Editor's choice paper

Experimental and kinetic modeling studies on the biphasic hydrogenation of levulinic acid to γ-valerolactone using a homogeneous water-soluble Ru–(TPPTS) catalyst

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ABSTRACT

γ-Valerolactone (GVL) is considered a very attractive biomass derived platform chemical. This paper describes the application of biphasic homogeneous catalysis for the hydrogenation of levulinic acid (LA) to GVL using molecular hydrogen. A water soluble Ru-catalyst made *in situ* from $RuCl_3 \cdot 3H_2O$ and sodium-tris(*m*-sulfonatophenyl)phosphine (Na_3TPPTS) in dichloromethane/water biphasic mixtures was used. The hydrogenations were performed at mild conditions in a batch hydrogenation reactor and essentially quantitative GVL yields were obtained at 45 bar, 90 °C and 80 min reaction time (1 mol% catalyst). The effects of process variables like LA concentration, hydrogen pressure, temperature, pH and the catalyst to substrate ratio on the LA conversion and GVL yield were determined. The experimental data were quantified by kinetic modeling and it was shown that the reaction is first order in LA. Catalyst recycle experiments show that the recycled catalyst is still active, though the activity is lower than for the first run (81% LA conversion for first run versus 55% for recycle experiment).

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1. Introduction

Levulinic acid (LA) is considered an important biobased platform chemical and may serve as a starting material for a wide range of interesting chemicals with a broad application range [1]. LA may be obtained in high yields by the acid catalysed hydrolysis of the C6-sugars present in lignocellulosic biomass [2].

A very attractive LA derivate is γ-valerolactone (GVL). It has potential as a solvent, a food additive [3,4] and as a biofuel, for instance as a substitute of ethanol in gasoline–ethanol blends [4]. GVL may also be converted to a number of interesting derivatives. Hydrogenation of GVL provides access to methyltetrahydrofuran (MTHF), which is a potential fuel additive [5]. The reaction with GVL and formaldehyde leads to the formation of α-methylene-γ-valerolactone (MGVL), a new acrylic monomer which may be converted to novel acrylic polymers with improved product properties (e.g. thermal stability) [6]. Another interesting option is the ring-opening reaction of GVL with methanol followed by dehydration to produce (isomeric) methylpentenoates (MP). These may be converted to well known bulk chemicals like caprolactone by hydroformylation, caprolactam by hydrocyanation or adipic acid by hydroxycarbonylation [7]. Recently, the conversion of GVL to 5-nonanone and subsequently to alkanes in the C_9 or C_{18}–C_{27} range has been reported [8].

GVL is typically obtained from LA by stoichiometric reduction reactions or catalytic hydrogenations [8,9]. The catalytic hydrogenation reactions, either starting with LA or ester derivatives, may be carried out either using heterogeneous [10–14] or homogeneous catalysts. The intermediate 4-hydroxyvaleric acid (4-HVA) is not very stable and cyclization to GVL occurs easily under reaction conditions (Scheme 1). Excellent GVL yields (>98%) have been reported for the hydrogenation of LA using a variety of Ru catalysts (Ru/C [6,15], Ru/Al_2O_3) [16]. Recently, good results were obtained for catalytic transfer hydrogenation reactions with formic acid as the hydrogen source using Ru/C as the catalyst [17].

Homogeneous catalysts have also been used for the hydrogenation of LA to GVL using both molecular hydrogen and formic acid as the reductants. Typically ruthenium complexes with chelating phosphine ligands are applied. Osakada et al. showed that $RuCl_2(PPh_3)_3$ is a good catalyst and 99% yield of GVL was obtained at 11.8 bar of H_2 pressure, 180 °C for a 24 h reaction time [18]. Joo et al. [19,20] demonstrated the use of water-soluble homogeneous ruthenium catalysts (e.g. $HRuCl(Dpm)_3$, Dpm = diphenylphosphinobenzene-m-sulphonic acid) for the hydrogenation of oxo- and keto acids. However, catalytic activity for the hydrogenation of keto-acids like LA was low. Chiral versions have also been developed, e.g. by using Ru-BINAP complexes [21,22]. For instance, ethyllevulinate

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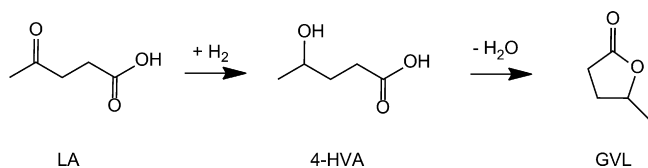
Scheme 1. Hydrogenation of LA to GVL.

was converted to GVL using a Ru-BINAP complex obtained *in situ* from Ru(acetate)$_2$BINAP with 2 equiv. of HCl at 25–25 °C in ethanol using 100 bar of hydrogen in 96% chemical yield and >99% ee with only 0.1 mol% of catalyst. The latter example nicely illustrates the potential of homogeneous catalysts for the synthesis of GVL, i.e. the possibility to obtain high reaction rates and selectivities at less severe reaction conditions than heterogeneous analogues.

Recently, the potential of homogeneous transfer hydrogenations with formic acid was also demonstrated. For instance, Horvath et al. [23] applied a homogeneous Ru compound [(η^6-C$_6$Me$_6$)Ru(bpy)(H$_2$O)][SO$_4$] in water for the transfer hydrogenation of LA using formic acid as the hydrogen donor. Both GVL and 1,4-pentanediol were obtained in 25% yield. Improved GVL yields (up to 94%) were reported using RuCl$_3$·3H$_2$O in combination with PPh$_3$ and a base (150–200 °C, solvent free) [24].

