Hydrogenation of fast pyrolyis oil and model compounds in a two-phase aqueous organic system using homogeneous ruthenium catalysts

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Abstract

The use of homogeneous ruthenium catalysts to hydrogenate the water-soluble fraction of pyrolysis oil is reported. Pyrolysis oil, which is obtained by fast pyrolysis of lignocellulosic biomass at 450–600 °C, contains significant amounts of aldehydes and ketones (e.g. 1-hydroxy-2-propanone (**1**) and 1-hydroxy-2-ethanal (**2**)), that are known to have a negative effect on the product properties (a.o. storage stability) of pyrolysis oil. The hydrogenation experiments were performed at mild conditions (40 bar, 90 °C) using a biphasic system (water/toluene) and $RuCl_2(PPh_3)_3$ as the toluene soluble catalyst. Significant reductions in the amounts of (**1**) and (**2**) were observed, demonstrating the potential of homogeneous Ru-catalysts to upgrade pyrolysis oils. Model studies showed that (**1**) and (**2**) are selectively hydrogenated to 1,2-propanediol and 1,2-ethanediol, respectively. The influence of the temperature (50–90 °C), pressure (20–40 bar) and initial substrate concentration on the reaction rates were investigated. For (**2**), the reaction was shown to be first order in substrate and zero order in hydrogen. An overall kinetic model for the hydrogenation of (**2**) was developed including the rate of active catalyst formation and the kinetic parameters were determined.
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1. Introduction

Fast pyrolysis oil, also known as bio-oil (BO), is a promising second generation bio-fuel. It is accessible by rapid heating of lignocellulosic biomass like for instance wood, straw and rice husk at elevated temperatures (450–600 °C). Typically, reactor configurations with short residence times (0.1–5 s) are applied. The product is a low viscous, brown-red liquid with a distinct odour [1]. Its direct-application for heat and power generation has been proven successfully on semi-commercial scale [2–4]. However, upgrading is required before the material can be applied as a liquid transportation fuel for in-stationary internal combustion engines. The objective of upgrading is to increase the caloric value of the product by reducing the oxygen content and to improve storage stability by reducing the levels of very reactive compounds like aldehydes.

Typical upgrading technologies for fossil oil like hydrodeoxygenation and hydrocracking have been applied to upgrade BO [1,5–7]. Promising results were obtained with classical hydrotreatment catalysts like NiMo and CoMo on alumina and hydrocarbon like products with a high caloric value and good storage stability were obtained [7–11]. However, severe process conditions are required ($P = 150$–200 bar; $T = 300$–400 °C), catalyst deactivation may be substantial and hydrogen consumption is excessive [12].

It is well established that homogeneous catalysts generally perform at much milder process conditions than typical heterogeneous catalysts [13]. We have recently shown that a homogenous water-soluble ruthenium catalyst ($RuCl_3$-TPPTS, TPPTS: triphenylphospine tris-sulphonate) is capable of hydrodeoxygenating BO model compounds (e.g. vanillin) at mild conditions ($P = 45$ bar hydrogen; $T = 45$ °C) [14]. A liquid–liquid (L–L) biphasic system is used to circumvent catalyst-product separation after the reaction.

We envisaged that this biphasic concept using a homogeneous catalyst might also be applicable to hydrogenate the water-soluble fraction of pyrolysis oil. This fraction contains

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Nomenclature

C_{cat}	catalyst precursor concentration (mol $L_{toluene}^{-1}$)
C_{cat*}	active catalyst concentration (mol $L_{toluene}^{-1}$)
C_1	acetol (**1**) concentration (mol L_{aq}^{-1})
C_2	hydroxyacetaldehyde (**2**) concentration (mol L_{aq}^{-1})
$C_{2,0}$	initial hydroxyacetaldehyde (**2**) concentration (mol L_{aq}^{-1})
Ea_{act}	activation energy for catalyst activation (kJ mol^{-1})
Ea_{R_2}	activation energy for the hydrogenation of **2** (kJ mol^{-1})
k_{act}	pseudo first order rate constant for catalyst activation (min^{-1})
k_R	kinetic constant of the hydrogenation of **2** at $T = T_R$ (min^{-1})
k'_{act}	actual rate constant for catalyst activation (min^{-1} bar^{-1})
k_2	kinetic constant of the hydrogenation of **2** (min^{-1})
P_{H_2}	hydrogen pressure (bar)
R	ideal gas constant, 8.314 J mol^{-1} K^{-1} (J mol^{-1} K^{-1})
R_{cat*}	reaction rate of catalyst activation (mol L^{-1} min^{-1})
R_2	reaction rate of the hydrogenation of **2** (mol L^{-1} min^{-1})
t	reaction time (min)
T_R	reference temperature, 353 (K)
X_i	conversion of component i

Greek symbols

α	order of reaction in **2**
β	order of reaction in hydrogen

significant amounts of highly reactive oxygenated compounds [15–17]. Hydrotreatment may lead to reduction in the oxygen content and thus an improvement in the caloric value. In addition, the water-soluble fraction also contains significant amounts of reactive aldehydes, e.g. 1-hydroxy-2-ethanal (hydroxyacetaldehyde), that are expected to have a negative influence on the storage stability of pyrolysis liquid due to reactions with a.o. lignin derived phenolics. RuCl$_2$(PPh$_3$)$_3$ was selected as the homogeneous, organic soluble catalyst of choice. This compound is known to be an outstanding catalyst for aldehyde and ketone reductions in homogeneous, single phase systems [18]. To the best of our knowledge, the catalyst has not been applied in a biphasic water/organic systems to hydrogenate water-soluble substrates [19–27].

