

# The application of water-soluble ruthenium catalysts for the hydrogenation of the dichloromethane soluble fraction of fast pyrolysis oil and related model compounds in a two phase aqueous–organic system

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## Abstract

The hydrogenation of a dichloromethane soluble fraction of flash pyrolysis oil (bio-oil, BO), obtained by treatment of BO with a water–dichloromethane solvent mixture, was investigated using a water-soluble homogeneous ruthenium catalyst ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/\text{tris}(m\text{-sulfonatophenyl})\text{phosphine}$ , TPPTS). The catalyst is active at mild conditions ( $<70^\circ\text{C}$ , 45 bar hydrogen) and particularly the levels of aldehydes in the BO fraction are reduced considerably. Model studies using vanillin (**1**), acetoguaiacone (**2**) and *iso*-eugenol (**3**) (45 bar hydrogen and  $45\text{--}70^\circ\text{C}$ ) showed that vanillin is the most reactive and unexpectedly forms creosol (**6**) instead of the vanillyl alcohol (**5**). An optimisation study was performed on the latter reaction and the highest TOF (36.4 mol/(mol h)) was obtained at  $60^\circ\text{C}$ , 45 bar hydrogen and a NaI concentration of 0.08 M. Kinetic studies imply that the formation of **6** proceeds via the intermediate alcohol **5** in a series type of mechanism. TEM-EDX measurements suggest that the reactions are most likely catalyzed by single metal homogeneous Ru complexes and not by Ru nanoparticles/colloids.

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**Keywords:** Hydrogenation; Biphasic catalysis;  $\text{RuCl}_3$ ;  $\text{Tris}(m\text{-sulfonatophenyl})\text{phosphine}$  (TPPTS); Homogeneous catalyst; Hydrodeoxygenation; Flash pyrolysis oil

## 1. Introduction

The development of renewable energy carriers as replacements for fossil-based fuels is rapidly progressing. An attractive second generation biofuel is fast pyrolysis oil, also known as bio-oil (BO), obtained from flash pyrolysis of lignocellulosic biomass at medium temperatures ( $375\text{--}450^\circ\text{C}$ ). Pyrolysis oil is a very complicated matrix consisting of up to 400 different chemical substances belonging to a broad range of chemical groups (acids, aldehydes, ketones, lignins and sugars).

Crude BO requires upgrading before it is suitable to be applied in non-stationary internal combustion engines. The caloric value of BO is relatively low (20 MJ/kg) compared to fossil oil (42 MJ/kg), it is rather acidic (pH 2.5) and improvements in storage stability are desirable [1,2]. Hydrotreatment of BO using heterogeneous catalysts has been studied and it

was shown that the caloric value and storage stability increased dramatically when using classical hydrotreatment catalysts like sulphidised NiMo and CoMo on alumina supports [3–7]. The process conditions for hydrotreatment of BO are rather severe ( $350\text{--}450^\circ\text{C}$ , 50–150 bar hydrogen), leading to the formation of substantial amounts of gases and (undesirable) char. As a result, the energy efficiency is relatively low. Therefore, there is a strong incentive to develop catalysts that operate at lower temperatures and pressure while still producing a modified BO with improved properties.

We envisaged that homogeneous catalysts could be attractive alternatives [8–13] as these operate at considerably milder conditions. However, the use of well defined homogeneous catalysts for the hydrotreatment of pyrolysis oil is still in a state of infancy. We have recently reported the use homogeneous ruthenium catalysts of the type  $\text{RuCl}_2(\text{PPh}_3)_3$  for the hydrogenation of the water-soluble fraction of BO in a two phase aqueous–organic system. At mild conditions (40 bar,  $90^\circ\text{C}$ ), the amounts of watersoluble aldehydes (e.g. 1-hydroxy-2-ethanal) were reduced considerably [14]. Although this earlier study has

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### Nomenclature

$C_i$	concentration of component $i$ (mol/L)
$k_{ij}$	reaction rate constant of the hydrogenation of component $i$ into component $j$ (mol/(L h))
$k'_{ij}$	pseudo-first order rate constant of the hydrogenation of component $i$ into component $j$ ( $\text{h}^{-1}$ )

### Subscripts

1	vanillin
5	vanillyl alcohol
6	creosol

### Superscripts

$n$	reaction order in vanillin
$m$	reaction order in vanillyl alcohol
$p$	reaction order of hydrogen in hydrogenation of vanillin reaction
$q$	reaction order of hydrogen in hydrogenation of vanillyl alcohol

demonstrated the potential of homogeneous catalysts for the hydrotreatment of BO, it is only a first step towards applications. The development of highly active and cheap catalysts is of utmost importance. With such systems, once through operation modes are possible without the use of catalyst recycling strategies. Only then, these homogeneous catalysts will be able to compete with the classical heterogeneous systems and may eventually be used to upgrade BO as a fuel for non-stationary combustion engines.

We here report our hydrogenation studies on the dichloromethane soluble fraction of a typical BO obtained by L–L extraction of BO with dichloromethane and water. This fraction contains large amounts of lignine derived compounds like low and medium molecular weight phenolics, syringols and guaiacols [15,16]. Typical examples of low molecular weight lignine derived compounds are guaiacol and alkyl substituted derivatives (4-methyl-guaiacol, 4-ethyl guaiacol, 4-propyl guaiacol), (substituted) syringols, *iso*-eugenol and vanillin.

Our focus was mainly on the hydrogenation of aldehyde functionalities in this pyrolysis oil fraction as the storage stability of BO is known to be negatively affected by the presence of aldehydes [17,18]. Various water-soluble ruthenium-based homogeneous catalysts have been developed that are capable of reducing aldehyde groups to alcohols [8,10–13,19–23]. For instance, water-soluble ruthenium–TPPTS complexes, generated *in situ* from  $\text{RuCl}_3$  and tris(*m*-sulfonatophenyl)phosphine (TPPTS) have proven to be very useful catalyst for the selective reduction of the carbonyl function of  $\alpha,\beta$ -unsaturated aldehydes at mild conditions (30–60 °C, 10–50 bar hydrogen). For some of the systems, conversion and the selectivity remained unaffected after catalyst recycle [11].

Our initial activity involved hydrogenation experiments to hydrogenate typical lignin model compounds (vanillin, acetoguaiacone and *iso*-eugenol) using a  $\text{RuCl}_3$ /TPPTS catalyst.

Subsequently, the potential of this catalyst for the hydrotreatment of the dichloromethane soluble fraction of BO was explored in a two phase aqueous–organic system.

## 2. Experimental

### 2.1. Materials and product analysis

Vanillin (**1**), *iso*-eugenol (**2**, mixture of *cis*- and *trans*-isomers) and acetoguaiacone (**3**), were obtained from ACROS (purity >99%). The metal catalyst precursor,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (purity 99%), was provided by Riedel-de Haen,  $\text{Na}_3\text{TPPTS}$  (TPPTS) from Fluka. NaI was purchased from ACROS (purity 99 wt%). *n*-Hexane and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were from Lab Scan (analytical grade, 99% purity), THF (99% purity) was obtained from ACROS.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  were purchased from Merck. Hydrogen and nitrogen gas were from Hoek-Loos (99.5 vol.% purity). All compounds were used without purification. Fast-pyrolysis oil (beech wood) obtained using rotating cone technology was provided by the Biomass Technology Group B.V., Enschede, The Netherlands.

