J. Phys. Chem. A **2005,** *109,* 4419−4424

Hydrogenation of Benzaldehyde and Cinnamaldehyde in Compressed CO_2 Medium with a Pt/C Catalyst: A Study on Molecular Interactions and Pressure Effects

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Received: January 4, 2005; In Final Form: March 28, 2005

The hydrogenation of benzaldehyde and cinnamaldehyde has been studied with a 5% Pt/C catalyst in compressed CO_2. The effect of CO_2 pressure on the total conversion was found to be different between the two aldehydes. The total conversion of benzaldehyde merely decreases with increasing CO_2 pressure, while that of cinnamaldehyde shows a maximum at a certain pressure. High-pressure FTIR measurements indicate the existence of interactions of CO_2 with the aldehydes. The absorption of $\nu(C{=}O)$ red-shifts at increasing CO_2 pressure, and this red-shift is more significant for cinnamaldehyde than for benzaldehyde, indicating that the C═O bond of the former becomes more reactive than the latter. The difference in the mode of interactions of CO_2 with these aldehydes has also been indicated by changes of $\nu(C{=}O)$ of CO_2. Thus, the conversion of benzaldehyde will decrease with increasing CO_2 pressure because of a simple dilution by introducing a larger quantity of CO_2. For cinnamaldehyde, the conversion will increase at low pressures because of increasing interactions with CO_2 molecules (increasing the reactivity of the C═O bond) but decrease at high pressures because of the simple dilution effect, similar to the case of benzaldehyde. The dense CO_2 molecules are not likely to change the catalytic activity of supported Pt particles, which was previously suggested from optical absorption of supported fine metal (Au) particles in a compressed CO_2 medium.

1. Introduction

Hydrogenation of organic compounds is an industrially important chemical transformation. Gaseous H_2 is an inexpensive and versatile reagent for hydrogenation, but the rate of hydrogenation is usually slow, because H_2 is less soluble in common organic solvents. By contrast, supercritical carbon dioxide ($scCO_2$) is completely miscible with H_2, and it is an environmentally benign medium with good mass and thermal transport properties.[1−4] So, the use of $scCO_2$ has been attracting much attention for developing green chemistry processes. Hydrogenation is one of the frequently studied reactions in $scCO_2$ using homogeneous[5−9] and heterogeneous catalysts.[10−20] Practical merits of the use of heterogeneous catalysts include ease of separation, recovery, and recycling.

It is known for hydrogenation as well as other reactions in $scCO_2$ that the CO_2 pressure often significantly affects the total conversion and product distribution in different manners depending on the reaction conditions. In most cases reported so far, the enhancement of the rate of catalytic hydrogenation of organic substrates in $scCO_2$ has been ascribed to high H_2 concentration in the liquid or gas phase in which the substrates and catalysts exist and/or to the elimination of mass transfer resistance due to complete miscibility of CO_2 and other reacting species. For example, Phiong et al. observed that $scCO_2$ significantly enhances the rate of α-methylstyrene hydrogenation with 1% Pd/C under three-phase conditions.[10] Tschan et al. indicated the importance of phase behavior in continuous semihydrogenation of phenylacetylene to styrene with a $Pd_{81}Si_{19}$ alloy. They showed that a single-phase mixture at low H_2 pressure is an ideal medium for this semi-hydrogenation. The hydrogenation in $scCO_2$ has also been studied in our laboratory using heterogeneous catalysts as well as homogeneous ones. Significant enhancement in activity and selectivity was shown for the hydrogenation of unsaturated aldehydes with supported transition-metal catalysts in $scCO_2$.[12−16] The above-mentioned effects of $scCO_2$ are also important for these hydrogenation reactions. In addition, we previously suggested the possibility that dense CO_2 changes the properties of supported metal particles. This was assumed from optical absorption measurements of small Au particles in dense CO_2 medium,[21] and this idea was invoked to explain the change of product distribution in Pt-catalyzed nitrobenzene hydrogenation with CO_2 pressure.[13,14] Furthermore, the coordination of CO_2 with active metal centers has been thorougly reviewed.[22,23] It is indicated that only a weak interaction between CO_2 and an active metal center is sufficient to bring about insertion of CO_2 into an M−X bond (M = metal), which could modify the catalytic activity of this metal in dense CO_2.

