

# Recyclability of water-soluble ruthenium–phosphine complex catalysts in multiphase selective hydrogenation of cinnamaldehyde using toluene and pressurized carbon dioxide

Shin-ichiro Fujita, Shuji Akihara, Masahiko Arai \*

*Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

Received 19 December 2005; accepted 4 January 2006

Available online 20 February 2006

## Abstract

The recyclability of water-soluble ruthenium–phosphine complex catalysts was investigated in water–toluene and in water–pressurized carbon dioxide systems for selective hydrogenation of *trans*-cinnamaldehyde (CAL). For the first hydrogenation run, the selectivity for cinnamyl alcohol (COL) is high for both toluene and dense CO<sub>2</sub>, because of interfacial catalysis in which the reaction mainly occurs at the interface between the aqueous phase and the other toluene or dense CO<sub>2</sub> phase. The total CAL conversion and the COL selectivity decrease on the second run, more significantly with dense CO<sub>2</sub> than toluene. On the subsequent runs, however, less significant changes were observed. During the first run, the active metal complexes should change to much less active ones such as Ru(H)<sub>2</sub>L<sub>*n*</sub>(TPPTS)<sub>*m*</sub> (L = COL) by accumulation of the main product of COL. This structural change may occur more easily in multiphase hydrogenation with dense CO<sub>2</sub> than that with toluene, probably because the solubility in the dense CO<sub>2</sub> gas phase is even smaller than that in toluene. For homogeneous reaction of COL in aqueous phase, Ru(H)<sub>2</sub>L<sub>*n*</sub>(TPPTS)<sub>*m*</sub> catalyzes the isomerization to HCAL compared with the hydrogenation to hydrocinnamyl alcohol. With those complexes, however, the selectivity for COL is still comparable to that for HCAL for multiphase hydrogenation reactions because the hydrogenation of an ampholytic substrate of CAL occurs mainly at interface between water and toluene or dense CO<sub>2</sub> gas phase. Interactions of CO<sub>2</sub> molecules with CAL would also increase the reactivity of carbonyl group of the substrate.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Multiphase hydrogenation; Cinnamaldehyde; Ruthenium–phosphine complex; Supercritical carbon dioxide; Catalyst recycling

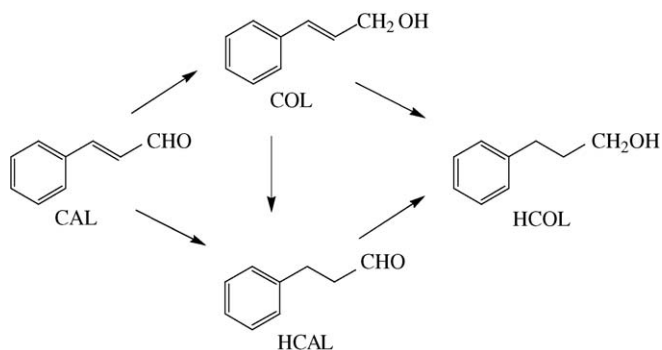
## 1. Introduction

Multiphase catalytic reactions are of industrial significance because of their distinctive features compared with homogeneous counterparts [1–4]. An interesting aspect is the change of product distribution, which is demonstrated by an example of selective hydrogenation of an  $\alpha,\beta$ -unsaturated aldehyde, *trans*-cinnamaldehyde (CAL) (Scheme 1). Such a selective hydrogenation is one of important reactions for the production of perfume and fine chemicals [5–7]. The selectivity for the corresponding unsaturated alcohol, cinnamyl alcohol (COL), can be improved by multiphase reactions using water–organic liquid systems [8–18], water–dense CO<sub>2</sub> systems [19], and supported liquid phase catalysts [20,21]. The present

authors have recently indicated that COL is selectively produced with a water-soluble complex of ruthenium–trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS), which exists in an aqueous phase being in contact with a bulk CAL phase in toluene, pure CAL, or dense CO<sub>2</sub> (Fig. 1) [19]. The high COL selectivity observed may be ascribed to that the reaction mainly occurs at the interface between the two phases having different solvent properties and the substrate CAL is of amphiphilic nature (like surfactants).

The possibility of the control of product distribution is a positive feature of multiphase catalytic reactions. Needless to say, another important aspect of these reactions is easy phase separation of a reaction mixture and easy recovery and recycling of a catalyst phase [1–4]. Although the recycling is an important aspect from practical point of view, it has little been studied so far for multiphase hydrogenation of CAL and other  $\alpha,\beta$ -unsaturated aldehydes. Sánchez-Delgado et al. studied selective hydrogenation of CAL in a water–toluene multiphase system using Os

\* Corresponding author. Tel.: +81 11 706 6594; fax: +81 11 706 6594.  
E-mail address: [marai@eng.hokudai.ac.jp](mailto:marai@eng.hokudai.ac.jp) (M. Arai).