Buffer solutions (pH 4.5, 7.28 and 9.25) were prepared using standard procedures [24] by dissolving the appropriate amount of phosphate salts in water (pH 4.5: 0.1 M  $\text{NaH}_2\text{PO}_4$ ; pH 7.28: mixture of 0.01 M  $\text{KH}_2\text{PO}_4$  and 0.01 M  $\text{Na}_2\text{HPO}_4$ ; pH 9.28: 0.1 M  $\text{Na}_2\text{HPO}_4$ ).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian AMS 100 spectrometer using  $\text{CDCl}_3$  as the solvent. The spectra were referenced to TMS ( $\delta = 0$  ppm). FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer (Spectrum 2000 series, resolution  $2.0\text{ cm}^{-1}$ , 100 scans). The samples were diluted with tetrahydrofuran (10 wt% solution) before measurement. The THF peaks were subtracted from the product spectra using the FT-IR software.

Elemental compositions (C, H, N, Cl) were determined using an Elemental Analyzer (Flash EA 1112, CE Instruments).

Samples for Transmission Electron Microscopy (TEM) were prepared by depositing a representative droplet of the aqueous phase containing the Ru–TPPTS catalyst (3.00 mmol/L<sub>w</sub>, taken from a typical reaction mixture performed at base case conditions, see Table 1) on a 10 nm thick silicon-nitride membrane and then drying the droplet under infra-red light for about half

Table 1  
Overview of experimental conditions for the hydrogenation of **1** using the  $\text{RuCl}_3$ /TPPTS catalyst

Process variable	Base case	Ranges
$T$ (°C)	45	45–70
$P$ (bar)	45	–
Stirring speed (rpm)	1300	200–2000
L/M (mol/mol)	3.0	1.0–4.0
Catalyst intake (mmol)	0.14	0.14 and 0.28
Substrate to catalyst ratio (mol/mol)	65	32.5 and 65
NaI addition (mol/L <sub>w</sub> )	–	0–0.50
Reaction time (h)	3	–
Organic solvent	<i>n</i> -Hexane	<i>n</i> -Hexane, dichloromethane

an hour. Bright-Field TEM images and selected area electron diffraction patterns were recorded (on CCD cameras) using a JEOL 2010F TEM operating at 200 kV. Energy dispersive X-ray spectrometry (EDAX) attached to the TEM was also used to determine the local chemical composition of the prepared TEM samples (with a spatial resolution down to about 1 nm).

## 2.2. Hydrogenation equipment

Hydrogenation experiments were performed in a 350 mL stainless steel batch autoclave (Buchii GmbH) equipped with an overhead magnetic stirrer, a pressure indicator and a thermocouple for temperature registration. The autoclave was equipped with an electrical heating/cooling system to control the temperature inside the reactor.

## 2.3. Typical experimental procedure for a hydrogenation experiment

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (37.5 mg, 0.14 mmol) and TPPTS (236.3 mg, 0.42 mmol) were charged to the autoclave. Subsequently, water (46 mL), organic solvent (164 mL), substrate (9.33 mmol) and, when appropriate, NaI (0.08, 0.12, and 0.5 M) were added. Typically, a substrate to catalyst ratio of 65 mol/mol was applied and the Ru to TPPTS ratio was typically set at 1:3 (mol/mol).

The autoclave was closed immediately and flushed three times with nitrogen gas to remove oxygen. The reactor was pressurized with 6.0 bar of  $\text{H}_2$  gas and heated to the pre-set temperature (45, 60 and 70 °C). After the reaction temperature was reached,  $\text{H}_2$  was introduced to the reactor to the desired reaction pressure (typically 45 bar). The hydrogen supply valve was closed and the hydrogen pressure in the reactor was measured as a function of time.

After reaction, the reactor was cooled down to room temperature and vented to atmospheric pressure. The reactor content was collected and the two liquid layers were separated. The organic phase was collected and the solvent was removed at reduced pressure (10 mbar, 30 °C). All phases and products were weighed to determine the mass balances. The composition of the organic phase was determined and quantified using  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

## 2.4. Hydrogenation of the dichloromethane soluble fraction of BO

The dichloromethane soluble fraction of BO was prepared by intensely mixing crude BO (7.15 g) dissolved in dichloromethane (164 mL) with water (46 mL). Subsequently, both liquid phases were separated using a separating funnel. The organic phase was used as a starting material for the hydrogenation studies. The dichloromethane layer was analysed with GC–MS and all model compounds used in this study could be detected within the multitude of lignin derived components present.

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (112.5 mg, 0.43 mmol), TPPTS (712.5 mg, 1.25 mmol) and NaI (0.08 mol/L<sub>w</sub>) were charged to the autoclave. Subsequently, water (46 mL) and the dichloromethane

soluble fraction of BO (see above for preparation) were added. The autoclave was closed and flushed three times with nitrogen gas to remove oxygen. The reactor was pressurized with 6.0 bar of  $\text{H}_2$  gas and heated to the pre-set temperature (45 and 70 °C). After the reaction temperature was reached,  $\text{H}_2$  was introduced to the reactor to the desired reaction pressure (typically 45 bar). The hydrogen supply valve was closed and the hydrogen pressure in the reactor was measured as a function of time.

After reaction, the reactor was cooled down to room temperature and vented to atmospheric pressure. The organic phase was collected and the organic solvent was removed at reduced pressure (10 mbar, 30 °C). All phases and products (dark brownish oils) were weighed to determine the mass balances. The composition of the organic phase was determined and quantified using  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and FT-IR. The elemental composition of the organic phase before and after reaction was determined after removal of the dichloromethane at reduced pressure (50 mbar, 40 °C).

## 2.5. Kinetic experiments and reaction modeling

For these experiments, 75 mg (0.28 mmol) of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 1.42 g (9.33 mmol) of vanillin were applied; giving a substrate to catalyst ratio of 32.5 mol/mol. The reaction was performed at 45 bar  $\text{H}_2$  pressure, a reaction temperature 70 °C and without NaI addition.

The kinetic parameters were estimated using a maximum likelihood approach, which is based on minimization of errors between the experimental data and the kinetic model. Details about this procedure can be found in the literature [25]. Minimization of the objective function was performed by providing initial guesses for each kinetic parameter. The best estimates were obtained using the MATLAB toolbox command *fminsearch*, which is based on the Nelder–Mead optimization method.

