

Regioselective Hydrogenation of Unsaturated Alcohol Using Platinum-Alumina Modified with Carboxylic Acid

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Platinum-alumina catalysts modified with carboxylic acid were prepared for the selective hydrogenation of unsaturated alcohols. These catalysts were stable in non-polar solvents. It has been demonstrated that the carbon-carbon double bond which is close to the hydroxyl group is preferentially hydrogenated in the case of several hexenols. This selectivity was applied to the regioselective hydrogenation of geraniol and citronellol was obtained in an 84.5% yield over one of the modified catalyst systems.

It has been difficult to achieve a high regioselective hydrogenation of compounds which had plural unsaturations over a heterogeneous catalyst. It was recently reported that a carbon-carbon double bond far from a hydrophobic site in unsaturated carboxylic acid was more quickly hydrogenated than that near by a hydrophilic site over colloidal palladium or platinum supported on a polymer in a water solution.¹⁾ This selectivity was due to the colloidal micelle. Further, the site-selective epoxidation was also performed over the micelle-type catalyst.²⁾ On the other hand, highly regioselective reactions, such as esterification,^{3,4)} were reported to be achieved by using a monomolecular layer which could be prepared on an inorganic solid with carboxylic acid.

In this investigation, the selective hydrogenation of the carbon-carbon double bond was carried out by the application of a monomolecular layer system. The platinum-alumina (Pt/Al₂O₃) catalysts modified with carboxylic acids were prepared and used as catalysts with a monomolecular layer system. The carboxylic acid was presumed to be chemisorbed on an inorganic support as carboxylate anions.⁵⁻⁸⁾ It was elucidated that the difference in the hydrogenation rates were found in the different positions of the carbon-carbon double bond in unsaturated alcohols. In this paper, we report that the hydrogenation rate of the carbon-carbon double bond is dependent on the distance between the double bond and the hydroxyl group in the unsaturated alcohol, and that the regioselective hydrogenation of geraniol is achieved in this catalyst system.

Experimental

Materials. Commercial reagents were used for the reactions without further purification. Five percent platinum on a powdered alumina (Nippon Engelhard Ltd.) was used for the preparation of modified catalysts.

Preparation of Carboxylic Acid-Modified Catalyst (Catalyst A).^{2,3)} Carboxylic acids (0.1 g) and tridecane or dodecane as an internal standard (0.1 g) were dissolved in 10 cm³ of *N,N*-dimethylformamide (DMF). A platinum-alumina catalyst (5 w/w% Pt) was immersed in the solution and stirred overnight at room temperature. A catalyst modified

with the carboxylic acid was filtered off, washed with a small amount of DMF and dried under reduced pressure. The filtrate was analyzed by gas chromatography (a capillary column OV 101 30 m) in order to determine the adsorbed amount of the carboxylic acid on the catalyst.

Hydrogenation of Hexenols. In a 30-cm³ round-bottom flask, 10 mg of Catalyst A, or 5 % platinum on alumina (Catalyst B), was suspended in 10 cm³ of hexane containing 0.1 g of tridecane, and 10 cm³ of hexane containing *trans*-2-hexen-1-ol (0.1 g or 0.2 g) and/or *trans*-4-hexen-1-ol (0.1 g or 0.2 g) was added with stirring at 0°C under a hydrogen atmosphere. The reactants and products were analyzed on gas chromatography (a capillary column PEG 20M 30 m). The compounds were assigned and their concentrations were determined using authentic samples and an internal standard.

Hydrogenation of Geraniol. In a 30-cm³ round-bottom flask, 20 cm³ of hexane containing tridecane (0.1 g) and geraniol (0.1 g) was stirred with 10 mg of Catalyst A or Catalyst B at 0°C under a hydrogen atmosphere. The reactants and products were analyzed in a similar manner as described above. The assignment of the products was performed with GC-MS and ¹H NMR spectroscopy.

Results and Discussion

Adsorption of Carboxylic Acid on Alumina. The amounts of several carboxylic acids adsorbed on Pt/Al₂O₃ are listed in Table 1. The amount of myristic acid on Pt/Al₂O₃ was smaller than those of the other carboxylic acids. Monocarboxylic acids were efficiently adsorbed on alumina in comparison with the dicarboxylic acid. The adsorption amounts were not changed when large amounts of carboxylic acids were used in the preparation of the modified catalysts.

