

Impact of Carbon Dioxide Pressurization on Catalytic Reactions

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Abstract

The present contribution briefly describes several catalytic reactions in the presence of dense phase CO₂, which the present authors have studied in recent years. The reactions described are hydrogenation reactions of cinnamaldehyde, nitro benzenes and phenol, Heck coupling, and Diels-Alder reactions. Dense phase CO₂ affects the overall reaction rates and/or the reaction selectivity in different modes of manner depending on the reactions examined and the catalysts used. Such effects can be connected with interactions of dense phase CO₂ with the substrate and/or the catalyst. Phase behavior of reaction mixture is also significant for the reactions. The pressurization of liquid reaction mixtures with CO₂ is sometimes more effective than doing the reaction under homogeneous conditions in supercritical CO₂ for accelerating the rate of reaction and modifying the product selectivity.

1. Introduction

In chemicals manufacturing, there is a growing need for processes that produce minimal waste and avoid, as much as possible, the use of toxic and/or hazardous organic reagents and solvents. From this viewpoint, supercritical carbon dioxide (scCO₂) has been gaining considerable interest as an ecologically benign and economically feasible new generation reaction medium, which can replace conventional toxic, flammable organic solvents. It allows various chemical substances to dissolve in it but it simply separates from them by depressurization, and its several other advantages are non-flammability, non-toxicity and absence of a gas-liquid phase boundary^[1-6]. The physicochemical properties of scCO₂ can be tuned within a certain range by adjusting the pressure and temperature, so that the reaction rate and the product selectivity in scCO₂ media can be altered by changing those parameters.

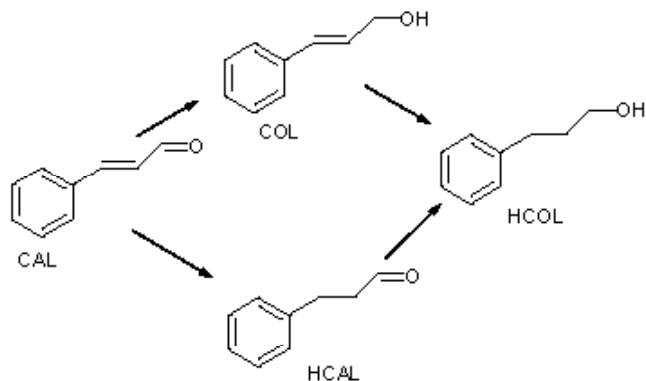
A biphasic mixture of dense phase CO₂ and an organic liquid (solvents or substrates) will often generate a CO₂-dissolved expanded liquid (CXL) phase. When a liquid solvent or substrate phase is pressurized by CO₂, it can expand by dissolution of a large quantity of CO₂. The extent of expansion depends on the nature of the liquid used as well as CO₂ pressure and temperature. In recent years, several groups have demonstrated CXLs are promising reaction media, as Subramaniam et al. already reviewed^[7,8]. CXL will facilitate the dissolution of other coexisting gases and may accelerate the reactions involved with these gaseous reactants although CO₂ is not a reactant but rather a diluent. For reactions in CXLs, there is no concern about the solubility of reacting species in CO₂ gas phase, the catalysts effective in organic or aqueous media may be used without structural modifications, and larger quantities of substrates may be processed. Some promotive effects of scCO₂ solvent may also appear in CXL systems. Although not described in the present paper, CXL will also make the catalyst-product separation easy^[9].

The present authors have studied several catalytic reactions in the presence of dense phase CO₂. It improves the overall reaction

rates and/or the reaction selectivity in different modes of manner depending on the reactions examined and the catalysts used. The present contribution briefly describes those reaction results in connection with interaction of dense phase CO₂ with the substrate and/or the catalyst. It has also been showed that phase behavior of reaction mixtures is sometimes an important factor for the reactions. The described reactions are hydrogenation reactions of cinnamaldehyde, nitro benzenes and phenol, Heck coupling reactions, and Diels-Alder reactions. The last two classes of the reactions do not include any gaseous reactants.

2. Hydrogenation of Cinnamaldehyde

Selective hydrogenation of α,β -unsaturated aldehydes is an important step in producing unsaturated alcohols, which are important intermediates in organic synthesis in fine chemical industries, such as flavor, fragrance and pharmaceutical industry. To get high selectivity to unsaturated alcohol is still an important task. In the case of hydrogenation of cinnamaldehyde (CAL), unsaturated alcohol of cinnamyl alcohol (COL), saturated aldehyde of hydrocinnamaldehyde (HCAL) are produced via the hydrogenations



Scheme 1. Hydrogenation of cinnamaldehyde. CAL: cinnamaldehyde; COL: cinnamyl alcohol; HCAL: hydrocinnamaldehyde; HCAL: hydrocinnamyl alcohol.

of C=O and C=C bonds, respectively. These products are further hydrogenated to hydrocinnamyl alcohol (HCOL). We carried out this reaction with a Pt/C catalyst^[10] or Ru-phosphine complexes^[11,12] in the presence of dense phase CO₂, to investigate the influence of CO₂ pressurization on it.

Fig. 1 shows the influence of CO₂ pressure on cinnamaldehyde (CAL) and benzaldehyde (BAL) hydrogenation reactions with a commercial 5 wt. % Pt/C catalyst. The latter reaction was conducted for comparison. The conversion of BAL merely decreases with CO₂ pressure up to 16 MPa. In contrast to this, the conversion of CAL changes significantly with increasing CO₂ pressure. It increases up to 55% at 10.5 MPa. At CO₂ higher pressures, smaller conversions are obtained. Thus, dense phase CO₂ has only a negative effect on the BAL hydrogenation, while it has a promotive effect on the COL hydrogenation. When N₂ was used instead of CO₂ for the pressurization, the conversions of both BAL and CAL were almost the same with those obtained in the absence of CO₂. Hence, the influence of CO₂ pressure is not a simple static pressure effect. It would arise from the chemical nature of dense phase CO₂.

Under the reaction conditions for Fig. 1, the reaction system changed from solid (catalyst)-liquid-gas three-phase mixture to

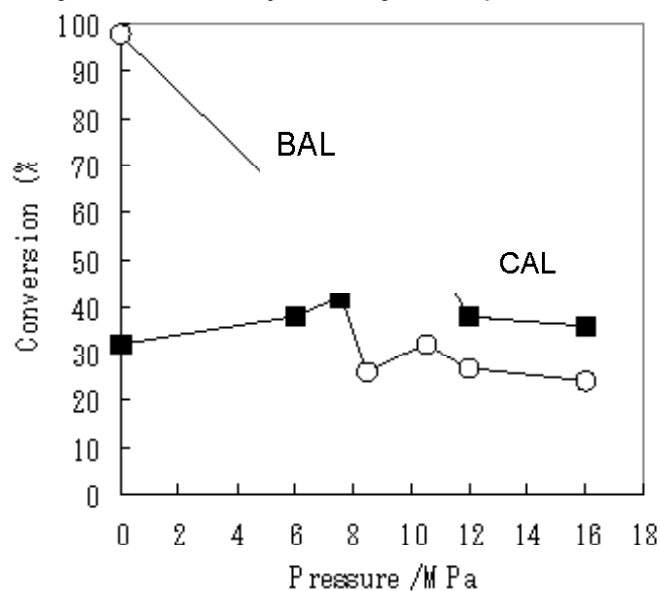


Figure 1 : Influence of CO₂ pressure on CAL and BAL hydrogenations with Pt/C at 50°C. Reaction conditions: reactor, 50 cm³; BAL, 5 mmol; CAL, 0.25 mmol; Pt/C, 0.5 mg (for CAL) and 10 mg (for BAL); H₂, 4 MPa; 50°C; 2 h.

solid-gas two-phase one around 10.5 MPa for both the reactions. The phase behavior cannot explain the difference in the influence of CO₂ pressure. It should also be noted that the maximum of COL conversion was observed at the CO₂ pressure where the phase change occurred.

