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

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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 CO₂, because of interfacial catalysis in which the reaction mainly occurs at the interface between the aqueous phase and the other toluene or dense CO₂ phase. The total CAL conversion and the COL selectivity decrease on the second run, more significantly with dense CO₂ 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)₂L_n(TPPTS)_m (L=COL) by accumulation of the main product of COL. This structural change may occur more easily in multiphase hydrogenation with dense CO₂ than that with toluene, probably because the solubility in the dense CO₂ gas phase is even smaller than that in toluene. For homogeneous reaction of COL in aqueous phase, Ru(H)₂L_n(TPPTS)_m 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 CO₂ gas phase. Interactions of CO₂ molecules with CAL would also increase the reactivity of carbonyl group of the substrate.

Keywords: Multiphase hydrogenation; Cinnamaldehyde; Palladium – 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 α,β -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 CO₂ 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 – TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine), which exists in an aqueous phase being in contact with a bulk CAL phase in toluene, pure CAL, or dense CO₂ (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 α, β -unsaturated aldehydes. Sánchez-Delgado et al. studied selective hydrogenation of CAL in a water – toluene multiphase system using Os and Ru complex catalysts [12]. They examined the recycling with OsCl₃ · 3H₂O/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 CO₂ 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 CO₂ molecules on the reactivity of CAL.

Scheme 1

Figure 1

2. Experimental

2.1. Catalyst preparation

For multiphase reactions using water, ruthenium (III) chloride (Wako) and TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine, Fluca) were charged into a high-pressure stainless steel reactor of 50 cm³, followed by introduction of water degassed by bubbling with argon. The reactor was heated up to 60 °C using a water bath and then charged with H₂ 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 Ru(H)(Cl)(TPPTS)₃ [20].

Another chlorine-free complex, Ru(H)₂(TPPTS)₄, was also prepared from Ru(Cl)₂(TPP)₃ (Aldrich) according to the literature [22, 23]. Ru(Cl)₂(TPP)₃ was dissolved in THF, an aqueous solution of TPPTS was added to this THF solution, and the mixture was stirred at 60 °C for 1 h under reflux conditions. Another aqueous solution of TPPTS was prepared and NaBH₄ 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 °C for a few hours, yielding a yellow solid, which was a complex of Ru(H)₂(TPPTS)₄, including NaCl and B(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 (CAL) was added to the reactor including the catalyst-containing water and the reactor was heated to a reaction temperature of 70 °C. Then the reactor was introduced with H₂ up to the desired pressure and then CO₂ 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 (Zebron ZB-50, 30 m x 0.25 mm x 0.5 μm) and GC mass spectrometry (Shimadzu GC-MS QP5050A) with a capillary column (GL Science TC-17, 30 m x 0.53 mm x 0.25 μm). For recycling, the catalyst-containing water phase was separated and washed with 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 scCO₂; 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 cm³ 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 (CAL) 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 CO₂ 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.

Figure 1

Fig. 2 shows the total conversion and product distribution for the first and recycled runs with the water-soluble Ru complex **1** [Ru(H)(Cl)(TPPTS)₃] using toluene and dense CO₂. One can see common trends that the total CAL conversion decreases and the product distribution changes in repeated runs. The selectivity for cinnamyl alcohol (COL) 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.

Figure 2

Table 1

Figure 3

Next, the other water-soluble Ru complex **2** [Ru(H)₂(TPPTS)₄] was examined. Fig. 4 gives the results of repeated runs of CAL hydrogenation with this complex using toluene and dense CO₂. 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 h 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 CO₂, 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 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.

Figure 4

Various water – soluble Ru/TPPTS complexes were compared in their catalytic performance for selective hydrogenation of CAL [14, 15]. Hernandez and Kalck indicate that $[\text{Ru}(\text{H})_2(\text{TPPTS})_4]$ is more active than $[\text{Ru}(\text{H})(\text{Cl})(\text{TPPTS})_3]$ 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 $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ 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%.

