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Selective hydrogenation of cinnamaldehyde using ruthenium–phosphine complex catalysts with multiphase reaction systems in and under pressurized carbon dioxide: Significance of pressurization and interfaces for the control of selectivity

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Abstract

The selective hydrogenation of *trans*-cinnamaldehyde (CAL) has been investigated with several types of multiphase reaction systems using Ru–phosphine complex catalysts in the presence of high-pressure CO_2. The selective formation of an unsaturated alcohol, cinnamyl alcohol (COL), can be achieved in an organic solvent free two-phase system, which includes the liquid (CAL, Ru complex) and gas (H_2, CO_2) phases. Both total conversion and COL selectivity are enhanced with increasing CO_2 pressure. This enhancement is due to the dissolution of CO_2 molecules into the CAL phase, which promotes the dissolution of H_2 and activates the reactivity of the carbonyl group of CAL molecules, and a high concentration of CAL in the reaction medium. The high COL selectivity can also be obtained in three- and two-phase reaction systems, which include a gas (H_2, CO_2) phase, a liquid (water-dissolving Ru complex) phase, and/or another liquid phase (CAL). The COL selectivity is high irrespective of CO_2 pressure because of a water–CAL interface or a water–CO_2 interface as a main reaction locus, but the total conversion is not enhanced by pressurization with CO_2, and it decreases at elevated CO_2 pressure under the two-phase conditions because of a simple dilution effect. In contrast, the highly selective formation of COL is not possible in a homogeneous dense CO_2 gas phase or in a two-phase system that includes a gas (H_2) phase and a liquid (DMF, CAL, Ru complex) phase. Pressurization with CO_2 is not effective in improving the conversion and COL selectivity for these systems.

Keywords: Hydrogenation; Cinnamaldehyde; Multiphase catalysis; Supercritical carbon dioxide; Ruthenium catalysts

1. Introduction

Compared with homogeneous catalytic reactions, multiphase catalytic reactions using biphasic catalysts, supported liquid-phase catalysts, conventional solid catalysts, and others have practical merits, including easy separation of catalysts and products, easy recovery and recycling of catalysts, and applicability to continuous operations [1–4]. In addition to these merits, we note another potential one of controlling the product selectivity due to the fact that interfaces existing in multiphase reactions play important roles in determining not only overall conversion, but also product distribution. For the hydrogenation of cinnamaldehyde (CAL) in biphasic catalysts [5–12] and supported liquid-phase catalysts [13] using water-soluble organometallic complexes, the interface between water and organic liquid (CAL substrate and/or another, less-polar solvent) is a locus for hydrogenation (see Scheme 1). For a CAL molecule at this interface, its polar C=O bond is oriented to the catalyst-containing water phase and so is easier to hydrogenate

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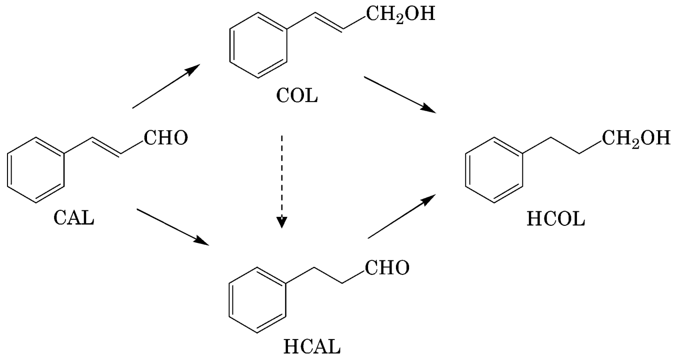
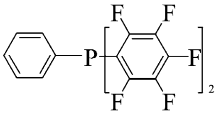


Scheme 1. Hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL). (Isomerization of COL to HCAL is thermodynamically possible but it did not occur under the present conditions.)

(I) Triphenylphosphine (II) Diphenyl(pentafluorophenyl)phosphine



(III) Bis(pentafluorophenyl) phenylphosphine

Scheme 2. Phosphine compounds used as ligands.

than the C=C bond oriented away from the water phase toward the organic phase. Thus, the selective hydrogenation of CAL to the corresponding unsaturated alcohol, cinnamyl alcohol (COL), can be achieved under two-phase conditions. Those results demonstrate that such an interface catalysis will be significant to selective chemical transformation of multifunctional substrates. The selective hydrogenation of α,β-unsaturated aldehydes is one of important reactions in the synthesis of various fine chemicals [14,15].

Recently, we reported that although CO_2 is not a reactant, the presence of high-pressure CO_2 promotes the selective hydrogenation of CAL to COL with a homogeneous Ru complex catalyst using a phosphine ligand or a heterogeneous Pt/C catalyst under organic solventless conditions [16,17]. This promotion depends on several factors: dissolution of CO_2 molecules into the CAL liquid phase, dissolution of H_2, and interactions between the dissolved CO_2 and CAL molecules (measured by high-pressure Fourier transform infrared (FTIR) spectroscopy). Subramaniam et al. previously demonstrated a similar effectiveness of pressurization with CO_2 for liquid-phase oxidation reactions [18–20]. From visual observation of our reaction mixture, the CAL liquid phase expands to some extent in the presence of both H_2 and CO_2 [16,17]. These findings provide a simple and useful way to control the rate of reaction and product selectivity in chemical reactions, in addition to the aforementioned interface catalysis.

On the basis of those previous results on multiphase reactions, the present work was undertaken to further investigate the significance of interfaces and the effectiveness of CO_2 pressurization in multiphase catalytic reactions using a model reaction of practical and scientific significance, selective hydrogenation of CAL with Ru complex catalysts that are soluble in water, CO_2, or organic phases. Our previous results on homogeneous CAL hydrogenation with similar complexes in dense CO_2 [21] and organic solvents [22] are also used for the present discussion. In these homogeneous reactions with CAL, COL is not produced with such a high selectivity as obtained in multiphase reactions.

2. Experimental

2.1. Catalyst preparation

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

For multiphase reactions in and under dense CO_2, the ruthenium–phosphine complex catalysts were prepared under H_2 atmosphere as described previously [21,22]. The 50 cm^3 stainless steel reactor was charged with ruthenium(III) chloride and phosphine compound in ethanol. Then the reactor was sealed and flushed with CO_2 (2 MPa) three times. Hydrogen was introduced into the reactor up to 2 MPa and heated up to 50 °C, after which stirring was started. The mixture was kept at 50 °C for 2 h while stirring, and then the solvent (ethanol) was evaporated. The solid ruthenium complexes that formed were collected and vacuum-dried at 80 °C for 6 h. Triphenylphosphine (TPP) was used mainly as a ligand, but the other two fluorinated phoshine compounds (as shown in Scheme 2) were also used in a few cases. For homogeneous and multiphase hydroformylation reactions using dense CO_2, we previously observed significant differences in the total conversion and the product distribution between TPP and fluorine-modified phosphine compounds [23–25].