Recently, IR spectroscopy has been used to study the mixture of organic compounds in dense CO_2 at different pressures. In a CO_2 molecule, the carbon atom is partially positive and the oxygen atoms are partially negative, and this polar nature is significant in compressed CO_2. Hyatt et al.[24] measured IR spectra of several probe compounds in both liquid and supercritical CO_2. They reported that red-shifts in the $\nu(C{=}O)$ of acetone and cyclohexanone in dense CO_2 were slightly greater than that in *n*-hexane but slightly smaller than those in aromatic solvents, which show a tendency for CO_2 to interact with basic carbonyl groups. Brokeman et al.[25] suggested that the specific interaction between CO_2 and carbonyl oxygen could be de-

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10.1021/jp050049x CCC: \$30.25

scribed as a Lewis acid−base reaction. Such molecular interactions have been investigated further by Raveendran et al.,[26] who indicated the interaction of CO_2 molecules with Lewis base groups, especially carbonyl groups, through a C−H···O hydrogen bond with the hydrogen atom attached to the carbonyl carbon or at the α-position. These interactions with CO_2 were suggested to affect the solubility of the substrate and the phase behavior of the reaction mixture in CO_2, changing the chemical reactions in dense CO_2. Recently, the application of various in situ spectroscopic techniques for the investigation of mixtures in supercritical fluids has been reviewed extensively.[27]

Although a number of homogeneously and heterogeneously catalytic reactions have been investigated in scCO_2, fundamental studies at molecular levels are still insufficient to understand the CO_2 pressure effects on catalytic and noncatalytic reactions in scCO_2. The present work has been undertaken to study in detail the CO_2 pressure effects in hydrogenation of two aldehydes, benzaldehyde and *trans*-cinnamaldehyde, with a Pt/C catalyst. It has been observed that the change of conversion with CO_2 pressure is significantly different between these two aldehydes. Other physicochemical measurements have been made to examine the effects of dense CO_2 medium observed, and the hydrogenation results have been discussed in terms of phase behavior, molecular interactions with CO_2 molecules (measured by in situ high-pressure FTIR), and change of the catalytic activity of Pt particles.

2. Experimental Section

2.1. Materials. All chemicals were purchased from Wako and used without further purification. A 5 wt. % Pt/C catalyst also purchased from Wako was reduced by hydrogen at 300 °C for 2 h before activity measurements. The size of the Pt particles obtained was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements and determined to be 8.3 nm, which gave a degree of metal dispersion of 0.11 from an approximate expression: metal dispersion = 0.9/diameter (in nm).[28]

2.2. Phase Behavior and Solubility. The examination of the phase behavior is important to study chemical reactions in scCO_2; it is significant to see whether the reaction is taking place homogeneously in a single phase or heterogeneously in two or more phases. A 10 cm^3 high-pressure sapphire-windowed view cell was used to determine the separate pressure from a two-phase (gas−liquid) state to a one-phase (scCO_2) state and estimate the solubility of the substrate in scCO_2. A certain amount of substrate was added into the cell, and then, the cell was flushed with 0.5 MPa CO_2 twice. After the cell was heated to 50 °C (reaction temperature) by circulation of preheated oil outside the cell, CO_2 was introduced into it. The pressure was increased slowly while stirring by a Teflon-coated magnetic stirrer. When the pressure reached a certain value, the stirring was continued for 3−5 min and stopped; then, the state of the mixture including the substrate and CO_2 was visually examined. This examination was made at intervals of 0.2−0.5 MPa to determine the pressure at which the substrate was completely dissolved into CO_2, forming a single phase. Then, the pressure was decreased in a similar way to determine the pressure at which droplets appeared (dew point), changing into a two-phase mixture. The pressures determined at increasing and decreasing pressures were less than ±0.3 MPa different, and the average value of the two pressures determined was used. Those observations were used to estimate the solubility of benzaldehyde and cinnamaldehyde in CO_2 at different pressures.

2.3. Hydrogenation of Aldehydes. Hydrogenation of the two aldehydes in scCO_2 was carried out in a 50 cm^3 high-pressure stainless steel reactor. The reactor was charged with reactant and catalyst and then sealed. It was flushed with CO_2 three times and heated to 50 °C. After the introduction of H_2, liquid CO_2 was introduced into the reactor with a high-pressure liquid pump to the desired pressure. The reaction was conducted while stirring the mixture with a magnetic stirrer for 2 h. The reactor was then cooled to room temperature with an ice bath and depressurized to atmospheric pressure. The reaction mixture was collected with acetone and analyzed with a gas chromatograph with a flame ionization detector. Previously, some authors reported that stainless steel reactors promoted chemical reactions such as hydrogenation and oxidation.[29−31] Hydrogenation reactions of benzaldehyde and cinnamaldehyde were conducted at pressures of 4 MPa H_2 and 10 MPa CO_2 in the absence of Pt/C catalyst. No products were observed to form with benzaldehyde, and a marginal quantity of hydrocinnamaldehyde was detected with cinnamaldehyde. Thus, the absence of reactor wall effects has been confirmed in the present cases.