Pyrolysis oil is a complex mixture of organic molecules and up to 400 different compounds have been identified in the matrix [28]. Therefore, we initially focused on the hydrogenation of water-soluble pyrolysis oil model compounds to gain information on the reaction rates and product composition. 1-Hydroxy-2-propanone (acetol, **1**) and 1-hydroxy-2-ethanal

(hydroxyacetaldehyde, **2**), were selected as both are present in pyrolysis liquid in considerable amounts [28]. The influence of temperature (50–90 °C), pressure (20–40 bar) and initial concentration of the reactants on the reaction rate was studied and a kinetic model for the hydrogenation of **2** was developed. Subsequently, the potential of the biphasic homogeneous catalytic system to hydrogenate the water-soluble fraction of pyrolysis oil was investigated.

2. Experimental

2.1. Chemicals

All chemicals were used as received: Tris(triphenylphosphine)-ruthenium(II)dichloride (98%, Acros), acetol (1-hydroxy-2-propanone in water, 90 wt.%, Sigma–Aldrich), hydroxyacetaldehyde (in the form of glycolaldehyde dimer, 99%, Sigma–Aldrich), 1,2-propanediol (99%, Merck), 1,2-ethanediol (99%, Merck), ethanol (analytical grade, Merck), toluene (>99%, Acros), nitrogen (Aga Gas BV) and hydrogen (99% Hoekloos). Fast pyrolysis oil was obtained from the Biomass Technology Group (BTG), Enschede, The Netherlands and used as received. The oil was prepared from beech wood and was produced using rotating cone flash pyrolysis technology [29].

2.2. Product analysis

GC analyses were carried out on a HP 5890 GC equipped with a flame ionization detector (FID) and an Altech (EC-1000) polar capillary column using a split ratio of 1:50. The injection and detector temperature were 280 °C and 300 °C, respectively. A heating program from 100 °C to 200 °C with a rate of 20 °C per minute was applied. The reaction products (1,2-propanediol and 1,2-ethanediol) were identified by comparing the retention time with that of the pure components.

Quantification of compounds **1**–**4** was done by GC. Ethanol was used as an internal standard. The concentration of the various components was determined using calibration lines.

^{1}H and ^{13}C NMR spectra were recorded on a Varian AMS 200 spectrometer using D$_2$O as the solvent. The spectra were referenced to TMS ($\delta = 0$ ppm).

2.3. Identification of the components present in the water-soluble fraction of pyrolysis oil

BO (1 mL) was mixed with D$_2$O (2 mL) at room temperature. The resulting turbid suspension was centrifuged for 15 min at 1000 rpm. The transparent brown liquid was separated from the brown solid and analyzed using ^{1}H and ^{13}C NMR.

2.4. Hydrogenation of model compounds

All hydrogenation experiments were conducted in a 350 mL stainless steel batch autoclave equipped with an electrical heating jacket and a mechanical overhead stirrer with a gas entrainment impeller (Fig. 1). High stirring speeds were applied (1500–1800 rpm) to avoid mass transfer limitations. A typical
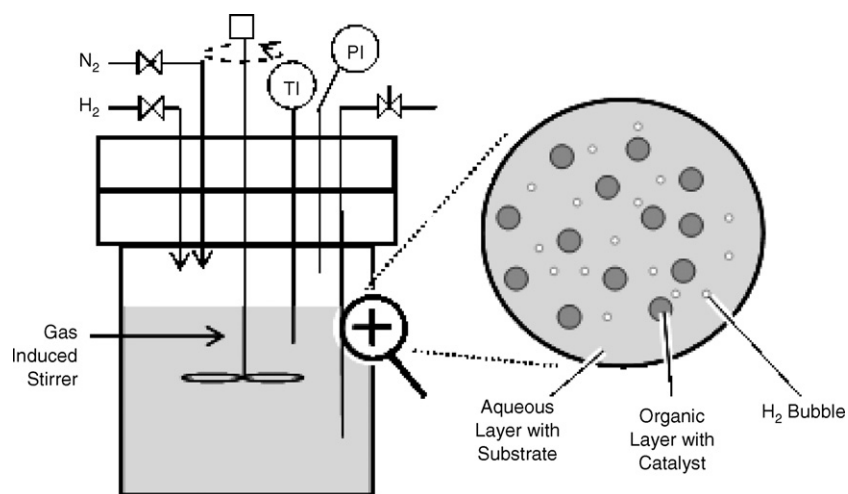
Fig. 1. Batch autoclave set-up (left) and a schematic representation of the G–L–L system (right). TI/PI = temperature/pressure indicator.

example of an hydrogenation experiment for **2** (entry 1 in Table 1) is provided below.

The autoclave was charged with **2** (0.3 g, 5 mmol), $RuCl_2(PPh_3)_3$ (0.16 g, 0.167 mmol), demi-water (165 mL) and toluene (45 mL). Prior to hydrogen addition, the autoclave was flushed three times with nitrogen to remove oxygen from the set-up. Subsequently, hydrogen was added until a pressure of 5 bar was reached. The reactor was heated to 90 °C. Subsequently, the hydrogen pressure inside the reactor was increased to 40 bar. During reaction, samples (1 mL) were taken from the reactor using a dip-tube. The liquid layers were separated and the composition of the water layer was determined using GC and NMR.

A range of experiments was carried out with temperatures in the range of 50–90 °C and pressures between 20 bar and 40 bar. Typical reaction times were 24–48 h for the hydrogenations of **1** and 120–420 min for the hydrogenation of **2**.

During all hydrogenation experiments, the pressure drop was less than 3% of the original value.

2.5. Isolation of the water-soluble fraction of fast pyrolysis oil

BO (3.5 g) was added under vigorous stirring to water (55 mL) at room temperature. The resulting turbid, milky-brown mixture was centrifuged for 1 h at 2000 rpm. The brown transparent top layer (35 mL) was separated from the residue and used as a substrate for the hydrogenation reaction.

2.6. Hydrogenation of the water-soluble fraction of fast pyrolysis oil

Hydrogenations were carried out in the batch set-up described above (Fig. 1). The reactor was loaded with the water-soluble fraction of pyrolysis oil (35 mL), water (130 mL), toluene (45 mL) and catalyst (0.16 g, 0.167 mmol). The mixture was stirred for 5 h at 40 bar, 90 °C and applying an agitating speed of 1500 rpm. After 5 h, the hydrogen was released and the reactor content was cooled down to room temperature. Subsequently, the organic layer and the yellow transparent water layer were separated. The water was removed at reduced pressure (70 °C, 200 mbar). The resulting brown liquid was analyzed by NMR (D_2O).