Scheme 1. Hydrogenation of *trans*-cinnamaldehyde (CAL) to cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL) and isomerization of COL to HCAL.

and Ru complex catalysts [12]. They examined the recycling with  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$  and found that this catalyst was recyclable with no appreciable loss of activity and selectivity for three repeated runs, indicating a stable COL selectivity of 85%. Hernandez and Kalck showed that initially active Ru/TPPTS complex catalysts changed in their structure showing less activity after water–toluene multiphase hydrogenation of CAL; so they remark that the recycling would be difficult in many cases [15]. The present work has thus been undertaken to examine the catalyst recycling for the three multiphase reaction systems given in Fig. 1, which are effective for the selective hydrogenation of CAL to COL, as above-mentioned. It has been observed that the activity of Ru/TPPTS complex catalysts changes during repeated runs; the overall CAL conversion and the COL selectivity decrease while the selectivity for the saturated aldehyde, hydrocinnamaldehyde (HCAL), increases. These changes occur

greatly between the starting and first recycling runs but become marginal during the subsequent recycling runs. An important reason for these changes is a change in the structure of the complex catalysts, which is easier to occur in the reactions with dense  $\text{CO}_2$  than those with toluene. The changed catalysts are less active to hydrogenation of CAL to COL in water but, for multiphase reactions, the COL selectivity is still comparable to that for HCAL, which may be ascribable to the interfacial catalysis and/or the influence of dense  $\text{CO}_2$  molecules on the reactivity of CAL.

## 2. Experimental

### 2.1. Catalyst preparation

For multiphase reactions using water, ruthenium(III) chloride (Wako) and TPPTS (Fluca) were charged into a high-pressure stainless steel reactor of  $50\text{ cm}^3$ , followed by introduction of water degassed by bubbling with argon. The reactor was heated up to  $60\text{ }^\circ\text{C}$  using a water bath and then charged with  $\text{H}_2$  up to 2 MPa. The mixture was stirred with a magnetic stirrer at this temperature for 1 h. The catalyst-containing water was used for hydrogenation of CAL as described below. The complex thus prepared will be herein referred to as complex **1**, for which an expected form is  $\text{Ru}(\text{H})(\text{Cl})(\text{TPPTS})_3$  [20].

Another chlorine-free complex,  $\text{Ru}(\text{H})_2(\text{TPPTS})_4$ , was also prepared from  $\text{Ru}(\text{Cl})_2(\text{TPP})_3$  (Aldrich) according to the literature [22,23].  $\text{Ru}(\text{Cl})_2(\text{TPP})_3$  was dissolved in THF, an aqueous solution of TPPTS was added to this THF solution, and the mixture was stirred at  $60\text{ }^\circ\text{C}$  for 1 h under reflux conditions. Another aqueous solution of TPPTS was prepared and  $\text{NaBH}_4$  was gradually added to this solution cooled with ice. Then, this solution was added to the previous aqueous solution and the mixture was stirred at room temperature for 10 min. Then, the aqueous solution was subjected to vacuum distillation at 0.08 MPa and at  $80\text{ }^\circ\text{C}$  for a few hours, yielding a yellow solid, which was a complex of  $\text{Ru}(\text{H})_2(\text{TPPTS})_4$ , including  $\text{NaCl}$  and  $\text{B}(\text{OH})_3$ . On the basis of weight of Ru, the yield of this complex was about 90%, and it will be referred to as complex **2** in the following.

### 2.2. Selective hydrogenation

For multiphase hydrogenation reactions using water, cinnamaldehyde was added to the reactor including the catalyst-containing water and the reactor was heated to a reaction temperature of  $70\text{ }^\circ\text{C}$ . Then the reactor was introduced with  $\text{H}_2$  up to the desired pressure and then  $\text{CO}_2$  up to the desired total pressure with a high-pressure liquid pump (JASCO SCF-Get). The reaction was conducted while stirring the mixture for 2 h. After the reaction, the reactor was cooled to room temperature with an ice-water bath and it was depressurized to atmospheric pressure. The reaction mixture was analyzed by gas chromatography (Shimadzu GC-14B) with a capillary column (Zebtron ZB-50,  $30\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$ ) and GC mass spectrometry (Shimadzu GC-MS QP5050A) with a capillary column (GL Science TC-17,  $30\text{ m} \times 0.53\text{ mm} \times 0.25\text{ }\mu\text{m}$ ). For recycling, the catalyst-containing water phase was separated and washed with

