Continuous gas-phase hydroformylation of propene with CO$_2$ using SILP catalysts

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ABSTRACT. Hydroformylation is an important process for the synthesis of aldehydes and alcohols in the chemical industry. Although this process uses toxic CO as one of the reactants, some types of Ru complex catalysts have been known to replace CO with CO_2 as a reactant in hydroformylation. Herein, we report the continuous hydroformylation of propene with CO_2, heterogeneously catalyzed by supported Ru complexes on silica using ionic liquids [*i.e.*, supported ionic liquid-phase (SILP) catalysts] in a flow reactor. When the reaction was carried out at 170 °C, 8.6 MPa and gas hourly space velocity (GHSV) of 1.13×10^3 h^{-1} using the SILP catalyst prepared from $Ru_3(CO)_{12}$, 1-ethyl-3-methylimidazolium chloride, and silica, the conversion of propene was 81.6% and the selectivity of hydroformylation was 66.1%. Kinetic analysis showed that the reaction rates of CO formation and hydroformylation were near-identical at 170 °C, indicating that the CO formed by the reverse water–gas shift reaction was readily used for the subsequent hydroformylation reaction. ESI-MS analysis of the ionic liquid phase showed the formation of trinuclear and mononuclear Ru complexes, and a plausible reaction mechanism was proposed based on these findings.

INTRODUCTION

Hydroformylation is a substantial chemical process in the chemical industry.[1] Its main products are aldehydes and alcohols, the total amount of which reaches more than 10 million tons per year. This process uses CO as a C1 unit and thus, if CO can be replaced with CO_2, it will be a greener process with a great impact on CO_2 utilization in the chemical industry.

As the first example to use CO_2 as a reactant in hydroformylation, our group reported that the $Ru_3(CO)_{12}$-catalyzed one-pot hydroformylation of alkenes with CO_2 instead of CO proceeded

smoothly to provide the corresponding alcohols in good yields.[2,3] Moreover, the yields and TONs (turn over numbers) were increased when ionic liquids were used instead of conventional organic solvents.[4,5] The addition of a halide salts is absolutely essential in these reactions because it forms several anionic Ru complexes, both in organic solvents and ionic liquids, that successively catalyze the conversion of CO_2 to CO, alkene hydroformylation with CO to form the aldehyde, and hydrogenation of the aldehyde to the alcohol.

Following our reports, Beller et al., reported that the introduction of bulky phosphine to $Ru_3(CO)_{12}$ increased the alcohol yield at lower temperatures.[6] Almost simultaneously, Dupont et al. reported that the addition of H_3PO_4 increased the catalytic activity of $Ru_3(CO)_{12}$ in ionic liquids to afford the corresponding alcohol in higher yields at lower reaction temperatures.[7] Additionally, Ding et al. reported the hydroformylation with CO_2 to afford aldehydes as the main products, using Rh complexes in the presence of hydrosilanes as oxygen scavengers.[8]

Hydroformylation is also a successful example of a homogeneous catalytic process in the chemical industry. Recently, in view of process intensification,[9] much attention has been devoted toward developing a heterogeneous catalyst for this reaction and its use in flow reactor systems. Supported ionic liquid-phase (SILP) technology is an effective method to fix homogeneous catalysts on solid supports. An SILP catalyst comprises a homogeneous transition metal complex confined in a thin ionic liquid film covering the large internal surface of a porous support.[10] It is much easier to prepare such a thin ionic liquid film on a porous support by the simple impregnation of a mixed solution of metal complexes and ionic liquid than a solid catalyst, where a homogeneous transition metal complex is immobilized on silica gel by chemical modification. Macroscopically, the SILP catalyst appears and can be handled as a dry solid; however, microscopically, it is a liquid solution. Moreover, it is robust and easily prepared and

processed. Because of the extremely low vapor pressure of ionic liquids, an SILP catalyst displays excellent stability, even at high temperatures, and is often used in gas-phase reactions such as hydrogenation,[11] carbonylation,[12] water–gas shift reaction,[13,14] and hydroformylation.[15-18]

Very recently, we investigated the reverse water–gas shift reaction (RWGSR), *i.e.*, the hydrogenation of CO_2 to CO, using a Ru-based SILP catalyst in a batch reactor system and observed that the reaction rate was 5.4 times faster than that of the same reaction under a homogeneous system.[19] The SILP catalyst could be reused for 20 times, and the total turnover number per Ru atom reached 3600. In addition, catalytic activity remained stable even after 30 h when the catalyst was used in a fixed-bed flow reactor system.[20]

In this study, we applied the SILP catalyst technology to the hydroformylation of propene with CO_2 catalyzed by Ru complexes derived from $Ru_3(CO)_{12}$ and imidazolium chlorides (Eq. 1). Surprisingly, the SILP catalyst not only enabled the use of CO_2 as a reactant in such a key reaction in chemical industry, but it also facilitated the replacement of the batch reaction process with a continuous flow reaction process.

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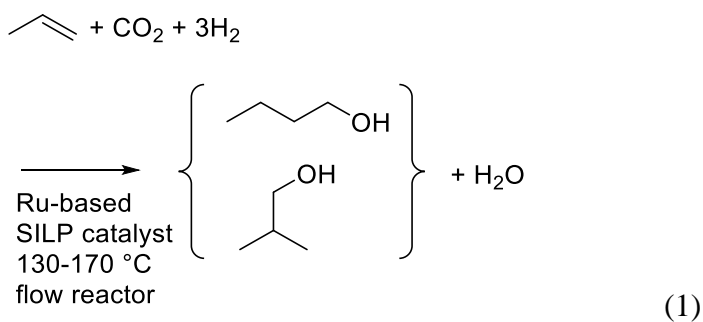
EXPERIMENTAL

Materials. Silica gel (Wakosil C-200) and $Ru_3(CO)_{12}$ were purchased from Fujifilm Wako Pure Chemical Corp. (Japan). Ionic liquids were obtained from the Tokyo Chemical Industry (Japan), while dehydrated super-grade dichloromethane (CH_2Cl_2) was purchased from Kanto

Chemical Co., Ltd (Japan). Wakosil C-200 was dried at 500 °C for 10 h under N_2 atmosphere. To prevent contamination with moisture, dried silica gel, $Ru_3(CO)_{12}$, and the ionic liquids were treated in a glovebox under N_2, where the oxygen content and dew point were controlled to <5 ppm and 45 °C, respectively. The raw material gas (propene: 4.0%, CO_2: 23.7%, and H_2: 72.3%) was purchased from Takachiho Shoji Co. Ltd (Japan).

