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Influence of electronic state and dispersion of platinum particles on the conversion and selectivity of hydrogenation of an α,β-unsaturated aldehyde in supercritical carbon dioxide

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Abstract

The selective hydrogenation of cinnamaldehyde (CAL) was investigated using silica supported platinum catalysts in supercritical carbon dioxide. Selectivity to cinnamyl alcohol (COL) is enhanced as Pt^0/Pt^{2+} ratio increases; namely, zero-valent metallic surface is beneficial to the formation of COL compared with less reduced surface. The influence of Pt^0/Pt^{2+} ratio is more significant on the selectivity than on the total conversion. For the catalyst with small Pt^0/Pt^{2+} value, the selectivity also depends on the degree of platinum dispersion. The selectivity to COL is higher for higher degree of platinum dispersion. The CO_2 pressure did not affect the conversion and selectivity so much. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective hydrogenation of α,β-unsaturated aldehyde to unsaturated alcohol is an important step in the preparation of various fine chemicals such as fragrances for the perfume industry [1]. The unsaturated alcohol is difficult to obtain since it is known that a C=C bond can be hydrogenated more easily compared with a C=O bond. Therefore, many studies have been devoted to improving the selectivity towards the unsaturated alcohol. It was reported that the selectivity to unsaturated alcohol is governed by the nature of supports [2–5], the presence of promoters [6,7], the metal particle size [8,9], and the reaction medium such as supercritical carbon dioxide ($scCO_2$) [10]. The existence of Lewis acid centers on the support was reported to benefit the formation of unsaturated alcohol because it provides suitable anchoring sites for C=O bond [2]. For the hydrogenation of CAL with supported platinum catalyst, when metal chlorides of $FeCl_2$ and $GeCl_4$ are added as promoters, the selectivity to cinnamyl alcohol (COL) has been found to increase since the electron deficient centers are formed on the catalyst surface and these electron acceptor sites tend to adsorb C=O groups through the unshared electron pairs of carbonyl oxygen [7]. It was reported

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that larger particles benefited the formation of COL for the hydrogenation of CAL, and this was attributed to a steric effect that the phenyl group prevents the close approach of the C=C to the surface of large particles. As a result, the molecule is tilted with C=O closer to the catalytic surface and, therefore, the selectivity to COL is higher [8,9]. The activity and selectivity were found to be enhanced significantly when CAL was hydrogenated with Pt/Al_2O_3 in $scCO_2$ compared with organic solvents [10]. It is considered that the complete miscibility between hydrogen and $scCO_2$ is particularly beneficial for hydrogenation reactions since hydrogenation reactions in liquids are proportional to hydrogen concentration and are sometimes limited by the rate of diffusion of hydrogen from gas to the liquid phase, and these problems are solved by the use of $scCO_2$ as a hydrogenation medium [11]. Furthermore, the absorption spectrum of small gold particles measured in $scCO_2$ depends significantly on pressure, suggesting there is a direct interaction between gold particles and $scCO_2$ medium [12]. $scCO_2$ is an environmentally benign fluid, which is cheap, nontoxic, and nonflammable, and the relatively mild critical point ($T_c = 31\,^{\circ}C$, $P_c = 7.29\,MPa$) and its benign nature are particularly attractive for catalytic applications. In the present work, we have investigated the CAL hydrogenation catalyzed with silica supported platinum catalysts in $scCO_2$, focusing our attention to the influence of electronic state and degree of platinum dispersion on their catalytic activity and selectivity.

2. Experimental

2.1. Catalyst preparation

The catalysts of 1 and 2 wt.% Pt/SiO_2 were prepared with a porous silica gel (Aldrich Davisil grade 646) and tetra-ammineplatinum dichloride (Aldrich) through ion-exchange method. Silica gel was immersed into an aqueous solution of this platinum precursor at pH = 12 adjusted using 25% NH_4OH solution at room temperature for 3 days. After filtration and washing with distilled water until pH = 7, the sample of platinum precursor adsorbed on the support was air dried at room temperature for 24 h and then vacuum dried at 120 °C for 5 h. In order to make different degrees of platinum dispersion the platinum-loaded samples were reduced under hydrogen atmosphere at different temperatures of 300, 400, 500, 750 and 800 °C. Some samples were treated at 500 °C with nitrogen instead of hydrogen.