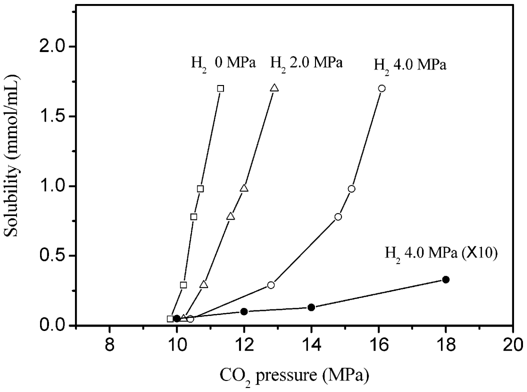


Figure 1. Estimated solubility of benzaldehyde in CO_2 and/or H_2 at 50 °C (open marks) along with the data of cinnamaldehyde at H_2 of 4 MPa (closed mark); for comparison, see ref 9.

2.4. High-Pressure FTIR Measurements. The information about interactions of dense CO_2 with the aldehydes dissolved at different pressures is significant in discussing the CO_2 effects during the reaction. In situ high-pressure FTIR spectra were measured at 50 °C with an FTIR spectrometer (FT/IR-620, JASCO) equipped with a 1.5 cm^3 high-pressure cell with a path length of 4 mm. The experimental procedure used is as follows: 10 μL substrate, benzaldehyde or cinnamaldehdye, was added to the cell, it was heated to 50 °C by the circulation of preheated oil outside it, and H_2 and/or CO_2 was introduced into the cell. The pressure was raised slowly while stirring by a Teflon-coated magnetic stirrer. When the pressure reached a certain value, the stirring was continued for 3−5 min and stopped; then, the IR spectra were measured with a triglycine sulfate (TGS) detector at 4 cm^{-1} wavenumber resolution by using pure CO_2 at the corresponding pressures as background.

3. Results and Discussion

3.1. Phase Behavior and Solubility of Aldehydes. The solubility of benzaldehdye in a mixture of CO_2 and H_2 was estimated from the phase behavior inspection at 50 °C in the same manner as that used for *trans*-cinnamaldehyde.[9] The results obtained are given in Figure 1, indicating that the solubility of benzaldehyde in pure CO_2 markedly increases with increasing CO_2 pressure at 9.8−11 MPa. At lower pressures, the quantity of benzaldehyde soluble in CO_2 was very small, and so, it was impossible to examine the phase behavior by visual inspection. Figure 1 also shows that the addition of H_2 significantly decreases the solubility of benzaldehyde, and this effect is larger

TABLE 1: Influence of CO_2 Pressure on Benzaldehyde Hydrogenation with Pt/C Catalyst at 50 °C[a]

entry	CO_2 pressure (MPa)	benzaldehyde conversion (%)	TOF[b] (s^{-1})	no. of phases
1	*c*	98	2.40	3
2	*d*	97	2.38	3
3	*e*	99	2.42	3
4	6.0	62	1.52	3
5	7.5	44	1.08	3
6	8.5	26	0.64	3
7	10.5	32	0.78	2
8	12.0	27	0.66	2
9	16.0	24	0.59	2

[a] Reaction conditions: benzaldehyde, 5 mmol; catalyst, 5% Pt/C, 10 mg (including Pt 2.56 μmol); H_2, 4.0 MPa; reaction time, 2 h. [b] Turnover frequency, (moles of benzaldehyde reacted)/((moles of surface-exposed Pt atoms) × (reaction time)). The number of surface-exposed Pt atoms was calculated from the metal dispersion estimated from an approximate expression (see text). [c] In the absence of CO_2. [d,e] In the presence of 6.0 and 10.1 MPa N_2, respectively, instead of CO_2.

TABLE 2: Influence of CO_2 Pressure on Benzaldehyde Hydrogenation at 50 °C[a]

	CO_2		H_2		benzaldehyde		
entry	MPa	mole fraction	MPa	mole fraction	mmol	mole fraction	conversion (%)
1	11	0.91	2.0	8.0×10^{-2}	3.0	6.4×10^{-3}	17
2	12	0.91	2.4	8.0	3.7	6.6	14
3	14	0.92	3.1	7.3	4.7	5.8	15
4	16	0.92	3.5	6.7	5.3	5.4	16

[a] Reaction conditions: 5% Pt/C catalyst, 5 mg (including Pt 1.23 μmol); reaction time, 2 h.