## 3. Results and discussion

### 3.1. Screening experiments with BO model compounds

Three typical model compounds representing the low molecular weight lignine fraction of BO, vanillin (**1**), *iso*-eugenol (**2**) and acetoguaiacone (**3**) (Fig. 1), were tested in a batch set-up using a catalyst consisting of  $\text{RuCl}_3$  and TPPTS (Ru:TPPTS mol ratio = 1:3) in a water–hexane biphasic system (45 °C, hydrogen

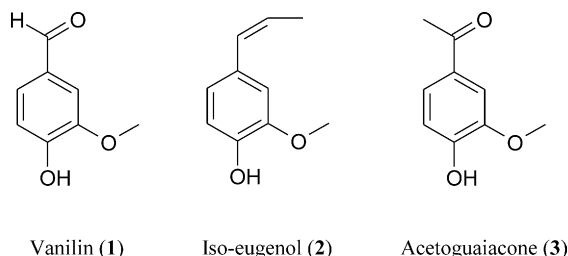
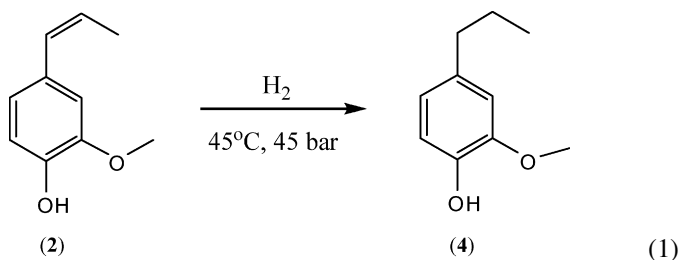


Fig. 1. Selected bio-oil model compounds.

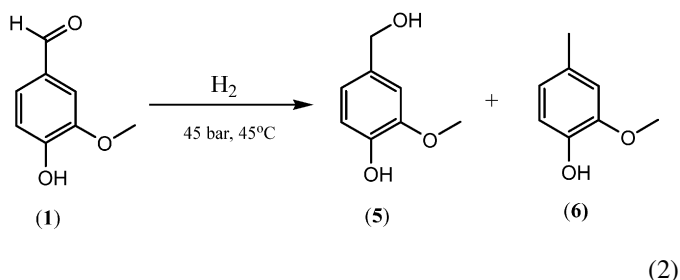
pressure of 45 bar and a substrate to catalyst ratio of 65:1). A typical reaction time was 3 h.

The hydrogenation of **2** resulted in the selective formation of 2-methoxy-4-*n*-propyl phenol (**4**, see Eq. (1)). Hydrogenation of the aromatic ring was not observed:



NMR spectra clearly showed the appearance of peaks arising from the *n*-propyl group of **4** ( $\delta$  1.5–2.5 ppm in  $^1\text{H}$  NMR and  $\delta$  24–37 ppm in  $^{13}\text{C}$  NMR). The reaction is relatively slow and the conversion was only 7% after a 3 h reaction time, corresponding to a TOF of 1.5 mol/(mol Ru h). Under similar conditions, (**3**) was not reactive and the starting material was recovered after the reaction.

Vanillin was considerably more reactive and a 32% conversion was observed after 3 h reaction time. Surprisingly, the major product was not the anticipated vanillyl alcohol (**5**) but 2-methoxy-4-methylphenol, (creosol, **6**) (see Eq. (2)). **5** and **6** were present in a 1:13.3 mol ratio:



This is particularly evident from NMR spectra of the product. A clear peak of the  $\text{CH}_2\text{OH}$  group of **5** ( $\delta$  4.6 ppm in  $^1\text{H}$  NMR and  $\delta$  68.8 ppm in  $^{13}\text{C}$  NMR) and the methyl group of **6** ( $\delta$  2.4 ppm in  $^1\text{H}$  NMR and  $\delta$  21.2 ppm in  $^{13}\text{C}$  NMR) appear as a result of hydrogenation of **1**. As with **2**, hydrogenation of the aromatic ring did not occur.

The formation of the hydrogenation product **6** was not anticipated at forehand for a homogeneous hydrogenation catalyst. The reaction is formally a hydrodeoxygenation reaction of an aldehyde to a saturated hydrocarbon. A number of synthetic routes using stoichiometric reagents is available for this transformation (hydrazine, base [26], Zn-amalgam, HCl [27],  $\text{NaBH}_3\text{CN}$  [28]). The catalytic conversion of vanillin to **6** is known to proceed with heterogeneous catalysts (e.g. CoMo on alumina,  $\text{MoS}_2$  on supports like alumina and carbon) [29,30]. However, to our best knowledge, it is the first example of the hydrodeoxygenation of vanillin to **6** using a biphasic homogeneous transition metal catalyst system. It also raises the question whether the reaction is catalyzed by a truly homogeneous transition metal compound or by Ru-nanoparticles or clusters (*vide infra*).

A comparison of the hydrogenation results for model compounds **1** and **3** by the  $\text{RuCl}_3/\text{TPPTS}$  catalyst indicates that aromatic aldehydes are more easily reduced than aromatic ketones, in line with literature data for this catalyst system [10–12,19,31].

### 3.2. Systematic studies on the conversion of vanillin to creosol

The biphasic hydrodeoxygenation reaction of **1–6** (Eq. (2)) using the  $\text{RuCl}_3/\text{TPPTS}$  catalyst was studied in more detail. The effects of various process variables like the ligand to metal ratio, solvents, temperature and the role of additives were determined (Table 1) with the aim to optimize the process conditions to achieve the highest conversion rates and selectivity for the reaction. Initially, the reproducibility of the reaction was tested at standard conditions (Table 1) and found to be satisfactorily (relative error in conversion 9% and 4% in selectivity).

#### 3.2.1. Mass transfer effects

The conversion rate as well as the selectivity in biphasic liquid–liquid systems may be affected by the rate of mass transfer of reactants from the supply to the reaction phase. Grosselin et al. [11] showed that the biphasic reduction of cinnamaldehyde using Ru/TPPTS was suffering from mass transfer limitations at lower stirring speeds (<1500 rpm). To probe possible mass transfer effects on the conversion of **1–6**, a number of experiments were performed using different agitating speeds while keeping all other variables at standard values (Table 1), with the exception that a double catalyst intake was employed to ensure significant vanillin conversion at lower agitation speeds. The results are provided in Fig. 2. It is clear that the conversion is a function of the agitation speed when the speed is less than about 1000 rpm. Above this value, the conversion remains essentially constant.

It clearly implies that the overall conversion is affected by mass transfer effects when the agitation speed is less than

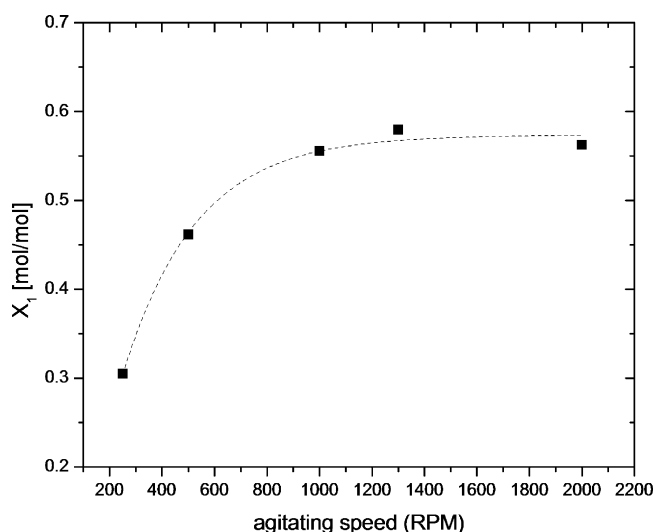


Fig. 2. Conversion of **1** at various stirring speeds. Conditions: Base case, except substrate/catalyst = 32.5 mol/mol and catalyst intake = 0.28 mmol.



