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Carbon dioxide-expanded liquid substrate phase: an effective medium for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol

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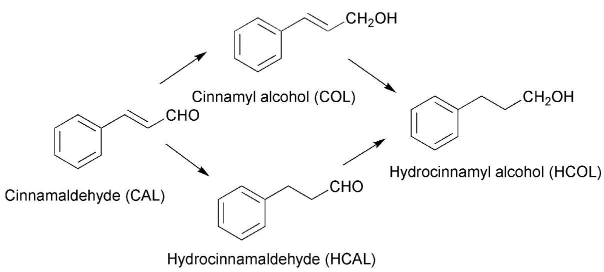
It has been shown that CO_2-expanded cinnamaldehyde liquid phase is a unique and effective medium for cinnamaldehyde hydrogenation to cinnamyl alcohol, due to interactions between the C=O group of the substrate and CO_2 molecules and increased solubility of H_2.

The use of supercritical carbon dioxide ($scCO_2$) as an environmentally benign solvent for organic synthetic reactions is currently receiving much attention. However, a drawback of $scCO_2$ prevents its utilization in homogeneous catalytic synthesis, due to its low ability to dissolve organometallic complexes. Some attention has been paid to enhancing the solubility of metal complexes in $scCO_2$ by using ligands with an affinity for CO_2.[1,2] Is the homogeneous phase really efficient for all the catalytic reactions in $scCO_2$? It was reported that insoluble rhodium complexes exhibited high activity and selectivity for hydroformylation of 1-hexene in $scCO_2$,[3] and a faster reaction rate was obtained in two-phase than in single-phase for α-pinene hydrogenation in $scCO_2$ with Pd/C catalysts.[4] Moreover, $scCO_2$ was reported to be dissolved in organic liquid substances and, in some cases, the solubility of CO_2 can approach a value much higher than 80 mol% in the vicinity of mixture critical point. The dissolution of CO_2 in an organic solvent is also accompanied by a significant volumetric expansion of the liquid phase. Subramaniam and Busch reported that CO_2-expanded CH_3CN solvent is an effective reaction medium for cyclohexene oxidation with TPP/FeCl catalyst.[5,6] And an increase in enantioselectivity has recently been reported for asymmetric hydrogenation of atropic acid in CO_2-expanded [bmim]PF_6 phase.[7] In the present communication, we will show that CO_2-expanded cinnamaldehyde (CAL) liquid phase using no organic solvent is a significantly effective medium for its selective hydrogenation to cinnamyl alcohol (COL) (Scheme 1) and that this is due to interactions between the substrate and CO_2 molecules, confirmed by *in situ* FTIR, and increased H_2 concentration in the liquid phase.

Table 1 shows the results of CAL hydrogenation and phase behaviour observations.† When the quantity of CAL was 0.2 mmol and that of Ru complex 0.075 or 0.15 μmol, the reaction system was in a single phase and the selectivity of COL was smaller than 30% (entries 1, 2). When 0.68 μmol of Ru complex was used at a higher CO_2 pressure of 16 MPa, the total CAL conversion increased to 55% while the COL selectivity did not change (entry 3). Under the conditions for this run, the system was in a two-phase mixture including a small volume of CAL-rich liquid phase. In addition, CAL hydrogenation was also examined under solvent-less conditions and in high pressure N_2 and CO_2 under two-phase conditions with using a large amount of CAL of 7.5 mmol (entries 4–7). Under the solvent-less conditions, a high COL selectivity of 88% was obtained (entry 4). When the CAL liquid phase was pressurized by 8.5 MPa N_2 (entry 5), the total conversion and COL selectivity did not change compared to these obtained under solvent-less conditions. However, 8.5 MPa CO_2 was used instead of N_2, the total conversion was enhanced to 24% from 11% and the COL selectivity to 91% from 88% (entry 6). When CO_2 pressure was further raised, the total conversion was further enhanced and the COL selectivity was also improved, which was 98% at 16 MPa (entry 7) in which the reaction mixture included a CO_2-rich gas phase and a large volume of CAL liquid phase dissolving CO_2 (CO_2-expanded liquid phase). Thus, the influence of phase



Scheme 1 Hydrogenation of cinnamaldehyde in compressed CO_2.

Table 1 Results of CAL hydrogenation with Ru complex in compressed CO_2

					Selectivity (%)			
Entry	Ru/μmol	CAL/mmol	CO_2 pressure/MPa	Conversion (%)	COL	HCAL	HCOL	Phase present[a]
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[b], L
4	50	7.5	—	11	88	9	3	G[c], L
5	50	7.5	8.5 N_2	12	88	10	2	G[d], L
6	50	7.5	8.5	24	91	7	2	G, L
7	50	7.5	16	54	98	1	1	G, L

[a] G: CO_2-rich gas phase, L: CO_2 expanded CAL liquid phase. [b] Very small droplets of CAL and/or catalyst were observed. [c] H_2-rich gas phase. [d] N_2-rich gas phase. Reaction conditions: bis(pentafluorophenyl)phenylphosphine/Ru = 3; H_2 pressure, 4 MPa; temperature, 50 °C; reaction time, 2 h. The Ru complex is completely soluble in CAL under these conditions used.