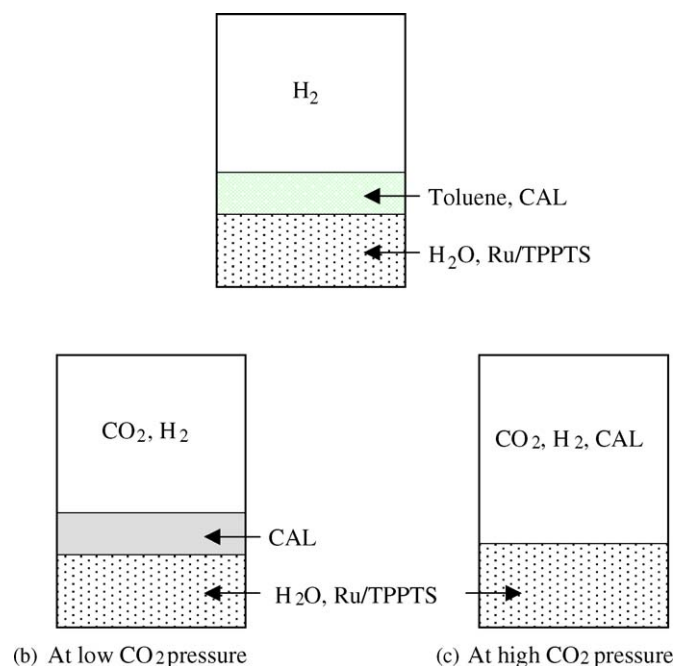


Fig. 1. Two- and three-phase hydrogenation reactions of CAL using an organic solvent of toluene (a) and dense  $\text{CO}_2$  at low (b) and high (c) pressures studied in this work.

toluene under argon atmosphere after a catalytic run and the next run was conducted with fresh substrate under the same conditions.

### 2.3. Phase behavior

The examination of the phase behavior is important to study chemical reactions in  $\text{scCO}_2$ ; it is significant to see whether the reaction is taking place homogeneously in a single phase or heterogeneously in two or more phases. A  $10\text{ cm}^3$  high-pressure sapphire-windowed view cell was used to determine the existing phases and the volume of these phases under the same conditions as used for hydrogenation reactions [17,18].

## 3. Results and discussion

### 3.1. Activity change on recycling

The two- and three-phase hydrogenation reactions of *trans*-cinnamaldehyde studied in this work are illustrated in Fig. 1, in which (a) is an ordinary gas–organic liquid–water system and (b) and (c) are, respectively, three- and two-phase systems using water-soluble ruthenium complex catalyst, which are pressurized by  $\text{CO}_2$  at low and high pressures. For each reaction system, hydrogenation run was conducted for a certain time, the catalyst-containing water phase was separated by decantation and washed with toluene, and this water phase was again used with fresh substrate for a second run under the same conditions. Further recycling runs were conducted in the same manner.

Fig. 2 shows the total conversion and product distribution for the first and recycled runs with the water-soluble Ru complex **1**  $[\text{Ru}(\text{H})(\text{Cl})(\text{TPPTS})_3]$  using toluene and dense  $\text{CO}_2$ . One can see common trends that the total CAL conversion decreases and the product distribution changes in repeated runs. The selectivity for cinnamyl alcohol decreases while that for hydrocinnamaldehyde (HCAL) increases. The selectivity for hydrocinnamyl alcohol (HCOL) little changes. These changes are much larger between the first and second runs than those between the subsequent repeated runs. The product selectivity does not depend on the total conversion so much, which is indicated from the results of Table 1 and Fig. 3. Table 1 shows the selectivity for COL to be slightly larger at a smaller conversion but this change is less significant as compared with the change observed during the recycling runs (Fig. 2). A typical time-course of Fig. 3 also indicates that the product selectivity is little influenced by the total conversion. Thus, the change of the product selectivity observed in Fig. 2 is not ascribable to that of the total conversion. During the repeated runs, no color changes were indicated for the organic and water phases and no colloidal metal particles were detected by visual observations. These observations indicate that the leaching of Ru species into the organic phase and the deposition of Ru species in the both phases did not occur under the reaction conditions used. Thus, the change of catalytic activity observed during repeated runs should be caused by a change of structure of the catalyst.

Next, the other water-soluble Ru complex **2**  $[\text{Ru}(\text{H})_2(\text{TPPTS})_4]$  was examined. Fig. 4 gives the results