2.2. Hydrogenation reactions

For multiphase 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 filled with H_2 up to the desired pressure and CO_2 up to the desired total pressure with a high-pressure liquid pump (JASCO SCF-Bpg). The reaction was run while stirring the mixture for 2 h. After the reaction, the reactor was cooled to room temperature in an ice water bath and depressurized to atmospheric pressure. The reaction mixture was analyzed by gas chromatography (GC; Shimadzu GC-14B) with a capillary column (Zebron ZB-50; 30 m × 0.25 mm × 0.5 µm) and GC mass spectrometry (GC-MS; Shimadzu GC-MS QP5050A) with a capillary column (GL Science TC-17; 30 m × 0.53 mm × 0.25 µm).

For multiphase reactions in and under dense CO_2, the reactor was charged with CAL and the catalyst, flushed with CO_2 three times, and heated up to 50 °C. After introduction of H_2, liquid CO_2 was introduced into the reactor up to the desired total pressure. The reaction was conducted while stirring the mixture for 2 h. After the reaction, the reaction mixture was removed with acetone and analyzed with GC and GC-MS.

2.3. Phase behavior observation

Examining the phase behavior is important for studying chemical reactions in $scCO_2$; it is significant to see whether the reaction is occurring homogeneously in a single phase or heterogeneously in two or more phases. A 10-cm^3 high-pressure sapphire-windowed view cell was used to determine the existing phases and the volume of these phases [21].

2.4. High-pressure FTIR measurements

Information about interactions of dense CO_2 with substances dissolved at different pressures is significant in discussing the CO_2 effects on the reaction. In situ high-pressure FTIR spectra were measured at 50 °C with an FTIR spectrometer (JASCO FTIR-620) equipped with a 1.5-cm^3 high-pressure cell with a path length of 4 mm. The following experimental procedure was used [16,17]: A certain volume of a substance was added to the cell and heated to 50 °C by circulation of preheated oil outside it, and then CO_2 and/or H_2 were introduced into the cell. The pressure was slowly raised while being stirred with a Teflon-coated magnetic stirrer. When the pressure reached a certain value, the stirring was continued for another 3–5 min and stopped; then the IR spectra were measured with a resolution of 4 cm^{-1} using pure CO_2 at the corresponding pressures as background.

2.5. Estimation of solubility

The solubility of CAL in water was measured by a simple method. A certain volume of CAL (1 cm^3) was contacted with distilled water (10 cm^3) at 70 °C for 20 min while stirring. Then the stirring was stopped, and the mixture was kept for 10 min to allow it to separate into two phases, water (above) and CAL (bottom). A small quantity of the water phase was sampled and analyzed by GC (Shimadzu 8A) with a capillary column (Restex Rtx-wax; 30 m × 0.53 mm × 0.25 µm). The results obtained were used to determine reaction conditions for homogeneous hydrogenation in the aqueous phase.

2.6. UV/vis measurements

The Ru–TPPTS complex catalysts in the aqueous phase were examined by UV/vis spectroscopy measurements made for the complex catalysts in the aqueous phase as prepared in the aforementioned manner and those after contact with a gaseous mixture of H_2 and CO_2 in the absence of CAL at 70 °C. The measurements were made with a UV/vis spectrometer (JASCO Ubest V-550) under ambient conditions.

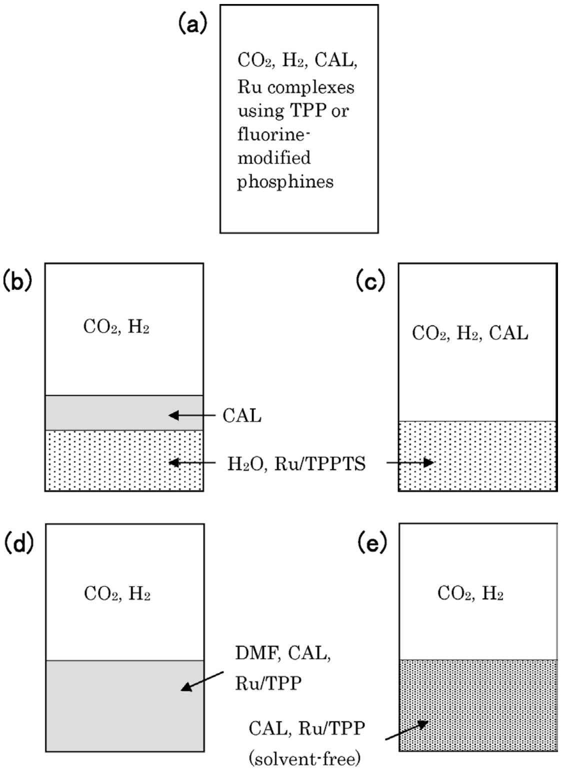


Fig. 1. A single phase system in dense CO_2 (a) and multi-phase systems (b, c, d, e) pressurized with CO_2 for hydrogenation of cinnamaldehyde (CAL) using H_2 and Ru/phosphine complex catalysts.

3. Results and discussion

Various multiphase reaction systems (Fig. 1) were investigated for the selective reduction of CAL with H_2: (a) a homogeneous reaction in a dense CO_2 phase in which all of the reacting species are soluble; (b) a gas (G)–liquid (L)–liquid (L) three-phase reaction in which the latter two phases are CAL substrate and water dissolving the catalyst; (c) a G–L (water) two-phase reaction; (d) and (e) G–L two-phase reactions in the presence and absence of an additional organic solvent. System (d) is a conventional reaction except for CO_2 pressurization. The product selectivity strongly depends on the reaction systems examined, as described in the following sections.

3.1. Hydrogenation in DMF under G–L (organic) conditions [system (d)]

Fig. 2 shows the influence of CO_2 pressure on total conversion and product distribution in the hydrogenation of CAL in a conventional solvent of DMF using a Ru–TPP complex catalyst [system (d) in Fig. 1]. The selectivity for HCAL was larger by a factor of about 2 compared with the selectivities for COL and HCOL, which were produced in comparable quantities. The total conversion of CAL and the selectivity for HCOL increased with increasing CO_2 pressure, whereas the selectivity for HCAL decreased. At a CO_2 pressure of 8 MPa, the conversion was 72% and the selectivity values for HCAL, COL, and HCOL were 54, 23, and 23%, respectively. When the amount of catalyst used was doubled with the other conditions kept unchanged, the conversion increased to 95%, and the selectivity values for HCAL, COL, and HCOL were 20, 29, and 51%, respectively. For the present reaction system, it was previously shown that HCOL was produced mainly through hydrogenation of HCAL, not COL [22]. Thus the increase in HCOL selectivity seen in Fig. 2 was due to the change of conversion (consecutive conversion of HCAL to HCOL), not CO_2 pressure. For this two-phase reaction in DMF, the influence of CO_2 pressurization was less significant for a wide range of pressure up to 20 MPa.