2.2. Catalyst characterization

The surface properties of platinum particles are considered in terms of the degree of platinum dispersion and electronic state (Pt^0/Pt^{2+} ratio). The degree of platinum dispersion was measured with hydrogen adsorption using a circulating system; after a catalyst was reduced and evacuated, the hydrogen adsorption was measured at room temperature and at different pressures in the range of 1.0–4.0 kPa. The number of exposed platinum atoms was calculated with a stoichiometry of $H/Pt = 1$ from the quantity of hydrogen adsorbed at extrapolated zero pressure.

X-ray photoelectron spectroscopy (ULVAC PHI ESCA 5600) was used to determine the nature of platinum species on the surface of catalysts with a resolution of 0.125 eV. A conventional Mg Kα X-ray excitation source ($h\nu = 1253.6\,eV$) was used and operated at 14.0 kV and 400 W. The residual vacuum in the spectrometer sample chamber was maintained below 1.33×10^{-5} Pa during data acquisition. The quantity of carbon species was observed to be less than 2 mol% and so the measurements were performed without any pretreatment like Ar^+ sputtering. The binding energies were determined by referencing to the Si 2p binding energy of 103.4 eV [13] with accuracy of about ±0.2 eV. The ratio of atomic concentrations on the surface layer was estimated from the XPS peak areas of the Pt $4f_{7/2}$, Si 2p, and O 1s. The spectrum was fitted by Gaussian spectra of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ by optimizing their peak heights and positions assuming a fixed peak to peak difference at 3.30 eV and at a full-width half-maximum of 2.0 eV. The ratio of platinum species, Pt^0/Pt^{2+}, was calculated with the peak areas of Pt $4f_{7/2}$.

2.3. CAL hydrogenation

Hydrogenation reactions were carried out in a 50 ml high-pressure stainless steel reactor. The 7.5 mmol CAL and a certain amount of catalyst were charged into the reactor, and the reactor was then sealed, flushed with 2.0 MPa carbon dioxide for three times and heated to 50 °C. After the introduction of hydrogen (4.0 MPa), liquid carbon dioxide 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. It was then cooled with an ice bath for about 10 min, carbon dioxide and hydrogen were carefully vented, and the liquid reaction mixture was separated from the catalyst through filtration. The conversion and selectivity were analyzed with a gas chromatograph (HP 6890, capillary column) with flame ionization detector.

3. Results and discussion

The hydrogenation of cinnamaldehyde (CAL) in $scCO_2$ was investigated using 1 and 2 wt.% Pt/SiO_2 catalysts, which were reduced under different conditions in order to change the metal dispersion and electronic state of supported platinum particles. Under the conditions used, COL, hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL) were produced (Scheme 1). The influence of the platinum dispersion and electronic state on the conversion and selectivity has been examined at different pressures of CO_2.