2.7. Kinetic modeling

The kinetic parameters were determined using the Scientist® software package. An error controlled fourth order Runge–Kutta numerical method was applied to solve the differential

Table 1
Overview of experiments for the hydrogenation of aldehyde **2**[a]

Entry	$C_{2,0}$[b] (mol L^{-1})	P (bar)	T (°C)	Catalyst intake (g)	Reaction time (total) (min)	Conversion of **2** (after t min) (mol%)
1	0.03	40	90	0.16	240	62 (30 min)
2	0.015	40	90	0.16	150	66 (30 min)
3	0.06	40	90	0.16	180	58 (30 min)
4	0.08	40	90	0.16	240	54 (30 min)
5	0.03	40	80	0.16	325	54 (40 min)
6	0.03	40	60	0.16	240	<1 (40 min)
7	0.06	40	50	0.16	220	2 (40 min)
8	0.03	20	90	0.16	120	64 (30 min)
9	0.03	40	90	0.32	420	66 (30 min)

[a] All experiments were performed in a batch set-up using a stirrer speed of 1500 rpm.
[b] Initial concentration of **2**.

equations. Error minimization to determine the best estimate of the kinetic parameters was performed using a simplex algorithm followed by a least squares minimization.

3. Results and discussion

In the first stage of this study, the hydrogenation of the water-soluble model compounds 1-hydroxy-2-propanone (acetol, **1**) and 1-hydroxy-2-ethanal (hydroxyacetaldehyde, **2**) was investigated in a biphasic system (toluene and water, 3.7:1 vol. ratio) with $RuCl_2(PPh_3)_3$ as the toluene soluble catalyst in a batch reactor set-up.

3.1. Hydrogenation of 1-hydroxy-2-propanone (acetol, 1)

The reaction of **1** (40 bar of hydrogen, 80 °C and using 1.1 mol% of catalyst) resulted in the selective formation of 1,2-propanediol (**3**) (GC and NMR, Eq. (1)).

$$\text{(1)} \quad + H_2 \xrightarrow{RuCl_2(PPh_3)_3} \text{(3)} \tag{1}$$
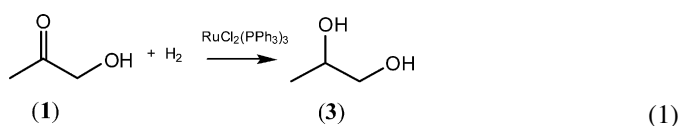
No traces of 1-propanol were detected, implying that the catalyst system is not capable of hydrodeoxygenating acetol to 1-propanol under these conditions. Hydrogenation products of toluene like methylcyclohexane were also not detected, in line with earlier studies using $RuCl_2(PPh_3)_3$ as a hydrogenation catalyst in toluene [30].

The hydrogenation reaction is relatively slow and the conversion of **1** was limited to about 10% after 16.5 h reaction time at 80 °C. Higher conversions are possible by adjusting the process parameters (*vide infra*).

Biphasic hydrogenation of ketones using Ru-catalyst have been reported in the literature [31–34]. However, in these cases, the Ru catalyst resides in the water phase by application of water-soluble phosphine ligands like Na_3TPPTS and the substrate is present in the organic phase. To best of our knowledge, hydrogenation of water-soluble substrates using a L–L system with an organic soluble $RuCl_2(PPh_3)_3$ catalyst has not been reported to date. Our results show that conversion of water-soluble ketones is well possible in biphasic systems using organic soluble homogeneous transition metal catalysts.

3.2. Effect of process conditions on the ruthenium catalyzed hydrogenation of 1

The effect of process conditions (pressure, temperature, reaction time) on the reaction rate for the conversion of **1** to 1,2-propanediol (**3**) was investigated in more detail. For all experiments, 1.1 mol% of catalyst was applied while the concentration of **1** was 0.09 mol L^{-1} water.

The influence of temperature was studied in the range 30–80 °C (40 bar, 16.5 h reaction time) and the results are given in Fig. 2. As expected, higher temperatures lead to higher conversions. The selectivity of the reaction is independent of the
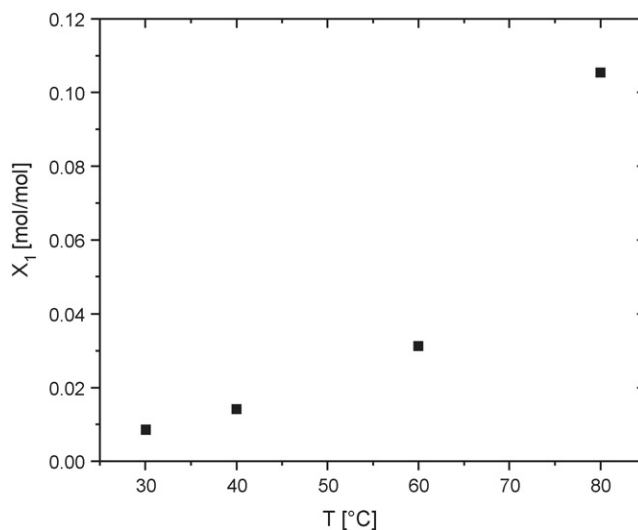

Fig. 2. Temperature influence on X_1. Conditions: $P = 40$ bar, agitation speed = 1800 rpm, reaction time = 16.5 h.

temperature and 1,2-propanediol was the sole reaction product identified after reaction.

The influence of the hydrogen pressure on the conversion of **1** was studied in the range of 10–40 bar, a fixed temperature of 80 °C and 16.5 h reaction time. The conversion of **1** is essentially independent of the hydrogen pressure, see Fig. 3 for details.

