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Hydrogenation of Unsaturated Carboxylic Acid Catalyzed by Platinum–Silica Coupled with Alkylsilyl Chloride

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Synopsis. Platinum–silica catalysts coupled with alkylsilyl chloride were prepared for the regioselective hydrogenation of unsaturated compounds. These catalysts were stable in polar solvents. It was found that the carbon–carbon double bond far from a hydrophilic site was more rapidly hydrogenated in this catalyst system.

It is still difficult to achieve high regioselective hydrogenation of compounds which have plural unsaturations over a heterogeneous catalysts. In a previous paper[1)] we reported achieving regioselective hydrogenation of unsaturated alcohols by using platinum–alumina modified with carboxylic acid. Since this catalyst is unstable in polar solvents, the application of this catalyst system is limited with regard to the reaction conditions. This catalyst is difficult to apply to the regioselective hydrogenation of unsaturated carboxylic acid because of the destruction of the carboxylic acid layer on platinum–alumina.

Platinum–silica coupled with alkylsilyl chrolide was prepared in order to overcome this disadvantage and to achieve regioselective hydrogenation of unsaturations. In this paper we report that the alkylsilyl-coupled catalyst can be applied to the regioselective hydrogenation of unsaturated carboxylic acids and that the hydrogenation rate of the carbon–carbon double bond is dependent on the distance between the double bond and the carboxyl group in unsaturated carboxylic acid.

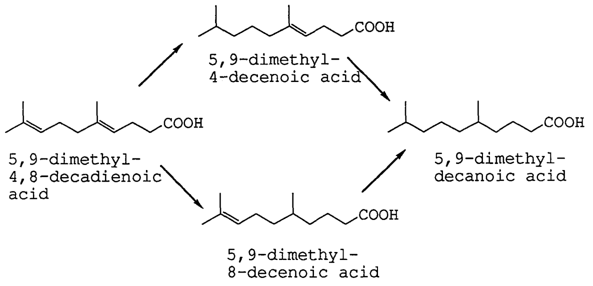
Experimental

Materials. Commericial reagents were used without further purification. Zero point five percent platinum on a powdered silica (N. E. Chemcat Corp.) was used for the preparation of modified catalysts.

Preparation of Alkylsilyl-Modified Catalyst.[2,3)] Dimethyloctadecylsilyl chloride (3.0 g) was dissolved in 15 cm^3 of hexane. Three grams of a platinum–silica catalyst (0.5% w/w Pt) was immersed in the solution and stirred overnight at room temperature. A catalyst coupled with the silylreagent was filtered off, washed with hexane and dried under reduced pressure. A catalyst prepared by the method described above was named catalyst A. A catalyst capped with trimethysilyl chloride (catalyst B) was prepared as follows: catalyst A was immersed in a hexane solution containing trimethylsilyl chloride (5.0 g); the solid was filtered off, washed with hexane and dried under reduced pressure. The characterizations of the catalysts A and B were analyzed by elemental analysis; catalyst A: C, 11.07; H, 2.26%, catalyst B: C, 11.24; H, 2.31%, platinum (0.5 w/w%)-silica: C, 0.14; H, 0.55%.

Hydrogenation of Decenoic Acids. In a 30-cm^3 round-bottom flask, 40 mg of catalyst A, B, or 0.5% platinum–silica, was suspended in 20 cm^3 of hexane containing 9-decenoic acid (25 mg), *trans*-2-decenoic acid (25 mg) and dodecane (25 mg) as an internal standard with stirring at 25 °C under a hydrogen atmosphere. Both the reactants and products were analyzed by gas chromatography (a capillary column PEG 20M 30 m and OV 101 30 m). These compounds were assigned and their concentrations were determined using authentic samples and an internal standard.

Hydrogenation of 5,9-Dimethyl-4,8-decadienoic Acid. 5,9-Dimethyl-4,8-decadienoic acid (**1**) was prepared in the manner described in a previous paper.[4)] In a 30-cm^3 round-bottom flask, 20 cm^3 of hexane containing 5,9-dimethyl-4,8-decadienoic acid (12.5 mg) and pentadecane (25 mg) as an internal standard was stirred with 80 mg of catalyst A or 0.5% platinum–silica at 25 °C under a hydrogen atmosphere. Both the reactants and products were analyzed in a similar manner to that described above. The assignments of the products were performed with GC-MS and ^{1}H NMR spectroscopy.



Results and Discussion

Hydrogenation of Mixture of 9-Decenoic Acid and *trans*-2-Decenoic Acid. Competitive hydrogenation of 9-decenoic acid and *trans*-2-decenoic acid was carried out over the catalysts A, B, and the control catalysts, and the results are shown in the table. The regioselectivities are listed as C1/C2 on the last column in the table. When using hexane as the solvent, the regioselectivity over catalyst A was much higher than those of the other catalysts. On the other hand, the selectivity over catalyst B was much higher than those of the other catalysts when using ethanol. In the case using both hexane and ethanol, a system of catalysts A and B led to a high regioselectivity in comparison with the control catalyst system. These phenomena result from the effect of alkylsiliyl-modification on the catalyst. This mechanism is thought to be as follows: the hydrophilic surface of the solid catalyst was converted to the hydrophobic one by alkylsilylation; the double bond in the hydrophobic part can more easily approach the active site than that in the hydrophilic part because of the strong affinity between the dimethyloctadecylsilyl (ODS)-layer and the hydro-

Table 1. Hydrogenation of Mixture of 9-Decenoic Acid (9-DA) and *trans*-2-Decenoic Acid (2-DA)

Catalyst	Solvent	React. time/min	Conversion/%		C1/C2
			9-DA (C1)	2-DA (C2)	
Catalyst A	Hexane	10.0	83.8	5.3	15.8
Catalyst B	Hexane	10.0	78.6	11.9	6.6
Control cat.	Hexane	10.0	76.0	27.3	2.8
Catalyst A	Ethanol	50.0	91.0	10.0	9.1
Catalyst B	Ethanol	150.0	91.7	5.4	17.0
Control cat.	Ethanol	240.0	91.5	25.0	3.6

Catalyst: 40 mg 9-decenoic acid: 0.1 mmol, *trans*-2-decenoic acid: 0.1 mmol, solvent: 20 cm^3, reaction temperature: 25 °C.

