

Full Research Paper

Hydroformylation of Cyclohexene with Carbon Dioxide and Hydrogen Using Ruthenium Carbonyl Catalyst: Influence of Pressures of Gaseous Components

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Abstract: Hydroformylation of cyclohexene was studied with a catalyst system of $\text{Ru}_3(\text{CO})_{12}$ and LiCl using H_2 and CO_2 instead of CO in NMP. The influence of H_2 and CO_2 pressures on the total conversion and the product distribution was examined. It was shown that increasing total pressure of H_2 and CO_2 promoted the reverse water gas shift reaction and increased the yield of cyclohexanecarboxaldehyde. Its hydrogenation to cyclohexanemethanol was promoted with increasing H_2 pressure but suppressed with increasing CO_2 pressure. Cyclohexane was also formed along with those products and this direct hydrogenation was suppressed with increasing CO_2 pressure. The roles of CO_2 as a promoter as well as a reactant were further examined by phase behavior observations and high pressure FTIR measurements.

Keywords: hydroformylation, ruthenium carbonyl catalyst, lithium chloride promoter, carbon dioxide, pressure effect

1. Introduction

Carbon dioxide (CO_2) has been attracting increasing attention from green chemistry concept because of its safety, cost, and wide utility as a reaction medium at high pressures [1-4] and as a reactant for several organic synthetic reactions [5-7]. When suitable catalysts and reaction conditions are chosen, CO_2 may replace conventional harmful organic solvents and reactants such as carbon

monoxide, phosgene, and so on. Hydroformylation is one of practically important chemical processes for the production of aldehydes and alcohols from olefins and syngas (CO, H₂) [8,9]. Many authors investigated hydroformylation reactions in dense CO₂ using homogeneous and heterogeneous catalysts and reported the positive features of such a high pressure CO₂ solvent [10]. However, few attempts were made so far to use CO₂ as a reactant instead of CO in hydroformylation reactions. Recently Tominaga and Sasaki have first shown that the hydroformylation can indeed proceed with a mixture of CO₂ and H₂ [11,12]. After screening several catalysts, they found an active catalyst system of Ru₃(CO)₁₂ with a promoter of LiCl. It can catalyze the reverse water gas shift reaction, CO₂ + H₂ → CO + H₂O, and CO formed will be used for hydroformylation. The presence of LiCl is crucial in suppressing undesired direct hydrogenation of substrates, according to the works of Tominaga and Sasaki [12] and Jääskeläinen and Haukka [13]. These authors also examined the influence of a few reaction variables but not that of CO₂ and H₂ pressures in detail.

On the course of their study on chemical reactions in and under pressurized CO₂, the present authors indicate an interesting chemical effect of dense CO₂ molecules, which interact strongly with a substrate molecule and affect its reactivity. Such interaction and effect occur with an α,β-unsaturated aldehyde of cinnamaldehyde and this is one of important factors for promoting the selective hydrogenation of its carbonyl group to the corresponding unsaturated alcohol [14-17]. It is thus noteworthy that CO₂ may act as not only a reaction medium but also a reaction promoter. Those previous results obtained by Tominaga and Sasaki, Jääskeläinen and Haukka, and our group have motivated us to study the influence of CO₂ and H₂ pressures in hydroformylation with CO₂ and H₂ using those previous authors' best catalyst system.

2. Results and Discussion

The hydroformylation of cyclohexene with CO₂/H₂ in NMP solvent was conducted under different conditions and the features of this hydroformylation reaction were examined and discussed.

2.1. Hydroformylation of cyclohexene at different pressures

The additive effect of LiCl was already reported in the literature [11-13] but it was briefly examined in this work as well. Table 1 gives the results obtained with different amounts of LiCl used. When LiCl was absent or its amount was smaller compared to that of Ru₃(CO)₁₂, hydrogenation of cyclohexene to cyclohexane and formation of methane and other hydrocarbons mainly occurred but hydroformylation scarcely took place. After these reaction runs, the remaining liquid mixture was black, suggesting that Ru₃(CO)₁₂ species released CO moieties and changed to ruthenium metal colloids. At a larger LiCl/Ru₃(CO)₁₂ ratio of 4/3, however, hydroformylation was observed to proceed, giving cyclohexanecarboxaldehyde **2** and cyclohexanemethanol **3** along with cyclohexane **4** (Scheme 1), but undesired hydrocarbons were not formed. The reaction mixture was reddish brown in color, indicating that the catalyst still remained in the form of Ru₃(CO)₁₂ after the reaction. The following experiments were made to examine the influence of CO₂ and H₂ pressures at this LiCl/Ru₃(CO)₁₂ ratio of 4/3.