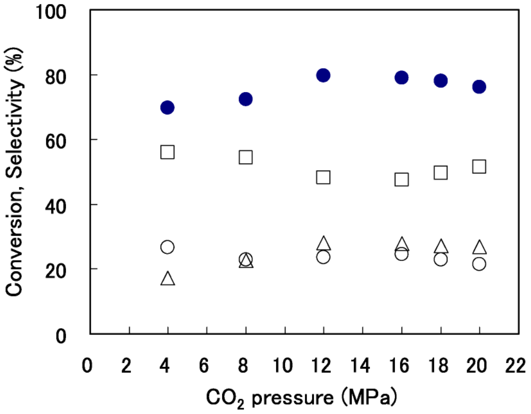


Fig. 2. Influence of CO_2 pressurization on hydrogenation of cinnamaldehyde (CAL) in a conventional solvent of DMF. (●) Conversion; (○) COL; (□) HCAL; (△) HCOL. Reaction conditions: CAL 8.0 mmol, DMF 10 cm^3, $RuCl_3$ 0.022 mmol, TPP 0.089 mmol, H_2 2 MPa, temperature 70 °C; time 2 h.

3.2. Hydrogenation in dense CO_2 under G–L (organic)–L (water) and G–L (water) conditions [systems (b) and (c)]

The next reaction systems studied are those illustrated in Figs. 1b and 1c, in which a water-soluble Ru–TPPTS complex catalyst was used. Fig. 3 presents the total conversion and product selectivity in hydrogenation of CAL using different initial amounts of CAL (1.1, 6.0, and 8.0 mmol) but otherwise the same conditions. The dashed lines indicate the pressure at which the reaction mixture changed from a three-phase (gas, water, CAL) state to a two-phase (gas, water) state as noted by visual observation. Above the threshold pressure, the reaction mixture included a single kind of liquid component in the form of small, colorless droplets. Hence the liquid component was water, and CAL was mostly dissolved in the gas phase at higher pressures. Note first that the selectivity for COL was much larger than that observed in DMF (Fig. 2). With increasing CO_2 pressure, the total conversion of CAL decreased marginally in the three-phase region and it decreased significantly in the two-phase region, particularly in the case of (1), in which the quantity of CAL was the smallest (1.1 mmol). The selectivity for unsaturated alcohol (COL) was high under any conditions used (>80%), with saturated aldehyde (HCAL) and saturated

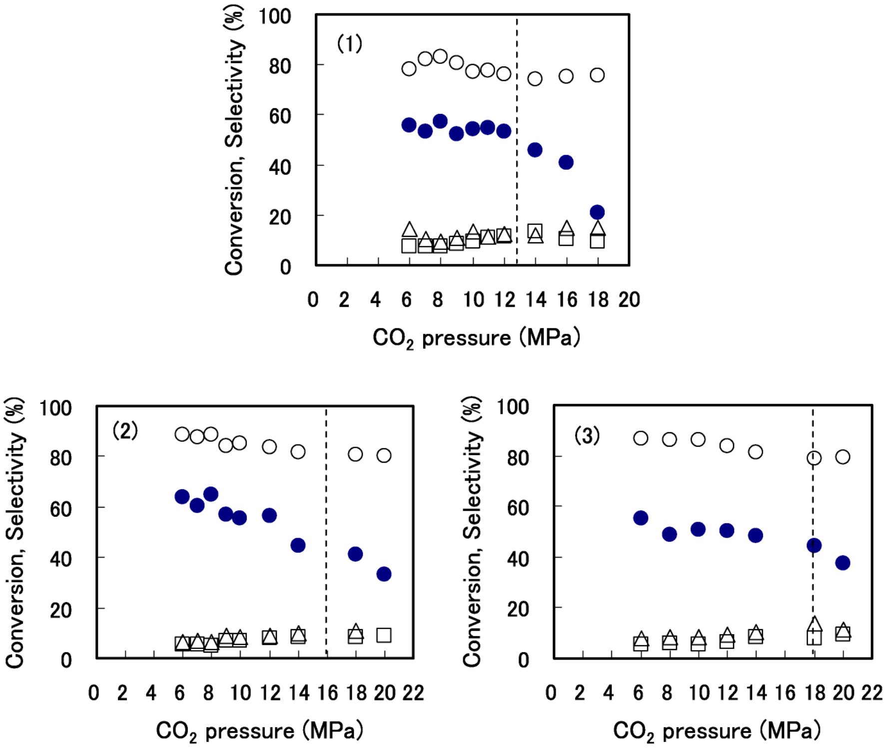


Fig. 3. Influence of CO_2 pressure on hydrogenation of cinnamaldehyde (CAL). (●) Conversion; (○) COL; (□) HCAL; (△) HCOL. Reaction conditions: CAL (1) 1.1 mmol, (2) 6.0 mmol, (3) 8.0 mmol; water 2 cm^3; $RuCl_3$ 0.089 mmol; TPPTS 0.356 mmol; H_2 2 MPa; temperature 70 °C; time 2 h. The reaction mixture is in a three-phase state ($CO_2 + H_2$ gas, CAL liquid, water) at low pressures below a certain pressure indicated by broken line and it is in a two-phase state ($CO_2 + H_2$ gas, water) at higher pressures.

alcohol (HCOL) produced in similar small quantities. The selectivity for COL decreased and that for either HCAL or HCOL increased with increasing CO_2 pressure, but these changes are of marginal significance. Two important points should be restated: The selectivity for COL was high at the CO_2 pressures examined, and total CAL conversion decreased with increasing pressure in the two-phase region in which CAL is mostly dissolved in the CO_2 gas phase. Fig. 3 illustrates the interesting fact that the total CAL conversion depended little on the initial amount of CAL used, as discussed later in the paper.