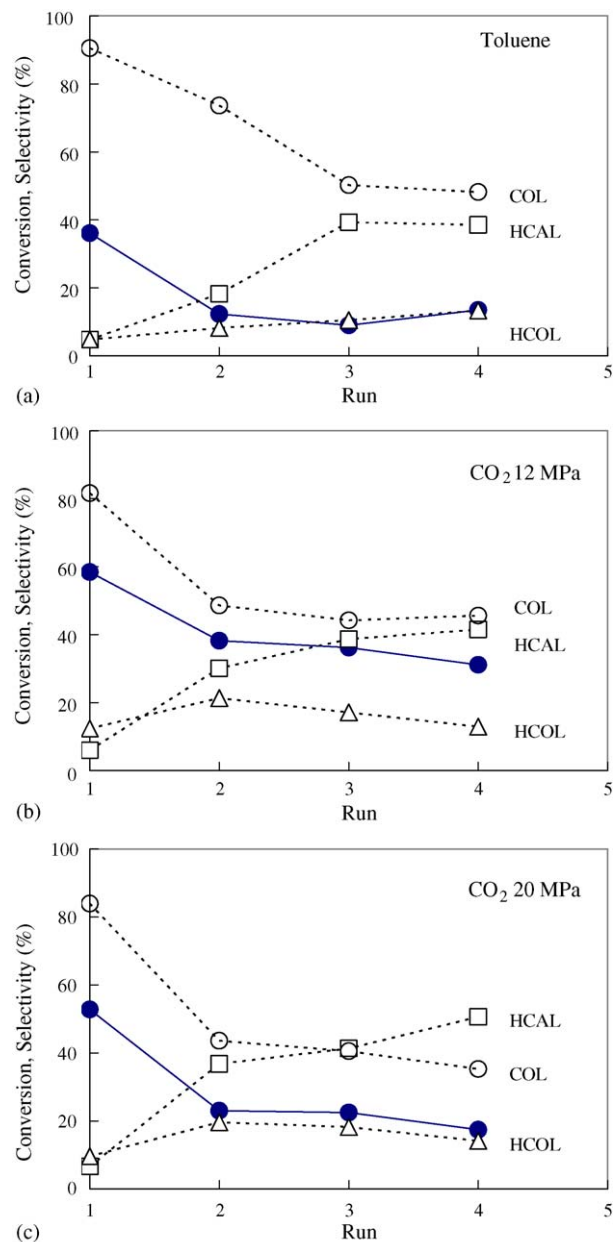


Fig. 2. Recycling results of the water-soluble Ru complex **1** for selective hydrogenation of cinnamaldehyde (CAL) using toluene (a) and  $\text{scCO}_2$  at 12 MPa (b) and 20 MPa (c). Total conversion (●) and product selectivity (○, □, △). Reaction conditions: CAL 8.0 mmol, water 4  $\text{cm}^3$ , toluene 10  $\text{cm}^3$ , Ru 0.0355  $\text{mmol cm}^{-3}$ ,  $P/\text{Ru}=4$ ,  $\text{H}_2$  2 MPa, 70 °C, 2 h. The state of reaction mixture is: gas–water–toluene three-phase (a), gas–water–CAL three-phase (b), and gas–water two-phase (c) (CAL is mostly dissolved in the gas phase).

of repeated runs of CAL hydrogenation with this complex using toluene and dense  $\text{CO}_2$ . Two series of runs were made, in each of which the first and recycled runs were conducted at the same reaction time of 0.5 or 2.0 h. When the first runs of Figs. 2 and 4 are compared, the complex **2** is more active and selective to the formation of COL. Similar to the complex **1**, however, the total conversion and COL selectivity decrease on recycling for the complex **2**. In the case of  $\text{CO}_2$ , the COL selectivity is similar between the complexes **1** and **2** after repeated runs, while, it is still higher for the complex **2** compared with the complex **1** in

Table 1  
Results of two- and three-phase hydrogenation of cinnamaldehyde (CAL) using the water-soluble Ru complex catalysts **1** and **2** using toluene and pressurized CO<sub>2</sub>

Catalyst	Solvent	Phases <sup>a</sup>	Time (h)	Conversion (%)	COL selectivity (%)
Complex 1: Ru(H)(Cl)(TPPTS) <sub>3</sub> (RuCl <sub>3</sub> + TPPTS)	Toluene	G–L–W	0.5	21	94
			2.0	36	91
	CO <sub>2</sub> (12 MPa)	G–L <sup>b</sup> –W	0.5	37	91
			2.0	58	82
	CO <sub>2</sub> (20 MPa)	G–W	0.5	32	87
			2.0	53	84
Complex 2: Ru(H) <sub>2</sub> (TPPTS) <sub>4</sub>	Toluene	G–L–W	0.5	85	98
			2.0	99	96
	CO <sub>2</sub> (12 MPa)	G–L <sup>b</sup> –W	0.5	87	98
			2.0	89	90
	CO <sub>2</sub> (20 MPa)	G–W	0.5	74	97
			2.0	80	89

Reaction conditions: CAL 8.0 mmol, water 4 cm<sup>3</sup>, toluene 10 cm<sup>3</sup>, Ru 0.0355 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 70 °C.

<sup>a</sup> G: CO<sub>2</sub>-rich gas phase, L: CAL-containing liquid phase, and W: catalyst-containing water phase (see Fig. 1 for the details of those multiphase reaction systems).

<sup>b</sup> CAL-rich liquid phase.

the case of toluene. Fig. 4 also shows that the extent of decrease in the COL selectivity on recycling is larger when a longer reaction time of 2.0 h is used. Note, again, that the change of the product distribution does not depend on the total conversion, as demonstrated from the results of Fig. 4 and Table 1. For the Ru complex **2** as well, the change of catalytic performance shown in Fig. 4 should be due to a change of structure of the catalyst during repeated runs, which may occur significantly during the first run and proceed further for a longer reaction time of 2.0 h than 0.5 h.

