraph, the most promising catalyst when considering activity and stability is Ru on carbon. However, stability was only so far assessed for a 6 h run. To determine the long-term stability, a 52 h run was carried out with the Ru/C (0.5 wt % Ru) catalyst at benchmark conditions (Table 3). The concentrations of LA, GVL, and 4-HPA versus run time are given in Figure 10.

Figure 10. Reaction profile for a continuous LA hydrogenation experiment over the Ru/C (0.5 wt % Ru) catalyst. Conditions: see Table 3.

The LA conversion at the start of the run was about 95%, and the main products were, as for the short runs, 4-HPA and GVL. Mass balance closure throughout the experiment was very good, indicating that significant amounts of products other than GVL and 4-HPA were not formed. Clearly, a small, though significant, increase in the concentration of LA in the outlet was observed after a runtime of 52 h (Figure 10), and the initial LA conversion (95%) decreased to 82%. Thus, some deactivation was observed during the run. These findings are in line with literature data for LA hydrogenation using Ru/C catalysts in the form of small particles ($d_p < 100 \mu\text{m}$). For instance, Serrano-Ruiz et al. performed experiments in a packed bed reactor (8.6 mol/L LA, 150 °C, and WHSV = 32 g_{feed}/g_{cat}·h) using the Ru/C (5 wt % of Ru) catalyst in powder form.²⁸ Here, a drop in the LA conversion from 90% to 68% after 106 h on stream was observed. Despite different reaction conditions, the extent of reduction of the LA conversion (approximately 0.2% per h) was similar to our experiments. Braden et al. used Ru/C (5 wt % of Ru) powder in a packed bed at 150 °C and 35 bar H₂ with a feed consisting of 0.3 mol/L of both LA and formic acid (FA).²⁹ A steady decrease in LA conversion over 50 h on stream was reported. In the group of Dumesic, a number of studies were performed to increase the stability of Ru/C catalyst for LA hydrogenation reaction in the presence and absence of acids (formic and sulfuric).^{31,33,35} The addition of tin to a Ru/C catalyst (5 wt % Ru and Ru/Sn molar ratio of 3.6:1) led to improved catalyst stability,³⁵ and stable perform-

ance was observed for runs exceeding 230 h. In a very recent paper, Abdelrahman et al. observed that the TOF's for the hydrogenation of LA using a Ru/C (5 wt % Ru) catalyst dropped to 20–30% of the initial values after 48–72 h on stream.³⁰

Literature findings, as well as the experimental data for the 6 h runs (*vide supra*), indicate that the loss of activity may be due to Ru leaching and loss of surface area due to, among others, coke deposition. As such, liquid samples taken during the 52 h run were analyzed with ICP-OES to determine the extent of ruthenium leaching. The results are given in Figure 11. A total of 0.37 mg Ru was leached, corresponding to 3.47 wt % on total Ru intake.

Figure 11. Ruthenium leaching level during an experiment with the Ru/C (0.5 wt % Ru) catalyst over 52 h on stream. Conditions: see Table 3.

Only a minor amount of ruthenium leached from the Ru/C catalyst was observed in the initial phase of the experiment (<45 min). The amount of ruthenium in the liquid phase was below the detection limit (ICP) for a sample taken after 45 min on stream. Similar behavior was observed for this catalyst during the catalyst screening study, indicating good reproducibility. As such, ruthenium leaching to the liquid is not the reason for the decrease in LA conversion upon longer runtimes.

Nitrogen physisorption experiments were performed on fresh and spent catalysts to determine changes in the surface area and pore volume. A significant decrease in the specific surface area (from 1110 to 390 m²/g) and pore volume (from 0.48 to 0.21 cm³/g) was observed after 52 h on stream. The reduction in specific surface area is 3 times higher than that measured for this catalyst after a 6 h run (*vide supra*). As already discussed, this decrease in specific surface area is probably caused by the formation of coke on the catalyst surface and/or sintering of the ruthenium particles.

