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The selective formation of unsaturated alcohols by hydrogenation of α,β-unsaturated aldehydes in supercritical carbon dioxide using unpromoted Pt/Al_2O_3 catalyst

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When α,β-unsaturated aldehydes are reduced by hydrogen in supercritical carbon dioxide using an unmodified Pt/Al_2O_3 catalyst, unsaturated alcohols are highly selectively produced, in contrast to previous results with organic solvents in which such a selective hydrogenation is difficult to achieve with monometallic Pt catalysts. The selectivity of unsaturated alcohols depends mainly on pressure of carbon dioxide while the conversion depends on both carbon dioxide and hydrogen pressures. The selectivity increases with increasing pressure and then does not change so much at higher pressures.

Keywords: hydrogenation, unsaturated aldehydes, Pt/Al_2O_3 catalyst, solvent effects, supercritical carbon dioxide

1. Introduction

The use of supercritical fluids as reaction media offers the opportunity to replace conventional organic solvents and due to its solvent properties it is possible to optimize product selectivity as well as reaction rate [1,2]. A unique and potentially advantageous characteristic of supercritical fluid solvents is that their density, polarity, viscosity, diffusivity, and solvent strength can be dramatically varied by relatively small changes in the pressure and/or temperature [2]. The relatively mild critical point of carbon dioxide ($T_c = 31\,^\circ\mathrm{C}$, $P_c = 72.9$ bar) and its benign nature are particularly attractive for catalytic applications. Several recent works have shown that supercritical carbon dioxide ($scCO_2$) can replace organic solvents in various transformations such as free radical reactions, polymerizations, and catalysis involving soluble metal complexes [3]. Homogeneous catalytic hydrogenation reactions in $scCO_2$ have been studied [4]. However, very few reports on the use of heterogeneous catalysts in $scCO_2$ have been reported [5]. Considering advantages of $scCO_2$ as a reaction medium and of heterogeneous catalysts for separation from reactants/products, it is worth combining these two advantages. Also hydrogenation of α,β-unsaturated aldehyde to unsaturated alcohol with higher selectivity is a challenging task due to several possible side reactions [6]. Herein, we report catalytic hydrogenation of α,β-unsaturated aldehydes in $scCO_2$, which gives very high selectivity towards unsaturated alcohols using an unmodified Pt/Al_2O_3 catalyst. It is known that such a selective hydrogenation is difficult to achieve with supported monometallic Pt catalysts in organic solvents [6,7].

2. Experimental

Hydrogenation reactions were carried out in sub- and supercritical CO_2 by charging a stainless-steel reactor (50 ml) with 1 wt% Pt/Al_2O_3 catalyst (500 mg) and α,β-unsaturated aldehyde (7.5 mmol), followed by pressurization with H_2 and CO_2 gases at 50 °C. The reaction was started by stirring the mixture with a magnetic stirrer and continued for 2 h. The reaction mixture was then analyzed by use of a gas chromatograph. We also conducted reaction experiments in ethanol with the same concentrations of catalyst and aldehyde using the same reactor for comparison. The Pt/Al_2O_3 catalyst used was prepared by wet impregnation followed by reduction with H_2 at 500 °C with the same procedures as described elsewhere [7a].

3. Results and discussion

The reaction can be represented as follows:

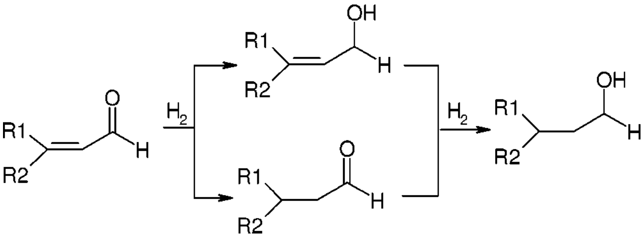

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Table 1
Hydrogenation of various substrates in $scCO_2$ and ethanol.

Serial No.	Substrate	Conversion (%)	Pressure (bar) H_2	CO_2	Total	Selectivity[a] (%) SAL	UOL
	In $scCO_2$[b]						
1	Cinnamaldehyde	40.3	40	140	180	6.6	92.6
2	α-methyl-*trans*-cinnamaldehyde	79.9	40	140	180	2.6	96.0
3	Crotonaldehyde	59.2	40	140	180	22.0	70.8
	In ethanol[c]						
4	Cinnamaldehyde	29.5	40	–	40	10.1	77.7
5	α-methyl-*trans*-cinnamaldehyde	42.3	40	–	40	21.0	79.0
6	Crotonaldehyde	41.8	40	–	40	33.3	45.8

[a] SAL: saturated aldehyde, UOL: unsaturated alcohol.
[b] Substrate 7.5 mmol; 1% Pt/Al_2O_3 500 mg; temperature 50 °C; time 2 h.
[c] Substrate 3.75 mmol; 1% Pt/Al_2O_3 250 mg; temperature 50 °C; time 2 h.