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_2 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_2 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_2 and toluene but more remarkably for the former.

Table 2

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 HCOL 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 HCOL while its total activity little changes for the reaction with COL but it becomes more active for the isomerization to HCOL than the hydrogenation to HCOL.

Table 3

According to the previous literature [23], a possible structure of the used Ru complex is $\text{Ru}(\text{H})_2(\text{COL})_n(\text{TPPTS})_m$, which is formed after the formation and accumulation of COL in toluene and dense CO_2 phases during multiphase hydrogenation of CAL. This structural change may be easier to occur for the reaction system with pressurized CO_2 than that with toluene because the solubility of COL in the dense CO_2 gas phase is even smaller than that in toluene and so such a structural change occurs more easily through water – CO_2 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_2 was estimated to be about $60 \mu\text{mol cm}^{-3}$ in 17 MPa CO_2 and $15 \mu\text{mol cm}^{-3}$ in 17 MPa $\text{CO}_2 + 2 \text{ MPa H}_2$. The present hydrogenation reactions were conducted at lower CO_2 pressures in the presence of 2 MPa H_2 , and so the quantity of COL soluble in the gas phase was even smaller. During the multiphase hydrogenation of CAL, the complexes **1** $[\text{Ru}(\text{H})(\text{Cl})(\text{TPPTS})_3]$ and **2** $[\text{Ru}(\text{H})_2(\text{TPPTS})_4]$ may change to those like $\text{Ru}(\text{H})_2(\text{COL})_n(\text{TPPTS})_m$ 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 $[\text{Ru}(\text{H})(\text{L})(\text{TPPTS})_2]\text{Cl}$ (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 $[\text{Ru}(\text{H})(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{TPPTS})_2]\text{Cl}$ did not catalyze hydrogenation of CAL in ether [15]. Although $\text{Ru}(\text{H})_2(\text{COL})_n(\text{TPPTS})_m$ 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_2) and the amphiphilic nature of CAL substrate [12, 20]. As pointed out by Sanchez-Delgado [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 CO₂ molecules on the reactivity of the carbonyl group of CAL; under high pressure conditions, CO₂ 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 CO₂ gas phase, as confirmed by high-pressure FTIR measurements [16-18]. Liquid phases (substrates or solvents) pressurized with CO₂, called as CO₂ – dissolved expanded liquid phases [25], have some merits in chemical transformations, which are not only to promote the dissolution of gaseous reactants (H₂, O₂, 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 CO₂ 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 CO₂ 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 CO₂, the catalytic performance of such water-soluble ruthenium – phosphine complexes as Ru(H)(Cl)(TPPTS)₃ and Ru(H)₂(TPPTS)₄ 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 CO₂ 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)₂(COL)_n(TPPTS)_m by accumulation of the main product of COL. This structural change may occur more easily in multiphase hydrogenation with dense CO₂ than that with toluene, probably because of difference in the solubility of COL between the dense CO₂ and toluene phases. For homogeneous reaction of COL in aqueous phase, Ru(H)₂COL_n(TPPTS)_m 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 CO₂ gas and/or the CO₂ molecules would enhance the reactivity of carbonyl group of CAL.

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Captions to Scheme and Figures

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

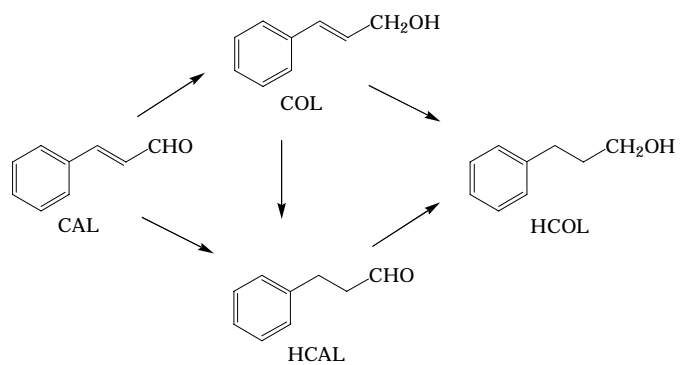
Figure 1 Two- and three-phase hydrogenation reactions of CAL using an organic solvent of toluene (a) and dense CO₂ at low (b) and high (c) pressures studied in this work.