Preparation of the SILP catalysts. The typical procedure was as follows: $Ru_3(CO)_{12}$ (50 mg, 78 μmol), 1-ethyl-3-methylimidazolium chloride ($[C_2C_1Im]Cl$: 1.6 g), and CH_2Cl_2 (15 mL) were mixed and stirred at 30 °C under N_2 to form a solution in a 50 mL two-necked flask, which was added to a 100 mL three-necked flask with Wakosil C-200 (10.0 g). The suspension was stirred for 10 min and CH_2Cl_2 was then distilled to form a pale-yellow residue. This was dried *in vacuo* to afford the SILP catalyst, which was stored in a glove box.[19]

Procedure for hydroformylation in the gas-phase flow reaction and catalytic activity evaluation. The continuous gas-phase experiments were carried out in a fixed-bed reactor equipped with an SUS316L stainless tubular reactor (internal diameter: 10.2 mm, thickness: 1.2 mm; Figure S1 in supporting information). The typical procedure was as follows: After placing the SILP catalyst (2.0 g) in the reaction tube in air (the Ru complex in the SILP catalyst is stable in air, however, this process should be carried out within several minutes to prevent contamination with moisture), the gas inside the line was replaced by passing the raw material gas (propene: 4.0%, CO_2: 23.7%, H_2: 72.3%) through the tubular reactor at room temperature. The flow rate and pressure were respectively controlled by a mass flow controller and back-pressure valve. The real gas flow rate was calibrated by measuring the amount of off-gas in the sampling bag connected to the integrated flowmeter (Kojima ACM-1A). The reaction temperature at the catalyst center was then measured with a thermocouple, and the tubular

reactor was heated to the reaction temperature and maintained for another 9 h. The off-gas collected in the sampling bag was analyzed using a gas chromatograph (Shimadzu GC-20B) equipped with a TCD detector, and the total amount of CO was calculated by the absolute calibration curve method. The amounts of propene and propane were analyzed using a gas chromatograph (Shimadzu GC-2010) equipped with a capillary column (Agilent, HP-PLOT Q, φ: 0.32 mm × 15 m) and an FID detector. The total amounts of propene and propane were calculated by the absolute calibration curve method. The liquid products were trapped in a collection tube equipped after the reactor, which was cooled with ice. After washing the collection tube with ethanol, the eluent was analyzed using a gas chromatograph (Shimadzu GC-14B) equipped with a capillary column (GL Science, TC-FFAP, φ: 0.25 mm × 30 m) and an FID detector, using ethylbenzene as the internal standard.

Characterization of the SILP catalysts. The surface area and pore volume of the SILP catalysts were determined by the N_2 absorption/desorption method at -196 °C, using a volumetric unit (Micromeritics ASAP 2020). The sample was pretreated by vacuuming at 150 °C for 10 h to remove water and volatile molecules from its surface. The thermal stability of the SILP catalyst was evaluated by thermogravimetry with differential thermal analysis (TG-DTA, Shimadzu DTG-60AH) at 2.0 °C/min under a flow of N_2 (50 mL/min). The Ru species were analyzed by electrospray ionization-mass spectrometry (Shimadzu LCMS-2020). After eluting from the SILP catalyst with ethanol in a glove box filled with N_2, the eluate was introduced in the LC-MS apparatus by a flow-injection method using acetonitrile as the mobile phase.

RESULTS AND DISCUSSION

Hydroformylation of propene with CO_2 using the Ru-based SILP catalyst in the gas-phase flow reactor. We first examined the activity and time course of the SILP catalyst prepared from 50.0 mg of $Ru_3(CO)_{12}$, 1600 mg of $[C_2C_1Im]Cl$, and 10.0 g of silica in the fixed-bed flow reactor. The silica support (Wakosil C-200) had a specific surface area of 555 m^2/g and a pore volume was 0.928 cm^3/g as determined by Brunauer–Emmett–Teller (BET) surface area analysis. Theoretically, the average thickness of this ionic liquid thin film was determined to be 2.0 nm and its average surface area to be 409 m^2/g-cat. Therefore, the density of Ru atom in this SILP catalyst was 42.2 $nmol/m^2$.

The reaction was carried out at 170 °C and 8.6 MPa, with the flow rate maintained at 42.5 mL/min (GHSV: 1.28×10^3 h^{-1}). The products were collected in a trap connected to the reactor, while the off-gas was collected in a sampling bag with an integrated flowmeter, both of which were analyzed after 1.5 h and then every 2 h. The conversion of propene was determined by quantitatively analyzing the off-gas. Product selectivity was determined by quantitatively analyzing the liquid products trapped in the collection tube and the propane in the off-gas. The total selectivity of the main products is defined as the sum of the *n*-butanal, *n*-butanol, *i*-butanal, and *i*-butanol selectivities, while the total selectivity of the by-products is defined as the sum of 2-methyl-3-hexanone, 4-heptanone, *i*-butyric acid, *n*-butyric acid, 2-methylbutanol, and pentanol selectivities; the result are in Figure 1. The reaction appeared to reach steady state after an induction of period for 90 min. The conversion of propene and the selectivities toward the hydroformylation products (butanol, butanol, and other products) and propane remained almost unchanged after 450 min.
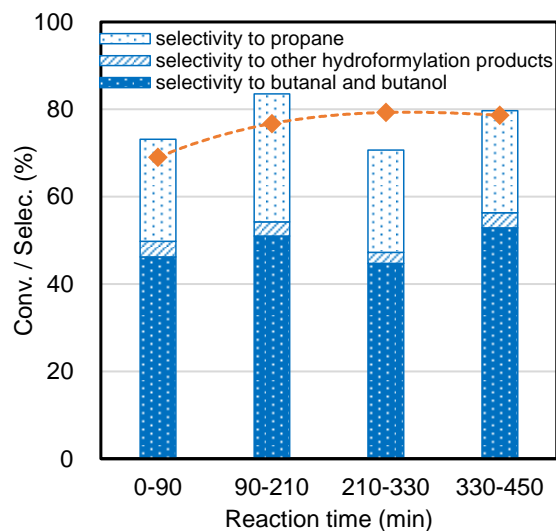
Figure 1. Time course of the reaction. Conditions: Supported ionic liquid-phase (SILP) catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg $[C_2C_1Im]Cl$, and 10.0 g silica), propene/CO_2/H_2 = 4.0/23.7/72.3, flow rate = 42.5 mL/min (GHSV: 1.28×10^3 h^{-1}), pressure = 8.6 MPa, and temp. = 170 °C. ◆ = conversion of propene.

