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Crucial parameters in the selective biphasic hydrogenation of cinnamaldehyde by biphasic Ru-TPPTS and $RhCl(TPPTS)_3$ catalysts

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Abstract

A number of important features in the selective hydrogenation of CALD by biphasic Ru-TPPTS catalysts (TPPTS = tris(m-sulfonatophenyl) phosphine trisodium salt) are discussed. These include the methods of synthesis of water-soluble Ru-TPPTS catalysts, the influence of pH during the synthesis and the hydrogenation reaction conditions (the concentration of catalysts, excess amounts of TPPTS, mass transfer characteristics). The Ru-TPPTS catalyst is not only selective at C=O bonds (which is generally known) but also at C=C bonds if certain parameters are controlled carefully. Ninety-six percentage selectivity to unsaturated alcohol and 97% selectivity to saturated aldehyde were achieved under optimum conditions. Some characteristics of the biphasic hydrogenation by $RhCl(TPPTS)_3$ catalyst are also mentioned and compared, particularly those promoting the high selectivity to saturated aldehyde.

Keywords: Biphasic; Cinnamaldehyde; Ru; Rh; TPPTS; Hydrogenation

1. Introduction

First developed more than two decades ago, biphasic catalysis, which generally consists of a catalytic complex dissolved in an aqueous phase and reactants and products soluble in an organic phase, can significantly repay time spent on further investigation for wider industrial application. A number of successful industrial biphasic processes such as hydroformylation of propene [1], hydrodimerisation of butadiene and C–C bond formation [2] have been reported. For an optimal design of a biphasic system it is important and much debated, in respect of where the reaction takes place (either at the aqueous–organic interface or in the aqueous phase) [3–5]. One method used for this evaluation is an observation of the reaction rate enhancement when co-solvents or surfactants are introduced. If the reaction rate is increased with the addition of co-solvents, the reaction is supposed to take place in the aqueous catalytic phase [6]. Alternatively, the reaction occurs at the aqueous–organic interface, if the reaction rate is increased with the introduction of surfactants [7]. From an engineering point of view, the reaction occurs either in the aqueous phase or at the interface subject to the relative rate of liquid–liquid mass transfer to the rate of reaction of the particular system. If the liquid–liquid mass transfer rate is relatively slow, the reaction occurs at the interface; otherwise the reaction takes place in the aqueous phase (e.g. for reactants that have finite solubility in water).

The mass transfer analysis of the biphasic system is quite complicated as there are many interfaces involved, especially when one of the reactants is gaseous (e.g. hydrogenation). The gas–liquid mass transfer is evidently affected by the presence of a second liquid phase. It has been reported that the liquid–liquid mass transfer rate of all reactants was assumed to be rapid compared with the gas–liquid mass transfer, therefore the liquid–liquid equilibrium was established [8–10]. This assumption needs to be examined when a development of the biphasic system comes reaches a manufacturing scale, since the liquid–liquid mass transfer may be limiting in large scale reactions as may the gas–liquid mass transfer.

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Hydrogenation of α,β-unsaturated aldehydes such as cinnamaldehyde (CALD) is an important application in the fine chemical industry. The hydrogenation can take place at both C=C and C=O bonds generating saturated aldehyde (hydrocinnamaldehyde, HCALD) and unsaturated alcohol (cinnamyl alcohol, CALH) respectively but only one product is preferred in practice. HCALD has been used as a food additive in the flavouring industry and was recently claimed to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV [11] while CALH has been employed in the manufacture of perfumes.

In the biphasic hydrogenation of CALD, the choice of the active metals is crucial to the selectivity to the desired product (either HCALD or CALH). For example, Ru-, Os-TPPTS catalysts are suitable for C=O bond hydrogenation [12–15] while Rh-, Pd-TPPTS favour C=C bond saturation [14–17].