A drawback of the use of homogeneous catalysts with limited activity is the necessity for catalyst recycle to improve the economic viability of the process. A possible solution is the application of biphasic catalysis, where the catalyst is present in a second, product immiscible phase after reaction and easily separated from the product phase and recycled [25–27]. A well known approach in homogeneous hydrogenation reactions is the use of aqueous/organic biphasic systems using water soluble ruthenium complexes with sulfonated phosphine ligands like sodium-tris(*m*-sulfonatophenyl)phosphine (Na$_3$TPPTS). Examples are the biphasic hydrogenation of α-β-unsaturated aldehydes [28], aromatic and aliphatic nitriles [29], alkenes and aromatics [30], and model compounds of fast pyrolysis oil (vanillin, *iso*-eugenol and acetoguaiacone) [31]. The biphasic hydrogenation of LA is to the best of our knowledge not reported in the literature. In this paper the feasibility of a biphasic hydrogenation of LA to GVL in a biphasic water/organic solvent system using the water soluble RuCl$_3$/TPPTS catalyst will be explored. The effect of process conditions on catalyst activity and stability have been determined and will be reported. Based on the experimental data, a kinetic model was developed. In addition, the possibility of effective catalyst recycling has also been studied.

2. Experimental

2.1. Materials

LA was purchased from Sigma–Aldrich (purity >98%). RuCl$_3$·3H$_2$O (purity 99%) and Na$_3$TPPTS were provided by Riedel-de Haen and Strem, respectively. Dichloromethane (DCM) was obtained from Lab Scan (analytical grade, purity 99%). Na$_2$HPO$_4$·12H$_2$O, HCl and NaOH were obtained from Merck Chemicals. Hydrogen and nitrogen gas were purchased from Hoek-Loos (purity 99.5%-v). All chemicals were used without further purification.

Buffer solutions were prepared using standard procedures [32] by dissolving the appropriate amount of the phosphate salts in reverse osmosis water (pH 9.0: 0.1 M Na$_2$HPO$_4$ and 0.1 M HCl; pH 11.0: 0.1 M Na$_2$HPO$_4$ and 0.1 M NaOH). Experiments at neutral pH were performed in deionised water.

2.2. Analytical procedures

^{1}H and ^{13}C NMR spectra were recorded on a Varian 200 MHz spectrometer using CDCl$_3$ as the solvent and tetramethylsilane (TMS) as an internal reference.

The composition of the aqueous phase after the partitioning experiments (*vide infra*) was analyzed using HPLC. A HPLC apparatus consisting of a Hewlett Packard 1050 pump, a Bio-Rad organic acid column (Aminex HPX-87H) and a Waters 410 refractive index detector was used. The mobile phase consisted of an aqueous solution of sulfuric acid (5 mmol/l) operated at a flow rate of 0.55 ml min^{-1}. The column was operated at 60 °C. The amounts of LA and GVL were calculated using calibration curves obtained from standard solutions of known concentrations.

2.3. Reactor set-up for catalytic hydrogenation experiments

The hydrogenation reaction was performed in a 350 ml stainless steel batch autoclave (Buchi GmBH). The autoclave was electrically heated and, when appropriate, may be cooled using water. The reactor content was stirred with an overhead stirrer, equipped with a Rushton type impeller. The reactor was equipped with a pressure indicator to monitor the pressure and a thermocouple to measure the temperature inside the reactor.

2.4. Typical example of a catalytic hydrogenation reaction

The autoclave was charged with Na$_3$TPPTS (90.4 mg, 0.15 mmol) in DCM (100 ml). Subsequently, LA (1.5 ml, 1.74 g, 15.0 mmol), RuCl$_3$·3H$_2$O (38.1 mg, 0.15 mmol) and water (25 ml) were added. The stirrer was started (2000 rpm) and the reactor was purged three times with nitrogen. The mixture was heated to 90 °C (about 30 min) and then hydrogen was charged to the reactor to a pressure of about 10 bar to saturate the solution with hydrogen and to form the active catalyst from the precursors (Na$_3$TPPTS and RuCl$_3$·3H$_2$O) [28]. After about 10 min, the pressure was increased to 45 bar by hydrogen addition and this point was taken as the start of the reaction. During reaction, hydrogen was admitted to the reactor to keep the pressure at 45 bar. After 60 min, a sample was taken from the reactor by a dip tube. The organic and water phase were allowed to settle and the organic phase was analyzed by NMR to determine the conversion of LA and the yield of GVL. NMR was used instead of HPLC for quantification of the amounts of GVL and LA. Though intrinsically less accurate, it was the method of choice as the HPLC method employed in this study for partitioning experiments does not allow determination/quantification of the possible intermediate 4-HVA due to cyclization to GVL by the slightly acidic eluent. Subsequently, the autoclave was cooled to room temperature and vented to atmospheric pressure.

2.5. Typical example for a kinetic hydrogenation experiment

The experiments were carried out as describe above. During the reaction, samples were withdrawn from the reaction mixture by a dip tube at pre-determined time intervals. The organic and water phase in the samples were allowed to settle and the organic phase was analyzed by NMR to determine the conversion of LA and the GVL yield.