To get insight into structural changes in the catalyst during reaction, the fresh and spent Ru/C were analyzed using TEM-HAADF (Figure S8 in the Supporting Information). An increase in the diameter of the Ru nanoparticles is visible after 52 h on stream, though quantification is difficult. This indicates the occurrence of considerable sintering of Ru nanoparticles on the catalyst surface, which is likely also an important contributor for the reduction in catalyst activity for the 52 h run. Sintering is typically considered a high temperature phenomenon; however, water can facilitate particle

agglomeration even close to room temperature.⁴⁹ These observations are supported by the works of Abdelrahman, who reported Ru cluster growth for the hydrogenation of LA in water at 50 °C from roughly 3.6 to 6.8 nm after 65 h on stream.³⁰ In addition, similar effects were found by Davis for the aqueous phase hydrogenation of glucose over Ru/SiO₂ at 100 °C.⁵⁰

Thus, we can conclude that both Ru sintering and reduction in the specific surface area of the catalyst are the most likely causes for catalyst deactivation. Future efforts aimed toward a rational design of stable supported LA hydrogenation catalyst based on Ru should consider strategies for maintaining high Ru dispersions in the support phase. A possible solution is the use of bimetallic catalysts. For instance, RuSn alloys were already shown to perform better in this respect, and negligible deactivation was observed for 300 h on stream.³³ However, despite a higher stability, the GVL production rate decreased from 0.5 to 0.1 mmol/min·g when Sn was added.

CONCLUSIONS

An experimental study on the catalytic hydrogenation of LA with Ru catalysts on various supports (Al₂O₃, TiO₂, and C) with particle sizes in the millimeter range in a continuous packed-bed reactor is reported. For these millimeter sized catalyst particles, intraparticle mass transfer limitation of both hydrogen and LA occurs to a significant extent, as was proven by calculations and experimental studies. As such, the experimental data are strongly biased by mass transfer limitations, limiting conclusions regarding the intrinsic activity and stability of the catalysts. The highest activity (STY up to 770 g_{LA}/g_{Ru}·h at 90 °C and a LA inlet feed concentration of 1.2 mol/L) and stability were observed for the Ru catalyst (0.5 wt %) on the carbon support. It was also shown that highly concentrated LA feeds may be used (>11 mol/L), though this goes at the expense of LA conversion. Long duration experiments (52 h) for the Ru/C (0.5 wt % Ru) catalyst reveal the occurrence of a small though significant reduction in catalyst performance (from 95 to 82% LA conversion), mainly caused by the loss of surface area (BET), likely by coke deposition, and Ru sintering (TEM-HAADF), whereas Ru leaching (below 3% on intake) appears to be of minor importance. However, the latter is of prime importance for further scale up, as loss of expensive Ru metal is highly undesirable and will have a strong negative effect on the techno-economic viability of the process. Further catalyst development will be required to reduce Ru leaching levels, e.g., by optimization of the catalyst synthesis procedure and the addition of promoters. In addition, coke removal strategies need to be developed, for instance by (mild) oxidation using air. This will require detailed insights in the nature of the coke, to avoid oxidation of the actual carbon support due to the regeneration step.

Finally, reactor modeling activities to identify optimum reactor configurations, given the fact that mass transfer plays an important role, are in progress and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00774.

Concentration–runtime profiles for LA, 4-HPA, and GVL for a number of continuous experiments with Ru catalysts on different supports and XRD data and TEM images for fresh and spent Ru/C catalysts (PDF)

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Funding

This research was conducted in the framework of the Dutch CatchBio program. Financial support from the Smart Mix Program of The Netherlands Ministry of Economic Affairs and The Netherlands Ministry of Education, Culture and Science is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the members of the CatchBio User Committee for valuable suggestions and discussions, the University of Utrecht for the TEM-HAADF measurements, and Marcel de Vries and Anne Appeldoorn for technical support.

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