Effect of the amount of ionic liquid used for SILP catalyst preparation. Next, we tested the effects of the loading amount of ionic liquid used for the SILP catalyst preparation. The tested loading amounts of $[C_2C_1Im]Cl$ were 800, 1200, 1600, 2000, and 3200 mg/10 g-silica, and the reaction was carried out at 150 °C and 6.0 MPa at a flow rate of 40.5 mL/min (GHSV: 1.22×10^3 h^{-1}). The reaction time was set to 540 min, during which entire off-gas was collected and then quantitatively analyzed. The liquid products were not only recovered from the collection tube but also from the catalyst by washing with EtOH, and then quantitatively analyzed.
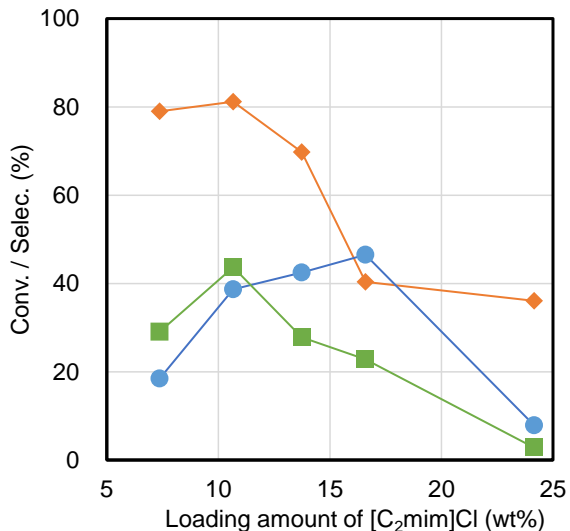
Figure 2. Effect of the amount of ionic liquid used for supported ionic liquid-phase (SILP) catalyst preparation. Conditions: SILP catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, a given amount of $[C_2C_1Im]Cl$, and 10.0 g silica), propene/CO_2/H_2 = 4.0/23.7/72.3, flow rate = 40.5 mL/min (GHSV: 1.22×10^3 h^{-1}), pressure = 6.0 MPa, temp. = 150 °C, and reaction time = 540 min. ◆ = conversion of propene, ● = selectivity to hydroformylation, and ■ = selectivity to propane.

The results are illustrated in Figure 2. The maximum conversion of propene was observed when the supported amount of $[C_2C_1Im]Cl$ was 10.7 wt% (1200 mg/10 g-silica), while the maximum selectivity toward hydroformylation was observed at a loading amount of 16.6 wt% (2000 mg/10 g-silica); however, at this loading amount, the conversion of propene was markedly decreased. In our previous research on the RWGSR with a Ru-based SILP catalyst using the same silica (Wakosil C-200), the optimum loading amount of imidazolium salt was 13.7 wt% (1600 mg/10 g-silica), over which, the catalyst activity was drastically decreased.[19] The

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difference between the exact pore volume of the SILP catalyst and the theoretical pore volume calculated from the surface area and the amount of ionic liquid increased with increasing amounts of ionic liquid, suggesting that the ionic liquid introduced in the silica pores became deposited in pore bottlenecks and is responsible for the decrease in catalyst activity. Similarly, in this hydroformylation, the decrease in conversion under the larger $[C_2C_1Im]Cl$ loading amount is also attributed to overloading with respect to the pore size, and therefore, the optimum amount of $[C_2C_1Im]Cl$ was determined to be between 10.7 and 13.7 wt%.

Effect of the ionic liquid used for the SILP catalyst. To investigate the effects of the alkyl chain length of imidazolium salts, we examined several imidazolium chlorides with different alkyl chain length as ionic liquids for the preparation of the SILP catalyst.

The results are summarized in Table 1. The conversion of propene slightly decreased from $[C_2C_1Im]Cl$ to $[C_4C_1Im]Cl$ and then increased from $[C_4C_1Im]Cl$ to $[C_{10}C_1Im]Cl$, while the best reaction selectivity toward hydroformylation was observed with $[C_2C_1Im]Cl$ (Table 1, entry 1). The reaction selectivity toward hydrogenation increased with increasing alkyl chain. This tendency was attributed to the solubility of propene and hydrogen, both of which increased in imidazolium chlorides with longer carbon chains,[21,22] and that of CO_2, which was not significantly influenced by the carbon chain length.[21,23−26] Notably, other gases display significantly lower solubilities than these gases, and the effects of the alkyl chain length would be very small. Therefore, the subsequent experiments were conducted using the SILP catalyst $[C_2C_1Im]Cl$.

Regarding hydroformylation regioselectivity, the linear/branch ratio was determined to be in the 1.4–1.6 range in all cases, indicating that the linear products were slightly more dominant. This ratio is almost same as those observed in the hydroformylation of linear alkenes using

homogeneous $Ru_3(CO)_{12}$-LiCl catalyst system in NMP,[3] suggesting that despite differences in the alkyl chain lengths of imidazolium salts known to moderately affect dipolarity and hydrogen bond donor/acceptor activity,[27] they influence regioselectivity little compared to reaction selectivity.

Table 1. Effects of the ionic liquids used for the SILP catalysts[a]

Entry	Ionic Liquids	Conv. of propene (%)	Select. (%)						
			n-butanal	n-butanol	i-butanal	i-butanol	by-products[b]	hydro-formylation products	propane
1	$[C_2C_1Im]Cl$	69.8	2.4	19.8	1.4	14.2	4.7	42.5	27.8
			l/b = 1.4[c]						
2	$[C_4C_1Im]Cl$	59.6	2.0	19.1	1.3	13.8	5.2	41.4	50.8
			l/b = 1.4						
3	$[C_6C_1Im]Cl$	76.7	0.7	10.7	0.4	7.2	1.8	20.8	54.0
			l/b = 1.5						
4	$[C_{10}C_1Im]Cl$	81.0	0.7	7.2	0.4	4.7	1.4	14.4	43.3
			l/b = 1.6						

[a] Conditions: SILP catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg ionic liquid, and 10.0 g silica), propene/CO_2/H_2 = 4.0/23.7/72.3, flow rate = 39.5 mL/min, pressure = 6.0 MPa, temp. = 150 °C, and reaction time = 540 min. [b] By-products: 2-Methyl-3-hexanone, 4-heptanone, i-butyric acid, n-butyric acid, 2-methylbutanol, and pentanol. [c] Linear/branch ratio.