2.6. Determination of the partitioning coefficient of LA and GVL in water/DCM mixtures

The experiments were performed by adding of LA (1.5 ml, 1.74 g, 15.0 mmol) or GVL (1.5 ml, 1.58 g, 15.6 mmol) into a solvent mixture consisting of water (25 ml) and DCM (75 ml) in a stainless steel batch autoclave equipped with an overhead stirrer and a dip

tube for sampling. The mixture was purged three times by nitrogen gas. The contents were heated to 90 °C, the nitrogen pressure was increased to 20 bar to avoid excessive solvent evaporation, and the mixture was stirred for 30 min under vigorous stirring (2000 rpm). After 30 min, the stirrer was stopped to induce phase separation. After 30 min, a sample of the aqueous phase was taken using the dip-tube and analyzed by HPLC to determine the LA (or GVL) content.

2.7. Catalyst recycling experiments

$RuCl_3 \cdot 3H_2O$ (38.1 mg, 0.15 mmol) dissolved in water (25 ml) and LA (1.54 ml, 1,74 g, 15 mmol) dissolved in DCM (75 ml) were charged to the batch autoclave. Subsequent purging, heating and hydrogen addition were performed as described above. After 60 min, a sample was taken from the reactor by a dip tube. The organic and water phase in the sample were allowed to settle and the organic phase was analyzed by NMR to determine the conversion of LA and the GVL yield. Subsequently, the autoclave was cooled to room temperature and vented to atmospheric pressure. Both phases were allowed to settle and the light-brown aqueous phase containing the Ru–TPPTS catalyst was collected. This solution was again charged to the batch autoclave together with LA (1.54 ml, 1.74 g, 15 mmol) dissolved in DCM (75 ml). The reaction was performed under similar conditions as described above. After 60 min reaction, a sample was taken from the reactor and subsequently analyzed by ^{1}H NMR.

2.8. Concentration and conversion calculations using ^{1}H NMR spectra

The LA conversion and the concentration of LA in water were determined using the composition of the organic phase as determined by ^{1}H NMR. The LA conversion (X_{LA}) is defined as

$$X_{LA} = \frac{n_{LA,0} - n_{LA}}{n_{LA,0}} = \frac{n_{GVL,org}}{n_{LA,0}} = \frac{n_{GVL,org}}{n_{GVL,org} + n_{LA}} \tag{1}$$

Here $n_{LA,0}$ is the initial intake of LA (in mol), $n_{GVL,org}$ the number of moles of GVL in the organic phase and n_{LA} the sum of the number of moles of LA in the aqueous and organic phase. In here, it is assumed that 1 mol of LA is converted to 1 mol of GVL (in line with the stoichiometry and selectivity of the reaction, *vide infra*), that LA distributes between both phases and that the GVL resides only in the organic phase. The latter is justified by partitioning experiments carried out for GVL in water–DCM mixtures (*vide infra*). These experiments also show that LA is soluble in both in the organic and aqueous phase and distributes between both phases. The conversion is calculated from ^{1}H NMR spectra of the organic phase (*vide infra*). To eliminate the concentration of LA in the water-phase in Eq. (1), the mol balance for LA over both phases (Eq. (2)) was combined with the definition of the partitioning coefficient of LA (m_{LA}) (Eq. (3)):

$$n_{LA} = n_{LA,org} + n_{LA,aq} \tag{2}$$

$$m_{LA} = \frac{n_{LA,org} V_{aq}}{n_{LA,aq} V_{org}} = \frac{n_{LA,org}}{n_{LA,aq}} \theta \tag{3}$$

where

$$\theta = \frac{V_{aq}}{V_{org}} \tag{4}$$

Elimination of $n_{LA,aq}$ by substitution of Eq. (2) into (3) leads to:

$$n_{LA} = a n_{LA,org} \tag{5}$$

Table 1
Base case and ranges of process variables.

Process variable	Base case conditions	Experimental ranges
Pressure of H_2 (bar)	45	5–45
Reaction time (min)	60	30–200
Phase ratio θ	0.25	–
Organic solvent	DCM	–
Stirring speed (rpm)	2000	200–2000
Temperature (°C)	90	50–115
Substrate/catalyst ratio (mmol/mmol)	100	67–520
TPPTS/Ru ratio	1.0	–
pH	7	7.0–11.0

where

$$a = \left[\frac{m_{LA} + \theta}{m_{LA}} \right] \tag{6}$$

Thus the conversion of LA is as follows:

$$X_{LA} = \frac{n_{GVL,org}}{n_{GVL,org} + a n_{LA,org}} \tag{7}$$

The X_{LA} was calculated by integration of the ^{1}H NMR spectra of the organic phase by rewriting Eq. (7):

$$X_{LA} = \frac{I_{GVL,org}}{I_{GVL,org} + a I_{LA,org}} \tag{8}$$

where I_i is the normalized area of one of the H atoms of component i. The concentration of LA in water ($C_{LA,aq}$), which is important input for the kinetic modeling, was determined using the conversion definition (Eq. (1)) and the definition of the partitioning coefficient for LA (Eq. (3)). This leads to:

$$C_{LA,aq} = \frac{n_{LA,0}}{V_{aq}} \left[\frac{\theta}{\theta + m_{LA}} \right] (1 - X_{LA}) \tag{9}$$

The initial rate of the reaction was determined from a plot of the concentration of LA in the aqueous phase versus reaction time. The profile was fitted by a fourth-order polynomial function using the *Polymath* software package. The initial rate was obtained by differentiation of the polynomial function and evaluation of this function at $t = 0$.