Various water-soluble Ru/TPPTS complexes were compared in their catalytic performance for selective hydrogenation of CAL [14,15]. Hernandez and Kalck indicate that [Ru(H)<sub>2</sub>(TPPTS)<sub>4</sub>] is more active than [Ru(H)(Cl)(TPPTS)<sub>3</sub>] in a water–toluene multiphase system at 40 °C but these are both selective to the formation of COL with a selectivity of 95% [15], which are similar to the present results obtained at 70 °C given in Figs. 2 and 4. Sánchez-Delgado et al. studied selective

hydrogenation of CAL in a water–toluene multiphase system at 100 °C using Os and Ru complex catalysts [12]. They examined the recycling with OsCl<sub>3</sub>·3H<sub>2</sub>O/TPPTS and found that this catalyst was recyclable with no appreciable loss of activity and selectivity for three repeated runs, indicating a stable COL selectivity of 85%.

### 3.2. Activity of used catalyst for aqueous homogeneous hydrogenation

As above-mentioned, the activity of the Ru complex catalysts changes during repeated runs of three-phase hydrogenation and this activity change is assumed to be caused by a change of structure of the catalysts. To inspect this structural change, the features of the used complex catalysts were examined for homogeneous hydrogenation of CAL in the aqueous phase. After a three-phase reaction run, the catalyst (complex **1**)-containing water phase was separated by decantation, washed with toluene a few times, added with a small quantity of fresh CAL below its solubility, and pressurized with H<sub>2</sub> to start hydrogenation under biphasic conditions, under which the reactions occurred in the aqueous phase. The results obtained are given in Table 2, including the results with the as-prepared complex **1** catalyst. Table 2 shows that the activity and selectivity significantly change after the multiphase reactions using either CO<sub>2</sub> or toluene; both the total conversion and the COL selectivity decrease. These results indicate that the complex **1** changes to a structure which is less active and selective to the formation of COL in the aqueous phase, after the multiphase reactions using CO<sub>2</sub> and toluene but more remarkably for the former.

In addition, the activity of the used Ru complex **1** was further examined for homogeneous hydrogenation reactions in the aqueous phase using either COL or HCAL as well as CAL for a starting substrate. The results obtained are given in Table 3, indicating that the used catalyst becomes less active for hydrogenation of HCAL to HCOL while its total activity little changes for the reaction with COL but it becomes more

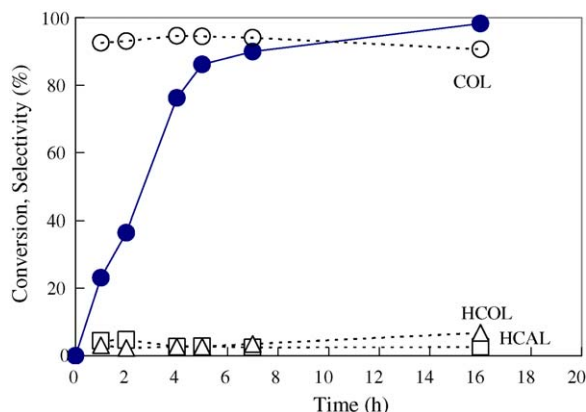


Fig. 3. The change of total conversion (●) and product selectivity (○, □, △) with time in selective hydrogenation of cinnamaldehyde (CAL) using the Ru complex **1** under three-phase (gas–water–toluene) conditions. Reaction conditions: CAL 8.0 mmol, water 1 cm<sup>3</sup>, toluene 10 cm<sup>3</sup>, Ru 0.044 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 4 MPa, 70 °C.