Effect of the reaction temperature, pressure and flow rate of the raw material gas. The reaction was carried out at several reaction temperatures in the range 130–190 °C under reaction

pressures of 6.0 and 8.6 MPa (Table 2). The results revealed that the reaction was markedly influenced by the reaction temperature and pressure of the raw material gas.

Table 2. Effects of the reaction temperature and pressure of the raw material gas[a]

Entry	Press. (MPa)	Temp. (°C)	GHSV ($\times 10^3$ h^{-1})	Time (min)	Conv. of propene (%)	Select. (%)				
						butanal	butanol	by-products[b]	hydro-formylation products	propane
1	6.0	190	1.22	510	66.7	2.2	36.8	2.4	41.4	33.4
2	6.0	170	1.19	520	83.8	1.9	46.8	3.2	50.0	32.0
3	6.0	150	1.21	517	69.8	3.8	34.0	4.7	42.5	27.8
4	6.0	130	1.19	515	34.5	3.2	9.3	5.2	17.7	10.1
5	8.6	190	1.34	570	82.8	1.1	34.2	2.7	38.0	30.7
6	8.6	170	1.13	495	81.6	1.1	60.1	5.0	66.1	31.7
7	8.6	150	1.34	570	78.1	1.4	35.9	4.6	41.9	35.2
8	8.6	130	1.28	540	34.5	9.6	32.1	10.1	51.8	42.9

[a] Conditions: SILP catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg $[C_2C_1Im]Cl$, and 10.0 g silica) and propene/CO_2/H_2 = 4.0/23.7/72.3. [b] By-products: 2-Methyl-3-hexanone, 4-heptanone, i-butyric acid, n-butyric acid, 2-methylbutanol, and pentanol.

When the reaction was carried out under 6.0 MPa at 150 °C, the conversion of propene was 69.8% and the selectivity toward hydroformylation was 42.5% (Table 2, entry 3), which increased to 83.8 and 50.0%, respectively, at 170 °C (Table 2, entry 2). The best results were obtained when the pressure of the raw material gas was increased to 8.6 MPa at 170 °C, wherein 81.6% propene conversion and 66.1% hydroformylation selectivity were observed (Table 2, entry 6). At the respective reaction temperature and pressure of 190 °C and 8.6 MPa, the

conversion of propene was 82.8%, whereas the selectivity toward hydroformylation was reduced to 38.0%, without any reduction in the selectivity to propane (Table 2, entry 5).

The effect of flow rate was investigated in the GHSV range of $0.55-1.77 \times 10^3$ h^{-1} (Figure 3). With an increase of the flow rate, the propene conversion decreased, while the average yield of CO per hour in gas phase increased and reached saturation over 1.48×10^3 h^{-1}. In addition, the selectivity to butanal slightly increased with an increase of the flow rate, while the selectivity to butanol decreased. These results suggest that as similarly observed in the homogeneous catalyst systems,[2–7] CO is a primary product of CO_2 formed by reverse water–gas shift reaction (RWGSR), followed by hydroformylation of propene with CO to form butanal, which is hydrogenated to butanol.
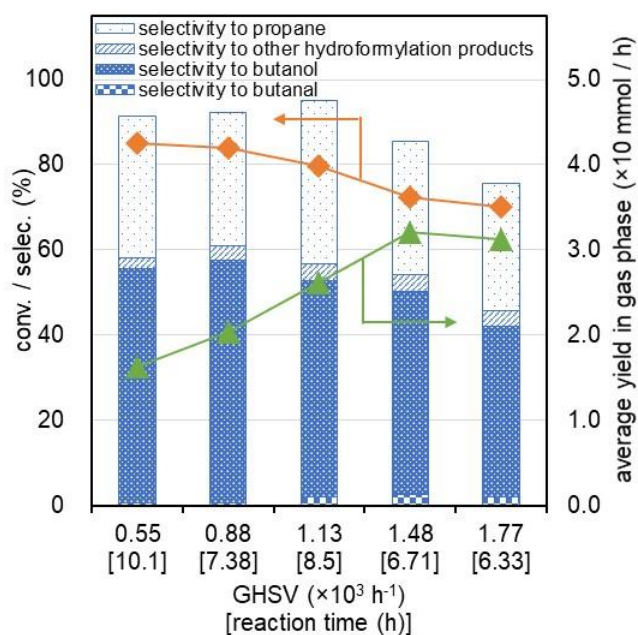

Figure 3. Effect of flow rate. Conditions: Supported ionic liquid-phase (SILP) catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg [C_2C_1Im]Cl, and 10.0 g silica) and propene/CO_2/H_2 = 4.0/23.7/72.3. ◆ = conversion of propene and ▲ = average yield of CO per hour in gas phase.

Figure 4 shows the Arrhenius plot of hydroformylation and RWGSR at 8.6 MPa. The reaction rates of hydroformylation were estimated as the total average yields of the hydroformylation products per second and those of the RWGSR as the total average yields of CO and the hydroformylation products per second. In the reaction temperature range 130–170 °C (2.26–2.48 $\times$ 10^{-3} K^{-1}), the apparent activation energy for hydroformylation (E_{ah}) was 42.5 kJ/mol and that for RWGSR (E_{ar}) was 41.5 kJ/mol.