COL hydrogenation was also conducted with Ru-phosphine complexes. Table I shows reaction results with a Ru complex and phase behavior observations. When the amounts of CAL and the Ru complex are small, the reaction system is a single phase and the selectivity to COL is lower than 30 % (entries 1-3). These COL selectivity values were comparable or lower than those obtained in conventional organic solvents^[13]. Phase behavior is important for the CAL hydrogenation again. When larger amounts of CAL and the

catalyst are used, the reaction system is in a G-L two-phase state, and the selectivity to COL is very high (entries 4, 5). Influence of CO₂ pressure on the reaction was further examined under the G-L two-phase conditions (entries 5-9). In the absence of both CO₂ and organic solvent, conversion is low, but the COL selectivity is high (entry 6). One possible reason for the high COL selectivity would be the high concentration of CAL in the liquid phase^[12]. With increasing CO₂ pressure, both the conversion and the COL selectivity are enhanced, although the extent of enhancement in the selectivity is small. Pressurization with N₂ has again no effect on the reaction (entry 6).

As shown above, pressurization with CO₂ can enhance the CAL conversion under the two-phase reaction system. One factor that should be taken into account for the improvement of conversion

Table I : CAL hydrogenation with Ru complex

Entry	Ru (μmol)	CAL (mmol)	CO ₂ (MPa)	Conversion (%)	Selectivity (%)			Phase
					COL	HCAL	HCOL	
1	0.075	0.2	10	21	25	48	27	G
2	0.15	0.2	10	22	23	51	26	G
3	0.68	0.2	16	55	24	50	26	G ^a
4	25	7.5	16	11	93	7	0	G, L
5	50	7.5	16	54	98	1	1	G, L
6	50	7.5	0	11	88	9	3	G, L
7	50	7.5	8.5 (N ₂) ^c	12	88	10	2	G, L
8	50	7.5	8.5	24	91	7	2	G, L
9	50	7.5	14	31	93	6	1	G, L

Reaction conditions: Ru/ligand (ligand: bis(pentafluorophenyl) phenylphosphine) = 1/3; reactor, 50 cm³; H₂, 4 MPa; temperature, 50°C; time, 2 h.

^a G: CO₂-rich gas phase; L: CAL-rich liquid phase.

^b Very small droplets of CAL and/or catalyst were observed.

^c N₂ was used instead of CO₂.

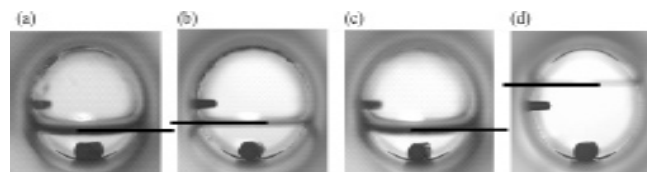


Figure 2 : Phase behavior of CAL and BAL liquid phase under pressurized CO₂ at 50°C. (a) CAL under 0.1 MPa of CO₂, (b) CAL under 16 MPa of CO₂, (c) CAL under 0.1 MPa of CO₂ and (d) BAL under 9.5 MPa of CO₂.

The amounts of CAL and BAL used were 2 cm³. The volume of view cell was 10 cm³. Note that the amounts of aldehydes and the substrate/reactor volume ratio were different from those for the reaction runs for Fig. 1 and Table I.

would be H₂ concentration in the CAL liquid phase, because the CAL phase expanded by CO₂ pressurization (Fig. 2 a and b), i.e. CXL, and this can enhance the dissolution of H₂ in it^[9]. Another possible factor is molecular interactions of CO₂ with the substrate. In a CO₂ molecule, the carbon atom is partially positive. So, it can interact with the oxygen atom of carbonyl group. The authors have recently reported a systematic FTIR study on molecular interactions of CO₂ with various carbonyl compounds of esters, ketones, and amides, which depend on their structures and CO₂ pressure^[14]. Fig. 3 illustrates FTIR spectra of CAL in dense phase CO₂. The spectra show strong absorption band of ν(C=O) and weak band of ν(C=C). The former band gradually red-shifts to smaller wavenumbers with increasing CO₂ pressure, while the position of the latter band does not change by the pressure. Thus, only the

reactivity of the C=O group is increased by CO₂ pressurization, resulting in the improvement in the CAL conversion. Furthermore, this can also enhance the selectivity to COL. For comparison, similar FTIR measurements were made for BAL and HCAL. Fig. 4 compares the band positions of $\nu(\text{C}=\text{O})$ bands of these aldehyde compounds. It is clear that the observed red-shift by CO₂ pressurization is the largest with CAL. The conjugation of C=C-C=O in CAL is important for the interactions between the CO₂ molecule and the C=O bond compared with the non-conjugated molecules of BAL and HCAL. Similar interactions would also occur in CO₂-dissolved expanded CAL liquid phase. Unfortunately, however, spectroscopic measurements of such interactions are difficult at present. The liquid phase expansion was also measured for BAL (Fig. 2 c and d). Even at a lower CO₂ pressure of 9.5 MPa, the expansion of BAL liquid phase is more significant than that of CAL at 16 MPa. Probably, there are promotional effects caused by the interactions between dissolved CO₂ and BAL, but they would be overcome by a simple dilution effect by CO₂ dissolution due to large extent of expansion, resulting in the simple decrease of BAL conversion, as shown in Fig. 1.

As shown in this section, when the CAL hydrogenation was carried out under CXL conditions, overall reaction rates and selectivity to COL obtained were higher than those obtained in homogeneous scCO₂ systems. Under the conditions of CXL in our studies, the

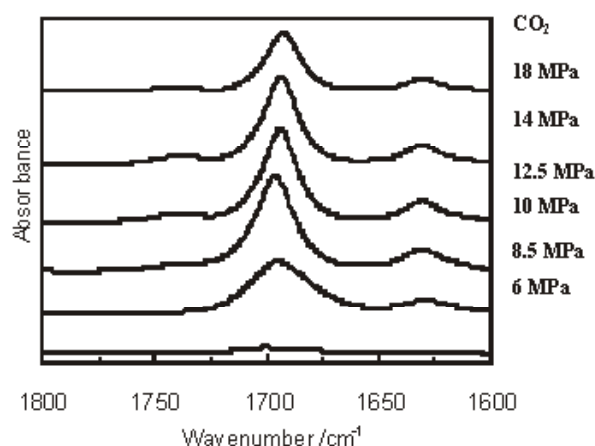


Figure 3 : FT-IR spectra of CAL dissolved in compressed CO₂ at different pressure at 50°C.

