Preparation of Alumina-supported Platinum Catalyst at Ambient Temperature for Selective Synthesis of Cinnamyl Alcohol by Liquid-phase Cinnamaldehyde Hydrogenation

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An alumina-supported platinum catalyst, indicating high activity to selective synthesis of cinnamyl alcohol in cinnamaldehyde hydrogenation, was prepared at ambient temperature by a novel method with the reduction of metal precursors adsorbed on the support by sodium tetrahydroborate solution.

Supported metal catalysts can be prepared in a variety of ways,[1] many of which require high-temperature activation and/or reduction. Non-heat-treated supported catalysts are expected to have different catalytic properties.

We have been investigating sodium tetrahydroborate solution as a reducing agent of dispersed metal precursors in catalyst preparation. Here, alumina-supported platinum catalysts have been prepared by the adsorption of metal precursors from chloroplatinic acid solution on the support followed by sodium tetrahydroborate reduction at ambient temperature. Platinum catalysts so prepared are highly selective in the synthesis of cinnamyl alcohol for liquid-phase cinnamaldehyde hydrogenation. Such catalytic hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is very difficult over monometallic platinum catalysts compared with the catalytic synthesis of saturated aldehydes under mild conditions.[2]

A porous gel alumina support, (Neobead C, Mizusawa Industrial Chemicals, Ltd) was used. Alumina particles (32/60 mesh) had a surface area of 130 m^2 g^{-1}. The adsorption of metal precursors was carried out under conditions given in Table 1, followed by removal of solvent by filtering and drying at about 380 K. The adsorbed precursors were then reduced at 303 K under conditions shown in Table 1, followed by washing with water and ethanol and drying under vacuum at about 330 K. A control catalyst was also prepared from the same alumina-supported platinum precursors through reduction by flowing hydrogen at 573 or 673 K for 2 h. In the following, the reductions with sodium tetrahydroborate solution and hydrogen are referred to as LLR (low-temperature liquid-

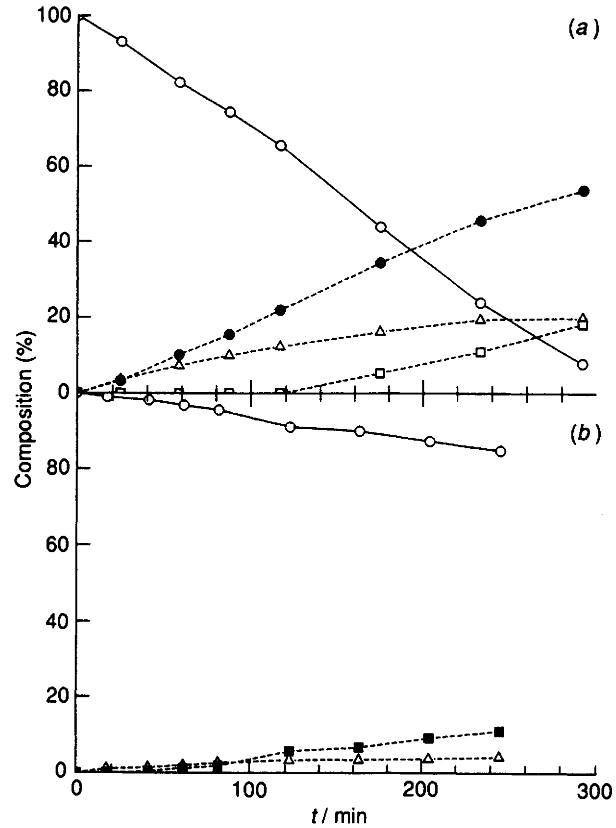

Fig. 1 Liquid-phase hydrogenation of cinnamaldehyde over alumina-supported platinum catalysts prepared by LLR for 30 min (*a*) and by HHR at 573 K (*b*). (○) cinnamaldehyde; (●) cinnamyl alcohol; (△) hydrocinnamaldehyde; (□) phenylpropanol; (■) hydrocinnamaldehyde diethylacetal.