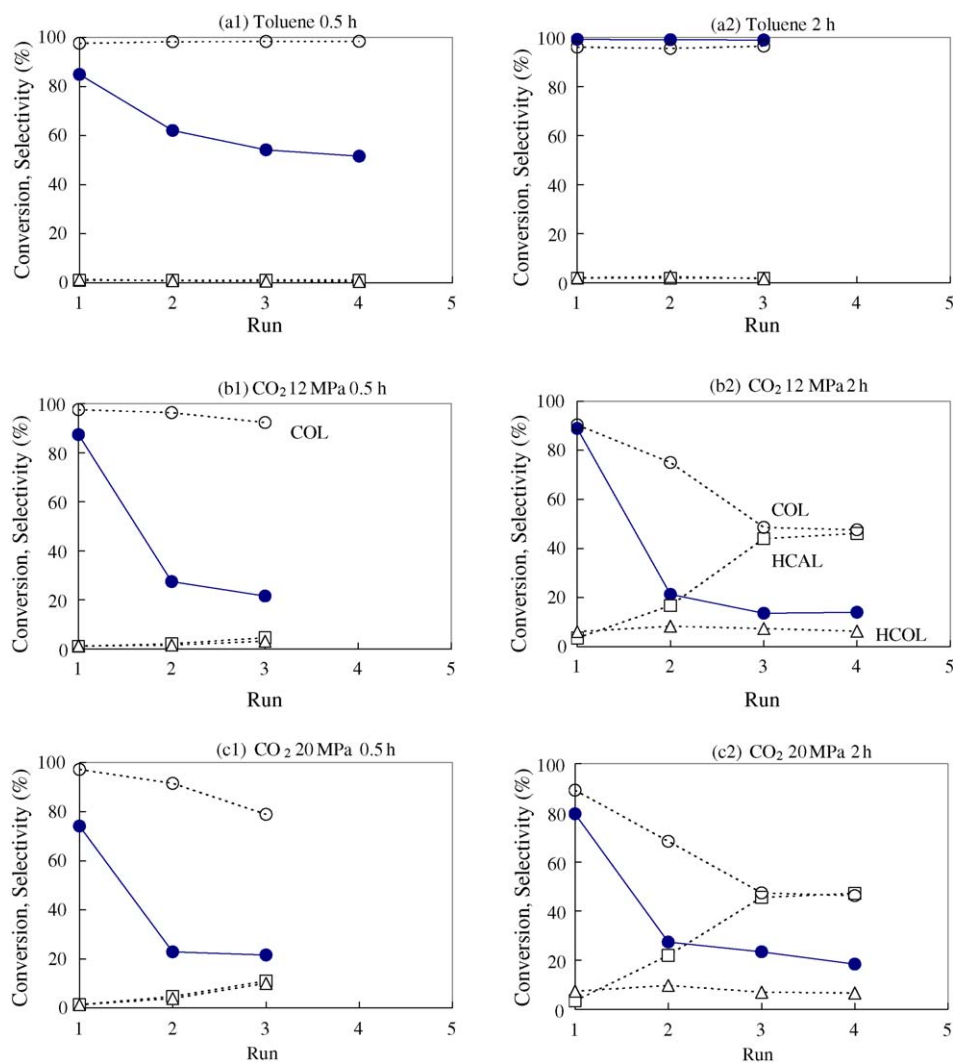


Fig. 4. Recycling results of the water-soluble Ru complex **2** for selective hydrogenation of cinnamaldehyde (CAL) in toluene (a) and in scCO<sub>2</sub> at 12 MPa (b) and 20 MPa. Total conversion (●) and product selectivity (○, □, △). Reaction conditions: CAL 8.0 mmol, water 4 cm<sup>3</sup>, toluene 10 cm<sup>3</sup>, Ru 0.0355 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 70 °C, 0.5 h (a1–c1) and 2.0 h (a2–c2). The state of reaction mixture is: (a) gas–water–toluene three-phase, (b) gas–water–CAL three-phase, and (c) gas–water two-phase (CAL is completely dissolved in the gas phase).

active for the isomerization to HCOL than the hydrogenation to HCOL.

According to the previous literature [23], a possible structure of the used Ru complex is Ru(H)<sub>2</sub>(COL)<sub>n</sub>(TPPTS)<sub>m</sub>, which is formed after the formation and accumulation of COL in toluene and dense CO<sub>2</sub> phases during multiphase hydrogenation of CAL. This structural change may be easier to occur for the reaction system with pressurized CO<sub>2</sub> than that with toluene because the solubility of COL in the dense CO<sub>2</sub> gas phase is even smaller than that in toluene and so such a structural change occurs more easily through water–CO<sub>2</sub> interface compared with water–toluene interface. The examination of phase behavior will give a rough estimation of the solubility, as described previously [24]. The solubility of COL in CO<sub>2</sub> was estimated to be about 60 μmol cm<sup>-3</sup> in 17 MPa CO<sub>2</sub> and 15 μmol cm<sup>-3</sup> in 17 MPa CO<sub>2</sub> + 2 MPa H<sub>2</sub>. The present hydrogenation reactions were conducted at lower CO<sub>2</sub> pressures in the presence of 2 MPa H<sub>2</sub>, and so the quantity of COL soluble in the gas phase was even smaller.

During the multiphase hydrogenation of CAL, the complexes **1** [Ru(H)(Cl)(TPPTS)<sub>3</sub>] and **2** [Ru(H)<sub>2</sub>(TPPTS)<sub>4</sub>] may change to those like Ru(H)<sub>2</sub>(COL)<sub>n</sub>(TPPTS)<sub>m</sub> which is less active and less selective to the transformation of CAL to COL but promotes the homogeneous isomerization of COL to HCOL in the aqueous phase (Table 3). A complex [Ru(H)(L)(TPPTS)<sub>2</sub>]Cl (L = COL or toluene) is unlikely to form under the present conditions since it would be an inactive form according to Hernandez and Kalck, who reported that a similar complex [Ru(H)(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)(TPPTS)<sub>2</sub>]Cl did not catalyze hydrogenation of CAL in ether [15]. Although Ru(H)<sub>2</sub>(COL)<sub>n</sub>(TPPTS)<sub>m</sub> may be selective to the isomerization of COL to HCOL than hydrogenation of COL to HCOL, the selectivity for COL is still comparable to that for HCOL in recycled runs under multiphase conditions as shown in Fig. 1. Important factors for this fact are the interfacial catalysis that the hydrogenation occurs mainly at interface between the catalyst-containing aqueous phase and the CAL-containing phase (toluene, CAL, or dense CO<sub>2</sub>) and the