Figure 1 gives typical changes of total conversion and product yields with reaction time. The reaction was timed just after the reaction temperature reached 423 K and so the reactions occurred to some

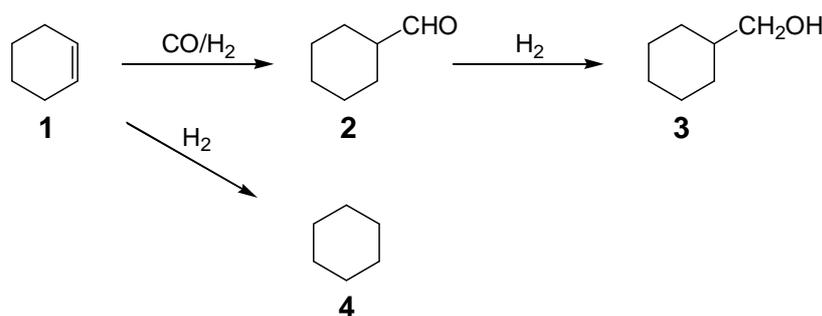
extent at increasing temperatures (the conversion and the yields are not zero at a reaction time of zero). Under the conditions used the three main products were observed to form from cyclohexene **1**, including cyclohexanecarboxaldehyde **2**, cyclohexylmethanol **3**, and cyclohexane **4** (Scheme 1). The conversion of **1** was almost completed in 5 h and the yield of the hydroformylation product **2** increased with time, had a maximum at about 2 h, and then decreased gradually. After about 2 h the yield of its hydrogenated product **3** went over the yield of **2** and further increased with time. Thus **3** was consecutively formed through the hydrogenation of **2**. The yield of **4**, hydrogenation product of **1**, increased slightly within 3 h and then did not change so much after the disappearance of the substrate **1**. It is indicated that the two paths from **1** to **2** (hydroformylation) and from **1** to **4** (hydrogenation) are parallel reactions. Very minor products such as cyclohexylmethyl cyclohexanecarboxylate, methylenecyclohexane, 1-methyl-1-cyclohexene, and 3-methyl-1-cyclohexene were detected.

Table 1. Influence of the amount of LiCl additive used on the reactions of cyclohexene with CO₂ and H₂ using Ru₃(CO)₁₂ catalyst.

Entry	LiCl/Ru ₃ (CO) ₁₂	Product yield (%)				Total CO ^a (mmol)
		Cyclohexane-carboxaldehyde	Cyclohexane-methanol	Cyclohexane	Hydro-carbons	
1	0/3	0	4	60	35	0.4
2	2/3	0	1	79	20	0.1
3	4/3	23	37	14	0	10.7

^a Total CO = cyclohexanecarboxaldehyde + cyclohexanemethanol + CO (see Scheme 1)

Reaction conditions: catalyst Ru₃(CO)₁₂ 0.3 mmol, substrate cyclohexene 1 cm³ (9.87 mmol), solvent NMP 8 cm³, pressure CO₂ 3 MPa, H₂ 3 MPa, temperature 423 K, time 3 h.



Scheme 1. Transformation of cyclohexene **1** to (path 1) cyclohexanecarboxaldehyde **2** via hydroformylation and then to cyclohexanemethanol **3** via hydrogenation and to (path 2) cyclohexane **4** via direct hydrogenation.