Figure 2 Recycling results of the water-soluble Ru complex **1** for selective hydrogenation of cinnamaldehyde (CAL) using toluene (a) and scCO₂ at 12 MPa (b) and 20 MPa (c). Total conversion () and product selectivity (, ,). Reaction conditions: CAL 8.0 mmol, water 4 cm³, toluene 10 cm³, Ru 0.0355 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C, 2 h. The state of reaction mixture is: gas-water-toluene three-phase (a); gas-water-CAL three-phase (b); gas-water two-phase (c) (CAL is mostly dissolved in the gas phase).

Figure 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 cm³, toluene 10 cm³, Ru 0.044 mmol cm⁻³, P/Ru = 4, H₂ 4 MPa, 70 °C.

Figure 4 Recycling results of the water-soluble Ru complex **2** for selective hydrogenation of cinnamaldehyde (CAL) in toluene (a) and in scCO₂ at 12 MPa (b) and 20 MPa (c). Total conversion () and product selectivity (, ,). Reaction conditions: CAL 8.0 mmol, water 4 cm³, toluene 10 cm³, Ru 0.0355 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C, 0.5 h (a1, b1, c1), 2.0 h (a2, b2, c2). The state of reaction mixture is: (a) gas-water-toluene three-phase; (b) gas-water-CAL three-phase; (c) gas-water two-phase (CAL is completely dissolved in the gas phase).

Scheme, Figures, Tables in the order of appearance:



