

Selective hydrogenation of α -, β -unsaturated aldehyde to unsaturated alcohol with supported platinum catalysts at high pressures of hydrogen

Masayuki Shirai^a, Tomonari Tanaka^a, Masahiko Arai^{b,*}

^a Institute for Chemical Reaction Science, Tohoku University, Katahita, Aoba-ku, Sendai 980-8577, Japan

^b Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan

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Abstract

Hydrogenation of an α , β -unsaturated aldehyde, cinnamaldehyde (CAL), was carried out with silica-supported platinum catalysts in ethanol under pressurized hydrogen atmosphere up to 12 MPa at 50°C. The initial rate of reaction (CAL consumption) was proportional to hydrogen pressure and independent of CAL concentration. Increasing hydrogen pressure decreased the selectivity of cinnamyl alcohol (COL) but increased that of hydrocinnamaldehyde (HCAL). The COL selectivity increased with CAL concentration. The effect of hydrogen pressure on the selectivity in ethanol is different from that observed previously in a solvent of supercritical carbon dioxide. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic hydrogenation of α , β -unsaturated aldehydes (UAL) to unsaturated alcohols (UOL) is a reaction of industrial importance [1–4]. Platinum is one of active metals for this reaction but it is difficult for conventional supported monometallic platinum catalysts to achieve high UOL selectivity. So the selection of promoters, supports and reduction conditions is important for the selective formation of UOL. A different way is the use of supercritical carbon dioxide (scCO₂) as a solvent instead of organic liquids. Supercritical fluids are demonstrated to be interesting media for several organic reactions

[5]. The present authors have recently indicated that high UOL selectivity can be attained in hydrogenation of a few UAL (cinnamaldehyde, crotonaldehyde, α -methyl-*trans*-cinnamaldehyde) with a conventionally prepared platinum catalyst in scCO₂ medium [6]. Note that increasing hydrogen partial pressure not only increases the rate of UAL hydrogenation but also enhances the selectivity of UOL. For comparison with these results in scCO₂, the present work has been undertaken to obtain reference data in organic solvents at high pressures of hydrogen. In the literature [4,7–10], there are only a few reports on selective hydrogenation of UAL to UOL under pressurized hydrogen and the results reported with homogeneous catalysts at two or three different pressures suggest that the UOL selectivity will increase with pressure. Englisch et al. studied hydrogenation of crotonalde-

* Corresponding author. Fax: +81-11-706-6594.
E-mail address: marai@eng.hokudai.ac.jp (M. Arai).

hyde in ethanol with silica-supported platinum catalysts at hydrogen pressures up to 6 MPa [11]. It was reported that the UOL selectivity decreased with hydrogen pressure. Further studies are needed to clarify the pressure effects on selective UAL hydrogenation for homogeneous and heterogeneous catalysts.

2. Experimental

Silica-supported platinum catalysts were prepared with a porous silica gel (Aldrich Davisil grade 646) and tetraammineplatinum dichloride through impregnation or ion-exchange. The metal loading was fixed to 1 wt.%. The platinum-loaded samples were reduced by flowing hydrogen at 400 or 500°C for 5 h. The details of catalyst preparation procedures are described elsewhere [12]. For the samples prepared by ion-exchange, the actual amounts of platinum loaded were determined by measuring the quantities of the precursors remaining in solution after ion-exchange. The metal loading was found to fall in a range of 0.90 to 1.03 wt.%, and the nominal value (1 wt.%) is used in the following. The catalysts prepared by impregnation and ion-exchange followed by reduction at 400 and 500°C are denoted as im-Pt/SiO₂ (400) and ie-Pt/SiO₂ (500), respectively. The catalysts prepared are listed in Table 1.

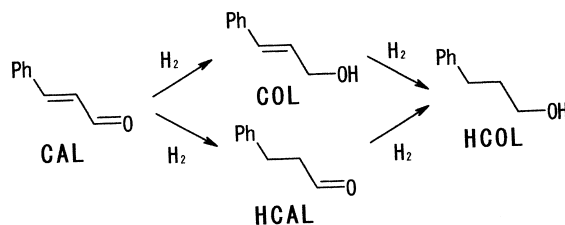
CAL hydrogenation was carried out in a 100 ml autoclave. The autoclave was filled in with a 50 ml solvent (ethanol in most cases) and a known volume of CAL and purged by repeatedly introducing nitrogen up to 5 MPa and releasing it down to ambient pressure three times. Then hydrogen was introduced up to the desired pressure and the reaction mixture was heated at 2°C/min up to a reaction temperature of 50°C. Small quantities of the reaction mixture were

repeatedly taken out and analyzed by gas chromatograph packed with Ucon oil 50HB 2000/Uniport B with flame ionization detector.

