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COVALENTLY IMMOBILIZED COLLOIDAL METAL PARTICLES AS SELECTIVE
CATALYSTS FOR OLEFIN HYDROGENATION

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Homogeneous colloidal dispersions of ultrafine noble metal particles have been prepared by the reduction of the corresponding metal ions in the presence of protective polymers. These colloidal metal particles show effective and selective catalyses in hydrogenation of olefins.¹ However, separation of these homogeneous catalysts from reaction mixtures for the repeated use is difficult. Thus, immobilization of these colloidal metal particles to supports is required. This paper reports immobilization of colloidal rhodium particles onto polymer support by use of covalent bonding between the protective polymer and the support. Activities and selectivities of the resultant immobilized catalysts for hydrogenation of olefins are shown.

Copolymer of N-vinyl-2-pyrrolidone and methyl acrylate (methyl acrylate content 32 mol%) and polyacrylamide gel having

aminoethyl groups (aminoethyl Bio-Gel P-150 from BIO·RAD Laboratories Co.) were used as protective polymer and support, respectively. Homogeneous dispersion of polymer protected colloidal rhodium particles was prepared as dark brown solution by refluxing for 1 h a solution of the protective polymer (2.0 g/dm^3) and RhCl_3 ($1.0 \times 10^{-3} \text{ mol/dm}^3$) in ethanol-water mixture (1/1, v/v).

The immobilization of colloidal rhodium particles was achieved as follows. One gram of dry polyacrylamide gel having aminoethyl groups was sufficiently swollen in 53 cm^3 of water. To this mixture, 20 cm^3 of the colloidal dispersion was added. After stirring the mixture for a few days, dark brown color of the liquid layer disappeared and the color of the gel turned from white to dark brown, due to the immobilization of the colloidal particles. These procedures are schematically shown in Fig. 1. The immobilization was stable in a wide range of pH (2-13), and no release of the colloidal particles was detected after repeated washing with water or methanol.

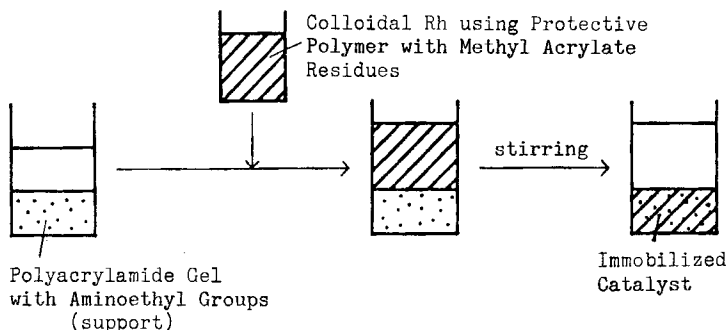


Fig. 1 Schematic Diagram for Immobilization Procedure of Colloidal Rhodium Particles

When homopolymer of N-vinyl-2-pyrrolidone was used as protective polymer, colloidal particles were not immobilized to the support at all. No immobilization occurred either, when a polyacrylamide gel without amino groups was used as support. These results indicate that the present immobilization is associated with formation of amide bonds between the methyl

acrylate residues in the protective polymer and the amino groups in the gel.

Table 1 shows catalytic activities of the resultant immobilized colloidal rhodium catalyst for hydrogenation of various olefins at 30°C under 1 atm, together with the ratios of the activities of the immobilized catalyst (r_i) to those of the homogeneous colloidal rhodium dispersion (r_d). The ratios (r_i/r_d), a measure for the magnitude of the effect of the immobilization on the catalytic activity, are small for hydrophobic olefins such as cyclohexene and 1-pentene, whereas the ratios are rather large for hydrophilic olefins such as ethyl vinyl ether and allyl alcohol. These facts show that the activities of the immobilized catalyst are mainly governed by the effective concentrations of the substrates in the vicinity of the catalyst. The effective concentrations are dependent on the interactions between the substrates and hydrophilic acrylamide gel as support. Quite significantly, the ratios for the hydrogenation

of acrylic acid and for 3-butenic acid are larger than 1. Here, the substrates are highly concentrated near the catalyst by electrostatic attractive force between carboxylate anion in the olefins and the ammonium group in the gel. The activities of the present immobilized catalyst for hydrogenation of 1-hexene, cyclohexene, and ethyl vinyl ether are 2,

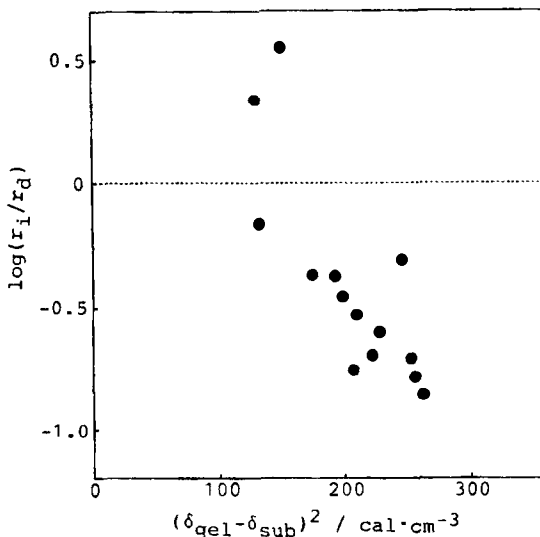
Tab. 1 Activities of the Immobilized Colloidal Rhodium Catalyst for Hydrogenation of Olefins

Substrate	Initial Rate of Hydrogenation ^{a)} (r_i)	r_i/r_d
Cyclohexene	140	0.21
Cyclopentene	280	0.26
1-Hexene	200	0.17
1-Pentene	140	0.14
Mesityl Oxide	86	0.18
2-Methyl-2-Pentene	13	0.20
Ethyl Vinyl Ether	570	0.50
Allyl Alcohol	130	0.45
3-Butene-1-ol	130	0.44
Allylamine	230	0.35
Methyl Vinyl Ketone	320	0.43
Methyl Acrylate	270	0.30
Acrylic Acid	150	2.2
3-Butenoic Acid	130	3.6

a) mmol H₂/mol Rh·s; at 30.0 °C under 1 atm in ethanol/water(1:1).

10, and 22 times as large as those of commercially obtained rhodium carbon catalyst, respectively.

Figure 2 depicts the plot of $\log(r_i/r_d)$ vs $(\delta_{\text{gel}} - \delta_{\text{sub}})^2$, where δ_{gel} and δ_{sub} are the solubility parameters of the gel as support and the substrates, respectively. Here, δ_{gel} was taken as identical with that of water, and δ_{sub} values were calculated



from the boiling point, density, and molecular weight.² A fair relationship is found: $\log(r_i/r_d)$ increases with decrease in $(\delta_{\text{gel}} - \delta_{\text{sub}})^2$. This result confirms the validity of the above argument showing the importance of the interactions between the substrate and the support, since smaller value of $(\delta_{\text{gel}} - \delta_{\text{sub}})^2$ corresponds to larger magnitude of the interaction.

The immobilized colloidal rhodium catalysts were easily recovered from the reaction mixtures by decantation without significant loss of activity. The activity in the fifth run for hydrogenation of cyclohexene was 98% of the value of the virgin catalyst.

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