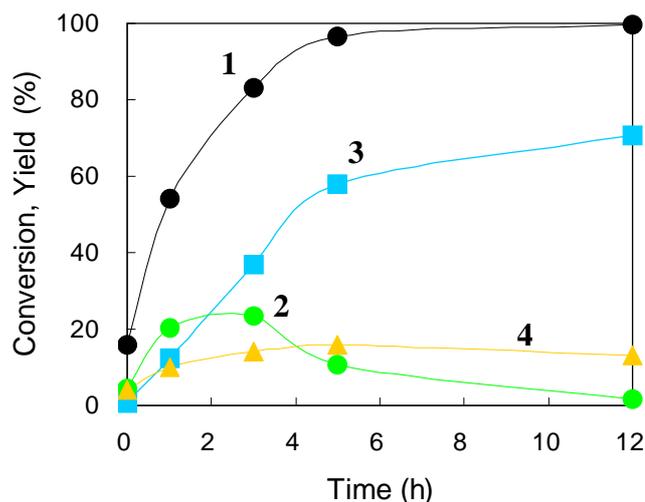


Figure 1. Typical time course of reactions of cyclohexene with CO₂ and H₂ under conditions: catalyst Ru₃(CO)₁₂ 0.3 mmol, substrate cyclohexene 1 cm³ (9.87 mmol), solvent NMP 8 cm³, pressure CO₂ 3 MPa, H₂ 3 MPa, temperature 423 K.

The present hydroformylation with CO₂ and H₂ is a two step process with the reverse water gas shift reaction (RWGSR) followed by the hydroformylation with CO formed. Table 2 shows the amounts of **2**, **3** and CO gas detected during the reaction run of Figure 1. The amount of CO gas is comparable to those of **2** and **3**, so the RWGSR is assumed to go faster compared with the following hydroformylation with CO formed and the latter determines the overall rate of the hydroformylation of **1** with CO₂ and H₂ to **2**.

Table 2. Amounts of **2**, **3**, and CO formed during hydroformylation of cyclohexene with CO₂ and H₂ using Ru₃(CO)₁₂ catalyst ^a.

Time (h)	Amount (mmol)			CO/(2 + 3 + CO) (%)
	2	3	CO	
1	2.0	1.2	2.2	41
3	2.3	3.6	4.7	44
5	1.0	5.7	8.2	55
12	0.18	7.0	8.0	53

^a See Figure 1 for reaction conditions used.

Next the influence of CO₂ and H₂ pressures has been examined. Figure 2 gives the results obtained at different total pressures while keeping the ratio of CO₂:H₂ to 1:1. It is indicated that the increasing total pressure promotes the hydroformylation and increases the yields of **2** and **3** but suppresses the direct hydrogenation of **1**, decreasing the yield of **4**. A higher pressure of 8 MPa gives a further increased yield of the aldehyde **2** while it does not change the yield of its hydrogenated product **3** so much. Higher total pressure is beneficial for higher rate of hydroformylation and higher selectivity to the hydroformylation product (aldehyde) compared to its further hydrogenated product (alcohol).

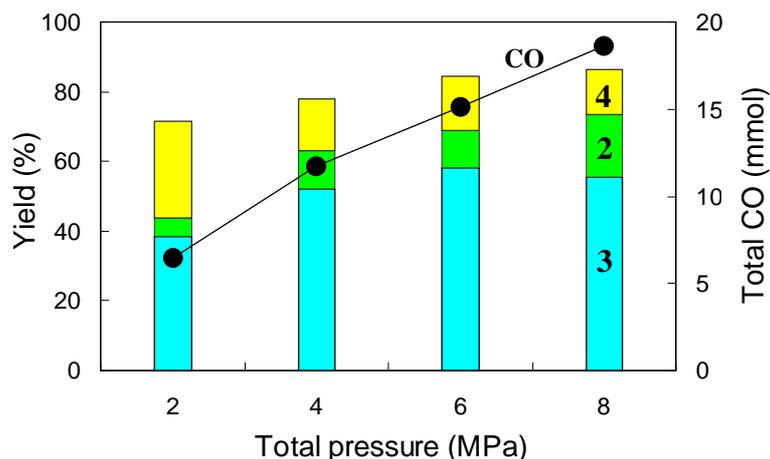


Figure 2. Influence of total pressure of CO₂ and H₂ (1:1) on the reactions under conditions: catalyst Ru₃(CO)₁₂ 0.3 mmol, additive LiCl 0.4 mmol, substrate cyclohexene 1 cm³ (9.87 mmol), solvent NMP 8 cm³, temperature 423 K, time 3 h. **2:** cyclohexanecarboxaldehyde, **3:** cyclohexanemethanol, **4:** cyclohexane.