A number of experiments were performed using prolonged reaction times ($T = 60$ °C, $P = 40$ bar, agitation speed = 1500 rpm, $C_{1,0} = 0.09$ mol L^{-1}). Conversions of up to 22% could be obtained after 70 h, see Fig. 4 for details. This implies that, although the catalyst is rather slow, it is remarkably stable under these conditions.
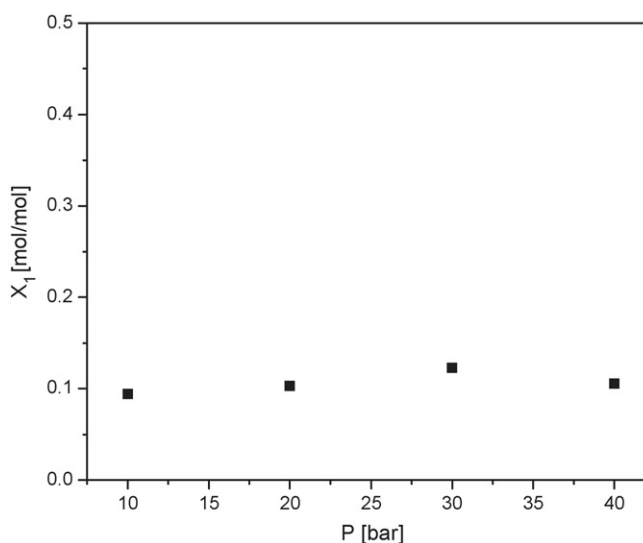

Fig. 3. Pressure influence on X_1. Conditions: $T = 80$ °C, agitation speed = 1800 rpm, reaction time = 16.5 h.
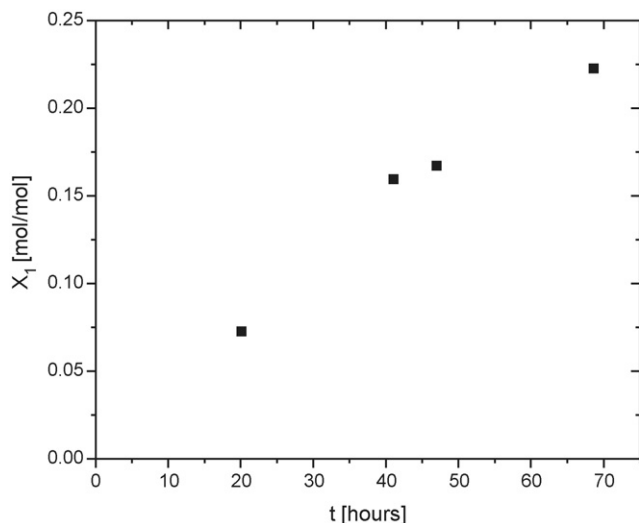
Fig. 4. Acetol conversion as a function of time. Conditions: $T = 60\,°C$, $P = 40$ bar, agitation speed = 1500 rpm, $C_{1,0} = 0.09$ mol L^{-1}.

3.3. Hydrogenation of 1-hydroxy-2-ethanal (hydroxyacetaldehyde, 2)

Catalytic hydrogenations of 1-hydroxy-2-ethanal (hydroxyacetaldehyde or glycolaldehyde, **2**) using the homogeneous RuCl$_2$(PPh$_3$)$_3$ catalyst were carried out in a batch reactor set-up ($T = 90\,°C$, $P = 40$ bar, 3.3 mol% RuCl$_2$(PPh$_3$)$_3$, water/toluene in a 3.7:1 vol. ratio and a substrate concentration of 0.03 mol L^{-1}). **2** is highly soluble in water (600 g/L at 25 °C) and resides in the aqueous phase. Whereas **2** is dimeric in the solid state [35], a variety of compounds is formed when **2** is dissolved in water [35,36]. For simplicity, **2** is represented as the monomeric aldehyde throughout this paper.

Using the aforementioned screening condition, **2** was selectively hydrogenated to 1,2-ethanediol (**4**) (GC, NMR, Eq. (2)).

$$ (2) $$
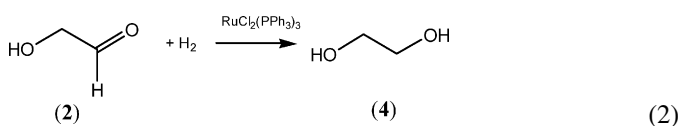
Hydrogenation of the solvent toluene did not occur under these conditions as is evident from the absence of hydrogenation products (GC).

In addition, ethanol could not be detected in the reaction mixture, implying that hydrodeoxygenation of the aldehyde functionality to a saturated hydrocarbon does not occur under these conditions. This is in marked contrast with the results obtained when hydrogenating an aromatic aldehyde like vanillin using a related Ru-catalyst (RuCl$_3$/TPPTS) [14]. Here, the main product was creosol, see Eq. (3):
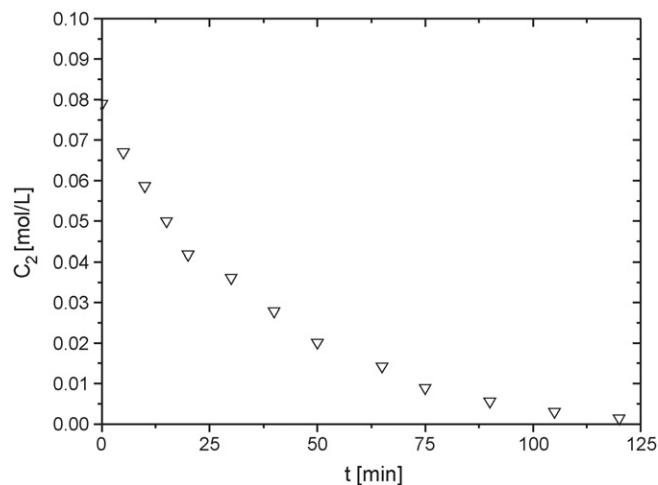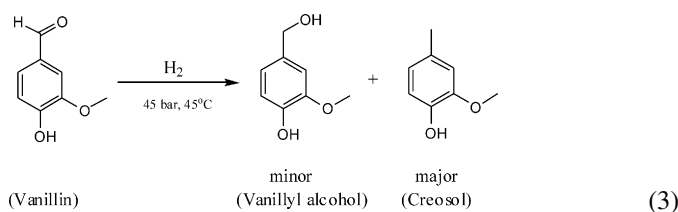

$$ (3) $$

Fig. 5. Typical concentration profile of **2** during the hydrogenation reaction. Conditions: $C_{2,0} = 0.08$ M, $T = 90\,°C$, agitation speed = 1500 rpm.