The aim of this work was to investigate the parameters that have a strong influence on the selectivity of the products in the hydrogenation of CALD by biphasic Ru-TPPTS catalysts, with respect to in both the synthesis method and reaction conditions. Some characteristics of the biphasic $RhCl(TPPTS)_3$ system are also included for comparison and to confirm the results.

2. Experimental

All manipulations were performed with a Schlenk technique under a nitrogen atmosphere. Analytical grade solvents and deionised water were deoxygenated prior to use. Ru-TPPTS catalysts were prepared by two different methods namely ligand exchange and redox reaction methods. The synthesis of $RhCl(TPPTS)_3$ solution has been reported in [17]. All synthesised catalytic solutions were characterised with ^{31}P NMR spectroscopy (a Bruker AMX400 instrument) using an external standard of 85%H_3PO_4/D_2O.

2.1. Synthesis of Ru-TPPTS catalysts

In the synthesis of $[RuCl_2(TPPTS)_2]_2$ with a ligand exchange method, the published procedure [18] was followed. A THF solution of $RuCl_2(PPh_3)_3$ (Johnson Matthey) (3.97×10^{-2} M Ru) was heated to 60 °C and added dropwise with an aqueous solution of TPPTS (Aldrich) (3.38×10^{-1} M). The mixture was stirred vigorously for 30 min, cooled down to room temperature and filtered. A red-brown filtrate solution was obtained and evaporated to dryness under vacuum at 50 °C. Chestnut-red solids were precipitated. Further addition of 10 mL of water, filtration, and evaporation led to final bright chestnut-red crystals which were later analysed by ^{31}P NMR spectroscopy.

For the redox reaction method, an aqueous solution of TPPTS (6.6×10^{-2} M) was heated to 50 °C. An aqueous solution of $RuCl_3$ (STREM Chemicals) (2.3×10^{-2} M Ru) was gradually added to the TPPTS solution under vigorous stirring. The reaction was continued for 8 h. The final red solution was cooled down to room temperature and analysed by ^{31}P NMR spectroscopy. In the case of pH control, a phosphate buffer (pH 7) solution (Aldrich or Fisher) was slowly added simultaneously with the addition of the $RuCl_3$ solution in order to maintain the solution pH during the synthesis at 7.

2.2. Hydrogenation reactions

The biphasic hydrogenation of CALD in toluene (100 mL) with aqueous solutions of Ru-TPPTS or $RhCl(TPPTS)_3$ catalysts (100 mL) was performed in a high-pressure autoclave reactor equipped with a 45° four-blade turbine impeller. Hydrogen gas was supplied by a hydrogenation control unit, maintaining constant pressure. During reaction, samples were withdrawn and analysed by gas chromatography (Philips PU 4550 instrument with a DB wax capillary column (30 m × 0.32 mm i.d. × 0.25 m) and a FI detector).

3. Results and discussion

3.1. Hydrogenation with Ru-TPPTS catalysts synthesised by different methods

The method of catalyst preparation was found to be influential on the performance of the hydrogenation reaction. Two well-known methods were employed for the synthesis of $[RuCl_2(TPPTS)_2]_2$: ligand exchange and redox reaction methods. After the synthesis, the composition of the catalytic products was analysed with ^{31}P NMR spectroscopy as shown in Fig. 1. A $[RuCl_2(TPPTS)_2]_2$ complex prepared by ligand exchange method of $RuCl_2(PPh_3)_3$ with TPPTS was obtained in a higher yield than that prepared from redox reaction method between $RuCl_3$ and TPPTS. This corresponds to the statement reported by Andriollo et al. [19] that ligand exchange method, compared with redox reaction method, offers compounds with higher purity. The unreacted TPPTS and oxide of TPPTS (OTPPTS) were present following these reactions.