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

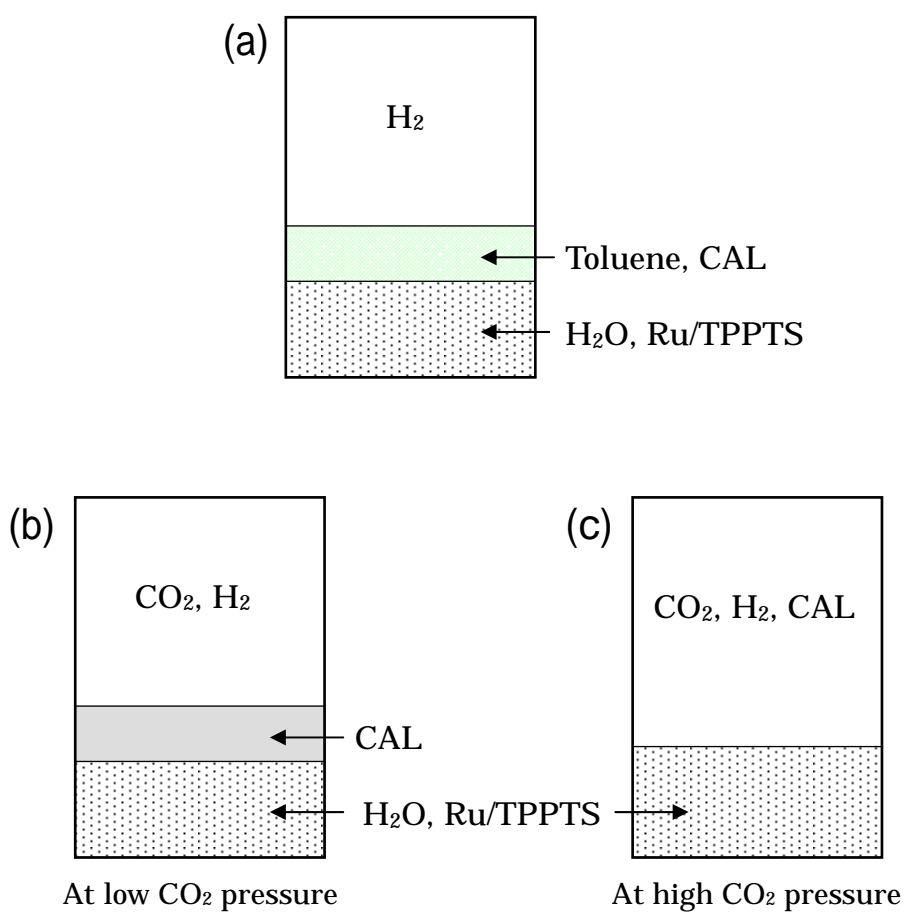


Figure 1 Two- and three-phase hydrogenation reactions of CAL using an organic solvent of toluene (a) and dense CO_2 at low (b) and high (c) pressures studied in this work.

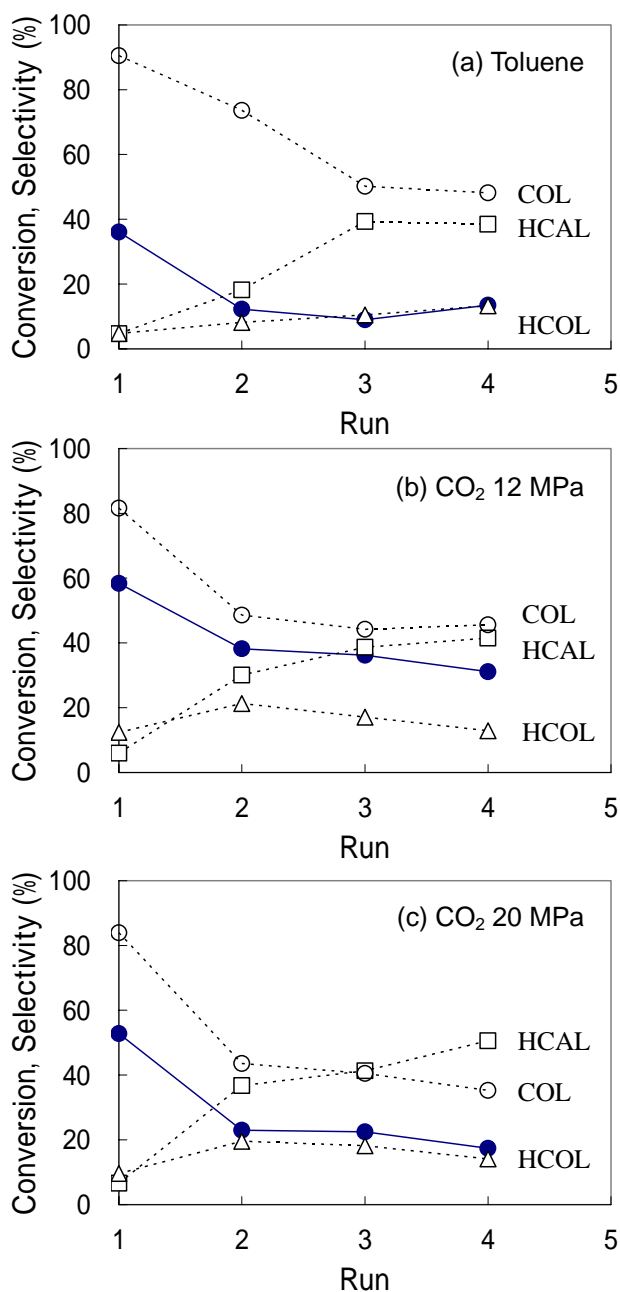


Figure 2 Recycling results of the water-soluble Ru complex **1** for selective hydrogenation of cinnamaldehyde (CAL) using toluene (a) and $scCO_2$ at 12 MPa (b) and 20 MPa (c). Total conversion () and product selectivity (, ,). Reaction conditions: CAL 8.0 mmol, water 4 cm^3 , toluene 10 cm^3 , Ru 0.0355 $mmol\ cm^{-3}$, P/Ru = 4, 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); gas-water two-phase (c) (CAL is mostly dissolved in the gas phase).

