NOTE

The Influence of Reduction Methods and Conditions on the Activity of Alumina-Supported Platinum Catalysts for the Liquid Phase Hydrogenation of Benzaldehyde in Ethanol

INTRODUCTION

The activities of supported metal catalysts depend on various preparation variables, including the method of reduction (1–3). A variety of reduction procedures can be applied to the preparation of supported metal catalysts (4). Previously we used a solid–liquid reduction by sodium tetrahydroborate solution for preparing supported platinum catalysts (5–7). In this reduction, platinum precursors adsorbed on supports were brought into contact with the reducing solution. The alumina-supported platinum catalysts prepared in this way were found to display interesting activities in the liquid-phase hydrogenation of α,β-unsaturated aldehydes; they were highly selective to the formation of unsaturated alcohols. The selective hydrogenation of C=O bonds of α,β-unsaturated aldehydes is difficult to achieve with platinum catalysts without using some additives like tin and iron (8, 9). The maximum temperature that our supported platinum catalysts went through was 110°C, required for the removal of water. This thermal history is a possible reason for the catalytic activity observed.

Following those observations, in the present work we have further examined the influence of reduction procedures by using hydrazine as well as sodium tetrahydroborate and different temperatures common during gas-phase reduction with hydrogen. The catalytic activity has been tested by the liquid-phase hydrogenation of benzaldehyde (BAL) in ethanol under mild conditions.

EXPERIMENTAL

The support material used was a porous alumina gel, Neobead C (Mizusawa Industrial Chemicals, Ltd.), with a surface area of 126 m^2 g^{-1}. Platinum precursors were adsorbed through ion exchange by immersing the support in an aqueous solution of tetraamine platinum dichloride at pH 12. The remaining solution was removed by filtering, washing with the distilled water, and drying in vacuum at 110°C. The amount of platinum loaded was 1% by weight. The precursor samples obtained were reduced by sodium tetrahydroborate, hydrazine, and hydrogen. The samples were brought into contact with the reducing solution at 30°C for 30 min. The molar ratio of the reducing agent to platinum was 400 : 1 in both cases. The reduced samples were washed with distilled water and vacuum dried at 60°C. In addition, the unreduced samples were reduced by flowing hydrogen at different temperatures. Those reductions in the liquid and gas phases are described with LR (liquid-phase reduction) and GR (gas-phase reduction), respectively, and the reducing agent and temperature used are specified when necessary, e.g., LR(NaBH$_4$) and GR(300).

The hydrogenation was conducted in a glass flask by using 0.1 g of catalyst, 0.5 ml of BAL, and 5 ml of ethanol at 35°C under atmospheric pressure of hydrogen. The reaction mixture was well mixed with a Teflon-coated magnetic stirrer. The reaction products were analyzed by gas chromatography. The details of catalyst preparation and liquid-phase hydrogenation have been described elsewhere (6, 7).

RESULTS AND DISCUSSION

In the present hydrogenation, benzyl alcohol (BOL) and benzaldehyde diethyl acetal (BALDA) were produced and the selectivities were significantly different depending on the catalyst used. Figure 1 compares the activities of variously reduced catalysts. Only BOL was formed by the LR catalysts and the GR catalysts reduced at 200°C or below. In contrast, the high-temperature GR catalysts produced large quantities of a byproduct, BALDA, as well as BOL. The major product was BALDA for the GR(400) and GR(500) catalysts. The activity of the formation of BOL was larger for the low-temperature reduced catalysts than for the high-temperature ones. The high activities of the LR catalysts during the hydrogenation of BAL to BOL are consistent with their high activities to the selective hydrogenation of the C=O bonds of α,β-unsaturated aldehydes (5–7). The low activity of the LR(N$_2$H$_4$) catalyst may be due to the lower reducing ability of hydrazine. When the platinum-free support was treated by GR at 400°C and used for the reaction, a small amount of BALDA was formed with a rate of 0.15 mmol g^{-1} min^{-1}. So platinum was required for the formation of BALDA as well as BOL.
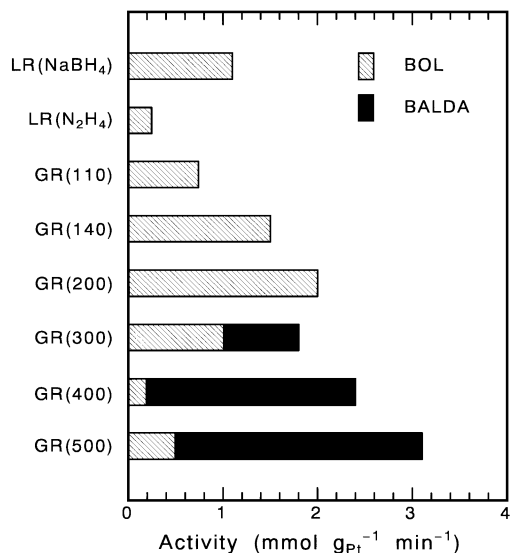
FIG. 1. Comparison of catalytic activities of alumina-supported LR and GR platinum catalysts. The reduction time was 30 min for LR and 3 h for GR, except GR(110), 24 h; GR(140), 120 h; and GR(200), 6 h.

The highly active LR(NaBH$_4$) catalyst was subjected to heat treatment in hydrogen (additional gas-phase reduction). Figure 2 gives the activity before and after the treatment at 380 and 500°C. The activity slightly decreased at 380°C, while it noticeably decreased at 500°C. It is interesting, however, that the catalyst still produced only BOL but no BALDA even after the treatment at 500°C.