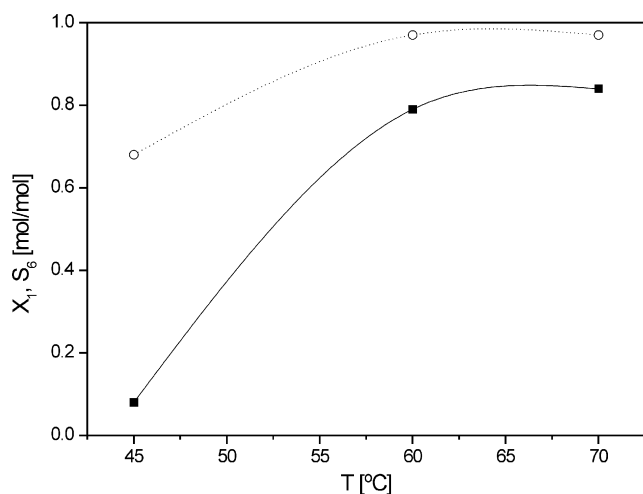


Fig. 3. Influence of  $T$  on the conversion and selectivity of the reaction of **1–6**. Conditions: see Table 1 for base case. Legends: (○) creosol selectivity ( $S_6$ ); (■) vanillin conversion ( $X_1$ ).

1300 rpm. To ensure the measurement of the intrinsic kinetics of the reaction and to exclude mass transfer effects, all further systematic studies were performed with a stirring speed >1300 rpm.

### 3.2.2. Effect of temperature

The effect of temperature on the conversion and selectivity of the hydrogenation of **1** was tested at 45, 60 and 70 °C. Temperature has a large impact on catalytic activity (Fig. 3) and the observed TOF at 60 °C (16.9 mol/(mol Ru h)) is more than 10 times higher than at 45 °C. The selectivity towards **6** also improves considerably when performing the reaction at higher temperatures (65% at 45 °C to ca. 95 mol% at  $T > 60$  °C, Fig. 3). However, catalytic activity levels off at temperatures above 60 °C, indicative for catalyst deactivation. The results indicate that the temperature is a critical process variable for optimizing the conversion and selectivity to **6**.

### 3.2.3. Effect of the ligand to metal (L/M) ratio

The effect of the ligand to metal ratio was probed in the range of 1–4 mol/mol (Table 1, base case). The hydrogenation results and particularly the conversion of **1** are a strong function of the L/M ratio (Fig. 4). Upon increasing the ratio from 1 to 2, the conversion increases from 12 to about 20%. A further increase of the L/M ratio has a negative effect and the conversion reduces to 7% and 2%, respectively. It appears that the optimum ratio with respect to conversion is about 2. The selectivity to **6** is reduced considerably when increasing the L/M ratio. At an L/M ratio of 4, the sole product is the alcohol **5**.

Previous studies on the hydrogenation of 3-methyl-2-butenal using the RuCl<sub>3</sub>/TPPTS catalyst have also shown that the conversion is a strong function of the ligand to metal ratio [11]. Selectivity changes as a function of the L/M ratio have also been observed, for instance for the hydrogenation of cinnamaldehyde to cinammyl alcohol using RuCl<sub>3</sub>/TPPTS catalysts [19]. This effect was explained by assuming a change in distribution of the

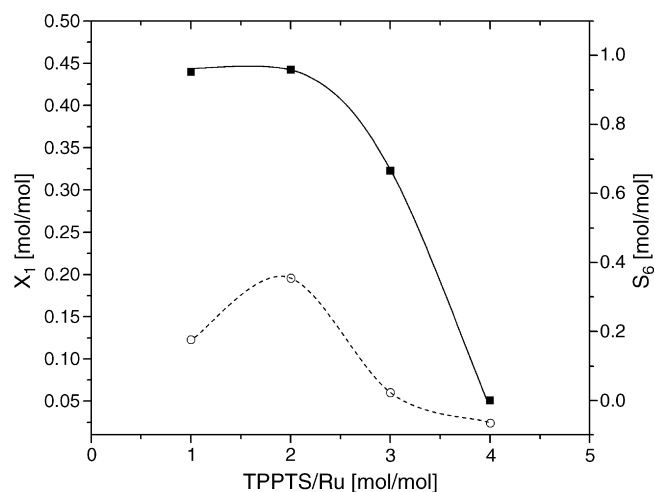


Fig. 4. Influence of L/M ratio on the conversion of **1** and selectivity towards **6**. Conditions: see Table 1 for the base case. Legends: (■) creosol selectivity; (○) vanillin conversion.

various ruthenium–TPPTS species in solution when varying the L/M ratio.

### 3.2.4. Solvent effects

To probe possible solvent effects, the biphasic aqueous–organic hydrogenation of **1** was also performed in a dichloromethane/water system. The results are given in Table 2. The conversion in dichloromethane after 3 h reaction time at standard conditions (Table 1) is slightly higher than in hexane. Remarkably, the reaction product in dichloromethane is the alcohol **5** and not the saturated compound **6**.

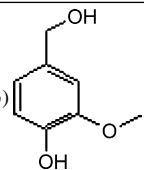
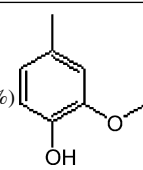
### 3.2.5. Effect of NaI addition

Basset and co-workers reported a very positive effect of NaI on the performance of well defined mono-nuclear Ru-catalyst precursors like RuHCl(TPPTS)<sub>3</sub> catalyst for the hydrogenation of propionaldehyde in water [23]. The presence of NaI (0.08 M) resulted in a dramatic increase the conversion of propionaldehyde and the reaction rate at 45 °C in the presence of NaI was even higher than at 70 °C in the absence of salt. We have performed a series of experiments to probe the effects of NaI on the hydrogenation of **1**. The results are given in Fig. 5.

A large positive effect of NaI addition on the conversion of **1** is observed. When going from 0 to 0.08 mol/L<sub>w</sub> NaI, the conversion increases from 7% to 79%, corresponding to a TOF of 17 mol/(mol Ru h). A further doubling of the TOF is possible at higher temperatures. At 60 °C instead of 45 °C and a reduced reaction time of 1 h, the conversion was 56%, corresponding with a TOF of 36.4 mol/(mol h).

There appears to be an optimum NaI concentration with respect to the conversion and a further increase from 0.08 to 0.5 mol/L<sub>w</sub> leads to a strong reduction in the conversion levels. The selectivity of the reaction improves in the presence of low levels of NaI (0.08 and 0.11 mol/L<sub>w</sub>) from 66% to 97%. However, in the case of a high NaI concentration (0.5 mol/L<sub>w</sub>) the selectivity drops to 76% and significant amounts of **5** are formed. The selectivity of the reaction appears to be a function

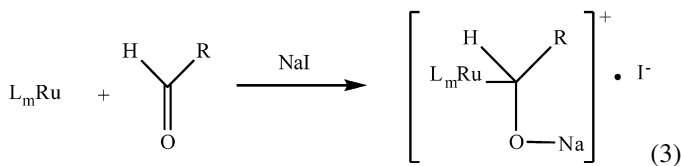
Table 2  
Influence of organic solvent on conversion and product selectivity

Solvent	Conversion, $X_1$ (mol%)	Chemical Structure	Selectivity, $S$ (mol%)	Chemical Structure
<i>n</i> -Hexane	7		13.0	
dichloromethane	9		100.0	

Conditions: see Table 1, base case.

of the conversion, with lower conversions leading to a reduced selectivity towards **6**. This aspect will be discussed in more detail in a subsequent paragraph on kinetic modeling of the reaction.