TABLE 3: Influence of CO_2 Pressure on Cinnamaldehyde Hydrogenation with Pt/C Catalyst at 50 °C[a]

			selectivity[b] (%)				
entry	CO_2 (MPa)	conversion (%)	COL	HCAL	HCOL	TOF (s^{-1})	no. phases
1	*c*	32	77	10	13	0.78	3
2	*d*	36	71	19	10	0.89	3
3	*e*	38	67	18	15	0.92	3
4	6.0	38	80	14	6	0.93	3
5	7.5	42	82	12	6	1.02	3
6	8.5	47	81	9	10	1.15	3
7	10.5	55	80	9	11	1.35	2
8	12.0	38	78	9	13	0.93	2
9	16.0	36	80	7	13	0.88	2

[a] Reaction conditions: cinnamaldehyde, 0.25 mmol; catalyst, 5% Pt/C, 0.5 mg; H_2, 4.0 MPa; time, 2 h. [b] COL: cinnamyl alcohol. HCOL: hydrocinnamyl alcohol. HCAL: hydrocinnamaldehyde. [c] In the absence of CO_2. [d,e] In the presence of 6.0 and 9.7 MPa N_2, respectively, instead of CO_2.

at higher H_2 pressure, in accordance with the previous results for cinnamaldehyde.[9] The solubility of cinnamaldehyde determined previously at H_2 of 4 MPa is also given in Figure 1 for comparison, which is much smaller than that of benzaldehyde. Reaction conditions for hydrogenation were selected on the basis of these solubility data. The H_2 pressure of 4 MPa was used for hydrogenation reactions described in the following section.

3.2. Influence of CO_2 Pressure on Benzaldehyde Hydrogenation. The benzaldehyde hydrogenation was carried out at an H_2 pressure of 4.0 MPa and at different CO_2 pressures using 5.0 mmol benzaldehyde. Under these conditions, the reaction occurred in a three-phase system (CO_2-rich gas, benzaldehyde-rich liquid, and catalyst solid phase) at CO_2 pressures below 10 MPa but in a two-phase system (CO_2-rich gas and catalyst solid phase) at CO_2 pressures above 10.5 MPa. Table 1 gives the results obtained, in which the selectivity to benzyl alcohol is 100%. The total conversion of benzaldehyde merely decreases with CO_2 pressure up to 16 MPa. Under solvent (CO_2)-free conditions, the reaction was almost completed in 2 h (entry 1), and this was not influenced by the presence of 6.0 and 10.1 MPa N_2 (entries 2, 3). In contrast, the use of 6.0 MPa CO_2 significantly decreased the conversion to 62% (entry 4). The conversion decreased with further increasing CO_2 pressure irrespective of the number of phases present, three or two phases. The highest conversion levels were obtained under solvent-less conditions and under pressurized N_2 atmosphere. Thus, dense CO_2 has only a negative effect on the hydrogenation of benzaldehyde, which is not the case for the hydrogenation of cinnamaldehyde as described below.

It should be noted here that the selectivity of benzyl alcohol is 100% in the presence of high-pressure CO_2 or N_2, in contrast to the results in conventional organic solvents such as ethanol, in which toluene and/or benzene are also formed in about 10−20% as byproducts.[32,33]

Furthermore, the influence of CO_2 pressure was also examined under different conditions at which the hydrogenation took place in a two-phase system, using a certain amount of 5% Pt/C catalyst of 5.0 mg (including Pt 1.23 μmol). The CO_2 pressure was varied from 11 to 16 MPa while keeping the benzaldehyde/H_2/CO_2 ratio unchanged (keeping the mole fraction of these species approximately unchanged) to minimize the influence of change of concentration of the reacting species on the reaction. For these experiments, we expected that the results did not include the influence of concentration change but did include the influence of CO_2 pressure, if it existed, on the activity of the Pt/C catalyst. The latter was expected from one of our previous results in which the natures of fine metal particles changed in compressed CO_2 medium depending on the CO_2 pressure from optical absorption measurements with supported Au particles.[21] Table 2 indicates, however, that the conversion changes very little with the CO_2 partial pressure, and so, the specific activity of the Pt particles on the C support is unlikely to change significantly in the presence of dense CO_2.