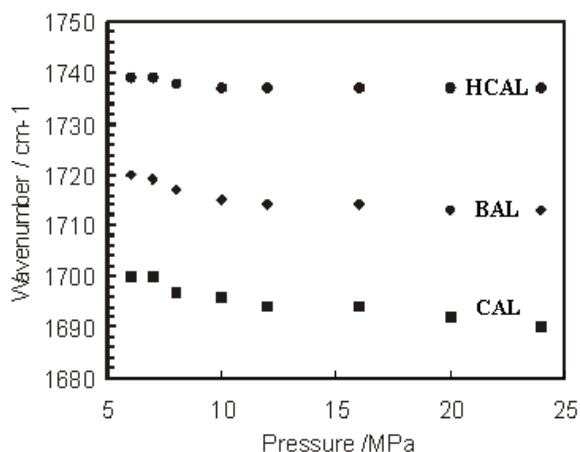


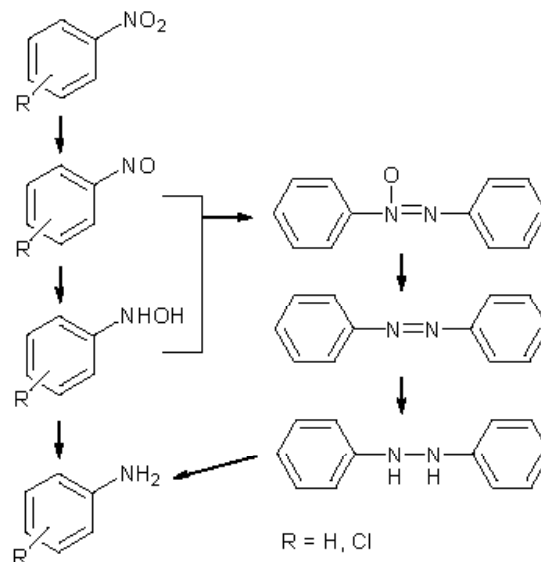
Figure 4 : Influence of CO₂ pressure on the peak positions of $\nu(\text{C}=\text{O})$ of CAL, HCAL and BAL at 50°C.

reaction locus is the CAL liquid phase. Recently, Zhao et al. reported the selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols with a Ru complex under compressed CO₂/PEG and CO₂/cyclohexane biphasic conditions^[15]. They also observed the improvement in the overall reaction rates and the selectivity to unsaturated alcohol by increasing CO₂ pressure. Thus, CXL systems are better reaction media for the reaction even in the presence of organic solvents.

3. Hydrogenation of Aryl Nitro Benzenes

The catalytic hydrogenation of nitro benzenes is commonly used to manufacture anilines, which are important intermediates for polyurethanes, dyes, pharmaceuticals, explosives, and agricultural products. In industrial processes, the reaction is generally carried out in the vapor phase over copper catalysts above 240°C. It can also be performed in the liquid phase by using noble metals (Pt and Pd) and organic solvents under milder conditions^[16, 17]. However, their use in large-scale production has not been practiced extensively due to their high costs. Furthermore, they sometimes show low selectivity to aniline because of the formations of several poisonous reaction intermediates. The formation and accumulation of these undesired intermediates should be avoided for the green production of anilines. Thus, it remains to be a challenging task to achieve selective hydrogenation of aryl nitro compounds to anilines. Under these circumstances, we examined hydrogenation of nitrobenzene (NB) and chloronitrobenzene (CNB), respectively, to aniline (AN) and chloroaniline (CAN) with supported Ni catalysts in the presence of pressurized CO₂^[18, 19]. Possible reaction pathways for these reactions are illustrated in Scheme 2. For the latter reaction, to avoid the formation of AN from CAN is also an important issue for practical application.

Table 2 shows influence of reaction media and catalysts. In ethanol, the selectivity to AN obtained with Ni/Al₂O₃ is not so high because of the formations of nitrosobenzene (NSB), N-phenylhydroxylamine (PHA), azoxybenzene (AOB), and azobenzene (AB) intermediates. As a reaction medium, scCO₂ is much better than ethanol. Higher



Scheme 2. Hydrogenation of Nitrobenzene and Chloronitrobenzene.

values of the conversion and the selectivity to AN are obtained in scCO_2 than in ethanol. Pt/C is more active than Ni/Al₂O₃. The conversion with Pt/C is higher even at a lower temperature (35°C) with a smaller catalyst amount (5 mg) than Ni/Al₂O₃ (50°C, 100 mg). However, the selectivity to AN is lower because of the intermediate formations that were observed in ethanol with Ni/Al₂O₃.

Fig. 5 shows the influence of CO₂ pressure on the total conversion of NB over Ni/Al₂O₃ at 35°C and 50°C. At 50°C, the conversion is maximal around 12 MPa but, at 35°C, a maximum conversion appears at a lower pressure around 9 MPa. Phase behavior of NB liquid was visually investigated. At 35°C, the NB liquid gradually

Table 2 : Hydrogenation of NB in scCO_2 and ethanol with Ni/Al₂O₃ and Pt/C catalysts.

Catalyst	Medium	Conversion (%)	Selectivity (%)	
			AN	Byprod. ^a
Ni/Al ₂ O ₃	Ethanol	25	81	19
	scCO_2	68	>99	<1
Pt/C ^b	scCO_2	72	75	25

Reaction conditions: reactor, 50 cm³; catalyst, 0.1 g; NB, 19.6 mmol; CO₂, 12 MPa; ethanol, 10 cm³; H₂, 4 MPa; temperature, 50°C; time, 50 min.

^a Byproducts mainly consist of NSB, AOB, PHA and AB.

^b Pt/C, 0.005 g, 35°C, 25 min, CO₂ 9 MPa.

expanded with introduction of CO₂ (CXL), and transformed into a single gas phase around the CO₂ pressure where the maximum conversion was observed. At 50°C, similar results were obtained. The increases in the conversion under CXL conditions would be ascribed to the enhancement of H₂ dissolution into NB liquid phase. Almost 100% selectivity to AN remained unchanged when the reaction mixture changed from G-L-S three-phase system to G-S two-phase system. It should be noted that, when the reaction was carried out in/under dense phase CO₂ for various periods of reaction time, the excellent selectivity to AN could be obtained for the whole range of total conversion irrespective of CO₂ pressures and temperatures.

Hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) was also conducted with Pt/C, Pd/C, Ni/Al₂O₃ and Ni/TiO₂. For Ni/TiO₂, ethanol was also used as the reaction solvent. Table 3 summarizes the reaction results obtained. Pt/C and Pd/C give very high conversions in scCO_2 . However, the selectivity to CAN is

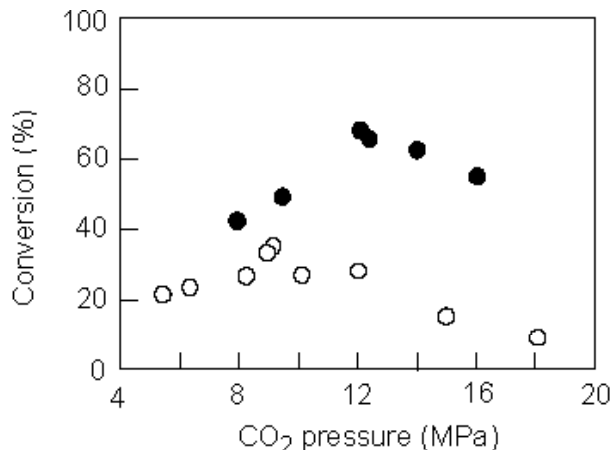


Figure 5 : Influence of CO₂ pressure on the conversion of NB over Ni/Al₂O₃ at 35°C and 50°C.

not satisfactory because of the formations of chloronitrosobenzene (CNSB), chloroazoxybenzene (CAOB), chloroazobenzene (CAB) and aniline (AN). The last byproduct is formed by dechlorination. Although the supported Ni catalysts are less active than Pt/C and Pd/C, they give excellent values of selectivity to CAN (entries 3 and 4). The highest selectivity to CAN is obtained with Ni/TiO₂. However, when this catalyst is used in ethanol, the selectivity is much lower (entry 5). As a reaction solvent, scCO_2 is better again than ethanol.

The reaction results described above show that the combination of supported Ni catalysts and scCO_2 gives excellent reaction systems for selective hydrogenation reactions of BN and CBN. Particularly, the presence of dense phase CO₂ is an important factor to get high selectivity to AN compounds. This is considered to arise from

Table 3 : Results of *o*-CNB hydrogenation using different catalysts in scCO_2 and in ethanol.