For the three-phase reactions, there were two possible reaction loci for CAL hydrogenation: at the water–CAL interface and in the bulk aqueous phase. The conversion of CAL in aqueous hydrogenation was measured with a smaller initial quantity of CAL under similar conditions as used for the three-phase reactions. To determine the CAL concentration, a simple method described in Section 2 was used to make a rough estimate of the solubility of CAL in water. The estimates obtained were 0.106 mmol cm^{-3} at 70 °C and 0.056 mmol cm^{-3} at 50 °C. The aqueous hydrogenation of CAL was carried out at 70 °C under the following conditions: CAL, 0.095 mmol; water, 2 cm^3; $RuCl_3$, 0.022 mmol; TPPTS, 0.089 mmol; H_2, 2 MPa; CO_2, 8 MPa; temperature, 70 °C. The CAL conversion reached 90% in a short reaction time of 5 min, and the COL selectivity was only 60% for the aqueous homogeneous hydrogenation. (The data collected at a lower reaction temperature of 60 °C are given later in Table 3.) That is, the hydrogenation of CAL occurred faster in the aqueous phase, but COL selectivity was lower than that obtained in the three-phase systems (Fig. 3). On the basis of these findings, we may characterize the three-phase reactions as follows. The CAL molecules and the Ru complex catalyst exist in the liquid phase and the aqueous phase (both in droplets), respectively. The substrate phase contacted with the aqueous phase, and the CAL molecules diffused into the aqueous phase. However, they were hydrogenated rapidly at the water–CAL interface layer because of the high activity of the catalyst, and they could not diffuse into the bulk aqueous phase. When the initial quantity of CAL used was increased, the likelihood of the water–CAL contacting and the contacting water–CAL interface areas also increased, enhancing the overall CAL conversion. As a result, the conversion did not depend so much on the CAL quantity used, as seen in Fig. 3. When the CO_2 pressure was raised, most of the CAL molecules were dissolved in the dense CO_2 gas phase, changing the reaction system to the two-phase state. At elevated CO_2 pressures, hydrogenation should occur at the interface between the aqueous and CO_2 gas phases because of the same reason mentioned above.

Hence we assume that the hydrogenation of CAL occurred at the water–CAL interface under the three-phase conditions at low CO_2 pressures and at the water–CO_2 gas interface under the two-phase conditions at higher CO_2 pressures. For the two-phase reaction conditions, the mole fraction of reacting species in the CO_2 gas phase at different pressures was estimated by a simple calculation. Moles of pure H_2 and CO_2 were calculated by an equation of state, $PV = ZnRT$; the compressibility factor Z was assumed to be unity for H_2, whereas it was determined as a function of pressure and temperature for CO_2 [26]. From these moles of pure components, the mole fraction was then calculated under the reaction conditions. The results are plotted against CO_2 pressure in Fig. 4. Below certain pressures (depending on the initial amounts of CAL used), the reaction mixture includes the three aforementioned phases, and so Fig. 4 gives apparent values at low pressures assuming that the CAL and CO_2 gas phases are mixed into a single phase. At elevated CO_2 pressures, the mole fraction of either CAL or H_2 decreased significantly with increasing pressure. This dilution will likely cause a decrease in CAL hydrogenation at the water–gas interface region, resulting in decreased total conversion values at elevated pressures, as is clearly seen in Fig. 3(1) for the smallest initial amount of CAL used. In contrast to the conversion, the product selectivity changed little with the CO_2 pressure (and the conversion), which is an important feature of the multiphase reactions examined.

Papp et al. [12] reported a marked pressure effect of H_2 on the selective hydrogenation of CAL in an aqueous–organic two-phase system using water-soluble Ru complexes. They observed that COL selectivity increased significantly with H_2 pressure in a range of 0.1–1 MPa (lower pressures than those used in the present work), but this effect leveled off at pressures above 0.7 MPa. They ascribed this pressure effect to a change in the structure of Ru complexes as indicated by UV/vis spectroscopic measurements. The complex was in the form of $[RuClH(m\text{TPPMS})_3]$ (cherry-red solution) and $[RuH_2(m\text{TPPMS})_4]$ (strong yellow solution) at low and high H_2 pressures, respectively ($m\text{TPPTM} =$ *meta*-monosulfonated triphenylphosphine). The latter is beneficial to the hydrogenation of C=O of CAL. The possibility of a similar structural change has been examined for the present catalyst system and, as described later, the complex structure was found to change with CO_2 pressure.

3.3. Hydrogenation in dense CO_2 under G–L (organic) conditions [systems (a) and (e)]

The reaction systems shown in Fig. 1a and 1e, in which no additional organic solvent was used, were investigated. The three different phosphine compounds given in Scheme 2 were used as ligands. First, the effectiveness of the three phosphine compounds was examined under homogeneous conditions at a CO_2 pressure of 10 MPa, confirmed by visual observations. Table 1 gives the differences in total conversion and product selectivity among the Ru complex catalysts using these phosphine ligands. The differences observed are much smaller than those observed previously for hydroformylation reactions [23–25], in which the modification of TPP with fluorine-containing groups significantly affected the reactions of mono- and di-olefins. Table 1 shows that the selectivity for COL is <30% for the present homogeneous reactions (entries 1–7), comparable to the level observed in DMF (Fig. 2).

The G–L two-phase reaction was further examined under different conditions using a phosphine compound III, bis(pentafluorophenyl) phenylphosphine. As shown in Table 1, the product distribution is little influenced by the quantity of catalyst used, so it does not depend on the conversion (entries

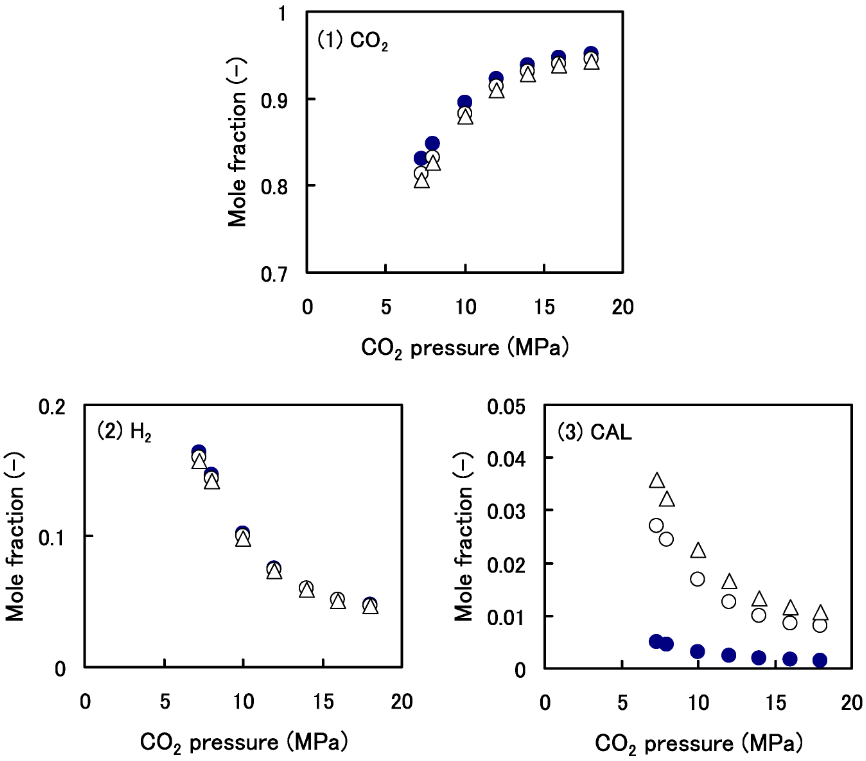


Fig. 4. Mole fraction of (1) CO_2, (2) H_2, and (3) cinnamaldehyde (CAL) as a function of CO_2 pressure at H_2 2 MPa and 70 °C. CAL: 1.1 mmol (●), 6.0 mmol (○), 8.0 mmol (△).