Our findings with respect to the activity of the systems as a function of the NaI concentration are in line with those reported by Basset for the hydrogenation of propionaldehyde in water using well defined mono-nuclear Ru-catalyst precursors like  $\text{RuHCl}(\text{TPPTS})_3$  [23]. For this system, the reaction order in NaI is also a function of the  $C_{\text{NaI}}$ . In the range  $C_{\text{NaI}} < 0.07 \text{ mol/L}_w$  the order in NaI was one, between 0.07 and 0.4 mol/L<sub>w</sub> zero and negative above 0.4 mol/L<sub>w</sub>. The positive role of NaI at lower concentrations was rationalized by assuming that reaction of the aldehyde at the metal center is assisted by NaI (Eq. (3)).



### 3.2.6. Effect of pH of the aqueous phase on catalyst activity and selectivity

A number of experiments in buffer solutions with different pH-values (4.5–9.25;  $T=60^\circ\text{C}$ , 45 bar  $\text{H}_2$ , TPPTS/Ru ratio of 3.0) were performed. The conversion of **1** and selectivity towards

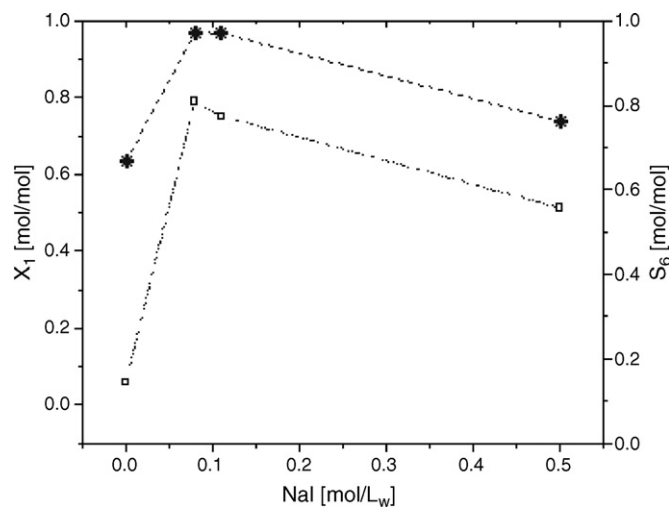


Fig. 5. Influence of NaI addition on vanillin conversion and product selectivity. Conditions: see Table 1 for base case. Legends: creosol selectivity (●); vanillin conversion (□). Lines are for illustrative purposes only.

**6** were measured and the results are shown in Fig. 6. A clear pH dependency was observed and the conversion and selectivity both peak at neutral conditions and are reduced in acidic and basic media.

The conversion in the buffered solution at pH 7.28 is actually higher than found for an experiment in the absence of a buffer (Fig. 6). The pH of the latter is about 7, thus pH effects are not likely the cause of this observation. It suggests that both the presence of salts and the pH affect the activity of the Ru–TPPTS system. Further experiments outside the scope of this paper with a range of pH values and a wide variety of salts with different anions and cations will be required to rationalize these findings.

The pH of the aqueous phase in biphasic aqueous–organic catalysis using homogeneous catalysts is known to affect catalytic activity and selectivity [9,32–34]. Joó et al. [34] studies the hydrogenation of unsaturated aldehydes with well defined homogeneous Ru–TPPTS catalysts and found that the composition of the various homogeneous Ru-species in solution drastically changed as a function of the pH with a concomitant change in the selectivity of the reaction. Daguinet and Dyson [33] observed a strong increase in activity when using various water-soluble Ru–arene complexes for the hydrogenation of benzene to cyclohexane in biphasic media. The activities of the catalysts were a clear function of the pH, with high pH values leading to high catalytic activity. These results were rationalized assuming that the active catalysts are actually colloidal

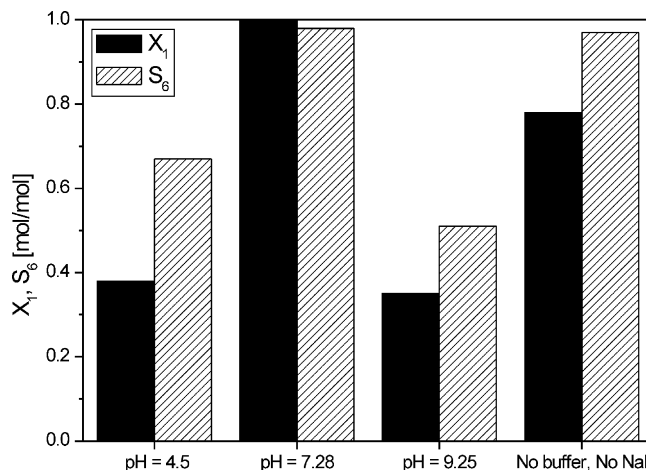
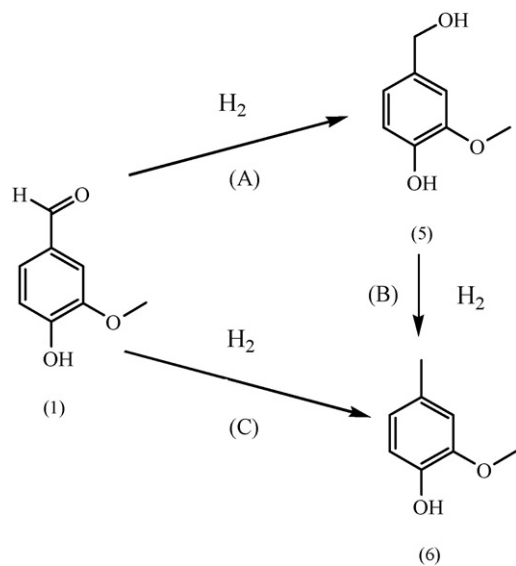


Fig. 6. Conversion of **1** and selectivity to **6** at different pH. Conditions:  $T=60^\circ\text{C}$ ,  $P=45 \text{ bar}$ ,  $\text{RPM}=1500$ , and  $\text{TPPTS/Ru}=3.0 \text{ mol/mol}$ , 3 h reaction time.

Scheme 1. Possible mechanistic pathways for the hydrogenation of **1**.

Ru-species and that the rate of colloid formation is pH dependent.

### 3.2.7. Kinetic modeling of the reaction of vanillin (**1**) to creosol (**6**)

The main reaction product of vanillin hydrogenation in the hexane–water biphasic using the RuCl<sub>3</sub>/TPPTS catalyst is **6**. Depending on reaction conditions and batch times, alcohol **5** may be present in significant amounts. The question arises whether the alcohol is an intermediate product and subsequently reacts to **6** or that vanillin reacts in a parallel mode to **5** and **6** (Scheme 1).