Very recently, we investigated the continuous RWGSR in a follow reactor using Ru-based SILP catalysts prepared from $[Ru(CO)_3Cl_2]_2$ and imidazolium chlorides, and determined apparent activation energy of 93.2 kJ/mol in the 130−170 °C temperature range.[21] Compared with the above mentioned results, the apparent activation energy for the RWGSR during hydroformylation using CO_2 is much lower and almost identical with the apparent activation energy for hydroformyltion, suggesting that the CO formed by RWGSR is readily consumed for hydroformylation. For this reason, the RWGSR equilibrium shifts to the product side and its apparent reaction rate is promoted.
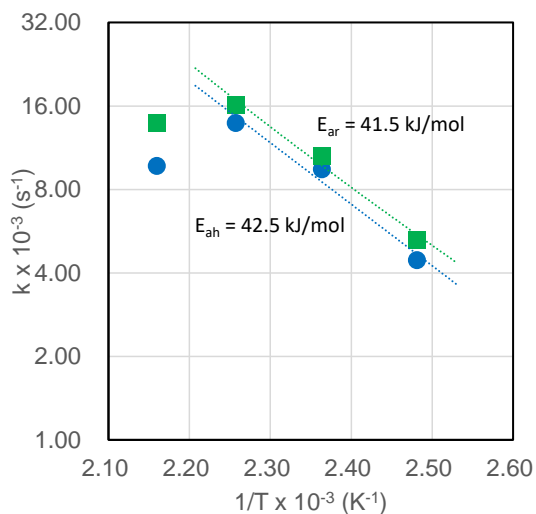
Figure 4. Arrhenius plot of the reverse water–gas shift reaction (RWGSR) and hydroformylation at 8.6Mpa. Conditions: Supported ionic liquid-phase (SILP) catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg $[C_2C_1Im]Cl$, and 10.0 g silica) and propene/CO_2/H_2 = 4.0/23.7/72.3. ● = reaction rate of hydroformylation and ■ = reaction rate of reverse water-gas shift reaction.

The rates of the RWGSR and the hydroformylation are both dramatically lower at 190 °C (2.16×10^{-3} K^{-1}). Because it has been known that the thermal stabilities of ionic liquids significantly reduce when they are immobilized on metal oxides,[28] we subjected the SILP catalyst used in Table 1, entry 1 to TG-DTA, the results of which are shown in Figure 5. The SILP catalyst began to thermally degrade at around 190 °C, which continued to around 420 °C with 13.4% of its mass lost. This result corresponds almost complete degradation of $[C_2C_1Im]Cl$ (13.7 wt%). The DTA curve shows two endothermic peaks and one exothermic peak. The small endothermic peak at 232.2 °C corresponds to the degradation of Ru carbonyl complexes, while the other larger peak at 289.5 °C corresponds to the degradation of $[C_2C_1Im]Cl$, and the

exothermic peak at 361.9 °C is due to sintering of the Ru metal. When the same experiment was carried out on a SILP catalyst without Ru complex, it also began to thermally degrade at around 190 °C and only one large endothermic peak was observed at 293.3 °C, which corresponds to the degradation of $[C_2C_1Im]Cl$ (Figure S2). These data reveal that the thermal degradation of the SILP catalyst is the main reason why the RWGSR and the hydroformylation rate decrease above 190 °C.
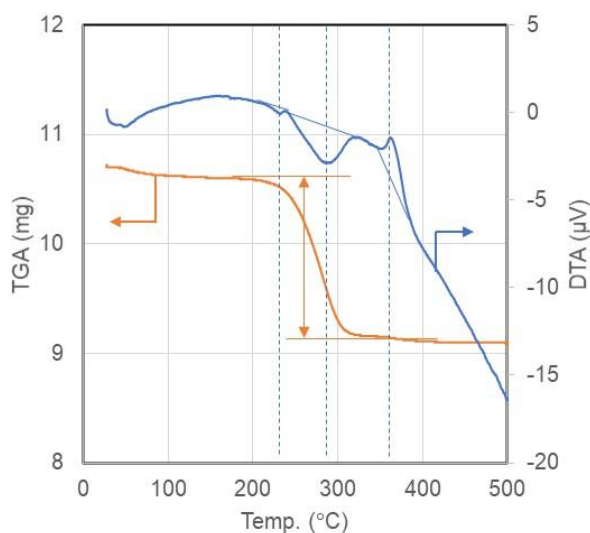

Figure 5. TG-DTA analysis of supported ionic liquid-phase (SILP) catalyst. Conditions: SILP catalyst = 10.72 mg (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg $[C_2C_1Im]Cl$, and 10.0 g silica), N_2 flow rate = 50 mL/min, and rate of temperature increase = 2.0 °C/min.

Active species in the SILP catalyst and reaction mechanism. According to our previous research on the Ru-complex catalyzed hydroformylation using CO_2 as a reactant,[2−5] $Ru_3(CO)_{12}$ is readily transform to several anionic complexes in the presence chloride salts, the combination of which successively catalyze the RWGSR, hydroformylation, and hydrogenation of aldehyde.

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These anionic Ru complexes can be homogeneously dissolved not only in polar organic solvents but also in ionic liquids and act as catalysts. To investigate the active species in the SILP catalyst, we recovered the SILP catalyst after reaction at 170 °C under 8.6 MPa for 3 h, dissolved the Ru species with EtOH, and analyzed it using ESI-MS in negative mode.
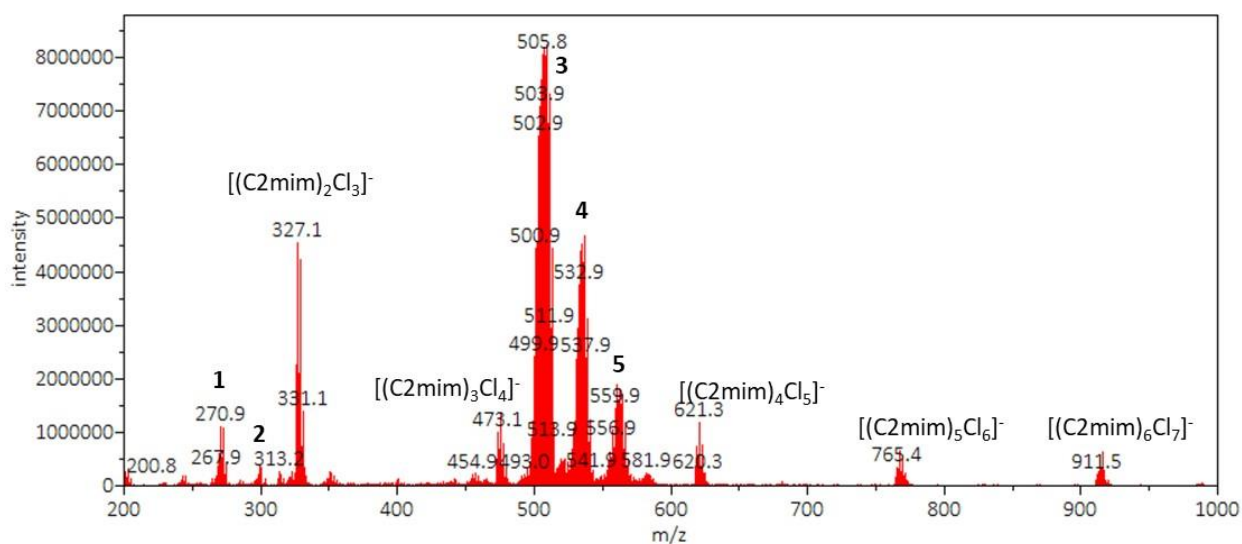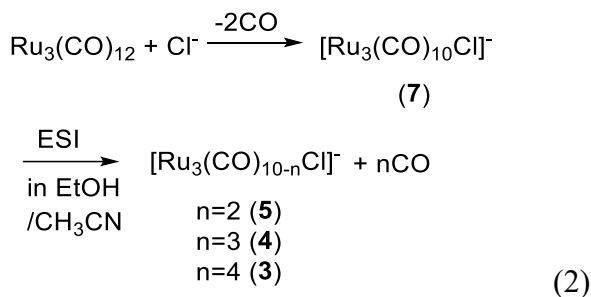