Apparently, hydrodeoxygenation activity by these homogeneous Ru-catalysts is restricted to aromatic aldehydes like vanillin only.

For one of the batch experiments, the concentration of **2** was measured by periodically taking samples from the hydrogenation mixture. A typical conversion–time graph is given in Fig. 5. Typically, full conversion of **2** is observed within 120 min of reaction time. This is in marked contrast with the results obtained for the ketone **1**, for which much lower activities were observed at similar conditions. These findings are in line with hydrogenation experiments by Kalck et al. using cinammaldehyde and benzyl acetone as the substrates and a Ru-TPPTS complex as the catalysts. It was shown that aldehydes are much more reactive than ketones [32].

3.4. Effects of acetic acid on catalyst performance

Fast pyrolysis oil contains up to 10 wt.% of acetic acid [28]. The presence of this acid may influence catalytic performance of the Ru-catalyst by a.o. anion exchange reactions and the formation of Ru-acetate species [37]. To probe the effects of the presence of acetic acid, a number of experiments were performed for substrate **2** in the presence of acetic acid (0.025 g, equal to a molar Ru to acetic acid ratio of 1:2.5, $T = 90\,°C$, $P = 40$ bar). The Ru-acetic acid molar ratio corresponds to the ratio applied in the hydrogenation experiments of fast pyrolysis oil using the RuCl$_2$(PPh$_3$)$_3$ catalyst (*vide infra*). The results are provided in Fig. 6. Evidently, the catalyst is still active in the presence of acetic acid, although activity is slightly lowered. Furthermore, the selectivity is also unchanged and 1,2-ethanediol is the sole product. The results imply that hydrogenation of **2** in the complex pyrolysis oil matrix with acetic acid present should be feasible using the selected catalyst (*vide infra*).

3.5. Effect of process conditions on the hydrogenation of 2

A number of experiments were performed to determine the effects of process conditions (initial concentration, temperature,
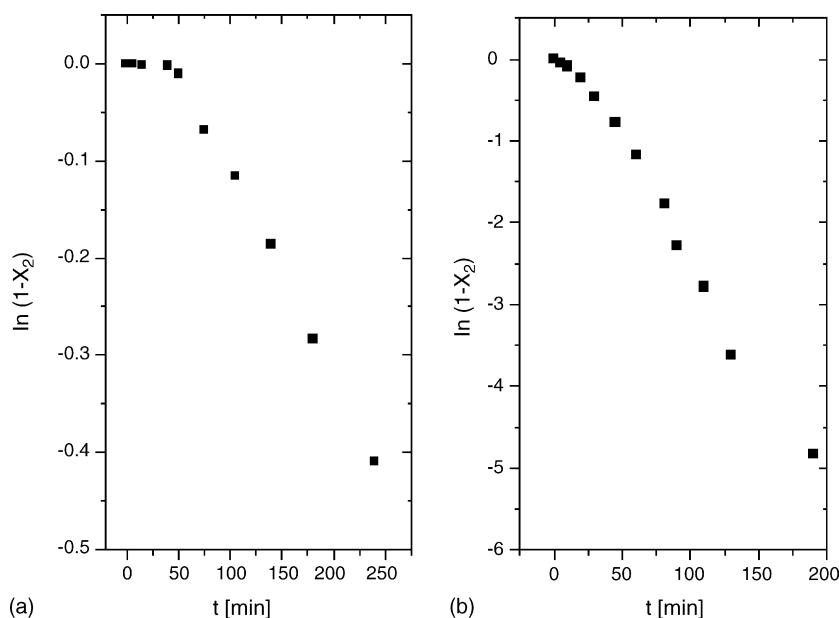
Fig. 6. Concentration of **2** without and with the presence of HOAc. (■) $W_{HOAc} = 0$ g; (○) $W_{HOAc} = 0.025$ g. Conditions: $P = 40$ bar, $T = 90\,^{\circ}$C, agitating speed = 1500 rpm.

Fig. 8. Product concentration (**4**) vs. time at different temperatures. Legends: (■) $90\,^{\circ}$C; (○) $80\,^{\circ}$C; (△) $60\,^{\circ}$C (entries 1, 5 and 6, respectively in Table 1).

hydrogen pressure) on the reaction rates for the hydrogenation of **2**. With this information, it is possible to determine the optimum process conditions for the hydrogenation of **2** to **4**. In addition, the data were applied to develop an overall kinetic model for the reaction. An overview of the experiments is given in Table 1.

The effect of hydrogen pressure on the reaction rate was determined at $90\,^{\circ}$C using two different pressures (20 and 40 bar, Table 1, entries 1 and 8). The results are given in Fig. 7. Apparently, the pressure does not have a profound effect on the kinetics when performing the reaction at $90\,^{\circ}$C, indicating that the reaction is zero order in hydrogen. These findings are in line with the results for acetol hydrogenation (*vide supra*).

The effect of temperature on catalyst performance was investigated in a temperature range of 60–$90\,^{\circ}$C. All other variables were kept constant (Table 1, entries 1, 5–6). The results are graphically provided in Fig. 8. Evidently, the highest reaction rates were observed at the highest temperature. Remarkably, a

lag time was observed when the reaction was performed at $60\,^{\circ}$C and significant amounts of product was formed only after 50 min of reaction time. This suggest that active catalyst formation from the catalyst precursor $RuCl_2(PPh_3)_3$ and hydrogen is relatively slow at $60\,^{\circ}$C (Scheme 1, *vide infra*).