Entry	Catalyst	Amount (g)	Time (min)	Conversion (%)	Selectivity (%)		
					<i>o</i> -CAN	AN	Other ^a
1	Pt/C	0.01	30	100	77	<1	>22
2	Pd/C	0.01	30	100	<97	3	<1
3	Ni/Al ₂ O ₃	0.1	60	78	>98	<1.5	<0.5
4	Ni/TiO ₂	0.15	50	78	>99.5	<0.5	—
5	Ni/TiO ₂ ^b	0.15	50	36	70	—	30

Reaction conditions: reactor 50 cm³, *o*-CNB 1.5 g (9.52 mmol), H₂ 4 MPa, CO₂ 9 MPa, 35°C.

^a Others include CNSB with trace amounts of CAOB, CAB, and CHAB.

^b in 10 cm³ of ethanol

the interactions of CO₂ with the reacting species. To study the interactions of CO₂ with NB, NSB and PHA, their FTIR spectra were collected in the presence of 4 MPa of H₂ and 0-20 MPa CO₂.

- 1) In the spectra of NB in dense phase CO₂, the peaks of symmetric and asymmetric stretching vibrations of nitro group, $\nu_s(\text{NO}_2)$ and $\nu_{as}(\text{NO}_2)$, appeared at different wavenumbers depending on CO₂ pressure. The shifts of these peaks are illustrated in Fig. 6. The peak positions of both $\nu_s(\text{NO}_2)$ and $\nu_{as}(\text{NO}_2)$ are blue-shifted with CO₂ pressure up to 6 MPa as compared to those of the gas phase. At higher pressures up to 20 MPa, these peak positions are slightly shifted to a lower wavenumber and then scarcely change. The absorption bands of nitro group in dense phase CO₂ at 20 MPa are located at larger wavenumbers than those in the ambient gas state and in the liquid state (neat and in ethanol). These FTIR results indicate that the N–O bond of nitro group becomes stronger in the presence of dense phase CO₂ compared to the ambient gas and liquid conditions.
- 2) In the spectra of NSB in dense phase CO₂, the peak of N=O stretching vibrations of nitroso group, $\nu(\text{N=O})$, red-shifted with increasing CO₂ pressure (Fig. 7). In a reverse manner, the stretching band of C–N bond was blue-shifted by CO₂ pressurization. Hence, it can be concluded that the reactivity of nitroso group is enhanced by CO₂ pressurization, in contrast to the reactivity of nitro group of NB.
- 3) In the spectra of PHA in dense phase CO₂, no shift of the N–O stretch band was observed. However, the ring-stretching band

split and red-shifted at higher CO_2 pressures, suggesting the occurrence of the interactions between CO_2 and PHA. Such spectral change cannot directly be correlated with the change in the reactivity of NHOH group of PHA; however, the reactivity may be altered by pressurized CO_2 through its interactions with the phenyl ring.

On the basis of the reaction pathways (scheme 2), the FTIR results can quantitatively explain the high AN selectivity obtained in the presence of dense phase CO_2 . NB is hydrogenated to NSB (step 1), which is further transformed to PHA (step 2). AN is formed by the hydrogenation of PHA (step 3). FTIR suggested dense phase CO_2

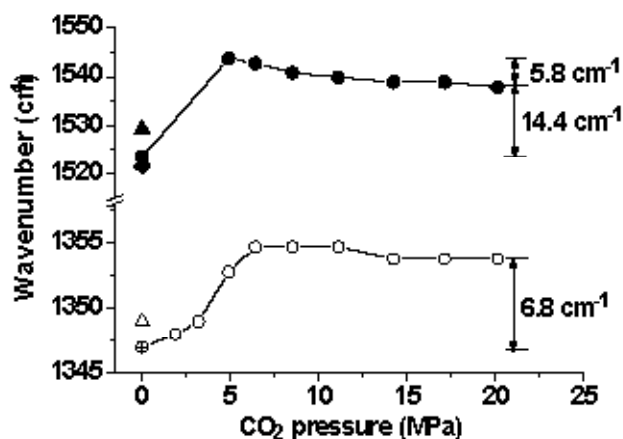


Figure 6 : FTIR results of the nitro group vibration for NB. (o) Symmetric and (●) asymmetric stretching vibrations in dense phase CO_2 at 50°C ; (+) symmetric and (◆) asymmetric stretch in liquid phase; (Δ) symmetric and (▲) asymmetric stretch in a mixture of NB and ethanol (NB / ethanol = 0.2, v / v) at room temperature.

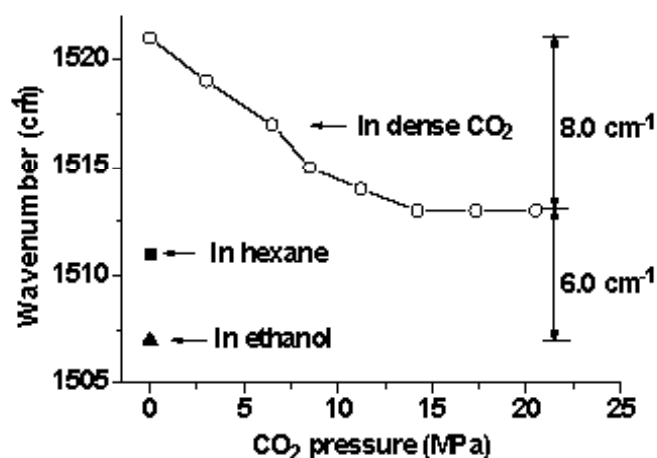


Figure 7 : Influence of CO_2 pressure on the peak position of nitroso group (O-interacted) vibration for NSB at 50°C . Also shown are the same group vibration in hexane (NSB saturated hexane) and in ethanol (NSB / ethanol = 0.11, molar ratio) at room temperature.

lowers the reaction rate of step 1. On the other hand, step 2 and 3 were suggested to be promoted by CO_2 . Hence, step 1 would be the rate determining step for the overall reaction rate of NB hydrogenation to AN in the presence of CO_2 . Because of this, the amounts of NSB and PHA in the reaction system would be lowered, resulting in the decrease of the formation of AOB, which is formed via the coupling of NSB and PHA. Thus, the high selectivity to AN is obtained in the presence of pressurized CO_2 .

As shown in this section, the combination of Ni catalysts with dense phase CO_2 can give excellent systems for the selective hydrogenation of aryl nitro compounds to aniline products.

4. Hydrogenation of Phenol

Catalytic hydrogenation of phenol is industrially important for the synthesis of cyclohexanone and cyclohexanol as the intermediate for the manufacture of nylon-6 and -66^[20]. Generally, the hydrogenation of phenol is carried out in the vapor phase over supported Pd catalysts^[20]. In the cases of vapor phase hydrogenation, high temperatures are needed, which usually cause catalyst deactivation by coking during the reaction. In a few studies, liquid phase hydrogenation of phenol was carried out with Pd catalysts^[21,22]. However, high reaction temperatures or long reaction time were still required to obtain high phenol conversions. A few research groups investigated this reaction in/under dense phase CO_2 . Rode et al.^[23] showed that a charcoal-supported rhodium (Rh/C) catalyst was highly active for the ring hydrogenation of phenol and cresols in scCO_2 , and high conversions of phenol were achieved over Rh/C under such conditions as 328 K, 10 MPa H_2 and 12 MPa CO_2 . Carbon supported Pd, Ru and Pt catalysts were much less active than Rh/C. Our group has also reported that a Rh catalyst supported on carbon nanofiber is active for the phenol hydrogenation in scCO_2 at a low temperature of 323 K and at a lower hydrogen pressure of 4 MPa^[24]. Thus, Rh catalysts supported on carbon materials are highly active for the phenol hydrogenation in scCO_2 . However, detail of this reaction system was still unknown. This led us to the initiation of further study on phenol hydrogenation in/under dense phase CO_2 ^[25].