The synthesised $[RuCl_2(TPPTS)_2]_2$ catalysts were further tested for the biphasic hydrogenation of CALD without extraction of the $[RuCl_2(TPPTS)_2]_2$ complex and it might be expected that the greater amounts of $[RuCl_2(TPPTS)_2]_2$ complex obtained with ligand exchange method should be more active for the biphasic hydrogenation of CALD, but, interestingly, it appeared to be less active than that prepared

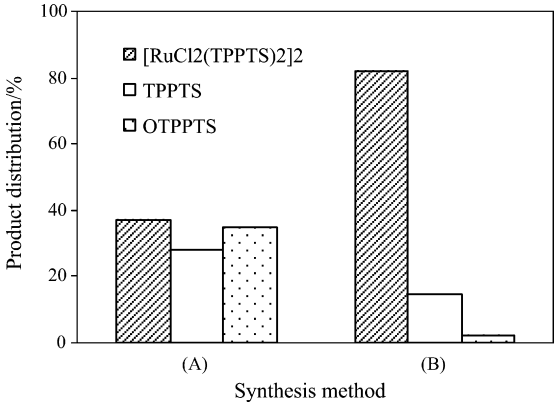

Fig. 1. Comparison in products yield obtained by different synthesis methods of $[RuCl_2(TPPTS)_2]_2$, (A) redox reaction method; (B) ligand exchange method.

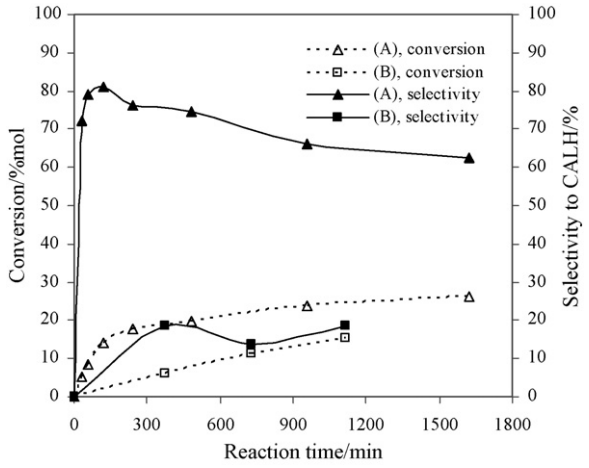

Fig. 2. Comparison in performance of $[RuCl_2(TPPTS)_2]_2$ catalytic solutions synthesised by different methods (1000 rpm, [CALD] = 0.227 M, [Ru] = 2×10^{-3} M, 40 °C, 20 barg), (A) redox reaction method; (B) ligand exchange method.

from redox reaction method as shown in Fig. 2. The low activity of $[RuCl_2(TPPTS)_2]_2$ catalyst prepared by the ligand exchange method is either due to a lack of excess TPPTS ligands or the difference in the type of active hydride species taking part in the hydrogenation mechanism of CALD. Lack of excess TPPTS ligand caused a decrease in catalyst activity and selectivity as evidenced by a previous study of a $RhCl(TPPTS)_3$ catalyst [17] and a study of biphasic and supported liquid-phase catalysts containing Ru-TPPTS complexes [20,21]. Later results concerning the effect of excess amounts of TPPTS (Section 3.4) have shown that the excess amounts of TPPTS are necessary. Under a hydrogen atmosphere, TPPTS can react with $[RuCl_2(TPPTS)_2]_2$ to form $RuHCl(TPPTS)_3$ as shown in Eq. (1) [18] and $RuHCl(TPPTS)_3$ was found to be more active than $[RuCl_2(TPPTS)_2]_2$ in the hydrogenation of cinnamaldehyde [12]. $[RuCl_2(TPPTS)_2]_2$ was also reported to give a poor conversion of cinnamaldehyde in water–toluene biphasic system compared with other water-soluble Ru-TPPTS complexes ($RuH_2(TPPTS)_4$, $RuCl_3{\cdot}3H_2O$/5TPPTS) [12]:

$$[RuCl_2(TPPTS)_2]_2 + 2TPPTS + 2H_2 \rightarrow 2RuHCl(TPPTS)_3 + 2HCl \quad (1)$$