3.1. CAL hydrogenation

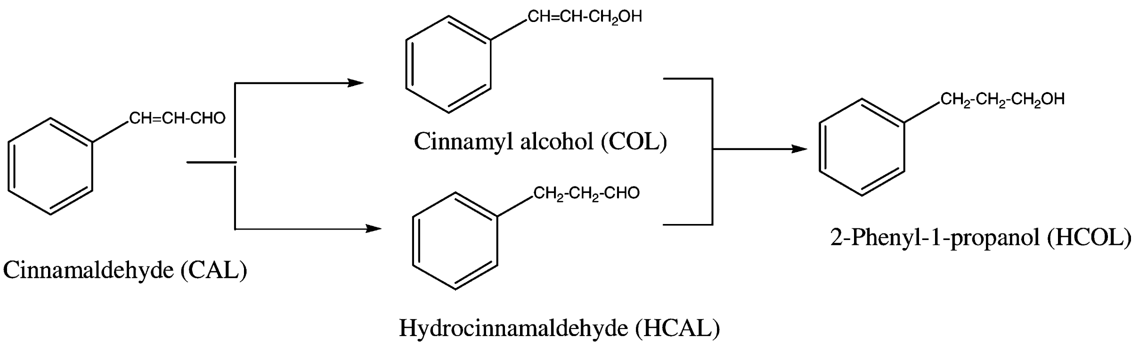
Table 1 shows the results of CAL hydrogenation with the catalysts reduced at different conditions. In these experiments, the total quantity of platinum used was the same. It was found that larger conversions were obtained at lower reduction temperatures for 1 and 2 wt.% Pt catalysts when CO_2 pressures applied were above its critical pressure. The selectivity to COL was also found to be higher at lower reduction temperature for 2 wt.% Pt catalysts. However, the 1 wt.% Pt catalysts reduced at 300, 400 and 500 °C showed similar COL selectivity values.

When N_2 was used instead of H_2 for the pre-treatment of 1 wt.% Pt catalyst at 500 °C, this reduced the conversion from 25 to 15% and the COL selectivity from 85 to 50%. Table 1 also indicates that the conversion and COL selectivity were little influenced by the pressure of CO_2 applied.

The catalyst recycling was also examined using a sample of 1 wt.% Pt/SiO_2 catalyst reduced at 500 °C for 3 h under the same standard reaction conditions (catalyst 0.2 g, CAL 7.5 mmol, H_2 4.0 MPa, CO_2 12.0 MPa, temperature 50 °C, time 2 h). When the catalyst was reused without any activation, the conversion decreased from 23.1 to 13.4% for the second run, due to the decrease in the Pt^0/Pt^{2+} ratio, as described below. However, the initial activity was regenerated after the catalyst was treated with hydrogen at 500 °C for 3 h.

3.2. Hydrogen adsorption and XPS

Table 2 shows the degree of platinum dispersion measured by hydrogen adsorption with a stoichiometry of $H/Pt = 1$. For 1 wt.% Pt catalysts reduced at 300, 400, and 500 °C, similar values of about 30% were obtained. The Pt dispersion was observed to increase up to 90% when the pre-treatment was conducted at 500 °C in N_2 instead of H_2. Compared with the 1 wt.% Pt catalyst reduced at 500 °C, 2 wt.% Pt



Scheme 1. Cinnamaldehyde hydrogenation.