Fig. 8 represents the variations of the phenol conversion and the product yields with reaction time obtained using Rh/C in the absence and presence of 16 MPa CO_2 . Fig. 8a indicates that the yield of cyclohexanone increases with time and then decreases through a maximum at around 30 min, while that of cyclohexanol increased monotonically in the absence of CO_2 . Similar trends were also observed in the presence of CO_2 at 16 MPa (Fig. 8b) and lower pressures. In Fig. 9, the selectivity to cyclohexanone is plotted against the phenol conversion. At zero phenol conversion, the selectivity to cyclohexanone is around 60% irrespective of CO_2 pressures used. When the conversion increased up to 70%, the selectivity to cyclohexanone gradually decreased. The presence of pressurized CO_2 has no effect on the product selectivity at conversions between 0 and 70%. At larger conversions, however, the selectivity to cyclohexanone decreases rapidly with the conversion in the absence of CO_2 , whereas the selectivity also decreases in the presence of CO_2 but gradually similar to the change at lower conversions. The selectivity to cyclohexanone at 100% conversion was < 10% in the absence of CO_2 but about 40% in the presence of CO_2 at 4-16 MPa. As a result, the selectivity to cyclohexanone obtained in the presence of CO_2 was always higher irrespective of CO_2 pressures than that in the absence of CO_2 .

As shown in Fig. 8, the yield of cyclohexanone was maximal in the course of the reaction with Rh/C, whereas that of cyclohexanol increased monotonously with time and it was likely to form at the expense of cyclohexanone in the latter stage of reaction. Similar results were obtained with Rh/ Al_2O_3 in the absence of CO_2 (shown

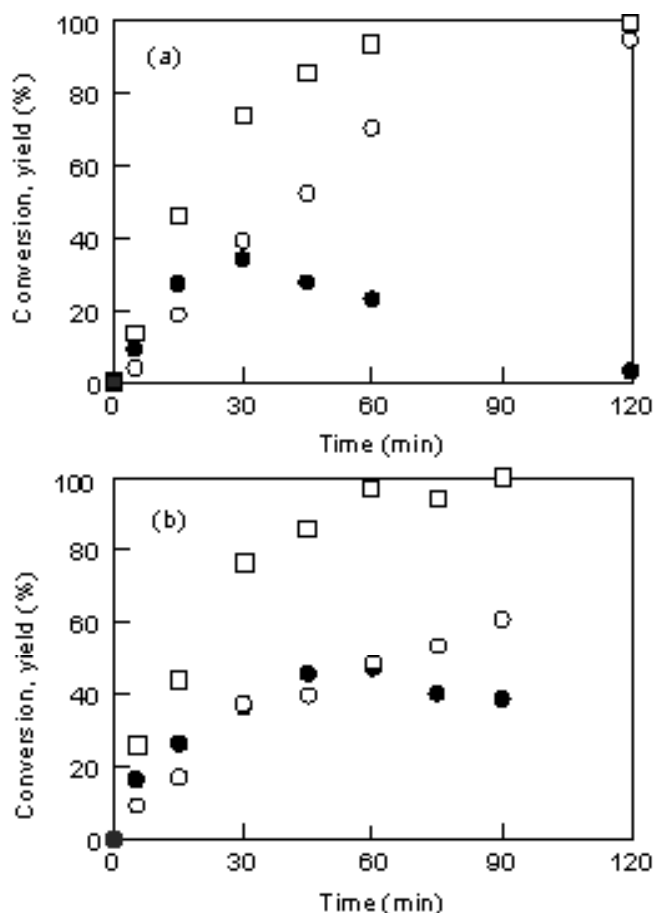


Figure 8. Variations of phenol conversion (\square) and yields of cyclohexanone (\bullet) and cyclohexanol (\circ) with time over Rh/C (a) in the absence of CO₂ and (b) in the presence of 16 MPa CO₂. Reaction conditions: Rh/C, 10 mg for (a) and 20 mg for (b); phenol, 10.6 mmol; H₂, 4 MPa; temperature, 323 K.

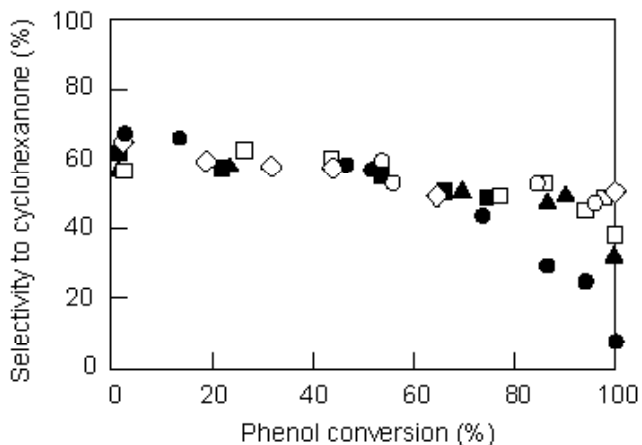
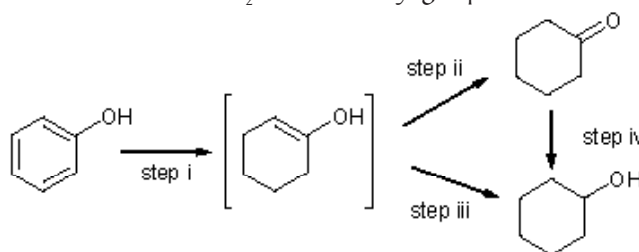


Figure 9: Influence of CO₂ on the relationship between selectivity to cyclohexanone and phenol conversion over Rh/C. CO₂ pressure = 0 (\bullet), 4 (\blacktriangle), 8 (\blacksquare), 11 (\circ), 14 (\diamond) and 16 MPa (\square).

later). These results strongly suggest that cyclohexanol is formed through the hydrogenation of cyclohexanone. If cyclohexanol was always produced by the hydrogenation of cyclohexanone, the selectivity to cyclohexanone would be 100% at zero conversion; however, this is not the case, as shown in Fig. 9. It is assumed, therefore, that cyclohexanone and cyclohexanol are produced through parallel pathways at low conversion levels. On the basis of these results, it can be concluded that the phenol hydrogenation

proceeds through the pathways illustrated in Scheme 3. The ring of phenol is sequentially hydrogenated to produce cyclohexenol (step i), which is isomerized to one product cyclohexanone (step ii) or further hydrogenated to the other product cyclohexanol (step iii). The cyclohexanol may also be produced via the hydrogenation of cyclohexanone (step iv). Based on the reaction scheme, one can conclude that dense phase CO₂ retards step iv, resulting in the higher selectivity to cyclohexanone at large conversion levels in the presence of CO₂ (Fig. 9).

However, FTIR measurements suggested that the reactivity of the C=O group of cyclohexanone was enhanced by dense phase CO₂. The absorption band of $\nu(\text{C}=\text{O})$ red-shifted with CO₂ pressure (Fig. 10). This red-shift would result from Lewis acid - base type interactions between CO₂ and its carbonyl group, as discussed for



Scheme 3: Hydrogenation of Phenol.

CAL hydrogenation. Other absorption bands due to C-H and C-C bonds were not observed to be shifted with CO₂ pressure. Thus, the retardation effects of CO₂ would arise from other reasons. One possible reason for the retardation effect of CO₂ can be the formation of adsorbed CO.