2.9. Kinetic modeling

The experimental concentration profiles were modeled using the Matlab® programming platform using the numerical integration toolbox *ode45*. The kinetic parameter values were determined by minimization of the sum of squared errors between all experimental data and the simulated data from the kinetic model. Error minimization was performed using the Matlab® toolbox *fminsearch,* which is based on the Nelder–Mead optimization method.

3. Results and discussion

All reactions were carried out in a biphasic system consisting of water and dichloromethane. The effect of important process variables (reaction temperature, pH, substrate concentration, catalyst concentration, hydrogen pressure) on the LA conversion was determined. An overview of the base case conditions and the range of process variables studied are given in Table 1. The catalyst was made *in situ* by adding the individual components ($RuCl_3 \cdot 3H_2O$ and sodium-tris(*m*-sulfonatophenyl)phosphine (Na_3TPPTS)) to the reaction mixture instead of an *ex situ* preparation procedure. This facilitates the experimental procedures considerably and has shown to lead to equal reactivity [31]. The use of a co-solvent or phase transfer agent to transfer the LA from the organic to the water
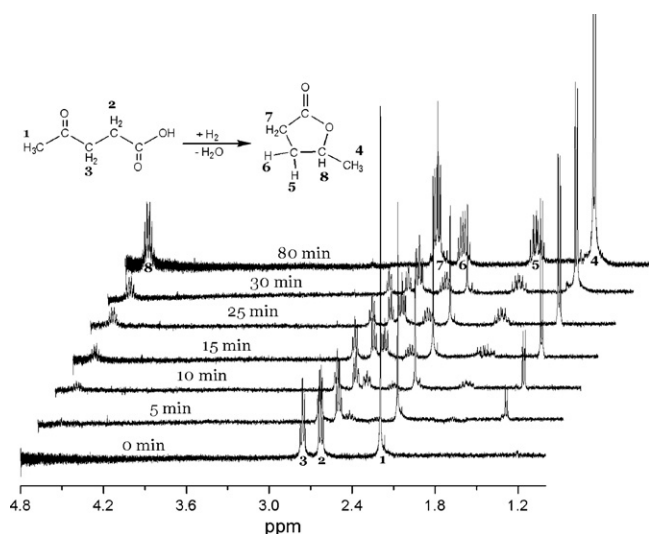
Fig. 1. ^{1}H NMR spectra for a representative LA hydrogenation run in DCM/water using the Ru–TPPTS catalyst (CDCl$_3$, base case as in Table 1).

Fig. 2. Conversion of LA at various agitation rates after 1 h. All other variables are at base conditions (Table 1).

phase is not necessary as LA is partly soluble in water (*vide infra*). After reaction, the reaction mixture was biphasic in nature and consisted of a light brown water phase and a slightly yellow organic phase.

The conversion of LA in the course of the reactions was monitored by taking samples at regular time intervals and subsequent analyses of the organic phase by ^{1}H NMR. A representative example for a typical experiment (at base case conditions) is given in Fig. 1. Clearly visible is the appearance of the methyl group of GVL as a doublet at δ 1.4 ppm and the disappearance of the characteristic singlet of the methyl group adjacent to the ketone moiety of LA at δ 2.2 ppm.

Selectivity towards GVL appears to be very high and near quantitative, as confirmed by NMR and GC analyses of the organic phase and HPLC analyses of the aqueous phase. The intermediate 4-hydroxyvalericacid (4-HVA) was not observed (Scheme 1), a clear indication that the subsequent lactonisation of 4-HVA to GVL is very fast in the system [33,34]. Subsequent hydrogenation products like methyltetrahydrofuran and pentanoic acid were also not detected in substantial amounts under the mild reaction conditions employed.

The conversion of LA after 1 h for an experiment at standard conditions as in Table 1 was 82%. This corresponds with an average turnover frequency (TOF) of about 100 mol mol^{-1} h^{-1}. The initial turnover frequency, determined from the initial reaction rate, was about 170 mol mol^{-1} h^{-1}.

The reproducibility of the reaction was checked by performing the experiment at base case conditions (Table 1) twice. The LA conversion was 82 and 81%, respectively, indicating that the reproducibility is good.