Table 1
Results of CAL hydrogenation in $scCO_2$ with Pt/SiO_2 catalysts

Catalysts[a]	Pressure of CO_2 (MPa)	Conversion (%)	Selectivity (%)		
			COL	HCAL	HCOL
1 wt.% Pt/SiO_2, 300 °C, 3 h (0.2 g)	6.0	16.8	79.7	16.1	4.2
	8.0	19.8	84.5	11.4	4.1
	10.0	23.0	85.4	10.3	4.2
	12.0	26.9	86.3	9.9	3.8
	14.0	25.9	88.1	8.6	3.3
1 wt.% Pt/SiO_2, 400 °C, 3 h (0.2 g)	6.0	18.1	70.0	24.1	6.0
	8.0	18.2	75.4	20.1	4.6
	10.0	18.8	80.0	16.6	3.4
	12.0	19.6	77.0	18.5	4.5
	14.0	21.7	78.8	17.8	3.4
1 wt.% Pt/SiO_2, 500 °C, 3 h (0.2 g)	6.0	11.2	86.1	13.9	–
	8.0	21.1	84.5	12.5	3.0
	10.0	22.2	83.6	13.0	3.4
	12.0	23.1	82.9	13.9	3.1
	14.0	24.2	83.2	13.7	3.1
1 wt.% Pt/SiO_2[b], 500 °C, 2.5 h (0.2 g)	6.0	16.0	50.3	44.9	4.8
	8.0	15.6	52.3	45.0	2.7
	10.0	15.0	52.0	45.3	2.7
	12.0	14.7	53.5	42.3	4.2
	14.0	15.7	53.3	41.3	5.4
2 wt.% Pt/SiO_2, 500 °C, 3 h (0.1 g)	6.0	19.0	50.0	45.0	5.0
	8.0	22.0	52.0	41.0	7.0
	10.0	27.0	53.0	38.0	9.0
	12.0	27.0	53.1	41.8	5.1
	14.0	20.0	51.0	44.0	5.0
2 wt.% Pt/SiO_2, 750 °C, 2 h (0.1 g)	6.0	20.8	35.5	55.4	9.1
	8.0	19.7	38.3	52.8	8.9
	10.0	20.5	44.9	49.4	5.7
	12.0	23.4	42.2	46.5	10.7
	14.0	21.6	33.0	60.4	6.6
2 wt.% Pt/SiO_2, 800 °C, 4 h (0.1 g)	6.0	17.0	33.5	58.0	8.5
	8.0	18.0	35.5	55.0	9.5
	10.0	17.5	38.5	55.8	5.4
	12.0	16.2	36.8	54.7	8.5
	14.0	16.2	33.0	59.0	8.0

[a] Reduced with hydrogen at conditions given; the weight used is given in parenthesis.

[b] Treated with nitrogen under the conditions given. Reaction conditions: H_2 4.0 MPa, CAL 7.5 mmol, temperature 50 °C, reaction time 2 h.

catalyst reduced at the same temperature showed a higher dispersion of 78%, but the Pt dispersion decreased with raising reduction temperature up to 750 and 800 °C.

Table 3 gives XPS results for 1 and 2 wt.% Pt catalysts reduced under different conditions before and after CAL hydrogenation. The Pt $4f_{7/2}$ and Pt $4f_{5/2}$ binding energies for the fresh catalysts are in the ranges of 70.06–71.32 and 73.36–74.63 eV, respectively. The binding energy was then compared with the platinum foil (Pt $4f_{7/2}$ and Pt $4f_{5/2}$ are 70.90 and 74.20 eV, respectively) and sputtered Pt films (Pt $4f_{7/2}$ and Pt $4f_{5/2}$ are 71.30 and 74.60 eV, respectively) [13–15]. The Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks merged

Table 2
Results on the degree of Pt dispersion for Pt/SiO_2 catalysts

Catalyst	Reduction conditions	Pt dispersion (%)
1 wt.% Pt/SiO_2	300 °C, 3 h	30
1 wt.% Pt/SiO_2	400 °C, 3 h	29
1 wt.% Pt/SiO_2	500 °C, 3 h	28
1 wt.% Pt/SiO_2[a]	500 °C, 2.5 h	98
2 wt.% Pt/SiO_2	500 °C, 3 h	78
2 wt.% Pt/SiO_2	750 °C, 3 h	44
2 wt.% Pt/SiO_2	800 °C, 4 h	20

[a] This catalyst was treated with N_2 instead of H_2.

and broadened to higher binding energies with decreasing reduction temperature and such a positive shift indicates larger degree of Pt dispersion at lower reduction temperature [14,15], which is consistent with the results of hydrogen adsorption. The Pt $4f_{7/2}$ and Pt $4f_{5/2}$ binding energies of 1 wt.% Pt catalyst treated with N_2 are the same as those of the sputtered Pt films, indicating that smaller platinum crystallites was formed, being in agreement with the result of hydrogen adsorption. The ratio of the quantities of Pt^0 and Pt^{2+} was calculated from Pt $4f_{7/2}$ peak areas. For the fresh 2 wt.% Pt catalysts, the Pt^0/Pt^{2+} ratio is decreasing with increasing reduction temperature. These catalysts indicate smaller Pt^0/Pt^{2+} values compared with the 1 wt.% Pt catalysts, which have similar Pt^0/Pt^{2+} values. When the pretreatment of 1 wt.% Pt catalyst was conducted in N_2 instead of H_2, this ratio decreased from 78/28 to 40/60. The use for CAL hydrogenation decreased the Pt^0/Pt^{2+} value from 79/21 to 26/74 and 40/60 to 30/70 for 1 wt.% Pt catalysts reduced with hydrogen at 300 °C for 3 h and treated with nitrogen at 500 °C for 2.5 h, respectively.