Table 2
Effect of pressure in hydrogenation of cinnamaldehyde.[a]

Serial No.	Pressure (bar) H_2	CO_2	Total	Conversion (%)	Selectivity[b] (%) SAL	UOL
Effect of total pressure						
1	15.5	54.5	70	16.0	13.9	85.4
2	22	78	100	33.9	11.8	87.0
3	40	140	180	40.3	6.6	92.6
4	50	170	220	48.7	5.3	93.1
Effect of hydrogen pressure						
5	10	140	150	32.3	11.7	85.7
6	20	140	160	34.8	9.0	89.5
7	40	140	180	40.3	6.6	92.6
8	60	140	200	69.4	7.7	91.5
Effect of $scCO_2$ *pressure*						
9	40	40	80	16.0	34.0	66.0
10	40	80	100	30.0	7.2	91.0
11	40	140	180	40.3	6.6	92.6

[a] Cinnamaldehyde 7.5 mmol; 1% Pt/Al_2O_3 500 mg; temperature 50 °C; time 2 h.
[b] SAL: saturated aldehyde, UOL: unsaturated alcohol.

Table 1 summarizes the results for three different α,β-unsaturated aldehydes using $scCO_2$ and ethanol. Under the conditions used, unsaturated alcohols and saturated aldehydes were the main products. Very small quantities of saturated alcohols were detected and in some cases other products should be formed in very small quantities but they were not identified. In the cases of α-methyl-*trans*-cinnamaldehyde and cinnamaldehyde, the selectivity towards unsaturated alcohol reached 96 and 93%, respectively, in $scCO_2$. A smaller selectivity of 71% was observed for crotonaldehyde, probably due to steric effects. These selectivity values are higher than those obtained in ethanol under 40 bar H_2. It is also interesting to see that the selectivity of unsaturated alcohol is relatively high, in particular for cinnamaldehyde and α-methyl-*trans*-cinnamaldehyde, in ethanol under 40 bar H_2. Under atmospheric pressure of H_2, the selectivity of unsaturated alcohol is low with conventional monometallic Pt catalysts [7], for which additives such as Sn and Ga are necessary to obtain high selectivities [6a,b]. After one run (table 1, serial No. 1), we added fresh cinnamaldehyde into the reaction mixture and the reaction was conducted again. The same activity and selectivity were observed in the second run, indicating no deactivation of catalyst under the present conditions. Minder et al. observed a strong deactivation of an alumina-supported platinum catalyst for enantioselective hydrogenation of ethyl pyruvate in $scCO_2$ [5d]; this catalyst deactivation was probably caused by the formation of poisoning species of CO_2 reduction on the surface of Pt.

In addition we have examined the influence of pressure on the selectivity and activity using cinnamaldehyde, and the results obtained are presented in table 2. As the pressure of H_2 *and/or* CO_2 is raised, both the selectivity and conversion are enhanced, being 93 and 49%, respectively, at 50 bar H_2 and 170 bar CO_2. The pressure effect on the selectivity of cinnamyl alcohol seems to level off at higher pressures. It is interesting to note that higher selectivity can be obtained only in the presence of $scCO_2$ (i.e., CO_2 pressure above 73 bar). At lower pressures of CO_2 (serial Nos. 1 and 9), the selectivity levels are low.

We can mention possible explanations for the improved selectivity of the unsaturated alcohols observed by using $scCO_2$. The dielectric constant of CO_2 increases with an increase in pressure [8]; in other words, the solvent is more polar at higher pressure. This may affect the reactivity of the polar C=O bond but not the less polar C=C bond. The C=O bonds are activated in $scCO_2$ and hydrogenated more easily, resulting in the selective formation of the unsaturated alcohols. In addition, the electronic state of supported platinum particles may be influenced by the polar solvent as suggested from our previous results on the optical absorption of supported silver particles in compressed CO_2 [9,10]. It was shown that the wavelength of maximum plasmon absorption increased with an increase in pressure, indicating that the electron density of silver particles was decreasing. The same effect is likely to occur for supported platinum particles, and it promotes the adsorption of the substrate with π electrons of its C=O group, enhancing the hydrogenation of this group. Under the reaction conditions used, H_2 is also in the supercritical state ($T_c = -240\,^\circ C$, $P_c = 12.9$ bar). High pressures of H_2 may have some effects on the activation of the C=O group and/or the catalytic properties of supported platinum particles.

The present reaction differs from conventional gas–liquid catalytic hydrogenation. Gas–liquid mass transfer is completely eliminated in the case of $scCO_2$ as a solvent and the concentration of H_2 is very high. The concentration of H_2 in a supercritical mixture of H_2 (85 bar) and CO_2 (120 bar) at 50 °C is 3.2 M, while the concentration of H_2 in THF under the same pressure is merely 0.4 M [11]. This is an important factor for the enhancement of the overall rate of reaction observed.

In conclusion, $scCO_2$ was shown to be a good solvent for the selective production of unsaturated alcohols by hydrogenation of α,β-unsaturated aldehydes even when we use a conventional Pt/Al_2O_3 catalyst without any promoters. The present reaction system is advantageous in that the separation of catalyst from products/reactant is easy at reduced pressure after reaction and the catalyst can be recycled.

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