As can be seen from Fig. 2, the selectivity to CALH was also strongly affected by different methods of synthesis. The $[RuCl_2(TPPTS)_2]_2$ complex prepared by redox reaction method preferentially hydrogenated at C=O bonds (62–81% selectivity to CALH) while the other was more selective at C=C bonds (14–19% selectivity to CALH and 56–69% selectivity to HCALD). This result emphasised that $[RuCl_2(TPPTS)_2]_2$ prepared by the ligand exchange method gave a lower performance (in terms of both activity and selectivity to CALH) compared with that prepared from the redox reaction method. Hernandez and Kalck [12] synthesied a $[RuCl_2(TPPTS)_2]_2$ solid by ligand exchange method and used it in a pure form for hydrogenation of cinnamaldehyde. It was found that this complex was selective to CALH formation (91% selectivity at 14% conversion of CALD). This is contrasted with our result in which a solution of $[RuCl_2(TPPTS)_2]_2$ complex was not selective to CALH but to HCALD. The presence of impurities such as cations has found to affect hydrogenation rate and selectivity [22] and this may be a cause.

^{31}P NMR spectra of both $[RuCl_2(TPPTS)_2]_2$ solutions prepared from redox reaction and ligand exchange methods are illustrated in Fig. 3 (A & B respectively). $[RuCl_2(TPPTS)_2]_2$ exhibits two singlets at chemical shift between 56.6 and 57.0 ppm because a hydrolysis equilibrium between the chloride ligand and water was established as observed by Hernandez and Kalck [18]. The inevitable oxide of TPPTS and unreacted TPPTS were also present in the both solutions. A small amount of an unknown compound (singlet at 37 ppm) was noticed in the $[RuCl_2(TPPTS)_2]_2$ solution prepared by the ligand exchange method. Since the reaction rates by both $[RuCl_2(TPPTS)_2]_2$ catalytic solutions in this study were very slow (<30% conversion in 27 h), a method to improve the reaction rate was sought (Section 3.2).

3.2. Influence of solution pH during the synthesis of $[RuCl_2(TPPTS)_2]_2$ with redox reaction method

Since pH was found to influence the synthesis of Pd-, Pt- and Rh-TPPTS catalysts [23], an investigation of the solution pH during the synthesis of $[RuCl_2(TPPTS)_2]_2$ catalyst with redox