The effect of the initial concentration of **2** on the rate of the hydrogenation reaction was probed by varying the concentration between 0.015 and 0.08 mol L^{-1} while keeping all other conditions at constant values (Table 1, entries 1–4). The conversion was found between 54 and 66%.

To gain insights in the order of the hydrogenation reaction in **2**, the concentration–time curves were linearised. In case the reaction is first order in **2**, a plot of $\ln(1 - X_2)$ versus the batch time is expected to lead to a linear dependency. The results of two experiments (entries 5 and 6 in Table 1) are provided in Fig. 9. In both cases, two distinct regimes are observed. At prolonged reaction times, a clear linear relation is observed, indicating first order behavior. However, at low reaction times the reactions are much slower than anticipated on the basis of first order behavior. This effect is most likely related to active catalyst formation from the catalyst precursor (Scheme 1). It is well possible that active catalyst formation by the reaction of $RuCl_2(PPh_3)_3$ with hydrogen is relatively slow and occurs on a similar time scale as the actual hydrogenation of the substrate. This explanation is also supported by the observation that first order behavior is obtained more rapidly at higher temperatures, viz. 20 min at $80\,^{\circ}$C and about 50 min at $60\,^{\circ}$C (Fig. 8).

Fig. 7. Concentration of **2** vs. time at two different pressures. (■) $P = 20$ bar; (○) $P = 40$ bar (entries 8 and 1, respectively, in Table 1), $T = 90\,^{\circ}$C.

Catalyst Activation

$RuCl_2(PPh_3)_3 + H_2 \rightarrow RuHCl(PPh_3)_3 + HCl$

Reaction with Substrate

Scheme 1.

Fig. 9. $\ln(1 - X_2)$ vs. the reaction time. Conditions: (a) $T = 60\,°C$, (b) $T = 80\,°C$, $C_{2,0} = 0.03$ M (entries 6 and 5, respectively, in Table 1).

3.6. Mechanistic aspects

Grosselin et al. [38] have proposed a catalytic cycle (Fig. 10) for the hydrogenation of aldehydes using water-soluble homogeneous ruthenium(II) complexes. A similar catalytic cycle is proposed here. In the first step, the catalyst precursor $RuCl_2(PPh_3)_3$ is converted to the active catalyst, $RuHCl(PPh_3)_3$, by reaction with hydrogen. Subsequent coordination of the aldehyde to the metal center followed by an insertion of the C=O double bond
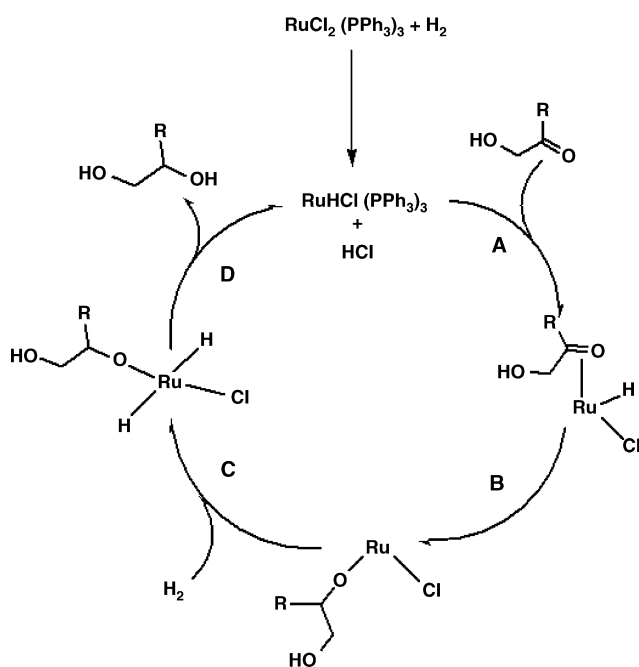
Fig. 10. Proposed catalytic cycle for the hydrogenation of **1** and **2** using $RuCl_2(PPh_3)_3$ R = CH$_3$ (**1**) or H (**2**); for clarity, phosphine ligands are omitted.

in the Ru–H bond produces a Ru-alkoxide species. Addition of hydrogen followed by reductive elimination results in the formation of the product, 1,2-ethanediol.

The experimental results described in the previous section provide insights in the importance of the various steps in the catalytic cycle. First of all, it was observed that, especially at low temperatures ($T < 60\,°C$), catalyst activation is relatively slow and has a major impact on the overall hydrogenation rate. Secondly, the reaction is first order in aldehyde **2** and zero order in hydrogen at conditions where catalyst activation is fast ($T > 70\,°C$). This implies that coordination/insertion of the aldehyde into a Ru–H species (step A/B in Fig. 10) is the rate determining step in the catalytic cycle.

A number of kinetic studies have been performed on the ruthenium catalysed hydrogenation of aldehydes, both in homogeneous as well as in biphasic systems. The order in both substrate (S) and hydrogen was found to vary between 0 and 1, see Table 2 for details.

On the basis of these kinetic data, it is well possible that both hydrogen and substrate display saturation kinetics, i.e. a first order dependency at low concentrations and zero order dependency at higher concentrations. This suggests that the overall rate law for Ru-catalysed aldehyde concentrations may be expressed as the product of two saturation terms (Eq. (4)):

$$R_2 = -\frac{k_1[\text{cat}][\text{S}]P_{H_2}}{(1 + k_2[\text{S}])(1 + k_3 P_{H_2})} \tag{4}$$

The observed order in substrate and hydrogen will depend on the value of the terms $k_2[\text{S}]$ and $k_3 P_{H_2}$ compared to 1. In case both terms are much smaller than 1, the reactions are first order in hydrogen and substrate whereas the order becomes zero when both terms are much larger than 1. Evidently, mixed combinations are possible as well. Apparently, the reported kinetic studies have all been performed in different regimes

Table 2
Kinetic data for aldehyde hydrogenations using homogeneous Ru-catalysts

Substrate	Catalyst	Solvent	Order in substrate	Order in H_2	Reference
Crotonic acid	$HRu(TPPTS)_3$	Water	1 at low [S] 0 at high [S]	1	[39]
Propionaldehyde	$(RuCl_2(TPPTS)_2)_2$	Water	1	1	[40]
Cinnamaldehyde	$RuCl_3/PPh_3$	DMF	1	1 at low P_{H_2}	[41]
		NMP	0	0 at high P_{H_2}	
Cinnamaldehyde	$RuCl_3/TPPTS$	Biphasic	0	1	[38]

leading to orders in substrate and hydrogen ranging between 0 and 1.

