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Supported liquid-phase catalysts containing ruthenium complexes for selective hydrogenation of α, β-unsaturated aldehyde: importance of interfaces between liquid film, solvent, and support for the control of product selectivity

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Abstract

Selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) has been investigated with supported liquid-phase catalysts (SLPC), which contain Ru–TPPTS complexes in water film supported on a porous silica gel, in organic solvent (toluene). It was shown that COL can be mainly produced with small quantities of hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL). The influence of various reaction and catalyst preparation parameters on the overall rate of reaction and the product selectivity have been examined. In addition, liquid-phase adsorption of CAL on water-loaded silica samples has also been measured. It is believed that the hydrogenation of CAL to COL occurs at the interface between the water film and the organic solvent while that to HCAL at the interface between silica, water, and toluene. The hydrophilic nature of the C=O bond of CAL is significant for the selective formation of COL at the water/toluene interface, to which polar C=O bonds of CAL molecules are pointing. The product, COL, also has a polar OH group, and so it is difficult for COL to be hydrogenated to HCOL at this interface. At the other silica/water/toluene interface, CAL molecules may be adsorbed with their C=C bonds as well, which enables the hydrogenation to HCAL. On recycling of SLPC, its activity and COL selectivity decrease. Both oxygen dissolved in toluene and change of active Ru complexes in the water film are responsible for the decrease of catalytic activity, and the change of the state of dispersion of the water film is significant for the decrease of COL selectivity.

Keywords: Supported liquid-phase catalyst; Selective hydrogenation; Ruthenium complexes; Cinnamaldehyde; Catalyst recycling; Interfacial catalysis

1. Introduction

It is important to consider catalyst product separation and catalyst recycling in addition to activity and selectivity performance for practical applications of noble metal complexes as catalysts [1,2]. From this point of view, heterogeneous catalyses are preferable to homogeneous ones, and heterogeneous reactions can be performed by using such heterogenized metal complexes as biphasic catalysts and supported liquid-phase catalysts. Some authors have applied biphasic catalysts using water-soluble metal complexes for an industrially important reaction, selective hydrogenation of α, β-unsaturated aldehydes to unsaturated alcohols or saturated aldehydes [3–9], which is an important step for the synthesis of various fine chemicals. Grosselin et al. indicated that the biphasic catalysis was effective for selective hydrogenation of these substrates to unsaturated alcohols [3]. Joo et al. studied hydrogenation of unsaturated aldehydes using water-soluble ruthenium hydrides in a water and organic liquid biphasic system [4,5]. One of their interesting findings is that the selectivity can be tuned by changing the pH value of the water phase. Tin et al. used a water and benzene biphasic system using a water-soluble palladium complex catalyst for hydrogenation of cinnamaldehyde [6]. They showed the selectivity to unsaturated alcohol to be increased by the addition of sodium carbonate to the water phase. Sanchez-Delgado et al. conducted hydrogenation of cinnamaldehyde using homogeneous ruthenium complex catalysts in organic solvent and using biphasic catalysts with water-soluble analogue complexes [7]. It has been reported that the selectivity to unsaturated alcohol is higher for biphasic reactions com-

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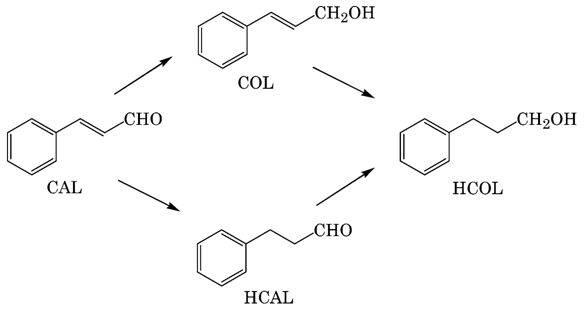

Scheme 1. Hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL).

pared with homogeneous ones (but unfortunately compared at different conversion levels). In addition, these authors have pointed out an important aspect that the hydrophilic nature of the C=O bond contributes to its selective hydrogenation. Those results demonstrate that one can find other factors, ineffective for homogeneous reactions, in controlling the catalytic performance of metal complexes for biphasic catalyses and similar heterogenized metal complex catalysts including supported liquid-phase catalysts (SLPC), in which active species exist in a liquid film dispersed on a support [10–14]. Water and other liquids like ethylene glycol have been used as supporting liquids and porous materials like silica gel as supports, and granular SLPC samples prepared have been used by dispersing in organic solvents for a few chemical transformations of hydrogenation, hydroformylation, and Heck coupling reactions [10–26].

In the present work, hydrogenation of cinnamaldehyde (CAL) has been studied by using ruthenium phosphine complexes in the form of SLPC as well as biphasic and homogeneous catalysts (Scheme 1). Ruthenium has been selected because it is less expensive and therefore more practical. Time profiles of total conversion and product selectivity have been collected for these heterogeneous and homogeneous hydrogenation reactions. It is interesting that the product selectivity strongly depends on the reaction phases used. The homogeneous reactions produce hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL); in contrast, the reactions with SLPC selectively produce cinnamyl alcohol (COL) with a small amount of HCOL. The use of SLPC is also valuable in controlling the catalytic performance of metal complexes, in addition to the easiness of catalyst separation and recycling. There has been discussion on the features of gas–liquid–liquid film–solid multiphase reactions using SLPC and factors determining the rate of reaction and the product selectivity.