Similar reaction runs were also carried out with Rh/Al₂O₃ catalyst for comparison. Fig. 11 represents the variations of the phenol conversion and the product yields with time in the absence of CO₂. The yield of cyclohexanone showed a maximum at around 30 min, whereas that of cyclohexanol increased monotonically with time.

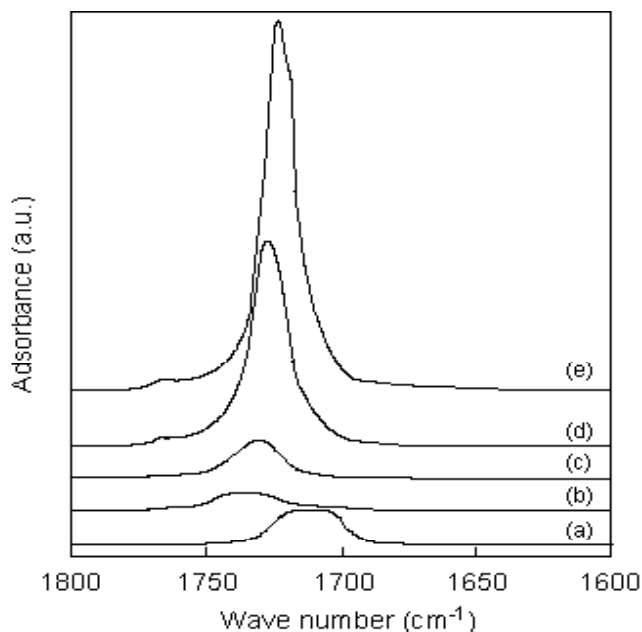


Figure 10. FT-IR spectra of cyclohexanone. (a), liquid; (b), gas; (c) in 4 MPa CO₂; (d), in 8 MPa CO₂; (e), in 16 MPa CO₂. Spectra c, d and e were measured in the presence of 4 MPa H₂.

Thus, the results obtained in the absence of CO_2 with $\text{Rh}/\text{Al}_2\text{O}_3$ were very similar to those obtained with Rh/C (Fig. 8). When the reaction was conducted in the presence of CO_2 , different results were obtained. Fig. 12 gives the results obtained at CO_2 pressures at 8 and 14 MPa, indicating that the hydrogenation reaction of phenol stopped in an early stage of reaction. That is, the activity of $\text{Rh}/\text{Al}_2\text{O}_3$ was rapidly and completely lost during the reaction. Note that the reaction stopped in about 30 min at 8 MPa but in a shorter time of 5 min at a higher pressure of 14 MPa.

For the purpose of obtaining direct evidence for the formation of adsorbed CO in the mixture of compressed CO_2 and H_2 , the authors made a stainless steel cell with ZnSe windows for in situ transmittance FTIR measurements at high pressures. Fig. 13 shows the FTIR spectra in the C–O stretching region for Rh/C

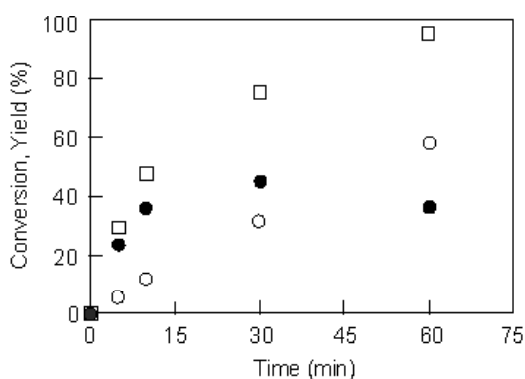


Figure 11 : Variations of phenol conversion (□) and yields of cyclohexanone (●) and cyclohexanol (○) with time over $\text{Rh}/\text{Al}_2\text{O}_3$ in the absence of CO_2 . Reaction conditions: $\text{Rh}/\text{Al}_2\text{O}_3$, 10 mg; phenol, 10.6 mmol; H_2 , 4 MPa; temperature, 323 K.

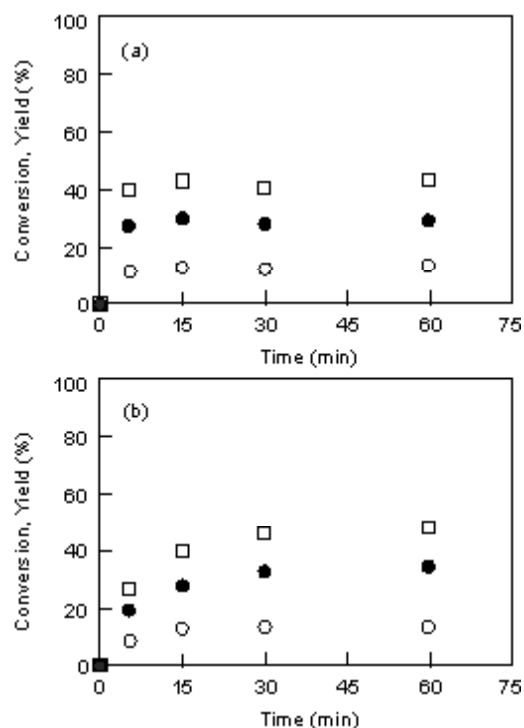


Figure 12. Variations of phenol conversion (□) and yields of cyclohexanone (●) and cyclohexanol (○) with time over $\text{Rh}/\text{Al}_2\text{O}_3$ in the presence of CO_2 at (a) 14 MPa and (b) 8 MPa. Reaction conditions: $\text{Rh}/\text{Al}_2\text{O}_3$, 50 mg; phenol, 10.6 mmol; H_2 , 4 MPa; temperature, 323 K.

and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts collected in the presence and absence of 16 MPa CO_2 . In the presence of CO_2 and H_2 , Rh/C indicated the adsorption bands of adsorbed CO at 2069 cm^{-1} , 2048 cm^{-1} and 1945 cm^{-1} (spectrum a). The former two bands and the last one can be ascribed to linearly and bridged adsorbed CO over Rh metal, respectively. On the other hand, $\text{Rh}/\text{Al}_2\text{O}_3$ exhibited the absorption bands at 2069 cm^{-1} , 2020 cm^{-1} and 1844 cm^{-1} (spectrum c). The bands at 2020 cm^{-1} and 1844 cm^{-1} can be assigned to linearly and bridged adsorbed CO, respectively, which were located at smaller wavenumbers from those observed over Rh/C . From the difference in the peak position of C–O vibration between Rh/C and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts, the adsorption of CO is assumed to be stronger on $\text{Rh}/\text{Al}_2\text{O}_3$ than on Rh/C . This was also indicated by the spectral change on the depressurization. When the pressure was reduced to atmospheric pressure, those CO absorption bands disappeared for Rh/C (spectrum b) but, in contrast, the corresponding absorption bands at 2020 and 1844 cm^{-1} still remained for $\text{Rh}/\text{Al}_2\text{O}_3$ (spectrum d). Those FTIR results gives direct evidence for the formation and adsorption of CO on the surface of supported Rh particles in the pressurized gaseous mixture of H_2 (4 MPa) and CO_2 (16 MPa). It is also confirmed that the adsorbed CO species exist on both Rh/C and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts under pressurized CO_2 conditions and these disappear on the depressurization for the former but still remain even at atmospheric pressure for the latter. That is, the stability of adsorbed CO species is significantly different between the two Rh/C and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts. As shown above, the reaction with $\text{Rh}/\text{Al}_2\text{O}_3$ in the presence of CO_2 stopped in a short period of reaction time, while 100% phenol conversion was obtained with Rh/C even in the presence for CO_2 . Considering the FTIR results, the difference in the reaction results between Rh/C and $\text{Rh}/\text{Al}_2\text{O}_3$ can be ascribed to the differences in the amounts and the stability of adsorbed CO species, which retard the reaction. This would also result in the higher selectivity to cyclohexanone in the presence of CO_2 .