Figure 6. ESI-MS spectrum of the reaction solution. Conditions: Supported ionic liquid-phase (SILP) catalyst = 2.0 g (prepared from 50.0 mg $Ru_3(CO)_{12}$, 1600 mg $[C_2C_1Im]Cl$, and 10.0 g silica), propene/CO_2/H_2 = 4.0/23.7/72.3, flow rate = 42.5 mL/min, pressure = 8.6 MPa, temp. = 170 °C, and time = 3 h.

As shown in Figure 6, the observed Ru species were $[Ru(CO)Cl_4H]^-$ (**1**), $[Ru(CO)_2Cl_4H]^-$ (**2**) $[Ru_3(CO)_6Cl]^-$ (**3**), $[Ru_3(CO)_7Cl]^-$ (**4**), and $[Ru_3(CO)_8Cl]^-$ (**5**), all of which were identified from the theoretical isotope distributions (Figure S3–S7). Mononuclear Ru complex **2** was adduct of $[Ru(CO)_2Cl_3]^-$ (**6**) and HCl, the former of which was also observed as one of the active species

of RWGSR.[19,29] On the other hand, the trinuclear Ru complexes **3**, **4**, and **5** were derived from [Ru$_3$(CO)$_{10}$Cl]$^-$ (**7**), which is known to be formed from Ru$_3$(CO)$_{12}$ and the chloride anion according to Eq. 2.[30]

$$\text{Ru}_3\text{(CO)}_{12} + \text{Cl}^- \xrightarrow{\text{-2CO}} \text{[Ru}_3\text{(CO)}_{10}\text{Cl]}^-$$

$$(\mathbf{7})$$

$$\xrightarrow[\substack{\text{in EtOH}\\ \text{/CH}_3\text{CN}}]{\text{ESI}} \text{[Ru}_3\text{(CO)}_{10\text{-}n}\text{Cl]}^- + n\text{CO}$$

$$\begin{array}{c} n=2\ (\mathbf{5}) \\ n=3\ (\mathbf{4}) \\ n=4\ (\mathbf{3}) \end{array} \qquad (2)$$

Based on the above findings, we elucidated a plausible reaction mechanism (Figure 7): In the ionic liquid film of the SILP catalyst, Ru$_3$(CO)$_{12}$ is converted into mononuclear complex **8** and trinuclear complex **7**. Complex **8** is known to be converted to complex **6** with releasing CO in the catalysis cycle of RWGSR, the mechanism of which was reported in our previous paper.[29] Complex **7** was considered to be in equilibrium with [Ru$_3$(CO)$_{11}$H]$^-$ (**9**) in the presence of H$_2$ and CO. Complex **9** is not only known to be an active species for hydroformylation,[31,32] but combines with complex **8** to enhance the hydroformylation reaction.[3] The CO formed by the RWGSR was used *in-situ* as a reactant for hydroformylation on the same complex (**8**), which is responsible for the efficient hydroformylation using CO$_2$.
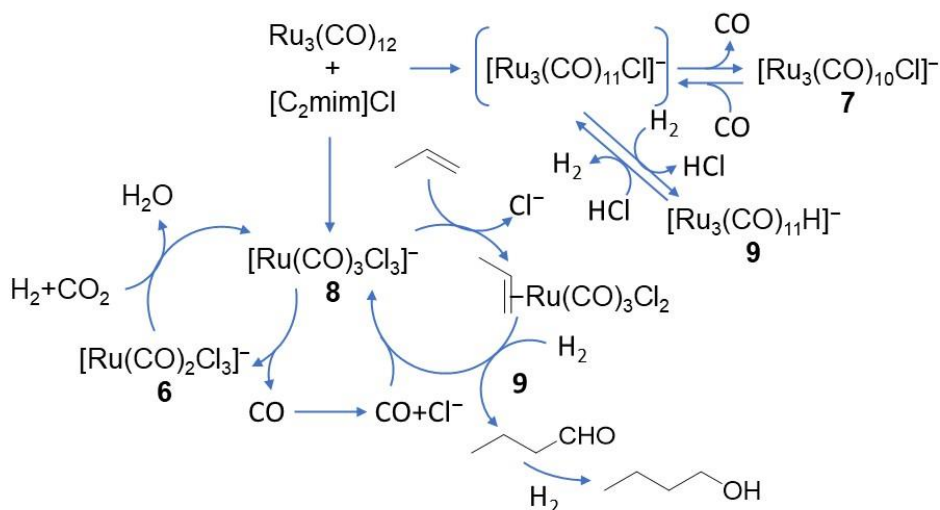
Ru$_3$(CO)$_{12}$ + [C$_2$mim]Cl → [Ru$_3$(CO)$_{11}$Cl]$^-$ ⇌ [Ru$_3$(CO)$_{10}$Cl]$^-$ **7**