Fig. 1 indicates Pt 4f XPS spectra for fresh 1 wt.% Pt catalysts reduced at 300 °C and treated with N_2 at 500 °C and for the same catalysts after CAL hydrogenation at CO_2 pressure of 12 MPa. The used catalysts were washed with acetone and dried in air after the reaction and then measured with XPS without further pretreatment. The Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks merged and broadened to higher binding energies after the use for CAL hydrogenation. This suggests that the electron density on platinum decreases; namely, platinum was oxidized during the reaction, which is in agreement with the decrease of the Pt^0/Pt^{2+} after reaction.

3.3. Catalytic activity and surface properties

According to the present results, the influence of reduction conditions is more significant on the product selectivity than on the total conversion. The reduction conditions will have effects on the properties of supported platinum particles and then on the catalytic activity of them. The surface properties of platinum particles are considered in terms of the degree of metal dispersion and the electronic state (Pt^0/Pt^{2+} ratio) in the following.

From the present results, the COL selectivity seems to be higher when the Pt^0/Pt^{2+} value is larger; namely, the hydrogenation of C=O bond of CAL is easier to occur than that of C=C bond. As this ratio is decreasing, the COL selectivity is decreasing while the HCAL selectivity is increasing. This would be

Table 3
XPS results for Pt/SiO_2 catalysts

Catalyst	Binding energy (eV)		Pt (4f) atomic concentration (%)	Pt^0/Pt^{2+}
	Pt $4f_{7/2}$	Pt $4f_{5/2}$		
1 wt.% Pt/SiO_2, 300 °C, 3 h	71.00	74.30	0.07	79/21
1 wt.% Pt/SiO_2, 400 °C, 3 h	70.96	74.26	0.03	72/28
1 wt.% Pt/SiO_2, 500 °C, 3 h	70.84	74.14	0.04	78/22
1 wt.% Pt/SiO_2, 500 °C, 2.5 h, N_2	71.32	74.62	0.07	40/60
2 wt.% Pt/SiO_2, 500 °C, 3 h	70.84	74.14	0.07	58/42
2 wt.% Pt/SiO_2, 750 °C, 2 h	70.84	74.14	0.17	49/51
2 wt.% Pt/SiO_2, 800 °C, 4 h	70.06	73.36	0.15	48/52
1 wt.% Pt/SiO_2, 300 °C, 3 h[a]	71.76	75.06	0.06	26/74
1 wt.% Pt/SiO_2, 500 °C, 2.5 h, N_2[a]	72.12	75.42	0.07	30/70

[a] After reaction at 16.0 MPa (H_2 4.0 MPa, CO_2 12.0 MPa) for 2 h.