3.1. Mass transfer limitations

The system under study is a three-phase G–L–L system, consisting of hydrogen gas, an aqueous phase with the homogeneous catalyst and an organic phase with the product. LA distributes between both liquid phases (*vide infra*). In such a multiphase reactive system, the overall conversion rate may be limited by, among others, gas-liquid mass transfer of hydrogen gas and transfer of substrates between both liquid phases. For determination of the intrinsic kinetics, it is advantageous to perform the experiments in the kinetic regime. To gain insights in possible mass transfer effects, some experiments were performed at different agitation
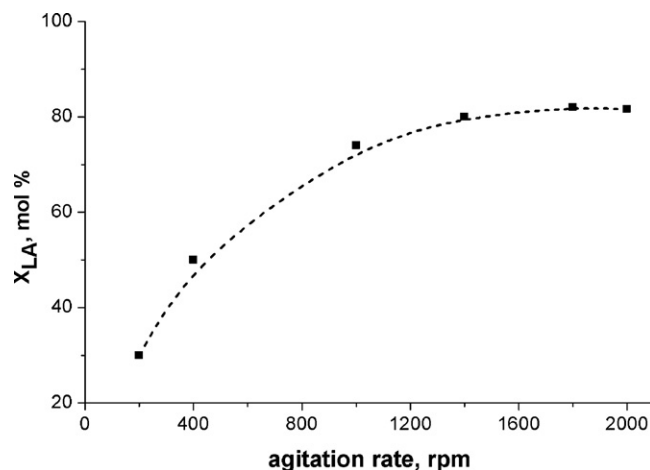
rates while keeping all other variables at base case conditions (Table 1). The conversion of LA for a 1 h reaction time as a function of the stirring speed is given in Fig. 2. The X_{LA} is a clear function of the agitation rate when the agitation rate is below 1400 rpm. This implies that the reactions below 1400 rpm are affected by mass transfer effects. Above 1400 rpm, the X_{LA} is essentially independent of the stirring rate, an indication that these experiments were performed in the kinetic regime. All further experiments were performed at agitation rate of 2000 rpm to ensure that the hydrogenation reactions take place in the kinetic region.

3.2. Effect of temperature

The effect of temperature on the X_{LA} was determined in the range 50–115 °C. All other conditions were set at base case conditions as given in Table 1. The conversion of LA for a 1 h reaction time at different temperatures is given in Fig. 3. It is clear that the hydrogenation reaction is very sensitive to the temperature. The LA conversion increases till about 90 °C (81%), at higher temperatures the conversion is considerably lower. This is indicative for the occurrence of catalyst deactivation at elevated temperatures. This is further confirmed by considering the LA hydrogenation profiles (Fig. 4). The initial reaction rate is highest at the highest temperature in the range. However, after about 10 min, a rapid decay of catalyst activity is observed, likely due to catalyst deactivation. Sim-
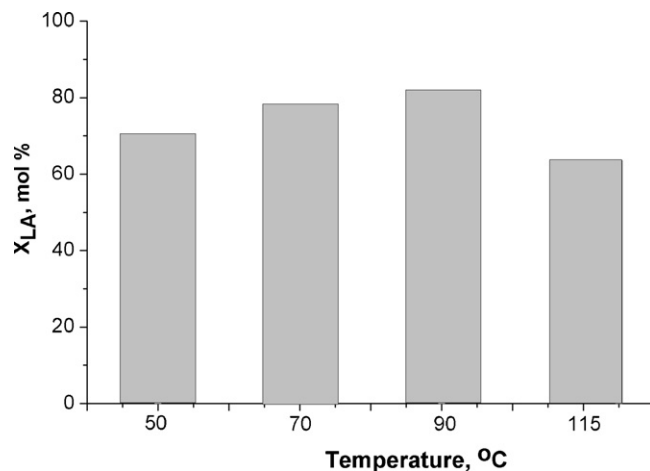
Fig. 3. Effect of the temperature on the conversion of LA after 1 h reaction time. *Conditions*: see Table 1 for base case conditions.
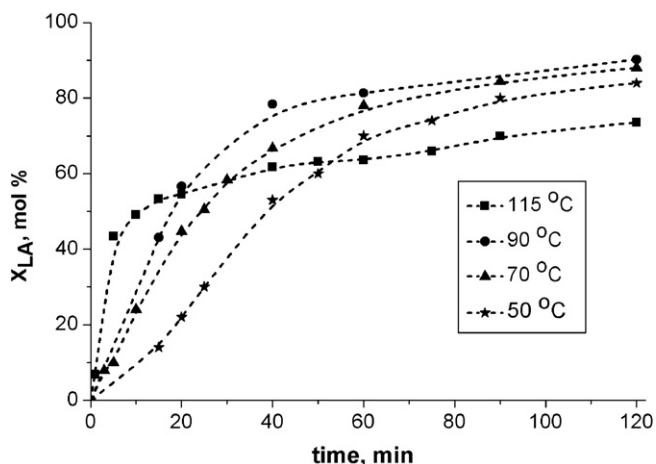
Fig. 4. LA conversion versus time at different temperatures. *Conditions*: see Table 1 for base case conditions. Lines are for illustrative purposes only.

Fig. 6. Determination of the order of reaction in LA (base case conditions, except $T = 70\,^\circ C$).

ilar observations were reported for related hydrogenations using the Ru–TPPTS system. Heinen et al. [35] studied the hydrogenation of D-fructose in aqueous systems and found that catalyst deactivation and the formation of Ru(0) particles (XRF) occurs easily above 90 °C. Mahfud et al. [31] reported the use of the Ru–TPPTS catalyst for the biphasic hydrogenation of vanillin to creosol in a water/DCM mixture and found that catalyst activity levels off above 60 °C. These examples indicate that the stability of the Ru–TPPTS catalysts is limited, though the temperature at which deactivation occurs to a considerable extent seems to be reaction-specific.

3.3. Effect of substrate concentration

The effect of the initial LA concentration on the reaction rate was determined at a fixed catalyst intake. All other experimental conditions were set at base case conditions (Table 1), except that the temperature was set at 70 °C to avoid excessive catalyst deactivation (Fig. 4). Typical concentration–time profiles are given in Fig. 5 for four different initial LA concentrations. With the profiles available, the initial rate of LA may be determined. This allows evaluation of the reaction order in LA by using the following equation:

$$R_{LA,water,0} = -kC_{LA,water,0}^{\alpha} \tag{10}$$

Here, the subscript 0 is related to initial conditions, k is the observed kinetic constant and α the reaction order in LA. The concentrations and rates are evaluated for the water phase, as this is expected to be the locus of the chemical reaction (*vide infra*).