3.7. Development of an overall kinetic model for the hydrogenation of 2

An overall kinetic model was developed for the hydrogenation of **2**. Both catalyst activation and the main reaction were taken into account (Scheme 1). Pressure effects were not considered and only experiments at 40 bar were used as the basis for the model (Table 1, entries 1–6 and 8–9).

When assuming elementary kinetics for catalyst activation, the rate expression for the formation of active catalyst reads:

$$R_{cat^*} = k'_{act} C_{cat} P_{H_2} \tag{5}$$

Here, R_{cat^*} is the rate of formation of the active catalyst (cat*) by reaction of $RuCl_2(PPh_3)_3$ (cat) with H_2 (Scheme 1). At constant pressure, this relation reduces to:

$$R_{cat^*} = k_{act} C_{cat} \tag{6}$$

The reaction rate of the main reaction may be expressed as

$$R_2 = -k_2 C_{cat^*} C_2^\alpha P_{H_2}^\beta \tag{7}$$

where α and β are the order in **2** and H_2, respectively. The reaction is first order in **2** (*vide supra*) and when performing the reaction at a fixed and constant pressure of 40 bar, β equals zero.

The effect of temperature on the kinetic constants k_{act} and k_2 are expressed in terms of modified Arrhenius equations:

$$k_{act} = k_{act,R} \exp\left[-\frac{Ea_{act}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{8}$$

$$k_2 = k_{2,R} \exp\left[-\frac{Ea_2}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{9}$$

where T_R is the reference temperature, arbitrarily set at 80 °C, and $k_{act,R}$ and $k_{2,R}$ are the kinetic constants at the reference temperature for catalyst activation and the main hydrogenation reaction, respectively.

When performing the reaction in a batch set-up, the concentrations of **2** and active catalyst (cat*) may be represented as follows:

$$\frac{dC_{cat^*}}{dt} = R_{cat^*} \tag{10}$$

$$\frac{dC_2}{dt} = R_2 \tag{11}$$

Table 3
Estimated kinetic parameters for the hydrogenation of **2** using $RuCl_2(PPh_3)_3$

Parameter	Estimate
Ea$_{act}$ (kJ/mol)	81 ± 17
Ea$_2$ (kJ/mol)	80 ± 6
$k_{act,R}$ (min^{-1})[a]	0.18 ± 0.04
$k_{2,R}$ (M^{-1} min^{-1})[a]	4.1 ± 0.2

[a] The values were determined at a reference temperature (T_R) of 80 °C.

Eqs. (10) and (11), combined with (6)–(9), were the basis for the kinetic model and used to estimate the kinetic parameters.

3.8. Modeling results

The best estimates of the kinetic parameters ($k_{act,R}$, Ea$_{act}$, $k_{2,R}$ and Ea$_2$) were determined by minimization of the errors between all experimental datapoints and the kinetic model. The results are given in Table 3. The set consisted of 122 data points (8 experiments, with 13–21 samples per experiment). Comparisons of the experimental data and the output of the kinetic model show a good fit for a broad range of reaction condition (Fig. 11). A parity chart (Fig. 12) shows the goodness of fit between the experimental and model data.

The distinct differences in the shape of the profiles when going from 50 °C to 90 °C is related to the amount of active
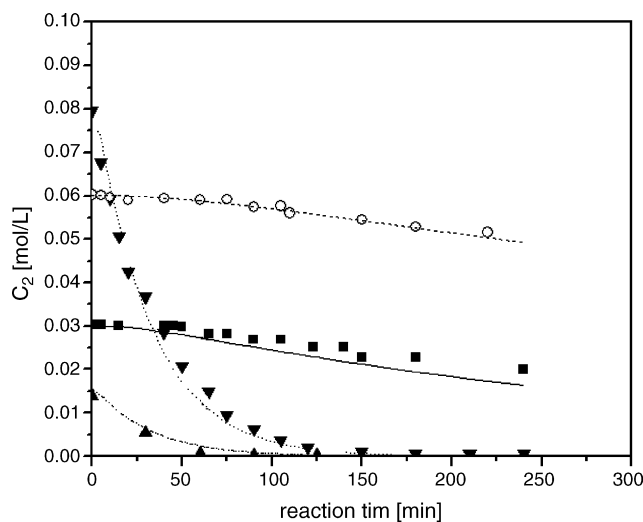

Fig. 11. Modeling results for the hydrogenation of **2** ($P = 40$ bar; agitation speed = 1500 rpm). Legends: (▲) $C_{2,0} = 0.015$ M, $T = 90$ °C; (■) $C_{2,0} = 0.03$ M, $T = 60$ °C; (▼) $C_{2,0} = 0.08$ M, $T = 90$ °C; (○) $C_{2,0} = 0.06$ M, $T = 50$ °C.
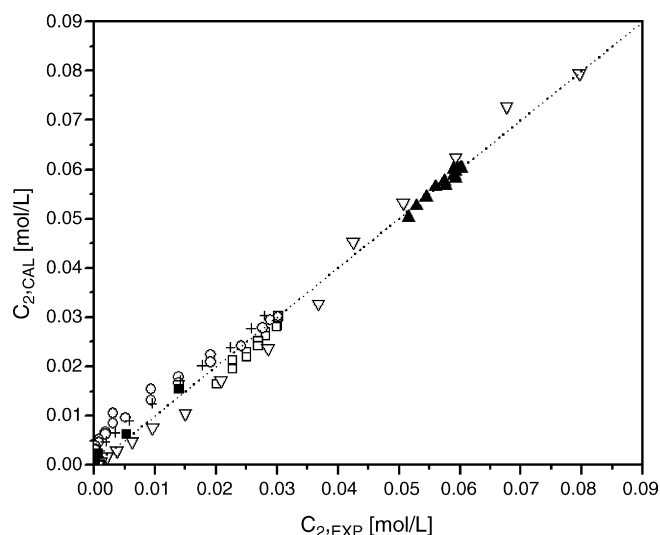
Fig. 12. Parity plot showing the experimental and modeled concentrations of **2**.