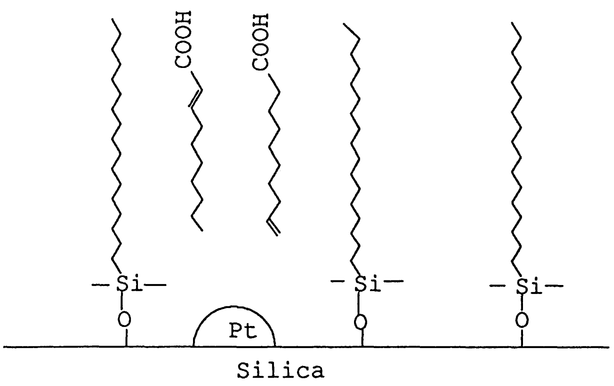


Fig. 1. Reaction model for the competitive hydrogenation of 9-decenoic acid and *trans*-2-decenoic acid in Catalyst A system.

hobic part in unsaturated carboxylic acid (Fig. 1).

Hydrogenation of 5,9-Dimethyl-4,8-decadienoic Acid (1). The hydrogenation of **1** was investigated by catalysis with the alkylsilyl-modified catalyst. Since the two double bonds were similar in a steric environment, regioselective hydrogenation could not be acheived over the usual heterogeneous catalyst. In fact, the regioselectivity in the hydrogenation of **1** was low over the control catalyst (Fig. 2-a). However, by catalysis over catalyst A, the regioselectivity in the hydrogenation was increased and the yield of 5,9-dimethyl-4-decenoic acid was 2-times that with catalysis over the control catalyst (Fig. 2-b). This result also originates from the effect of the ODS layer on platinum-silica. Uzuki and Suzuki[2] reported that alkylsilyl chloride was coupled with silica and that they covalently bonded with each other. In our case, the preparation method was similar to that of Uzuki and Suzuki, and the alkylsilyl reagent was thought to be bound to platinum–silica by a covalent bond. The results of the elemental analysis supported this view. It is possible to use carboxylic acid as the substrate and a polar solvent in the catalysis with the ODS-coupled catalyst. Consequently, the application range of this catalyst system is very wide in comparison with the carboxylic acid-modified catalyst.[1]

In conclusion, it was elucidated that an alkylsilyl-coupled catalyst makes it possible to achieve the regioselective hydrogenation of unsaturated acids.

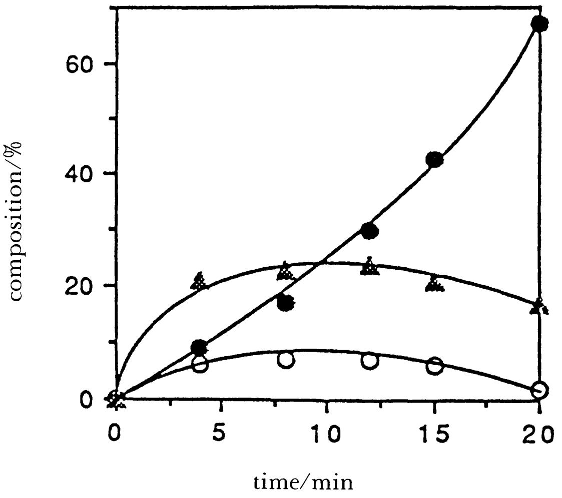


Fig. 2-a.

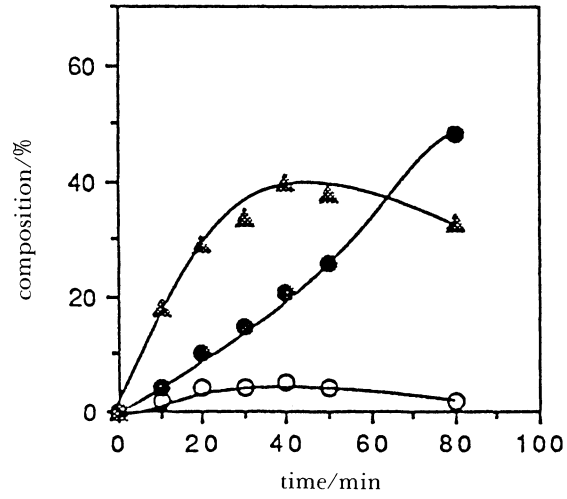
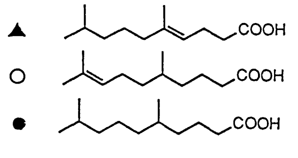


Fig. 2-b.

Fig. 2. Hydrogenation of 5,9-dimethyl-4,8-decadienoic acid: a) Control catalyst; b) Catalyst A. Conditions: Catalyst: 80 mg, 5,9-dimethyl-4,8-decadienoic acid: 12.5 mg, pentadecane: 25 mg, hexane: 20 cm^3, reaction temperature: 25 °C.



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