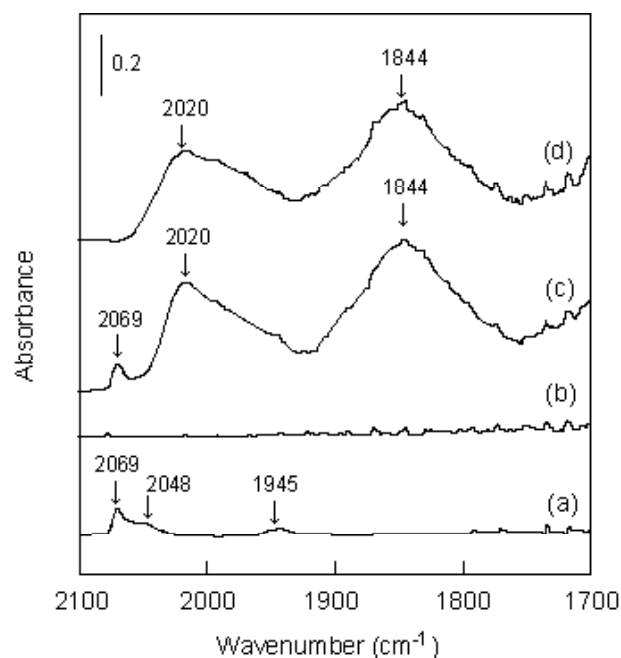
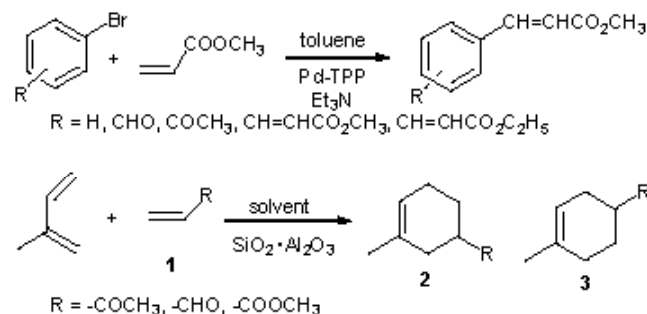


Figure 13 : FT-IR spectra of Rh/C (a, b) and $\text{Rh}/\text{Al}_2\text{O}_3$ (c, d). Spectra a and c were measured in the presence of 16 MPa CO_2 and 4 MPa H_2 , and spectra b and d were measured after depressurization of the IR cell to an ambient pressure.

5. Heck Coupling and Diels-Alder Reactions

As shown in the foregoing sections, pressurized CO₂ influences the hydrogenation reactions in different modes of manner depending on the reaction and the catalyst. It is also interesting to investigate whether the potential of CO₂ pressurization appears for liquid phase reactions including no gaseous reactants. So, we carried out Heck and Diels-Alder reactions in organic solvents (Scheme 4) in the presence of dense phase CO₂ [26].

At first, Heck coupling of methyl acrylate with various bromobenzenes with a Pd-TPP catalyst in toluene was examined. Fig. 14 shows the influence of CO₂ pressurization on the reactions of 2-, 3- and 4-isomers of bromoacetophenones with methylacrylate. The conversion increases with the pressure in a range up to 3 MPa for 2-bromoacetophenone. The maximum conversion is larger by a



Scheme 4 : Heck coupling and Diels-Alder reactions.

factor of 3 compared with that under ambient pressure. However, such promotional effect is marginal or absent with the other two isomers. Similar results were obtained with methyl bromocinnamates (Fig. 15). On the other hand, with the other aryl bromo compounds (R = H, CHO, CH=CHCO₂CH₃), a significant or marginal decrease in conversion was observed with CO₂ pressurization. Thus, the promotional effect is limited to a few selected bromobenzenes depending on their structures.

The liquid reaction mixtures were found to be simply expanded by

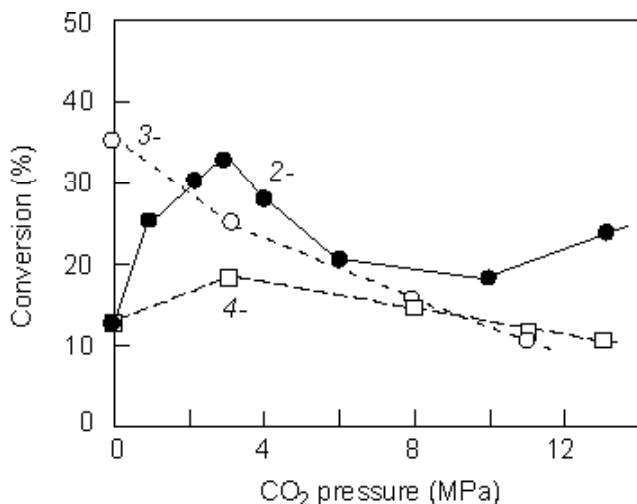


Figure 14 : Influence of CO₂ pressurization on the Heck reactions of 2-, 3-, 4-isomers of bromoacetophenones with methyl acrylate. Reaction conditions: bromoacetophenone 10 mmol, methyl acrylate 10 mmol, Pd(OAc)₂ 0.1 mmol, TPP 0.4 mmol, triethylamine 10 mmol, toluene 10 cm³, temperature 393 K, time 2 h.

CO₂ pressurization. Two phase condition was kept up to 14 MPa CO₂ pressure. According to the literature [27], the overall reaction rate significantly decreases with the dilution of the substrates, catalyst and amine (caused by the expansion). Hence, the interactions of dissolved CO₂ and the substrates (aryl bromo compounds) would overcome such dilution effect, at least for 2-bromoacetophenone

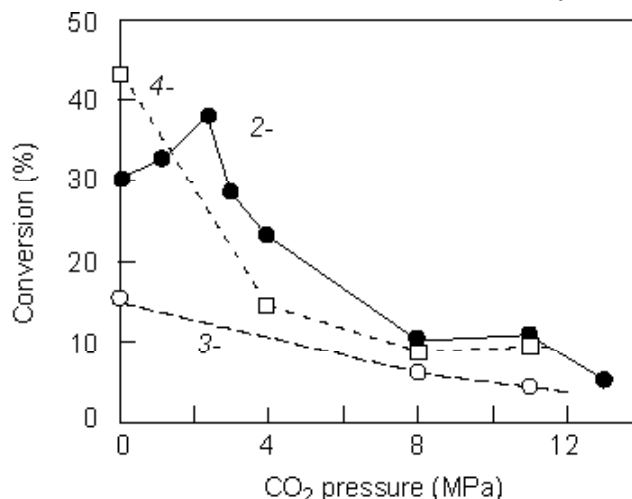


Figure 15 : Influence of CO₂ pressurization on the Heck reactions of 2-, 3-, 4-isomers of ethyl bromocinnamate with methyl acrylate. Reaction conditions: ethyl bromocinnamate 10 mmol, methyl acrylate 10 mmol, Pd(OAc)₂ 0.1 mmol, TPP 0.4 mmol, triethylamine 10 mmol, toluene 10 cm³, temperature 393 K, time 2 h.

and ethyl 2-bromocinnamate. FTIR measurements were used to examine the interaction of CO₂ with bromoacetophenones. The peak position of ν(C=O) absorption of 2-bromoacetophenone changes with CO₂ pressure in a different manner as compared with those of 3- and 4-bromoacetophenones (Figure 16). The ν(C=O) absorption band of the former substrate in dense phase CO₂ appeared at larger wavenumbers by 7–10 cm⁻¹ than those of the latter two ones. Dissociation of C-Br bond is important for Heck reactions, because it is required for initiating the reaction [28]. Unfortunately it is difficult to examine the C-Br bond of aryl bromides due to the limitation of the FT-IR apparatus used. However, it is probable that the C-Br bonds of the three substrates are modified by the presence of dense phase CO₂, indirectly through interactions of CO₂ with the other moieties or directly with the C-Br moiety. In addition, the modification for 2-bromoacetophenone should be different from that of 3- or 4- bromoacetophenone.