Figure 3 shows the effects of CO₂ and H₂ pressures at certain H₂ and CO₂ pressures. The effects of CO₂ pressure are similar to those of the total CO₂ + H₂ pressure as above-mentioned. Figure 3(b) shows that increasing H₂ pressure enhances the rates of hydrofomylation and hydrogenation reactions. The yield of **3** increases with H₂ pressure, while the yield of **2** decreases. The yield of **4** increases on going from 1 MPa to 2 MPa but does not change at higher H₂ pressures. Higher H₂ pressure is suitable for higher selectivity for the hydrofomylation and the subsequent hydrogenation than the undesired direct hydrogenation to **4**.

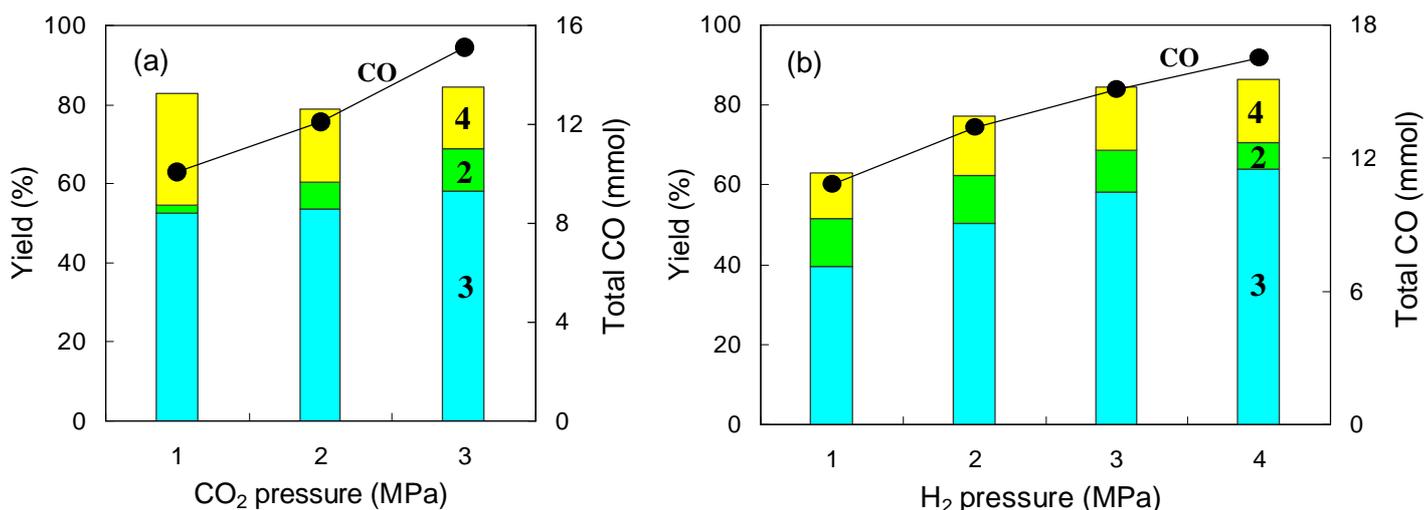


Figure 3. Influence of (a) CO₂ pressure at H₂ 3 MPa and (b) H₂ pressure at CO₂ 3 MPa under conditions: catalyst Ru₃(CO)₁₂ 0.3 mmol, additive LiCl 0.4 mmol, substrate cyclohexene 1 cm³ (9.87 mmol), solvent NMP 8 cm³, temperature 423 K, time 3 h. **2:** cyclohexanecarboxaldehyde, **3:** cyclohexanemethanol, **4:** cyclohexane.