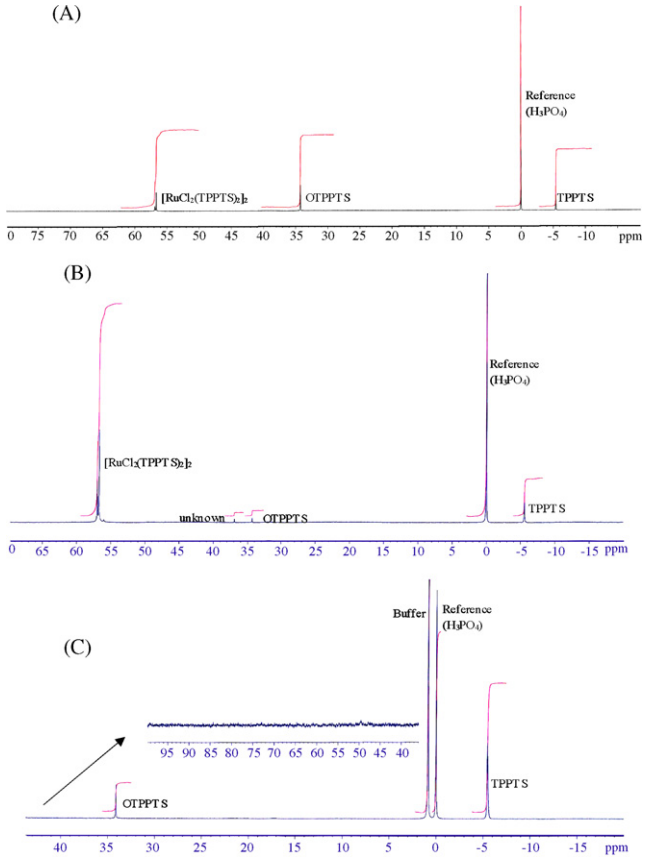

Fig. 3. ^{31}P NMR spectra of $[RuCl_2(TPPTS)_2]_2$ solutions synthesised by different methods, (A) redox reaction method, (B) ligand exchange method, (C) redox reaction method with pH control by a buffer solution.

reaction method was performed. The results showed that the solution pH greatly affected on the yield of $[RuCl_2(TPPTS)_2]_2$ which eventually resulted in the different outcomes in the biphasic hydrogenation of CALD.

To our knowledge, it was the first time that a pH control was used in the *ex situ* synthesis of water-soluble Ru-TPPTS catalysts. The synthesis of Ru-TPPTS catalyst with an addition of a phosphate buffer solution to maintain the pH at 7 showed no signal of $[RuCl_2(TPPTS)_2]_2$ on ^{31}P NMR spectrum (Fig. 3(C)) but interestingly its activity for biphasic hydrogenation of CALD was much more impressive than the $[RuCl_2(TPPTS)_2]_2$ solution prepared without pH control (final solution pH 2) as shown in Fig. 4. Blank experiments were carried out to ensure that the hydrogenation was not catalysed by either the water-soluble $RuCl_3$ or TPPTS but by an association of $RuCl_3$ and TPPTS in the presence of the buffer solution [24] and the results suggested that an active catalytic species was generated during the hydrogenation and this species was responsible for the impressive activity.

The formation of various hydride species or change in concentration of active hydride species can occur when solution pH is altered. Hernandez and Kalck [12] gave an evidence that $[RuCl_2(TPPTS)_2]_2$ was less active than other water soluble Ru-TPPTS complexes. As hydrogen is one of the reactants and is concerned with the catalytic mechanism of hydrogenation reaction, the active species is probably the ruthenium hydride species, for example, $H_2Ru(TPPTS)_4$ or $HRuCl(TPPTS)_3$. Fujita et al. [25] synthesised $H_2Ru(TPPTS)_4$ and $HRuCl(TPPTS)_3$ complexes from ligand exchange and redox reaction methods respectively and these two complexes had different activity and selectivity to CALH; the former was more active and selective to the formation of CALH. In addition Hernandez and Kalck [12] reported that $H_2Ru(TPPTS)_4$ was more active than $HRuCl(TPPTS)_3$ in a water–toluene biphasic system but both more selective to the formation of CALH with a selectivity of 95%. Without a pH control, $HRuCl(TPPTS)_3$ was generated *in situ* from the redox reaction between $RuCl_3$ and TPPTS and found in the reaction medium after catalysis. However this complex could alter to $H_2Ru(TPPTS)_4$ (Eq. (2)) as suggested by Grosselin et al. [14]. In addition the influence of pH on the formation of different water soluble Ru-TPPMS[1] complexes and the selectivity to CALH was studied by Joó et al. [21]. It was found from their study that at pH $\leq$ 3.3 the dominant complex was $HRuCl(TPPMS)_3$ while at pH $\geq$ 7 it was $H_2Ru(TPPMS)_4$. $H_2Ru(TPPMS)_4$ was also expected to be the true catalytic species in the selective hydrogenation of CALD to CALH. Regarding to the structural similarity between TPPMS and TPPTS, therefore it is likely that the active species in our study is $H_2Ru(TPPTS)_4$. However further investigation (e.g. *in situ* NMR analysis) is required to identify the genuine species.