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 CO₂

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

Reaction conditions: CAL 8.0 mmol, water 4 cm³, toluene 10 cm³, Ru 0.0355 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C.

a. G: CO₂-rich gas phase, L: CAL-containing liquid phase, W: catalyst-containing water phase (see Fig. 1 for the details of those multiphase reaction systems).

b. CAL-rich liquid phase

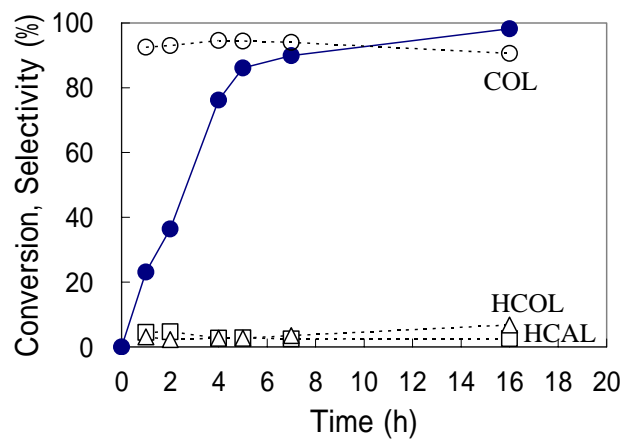


Figure 3 The change of total conversion () and product selectivity (, ,) with time in selective hydrogenation of cinnamaldehyde (CAL) using the Ru complex **1** under three-phase (gas-water-toluene) conditions. Reaction conditions: CAL 8.0 mmol, water 1 cm³, toluene 10 cm³, Ru 0.044 mmol cm⁻³, P/Ru = 4, H₂ 4 MPa, 70 .