2. Experimental

2.1. Preparation of SLPC and hydrogenation of CAL

trans-Cinnamaldehyde, a metal precursor of ruthenium trichloride hydrate, a ligand of triphenylphosphine trisulfonate trisodium salt (TPPTS), and a porous silica gel (Aldrich Davisil 646) were used as received. The BET surface area of the silica was 294 $m^2\ g^{-1}$, the total pore volume 0.96 $cm^3\ g^{-1}$, and the average pore diameter 20 nm. Toluene was used as a solvent. The preparation of SLPC and the hydrogenation of CAL were carried out in a 100 cm^3 autoclave. In a typical experiment, 1 cm^3 of distilled water containing 0.3 mmol of ruthenium trichloride hydrate and an appropriate amount of TPPTS was well mixed with a weighed amount of the silica powder in the reactor. Twenty cubic centimeters of the solvent was introduced into the reactor and the reactor was purged with N_2 three times. The mixture was then treated at 60 °C for 1 h under 1 MPa H_2 for the formation of Ru complexes. After this treatment, the reactor was cooled and depressurized. Then, CAL (24 mmol) and toluene (40 cm^3) were added into the reactor and it was purged with atmospheric H_2 three times. The reactor was heated again to a reaction temperature of 60 °C and H_2 was further introduced under stirring. When the H_2 pressure reached the desired value, reaction time was counted. During the reaction, small amounts of the reaction mixture were sampled at desired intervals and analyzed using gas chromatography. Procedures of the preparation of similar SLPC samples containing Pd, Pt, and Ru in water or ethylene glycol film were described elsewhere [27,28] and those of CAL hydrogenation were previously given for homogeneous and heterogeneous reaction systems [29,30].

2.2. Adsorption of CAL to water-loaded silica

This adsorption was examined at room temperature to obtain information about the liquid-phase adsorption of CAL on SLPC, using a 50 cm^3 reactor and silica supports in which water was loaded but Ru complexes were not included. Two grams of silica and a certain volume of water were well mixed in the reactor in the same way as used in the preparation of SLPC samples. Then, 10 cm^3 toluene and 4.8 mmol CAL were charged into the reactor. After the mixture was left for 30 min under stirring, the amount of CAL adsorbed by the silica sample was evaluated from a decrease in the concentration of CAL in the liquid phase.

2.3. NMR spectroscopy

The structure of Ru complexes in the supported water film was analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectrometry. The samples were prepared by using D_2O instead of H_2O as the supported film. After H_2 pretreatment, hydrogenation, or recycling, the SLPC sample was washed with toluene degassed by bubbling with argon, Ru complexes contained in the sample were extracted with D_2O from the silica support, and then ^1H and ^{31}P NMR spectra were measured on a JEOL JNM-400II spectrometer using TMS or H_3PO_4 as external standards. The washing and extraction were carried out under argon atmosphere.

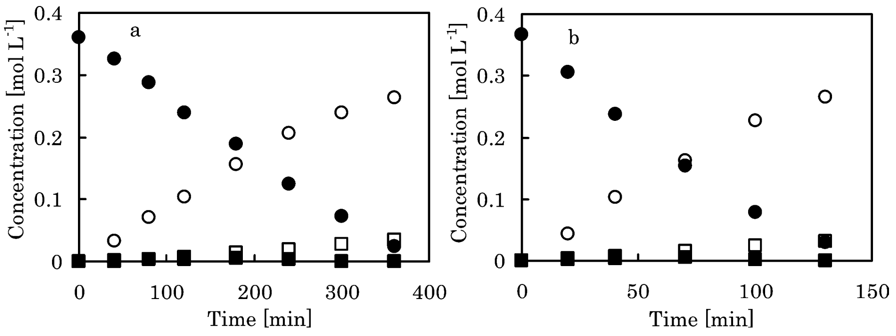

Fig. 1. Typical concentration–time curves of cinnamaldehyde hydrogenation using a SLPC in toluene. Substrate (●) CAL; products (○) COL, (■) HCAL, (□) HCOL. SLPC: SiO_2 2 g, H_2O 1 cm^3, Ru 0.3 mmol, TPPTS/Ru = 4. Reaction conditions: toluene 60 cm^3, CAL 24 mmol, temperature 60 °C, H_2 pressure (a) 2 MPa, (b) 8 MPa.

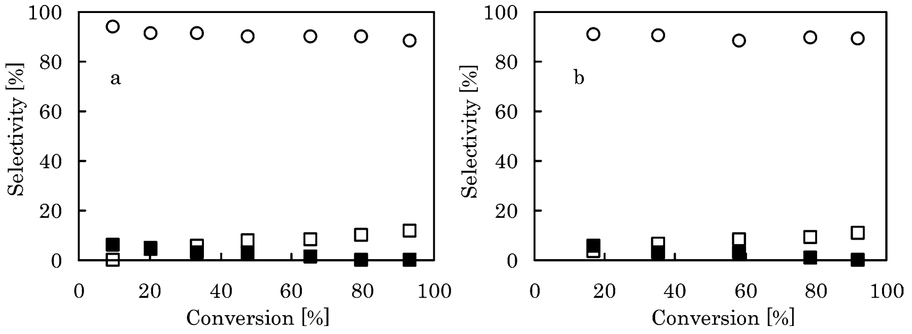

Fig. 2. Plots of the selectivity of COL (○), HCAL (■), and HCOL (□) against total CAL conversion in cinnamaldehyde hydrogenation using a SLPC at H_2 pressures of (a) 2 MPa and (b) 8 MPa. For SLPC and reaction conditions, see Fig. 1.

3. Results and discussion

3.1. Effects of reaction parameters in SLPC system

The heterogeneous reaction systems using SLPC are more complicated compared with homogeneous ones. The rate of such a heterogeneous reaction depends on several reaction and catalyst preparation conditions, and their effects have been examined in detail. Typical concentration–time curves obtained are shown in Fig. 1. The (initial) rate of reaction, disappearance of substrate, or formation of products have been determined from the data at an initial stage of the reaction, which give a good linear concentration–time relationship. Here we note an important point that the selectivity to cinnamyl alcohol (COL) is significantly high, and will be discussed in detail later.