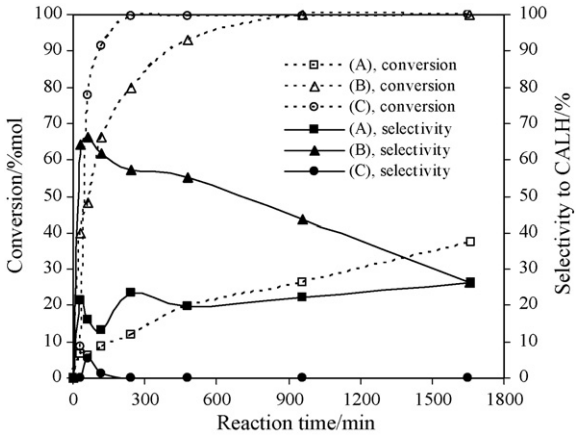

Fig. 4. Comparison in performance of Ru-TPPTS catalytic solutions synthesised by redox reaction method with and without pH control (1000 rpm, [CALD] = 0.227 M, 40 barg, 70 °C, [Ru] = 2.0×10^{-3} M, TPPTS/Ru = 4.5), (A) without pH control, (B) with pH control at 7 by buffer solution, (C) $RhCl(TPPTS)_3$ solution, [Rh] = 2.3×10^{-3} M, TPPTS/Rh = 4.1.

$$HRuCl(TPPTS)_3 + H_2 + TPPTS \rightarrow H_2Ru(TPPTS)_4 + HCl \quad (2)$$

The selectivity to CALH was also increased with the neutral pH Ru-TPPTS solution (Fig. 4) but it was not high enough (maximum 66% at 48% conversion and dropped to 44% at 100% conversion) since the concurrent hydrogenation took place at C=C bonds to generate the saturated alcohol (hydrocinnamyl alcohol, HCALH). The selectivity to HCALH was 50% at 100% conversion. The conversion curve of CALD by the neutral Ru-TPPTS solution was similar to that by a $RhCl(TPPTS)_3$ solution but the selectivity of the products was the opposite. The neutral Ru-TPPTS solution selectively hydrogenated at C=O bonds while the $RhCl(TPPTS)_3$ solution preferred C=C bonds (almost flat selectivity curve to CALH was obtained). However both catalysts generated HCALH as the final product when the reaction was left to continue after the complete conversion of CALD.

3.3. Effect of concentration of Ru-TPPTS catalyst

The concentration of the Ru-TPPTS catalytic solution (prepared from the redox reaction method at pH 7) is another crucial factor in the selectivity to the required products. Although the Ru-TPPTS catalyst was previously shown to be selective at C=O bonds (solid curve B in Fig. 4), with the low concentration of Ru-TPPTS (3.4×10^{-4} M of Ru), the hydrogenation was exceptionally selective at C=C bonds (97% selectivity to HCALD at 72% conversion) as shown in Fig. 5. A selective hydrogenation for HCALD was also obtained with $RhCl(TPPTS)_3$ catalyst (84% selectivity at 74% conversion) at a similar concentration of Rh (3.2×10^{-4} M). Although the selectivity to HCALD with $RhCl(TPPTS)_3$ catalyst was lower than Ru-TPPTS catalyst, its activity was higher (100% conversion within 5 h of reaction compared with 72% conversion at 8.5 h of reaction).

When the higher concentration of Ru-TPPTS catalyst (2.0×10^{-3} M of Ru) was introduced, the selectivity was switched to favour CALH as shown in Fig. 5 (selectivity to HCALD and CALH were 18% and 73%, respectively at 72% conversion). A similar result was obtained with a different

[1] TPPMS: (3-sulfonatophenyl) diphenylphosphine sodium salt.