2.2 Phase behavior and high pressure FTIR

Under the reaction conditions used, the reaction mixture is a biphasic system of gas and liquid phases. The phase behavior was confirmed by visual observations at 403 K (Figure 4), which is a little lower than the reaction temperature (423 K) due to limitation of the observation system used. The presence of CO₂ seems to cause the expansion of the liquid phase but marginally. The hydrofomylation and hydrogenation reactions occur in the liquid phase (NMP solvent).

Previously the present authors show from in situ high pressure FTIR measurements that dense CO₂ molecules may strongly interact with organic molecules and modify the reactivity of some of their functional groups [14-17]. There are indeed strong interactions between dense CO₂ molecules and an α,β -unsaturated aldehyde, cinnamaldehyde, in particular with its carbonyl group. This is of significance in promoting the selective hydrogenation to the corresponding unsaturated alcohol,

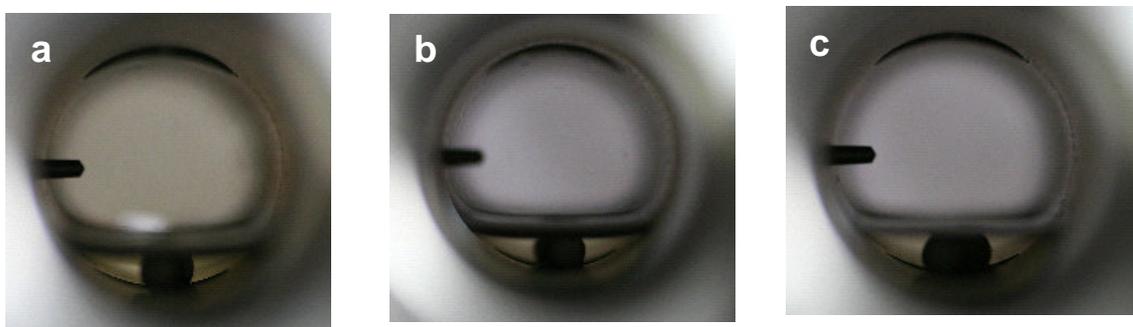


Figure 4. Visual observations of liquid (NMP) - gas biphasic mixtures at 403 K. These are NMP under (a) 4 MPa H₂, (b) 4 MPa H₂ + 4 MPa CO₂ MPa, (c) 4 MPa H₂ + 16 MPa CO₂. A dark body in the liquid phase is a Teflon stirrer.

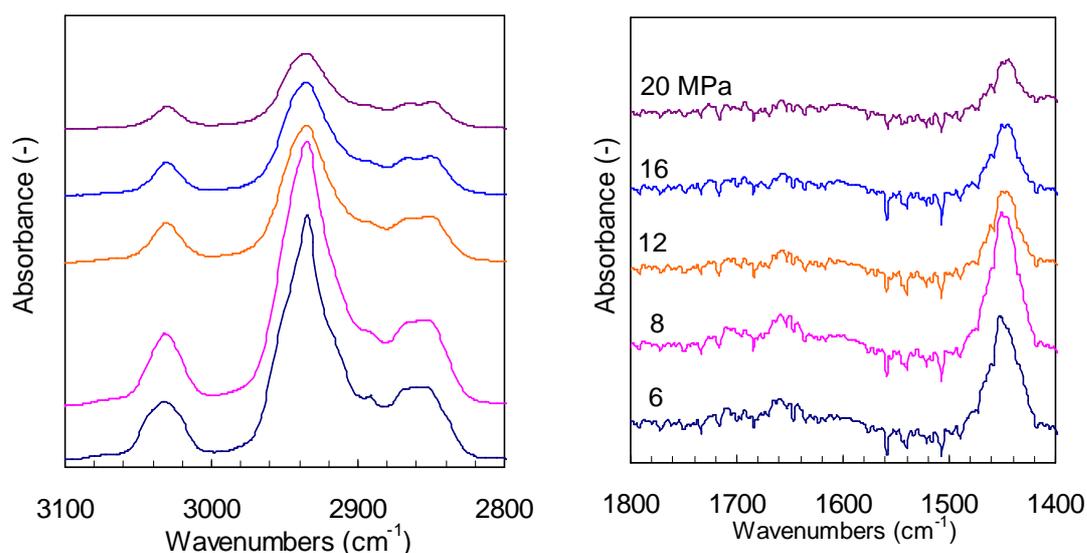
cinnamyl alcohol. To examine such a chemical effect of CO₂ for the present cases, similar FTIR measurements were also made for the substrate **1** and the hydrofomylation product **2**, which were dissolved in the dense CO₂ medium at different pressures. Figure 5 presents FTIR spectra of **1** and **2** in a mixture of 4 MPa H₂ and CO₂ at different pressures and at 387 K. Figure 5(a) shows an IR band at around 3030 cm⁻¹ and a very weak band at around 1660 cm⁻¹, which are assigned to the absorption of =CH- and -C=C-, respectively. The both bands decrease in the strength with CO₂ pressure, due to a simple dilution. Their peak positions little change with the pressure. For **2**, on the other hand, Figure 5(b) indicates a single peak at 1743 cm⁻¹ assignable to the absorption of C=O at a CO₂ pressure of 4 MPa and a new shoulder peak appears at 8 MPa; it marginally increases with the pressure but the peak position remains almost unchanged. The two IR bands assignable to -CH₂- in the region of 2980 - 2840 cm⁻¹ do not change their peak positions with CO₂ pressure. Thus we believe that dense CO₂ molecules indicate no effects on the reactivity of **1** and **2** to hydrogenation and hydroformylation, respectively, under the present CO₂ pressure conditions.