X-ray diffraction line broadening and hydrogen adsorption were used to examine the dispersion of platinum loaded. Hydrogen adsorption was measured by a closed circulating glass system. After reduction of a catalyst in the system, the amount of hydrogen adsorbed was determined at an introduction pressure of 0.7 to 1.3 kPa.

3. Results and discussion

The hydrogenation of cinnamaldehyde (CAL) produces a mixture of cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL) depending on reaction conditions used.



The influence of solvent on CAL hydrogenation was first examined using four different solvents for a catalyst of im-Pt/SiO₂ (400). Fig. 1 shows the results obtained at a hydrogen pressure of 4.9 MPa and a reaction time of 120 min. Methanol indicated a maximum conversion but it gave appreciable quantities of by-products like acetal. Although, the conversion decreased in the order of ethanol > 2-propanol > cyclohexane (of polarity), these did not give other products than COL, HCAL and HCOL. Thus, we used ethanol in further experiments.

Typical changes of quantities of reactant and products with time are shown in Fig. 2, for im-Pt/SiO₂ (400) in ethanol. Similar results were also observed for other catalysts and reaction conditions examined. Fig. 2 shows that COL and HCAL are produced as CAL is disappearing. The amount of the former product simply increases with time and becomes constant at the complete expense of CAL, while that of the latter has a maximum and decreases when some CAL remains unreacted. The amount of HCOL is simply

Table 1
Catalysts prepared and average crystallite size and degree of metal dispersion measured by X-ray diffraction line broadening and hydrogen adsorption

Catalyst	XRD	H ₂ adsorption (%)
im-Pt/SiO ₂ (400)	11 nm	4
im-Pt/SiO ₂ (500)	–	6
ie-Pt/SiO ₂ (400)	10 nm	10
ie-Pt/SiO ₂ (500)	–	9

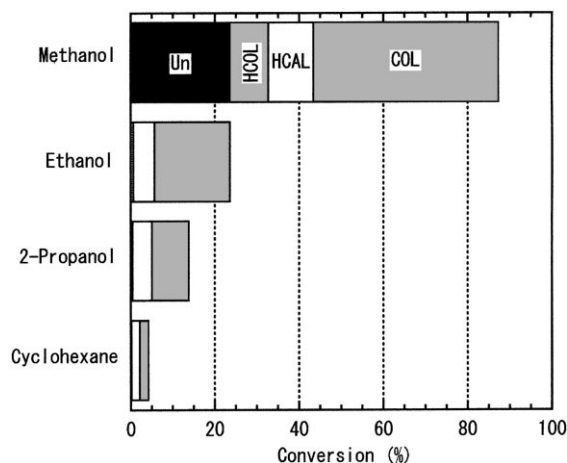


Fig. 1. Results of CAL hydrogenation with *im*-Pt/SiO₂ (400) in different solvents at a reaction time of 120 min. Hydrogen pressure 4.9 MPa and CAL concentration 0.16 mol/l.

increasing before and after the consumption of CAL. It was found that COL decreased and HCOL further increased for a longer period of reaction and in addition, only HCOL was formed when COL was used as a starting reactant. Thus, one can say that HCOL was not produced from COL but mostly from HCOL during CAL hydrogenation when HCOL remained. These results suggest that the adsorption on catalyst is easier to occur in the order of CAL > HCOL > COL. As a

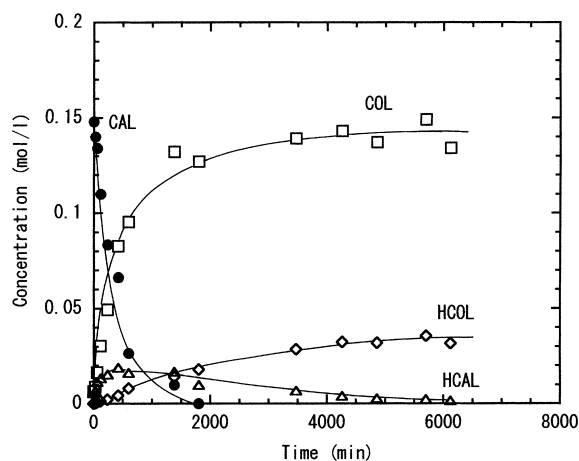


Fig. 2. Changes of reactant and products concentrations during CAL hydrogenation with *im*-Pt/SiO₂ (400) in ethanol at 6.9 MPa hydrogen pressure and 0.16 mol/l CAL concentration.