Eq. (10) may be rewritten as

$$\ln(-R_{LA,water,0}) = \ln k + \alpha \ln(C_{LA,water,0}) \tag{11}$$

The experimental data for the hydrogenation at various initial LA concentrations at 70 °C, are plotted according to Eq. (11) and the results are given in Fig. 6. The figure shows that the reaction is approximately first order in LA concentration with a k value of about 0.025 min^{-1}.

3.4. Effect of catalyst concentration

The effect of catalyst intake on the initial LA reaction rate was studied by performing experiments with a variable catalyst intake at a fixed initial LA intake at base case conditions (Table 1). The experimental results, as shown in Fig. 7, suggest that the hydrogenation reaction is first order in catalyst for this hydrogenation system.
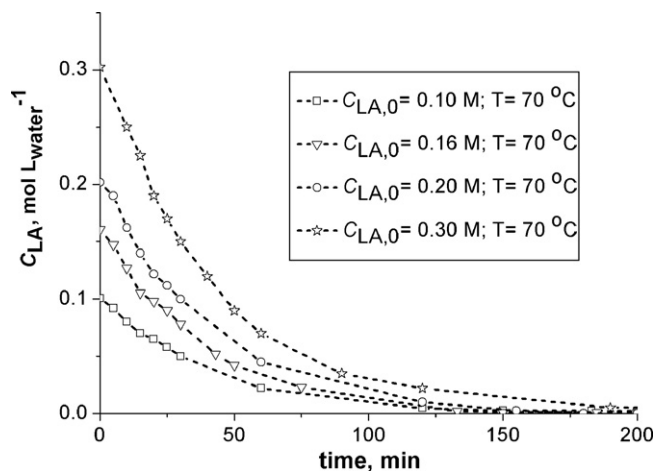

Fig. 5. LA concentrations in water versus time for various initial LA concentrations. *Conditions*: see Table 1 for base case conditions, except $T = 70\,^\circ C$. Lines are for illustrative purposes only.
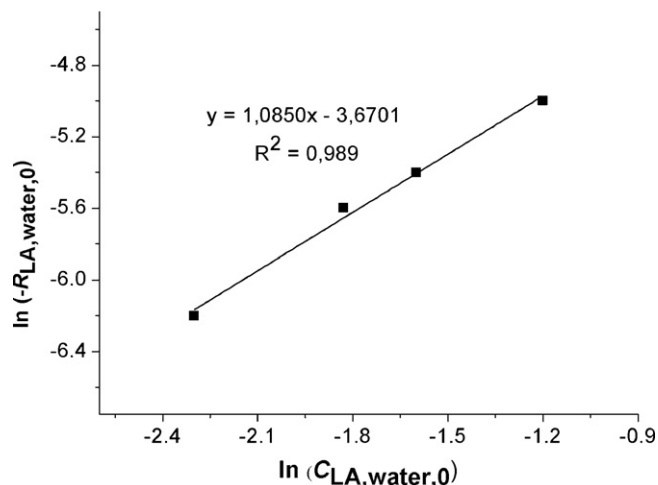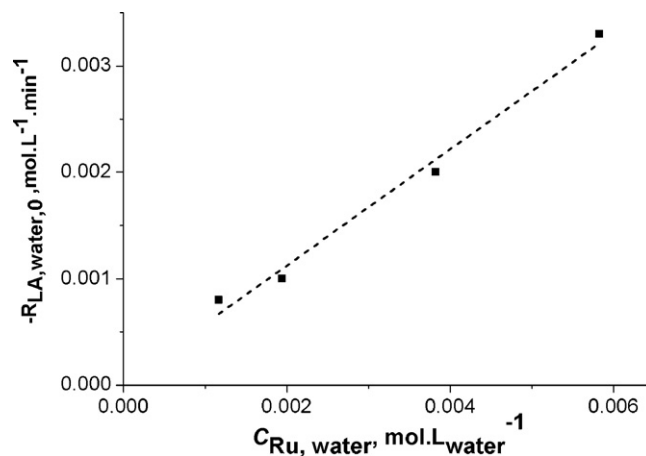

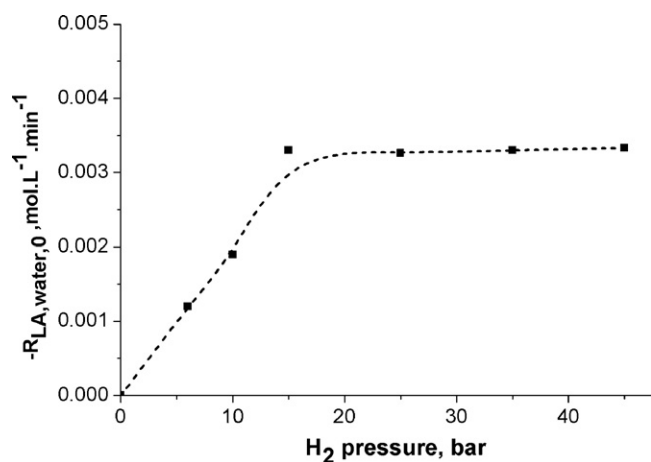**Fig. 7.** Effect of the catalyst intake on the initial rate of LA at base case conditions (Table 1).