The reaction runs were carried out at various H_2 pressures. It was found that the overall rate of reaction increases linearly with the pressure, in accordance with several previous works reporting similar simple pressure effects [3,6,8,30,31]. The COL selectivity, moles of COL formed against total moles of all the products of COL, hydrocinnamaldehyde, and hydrocinnamyl alcohol, are plotted against total conversion in Fig. 2. A COL selectivity as high as 90% remains unchanged during the reactions at different H_2 pressures examined. Very recently, Joo and co-workers reported that the COL selectivity for CAL hydrogenation with Ru complexes in a water/chlorobenzene biphasic reaction depends on the H_2 pressure in a region below 1 MPa [32]. The COL selectivity of the present reaction system might change at such low H_2 pressures.

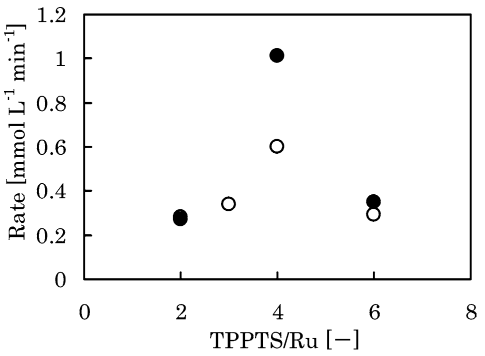

Fig. 3. Influence of TPPTS/Ru ratio on the overall rate of reaction in cinnamaldehyde hydrogenation using a SLPC in toluene. SLPC: SiO_2 2 g, H_2O 1 cm^3, Ru (●) 0.20 mmol, (○) 0.15 mmol. Reaction conditions: toluene 60 cm^3, CAL 24 mmol, temperature 60 °C, H_2 pressure 4 MPa.

The influence of the ratio of Ru to TPPTS in the supported water film is shown in Fig. 3. With an increase in this ratio, the overall rate of reaction increases, has a maximum at 4, and then decreases. The rate of COL formation has been shown to mainly change and so the COL selectivity also changes in a similar fashion. This may be explained by a change of the structure of active Ru complexes formed at different Ru/TPPTS ratios [3,4,7]. The effect of Ru/TPPTS ratio observed is different from that in homogeneous reactions using N,N'-dimethylformamide (DMF), N-methyl-

Table 1
Results of CAL hydrogenation using different quantities of SLPC and CAL used

Entry	SLPC[a]			CAL quantity (cm^3)	Overall rate (mmol L^{-1} min^{-1})	COL selectivity[b] (%)
	Silica (g)	Water (cm^3)	Ru (mmol)			
A						
1	1.0	0.5	0.15	1.5	0.22	70
2	1.0	0.5	0.15	3.0	0.27	66[c]
3	1.0	0.5	0.15	6.0	0.24	60[d]
B						
1	1.5	0.75	0.23	2.3	0.76	78
2	1.5	0.75	0.23	3.0	0.82	81
3	1.5	0.75	0.23	4.5	0.67	66
C						
1	2.0	1.0	0.30	1.5	1.25	92
2	2.0	1.0	0.30	3.0	1.60	90
3	2.0	1.0	0.30	6.0	1.53	85

Reaction conditions: toluene 60 cm^3; temperature 60 °C; H_2 pressure 4 MPa.

[a] TPPTS/Ru = 4; silica (g)/water (cm^3)/Ru (mmol) = 1/0.5/0.15.

[b] At a conversion of 20%.

[c] At a conversion of 10%.

[d] At a conversion of 5%.

pyrrolidone (NMP), and ethyl acetate, which have the possibility of having interactions with active Ru species [30]. In the case of NMP, the COL selectivity was the highest in the absence of TPP ligands.

Table 1 shows the influence of the quantity of SLPC and the concentration of CAL substrate in toluene. With an increase in the SLPC quantity, the overall rate of reaction increases significantly (entries A, B, and C). The rate is not proportional to the SLPC quantity; the increase of the rate observed is more significant than expected. The COL selectivity also increases with increasing SLPC quantity (A, B, and C) and tends to decrease with increasing CAL concentration (entries 1, 2, and 3). The influence of CAL concentration on the overall rate is not clear.

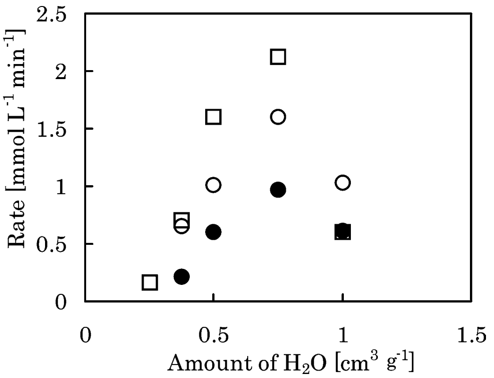

Fig. 4. Influence of the amount of H_2O loaded onto SiO_2 on the rate of reaction in cinnamaldehyde hydrogenation using a SLPC in toluene. SLPC: SiO_2 2 g, TPPTS/Ru = 4, Ru concentration in H_2O (□) 0.30 mmol cm^{-3}, (●) 0.20 mmol cm^{-3}, (○) 0.15 mmol cm^{-3}. Reaction conditions: toluene 60 cm^3, CAL 24 mmol, temperature 60 °C, H_2 pressure 4 MPa.

Table 2
Influence of the amount of supported water on the product distribution[a]

Amount of supported water (cm^3 g^{-1})	Selectivity[b] (%)		
	COL	HCAL	HCOL
0.25	70[c]	30[c]	0[c]
0.38	72	17	10
0.50	90	3	7
0.75	95	0	5

[a] Reaction conditions: Ru concentration 0.3 mmol cm^{-3}, P/Ru = 4, SiO_2 2 g, H_2 4 MPa, toluene 60 cm^3, 60 °C.