To gain insight in the dominant reaction pathway, eight batch experiments with different reaction times (20 min–7 h) were performed. The reaction conditions are as for the base provided in Table 1, with the exception that a higher catalyst intake

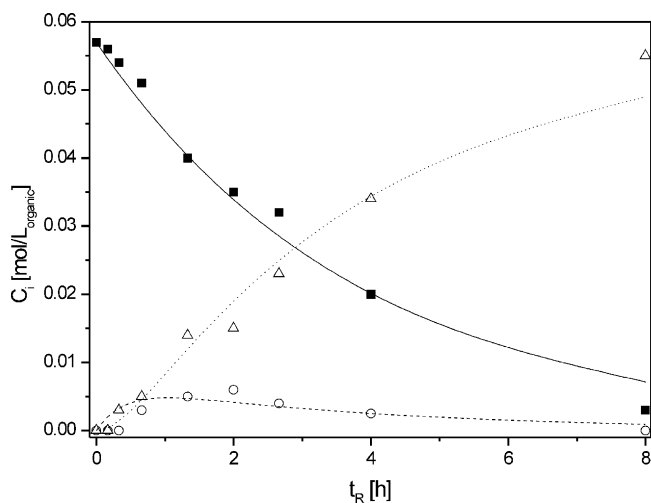


Fig. 7. Batch concentration profiles for the hydrogenation of **1** using the RuCl<sub>3</sub>/TPPTS catalyst. For conditions: see Table 1, base case with 0.28 mmol catalyst intake. Legends: C<sub>1</sub> (■), C<sub>5</sub> (○), C<sub>6</sub> (△). Lines are according to the kinetic model.

(0.28 mmol) and lower substrate to catalyst ratio (32.5 mol/mol) were applied. The results are graphically depicted in Fig. 7.

From the figure, it can be concluded that alcohol **5** is an intermediate product, with a concentration peaking after about 1 h reaction time. This implies that the reaction proceeds via a series mechanism (path A and B in Scheme 1).

With the kinetic profiles available (Fig. 6) and assuming a series mechanism (route A and B in Scheme 1), it is possible to determine the kinetic parameters for the reaction of **1–5** and that of **5–6**.

For the proposed kinetic scheme, the following relations hold for a batch reactor:

$$\frac{dC_1}{dt} = -k_{15}C_1^m C_{H_2}^p \quad (4)$$

$$\frac{dC_5}{dt} = k_{15}C_1^m C_{H_2}^p - k_{56}C_5^n C_{H_2}^q \quad (5)$$

$$\frac{dC_6}{dt} = k_{56}C_5^n C_{H_2}^q \quad (6)$$

where  $k_{15}$  is the rate constant of the reaction of **1–5**,  $k_{56}$  the rate constant of the reaction of **5–6** and  $n$ ,  $m$ ,  $p$  and  $q$  are the orders in substrates. When assuming that all reactions are elementary and considering that during an experiment the pressure drop in the batch reactor is less than 10%, Eqs. (4)–(6) simplify to:

$$\frac{dC_1}{dt} = -k'_{15}C_1 \quad (7)$$

$$\frac{dC_5}{dt} = k'_{15}C_1 - k'_{56}C_5 \quad (8)$$

$$\frac{dC_6}{dt} = k'_{56}C_5 \quad (9)$$

The software package MATLAB was used to determine the kinetic parameter  $k'_{15}$  and  $k'_{56}$ . The results for the optimized values of the parameters are shown in Fig. 7 and presented in Table 3. The pseudo-first-order kinetic constant for the reduction of the alcohol **5** to the saturated hydrocarbon **6** (path B in Scheme 1) is a factor of 10 higher than that of the reaction of aldehyde **1** to alcohol **5**. With these kinetic rate constants available, it is possible to predict the selectivity towards creosol **6** as a function of the conversion (Fig. 8). The model suggests that the selectivity towards creosol is always higher than the conversion at a certain batch time, in line with the experimental findings.

With this kinetic information available, it is also possible to rationalize some of the experimental trends. For instance, when studying the effects of the L/M ratio on catalyst performance (Fig. 4), it was observed that the selectivity of the reaction increased considerably at higher conversions. Similar effects were observed when studying the effects of NaI addition (Fig. 5) and temperature (Fig. 3). All of these findings are in line with

Table 3  
Pseudo-first-order kinetic constants for the hydrogenation reaction

Parameter	Value (h <sup>-1</sup> )
$k'_{15}$	0.26 ± 0.02
$k'_{56}$	2.35 ± 0.95

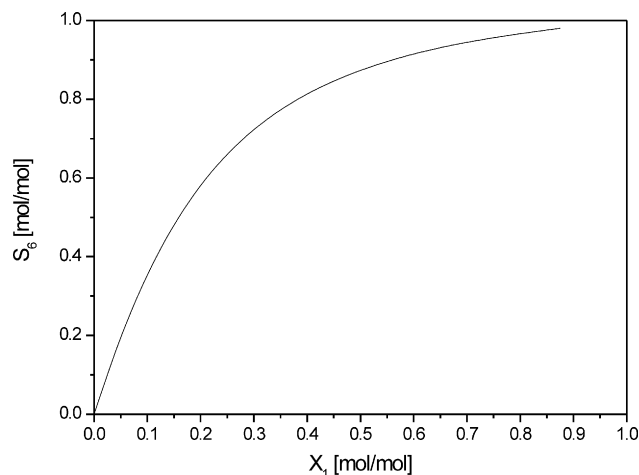


Fig. 8. Modeled selectivity to creosol ( $S_6$ ) as a function of vanillin conversion  $X_1$ .

the series mechanism proposed here for the formation of **6** for which the kinetic constant of the second reaction is considerably higher than the first.

### 3.3. Catalytic hydrogenation of the dichloromethane soluble fraction of bio-oil

The hydrogenation of the dichloromethane soluble fraction of BO, was performed using a biphasic liquid–liquid system consisting of dichloromethane and water. The dichloromethane soluble fraction was obtained by dissolving the BO in dichloromethane followed by water addition and phase separation. About 20 wt% of the original BO was present in the dark-brown dichloromethane layer. Two experiments were performed, slightly differing in process conditions. In both cases, Ru–TPPTS (L/M ratio of 3) was used as the catalyst in the presence of NaI (0.08 mol/L<sub>w</sub>).