3.3. Influence of CO_2 Pressure on Cinnamaldehdye Hydrogenation. The hydrogenation of cinnamaldehyde was conducted under similar conditions as those used with benzaldehyde. Table 3 shows that the total conversion is 32% and the selectivity of cinnamyl alcohol is 77% under solvent (CO_2)-free conditions (entry 1). The reaction was conducted under pressurized N_2 conditions at 6.0 and 9.7 MPa (entries 2, 3). It seems that the pressurization with N_2 increases the total conversion and decreases the selectivity of cinnamyl alcohol, while it decreases the selectivity of hydrocinnamaldehyde. However, these effects of N_2 are even less marked as compared with those observed under pressurized CO_2 conditions. The conversion and product distribution change significantly with increasing CO_2 pressure (entries 3−8), in contrast to the case of benzaldehyde. The conversion increased up to 55% at 10.5 MPa, at which the reaction system changed from a three-phase mixture to a two-phase mixture. At higher pressures, smaller conversions were obtained. The selectivity of cinnamyl alcohol was slightly improved in the presence of compressed CO_2. Thus, the influence of CO_2 pressure observed in cinnamaldehyde hydrogenation is markedly different from that in benzaldehyde hydrogenation. The reasons for the difference in CO_2 pressure effects between these two substrates will be discussed later.

It is well-known that Pt is not a good catalyst for the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols under ordinary conditions.[34] The selectivity may be

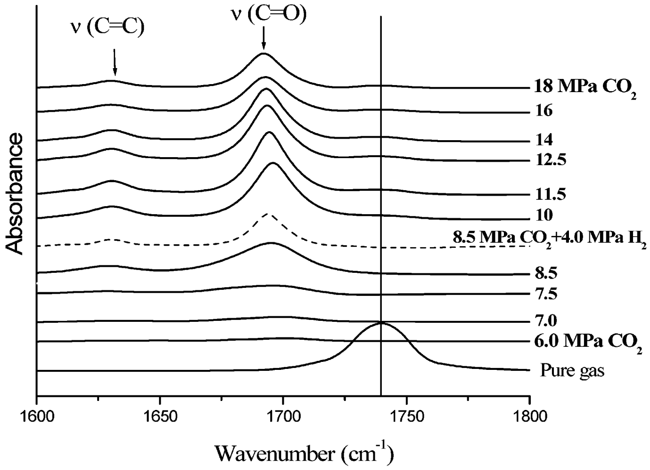


Figure 2. FTIR spectra of pure gaseous cinnamaldehyde and cinnamaldehyde dissolved in compressed CO_2 at 50 °C. Broken line is a spectrum in the presence of 4 MPa H_2 and 8.5 MPa CO_2.

improved by alloying with other metal species such as tin. It is interesting that the selectivity of a Pt/C catalyst for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol can be improved when the reaction occurs under dense CO_2 conditions.

3.4. Interactions between CO_2 and Aldehyde Molecules Measured by High-Pressure FTIR. It is reported that interactions should exist between solutes and CO_2 molecules,[24−27] which would affect the reaction rate and product distribution in reactions in $scCO_2$. So, high-pressure FTIR was used to examine such interactions in our reaction systems with cinnamaldehyde and benzaldehyde. Figure 2 gives FTIR spectra from 1800 to 1600 cm^{-1} for the former substrate dissolved in compressed CO_2 at 50 °C. Gaseous cinnamaldehyde was examined as a reference, and its spectrum shows an absorption of ν(C=O) at 1740 cm^{-1}. In compressed CO_2, the spectra have strong ν(C=O) absorption and weak ν(C=C) absorption. The former absorption peak red-shifts to a smaller wavenumber with increasing CO_2 pressure compared with the gaseous substrate. This pressure effect on ν(C=O) is larger than that on ν(C=C). The results indicate the existence of interactions between cinnamaldehyde and dense CO_2 molecules, and these interactions are more significant for the C=O bond than the C=C bond. Figure 3 gives FTIR spectra for benzaldehyde, showing an absorption of ν(C=O) to red-shift in the presence of dense CO_2. The extent of this red-shift is larger with increasing CO_2 pressure, but it is much smaller compared with the results of cinnamaldehyde, as clearly shown in Figure 4. The presence of 4 MPa H_2 does not change the peak position of ν(C=O) for both cinnamaldehdye and benzaldehyde, but the peak in the presence of H_2 is broader than that in the pure CO_2 for benzaldehyde. The results obtained from the FTIR measurements are summarized: A stronger interaction exists between CO_2 and cinnamaldehyde molecules than that between benzaldehyde and CO_2 molecules; the interaction with C=O of cinnamaldehyde is larger than that with C=C, and this interaction is not influenced by H_2 so much.