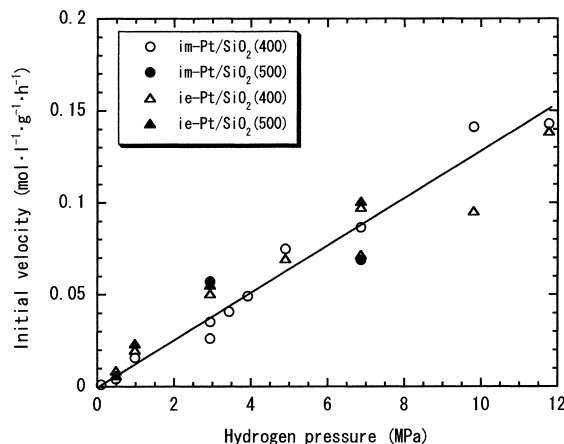


Fig. 3. Relationship between the initial rate of CAL hydrogenation in ethanol and hydrogen pressure at 0.16 mol/l CAL concentration.

result, COL could be further hydrogenated to HCOL after HCOL was consumed.

In the following, the initial rates of reaction determined from the initial time-concentration data for the disappearance of CAL as shown in Fig. 2 are used to examine the influence of reaction conditions. Fig. 3 shows the relationship between the initial rate and hydrogen pressure, indicating that the rate is proportional to the pressure. Fig. 4 gives the influence of CAL concentration and the initial rate of reaction is independent of it. It can be then assumed that CAL is much more abundant on catalysts than hydrogen. According

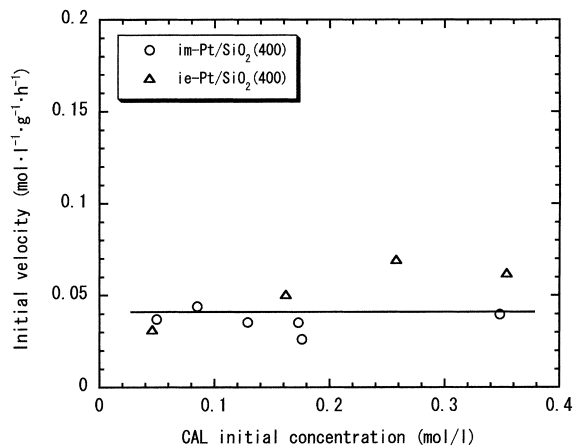


Fig. 4. Relationship between the initial rate of CAL hydrogenation in ethanol and CAL concentration at 2.9 MPa hydrogen pressure.

to Deshpande and Chaudhari [13], the concentration of hydrogen in ethanol at 50°C and at 10 MPa is estimated to be 0.4 mol/l, which is comparable to that of CAL. So, it should be more difficult for hydrogen to adsorb on catalysts in ethanol than CAL. In the case of scCO₂ as well, the CAL conversion increased with hydrogen pressure [6]. The increase in the rate of CAL hydrogenation with pressure should be simply due to the increase of hydrogen concentration in the solvents.

The data obtained at a CAL conversion of 20% are used to examine the product selectivity. Fig. 5 shows the influence of hydrogen pressure, indicating that the COL selectivity decreases with pressure while the