[b] At conversion of 20%.

[c] At conversion of 5%.

Finally, the influence of the concentration of Ru–TPPTS complexes in the water film and of the volume of water has been examined (Fig. 4). The catalyst concentration is significant, which increases the overall rate of reaction when compared at the same volume of water. The effect of catalyst concentration on the overall reaction rate observed is similar to that in our previous Heck reactions using SLPC in which Pd–TPPTS complexes are dispersed in ethylene glycol film on the same silica gel [27,28]. Fig. 4 also shows that even at the same catalyst concentration in water film, the overall reaction rate increases with an increase in the water volume up to 0.75 cm^3 per 1 g of silica support. In the previous Heck reactions as noted above, the rate of reaction depends little on the volume of ethylene glycol used [28]. The dispersion (wetting) of the liquid film on the same silica gel would be different between water and ethylene glycol. At a higher water loading of 1 cm^3 g^{-1}, all the water was not able to be stably dispersed on the support. The influence of water loading was examined by previous authors for hydroformylation reactions [15–17,21,22], reporting similar changes. For example, Naughton and Drago indicated that optimal activities occurred when the pore volume of the support materials was fully filled [21].

The product distribution did not change with the catalyst concentration in the water film and the high COL selectivity remains unchanged under the conditions examined. However, the amount of water film affects the product distribution as shown in Table 2. A larger amount of water causes higher COL selectivity and lower HCAL selectivity. Joo et al. showed that the pH value of water affects the COL selectivity for the CAL hydrogenation in a biphasic reaction [4,5]. The water film of SLPC prepared in the present study would be acidic because of the presence of HCl originating from the precursor of $RuCl_3$. However, the experiments in Table 2 were carried out at the same catalyst concentration and, hence, it is assumed that the pH value of the water film did not change with its volume. So, the change of the COL selectivity would result from reasons other than the change in the pH value.

3.2. Reactions with COL and HCAL in SLPC system

Hydrogenation experiments have also been carried out using the two products of COL and HCAL as starting substrates under such conditions: catalyst, $RuCl_3$ 0.3 mmol, TPPTS/Ru = 4, water 1 cm^3, silica 2 g; reaction CAL 3 cm^3, toluene 60 cm^3, temperature 60 °C, H_2 4 MPa. Both COL and HCAL have been found to be hydrogenated to HCOL but at different rates of reaction. The rate of COL hydrogenation (0.12 $mmol\,L^{-1}\,min^{-1}$) is smaller by more than one order of magnitude than that of HCAL hydrogenation (2.3 $mmol\,L^{-1}\,min^{-1}$). This difference is the same as observed in homogeneous hydrogenation reactions of COL and HCAL [30] under similar conditions as used in the present work.

3.3. Adsorption of substrate on SLPC

This adsorption has been examined at room temperature using catalyst-free silica gel samples, similar to SLPC, in which different volumes of water are loaded. The amount of substrate, CAL, adsorbed on such a water-coated silica gel has been measured at an initial CAL concentration of 0.45 $mol\,L^{-1}$ (Fig. 5). The water-free silica can adsorb CAL in 0.56 $mmol\,g^{-1}$ and the amount of CAL adsorbed decreases simply with the water volume coated. The solubility of CAL in water is very low (about 0.14 g per 100 g of water, ca. 0.01 $mmol\,cm^{-3}$, at 25 °C [6]) and so the quantity of CAL absorbed in water is negligibly small. The water can spread over the hydrophilic surface of the silica gel and the free surface that can adsorb CAL decreases with the water volume. At a volume of 1 cm^3 per 1 g of silica, the water-free surface is likely to disappear, at which the average water film thickness is estimated to be 3.6 nm. Such a water film may contain the Ru–TPPTS complexes. Probably, in the present case of water, the water–silica contact area increases with the volume of water used while maintaining the film thickness. This is different from the previous case of SLPC using ethylene glycol, which can spread over the silica surface to some limited extent and so the silica–ethylene glycol contact area changes little with the volume of ethylene glycol used, but the film thickness increases. This means that the interfacial area between ethylene glycol film and organic solvent (toluene) changes little and, as a result, the rate of Heck reaction does not depend on the quantity of ethylene glycol used, as reported previously [26]. Fig. 5b shows that the (total) amount of CAL adsorbed increases with an increase in the initial concentration of CAL in toluene and it is proportional to the quantity of water-loaded silica sample used. The amount of CAL adsorbed becomes saturated at higher CAL concentrations.

3.4. Effects of reaction parameters in biphasic and homogeneous systems

To examine the features of SLPC reaction systems, some additional experiments were performed for biphasic systems. Typical concentration–time curves are given in Fig. 6. It has been found for biphasic reactions that CAL is selectively hydrogenated to COL and the high COL selectiv-

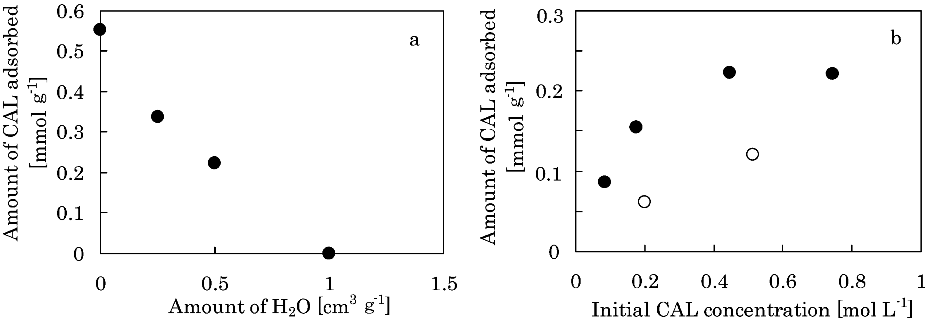

Fig. 5. Results of adsorption of cinnamaldehyde by H_2O-loaded SiO_2 samples at room temperature. Influence of (a) amount of H_2O loaded onto SiO_2 and (b) initial CAL concentration in toluene. For (a), toluene 60 cm^3, SiO_2 2 g, initial CAL concentration 0.45 $mmol\,cm^{-3}$. For (b), toluene 10 cm^3, (●) SiO_2 2.0 g, H_2O 1 cm^3, (○) SiO_2 1.0 g, H_2O 0.5 cm^3.