Table 1 Typical conditions employed for the adsorption and reduction of platinum precursor on alumina support

	Adsorption	Reduction
Agent	H_2PtCl_6	$NaBH_4$
Concentration	1.46×10^{-5} mol Pt ml^{-1}	1.0×10^{-4} mol ml^{-1}
Volume	23.5 ml	10.0 ml
Initial pH	1.8	11.6
Weight of alumina	6.00 g	490 mg
Temperature	303 K	303 K
Time	5 days	1 min–30 h

phase reduction) and HHR (high-temperature hydrogen reduction), respectively. The amount of platinum loaded was fixed to 1 wt% for LLR and HHR catalysts. The catalysts so prepared were handled carefully to avoid exposure to the atmosphere between reductions and measurement of their catalytic activity. The reaction was carried out in a well-stirred glass flask under hydrogen (1 atm). Typical conditions were: solvent (ethanol), 5 ml; substrate, 0.5 ml; catalyst, 0.75 g; temperature, 308 K. The reaction rate and the product distribution were followed by repetitive sampling and GC.

The main products of cinnamaldehyde ($C_6H_5CH{=}CHCH{=}O$) hydrogenation are cinnamyl alcohol ($C_6H_5CH{=}CHCH_2OH$), hydrocinnamaldehyde ($C_6H_5CH_2CH_2CH{=}O$), and phenylpropanol ($C_6H_5CH_2CH_2CH_2OH$) for the LLR catalysts. In contrast for the HHR catalysts, the main products are hydrocinnamaldehyde and hydrocinnamaldehyde diethylacetal [$C_6H_5CH_2CH_2CH(C_2H_5O)_2$] and only a little cinnamyl alcohol is produced. Fig. 1 shows the time-course of the hydrogenation over the two catalysts prepared by LLR at 303 K for 30 min and HHR at 573 K for 2 h. Table 2 presents the performance of all of the catalysts prepared. The LLR

Table 2 Catalytic activities of alumina-supported platinum catalysts prepared by LLR and HHR in cinnamaldehyde hydrogenation

Reduction	Initial rate[a]/ mol min^{-1} g_{Pt}^{-1}	Selectivity[b] (mol%)
LLR 303 K, 1 min	0.27	36
303 K, 30 min	0.48	62
303 K, 30 h	0.56	78
HHR 573 K, 2 h	0.09	≈0
673 K, 2 h	0.11	≈0

[a] Moles of cinnamaldehyde converted. [b] To cinnamyl alcohol at the total conversion of about 50% except for HHR catalysts, for which the conversions achieved are smaller than 20% even after the reaction for 5 h.

catalysts indicate higher activities and higher selectivities to cinnamyl alcohol compared with the HHR catalysts. Increasing time of LLR results in the increase in the activity and selectivity. The LLR catalysts can maintain their high activities during the reaction and complete conversion of the substrate can, for example be achieved in *ca.* 5 h by the 30-min-LLR catalyst. In contrast, the activity of the HHR catalysts decreases and the conversions achieved in 5 h are less than 20%. There is little difference in the catalytic performance between the HHR catalysts prepared at 572 and 673 K. It is far harder to achieve selective synthesis of unsaturated alcohols by hydrogenation of α,β-unsaturated aldehydes over monometallic platinum catalysts. However, our LLR platinum catalysts require only mild conditions.

Richard *et al.* showed that graphite-supported platinum catalysts produce cinnamyl alcohol in high selectivities on liquid-phase cinnamaldehyde hydrogenation,[3,4] but need 4MPa hydrogen pressure. To be selective to the production of cinnamyl alcohol under mild conditions, platinum catalysts have to be modified by such additives as iron, tin and germanium,[3,5,6] possibly for electron transfer from additive to platinum. Increased charge density on platinum does not favour the activation of the C=C bond and cationic character of the additives favours the activation of the C=O bond. Metal particle morphology also affects selectivity.

The state of platinum species in our catalysts was briefly examined by hydrogen adsorption/spillover[7] by the method of Khoobiar.[8] The catalyst was mixed with a WO_3 powder with a ratio of 1:9 in mass and exposed to flowing hydrogen at ambient temperature for 5 min. It was found that the WO_3 changed from yellow to dark blue for all the catalysts prepared. This indicates that the LLR catalysts have similar platinum sites for hydrogen adsorption/spillover as those in the HHR catalysts, but these sites differ for the LLR and HHR catalysts and/or the former catalysts include other different active sites. Transmission electron microscopy failed to detect platinum particles, probably because particle size was < 1 nm for LLR and HHR catalysts.

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