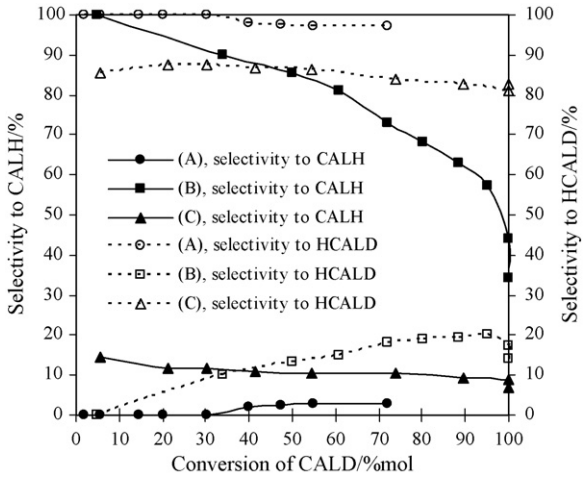

Fig. 5. Effect of concentration of Ru-TPPTS catalysts synthesised by redox reaction at pH 7 (1000 rpm, [CALD] = 0.227 M, 40 barg, 70 °C, TPPTS/Ru = 4.2), (A) [Ru] = 3.4×10^{-4} M, (B) [Ru] = 2.0×10^{-3} M, (C) $RhCl(TPPTS)_3$ catalyst, [Rh] = 3.2×10^{-4} M, TPPTS/Rh = 4.1.

ligand bonded to Ru, Ru-TPPMS system, in which the selectivity to CALH was increased when the substrate to metal ratio was decreased [26]. This behaviour change with concentration of Ru-TPPTS catalyst is promising. However a continuous drop in selectivity to CALH was observed, mainly because of the consecutive formation of HCALH (the selectivity to HCALD was less than 20% over the whole range of conversion).

It is worth mentioning that in the small-laboratory scale (i.e. total volume of solutions = 10 mL), a very high selectivity to CALH (99%) by a biphasic Ru-TPPTS catalyst was achieved by a Grosselin et al. [14] as compared in Table 1. Although the direct comparison could not be made, it can be seen that when hydrogenation was performed on bigger scale, both activity and selectivity to CALH decreased. The lower activity is because the concentration of Ru catalyst was lower in the bigger reactor which also affected on the selectivity. Less than 1% of the Ru catalyst to the CALD reactant was enough to accelerate the reaction and to achieve the reasonable selectivity to CALH unless the Ru concentration in the aqueous phase was too low (the reaction was selective to HCALD when Ru concentration was 3.4×10^{-4} M).

Table 1
Comparison in biphasic hydrogenation of CALD with Grosselin et al. [14]

Parameters	Grosselin et al. (1991)	This study	
$RuCl_3$ (mmol)	0.1	0.034	0.203
TPPTS (mmol)	0.5	0.143	0.853
CALD (mmol)	20	7.57	22.7
Water (mL)	5	100	100
Toluene (mL)	5	100	100
[Ru] in aqueous phase (M)	0.02	0.00034	0.002
Ru/CALD (%)	0.50	0.45	0.89
P_{H_2} (bar)	20	40	40
Temperature (°C)	35	70	70
Conversion at 3 h (%)	99	100	71.98
Selectivity to CALH (%)	98	0.01	72.80

3.4. Effect of excess TPPTS

As it is known from the results of the biphasic $RhCl(TPPTS)_3$ catalyst system that the addition of excess TPPTS improved both the activity and selectivity to HCALD [17], a similar result was expected with the Ru-TPPTS catalysts. As shown in Fig. 6, an addition of free TPPTS powder (1.69 mmol) into the Ru-TPPTS aqueous solution (initial ratio of TPPTS/Ru = 4.2) to make up the total ratio of TPPTS/Ru of 12.5 improved both reaction rate and selectivity to CALH (96% at the first 100% conversion). However, after all CALD was consumed, the reaction continued and CALH hydrogenated, giving HCALH as the final product. The high selectivity to CALH with high ligand excess was also observed with Ru-TPPMS system and the C=C reduction could not be eliminated completely [21]. In practice the high selectivity to CALH can be obtained if the reaction is stopped when all CALD is utilised. It may be helpful to use a lower concentration of CALD (i.e. 0.076 M) as it was shown to be an effective way to stop the consecutive reaction of HCALD to HCALH in the biphasic $RhCl(TPPTS)_3$ system; 99.9% selectivity to HCALD was obtained and remained constant even at 100% conversion of CALD [17].