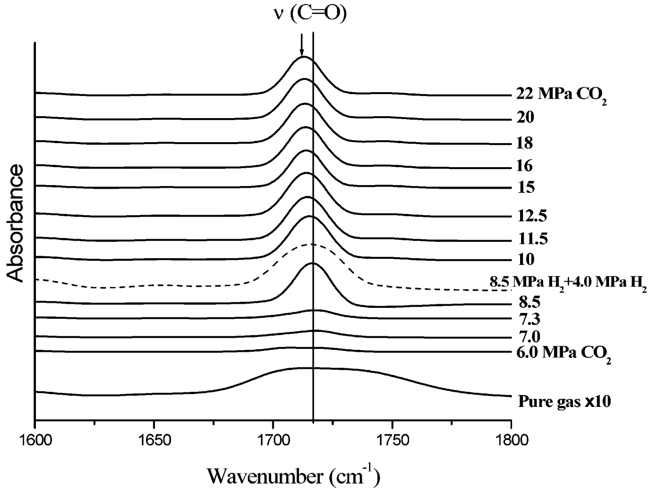


Figure 3. FTIR spectra of gaseous benzaldehyde and benzaldehyde dissolved in compressed CO_2 at 50 °C. Broken line is a spectrum in the presence of 4 MPa H_2 and 8.5 MPa CO_2.

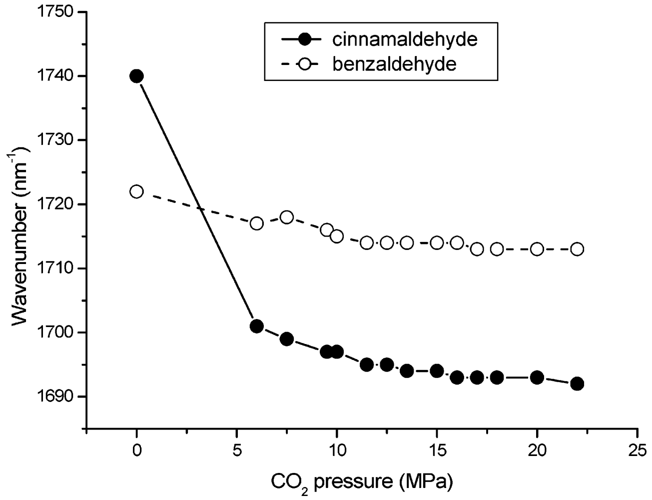


Figure 4. Influence of CO_2 pressure on the peak positions of ν(C=O) for cinnamaldehyde and benzaldehyde at 50 °C.

Moreover, the absorption of ν(C=O) in the CO_2 molecule was also examined. Figure 5 gives FTIR spectra obtained in the presence and absence of cinnamaldehyde and benzaldehyde in compressed CO_2. The absorption peak of pure CO_2 is single at 1.5 MPa, but it splits into two peaks at higher pressures, indicating that CO_2 is not a nonpolar molecule in the supercritical region, although the net dipole moment of CO_2 is zero. The difference between these two peaks increases at increasing CO_2 pressure. Furthermore, note that these peaks split into four peaks in the presence of cinnamaldehyde at high CO_2 pressures of 12.5 and 16 MPa, while in the presence of benzaldehyde, one of the two peaks located at a larger wavenumber splits into two peaks. It is suggested that CO_2 molecules can interact with cinnamaldehyde and benzaldehyde molecules, but the modes of this interaction should be different between them.

In a CO_2 molecule, the carbon atom is partially positive and the oxygen atoms are partially negative. Thus, compressed CO_2 is not a nonpolar medium but a polar medium. In the literature, a specific interaction of CO_2 molecules with Lewis base groups, especially carbonyl groups, through a C—H···O hydrogen bond with the hydrogen atom attached to the carbonyl carbon or at the α-position has been reported.[26] Such hydrogen bonds for cinnamaldehyde can occur, while in the case of benzaldehyde having no hydrogen atom at the α-position, only one hydrogen bond can form with the hydrogen atom attached to carbonyl carbon. Possible interaction modes are illustrated in Scheme 1, which may explain the difference in the splitting of ν(C=O) absorption peaks in the presence of the two substrates (Figure 5). The two C=O bonds of a CO_2 molecule of configuration (a) are different from each other, and this may cause the second splitting in the presence of cinnamaldehyde at high CO_2 pressures. The two C=O bonds of a CO_2 molecule of config-