Table 2  
Results of homogeneous hydrogenation<sup>a</sup> of CAL in water using the Ru complex **1** before and after multiphase hydrogenation reactions<sup>b</sup> using a solvent of toluene or dense CO<sub>2</sub>

Catalyst	Phases <sup>b</sup>	Time <sup>b</sup> (h)	Conversion <sup>a</sup> (%)	Selectivity <sup>a</sup> (%)		
				COL	HCAL	HCOL
As prepared <sup>c</sup>	–	–	87	67	6	27
After multiphase reaction in CO <sub>2</sub> (8 MPa)	G–L <sup>d</sup> –W	0.5	72	19	32	49
		2.0	52	17	35	48
After multiphase reaction in toluene	G–L–W	0.5	73	29	22	50
		2.0	73	28	20	52

<sup>a</sup> Homogeneous reaction in water in the absence of CO<sub>2</sub>. Reaction conditions: CAL 0.095 mmol, water 2 cm<sup>3</sup>, Ru 0.011 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 60 °C, 5 min.

<sup>b</sup> For multiphase reactions. Reaction conditions: CAL 8.0 mmol, water 2 cm<sup>3</sup>, toluene 10 cm<sup>3</sup>, CO<sub>2</sub> 8 MPa, Ru 0.011 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 70 °C.

<sup>c</sup> Complex **1** Ru(H)(Cl)(TPPTS)<sub>3</sub>.

<sup>d</sup> CAL-rich liquid phase.

amphiphilic nature of CAL substrate [12,20]. As pointed out by Sánchez-Delgado et al. [12], the polar C=O bond points towards the catalyst-containing water phase but the less hydrophilic C=C bond points away from the water phase. As a result, the former is selectively hydrogenated, yielding COL; the COL formed remains its amphiphilic nature and its C=C bond is difficult to hydrogenate at the water–organic liquid interface. Another possible factor is the effect of CO<sub>2</sub> molecules on the reactivity of the carbonyl group of CAL; under high-pressure conditions, CO<sub>2</sub> may selectively increase the reactivity of the C=O bond, compared with the C=C bond, of CAL molecules in the CAL liquid phase or in the dense CO<sub>2</sub> gas phase, as confirmed by high-pressure FTIR measurements [16–18]. Liquid phases (substrates or solvents) pressurized with CO<sub>2</sub>, called as CO<sub>2</sub>-dissolved expanded liquid phases [25], have some merits in chemical transformations, which are not only to promote the dissolution of gaseous reactants (H<sub>2</sub>, O<sub>2</sub>, for example) into the liquid phases but also to modify the chemical reactions [16–18,26].

It is thus demonstrated that the water-soluble Ru/TPPTS complex catalysts change in their structure and performance during

repeated multiphase hydrogenation reactions of CAL in both water–toluene and water–dense CO<sub>2</sub> systems. The total activity and the selectivity for COL decrease significantly after the first catalytic run but marginally after the second and subsequent runs. The catalysts change to those which are less active and more selective to the homogeneous isomerization of COL to HCAL in water. For multiphase reactions, however, the COL selectivity is comparable to that for HCAL as resulted from the interfacial catalysis and/or the influence of CO<sub>2</sub> molecules on the reactivity of CAL. Even if the total activity is still satisfactory and the interfacial catalysis has some merits, the recycling would be difficult with respect to the selective production of COL.

#### 4. Conclusion

For selective hydrogenation of CAL in multiphase systems using water and toluene or dense CO<sub>2</sub>, the catalytic performance of such water-soluble ruthenium–phosphine complexes as Ru(H)(Cl)(TPPTS)<sub>3</sub> and Ru(H)<sub>2</sub>(TPPTS)<sub>4</sub> was shown to decrease during repeated runs. The total CAL conversion and the COL selectivity decreased after the first run and these changes were more significant with dense CO<sub>2</sub> than toluene. On the subsequent runs, however, less significant changes were observed. During the first run, the active Ru complexes should change to less active ones such as Ru(H)<sub>2</sub>(COL)<sub>n</sub>(TPPTS)<sub>m</sub> by accumulation of the main product of COL. This structural change may occur more easily in multiphase hydrogenation with dense CO<sub>2</sub> than that with toluene, probably because of difference in the solubility of COL between the dense CO<sub>2</sub> and toluene phases. For homogeneous reaction of COL in aqueous phase, Ru(H)<sub>2</sub>COL<sub>n</sub>(TPPTS)<sub>m</sub> was indicated to catalyze the isomerization to HCAL compared with the hydrogenation to hydrocinnamyl alcohol. With those complexes, however, the selectivity for COL is still comparable to that for HCAL for multiphase hydrogenation reactions of CAL because the hydrogenation of an amphiphilic substrate of CAL occurs mainly at interface between water and toluene or dense CO<sub>2</sub> gas and/or the CO<sub>2</sub> molecules would enhance the reactivity of carbonyl group of CAL.