2.3. Pressure effects

The structure of Ru complexes prepared at different CO₂ and H₂ pressures was examined by FTIR measurements. Figure 6 shows that the complexes (a) – (c) exhibit three strong and two weak IR bands

in the CO region at 2038, 2018, 1999, 1976, and 1949 cm^{-1} , which are very similar independent of the pressures of CO_2 and H_2 used for the preparation of them. Previously Tominaga and Sasaki observed similar IR bands [11] and pointed out that these IR bands indicated the presence of two different Ru complexes, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^{-1}$ and $[\text{HRu}_3(\text{CO})_{11}]^{-1}$, which may be active for the hydrogenation of CO_2 to CO and the hydrofomylation of alkene with CO, respectively. Those two Ru complexes should also be formed in our cases and their structure and relative quantities do not change with the CO_2 and H_2 pressures under the present conditions. Thus, other factors should be considered to explain the pressure effects observed.

(a) **1** (cyclohexene)



(b) **2** (cyclohexanecarboxaldehyde)

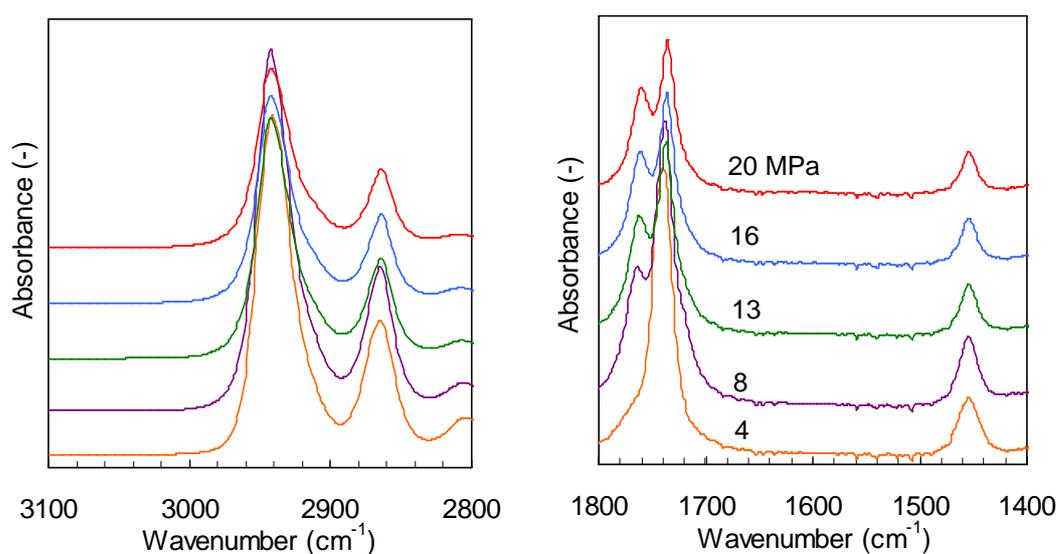


Figure 5. High pressure FTIR spectra of **1** and **2** in 4 MPa H_2 and dense CO_2 at different pressures given and at 387 K.