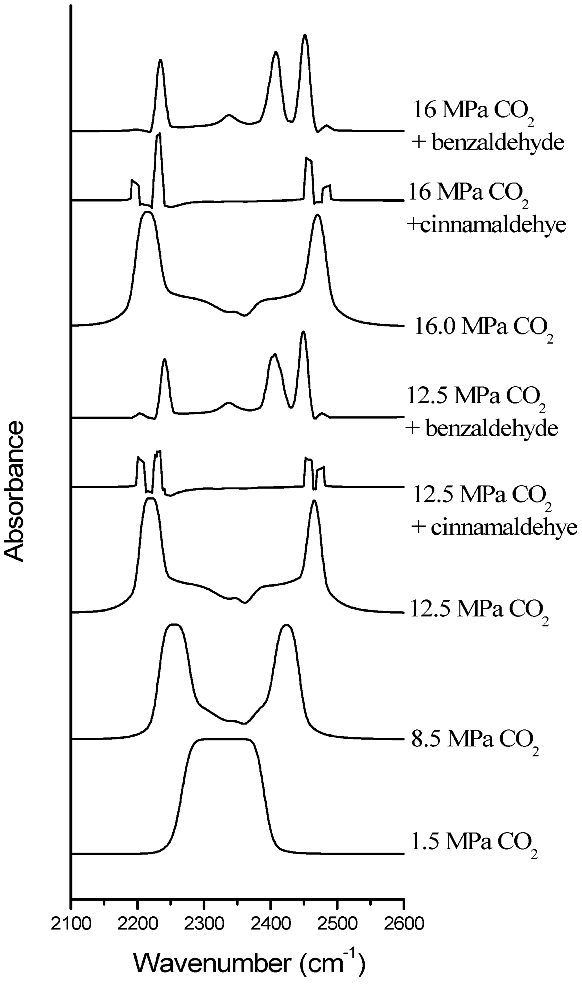
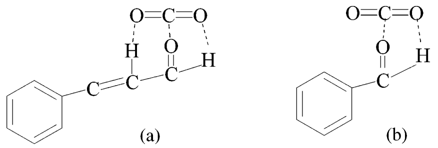


Figure 5. FTIR spectra of CO_2 at different pressures in the absence and presence of cinnamaldehyde and benzaldehyde at 50 °C.

SCHEME 1: Possible Modes of Interaction of CO_2 with Cinnamaldehdye (a) or Benzaldehdye (b)



uration (b) are also different, but the one bond may not be so different from the C═O bonds of the CO_2 molecules around this CO_2 molecule interacting with the carbonyl group. So, the second splitting should occur for the one peak only with benzaldehyde. The detail of the configuration of the CO_2 molecules nearest and second-nearest to a cinnamaldehyde or benzaldehyde molecule needs further investigation, in particular, theoretical modeling and calculation. The interaction of CO_2 with the carbonyl group of benzaldehdye should be weaker because of steric hindrance from the benzene ring, while such steric hindrance is not strong in cinnamaldehyde, because its carbonyl group is not located directly adjacent to the benzene ring. Nelson et al.[25] suggested that a specific interaction between CO_2 and the carbonyl oxygen could be described as a Lewis acid−base reaction; when a steric hindrance is present, the interaction of CO_2 and the carbonyl groups becomes weaker, resulting in a smaller degree of splitting of ν(C═O) of CO_2, which is in agreement with our present results.

3.5. Pressure Effects on Hydrogenation of Aldehydes in Dense CO_2. As described above, the conversion of benzaldehyde simply decreases with CO_2 pressure, while the conversion of cinnamaldehyde has a maximum at a certain CO_2 pressure (Tables 1 and 3). The possible effects, both positive and negative, of CO_2 pressure on the hydrogenation of aldehydes are as follows: (a) dilution of reacting species, (b) modification of the reactivity of the C═O bond, and (c) change of the specific activity of catalyst.

In the case of benzaldehyde, (b) is insignificant from FTIR results and (c) is not significant for the present catalyst used (Table 2). In the experiments of Table 2, the relative quantities of benzaldehyde, H_2, and CO_2 are approximately the same even at different CO_2 pressures. Under these conditions, the influence of the concentration (mole fraction) of reacting species on the conversion of benzaldehyde was insignificant, and we expected to consider independently the influence of CO_2 pressure on the activity of supported Pt particles. On the basis of the results of Tables 1 and 2, we may say that compressed CO_2 does not have a positive effect on enhancement of the catalytic activity. Thus, (a) is the main reason for the simple decrease in the benzaldehyde conversion with CO_2 pressure. At high pressures, there are a CO_2-rich gas phase, in which all benzaldehyde is soluble, and a catalyst solid phase. Increasing the CO_2 pressure merely decreases the concentration of the substrate in the gas phase, resulting in a decrease in the conversion (simple dilution effect). The situation is not simple at low pressures, because the reaction may occur in the benzaldehyde liquid phase and in the CO_2-rich gas phase. When the CO_2 pressure is raised, more benzaldehyde is soluble in the gas phase and more CO_2 and H_2 are soluble in the liquid phase. The solubility of benzaldehyde in the gas phase at low pressures is very small (Figure 1), and so, the reaction is likely to occur mainly in the liquid phase. The dilution of benzaldehyde with dissolved CO_2 and H_2 should be responsible for the decrease in the conversion with CO_2 pressure at low pressures as well.