Table 1. Amount of Adsorbed Carboxylic Acids on Pt/Al₂O₃

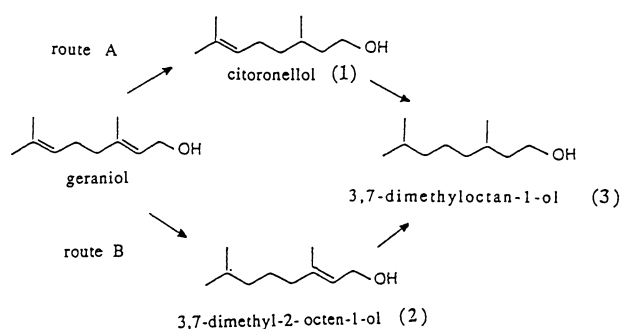
Carboxylic acid	Adsorption amount/mmol g ⁻¹
Decanoic acid	0.233
Hexanoic acid	0.240
Myristic acid	0.123
Benzoic acid	0.277
Adipic acid	0.166

Carboxylic acid: 0.1 g, 5% platinum-alumina: 1.0 g, in DMF solution, for overnight at room temperature.

These results showed that an almost saturated amount of the carboxylic acids were adsorbed on Pt/Al₂O₃. Although the prepared Catalyst A was immersed in hexane and stirred under a hydrogen atmosphere overnight, the eliminated carboxylic acid was not detected. Catalyst A was stable in hexane.

Hydrogenation of Some Unsaturated Alcohols.

The hydrogenation of *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol was carried out with catalysts modified by three kinds of carboxylic acids, decanoic acid (Catalyst A-1), hexanoic acid (Catalyst A-2), and myristic acid (Catalyst A-3), and with a non-modified catalyst (Catalyst B). The time-courses of the hydrogenation over Catalyst A-1 are shown in Fig. 1-a. The hydrogenation rate of *trans*-2-hexen-1-ol was higher than that of *trans*-4-hexen-1-ol over Catalyst A-1, while the two hexenols were hydrogenated at similar



reaction rates over Catalyst B (Fig. 1-b). These results could be explained as follows: in the case of the Catalyst A-1 system, hexenols were adsorbed on the catalyst surface at the hydroxyl group. It was difficult for the carbon-carbon double bond far from the hydroxyl group to approach the active site compared with that of the hydroxyl group nearby because of the long hydrophobic carbon chain of the carboxylic acid which had adsorbed on Pt/Al₂O₃. It is considered that these phenomena are attributable to two effects. One of them is the hydrophilic-hydrophobic effect⁹⁾ which is caused by the attached carboxylic acid. Another effect is caused by a steric regulation in the carboxylic acid layer on Pt/Al₂O₃ (matrix effect).¹⁰⁾ Therefore, the hydrogenation of the carbon-carbon double bond near the hydroxyl group was faster than that far from the hydroxyl group. The hydrogenation over Catalyst A-2 or Catalyst A-3 was similar to that over Catalyst A-1. The difference in the rates between *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol over Catalyst A-1 was largest. It was reasonable that the effect increased with increasing the carbon chain of the adsorbed carboxylic acid; therefore, the matrix effect in Catalyst A-2 was smaller than that in Catalyst A-1. In the case of Catalyst A-3, the matrix effect was lowered because of the small amount of the adsorbed myristic acid.

Competitive hydrogenation of *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol was carried out on Catalyst A-1, and the results are shown in Fig. 2. Although the hydrogenation rates of the two hexenols were almost the same in the case of the Catalyst B system, *trans*-2-