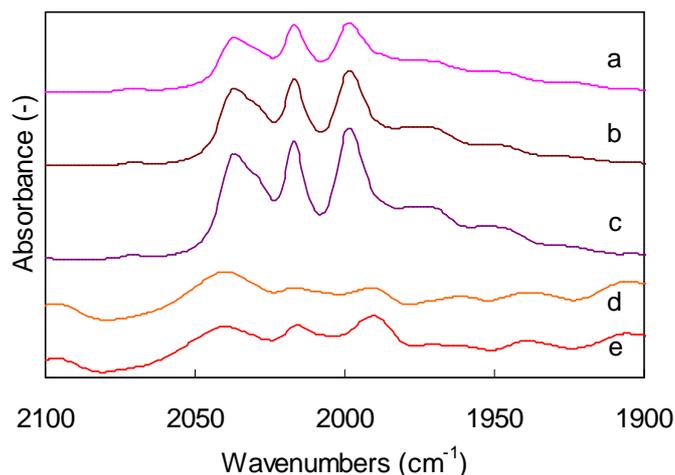


Figure 6. FTIR spectra of catalytically active species prepared in NMP at different CO₂ and H₂ pressures. Ru₃(CO)₁₂ + LiCl in NMP at (a) CO₂ 3 MPa, H₂ 3 MPa; (b) CO₂ 1 MPa, H₂ 3 MPa; (c) CO₂ 1 MPa, H₂ 1 MPa. (d) Ru₃(CO)₁₂ + LiCl in NMP. (e) Ru₃(CO)₁₂ in NMP.

The reactions occur in the liquid phase (NMP) under the conditions used, as confirmed by visual observations (Figure 4). When CO₂ and H₂ pressures are raised, larger quantities of these gaseous reactants are dissolved in the liquid phase and this promotes the hydroformylation and the following hydrogenation. Thus, the yields of **2** and **3** tend to increase with the CO₂ and H₂ pressures (Figures 1-3). It is interesting to note that the yield of **4** does not increase with H₂ pressure and the coexistence of CO₂ may be important for this. When H₂ pressure is raised at a certain CO₂ pressure, the dissolution of CO₂ into the liquid phase may also be facilitated. The dissolved CO₂ species should suppress the direct hydrogenation of **1** to **4**. This may be due to a simple dilution effect that the reactants of **1** and H₂ in the liquid phase are diluted by the dissolved CO₂ molecules. The FTIR results do not indicate that the reactivity of **1** is modified through interactions with the CO₂ molecules. Additional reaction runs were attempted with the same catalyst system but at lower reaction temperatures (393 K – 323 K) to examine the influence of CO₂ pressures on the hydrogenation of **1**. In those runs, unfortunately, hydroformylation also took place or the overall conversion was small, and these attempts were not successful.

The dissolution of CO₂ into the solvent phase would decrease the concentration of **1** (and **2**) and H₂ and this might reduce the rate of hydrogenation of both **1** and **2**. However, the present results show that the conversion of **2** to **3** is not suppressed. For **2** as well, the dense CO₂ molecules little affect the reactivity of **2** (suggested from FTIR results). The simple hydrogenation of **2** was tested with the same catalyst system at a H₂ pressure of 3 MPa (in the absence of CO₂); the conversion was found to be more than 90 % and 60 % at 423 K (used for hydrofomylation runs) and 393 K, respectively (the conversion was observed to decrease in the presence of CO₂ for this hydrogenation of **2**, due to the dilution effect). The hydrogenation of **2** to **3** is assumed to be faster than the hydrofomylation of **1** to **2**. Under the hydroformylation conditions used, the hydroformylation of **1** is promoted with CO₂ pressure; this is positive for promoting the subsequent hydrogenation of **2**, which is against the negative dilution effect. As a result of the balance of these positive and negative effects the hydrogenation of **2** to **3** should not be suppressed with CO₂ pressure, in contrast to that of **1** to **4** (the simple dilution effect only).