Fig. 8. Effect of hydrogen pressure on the initial rate at base case conditions (Table 1).

3.5. Effect of hydrogen pressure

Six experiments with hydrogen pressures ranging from 5 to 45 bar were performed at base case conditions (Table 1) to determine the effect of hydrogen on the initial reaction rate of LA. The results are given in Fig. 8. The figure indicates that the initial reaction rate of LA is independent of the hydrogen pressure when the pressure exceeds 15 bar. At lower pressures, a first order dependency is observed. Similar saturation kinetics has been observed for related hydrogenations using homogeneous Ru-catalyst systems [36].

3.6. Effect of the pH of the aqueous phase

A number of experiments in buffer solutions at different pH values in the range 7–11 were performed while keeping all other conditions at base case conditions (Table 1). The results are given in Fig. 9 for a 1 h reaction time. Clearly the conversion of LA is a function of the pH and the highest conversions were found at pH = 11. The pH of the aqueous phase for biphasic organic-aqueous phase hydrogenations with water soluble Ru-based catalysts is known to affect the catalytic activity and selectivity of the reactions. For instance, Joo et al. [37] showed that the rate and selectivity of the hydrogenation reaction of unsaturated aldehydes using well defined Ru–TPPTS compounds is a strong function of the pH of
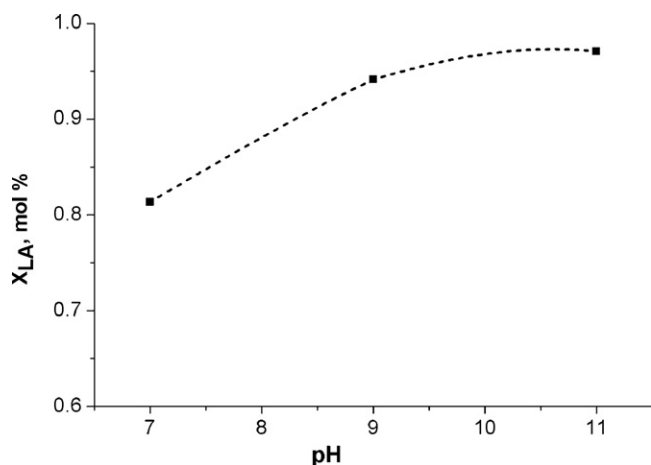

Fig. 9. Conversion of LA after 1 h as a function of the pH. Conditions: see Table 1 for base case conditions.
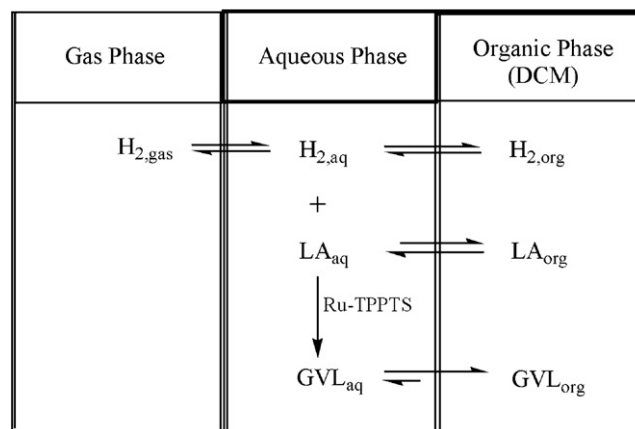

Fig. 10. Schematic representation of the biphasic hydrogenation of LA with the water-soluble Ru–TPPTS catalyst.

the solution. These findings were rationalized by assuming the existence of various Ru complexes in solution, of which the concentration is a function of the pH. However, other studies suggest that the reactions are not catalysed by homogeneous Ru-species but by Ru-colloids [38]. The rate of colloid formation is assumed to be a function of the pH. In addition, the pH will also affect the distribution of LA between the organic and water phase and this may also affect the overall reaction rate. Further studies, beyond the scope of this paper, will be required to draw definite conclusions on the origin of pH effects on catalytic performance.

3.7. Kinetic modeling

A kinetic model was developed for the biphasic hydrogenation of LA to GVL in water/DCM using the Ru–TPPTS catalyst on the basis of the following considerations and assumptions:

1. It is assumed that the water phase is the reactive phase and the organic phase the transport phase. This is rationalised by the high solubility of the Ru–TPPTS catalyst in water [28,39]. The substrates and product participate between the two liquid phases, see Fig. 10 for a schematic representation.
2. To avoid possible mass transfer effects and to measure intrinsic kinetics, all experiments were performed at an agitation rate of 2000 rpm (Fig. 2).
3. The reaction rate for the hydrogenation of LA in the water phase is expressed by the following general equation:

$$R_{LA,water} = -kC_{LA,water}^{\alpha}P_{H_2,water}^{\beta} \tag{12}$$

where α and β are the reaction order in LA and H_2, respectively.

The reaction rate constant is defined in terms of a modified Arrhenius equation which combines both the effects of temperature and the Ru–TPPTS concentration:

$$k = C_{RuTPPTS}^{\gamma}k_R \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{13}$$

Here k_R is the kinetic constant at reference temperature T_R, arbitrarily set at 70 °C, and γ the order in catalyst.