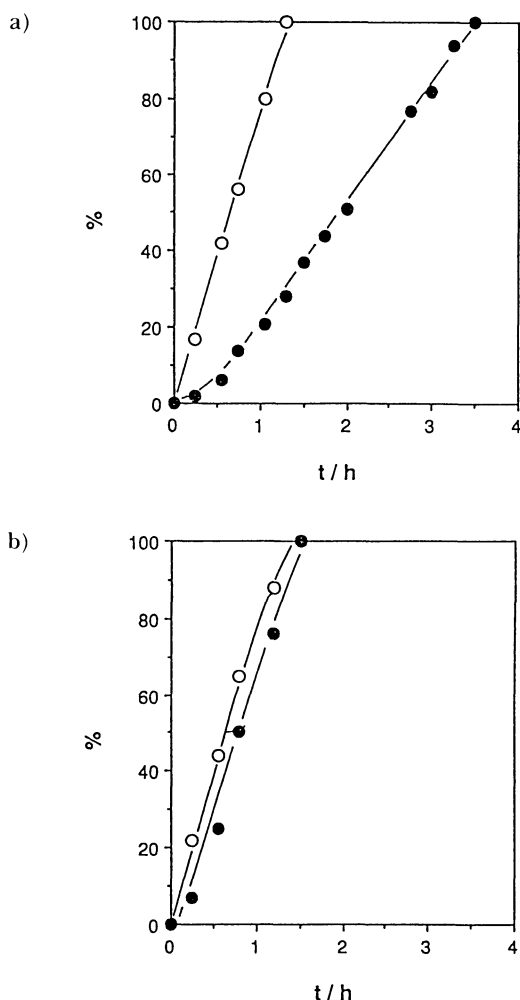


Fig. 1. Hydrogenation of *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol: a) Catalyst A-1; b) Catalyst B. ○; H₂ uptake in *trans*-2-hexen-1-ol hydrogenation. Conditions: Catalyst: 10 mg, *trans*-2-hexen-1-ol: 0.2 g, tridecane: 0.1 g, hexane: 20 cm³, reaction temperature: 0°C. ●; H₂ uptake in *trans*-4-hexen-1-ol hydrogenation. Conditions: Catalyst: 10 mg, *trans*-4-hexen-1-ol: 0.2 g, tridecane: 0.1 g, hexane: 20 cm³, reaction temperature: 0°C.

Table 2. Rate of Hydrogenation for *trans*-2-Hexen-1-ol and *trans*-4-Hexen-1-ol

Catalyst	Initial rate of reaction/mol g ⁻¹ h ⁻¹	
	<i>trans</i> -2-Hexen-1-ol	<i>trans</i> -4-Hexen-1-ol
Catalyst A-1	3.5×10 ⁻²	2.2×10 ⁻³
Catalyst A-2	7.0×10 ⁻²	8.2×10 ⁻³
Catalyst A-3	5.2×10 ⁻²	7.9×10 ⁻³
Catalyst A-4	4.2×10 ⁻²	5.9×10 ⁻³
Catalyst A-5	4.5×10 ⁻²	5.5×10 ⁻³
Catalyst B	7.1×10 ⁻²	5.2×10 ⁻²

Catalyst: 10 mg, *trans*-2-hexen-1-ol: 0.1 g, *trans*-4-hexen-1-ol: 0.1 g, tridecane: 0.1 g, hexane: 20 cm³, reaction temperature: 0°C

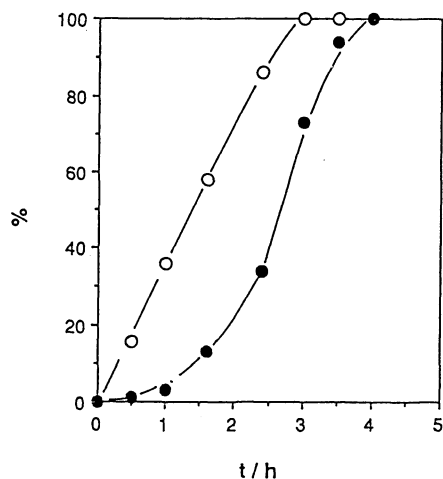


Fig. 2. Hydrogenation of the mixture of *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol (Catalyst A-1). Conditions: Catalyst: 10 mg, *trans*-2-hexen-1-ol: 0.1 g, *trans*-4-hexen-1-ol: 0.1 g, tridecane: 0.1 g, hexane: 20 cm³, reaction temperature: 0 °C. ○; H₂ uptake in *trans*-2-hexen-1-ol hydrogenation. ●; H₂ uptake in *trans*-4-hexen-1-ol hydrogenation.

hexen-1-ol was selectively hydrogenated over Catalyst A-1.

As shown in Table 2, the selective hydrogenation was observed by the use of catalysts modified by hexanoic acid (Catalyst A-2), myristic acid (Catalyst A-3), benzoic acid (Catalyst A-4), and adipic acid (Catalyst A-5). This tendency was independent of the variety of the modified carboxylic acids on Pt/Al₂O₃. Thus, selective hydrogenation could be performed for a mixture of some unsaturated alcohols by a catalyst modified with carboxylic acid.

It was expected that the regioselective hydrogenation of an alcohol possessing a plural of carbon-carbon double bonds could be applied, since a difference in the hydrogenation rates was found in a different position of the carbon-carbon double bond in hexenols. The hydrogenation of geraniol was investigated by catalysis with carboxylic acid-modified catalysts. Since the two double bonds were similar in a steric environment, regioselective hydrogenation could not be achieved over the usual heterogeneous catalyst. In fact, the regioselectivity in the hydrogenation of geraniol was low over Catalyst B, as shown in Fig. 3-b. However, by catalysis with Catalyst A-1, a high regioselective hydrogenation of geraniol was achieved and citronellol was obtained in an 84.5% yield (Fig. 3-a). The catalytic hydrogenation of geraniol proceeds via two kinds of pathways, shown to be routes A and B in the scheme; citronellol (1) and 3,7-dimethyl-2-octen-1-ol (2) were obtained as intermediates between geraniol and 3,7-dimethyloctan-1-ol (3). In the case of hydrogenation over Catalyst B, a slightly regioselective hydrogenation was observed, and 2 was detected during an early stage of the reaction. Furthermore, 3 was rapidly produced. In the