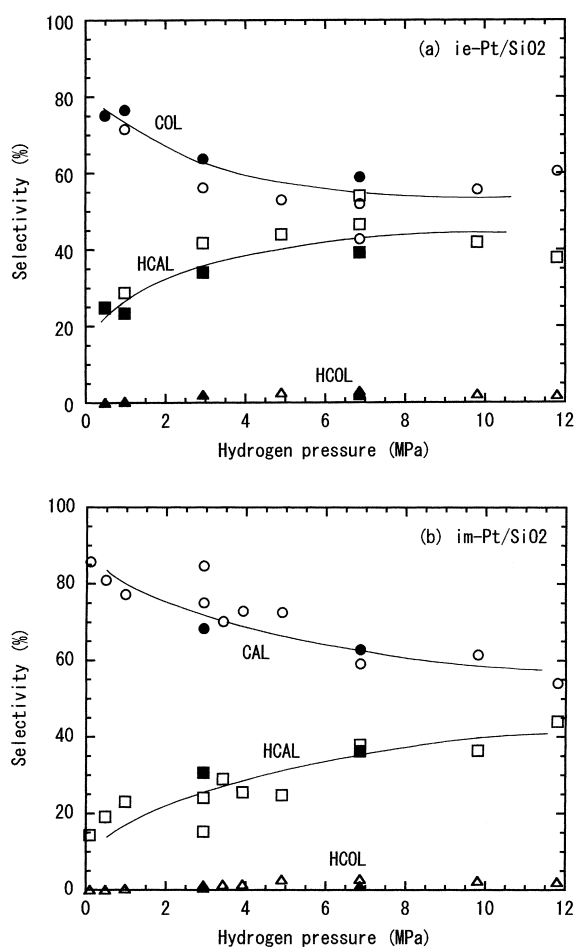


Fig. 5. Influence of hydrogen pressure on the product selectivity at 20% CAL conversion at 0.16 mol/l CAL concentration in ethanol. Reduction temperature (○, □, △) 400°C and (●, ■, ▲) 500°C.

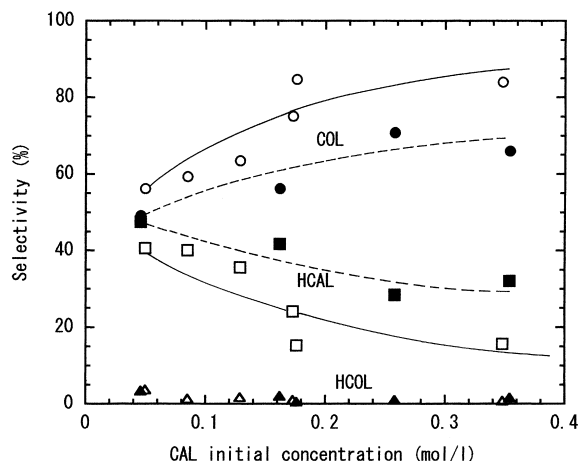


Fig. 6. Influence of CAL concentration on the product selectivity at 20% CAL conversion with im-Pt/SiO₂ (400) (○, □, △) and ie-Pt/SiO₂ (400) (●, ■, ▲) in ethanol at 2.9 MPa hydrogen pressure.

HCAL selectivity increases and both the selectivities level off at higher pressures. These trends are very similar for all the catalysts examined, irrespective of reduction temperature and the method of metal loading, although, the COL selectivity is larger for im-Pt/SiO₂ than for ie-Pt/SiO₂. This pressure effect of decreasing the COL selectivity is opposite to that observed in scCO₂ solvent [6]. The product selectivity is also influenced by CAL concentration. Fig. 6 indicates that the COL selectivity increases with the concentration while the HCAL selectivity decreases. For a selected catalyst of im-Pt/SiO₂ (400), it was further found that the COL selectivity was about 90% at partial pressures of hydrogen and nitrogen (diluent) of 0.1 and 4.8 MPa. This selectivity is similar to that obtained at 0.1 MPa pure hydrogen, and so the total gas pressure is not important but the partial pressure of hydrogen is significant.

As mentioned above, the surface of supported platinum particles should be occupied with CAL molecules rather than hydrogen during the initial period of reaction. When the CAL concentration increases, the amount of CAL molecules adsorbed increases and the state of adsorption would change, one possibility is that the adsorption occurs more favorably with C=O groups than C=C groups due to steric hindrance between bulky phenyl groups. This may explain the increase in the COL selectivity with

CAL concentration as shown in Fig. 6. The effect of hydrogen pressure is difficult to explain but we say that the nature of solvent (ethanol with hydrogen dissolved) is likely to change with hydrogen pressure and this would affect the properties of platinum particles and/or CAL molecules adsorbed. In scCO_2 solvent, the nature of supported platinum particles is suggested to change with pressure from optical absorption of supported silver particles [6]. Comparison with homogeneous reactions is of significance to do in further work.

Englisch et al. previously reported a similar effect of hydrogen pressure on UOL selectivity in liquid-phase hydrogenation of crotonaldehyde over silica-supported platinum catalysts [11]. These authors also reported that the UOL selectivity increased with increasing number of turnovers per metal site and they assumed that this could be explained with a preferential blocking of non-selective active sites by carbon monoxide formed during reaction and by a slow surface modification with organic deposits.

4. Conclusion

The initial rate of CAL hydrogenation with silica-supported platinum catalysts in ethanol is proportional to hydrogen pressure and independent of CAL concentration. When CAL remained in the reaction mixture, CAL and HCOL were produced and the latter was further hydrogenated to HCOL. After the complete hydrogenation of HCOL, COL was then

further hydrogenated to HCOL. The COL selectivity decreases with hydrogen pressure but increases with CAL concentration. The CAL concentration should affect the state of CAL molecules adsorbed on platinum particles and hydrogen pressure should change the nature of solvent and/or platinum particles.

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