In addition, we tried the treatment with sodium tetrahydroborate solution for GR catalysts in the same manner as that used in the LR catalyst preparation. Figure 3 shows the influence of this treatment on the catalytic activity. It
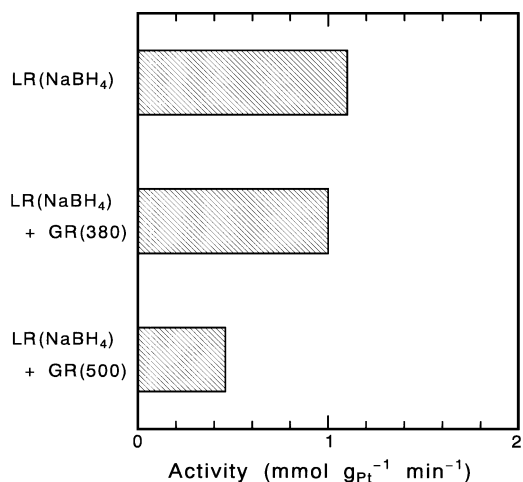

FIG. 2. The activities of an alumina-supported LR(NaBH$_4$) platinum catalyst before and after heat treatment in hydrogen (additional reduction) at 380 and 500°C for 3 h each. +GR(380) and +GR(500) indicate these additional treatments.
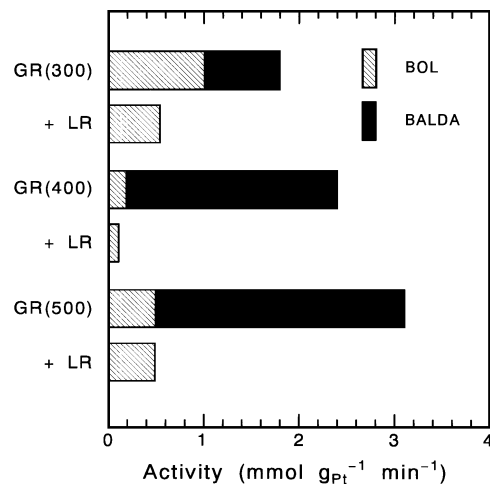

FIG. 3. The influence of treatment with NaBH$_4$ solution (additional liquid-phase reduction) on the activities of alumina-supported GR platinum catalysts. +LR indicates this additional treatment.

is found that this LR treatment completely inhibited the formation of BALDA while it slightly affected the activity of the formation of BOL.

It is demonstrated from the present work that the reduction conditions have significant effects on the catalytic activity of alumina-supported platinum catalysts for the hydrogenation of BAL in ethanol. The results of Fig. 3 imply that the high-temperature GR catalysts have two different active sites for the formation of BOL and BALDA, which are referred to as BOL and BALDA sites, respectively. When these GR catalysts were treated with LR(NaBH$_4$), their BALDA sites were completely deactivated. In contrast, the LR and low-temperature GR catalysts have BOL sites only (Fig. 1). This is also the case for the LR(NaBH$_4$) catalyst treated by high-temperature GR (Fig. 2). Thus, the BALDA sites appear with the high-temperature GR of the unreduced platinum precursors but do not for platinum reduced with sodium tetrahydroborate. It seems that low reduction temperatures are important for the presence of BOL sites, while high reduction temperatures are necessary for the presence of BALDA sites.

For catalytic reactions in the liquid phase, the state of mixing has some effect on them. In the present work, the reaction mixture was well stirred but the mixing was not very carefully controlled. However, there are obvious effects due to the reduction conditions on the catalytic activity and selectivity. We do not still have a clear explanation for the effects observed but we can mention a few important possibilities with respect to the BOL and BALDA sites.

The surface morphology of dispersed platinum particles may be important for the BOL sites present in the LR and low-temperature GR catalysts. It is likely that the platinum particles of these catalysts expose higher Miller index planes and some defects, and the sites on

the surface of these platinum particles are favorable to the activation of the C=O bonds of BAL as well as α,β-unsaturated aldehydes, cinnamaldehyde, crotonaldehyde, and 3-methylcrotonaldehyde (6, 7). Thus, the LR and low-temperature GR catalysts are highly active to the production of BOL as well as the corresponding unsaturated alcohols. More detail discussion for the case of the α,β-unsaturated aldehydes has been given in previous works (6, 7).

The formation of BALDA may depend on the ability of the catalyst to adsorb the solvent, ethanol. It is likely that this ability of the high-temperature GR catalysts is even more significant and the surface concentration of ethanol is larger compared with the LR and low-temperature GR catalysts. As a result, the high-temperature GR catalysts have been observed to produce larger quantities of BALDA. It is known that the formation of BALDA from BAL and ethanol is an acid catalyzed reaction (10). Probably some electron deficient platinum sites are favorable for this reaction. The BALDA sites are present in the high-temperature GR catalysts only, and so such electron-deficient sites would appear through metal–support interactions (11). It was indicated that high-temperature reduction of an alumina-supported platinum catalyst decreased its ability to adsorb hydrogen, due to the formation of an alloy between aluminum and platinum (12).

There is another possibility that some residual species from sodium tetrahydroborate, particularly boron, play an important role in the catalytic activity. This is because the activities of the LR catalysts for the BOL formation were little changed by additional high-temperature GR and the high-temperature GR catalysts lost their activities for the BALDA formation on the treatment with sodium tetrahydroborate solution. Very small amounts of boron species were indicated to be present in the LR catalysts from X-ray photoelectron spectroscopy measurements (7).

In conclusion, it should be noted again that the reduction procedures and conditions show marked effects on the activity and selectivity of alumina-supported platinum catalysts for the hydrogenation of BAL in ethanol. Further characterizations of the LR and GR catalysts are in progress to explain the catalytic features observed.

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