3.5. Mass transfer resistance

A final concern in the biphasic hydrogenation of CALD is the mass transfer process which can be a limiting process in a large scale production as intense stirring may be difficult and there are many interfaces involved. Our investigation in the biphasic catalysis of $RhCl(TPPTS)_3$ showed that the system was significantly transport controlled, which can be gas–liquid or liquid–liquid mass transfer [17]. A similar result (the evaluated activation energy value of 7 kcal/mol) was reported even in the smaller laboratory scale [14] in which mass transfer resistance should be less important and minimised because of the intensive stirring. Furthermore it was noted that in the

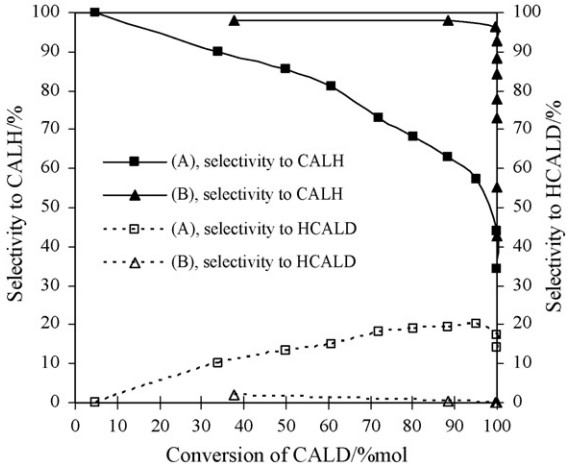

Fig. 6. Effect of excess amounts of TPPTS in Ru-TPPTS solutions synthesised by redox reaction at pH 7 (1000 rpm, [CALD] = 0.227 M, 40 barg, 70 °C, initial TPPTS/Ru = 4.2), (A) [Ru] = 2.0×10^{-3} M, (B) [Ru] = 2.0×10^{-3} M and excess TPPTS (1.69 mmol).

supported aqueous phase catalyst of $RhCl(TPPTS)_3$, the gas–liquid mass transfer resistance was significant [24] and this perhaps was an explanation for the biphasic system too because the catalyst is located in the aqueous phase in which hydrogen has a low solubility compared with the organic phase. The use of a higher pressure could perhaps overcome this as long as relatively low concentrations of CALD are employed to give high selectivity.

4. Conclusions

The selective hydrogenation can be made successful by careful choice of the nature of the metal so that cinnamaldehyde can be reduced either to the corresponding cinnamyl alcohol with the Ru-TPPTS catalyst or to the saturated hydrocinnamaldehyde with the $RhCl(TPPTS)_3$ catalyst or the Ru-TPPTS catalyst under particular conditions. $[RuCl_2(TPPTS)_2]_2$ can be synthesised with different methods but its activity was found to be different and the selectivity to the hydrogenated products was also affected. In order to obtain the highest selectivity to cinnamyl alcohol, the Ru-TPPTS catalysts synthesised by redox reaction method are recommended. During the synthesis, the solution pH also influenced on the formation of $[RuCl_2(TPPTS)_2]_2$. A particular advantage to be gained by synthesising the Ru-TPPTS catalyst in a neutral buffered medium; the most efficient catalyst for the reduction of C=O was, if the concentration of Ru-TPPTS catalyst was not too low, prepared from $RuCl_3$ and TPPTS with an addition of a buffer (pH 7) solution. An excess amount of TPPTS considerably improved both the activity and selectivity to cinnamyl alcohol and this finding should be further investigated for the supported aqueous phase systems utilising both Rh and Ru complexes.

Acknowledgements

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