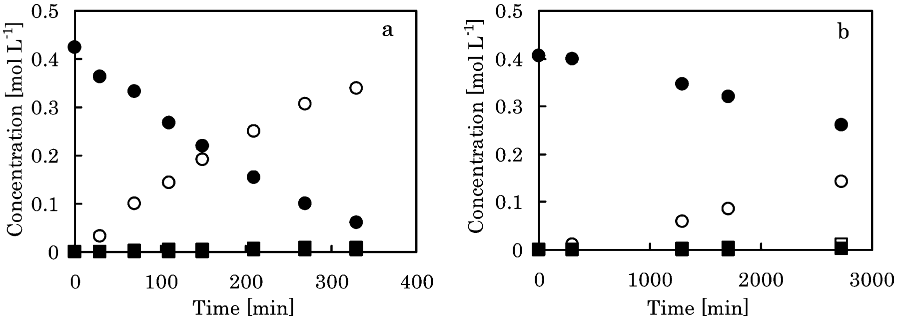

Fig. 6. Results of cinnamaldehyde hydrogenation in water/toluene biphasic system using Ru–TPPTS catalyst with (a) and without (b) stirring. Substrate CAL (●), products COL (○), HCAL (■), HCOL (□). Reaction conditions: H_2O 5 cm^3, Ru 0.6 mmol, TPPTS/Ru = 4, toluene 55 cm^3, CAL 24 mmol, H_2 pressure 4 MPa, temperature 60 °C.

ity remains unchanged during the reactions, in accordance with the above-noted results of SLPC systems. For homogeneous reactions, the rate of reaction and the product selectivity strongly depend on the nature of solvents and the Ru/TPP ratio [30]. The COL selectivity is lower compared with SLPC and biphasic systems and the product selectivity changes with time, in contrast to the two multiphase systems. For example, the COL selectivity values at 20% conversion were 50 and 20% for DMF and ethyl acetate, respectively, at 60 °C and H_2 4 MPa with a TPP/Ru of 4. For NMP, the COL selectivity was the best (15% at 20% conversion) in the absence of TPP.

For the biphasic system, the reactions with and without agitation have been compared to examine the influence of the water–toluene interfacial area (Fig. 6). As expected, the overall rate of reaction with agitation is larger than that without agitation; however, the high COL selectivity is the same between these two cases. Grosselin et al. reported that the rate of reaction increased with stirring rate up to a certain rate beyond which it did not change [3], but they did not note its influence on the product selectivity. In addition, biphasic reactions have been conducted at two different water/toluene volume ratios, 2.5/57.5 and 5.0/55.0. The overall rate of the former reaction was 0.55 $\mathrm{mmol\,L^{-1}\,min^{-1}}$ and that of the latter was 1.1 $\mathrm{mmol\,L^{-1}\,min^{-1}}$, indicating that the rate is proportional to the water/toluene interfacial area. However, the high COL selectivity changed little. Tin et al. reported for biphasic reactions using water and benzene that the concentration of Pd complexes in the water phase increased the CAL conversion but did not affect the product selectivity [6]. Grosselin et al. also observed a linear dependence of the rate of reaction on the Ru catalyst concentration [3]. Those results indicate that the rate of CAL hydrogenation in biphasic systems depends on the catalyst concentration in the water phase and the volume ratio of water and organic solvent phases, while the product selectivity (high COL selectivity) does not change with these factors.

3.5. Importance of interface as the reaction locus in SLPC and biphasic systems

The present reactions with SLPC are not controlled by diffusion of reacting species in the bulk organic phase and in the pores of SLPC because the concentration of substrate in the organic phase has only a marginal effect on the overall rate of reaction and the concentration of active Ru species in the supported water film increases the reaction rate as described above.

In addition to low solubility of CAL and H_2 in water, the present results demonstrate that the interface between the continuous organic phase (toluene) and the supported water film phase (or bulk water phase in biphasic system) is the sole reaction locus for hydrogenation of CAL to COL. Previously, Sanchez-Delgado et al. pointed out that the more hydrophilic nature of the aldehyde group of CAL compared with the C=C bond is important for the selective hydrogenation of CAL to COL in their water–benzene biphasic system [7]. The C=O bond points toward the water phase in which active Ru complexes exist, but the less hydrophilic C=C bond points away from the water film to the organic phase. As a result, the C=O bond can selectively be hydrogenated to COL. The same explanation may be possible for our SLPC system. In addition, we should note that the product, COL, has a hydrophilic end group of OH and so it is still not easy for its C=C bond to be hydrogenated. This explains the result that the rate of hydrogenation of COL alone is much smaller than that of HCAL alone, in which the hydrophilic C=O bond remains unaltered. It is interesting to compare these results with those obtained with a heterogeneous Pt/SiO_2 catalyst [31], for which competitive adsorption of substrate (CAL) and products (COL and HCAL) is also important but in a different way. The adsorption on the catalyst occurs easier in the order CAL > HCAL > COL; the fully hydrogenated product, HCOL, is produced mainly from COL and so the formation of HCOL starts after the disappearance of CAL and HCAL.