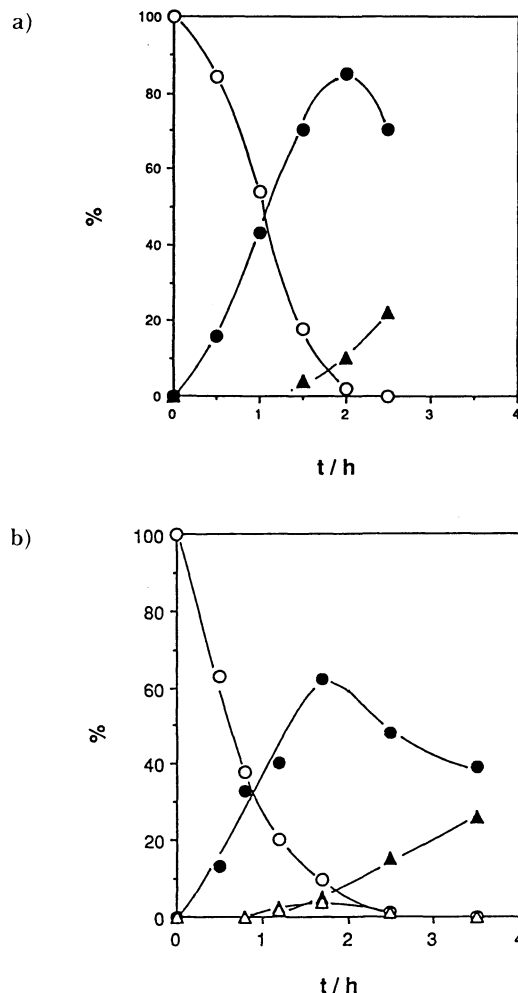


Fig. 3. Hydrogenation of geraniol: a) Catalyst A-1; b) Catalyst B. Conditions: Catalyst: 10 mg, geraniol: 0.1 g, tridecane: 0.1 g, hexane: 20 cm³, reaction temperature: 0 °C. ○; Ratio of geraniol. ●; Ratio of citronellol. △; Ratio of 3,7-dimethyl-2-octen-1-ol. ▲; Ratio of 3,7-dimethyloctan-1-ol.

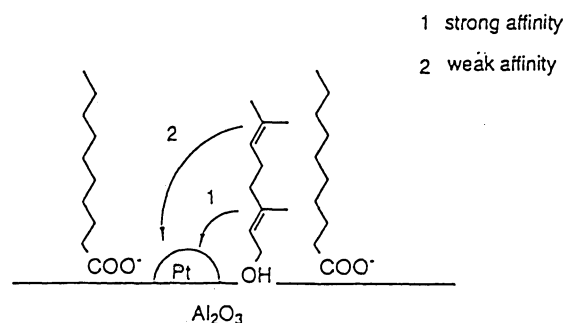


Fig. 4. Reaction model for the hydrogenation of geraniol in Catalyst A system.

hydrogenation on Catalyst A, 2 was never detected and 3 was slowly yielded. As a result, a high regioselectivity was achieved over Catalyst A. By the use of a catalyst modified by other carboxylic acids (for

instance, hexanoic acid, myristic acid, benzoic acid, or adipic acid) high regioselective hydrogenation of geraniol could also be achieved. However, a catalyst modified by decanoic acid was superior in selectivity to the other catalysts.

From these results, the reaction mechanism in the Catalyst A system was assumed to be as follows: by way of the hydroxyl group, as a hydrophilic label, the unsaturated alcohol is attracted in the hydrophilic phase to the surface of alumina and the double bond near the hydroxyl group can more easily approach the platinum by the carboxylic acid layer (Fig. 4). Consequently, the carbon-carbon double bond which was close to the hydroxyl group was easily hydrogenated.

In conclusion, a highly regioselective hydrogenation of the carbon-carbon double bond of the unsaturated alcohol was achieved by carboxylic acid-modified catalysts.

References

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 - 9) The hydrophilic part in unsaturated alcohol has an affinity for the carboxyl group adsorbed on the surface of Pt/Al₂O₃. On the other hand, the hydrophobic part in the substrate has an affinity for the hydrophobic core in the carboxylic acid. Accordingly, the carbon-carbon double bond near the hydroxyl group can preferentially close to the active site in comparison with the double bond in the hydrophobic part.
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