The effect of CO₂ and H₂ pressures on the hydroformylation and hydrogenation reactions also includes that of CO and H₂O formed via the reverse water gas shift reaction (RWGSR). As mentioned in 2.1., the RWGSR is assumed to go faster compared with the following hydroformylation with CO formed in the former reaction and the latter should determine the overall rate of hydroformylation of **1** with CO₂ and H₂ under the conditions used. The further detailed discussion on the pressure effects at molecular level should consider the roles of those intermediate and byproduct gases. The volume of NMP liquid phase little changes on the pressurization with CO₂ and H₂ (Figure 4), and so the species of **1** and **2** are likely to exist mainly in the liquid phase. This should be confirmed by measurements of the solubility of these species in either NMP liquid phase or dense CO₂ gas phase.

In the present work a homogeneous catalyst of Ru₃(CO)₁₂ and LiCl was used, which were soluble and functioned in the solvent phase (NMP in the present case). For practical operation, the separation and recycling of a catalyst is an important aspect for hydroformylation and other reaction processes [9,18]. Recently Tominaga and Sasaki attempted to use a biphasic system of an organic solvent and an ionic liquid for hydroformylation using CO₂ and H₂ [19,20]. They screened several couples of organic solvents and ionic liquids and showed that the hydroformylation of 1-hexene proceeded and Ru complex catalysts were recyclable for some couples. Under the conditions, however, alcohol was selectively formed but no aldehyde was obtained. The heterogenization of catalytic reaction systems and the control of product selectivity are also interesting and challenging tasks for hydroformylation with CO₂ and H₂.

3. Experimental Section

Commercially available reagents were used without further purification: catalyst Ru₃(CO)₁₂ purchased from Aldrich and LiCl, NMP (solvent), and cyclohexene from Wako. Ru₃(CO)₁₂ 0.3 mmol, LiCl 0.4 mmol, cyclohexene 1 cm³ (9.87 mmol), and NMP 8 cm³ were mixed in a 100 cm³ stainless reactor with Teflon-coated inner wall. Then CO₂ and H₂ (reagent grade) were introduced into the reactor up to the desired pressures at room temperature and the reactor was sealed and heated to a reaction temperature of 423 K while mixing the reaction mixture. In this work, these initial CO₂ and H₂ pressures are given in reaction conditions. After reaction runs, the mixing was stopped and the reactor was cooled down to room temperature. The reaction products, liquid and gaseous species, were analyzed with gas chromatographs, GL Science GC390B, Hitachi G-3000, Shimadzu GC-14B and a gas chromatograph - mass spectrometer Shimadzu GCMS-QP5050A. The conversion of cyclohexene was determined by (initial amount (9.87 mmol) – residual amount measured) / initial amount. The total quantity of CO formed was estimated by summing the amounts of hydroformylation product (cyclohexanecarboxaldehyde), its further hydrogenation product (cyclohexanemethanol), and CO remaining in the gas phase.

The phase behavior of reaction mixture was examined by the naked eye using another reactor attached with transparent quartz windows. The liquid phase used was NMP alone since the concentration of cyclohexene used in the reaction runs was small. In addition, in situ high pressure FTIR was used to study interactions of cyclohexene and some products with dense CO₂ molecules. The experimental setups and procedures for these visual observation and FTIR measurement were described in previous works [15,16]. The structure of catalytically active species was also examined by FTIR. The Ru complexes were prepared at different CO₂ and H₂ pressures in the abovementioned

manners, kept for 1 h under the reaction conditions (in the absence of cyclohexene), and were then subjected to FTIR measurements under ambient conditions. For the FTIR measurements a small quantity of NMP liquid containing the active species was held between two KBr plates but it was not precisely measured and so the absolute strength of IR bands observed was not considered in this work.

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