Table 1
Results of CAL hydrogenation with Ru complexes in compressed CO_2[a]

Entry	Precursor/ ligand	Ru (µmol)	CAL (mmol)	CO_2 pressure (MPa)	Conversion (%)	Selectivity (%)			Phase present[b]
						COL	HCAL	HCOL	
1	$RuCl_3$/I	0.075	0.2	10	18	30	50	20	G
2		0.15	0.2	10	23	24	56	20	G
3	$RuCl_3$/II	0.075	0.2	10	17	26	43	31	G
4		0.15	0.2	10	22	23	51	26	G
5	$RuCl_3$/III	0.035	0.2	10	18	25	50	25	G
6		0.075	0.2	10	21	25	48	27	G
7		0.15	0.2	10	22	23	51	26	G
8		0.68	0.2	16	55	24	50	26	G[c], L
9		25	7.5	16	11	93	7	0	G, L
10		50	7.5	16	54	98	1	1	G, L

[a] Reaction conditions: Ru/ligand = 1/3; H_2 pressure 4.0 MPa; temperature 50 °C; time 2 h.
[b] G: CO_2-rich gas phase, L: CAL-rich liquid phase.
[c] Very small droplets of CAL and/or catalyst were observed.

5–8). However, the COL selectivity improved when the quantity of the substrate used was increased. When a larger quantity of CAL of 7.5 mmol was used in CO_2, the reaction mixture changed to a G–L two-phase system, including CO_2-rich and CAL-rich phases (entries 9 and 10), and the COL selectivity improved significantly to >90%, in contrast to a low value of 24% at a small CAL quantity of 0.20 mmol. Although the same CAL/Ru ratio (300) was used for entries 8 and 9, the reaction results were significantly different. This difference may be explained by the difference in the state of reaction mixtures; the system of entry 8 is similar to the single G phase, whereas the system of entry 9 is in the G–L two-phase state.

The influence of CO_2 pressurization was further examined under two-phase conditions. Table 2 gives the results in the presence and absence of dense CO_2, demonstrating several interesting results. A high COL selectivity (about 90%) was obtained in the absence of both CO_2 and organic solvent (entries 6–10), in which CAL concentration was than that with reactions using organic solvents. This improved COL selectivity is in accordance with the previous observations that larger the quantity of CAL, the higher the COL selectivity for supported Pt catalysts [27,28]. When the reaction mixture was pressurized by N_2, the total conversion and the product selectivity did not change so much (entries 1 and 2). However, when CO_2 was used in-

Table 2
Results of CAL hydrogenation with Ru complexes in two-phase systems

Entry	Pressure (MPa)		Time (h)	Conversion (%)	Selectivity (%)		
	H_2	CO_2			COL	HCAL	HCOL
In $scCO_2$							
1	4.0	0	2	11	88	9	3
2	4.0	8.5 N_2	2	12	88	10	2
3	4.0	8.5	2	24	91	7	2
4	4.0	14	2	31	93	6	1
5	4.0	16	2	54	98	1	1
In the absence of $scCO_2$							
6	2.0	–	2	10	88	10	5
7	4.0	–	2	11	88	9	3
8	4.0	–	4	22	88	10	2
9	4.0	–	18	62	89	5	6
10	6.0	–	2	27	91	8	1

Reaction conditions: catalyst 0.05 mmol, Ru/ligand (III) = 1/3, CAL 7.5 mmol, temperature 50 °C.

stead of N_2, total conversion increased from 11 to 24% (entry 3). When CO_2 pressure was further raised, total conversion was further enhanced and COL selectivity was also improved, to 98% at 16 MPa (entries 3–5). These positive effects of compressed CO_2 are the same as previously observed with a solid catalyst of Pt/Al_2O_3 [17]. The results at 4 MPa H_2 in 8.5 MPa CO_2 are comparable to those at 6.0 MPa H_2 in CAL (entries 3 and 10). It should be noted again that COL selectivity was high under organic solvent-free conditions, and both the conversion and selectivity were further improved in the presence of compressed CO_2.

3.4. *UV/vis and FTIR spectroscopic measurements*

The possibility of a structural change in Ru complexes under different conditions was examined by UV/vis spectroscopy. The aqueous Ru complex solution was prepared as described in the Experimental section. The spectrum (a) in Fig. 5(1) indicates the starting complex solution so prepared, which is reddish-brown. This solution was further treated in the presence of different compressed gases and then subjected to UV/vis measurement under ambient conditions. When the treatment was done with 8 MPa H_2 or 2 MPa H_2 + 10 MPa N_2 for 120 min, the spectrum did not change much [spectra (b) and (c)]. Under 2 MPa H_2 + 8 MPa CO_2, however, the solution changed to orange-yellow in color, and the spectrum (d) was obtained. The treatments were also conducted for a shorter time (15 min) and at a higher CO_2 pressure (16 MPa) in the presence of 2 MPa H_2 [Fig. 5(2)]. This change occurred more rapidly at a higher CO_2 pressure of 16 MPa. In all likelihood, more H_2 molecules are soluble in the aqueous phase under pressurized CO_2 atmosphere, but this increased H_2 dissolution should be less significant for the Ru complex to change in structure; compare spectra (a), (b), and (d) of Fig. 5(1). Thus it is likely that the existence of CO_2 molecules dissolved in the aqueous phase promotes the structural change of the Ru complex, and the chemical nature of CO_2 molecules different from H_2 and N_2 should be important. The detailed structure of the Ru complexes is not known at present and requires further physicochemical structural analysis, but possible forms are $RuClH(TPPTS)_3$ and $RuH_2(TPPTS)_4$ for the complexes in the starting aqueous solution [spectrum (a) of Fig. 5(1)] and in the solution after treatment with compressed CO_2 [spectrum (d) of Fig. 5(1)]. The activity of the Ru complexes treated under different conditions was examined for aqueous homogeneous hydrogenation (in an H_2–water two-phase system), as described later.