The orders in LA and catalyst were determined experimentally (Figs. 6 and 7) and shown to be about 1. The kinetic experiments were carried out at constant hydrogen pressure (45 bar) through continuously feeding from a high pressure reservoir, meaning that the effect of hydrogen was not evaluated in the kinetic model. However, it was shown experimentally that the order in hydrogen is zero when the pressure exceeds 15 bar (Fig. 8). Thus, the kinetic model presented here is valid at hydrogen pressures above 15 bar.

Table 2
Estimated kinetic parameters for the biphasic hydrogenation of LA with Ru–TPPTS.[a]

Parameter	Estimate
E_a (kJ mol^{-1})	61 ± 2
k_R (l$_{aq}$ mol^{-1} min^{-1})	64 ± 1

[a] Reference temperature (T_R) of 70 °C.

A more extensive model, including a more complex relation for the hydrogen pressure will be required to model the complete pressure range.

With the orders in substrates and catalyst taken into account, Eqs. (12) and (13) simplify to Eqs. (14) and (15):

$$R_{LA,water} = -kC_{LA,water} \tag{14}$$

$$k = C_{Ru\,TPPTS}k_R \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{15}$$

A mass balance equation for LA in the waterphase for a batch reactor (Eq. (16)) completes the mathematical description of the model:

$$\frac{dC_{LA,water}}{dt} = R_{LA,water} \tag{16}$$

The kinetic model is set up for the waterphase and involves LA waterphase concentrations. LA is expected to distribute between both phases. The partitioning coefficients of LA and GVL (m_i with i = LA and GVL) as a function of the temperature (50–115 °C) were determined experimentally for the water–DCM system.

Here m_i is defined as

$$m_i = \frac{C_{i,DCM}}{C_{i,water}} \tag{17}$$

Within the experimental window, good linear correlations were observed for the equilibrium concentrations of LA in water and dichloromethane. The experimental values for m_{LA} are between 0.9 and 2.2 and indicate that LA has affinity for both phases. Similar experiments were performed for GVL. The amount of GVL in the water phase of the water–DCM biphasic system appeared to be very low and the value of m is below 10^{-6} in the experimental temperature range. Thus, it is assumed that GVL is not present in the water phase.

To determine the kinetic parameters, a total of 6 batch experiments were performed at 50, 70 and 90 °C at different initial LA concentrations, giving a total of 76 data points. All other conditions were as for the base case given in Table 1. The experimental concentration profiles were modeled using Eqs. (14), (15) and (16) using the Matlab® programming platform. The optimized kinetic parameters and their 95% confidence limits are shown in Table 2. Agreement between model and experiment is good, as is clearly seen when comparing the experimental and the modeled data (Fig. 11). The value of the activation energy (61 kJ/mol) implies that the kinetic data are not biased by mass transfer effects. In such cases, activation energies below 20–30 kJ/mol are expected [40].

3.8. Catalyst recycling

The feasibility for catalyst recycling was determined by performing a hydrogenation experiment at standard conditions (Table 1). The LA conversion after 1 h was 81%. The aqueous phase with catalysts was separated from the organic phase and charged to the reactor together with a fresh solution of LA in DCM. The LA conversion after the second run at standard conditions (Table 1) was 55%. This value is considerably lower than for the first run, though clearly indicates the proof of concept for catalyst recycle. Further optimization experiments (i.e. experiments at lower temperatures to avoid catalyst deactivation during a run and work-up
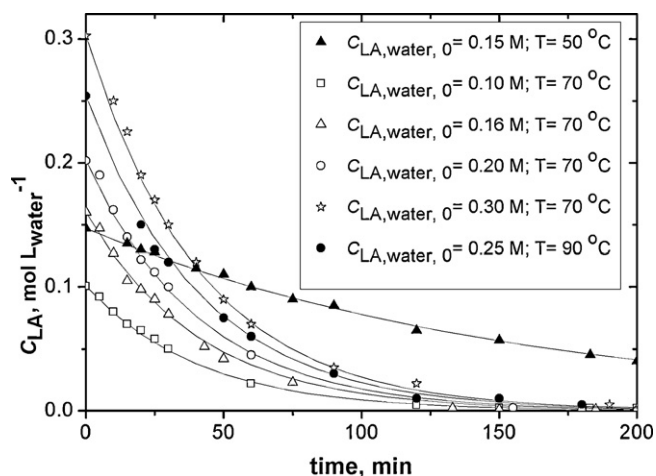
Fig. 11. Experimental and modeling results for the hydrogenation of LA. *Conditions*: see Table 1 for base case conditions at various temperatures and substrate concentrations.

of the aqueous phase after reaction under the rigorous exclusion of air) will be required to improve the recyclability.

4. Conclusions

It has been shown that biphasic catalysis in a DCM/water mixture using a homogeneous Ru-catalyst made *in situ* from RuCl$_3$·3H$_2$O and Na$_3$TPPTS allows the synthesis of GVL in near quantitative yields at mild conditions. Catalyst recycle by phase separation is possible, though further studies are required to reduce loss of activity in subsequent recycles and to become an attractive alternative for conventional heterogeneous catalysts like Ru/C. The kinetics in the biphasic system were determined using chemical reaction engineering models and it was shown that the reaction is first order in LA, zero order hydrogen in hydrogen at hydrogen pressures above 15 bar and first order below 15 bar.

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