The overall rate of reaction may be a function of the concentrations of CAL and H_2 in toluene phase and the area of water film of SLPC. The concentration of H_2 in water is very low at H_2 pressures examined; the concentration of H_2 dissolved in pure water at 60 °C is estimated to be 0.018 $\mathrm{mol\,L^{-1}}$ at 2.5 MPa and 0.036 $\mathrm{mol\,L^{-1}}$ at 5.0 MPa using Henry's constant and so the structure of active Ru complexes is not influenced by H_2 pressure. As a result, the rate of reaction simply increases with H_2 pressure (H_2 concentration in toluene). Thus, the Ru/TPPTS is only a factor affecting the structure and specific activity of Ru complexes, which do not change with the volume of water used. The rate of reaction simply increases with the volume of water (the area of water film), as seen in Fig. 4. When the quantity of water used is increased, the water–toluene interfacial area is assumed to increase while the film thickness is unchanged. Such a wetting is modeled in Fig. 7: water is supported in the form of islets of a certain thickness on the wall of cylindrical pores and the islets grow in size (and may coalesce sometimes) with an increase in the amount of water (water–toluene interface expands) but the thickness of the islets remains unchanged. This may explain the fact observed that the COL selectivity increases with an increase in the water loading, as discussed in the following with respect to the reaction sites for the COL and HCAL formation.

In SLPC systems, we should consider another locus for hydrogenation of CAL to HCAL in addition to the surface of water film (water/toluene interface) for the CAL hydrogenation to COL (Fig. 7). The water/silica/toluene interface is likely to be such a reaction locus, in which CAL exists on the silica close to the water film containing the Ru complexes. The CAL molecule would be adsorbed on some acidic sites such as Si^{4+} or surface OH with its C=O bond and it may be hydrogenated to HCAL. Such sites are, needless to say, absent in biphasic systems. The quantity of CAL molecules adsorbed on the surface of water film of SLPC is probably

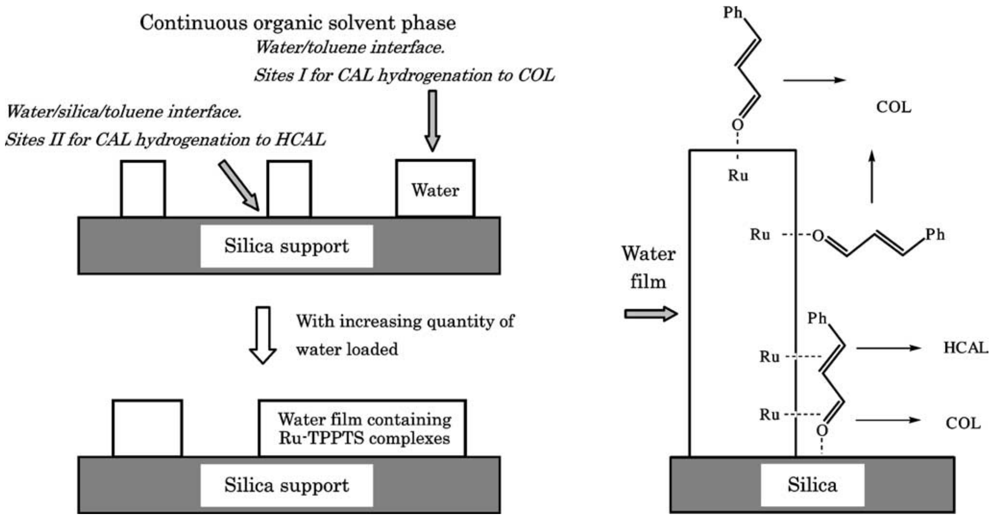

Fig. 7. Two possible reaction loci for hydrogenation of CAL to either COL or HCAL in a multiphase system using SLPC. The site II is absent when the whole surface of silica support is covered by water film. A biphasic system has site I only. When the quantity of water loaded increases, the water film spreads while the thickness remains.

saturated and small under the reaction conditions examined. However, the quantity of CAL molecules adsorbed on the silica surface should depend on the CAL concentration in toluene and the area of silica unoccupied by water film. On the basis of those considerations, it is believed that with an increase in CAL concentration, the quantity of CAL adsorbed on the water–silica interface increases while that on the water film does not change; so, the rate of HCAL formation increases while that of COL formation does not change, resulting in a decrease in the COL selectivity with the CAL concentration as observed (Table 1). With an increase of SLPC quantity (CAL/SLPC decreases), the quantity of CAL adsorbed on the silica–water interface decreases while that on the water film does not change. The rate of HCAL formation decreases while that of COL formation increases, resulting in an increase in the COL selectivity, as observed (Table 1). The ratio of the water/toluene interface against the water/silica/toluene interface cannot be determined quantitatively; however, it is obvious that this ratio is larger with an increasing amount of water. Hence, an increase in the volume of the supported water would cause higher COL selectivity and lower HCAL selectivity (Table 2).

If the whole surface of silica is covered by water film, such an effect of CAL concentration as discussed above would not appear; probably high COL selectivity would occur at any CAL concentrations, as in biphasic reactions. The whole surface of 1 g silica may be covered by more than 1 cm^3 water according to the results given in Fig. 5, for which the Ru complexes were absent. Unfortunately, such a SLPC sample containing the catalyst was not stably dispersed in toluene, making it difficult to perform reaction experiments. However, the above discussion may be indirectly/partially supported by the results of biphasic system, in which there is only a water–toluene interface, that high COL selectivity can be seen irrespective of the stirring condition and the water–toluene volume ratio.