CO

H$_2$ CO

H$_2$ HCl

[Ru$_3$(CO)$_{11}$H]$^-$ **9**

H$_2$O

H$_2$+CO$_2$

[Ru(CO)$_3$Cl$_3$]$^-$ **8**

Cl$^-$ HCl

[Ru(CO)$_2$Cl$_3$]$^-$ **6**

⊢Ru(CO)$_3$Cl$_2$

H$_2$

9

CO → CO+Cl$^-$

CHO

H$_2$ OH

Figure 7. Plausible reaction mechanism

CONCLUSION

The SILP system is an effective technology for supporting metal complexes on porous materials and enables the use of metal complexes in continuous gas flow reactions. In this study, Ru-based SILP catalysts prepared from Ru$_3$(CO)$_{12}$ and imidazolium chloride were found to be effective for the hydroformylation of propene with CO$_2$. The catalytic activity of the SILP catalyst was highly dependent on the amount of ionic liquid used for the SILP catalyst preparation, reaction temperature, and reaction pressure. The best result was 81.6% propene conversion and 66.1% hydroformylation selectivity by the reaction at 170 °C, 8.6 MPa and GHSV of 1.13×10^3 h^{-1}. Under this condition, turnover frequency of hydroformylation reached 50 h^{-1} per single Ru atom. Considering that the corresponding turnover frequency in the homogeneous catalyst systems using batch reactor was about 5 h^{-1} or less, [5–7] this continuous reaction system using SILP catalysts enabled about 10 times higher productivity. ESI-MS analysis showed the formation of mononuclear and trinuclear Ru complexes in the ionic liquid

film, wherein the former is an active species for RWGSR and the latter for hydroformylation. According to the kinetic analysis results, the CO formed by RWGSR was readily used for hydroformylation. Because hydroformylation is one of the key processes in chemical industry, this new catalyst process holds the potential of contributing to circulative utilization of CO_2.

ASSOCIATED CONTENT

Supporting Information

Schematic view of the experimental set-up; TG-DTA analysis of supported ionic liquid-phase (SILP) catalyst without metal complex; ESI-MS spectra of Complex **1−5** in the reaction solution and their isotope distribution.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ABBREVIATIONS

SILP, supported ionic liquid-phase; [C_2C_1Im]Cl, 1-ethyl-3-methylimidazolium chloride; [C_4C_1Im]Cl, 1-butyl-3-methylimidazolium chloride; [C_6C_1Im]Cl, 1-hexyl-3-methylimidazolium chloride; [$C_{10}C_1$Im]Cl, 1-dodecyl-3-methylimidazolium chloride.

REFERENCES

(1) Franke, R., Selent D., Börner A. Applied Hydroformylation. *Chem. Rev.* 2012, *112*, 5675−5732. DOI: 10.1021/cr3001803

(2) Tominaga K.; Sasaki Y. Ruthenium complex-catalyzed hydroformylation of alkenes with carbon dioxide. *Catal. Commun.* 2000, *1*, 1−3. DOI: 10.1016/S1566-7367(00)00006-6

(3) Tominaga K.; Sasaki Y. Ruthenium-catalyzed one-pot hydroformylation of alkenes using carbon dioxide as a reactant. *J. Mol. Catal. A* 2004, *220*, 159−165. DOI: 10.1016/j.molcata.2004.06.009

(4) Tominaga K.; Sasaki Y. Biphasic Hydroformylation of 1-Hexene with Carbon Dioxide Catalyzed by Ruthenium Complex in Ionic Liquids. *Chem. Lett.* 2004, *33*, 14−15. DOI: 10.1246/cl.2004.14

(5) Tominaga K. An environmentally friendly hydroformylation using carbon dioxide as a reactant catalyzed by immobilized Ru-complex in ionic liquids. *Catal. Today* 2006, *115*, 70−72. DOI: 10.1016/j.cattod.2006.02.019

(6) Liu Q.; Wu L.; Fleischer I.; Selent D.; Franke R.; Jackstell R.; Beller M. Development of a Ruthenium/Phosphite Catalyst System for Domino Hydroformylation–Reduction of Olefins with Carbon Dioxide. *Chem. Eur. J.* 2014, *20*, 6888−6894. DOI: 10.1002/chem.201400435

(7) Ali M.; Gual A.; Ebeling G.; Dupont J. Ruthenium-Catalyzed Hydroformylation of Alkenes by using Carbon Dioxide as the Carbon Monoxide Source in the Presence of Ionic Liquids. *ChemCatChem* 2014, *6*, 2224−2228. DOI: 10.1002/cctc.201402226

(8) Ren X.; Zheng Z.; Zhang L.; Wang Z.; Xia C.; Ding K. Rhodium-Complex-Catalyzed Hydroformylation of Olefins with CO_2 and Hydrosilane. *Angew. Chem. Int. Ed.* 2017, *56*, 310−313. DOI: 10.1002/anie.201608628

(9) Van Gerven T.; Stankiewicz A. Structure, Energy, Synergy, Time − The Fundamentals of Process Intensification. *Ind. Eng. Chem. Res.* 2009, *48*, 2465−2474. DOI: 10.1021/ie801501y

(10) Van Doorslaer C.; Wahlen J.; Metrens P.; Binnemans K.; De Vos D. Immobilization of molecular catalysts in supported ionic liquid phases. *Dalton. Trans.* 2010, *39*, 8377−8390. DOI: 10.1039/C001285H

(11) Mehnert C. P.; Mozeleski E. J.; Cook R. A. Supported ionic liquid catalysis investigated for hydrogenation reactions. *Chem. Commun.* 2002, 3010−3011. DOI: 10.1039/B210214E

(12) Riisager A.; Jørgensen B.; Wasserscheid P.; Fehrmann R. First application of supported ionic liquid phase (SILP) catalysis for continuous methanol carbonylation. *Chem. Commun.* 2006, 994−996. DOI: 10.1039/B516314E

(13) Werner S.; Szesni N.; Kaiser M.; Fischer R. W.; Haumann M.; Wasserscheid P. Ultra-Low-Temperature Water‑Gas Shift Catalysis using Supported Ionic Liquid Phase (SILP) Materials. *ChemCatChem* 2010, *2*, 1399−1402. DOI: 10.1002/cctc.201000245