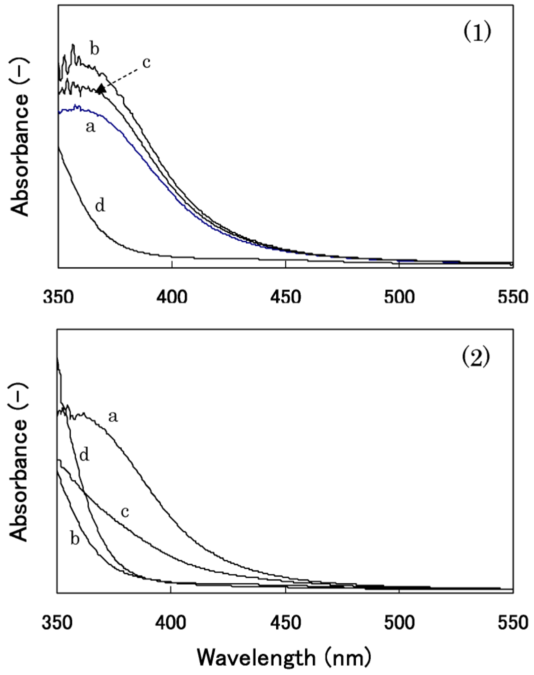


Fig. 5. UV/vis spectra for aqueous Ru/TPPTS complex solutions prepared at 70 °C under different conditions. For (1), (a) is a solution after prepared by normal procedures described in Section 2; this solution was further treated under (b) H_2 8 MPa, (c) 2 MPa H_2 + 10 MPa N_2, or (d) 2 MPa H_2 + 8 MPa CO_2 for 120 min each. For (2), the solution prepared by the normal procedures was further treated under 2 MPa H_2 + 8 MPa CO_2 for (a) 15 min or (b) 120 min or under 2 MPa H_2 + 16 MPa CO_2 for (c) 15 min or (d) 120 min. The spectra were collected under ambient conditions just after the preparation and the treatments under those different conditions.

Recently we reported that ν(CO) of the C=O bond of CAL in compressed CO_2 showed a red shift with CO_2 pressure, whereas ν(C=C) did not change so much; namely, there were interactions between CO_2 molecules and the C=O bond, increasing its reactivity [16,17]. This is of significance for the selective hydrogenation of CAL to COL under dense CO_2 conditions. For benzaldehyde as well, a similar red shift of ν(CO) was observed, but less marked than that of CAL. In the present work, the same FTIR measurements were conducted for HCAL (saturated aldehydes) in dense CO_2 for comparison. Fig. 6 shows in situ high-pressure FTIR spectra of HCAL at different CO_2 pressures at 50 °C. The spectrum of HCAL vapor at an atmospheric pressure of CO_2 was collected at a higher temperature (70 °C), because the absorption was very weak at 50 °C due to its lower vapor pressure (i.e., lower solubility in atmospheric CO_2). Fig. 6 shows that the absorption intensity increased with CO_2 pressure because more HCAL molecules became soluble. A red shift of ν(CO) of the C=O bond of HCAL is also visible; however, this red shift is less significant than the red shift for CAL, in which the ν(CO) absorption peak changed from 1740

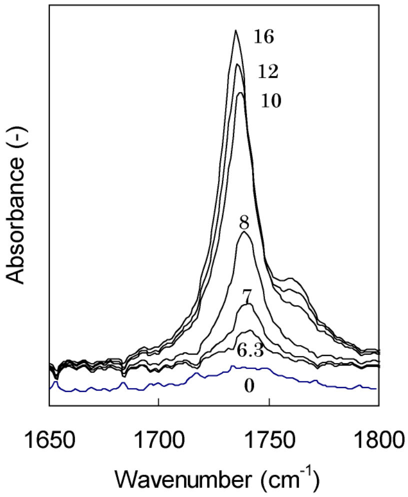


Fig. 6. FTIR spectra of hydrocinnamaldehyde (HCAL) dissolved in compressed CO_2 at pressures given and at 50 °C. The spectrum oh HCAL vapor at atmospheric pressure (indicated by 0) was collected at 70 °C since the absorption was very weak at 50 °C due to its lower vapor pressure. This spectrum is shifted down by a certain level.

to 1690 cm^{-1} at CO_2 pressures up to 20 MPa. The ν(CO) absorption was little influenced by the coexistence of 4 MPa H_2 for both HCAL and COL. The reactivity of the C=O bond of CAL was enhanced by the presence of dense CO_2, whereas that of HCAL was little modified. That is, the dense CO_2 promoted the hydrogenation of CAL to COL, but not the hydrogenation of HCAL to HCOL. The conjugation of C=C–C=O in CAL is important for the interactions between the CO_2 molecules and the C=O bond compared with the nonconjugated molecule of HCAL (C–C–C=O), enhancing the hydrogenation to COL.

3.5. *Aqueous homogeneous hydrogenation with different Ru complexes*

The homogeneous hydrogenation of CAL in the aqueous phase was also examined under similar reaction conditions as used for the aforementioned three- and two-phase reactions. The conversion of CAL was observed to occur very rapidly because of a low substrate/catalyst ratio. Table 3 gives the results obtained at 60 °C for the two complex catalysts prepared in different manners, which correspond to the UV/vis spectra (a) and (d) of Fig. 5(1). For complex catalyst (i), a total CAL conversion of 87% was achieved in only 5 min, and COL was produced in the largest quantity as compared with the other products (entry 1). However, the COL selectivity was only 67%, and a large quantity of HCOL was also produced. Note that this product distribution is significantly different than that observed under the multiphase conditions shown in Fig. 3. When the reaction mixture was pressurized by 8 MPa CO_2, the conversion marginally decreased, but COL selectivity decreased to 51% and HCOL selectivity increased to 41% (entry 2). This CO_2 pressure effect presents a contrast to that observed for the H_2–CAL two-phase system (Tables 1 and 2). For complex catalyst (ii), CAL conversion was also fast, but the conversion was smaller and the COL selectivity larger compared with complex (i) under the same conditions. It should be noted again that CAL hydrogenation occurred very rapidly in the aqueous phase and that COL selectivity was <75%.

Table 3
Results of homogeneous CAL hydrogenation with different Ru complexes in the aqueous phase[a]

Entry	Catalyst	CO_2 pressure[b] (MPa)	Conversion (%)	Selectivity (%)		
				COL	HCAL	HCOL
1	Complex (i)[c]	–[e]	87	67	6	27
2		8	82	51	8	41
3	Complex (ii)[d]	–[e]	78	74	10	16
4		8	62	70	18	12

[a] Reaction conditions: CAL 0.095 mmol; water 2 cm^3; $RuCl_3$ 0.022 mmol; TPPTS 0.089 mmol; H_2 2 MPa; temperature 60 °C; time 5 min.

[b] For hydrogenation runs.