A first experiment was performed at 45 bar hydrogen and 45 °C for 3 h. The isolated product after reaction was analysed using FT-IR (Fig. 9). When comparing the spectra of the solutions before and after hydrogenation, it appears that the absorbance in the 1850–1550 cm<sup>-1</sup> range is reduced significantly. The absorptions in this region arise from carbonyl and aromatic skeleton vibrations [35]. The Ru/TPPTS catalyst does

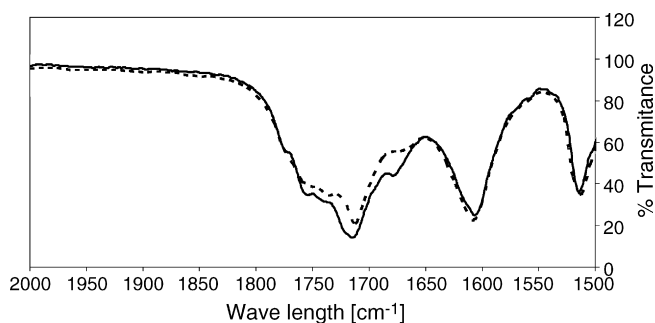


Fig. 9. FTIR spectra of the dichloromethane soluble fraction of BO and the hydrogenated product in CH<sub>2</sub>Cl<sub>2</sub>. Legends: before hydrogenation (—), after hydrogenation (---).

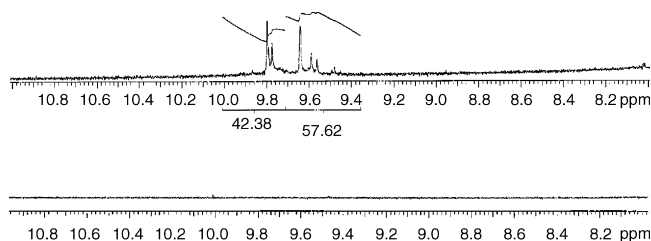


Fig. 10. <sup>1</sup>H NMR spectra of dichloromethane soluble BO fraction before (top) and after (bottom) hydrogenation using the Ru–TPPTS catalyst.

not show aromatic hydrogenation activity (*vide supra*) under the conditions applied in this study. This suggests, although not conclusive, that the concentrations of carbonyl containing compounds (aldehydes and/or ketones) are reduced considerably upon catalytic hydrotreatment.

To gain more insights in the various reactions taking place, a second experiment was performed (0.113 g Ru-precursor, 70 °C, 18 h and using the dichloromethane layer obtained by treatment of 7.15 g of pyrolysis oil with a water–dichloromethane mixture) and the product was analysed by <sup>1</sup>H NMR spectroscopy and elemental analysis. Comparison of the <sup>1</sup>H NMR spectra before and after reaction (Fig. 10) shows that typical aldehyde proton resonances in the range of 8–10 ppm are absent after reaction. This clearly implies that the hydrogenation reaction using the Ru/TPPTS catalysts leads to reductions in the amounts of aldehyde species, even in a complex matrix of dichloromethane soluble BO components.

This is further confirmed by elemental analysis on the dichloromethane soluble of BO, obtained by the L–L extraction of BO with dichloromethane and water, before and after the hydrogenation reaction. The results are given in Table 4.

The elemental analyses show a clear reduction (10 wt% relative) of the oxygen content of the water-insoluble fraction of BO upon hydrogenation with the RuCl<sub>3</sub>/TPPTS catalyst system. Combined with the NMR data, it is likely that these reduced oxygen contents are due to the hydrogenation of aldehydes (e.g. vanillin) to alcohols and/or saturated hydrocarbons.

### 3.4. Mechanistic aspects; single site metal catalysts or nanoparticles/colloids

The question arises whether the reactions are catalyzed by a truly single metal homogeneous Ru-metal compound or by soluble Ru-nanoparticles and/or colloids. In the literature on biphasic hydrogenations of aldehydes with molecular hydrogen using the

Table 4  
Elemental composition of the dichloromethane soluble fraction of BO before and after hydrogenation<sup>a</sup>

Sample	C (wt%)	H (wt%)	N (wt%)	O <sup>b</sup> (wt%)
Before hydrogenation	53.8	6.00	1.34	38.86
After hydrogenation	57.0	6.51	1.76	34.73

<sup>a</sup> Analyses performed after dichloromethane removal in vacuo. Dichloromethane removal was quantitative as indicated by low Cl contents of both products (<65 ppm).

<sup>b</sup> Calculated by differences.



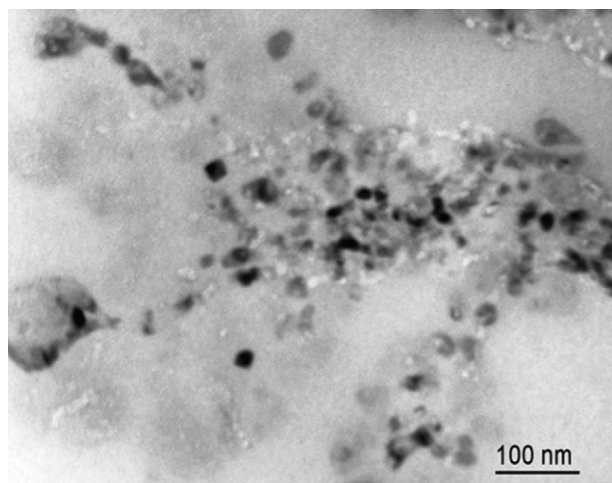


Fig. 11. TEM bright-field image of the dried aqueous phase containing the Ru catalyst.

RuCl<sub>3</sub>/TPPTS catalyst, it is always assumed that the catalyst is truly a homogeneous single metal catalyst. Experimental findings are commonly explained using mechanistic models with single metal catalysts [36–40]. However, there is an ongoing debate in the literature about whether simple metal salt precursors (e.g. RuCl<sub>3</sub>, RhCl<sub>3</sub>) under reducing conditions and in the presence of Lewis bases form truly single metal complexes or zero-valent nano-particles, see for instance a critical overview of Finke and co-workers on soluble arene hydrogenation catalysts [33,41–43]. Catalysts systems that were originally thought to be single site homogeneous were actually consisting of nanoparticles and colloids. However, it is experimentally difficult to unequivocally distinguish whether the catalyst is a single metal catalyst or consists of soluble metal-nanoparticles [41]. To gain more insights in the catalyst system described in this paper, we have performed TEM-EDX measurements on the aqueous phase after reaction. A typical example of a TEM image is provided in Fig. 11.

The TEM analysis shows the presence of different types of small particles <100 nm. The particles have various shapes, some are irregular and some are cubic. EDX analyses on a number of different particle types do not reveal the presence of significant amounts of Ru in them. The regular particles are rich in both sodium and chlorine, suggesting that these consist of, among others, NaCl, presumably arising from the reaction between the catalyst precursor RuCl<sub>3</sub>·3H<sub>2</sub>O and TPPTS. Further EDX measurements on various locations of the sample reveal that Ru is distributed uniformly throughout the sample and is not enriched in particles encountered. These findings, in combination with the good reproducibility of the catalytic experiments, indicate that the catalyst system used in this study is actually a single metal catalyst.

#### 4. Conclusions

A water-soluble homogeneous catalyst prepared by reacting RuCl<sub>3</sub>·3H<sub>2</sub>O and tris(*m*-sulfonatophenyl)phosphine (TPPTS) is an active hydrogenation catalyst for the dichloromethane sol-

uble fraction of BO in an aqueous biphasic aqueous–organic system. NMR, IR and elemental analysis indicate that particularly the levels of aldehydes are reduced considerably upon hydrotreating. Although this research demonstrates the potential of homogeneous catalysts for BO upgrading, substantial research efforts will be required to develop catalysts which are as active or even exceed the activity of heterogeneous systems and which may also be used to hydrogenate BO as a whole and not only certain fractions of the BO. Only then, applications of these catalysts for the production of energy carriers for the use in non-stationary combustion engines come within reach.