Fig. 13. Preliminary process flow diagram for the mild hydrogenation of BO using a homogenous transition metal catalyst.

catalyst present. At 50 °C, the concentration of active catalyst is only 15% of the theoretical maximum after 10 min reaction time, whereas active catalyst formation is quantitative after 10 min at 90 °C.

The value of the activation energy for the main reaction (Ea_2) is close to the value reported by Basset et al. (80 kJ/mol) for the hydrogenation of propionaldehyde using a homogeneous Ru-TPPTS complex in water [40].

The values of the activation energies also indicate that the hydrogenation experiments were carried out in the kinetic regime and were not biased by mass transfer effects. In the case mass transfer effects play a major role and interfere with the kinetics, as is well possible in biphasic reactive L–L systems, activation energies below 20–30 kJ/mol are expected [42].

3.9. Hydrogenation of the water-soluble fraction of pyrolysis oil using RuCl₂(PPh₃)₃

In a separate experiment, the water-soluble fraction of a typical pyrolysis oil was hydrogenated using the RuCl₂(PPh₃)₃ catalyst. The water-soluble fraction was obtained by extracting pyrolysis oil with water. The composition of the water fraction was determined by NMR. The main components were acetic acid, ketone **1** and aldehyde **2**, in line with literature data [28]. Quantification was hampered due to the presence of small amounts of various other components. Integration of ¹H NMR spectra indicate that **1** and **2** are presents in a 0.67 mol/mol ratio.

The water-soluble fraction was hydrogenated at 90 °C, 40 bar using the RuCl₂(PPh₃)₃ catalyst for a reaction time of 5 h. After reaction, the water layer was separated and analyzed by NMR. The expected product of the hydrogenation of **2**, 1,2-ethanediol (**4**), was present in significant amounts (singlet at $\delta = 3.30$ ppm in ¹H NMR in D_2O), confirmed by spiking with pure **4**. In addition, 1,3-propanediol (**3**), the hydrogenation product of ketone **1**, was also present, as indicated by a doublet at δ 0.95 ppm in ¹H NMR in D_2O. The ratio of **3** and **4** was determined by NMR integration and was about 0.08. This result implies that at the conditions

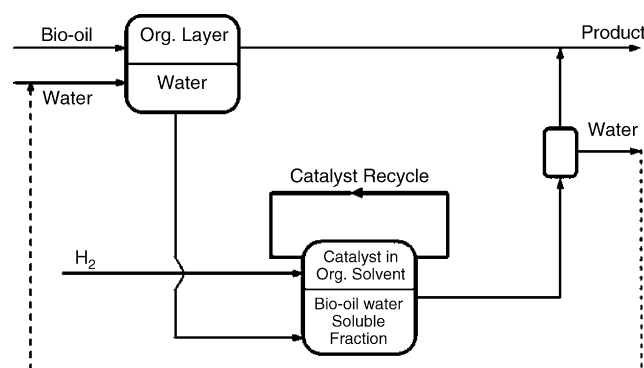applied, the conversion of **2**–**4** is much faster than the conversion of **1**–**3**. These results are inline with the hydrogenation results using the model compounds (**1** and **2**), which clearly indicated that aldehydes are much more reactive than ketones.

¹H NMR spectra of the starting material also contain several peaks in the 8–10 ppm range, indicative for the presence of various aldehyde species other than **2**. After hydrogenation, these peaks have fully disappeared, a clear indication for aldehyde reduction. These findings imply that even in a complex matrix with a variety of organic molecules, biphasic hydrogenations using a homogeneous Ru-catalyst allow the reduction of aldehydes and ketones to the corresponding alcohols. On the basis of our studies, an upgrading concept for pyrolysis oil at mild conditions could be envisaged (Fig. 12). Further process optimization studies, with as strong focus on achieving high catalyst productivities, will be required to determine the economic feasibility of this concept (Fig. 13).

4. Conclusions

Proof of principle for the upgrading of pyrolysis oil by hydrotreatment at mild conditions using a homogeneous Ru-catalyst in a two phase aqueous organic system has been shown. The reaction is a rare example of a biphasic water/organic hydrogenation system using an organic phase soluble catalyst and water-soluble substrates. Upon reaction, the amounts of reactive aldehydes in the pyrolysis oil are reduced significantly, which is expected to have a positive effect on the product properties. A process concept is proposed to apply these findings on a larger scale.

Model studies showed that 1-hydroxy-2-propanone (**1**) and 1-hydroxy-2-ethanal (**2**), both present in significant amounts in pyrolysis oil, are selectively hydrogenated to 1,2-propanediol and 1,2-ethanediol, respectively. The influence of the temperature (50–90 °C), pressure (20–40 bar) and initial substrate concentration on the reaction rates were investigated. Both reactions were first order in substrate and zero order in hydrogen, suggesting that coordination/insertion of the substrate to an unsaturated Ru–H is the rate determining step in the catalytic cycle. Activation of the catalyst precursor RuCl₂(PPh₃)₃ to an active Ru compound by the reaction with H_2 is an important step in the catalytic cycle that controls the overall hydrogenation rate at

temperatures below 60 °C. An overall kinetic model for the hydrogenation reaction, including the catalyst activation step, was developed.

Acknowledgements

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