(14) Wolf P.; Aubermann M.; Wolf M.; Bauer T.; Blaumeiser D.; Stepic R.; Wick C. R.; Smith D. M.; Smith A-S; Wasserscheid P.; Libuda J.; Haumann M. Improving the performance of supported ionic liquid phase (SILP) catalysts for the ultra-low-temperature water–gas shift reaction using metal salt additives. *Green Chem.* 2019, *21*, 5008−5018. DOI: 10.1039/C9GC02153A

(15) Riisager, A.; Wasserscheid P.; van Hal R. V.; Fehrmann R. Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid-phase (SILP) Rh catalysts. *J. Catal.* 2003, *219*, 452−455. DOI: 10.1016/S0021-9517(03)00223-9

(16) Riisager A.; Eriksen K. M.; Wasserscheid P.; Hal R. V.; Fehrmann R. Propene and 1-octene hydroformylation with silica-supported, ionic liquid-phase (SILP) Rh-phosphine catalysts in continuous fixed-bed mode. *Catal. Lett.* 2003, *90,* 149−153. DOI: 10.1023/B:CATL.0000004109.46005.be

(17) Riisager A.; Fehrmann R.; Haumann M.; Gorle B. S. K.; Wasserscheid P. Stability and kinetic studies of supported ionic liquid phase catalysts for hydroformylation of propene. *Ind. Eng. Chem. Res.* 2005, *44*, 9853−9859. DOI: 10.1021/ie050629g

(18) Haumann M.; Dentler K.; Joni J.; Riisager A.; Wasserscheid P. Continuous gas-phase hydroformylation of 1-butene using supported ionic liquid phase (SILP) catalysts. *Adv. Synth. Catal.* 2007, *349*, 425−431. DOI: 10.1002/adsc.200600413

(19) Yasuda T.; Uchiage E.; Fujitani T.; Tominaga K.; Nishida M. Reverse water gas shift reaction using supported ionic liquid phase catalysts. *Appl. Catal. B* 2018, *232*, 299−305. DOI: 10.1016/j.apcatb.2018.03.057

(20) Hatanaka M.; Uchiage E.; Nishida M.; Tominaga K. Low-Temperature Reverse Water-Gas Shift Reaction Using SILP Ru Catalysts Under Continuous-Flow Conditions. *Chem. Lett.* 2021, 50, 1586−1588. DOI: 10.1246/cl.210184

(21) Finotello A.; Bara J. E.; Camper D.; Noble R. D. Room-Temperature Ionic Liquids: Temperature Dependence of Gas Solubility Selectivity. *Ind. Eng. Chem. Res.* 2008, *47*, 3453−3459. DOI: 10.1021/ie0704142

(22) Makino T.; Kanakubo M.; Absorption of *n*-butane in imidazolium and phosphonium ionic liquids and application to separation of hydrocarbon gases. *Sep. Pur. Tech.* 2019, *214*, 139−147. DOI: 10.1016/j.seppur.2018.04.032

(23) Lei Z.; Dai C.; Chen B.; Gas Solubility in Ionic Liquids. *Chem. Rev.* 2014, *114*, 1289−1326. DOI: 10.1021/cr300497a

(24) Shannon M. S.; Tedstone J. M.; Danielsen S. P. O.; Hindman M. S.; Irvin A. C.; Bara J. E. Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.* 2012, *51*, 5565−5576. DOI: 10.1021/ie202916e

(25) Makino T.; Kanakubo M.; Umecky T.; Suzuki A.; Nishida T.; Takano J. Pressure-volume-temperature-composition relations for carbon dioxide + pyrrolidinium-based ionic liquid binary systems. *Fluid Phase Equil.* 2013, *360*, 253−259. DOI: 10.1016/j.fluid.2013.09.036

(26) Anderson J. L.; Dixon J. K.; Brennecke J. F. Solubility of CO_2, CH_4, C_2H_6, C_2H_4, O_2 and N_2 in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids. *Acc. Chem. Res.* 2007, *40*, 1208−1216. DOI: 10.1021/ar7001649

(27) Chiappe C.; Pomelli C. S.; Rajamani S.; Influence of Structural Variations in Cationic and Anionic Moieties on the Polarity of Ionic Liquids. *J. Phys. Chem. B* 2011, *115*, 9653–9661. DOI: 10.1021/jp2045788

(28) Babucci M.; Akfay A.; Balcijf V.; Uzun A.; Thermal Stability Limits of Imidazolium Ionic Liquids Immobilized on Metal-Oxides. *Langmuir* 2015, *31*, 9163 − 9176. DOI: 10.1021/acslangmuir.5b02519

(29) Tsuchiya K.; Huang J.-D.; Tominaga K. Reverse Water-Gas Shift Reaction Catalyzed by Mononuclear Ru Complexes. *ACS Catal.* 2013, *3*, 2865−2868. DOI: 10.1021/cs400809k

(30) Han S.-H.; Geoffroy G. L.; Dombek B. D.; Rheingold A. L. Equilibria within the $Ru_3(CO)_{12}$/Halide System. *Inorg. Chem.* 1988, *27*, 4355−4361. DOI: 10.1021/ic00297a006

(31) Süss-Fink G.; Reiner J. The cluster anion $[HRu3(CO)11]^−$ as catalyst in hydroformylation, hydrogenation, silacarbonylation and hydrosilylation reactions of ethylene and propylene. *J. Mol. Catal.* 1982, *16*, 231−242. DOI: 10.1016/0304-5102(82)85011-6

(32) Süss-Fink G.; Schmidt G. F. Selectivity studies on the hydroformylation of propylene catalysed by the cluster anion $[HRu_3(CO)_{11}]^−$. *J. Mol. Catal.* 1987, *42*, 361−366. DOI: 10.1016/0304-5102(87)85012-5

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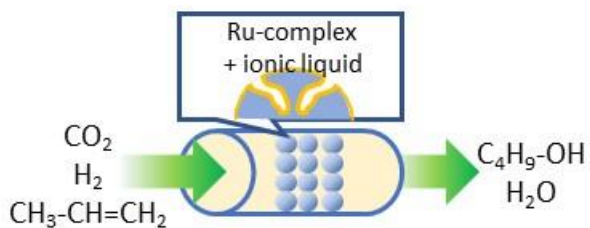
The continuous hydroformylation of propene with CO_2 is heterogeneously catalyzed by a supported ionic liquid-phase catalyst in a flow reactor.