To gain molecular insights in the reactions occurring in the complex BO matrix, model studies using vanillin (**1**), acetoguaiacone (**2**) and *iso*-eugenol (**3**) were conducted (45 bar hydrogen and 45–70 °C). *iso*-eugenol was selectively hydrogenated to 2-methoxy-4-propyl phenol (**4**) whereas no reaction was observed with acetoguaiacone. Surprisingly, the aldehyde group of vanillin was selectively hydrogenated to a saturated hydrocarbon and creosol (**6**) was the major product. This suggests that these ruthenium catalysts are capable of hydro-deoxygenating aldehyde functionalities. For vanillin, a systematic study was performed to assess the effects of process parameters on catalyst activity and product selectivity. Catalyst performance is a strong function of the temperature, TPPTS/Ru ratio and the presence of salts. The highest TOF (36.4 mol/(mol Ru h)) was obtained at 60 °C, 45 bar and in the presence of NaI (0.08 M).

Kinetic modeling implies that the formation of **6** proceeds via the intermediate alcohol **5** in a series type of mechanism. TEM-EDX measurements suggest that the reactions are most likely catalysed by truly single metal homogeneous Ru complexes and not by Ru colloids/nanoparticles.

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#### References

- [1] S. Czernik, A.V. Bridgwater, *Energy Fuels* 18 (2004) 590.
- [2] A. Oasmaa, S. Czernik, *Energy Fuels* 13 (1999) 914.
- [3] R. Maggi, B. Delmon, *Hydrotreat. Hydrocrack. Oil Fract. Stud. Surf. Sci. Catal.* 106 (1997) 99.
- [4] E. Laurent, B. Delmon, *Appl. Catal. A: Gen.* 109 (1994) 97.
- [5] E. Laurent, B. Delmon, *Appl. Catal. A: Gen.* 109 (1994) 77.
- [6] E. Laurent, B. Delmon, *Ind. Eng. Chem. Res.* 32 (1993) 2516.
- [7] W. Baldauf, U. Balfanz, M. Rupp, *Biomass Bioenergy* 7 (1994) 237.
- [8] V.S.S. Kolaric, *J. Mol. Catal. A: Chem.* 111 (1996) 239.
- [9] F.J.A. Bényei, *J. Mol. Catal.* 58 (1990) 151.
- [10] P.K.M. Hernandez, *J. Mol. Catal. A: Chem.* 116 (1997) 131.
- [11] J.M. Gosselin, C. Mercier, G. Allmang, F. Grass, *Organometallics* 10 (1991) 2126.
- [12] A. Andriollo, J. Carrasquel, J. Marino, F.A. Lopez, D.E. Paez, I. Rojas, N. Valencia, *J. Mol. Catal. A: Chem.* 116 (1997) 157.
- [13] S. Fujita, Y. Sano, B.M. Bhanage, M. Arai, *J. Chem. Eng. Jpn.* 36 (2003) 155.
- [14] F.H. Mahfud, F. Ghijssen, H.J. Heeres, *J. Mol. Catal. A: Chem.* 264 (2007) 227.

- [15] A.V. Bridgwater, S. Czernik, J. Diebold, D. Meier, A. Oasma, C. Peacocke, J. Pizkorz, D. Radlein, *Fast Pyrolysis of Biomass: A Handbook*, vol. 1, CPL Press, Newbury Berkshire, UK, 1999.
- [16] A. Oasma, E. Kuoppala, Y. Solantausta, *Energy Fuels* 17 (2003) 433.
- [17] S. Czernik, D.K. Johnson, S. Black, *Biomass Bioenergy* 7 (1994) 187.
- [18] A. Oasma, E. Kuoppala, *Energy Fuels* 17 (2003) 1075.
- [19] S.I. Fujita, Y. Sano, B.M. Bhanage, M. Arai, *J. Catal.* 225 (2004) 95.
- [20] C. de Bellefon, N. Tanchoux, S. Caravieilhès, *J. Organomet. Chem.* 567 (1998) 143.
- [21] P. Gallezot, D. Richard, *Catal. Rev.: Sci. Eng.* 40 (1998) 81.
- [22] B. Coq, P.S. Kumbhar, C. Moreau, P. Moreau, M.G. Warawdekar, *J. Mol. Catal.* 85 (1993) 215.
- [23] E. Fache, C. Santini, F. Senocq, J.M. Basset, *J. Mol. Catal.* 72 (1992) 337.
- [24] J. Basset, R.C. Denney, G.H. Jeffrey, J. Mendham, *A Textbook of Quantitative Inorganic Analysis*, Longman Group Ltd., London, 1978.
- [25] C.D. Knightes, C.A. Peters, *Biotechnol. Bioeng.* 69 (2000) 160.
- [26] P. Jaisankar, B. Pal, V.S. Giri, *Synth. Commun.* 32 (2002) 2569.
- [27] R. Schwarz, H. Hering, *Org. Synth.* 4 (1953) 203.
- [28] C.A. Elliger, *Synth. Commun.* 15 (1985) 1315.
- [29] R. Maggi, B. Delmon, *Biomass Bioenergy* 7 (1994) 245.
- [30] F.P. Petrocelli, M.T. Klein, *Fuel Sci. Tech. Int.* 5 (1987) 25.
- [31] S.-i. Fujita, S. Akihara, M. Arai, *J. Mol. Catal. A: Chem.* 249 (2006) 223.
- [32] F. Joó, J. Kovacs, A. Benyei, L. Nadashi, G. Laurency, *Chem. Eur. J.* 7 (2001) 193.
- [33] C. Daguénet, P.J. Dyson, *Catal. Commun.* 4 (2003) 153.
- [34] F. Joó, J. Kovacs, A. Benyei, A. Katho, *Angew. Chem. Int. Ed.* 37 (1998) 969.
- [35] B. Scholze, D. Meier, *J. Anal. Appl. Pyrol.* 60 (2001) 41.
- [36] F. Launay, A. Roucoux, H. Patin, *Tetrahedron Lett.* 39 (1998) 1353.
- [37] F. Fache, S. Lehuédé, M. Lemaire, *Tetrahedron Lett.* 36 (1995) 885.
- [38] W. Yu, M. Liu, H. Liu, X. Ma, Z. Liu, *J. Colloid Interf. Sci.* 208 (1998) 439.
- [39] M. Liu, W. Yu, H. Liu, *J. Mol. Catal. A: Chem.* 138 (1999) 295.
- [40] J. Foise, R. Kershaw, K. Dwight, A. Wold, *Mater. Res. Bull.* 20 (1985) 147.
- [41] C. Besson, E.E. Finney, R.G. Finke, *J. Am. Chem. Soc.* 127 (2005) 8179.
- [42] J.A. Widegren, R.G. Finke, *J. Mol. Catal. A: Chem.* 191 (2003) 187.
- [43] J.A. Widegren, R.G. Finke, *J. Mol. Catal. A: Chem.* 198 (2003) 317.