Table 3
Comparison of SLPC, biphasic, and homogeneous systems in the performance for CAL hydrogenation

Entry	System and conditions[a]	Overall rate[b] (mmol L^{-1} min^{-1})	COL selectivity[c] (%)
1	SLPC $RuCl_3$ 0.3 mmol; TPPTS/Ru = 4; water 1 cm^3; silica 2 g; toluene 60 cm^3	1.6	89
2	Biphasic $RuCl_3$ 0.3 mmol; TPPTS/Ru = 4; water 1 cm^3; toluene 60 cm^3 (the same conditions as in SLPC)	0.07	100
3	$RuCl_3$ 0.6 mmol; TPPTS/Ru = 4; water 5 cm^3; toluene 55 cm^3	1.1	96
4	Homogeneous $RuCl_3$ 0.15 mmol; TPP/Ru = 4; DMF 60 cm^3	17.3	48

[a] CAL 3 cm^3; temperature 60 °C; H_2 pressure 4 MPa.
[b] Initial rate.
[c] At a total conversion of 80%.

3.6. Comparison of the performance in CAL hydrogenation among SLPC, biphasic, and homogeneous systems

It is not easy to compare the performance of different multiphase reaction systems on an equal basis since the comparison depends on how standard reaction conditions are selected. Table 3 compares the overall rate of reaction and the COL selectivity between the three reaction systems. In homogeneous system, all the reacting species are soluble in a single phase and the contact of those species is better, leading to a larger rate of reaction. This is the case for the present CAL hydrogenation; however, the selectivity to COL is smaller than 50% (entry 4). Compared with this homogeneous system, the COL selectivity is much larger in

SLPC and biphasic systems (entries 1–3). When compared at the same amounts of Ru and water, the overall rate in the SLPC system is significantly larger than that in the biphasic system (entries 1 and 2). A reason for this is the smaller water–toluene interfacial area in the latter system. When the amounts of Ru and water are increased, the rate in the biphasic system may be improved (entry 3).

Another merit of SLPC systems should be noted here: multifunctional catalytic systems may be designed by using different SLPC samples at the same time, which has recently been demonstrated by a few model reactions [29]. For example, simultaneous hydrogenation of 3-phenylpropionaldehyde and 1,2-diphenylethylene is possible with a mixture of Ru–SLPC and Pd–SLPC. This is due to the fact that an active metal complex in a SLPC can be separated from another metal complex in another SLPC, and the respective catalytic activities remain unaltered. However, for biphasic and homogeneous systems in which different metal complexes coexist in the same solvent, some negative effects will often appear, by which one kind of metal complex loses its specific activity [29].

3.7. *Recycling performance and stability*

Finally, the recycling of SLPC has been examined. After the first hydrogenation run with a SLPC sample, the solvent (toluene) phase was removed by decantation leaving the catalyst in a small volume of toluene and washed by adding a certain volume of fresh toluene. These procedures were repeated a few times and then fresh toluene and CAL substrate were added for the second run. The rate of reaction was found to decrease by a factor of about 2/3 in the second run, as shown in Fig. 8. In the third run, the catalyst had no activity. It was also found that treatments with 4 MPa of H_2 at 60 °C during the repeated reaction runs had no effect on the catalyst deactivation. When toluene was degassed by bubbling with argon for about 60 min and used for the reaction and washing the SLPC sample, the activity also decreased but to a smaller extent. Using the degassed toluene, about half the initial activity appeared for the second run but the activity decreased gradually on the further repeated runs. It should be noted that, when the procedures for recycling were conducted in a globe box under argon atmosphere, the same results as those shown in Fig. 8 were obtained. These observations indicate that the deactivation by the recycling is caused from not only oxygen dissolved in toluene but some other reasons.

The change of activity on the recycling of SLPC was also investigated by ^{1}H and ^{31}P NMR spectroscopy. Signals observed were assigned on the basis of the literature [33–35]. After the H_2 pretreatment, [Ru(H)(Cl)(TPPTS)$_3$] [34] having broad singlets in ^{31}P NMR at 61.77 ppm and in ^{1}H NMR at −18.48 ppm (Ru–H) was formed. After the first reaction run, this complex changed to a mixture of [RuH$_2$(TPPTS)$_3$] having a singlet in ^{31}P NMR at 58.15 ppm and a quartet in ^{1}H NMR at −9.58 ppm [33] and several complexes like [RuH(η^6-arene)(TPPTS)$_2$]Cl, which showed five ^{31}P NMR signals in a region between 56.83 and 58.51 ppm [34]. Integration of the ^{31}P NMR signals showed that the total amount of the arene complexes was about 15% of the dihydride complex. After the recycling, the amount of the dihydride complex decreased while the total amount of the arene-type complexes increased. Hernandez and Kalck showed that the arene complex had no activity for CAL hydrogenation [35]. Along with these Ru complexes, a phosphine complex having a singlet in ^{31}P NMR at 27.08 ppm was detected after the reaction and its amount increased by the recycling. The structure of this phosphine complex is unknown at the present stage. On the basis of these results, it was concluded that the dihydride complex is an active species or its precursor and converted to the arene complexes during the reaction, resulting in the deactivation of SLPC by the recycling. In conformity with the present results, Fache et al. reported that the recycling of Ru–SLPC caused its deactivation for hydrogenation of prenal, and carbon content in the catalyst increased on the recycling [18]. TPPTS is liberated by the transformation of the dihydride complex to the arene complexes. Probably, the unknown phosphine compounds should be produced via the reaction of TPPTS so liberated with the substrate or one of the products.