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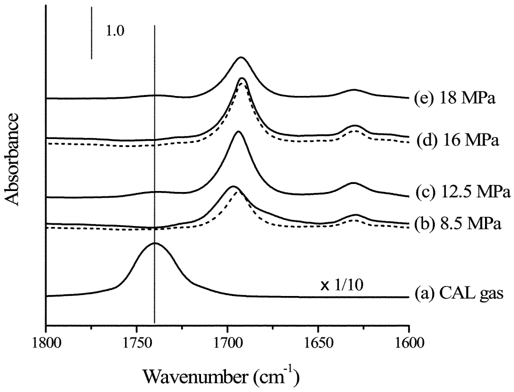

Fig. 1 FTIR spectra of pure CAL (gas) and CAL dissolved in compressed CO_2 as well as in H_2 and CO_2 mixture (dotted line) at 50 °C.

behaviour was significant and the presence of high-pressure CO_2 was requisite for selective CAL hydrogenation.

The present results demonstrate that larger conversion and larger COL selectivity can be obtained for CAL hydrogenation in CO_2-expanded CAL liquid phase. A few factors should be taken into account to explain these results. (1) CAL concentration. Although CO_2 and H_2 are dissolved in the CAL phase, the CAL concentration is still large in this phase. High CAL concentration was previously reported to benefit the formation of COL with heterogeneous catalysts.[9,10] (2) H_2 concentration. The concentration of H_2 in the CO_2-expanded CAL phase should be larger compared with that in the absence of CO_2 because a large quantity of CO_2 dissolved in the CAL phase favors the dissolution of H_2. (3) Compressed CO_2. The mass transfer resistance and substrate inhibition, if existed, should be reduced in CO_2-expanded CAL and $scCO_2$ phases. Note that compressed CO_2 increases the CAL conversion and the COL selectivity but compressed N_2 does not; hence, hydrostatic pressure to the CAL liquid phase is insignificant. So, direct effects of CO_2 may be assumed, and this was examined by FTIR.‡ Fig. 1 shows FTIR spectra from 1800 to 1600 cm^{-1} for CAL molecules dissolved in different gaseous mixtures at 50 °C. The spectrum (a) is a reference of gaseous pure CAL, indicating ν(C=O) at 1740 cm^{-1}. ν(C=C) was too weak under the conditions used. The absorbance in N_2 was very weak due to a less solubility of CAL in N_2. In contrast, CAL can be more soluble in dense CO_2, leading to stronger absorption (b–e). The absorption of ν(C=O) in dense CO_2 red-shifted compared with gaseous CAL and ν(C=C) appeared at 1630 cm^{-1} in 8.5 MPa CO_2. Further it was red-shifted a little with increasing CO_2 pressure. The dotted lines show the results in the presence of 4.0 MPa H_2, which has only a marginal effect. Moreover, the absorbance of ν(C=O) of CO_2 split into two peaks at 8.5 MPa from a single peak at 1.5 MPa, and these peaks split further to four peaks in the presence of CAL (Fig. 2), indicating the existence of interactions between CAL and CO_2 molecules in a gas state. For a CO_2 molecule, the carbon atom is partially positive and the oxygen atoms are partially negative. Thus, a C–H···O hydrogen bond should exist between CO_2 molecules and carbonyl groups even though it is weaker than O–H···O bonds.[11] The specific interaction of CO_2 molecules with Lewis base groups, especially carbonyl groups, through a C–H···O hydrogen bond has been reported.[11,12] In addition, interactions are known to exist between CO_2 and transition metal complexes, as reviewed by Leitner.[13] We may assume that the above mentioned interactions exist in the CO_2-expanded CAL liquid phase as well.

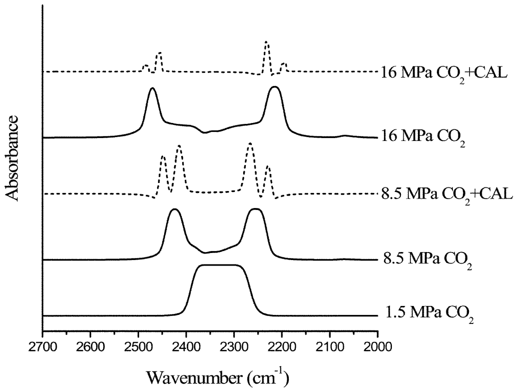

Fig. 2 FTIR spectra of pure CO_2 and mixture of CO_2 and CAL at 50 °C.

When the reaction occurs in the CO_2-expanded CAL phase, the high H_2 concentration (factor 1) is chiefly responsible for the increased CAL conversion and the high CAL concentration (factor 2) and CAL–CO_2 interactions (factor 3) for the high COL selectivity. The interactions may make the carbonyl group of CAL molecules more polar and reactive. It still remains unsolved whether CO_2 molecules have effects on the specific activity of the Ru complex in the CO_2-expanded CAL liquid phase (and in the CO_2-rich gas phase). For a catalyst of supported metal particles, direct effects of CO_2 on their properties were previously suggested.[14]

In summary, the CO_2-expanded substrate liquid phase has potential as a green reaction medium that does not need additional organic solvent.

Notes and references

† Hydrogenation of CAL in $scCO_2$ was carried out at 50 °C in a 50 mL high-pressure stainless steel reactor and a catalyst prepared from $RuCl_3$ and bis(pentafluorophenyl) phenylphosphine was used. This ligand was selected due to its high effectiveness in $scCO_2$ and the method of Ru complex preparation was described elsewhere.[8] The phase behavior and solubility of Ru complex and CAL in pure CO_2 and in H_2 + CO_2 were examined by visual observations with a 10 mL high-pressure sapphire-windowed view cell.[8] The reaction was conducted under different conditions, at which the reaction system was homogeneous or heterogeneous.

‡ The FTIR spectra were measured with 0.01 mL CAL using a 1.5 mL high pressure cell in a path length of 4 mm at 50 °C.

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