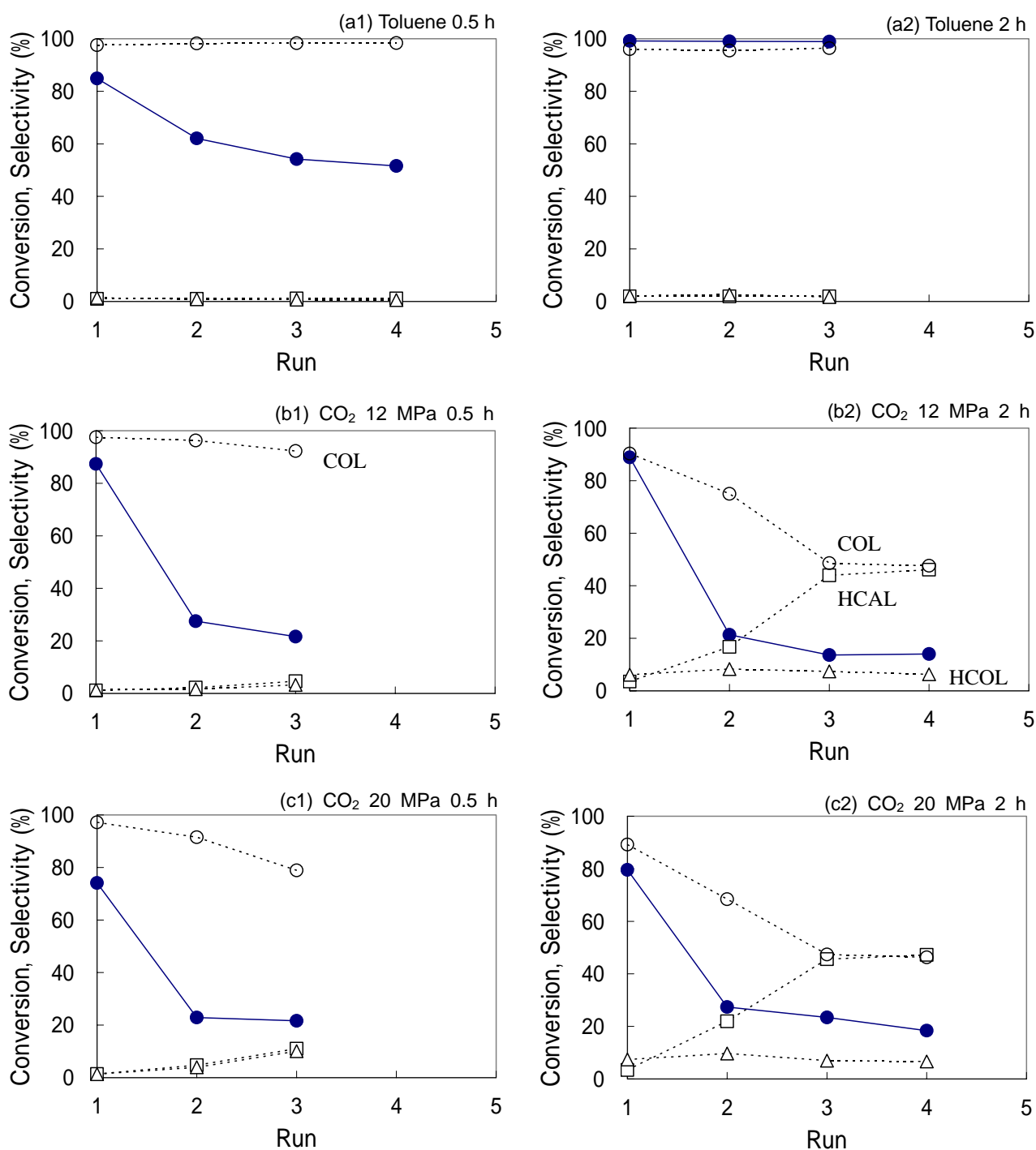


Figure 4 Recycling results of the water-soluble Ru complex **2** for selective hydrogenation of cinnamaldehyde (CAL) in toluene (a) and in scCO₂ at 12 MPa (b) and 20 MPa. Total conversion (○) and product selectivity (●, □, △). Reaction conditions: CAL 8.0 mmol, water 4 cm³, toluene 10 cm³, Ru 0.0355 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C, 0.5 h (a1, b1, c1), 2.0 h (a2, b2, c2). The state of reaction mixture is: (a) gas-water-toluene three-phase; (b) gas-water-CAL three-phase; (c) gas-water two-phase (CAL is completely dissolved in the gas phase).

Table 2 Results of homogeneous hydrogenation of CAL in water using the Ru complex **1** before and after multiphase hydrogenation reactions ^b using a solvent of toluene or dense CO₂

Pretreatment			Conversion ^c (%)	Selectivity ^c (%)		
				COL	HCAL	HCOL
<i>As prepared</i> ^a			87	67	6	27
<hr style="border-top: 1px dashed black;"/>						
<i>Multiphase reaction</i> ^b						
Solvent ^b	Phases ^b	Time ^b				
CO ₂ (8 MPa)	G-L ^d -W	0.5 h	72	19	32	49
		2.0 h	52	17	35	48
Toluene	G-L-W	0.5 h	73	29	22	50
		2.0 h	73	28	20	52

a. Complex **1** Ru(H)(Cl)(TPPTS)₃

b. For multiphase reactions. Reaction conditions: CAL 8.0 mmol, water 2 cm³, toluene 10 cm³, CO₂ 8 MPa, Ru 0.011 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C.

c. Homogeneous reaction in water in the absence of CO₂. Reaction conditions: CAL 0.095 mmol, water 2 cm³, Ru 0.011 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 60 °C, 5 min.

d. CAL-rich liquid phase

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

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

a. Complex **1** Ru(H)(Cl)(TPPTS)₃

b. Multiphase reaction using CO₂ under conditions: CAL 8.0 mmol, water 2 cm³, CO₂ 8 MPa, Ru 0.011 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 70 °C, 2 h.

c. Homogeneous reaction in water under conditions: CAL 0.095 mmol, COL 0.030 mmol, HCAL 0.095 mmol, water 2 cm³, Ru 0.011 mmol cm⁻³, P/Ru = 4, H₂ 2 MPa, 60 °C, 5 min.