Table 3  
Results of homogeneous hydrogenation reactions of different substrates in water using the Ru complex **1**

Substrate	Catalyst	Conversion <sup>a</sup> (%)	Selectivity <sup>a</sup> (%)		
			COL	HCAL	HCOL
CAL	As prepared <sup>b</sup>	82	51	8	40
	After one run <sup>c</sup>	69	12	26	63
COL	As prepared <sup>b</sup>	95	–	20	80
	After one run <sup>c</sup>	90	–	73	27
HCAL	As prepared <sup>b</sup>	71	0	–	100
	After one run <sup>c</sup>	45	0	–	100

<sup>a</sup> Homogeneous reaction in water under conditions: CAL 0.095 mmol, COL 0.030 mmol, HCAL 0.095 mmol, water 2 cm<sup>3</sup>, Ru 0.011 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 60 °C, 5 min.

<sup>b</sup> Complex **1** Ru(H)(Cl)(TPPTS)<sub>3</sub>.

<sup>c</sup> Multiphase reaction using CO<sub>2</sub> under conditions: CAL 8.0 mmol, water 2 cm<sup>3</sup>, CO<sub>2</sub> 8 MPa, Ru 0.011 mmol cm<sup>-3</sup>, P/Ru = 4, H<sub>2</sub> 2 MPa, 70 °C, 2 h.

## References

- [1] B. Cornils, *J. Mol. Catal. A Chem.* 143 (1999) 1.
- [2] B. Cornils, W.A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH, New York, 2000.
- [3] B.M. Bhanage, M. Arai, *Catal. Rev. Sci. Eng.* 43 (2001) 315.
- [4] R.A. Sheldon, H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, New York, 2001.
- [5] P. Gallezot, D. Richard, *Catal. Rev. Sci. Eng.* 40 (1998) 81.
- [6] G.V. Smith, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic Press, New York, 1995.
- [7] H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* 345 (2003) 103.
- [8] J.M. Gosselin, C. Mercier, G. Allmang, F. Grass, *Organometallics* 10 (1991) 2126.
- [9] F. Joo, J. Kovacs, A.C. Benyei, A. Katho, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 969.
- [10] F. Joo, J. Kovacs, A.C. Benyei, A. Katho, *Catal. Today* 42 (1998) 441.
- [11] K.-C. Tin, N.-B. Wong, R.-X. Li, Y.-Z. Li, J.-Y. Hu, X.-J. Li, *J. Mol. Catal. A Chem.* 137 (1999) 121.
- [12] R.A. Sánchez-Delgado, M. Medina, F. Lopez-Linares, A. Fuentes, *J. Mol. Catal. A Chem.* 116 (1997) 167.
- [13] A. Andriollo, J. Carrasquel, J. Marino, F.A. Lopez, D.E. Paez, I. Rojas, N. Valencia, *J. Mol. Catal. A Chem.* 116 (1997) 157.
- [14] F. Lopez-Linares, M.G. Gonzalez, D.E. Paez, *J. Mol. Catal. A Chem.* 145 (1999) 61.
- [15] M. Hernandez, P. Kalck, *J. Mol. Catal. A Chem.* 116 (1997) 131.
- [16] F. Zhao, S. Fujita, J. Sun, Y. Ikushima, M. Arai, *Chem. Commun.* (2004) 2326.
- [17] F. Zhao, S. Fujita, S. Akihara, M. Arai, *J. Phys. Chem. A* 109 (2005) 4419.
- [18] S. Fujita, S. Akihara, F. Zhao, R. Liu, M. Hasegawa, M. Arai, *J. Catal.* 236 (2005) 101.
- [19] B.M. Bhanage, Y. Ikushima, M. Shirai, M. Arai, *Chem. Commun.* (1999) 1277.
- [20] S. Fujita, Y. Sano, B.M. Bhanage, M. Arai, *J. Catal.* 225 (2004) 95.
- [21] F. Zhao, S. Fujita, M. Arai, *Curr. Org. Chem.*, in press.
- [22] E. Fache, C. Santini, F. Senocq, J.M. Basset, *J. Mol. Catal.* 72 (1992) 331.
- [23] M. Hernandez, P. Kalck, *J. Mol. Catal. A Chem.* 116 (1997) 117.
- [24] F. Zhao, Y. Ikushima, M. Chatterjee, O. Sato, M. Arai, *J. Supercrit. Fluids* 27 (2003) 65.
- [25] G. Musie, M. Wei, B. Subramaniam, D.H. Busch, *Coord. Chem. Rev.* 219–221 (2001) 789.
- [26] X. Xie, C.L. Liotta, C.A. Eckert, *Ind. Eng. Chem. Res.* 43 (2004) 7907.