[c] After prepared in the normal procedures with 2 MPa H_2 at 60 °C for 1 h (corresponding to spectrum (a) of Fig. 5(1)).

[d] After prepared in the normal procedures followed by the treatment with 2 MPa H_2 in the presence of 8 MPa CO_2 at 70 °C for 2 h (corresponding to spectrum (d) of Fig. 5(1)).

[e] Not applied.

3.6. *Comparison of the multiphase hydrogenation reactions*

The different types of multiphase reaction systems dealt with in this work are illustrated in Fig. 1. The kinetic analysis of multiphase catalytic reactions requires various pieces of information on the concentration of reacting species, the reaction kinetics in existing phases, the volume of the phases, and the transport phenomena between the phases. A detailed analysis of the present two- and three-phase reaction systems is hindered by the lack of such information. Nonetheless, we believe that it is important to compare those systems and discuss factors governing the selective hydrogenation of CAL to COL, including the significance of pressurization with CO_2 and the presence of interfaces. It was previously reported that isomerization of COL to HCAL did not occur with homogeneous and heterogeneous catalysts under similar conditions as used in the present work [22,28]. It also is unlikely that COL–HCAL isomerization occurs in the present multiphase reaction systems.

3.6.1. *Systems (a), (b), and (c)*

Earlier we studied the homogeneous hydrogenation of CAL in dense CO_2 with Ru complex catalysts using TPP and fluorine-modified phosphine compounds [21]. In these homogeneous reactions [system (a) in Fig. 1], the selectivity for COL was shown to be <50% irrespective of the phosphine compounds used. In contrast, in multiphase reactions using the similar water-soluble Ru–phosphine complexes, selectivity for COL was high at any conversion level (Fig. 3). Based on previous data [8] and the present solubility estimation, the solubility of CAL in water was not great, but the conversion of CAL was fast in the aqueous phase under homogeneous conditions. For the multiphase reaction systems, the hydrogenation of CAL should occur at the interface between the catalyst-containing aqueous phase and the CAL-containing fluid phase under the reaction conditions used. The CAL molecules diffusing from its liquid phase or the dense CO_2 phase can be hydrogenated at the interfaces but cannot enter into the bulk aqueous phase. The present work demonstrates that greater COL selectivity can be achieved when the interface between the water and organic phases is a main reaction locus [system (b)]. Selectivity for COL was also high at higher CO_2 pressures under which the reaction occurs at the interface between water and CO_2-rich gas phases [system (c)]. One can say that the COL selectivity is high when the catalyst-containing water phase contacts with the organic or CO_2 gas phase dissolving the substrate, CAL. For these three- and two-phase reactions, increasing CO_2 pressure was not effective in improving COL selectivity. A very important point for the high selectivity for COL in these two-phase systems is the nature of the substrate; namely, CAL is much less soluble in water but contains a hydrophilic carbonyl group, and so it may act as a surfactant in these reaction systems. As pointed out by Sanchez-Delgado et al. [9], this polar group is oriented toward the water phase, and the active species in this phase can catalyze the hydrogenation of this group, whereas hydrogenation of the nonpolar C=C group of CAL is much more difficult. This is also the case for hydrogenation of CAL using supported aqueous phase catalysts with Ru–TPPTS complex in an organic solvent (toluene) [13]. In this reaction system, interface between the support (silica gel) surface and the organic solvent also exists, in addition to the supported water–solvent interface. The former interface should contribute to the hydrogenation of C=C bond, and so the selectivity for COL would be slightly less than that of bulk water–toluene two-phase systems, although still much higher than that of homogeneous reaction systems [22]. Another possible factor contributing to the high selectivity for COL is the molecular interaction between the carbonyl group of CAL and CO_2 molecules dissolved in the CAL liquid phase, which we discuss in the following.

The results of UV/vis measurements (Fig. 5) indicate that the structure of complex catalyst changed during the reaction under pressurized CO_2 atmosphere, going from complex (i) to complex (ii) of Table 3. This change could influence the reaction; however, this should be insignificant, because the COL selectivity observed for the multiphase reactions is larger than that observed for the aqueous homogeneous reaction with complex (ii), because the reaction occurs at the water–CAL or water–CO_2 interface, and because the catalytic performance is not so different in complexes (i) and (ii) (Table 3).

3.6.2. *System (d)*

This reaction mixture is a conventional two-phase system using an organic solvent of DMF in which the catalyst and CAL are soluble. COL selectivity was <30%, and the total conversion of CAL and the product selectivity were not influenced by the pressurization of CO_2 (Fig. 2). When no organic solvent was used, COL selectivity improved even in the absence of CO_2 (Table 2, entries 6–10). In these cases, the CAL concentration in the liquid phase was high. The fact that high CAL concentration benefits the formation of COL with heterogeneous catalysts was reported previously [14,27–29]. Vergunst et al. [27] suggested a reasonable explanation that the state of adsorption of CAL on the surface of catalyst depends on the concentration of CAL. With increasing concentration, the space of the catalyst surface is relatively decreased, and so a CAL molecule will be adsorbed with its C=O group only, resulting in the enhancement of COL-selective hydrogenation. Gallezot and Richard [14] described this adsorption orientation, and Jin et al. [29] described the effect of concentration-dependent adsorption modes. In addition, the adsorption of a product of COL with its C=C group is also suppressed, hindering further hydrogenation of COL to HCOL. For homogeneous Ru complexes, however, the effect of CAL concentration at molecular levels is not easily explained. The structure of reaction intermediates (complexes) coordinated with CAL species and the rate of change between these intermediates may depend on the CAL concentration. The details of the reaction mechanisms merit further physicochemical investigation.

In addition, the polarity of the solvent used is significant in determining product selectivity in CAL hydrogenation with Ru/TPP [22] and Pt/C catalysts [30]. For both the homogeneous and heterogeneous catalysts, COL selectivity is higher when a more polar organic solvent is used. Comparison of the relative permittivity, ε_r, indicates that CAL ($\varepsilon_r = 16.9$ at 24 °C) is less polar than DMF ($\varepsilon_r = 36.7$ at 25 °C) [31,32], and so the dilution of CAL with DMF, which would make the reaction medium more polar, is unlikely responsible for the lower COL selectivity observed in DMF.