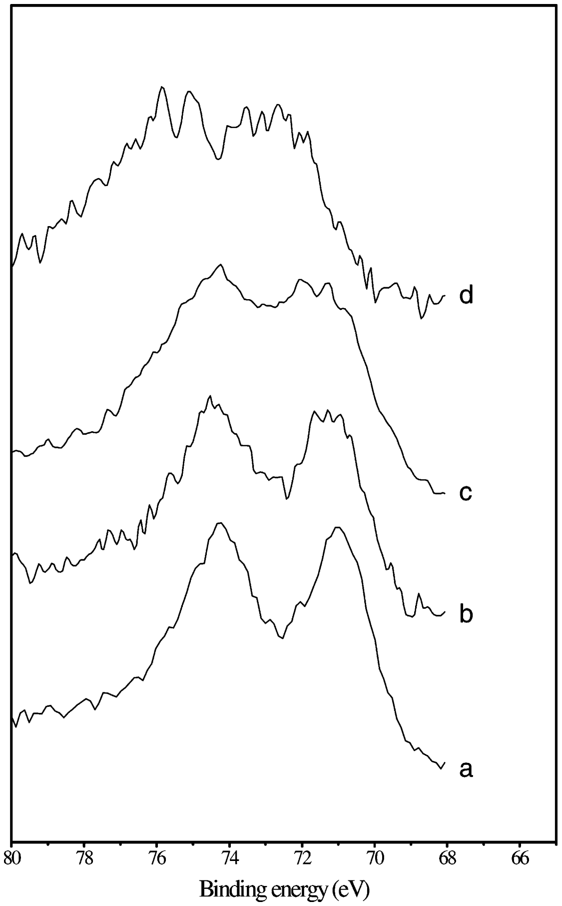


Fig. 1. XPS spectra for 1 wt.% Pt/SiO_2 catalysts before and after CAL hydrogenation: (a) reduced with H_2 at 300 °C, 3 h, before reaction; (b) reduced with H_2 at 300 °C, 3 h, after reaction at 12.0 MPa; (c) treated with N_2 at 500 °C, 2.5 h, before reaction; (d) treated with N_2 at 500 °C, 2.5 h, after reaction at 12.0 MPa.

explained with a difference in the adsorption of the C=O group; the surface exposing more metallic (less positive, more reduced) platinum species is more favorable to the adsorption of this group, resulting in more selective hydrogenation to the formation of COL, which can be explained by the different polarity of C=O and C=C bonds; the hydrogen dissociated on the platinum metallic atoms is more likely to do nucleophilic attack on the carbon atom of C=O due to more positive nature of this carbon atom induced by higher electronegativity of oxygen.

For the catalysts with small Pt^0/Pt^{2+} values, the selectivity also depends on the degree of platinum dispersion. The COL selectivity is higher for higher dispersion, namely, for smaller platinum particles. This cannot be explained by the steric effect that was previously proposed in the literature [8,9]. A large phenyl group is bonded to C=C of CAL, and so the adsorption of this C=C bond is suppressed on a flatter surface of larger metal particles due to steric hindrance, leading to the less selective hydrogenation of C=C bond compared with C=O bond. However, the present results indicate that the smaller platinum particles benefited the hydrogenation of C=O, in agreement with the previous results with Pt/SiO_2 catalysts in isopropyl alcohol solvent [16]. Szollosi et al. reported that the metal particle size of supported platinum catalysts decreased after ultrasonic treatment, resulting in higher selectivity of COL, and they explained this result by assuming that an effective metal–support active center was formed, which provides stronger acceptor sites for C=O adsorption.

Previously, Bhanage et al. [10] studied CAL hydrogenation with a Pt/Al_2O_3 catalyst in $scCO_2$. They reported an important result that the CAL conversion increased with CO_2 pressure as well as H_2 pressure while high COL selectivity was maintained. For the present CAL hydrogenation with Pt/SiO_2 catalysts, however, the CO_2 pressure did not vary the conversion and selectivity so much. Nevertheless, this is important, in accordance with the previous results. That is, the CAL conversion did not decrease due to dilution of the reactants of CAL and H_2 with applying higher CO_2 pressure. Thus, we may say again that dense CO_2 medium has some effect on the activity of Pt/SiO_2 catalysts, similar to Pt/Al_2O_3 catalysts, and/or the reactivity of CAL, as discussed previously [10].

In conclusion, the influence of Pt^0/Pt^{2+} ratio is more significant on the selectivity than on the total conversion. Selectivity to COL is enhanced as Pt^0/Pt^{2+} ratio increases. For the catalyst with small Pt^0/Pt^{2+} value, the selectivity also depends on the degree of platinum dispersion. The selectivity to COL is higher for higher degree of platinum dispersion.

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