Next, we will consider (a) and (b) in the case of cinnamaldehyde hydrogenation. The reaction is also likely to occur in the cinnamaldehyde liquid phase at low CO_2 pressures for the same reasons as already mentioned for benzaldehyde. When the CO_2 pressure is raised, the concentration of H_2 in the liquid phase increases because of the dissolution of CO_2, and in addition, the C═O bond of cinnamaldehyde becomes more reactive through interactions with the CO_2 molecule (red-shift increases with CO_2 pressure as illustrated in Figures 2 and 4), resulting in the enhancement of cinnamaldehyde conversion as observed (Table 3). At elevated pressures producing a two-phase mixture, the reaction occurs in a CO_2-gas phase, causing the decrease in the conversion with CO_2 pressure due to the simple dilution effects.

The mole fractions of substrates, H_2, and CO_2 in the reaction mixture were estimated at different CO_2 pressures by a simple calculation. Moles of pure H_2 and CO_2 were calculated by an equation of state, $PV = ZnRT$; the compressibility factor Z was assumed to be unity for H_2, while it was determined as a function of pressure for CO_2.[35] From the moles of pure components determined, the mole fraction was then calculated under the reaction conditions. The results calculated are plotted against CO_2 pressure in Figure 6. The reaction mixture includes liquid and gas phases (in addition to catalyst solid phase) at low pressures, and so, the results are average values within the reactor. At high pressures above 10 MPa, the reaction mixture is a single gas phase, and the concentrations of substrates and H_2 significantly decrease with CO_2 pressure. This should be responsible for the decrease observed in the conversion of hydrogenation of cinnamaldehyde and benzaldehyde at elevated pressures.

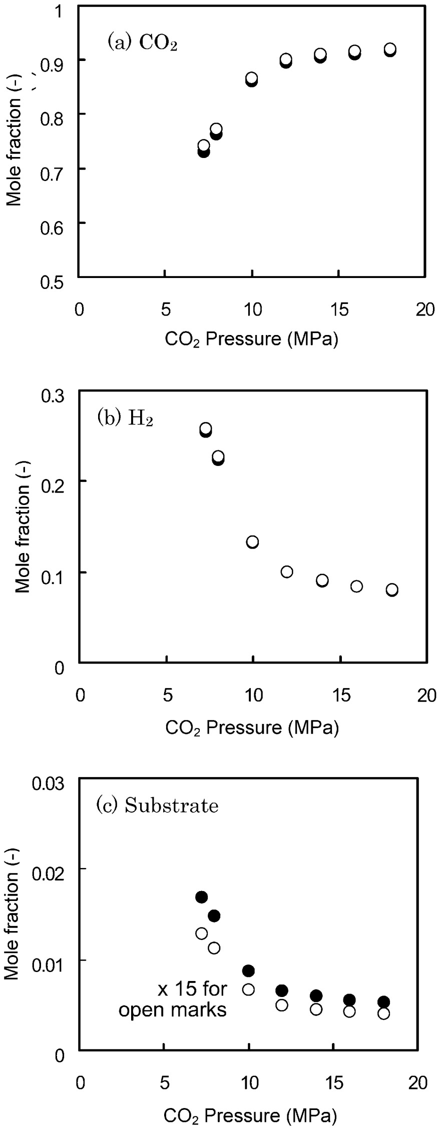


Figure 6. Mole fraction of substrates, H_2, and CO_2 as a function of CO_2 pressure for benzaldehyde−H_2−CO_2 (closed marks) and cinnamaldehyde−H_2−CO_2 (open marks) reaction systems under hydrogenation conditions. Substrate benzaldehyde, 0.25 mmol; cinnamaldehyde, 5.0 mmol; H_2, 4 MPa; temperature, 50 °C.

4. Conclusion

The influence of CO_2 pressure in the hydrogenation of benzaldehyde is significantly different from that of cinnamaldehyde. There are interactions of compressed CO_2 molecules with these two aldehydes. The mode and strength of the interactions are different, and the C═O bond of cinnamaldehyde becomes more reactive, but this promotion effect is less significant with benzaldehyde. Thus, the conversion of benzaldehyde hydrogenation simply decreases with CO_2 pressure because of a dilution effect, while that of cinnamaldehyde hydrogenation has a maximum at a certain pressure depending on the activation of the C═O bond at low pressures and the simple dilution at higher pressures. The specific activity of the Pt/C catalyst is unlikely to be enhanced in the presence of dense CO_2.

Acknowledgment. The authors greatly appreciate financial support for this work from Japan Science and Technology Agency (JST) under a CREST program.

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