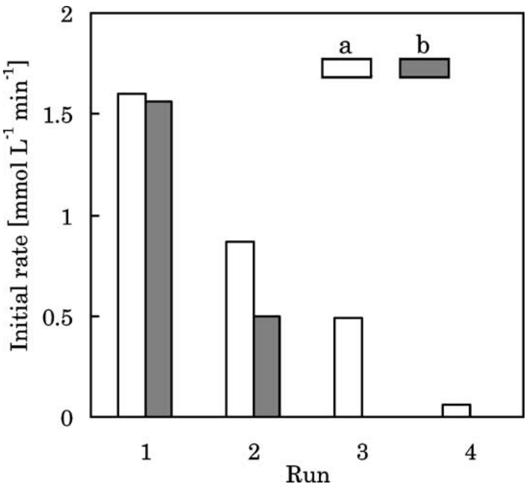

Fig. 8. Change of the initial rate of CAL hydrogenation on recycling of two SLPC samples of (a) and (b), which were prepared in the same way but samples (a) and (b) were washed with degassed toluene and untreated toluene, respectively, between the runs. The latter sample was reused twice. Reaction conditions: Ru 0.3 mmol, P/Ru = 4, H_2O 1 cm^3, SiO_2 2 g, toluene 60 cm^3, H_2 4 MPa, 60 °C.

Along with the decrease in the activity, the change of product selectivity was also observed. Table 4 shows the product selectivity and the initial rate of reaction for four repeated runs, in which the degassed toluene was used. The selectivity to COL decreased during the recycling while those to HCAL and HCOL increased and the extent of change is larger for HCAL than for HCOL (runs 2 and 3). As reported by Horvath [36], there is a possibility of a change of the state of water film dispersed on silica support, which may occur during the hydrogenation run and/or the wash-

Table 4
Results of recycling of SLPC sample for CAL hydrogenation[a]

Run	Initial rate ($mmol\,L^{-1}\,min^{-1}$)	Selectivity[b] (%) COL	HCAL	HCOL
1	1.60	100	0	0
2	0.87	72	15	14
3	0.49	35	42	24
4	0.06	38	38	23

[a] Reaction conditions: Ru 0.3 mmol, P/Ru = 4, H_2O 1 cm^3, SiO_2 2 g, H_2 4 MPa, toluene 60 cm^3, 60 °C. Degassed toluene was used to wash the SLPC sample between the runs (see text).

[b] At conversion of 20% for runs 1–3 and 4% for run 4.

Table 5
Results of TG and CAL adsorption measurements for water-loaded silica gel samples

Amount of H_2O film ($cm^3\,g^{-1}$)	Pretreatment[a]	Weight loss[b] (%)	Amount of CAL adsorbed ($mmol\,g^{-1}$)
0	–	7	0.55
0.5	–	34	0.22
0.5	60 °C, 1 h	23	0.39
0.5	60 °C, 3 h	19	0.47
0.75	–	44	–[c]

[a] After the loading of H_2O onto SiO_2 gel, the sample was dispersed in toluene at 60 °C for 1 or 3 h while stirring. Then the sample was dried under ambient conditions. For CAL adsorption, the treatment of the sample in toluene was made at the same temperature for 1 min and 3 h.

[b] After heating up to 800 °C.

[c] Not measured.

ing with toluene. This possibility has been examined with thermogravimetry (TG) and CAL adsorption measurements, for which silica gels were loaded with water only (in the absence of metal complexes). Table 5 gives the results of those measurements. The silica gel lost its weight by 7% after heating in air up to 800 °C, mainly due to the disappearance of surface hydroxyl groups. The weight loss for the untreated samples including 0.5 and 0.75 $cm^3\,g^{-1}$ water was in accordance with the quantity of water loaded. When the former sample was pretreated in toluene for 1 and 3 h, the weight loss decreased to 23 and 19%, respectively. Compared with the untreated sample, the pretreated samples adsorbed larger amounts of CAL, being 0.39 and 0.47 $mmol\,g^{-1}$. These amounts of CAL adsorbed are similar to those estimated from the results of Fig. 5 and the amounts of water estimated assuming that the weight loss is due to the disappearance of water. Those results suggest that some amount of water disappears from the surface of silica support during the reaction runs and/or the washing between them. It was observed, however, that the color of toluene did not change after the reaction and washing of SLPC and so no leaching of Ru species occurred during the recycling runs. The decrease in the quantity of water should cause a decrease in the interfacial area between water film and toluene solvent, which can explain the decrease in the activity and the COL selectivity observed (Table 4), on the basis of the above-noted reaction sites (Fig. 7). As described above, the quantity of water film affects the activity of SLPC. However, in the case of the recycling of SLPC, this effect would be canceled by the increase of Ru concentration in the film, since no Ru leaching occurred.

The results of NMR and TG indicate that, besides oxygen dissolved in toluene, the change of active Ru species in the water film and that of the state of dispersion of the water film (the decrease of the water–toluene interfacial area) are responsible for the loss of catalytic activity and the latter change for the decrease of COL selectivity on the recycling, respectively. These explanations are supported by additional results with biphasic reactions, for which the rate of hydrogenation was found to decrease on the recycling similar to the SLPC, while the product distribution was not observed to change. In the biphasic reactions, the contact between water and toluene phases did not change.

4. Conclusion

The selective hydrogenation of CAL to COL occurs with SLPC, which contains Ru–TPPTS complexes in water film on porous silica gel, in toluene, similar to a biphasic system with the same catalyst. The overall rate of reaction increases with the area of water film and the concentration of catalyst in the water film. The COL selectivity also increases with the area of water film but does not depend on the catalyst concentration. The COL selectivity tends to decrease with an increase of CAL concentration in toluene. It is assumed that the hydrogenation of CAL to COL occurs at the water/toluene interface and that to HCAL at the silica/water/toluene interface due to difference in the nature of C=O bond and C=C bond of CAL molecule. The quantity of CAL adsorbed at the former interface is saturated while that at the latter changes. The areas of these interfaces change with the reaction and catalyst preparation conditions, leading to a change in the overall rate of reaction and/or the COL selectivity. By the recycling of SLPC, its activity and COL selectivity decrease. Both the oxygen dissolved in toluene and the change of active Ru species in the water film are responsible for the decrease of catalytic activity and that of the state of dispersion of the water film is responsible for the decrease of COL selectivity.

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