3.6.3. *System (e)*

The reaction systems with which higher COL selectivity can be achieved are systems (b), (c), and (e) of Fig. 1. System (e) is a CAL liquid phase pressurized with a reactant H_2 and a nonreactant CO_2. It is interesting to note that both the total conversion and the COL selectivity can be enhanced by pressurizing the system with CO_2 (Tables 1 and 2). Similar positive effects of high-pressure CO_2 were perviously observed for the organic solvent-free hydrogenation of CAL with a heterogeneous Pt/C catalyst [16,17]. A few factors are responsible for these enhancements, in addition to the CAL concentration mentioned above. When the liquid CAL phase is pressurized by CO_2, more CO_2 molecules can be dissolved in this phase, which promotes the dissolution of a gaseous reactant of H_2. This is confirmed by visual observation of the CAL–gas mixture under varying pressure conditions (Fig. 7). The volume of the CAL liquid phase expands in the presence of compressed H_2 and CO_2, due mainly to the dissolution of H_2 and CO_2. The solubility of CAL in CO_2 gas phase is reduced by the presence of H_2 [21], but this is not responsible for the volume expansion observed, because the solubility of CAL is low even in the absence of H_2. Of course, the increased dissolution of H_2 will increase the rate of hydrogenation reaction. In addition, the reactivity of the carbonyl group of CAL may be increased by interactions with CO_2 molecules. In situ high-pressure FTIR measurements show that the presence of dense CO_2 causes a red shift of ν(CO) of the carbonyl group of CAL that is slightly larger at higher CO_2 pressure [16,17]. FTIR measurements were obtained for the gaseous mixture of dense CO_2 gas and soluble CAL molecules. The interactions between the CO_2 and CAL molecules should also occur in the CAL liquid phase, in which CO_2 molecules are

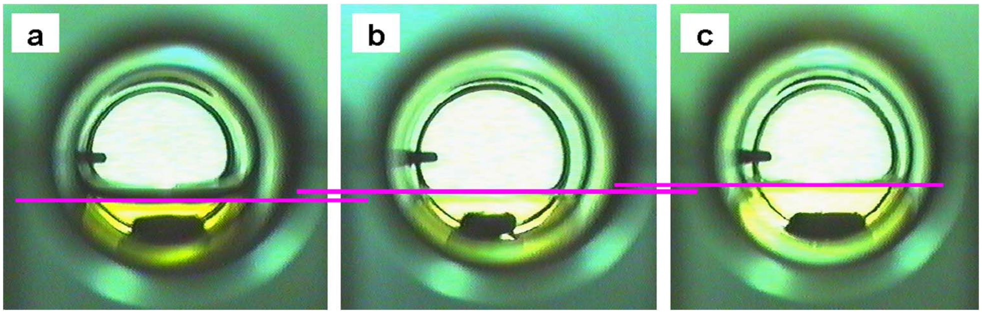


Fig. 7. The visual observation of CAL (a) under atmospheric pressure, (b) pressurized by 16 MPa CO_2, and (c) pressurized by 4 MPa H_2 and 16 MPa CO_2 at 50 °C. The volume of the CAL liquid phase expands in the presence of both compressed H_2 and CO_2.

Table 4
Features of various multiphase reaction systems using Ru–phosphine complex catalysts for selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL)

Reaction system[a]	Catalyst phase[a,b]	Selectivity for COL[c]	Influence of CO_2 pressurization	Remark
(a) Homogeneous in dense CO_2	G	Low (<30%)	Decreasing the overall CAL conversion	CO_2 is a solvent/diluent
(b) Three-phase, G–L_1–L_2 (at low CO_2 pressures)	L_2	High (>80%)	Less significant on the COL selectivity Decreasing the overall CAL conversion	The presence of L_1–L_2 and G–L_2 interfaces is significant for the high COL selectivity. The pressurization with CO_2 is less effective for the improvement of the selectivity
(c) Two-phase, G–L_2 (at high CO_2 pressures)	L_2	High (>80%)	Less significant on the COL selectivity Significantly decreasing the overall CAL conversion	
(d) Two-phase, G–L_3 (conventional system)	L_3	Low (around 30%)	Little effect on the COL selectivity Marginally increasing the conversion	CO_2 pressurization may increase the amount of H_2 dissolved in the liquid phase
(e) Two-phase, G–L_1	L_1	Very high (>90%)	Enhancing the overall CAL conversion and the COL selectivity	Dissolved CO_2 molecules promote the reactivity of the C=O bond of CAL molecules

[a] See Fig. 1. G: CO_2-rich gas phase; L_1: CAL phase; L_2: aqueous phase; L_3: organic phase (DMF).
[b] In which the catalyst exists.
[c] Under the reaction conditions used.

dissolved under high-pressure conditions. Thus we may point out two important factors for the enhancement of the total conversion and the COL selectivity in system (e): (1) increased H_2 concentration in the CAL liquid phase, and (2) increased reactivity of the carbonyl group of CAL through interactions with the dissolved CO_2 molecules. In addition, high concentration of CAL in the liquid phase with no organic solvent may be another important factor. At present, however, it is difficult to explain at the molecular level the CAL concentration effect (if it in fact exists) for homogeneous complex catalysts as used in this work compared with heterogeneous catalysts (supported metal catalysts, as described above).

But the presence of CO_2 has a negative effect as well as the aforementioned positive effects, depending on the reaction conditions used. For systems (a) and (c) of Fig. 1, the gas phase is simply diluted by CO_2, and this dilution effect is more significant, resulting in a decreased rate of reaction [Fig. 3 for system (c)]. High COL selectivity can still be achieved in system (c) because of the presence of the water–gas interface as a main hydrogenation locus, whereas COL selectivity is low for the homogeneous system (a). Although the interaction of CAL with CO_2 exists in system (a), it does not result in the selective hydrogenation of the carbonyl group of CAL to COL, probably because of the different nature of this gas phase compared with the homogeneous CAL liquid phase of system (e). In system (b), CO_2 is soluble in the CAL phase, but the catalyst exists in the different water phase, and the main reaction locus is the water–CAL interface. In this case as well, the interaction of CAL with CO_2 does not contribute to the selective hydrogenation to COL, and the selectivity does not change with altered CO_2 pressure, as observed in Fig. 3.

4. Conclusion

The present work has dealt with various multiphase reaction systems, as illustrated in Fig. 1. These systems have both different and similar features for the selective hydrogenation of CAL, as summarized in Table 4. Our results demonstrate that systems (b), (c), and (e) in Fig. 1 are beneficial to the selective hydrogenation of CAL to COL and that these systems use no organic solvent. Pressurization with CO_2 is very effective in improving total conversion and COL selectivity in system (e), but less effective for improving total conversion in the other two systems. But in systems (b) and (c), high COL selectivity can be obtained because of the interface catalysis. For system (e), the increased concentration of H_2 in the liquid phase caused by the dissolution of CO_2, the enhanced reactivity of the carbonyl group of CAL molecules due to interactions with dissolved CO_2, and the high concentration of CAL in the liquid phase are responsible for the high conversion and high COL selectivity observed. For systems (b) and (c), the interface between the water phase and the CAL liquid phase or the CO_2 gas phase is a main reaction locus, resulting in the selective hydrogenation of CAL to COL.

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