The impact of CO₂ pressurization was also studied for a different reaction system, the Diels-Alder reaction with a heterogeneous SiO₂·Al₂O₃ catalyst, which was a liquid-solid biphasic system including no gaseous reactant. Figure 17 represents the results obtained with three different carbonyl compounds (dienophiles). Unfortunately, the conversion was observed to merely decrease with the CO₂ pressure. This simple decrease of the conversion should result from a simple dilution effect of CO₂ molecules into the liquid phase at high pressures. One may consider another possibility that CO₂ molecules are adsorbed on the surface of the SiO₂·Al₂O₃ catalyst and this may mask the catalytically active sites and decrease the total activity.

The reaction runs were also conducted with methyl acrylate or acrolein in ethanol instead of toluene. Although toluene and

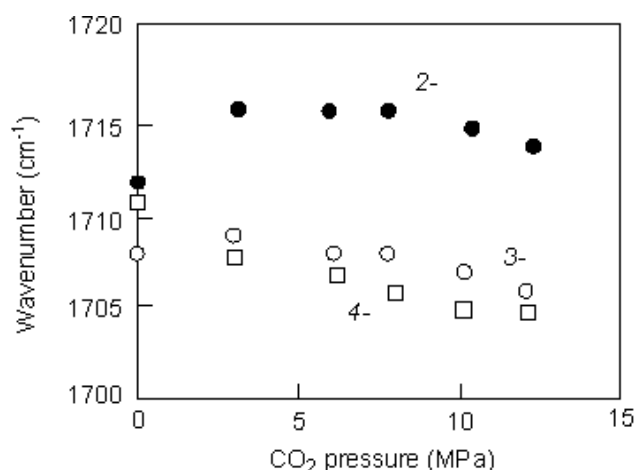


Figure 16. Dependence of $\nu(\text{C}=\text{O})$ absorption peak position on CO_2 pressure for 2-, 3-, 4-bromoacetophenones.

ethanol are different in solvent properties, the results of Diels–Alder reactions in these organic solvents were similar for the ester methyl acrylate. For the aldehyde acrolein, however, the conversion in ethanol was larger as compared with those in toluene.

Table 4 summarizes the product selectivity at different CO_2 pressures in the Diels–Alder reactions of isoprene with the three dienophiles. The results show that the ratio of para adduct 3 to meta adduct 2 can be altered by the CO_2 pressure, and the extent of change is large at around the critical pressure of pure CO_2 . The ratio changes most extensively from 47:53 to 73:27 at pressures up to 16 MPa for acrolein. The change is less significant for the other dienophiles but the ratio does also change from 63:37 to 73:27 and from 70:30 to 75:25 for methyl vinyl ketone and methyl acrylate, respectively, in the same pressure range. In other words, the ratio of 3 to 2 and the effect of CO_2 pressure on this ratio are larger in the order of acrolein > methyl vinyl ketone > methyl acrylate. This ratio for acrolein is again larger in ethanol than in toluene.

The enhancement of Diels–Alder reactions by solvent effects in hydrogen-bonded donor (HBD) solvents is known with carbonyl-containing reactants and the hydrogen bonding between the substrate and the solvent, $\text{C}=\text{O}\cdots\text{H}-\text{O}-\text{R}$, is significant in accelerating the reactions. Such a hydrogen bond may also cause the increase of the 3 to 2 ratio in ethanol. FTIR measurements of dienophiles dissolved in CO_2 at different pressures revealed the presence of interactions between CO_2 and $\text{C}=\text{O}$. In conformity with the reaction results on

Table 4 : Influence of CO_2 pressure on the selectivity of Diels–Alder reactions of isoprene with methyl acrylate, methyl vinyl ketone, and acrolein

CO_2 pressure (MPa)	Product selectivity (para:meta ratio)		
	Methylacrylate	Methylvinyl ketone	Acrolein
0.1	70 : 30 (71:29) ^a	63 : 37	47 : 53 (68 : 32) ^a
4	70 : 30 (71:29) ^a	66 : 34	55 : 45 (69 : 31) ^a
8	70 : 30 (71:29) ^a	69 : 31	69 : 31 (83 : 17) ^a
12	76 : 24 (74:26) ^a	70 : 30	70 : 30 (83 : 17) ^a
16	75 : 25 (76:24) ^a	73 : 27	73 : 27 (83 : 17) ^a

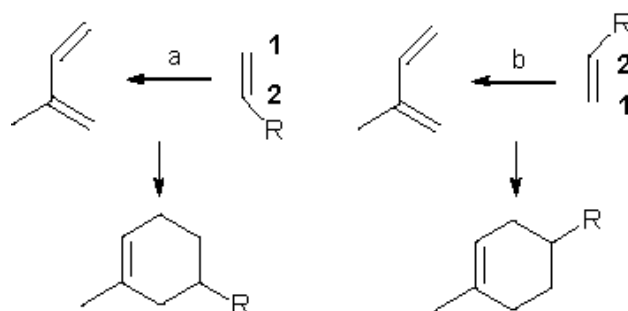
Reaction conditions: $\text{SiO}_2 \cdot \text{EAl}_2\text{O}_3$ catalyst 0.2 g, isoprene 20 mmol, $\text{CH}_2=\text{CH}-\text{R}$ 10 mmol, toluene 4 cm^3 , temperature 353 K, time 2 h (4 h for methyl acrylate).

^a Data collected with ethanol instead of toluene.

the product selectivity, the interactions were suggested to be most significant for acrolein compared with methyl acrylate and methyl vinyl ketone. The interaction may change the electronic states of C-1 and C-2 carbon atoms of dienophiles (Scheme 5). This would make the approach b in Scheme 5 more favorable, resulting in the alteration in the product selectivity. Steric effect of CO_2 interaction with $\text{C}=\text{O}$ group may also make the approach b more likely to occur, resulting in the increase in the 3 to 2 ratio.

6. Concluding Remark

Our Selected previous works on catalytic reactions in/under dense phase CO_2 are briefly reviewed. Dense phase CO_2 affects the overall reaction rates and/or the reaction selectivity in different modes of manner depending on the reactions examined and the catalysts used. Phase behavior of reaction mixture is also significant for the reactions. The pressurization of liquid reaction mixtures with CO_2 (CXL) is sometimes more effective for accelerating the



Scheme 5 : Two approaches, a and b, yielding meta- and para-adducts.

rate of reaction and modifying the product selectivity than doing the reaction under homogeneous conditions in supercritical CO_2 (CAL hydrogenation and NB hydrogenation). Adsorbed CO is formed over Rh catalysts. This can lower the reaction rate (phenol hydrogenation), but it improves the selectivity to cyclohexanone. The effects of CO_2 pressurization of liquid phase can appear for not only the hydrogenation reactions but also the reactions that do not include any gaseous reactants. The reaction rate is enhanced in a few cases (Heck coupling). Selectivity can also be changed (Diels–Alder reaction). The effects of CO_2 pressurization are ascribable to physical and chemical features of dense phase CO_2 , which will change the properties of the liquid phase as a continuum of reaction medium and the reactivity of reacting species through molecular interactions. CXL systems may be designed and applicable for various chemical transformations. However, they are complicated and so further works are still required to elucidate the roles of dense phase CO_2 and the reaction kinetics and to simulate the reaction outcomes by chemical engineering modeling.

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