CHEMISTRY LETTERS, pp. 149-152, 1987.

Preparation of Highly Active Hydrogenation Catalyst by Immobilization of Polymer-Protected Colloidal Rhodium Particles

Hidefumi HIRAI,* Michitaka OHTAKI, and Makoto KOMIYAMA
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Colloidal dispersion of rhodium protected by copolymer of methyl acrylate and N-vinyl-2-pyrrolidone is treated with polyacrylamide gel having amino groups, resulting in immobilization of the rhodium particles onto the gel. The gel-immobilized rhodium particles exhibit 2-22 fold larger catalytic activities than a rhodium carbon catalyst for hydrogenation of olefins at 30 °C under 1 atm.

Colloidal dispersions of ultrafine metal particles of diameters 5-100 Å were prepared by reduction of the corresponding metal ions in the presence of protective polymers.[1)] These dispersions showed effective and selective catalyses in hydrogenation of olefins[1,2)] and hydration of unsaturated nitriles to amides.[3)] Thus immobilization of the colloidal metal particles onto supports should provide quite useful catalysts for various reactions, if it is achieved without significant loss in the catalytic activities. However, informations on the immobilizations of colloidal metal particles have been rather scanty.

In a previous paper,[4)] the authors succeeded in the immobilization of colloidal platinum particles, protected by copolymer of acrylamide and N-vinyl-2-pyrrolidone, onto polyacrylamide gel having amino groups. The immobilization, which effectively proceeded in acidic solutions, was attributed to formation of amide bonds between the acrylamide residues in the protective polymer and the amino groups in the gel.

This paper reports on preparation of highly active hydrogenation catalysts by immobilization of colloidal rhodium particles onto a polyacrylamide gel having amino groups. The immobilization takes advantage of the reaction between the the gel and the protective polymer, a copolymer of methyl acrylate and N-vinyl-2-

pyrrolidone. The catalytic activities of the resulting immobilized catalysts for hydrogenation of olefins are shown.

A copolymer of N-vinyl-2-pyrrolidone and methyl acrylate as protective polymer was prepared in ethanol by use of benzoyl peroxide as radical initiator. The content of methyl acrylate residue in the copolymer was 32 mol%, as determined by elemental analysis: Obsd N, 8.60%. Calcd N, 8.58%. Polyacrylamide gel having aminoethyl groups (Aminoethyl Bio-Gel P-150, aminoethyl content 1.74 milliequivalent per 1 g of dry gel) was purchased from Bio-Rad Laboratories. Particle size of the gel in the hydrated state was 100-200 mesh.

Colloidal dispersions of metallic rhodium were prepared as dark brown homogeneous solutions by refluxing ethanol-water mixture (1:1 in volume) of rhodium(III) chloride for 1 h in the presence of the methyl acrylate-N-vinylpyrrolidone copolymer. The charged concentrations of rhodium chloride and the copolymer were 1.0 mmol dm^{-3} and 2.0 g dm^{-3} (the methyl acrylate residue 6.4 mmol dm^{-3}), respectively. Electron microscopy showed that rhodium particles having diameters 20-80 Å were highly dispersed without coaggregation and their average diameter was 50 Å.

Immobilization of colloidal rhodium particles onto the polyacrylamide gel having amino groups was carried out as follows. The gel (1.0 g) was sufficiently swollen in 53 cm^3 of water, and then the colloidal dispersion (20 cm^3) of rhodium was added. The mixture, which contained 0.128 mmol of methyl acrylate residue in the protective polymer and 1.74 mmol of the amino residue in the gel, was stirred at room temperature by use of a magnetic stirrer. The color of the gel gradually changed from white to dark brown, showing immobilization of colloidal rhodium particles onto the gel. After 3 days, almost all the rhodium particles were immobilized onto the gel and an immobilized catalyst was obtained as dark brown colored gel. The supernatant was virtually colorless, confirming absence of colloidal rhodium particles there.

The immobilization was stable, and no release of the colloidal particles from the gel was detected when pH of the mixture was changed in a wide range (from 2 to 13) after the immobilization. The immobilized catalyst remained also intact when it was repeatedly washed with water. These results rule out a possibility that the rhodium particles are simply attached to the gel either by electrostatically attractive force or by physical adsorption.

The present immobilization was successfully achieved in the pH region 4-9. In contrast, the immobilization of colloidal rhodium particles, protected by a copolymer of acrylamide and N-vinyl-2-pyrrolidone (acrylamide content 37 mol%), onto the gel having amino groups did not proceed at all at pH 9. Colloidal platinum particles, protected by the acrylamide-N-vinylpyrrolidone copolymer, were not immobilized onto the gel at pH 9 either. Immobilizations of these dispersions with the acrylamide-N-vinylpyrrolidone copolymer were successful only in acidic solutions.

When a polyacrylamide gel having no aminoethyl groups was used as support in place of the gel having amino groups, no immobilization occurred. Immobilization of colloidal particles of rhodium, prepared by use of homopolymer of N-vinyl-2-pyrrolidone as protective polymer, onto the gel having amino groups was not successful either. Thus the immobilization definitely requires both amino groups in the gel and methyl acrylate residues in the protective polymer.

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 residues in the gel. These reactions, which involve nucleophilic attack of the amino residues to the ester functions, efficiently proceed in alkaline solutions, since amount of the neutral amino residue as nucleophile is large here. Release of methoxide ion from the tetrahedral intermediate, formed by the nucleophilic attack, effectively proceeds without acid catalysis, since methoxide ion is rather good leaving group.5) In the immobilization of the metal particles protected by the acrylamide-N-vinylpyrrolidone copolymer, however, amide bonds are formed by the reactions between the acrylamide residues in the protective polymer and the amino residues in the gel.4) These reactions require acid catalyses, since the leaving group NH_2^- is so unstable that it must be protonated prior to being released from the tetrahedral intermediate.5)

Table 1 shows the catalytic activities of the gel-immobilized colloidal rhodium particles for the hydrogenation of various olefins. For all the olefins investigated, the catalytic activities of the present catalyst are much larger than those of 5% rhodium carbon catalyst obtained from Nippon Engelhard Co. The activities in the hydrogenation of ethyl vinyl ether and acrylonitrile are 22 and 12 times as large as those for the commercial catalyst.

Table 1. Catalytic Activities of Immobilized Colloidal Rhodium Particles for Hydrogenation of Olefins

Substrate	Initial hydrogenation rate[a)] Immobilized colloidal particles (r_i)	5% rhodium carbon (r_c)	r_i/r_c
Ethyl vinyl ether	170	7.7	22
Acrylonitrile	92	7.5	12
Cyclohexene	72	7.0	10
Mesityl oxide	56	12	4.7
1-Hexene	75	38	2.0

a) mmol H_2/mol Rh·s; at 30.0 °C under 1 atm in ethanol/water(1:1).

The present immobilized catalyst was easily separated by decantation from the reaction mixture after the reaction. When it was repeatedly used for the following runs, the catalytic activity remained virtually unchanged. In the hydrogenation of cyclohexene, for example, the catalytic activity in the fifth run was 97% of that in the first run.

The high activity of the present immobilized catalyst is mainly ascribed to quite large surface area of metallic rhodium particles. Here rhodium particles in the colloidal dispersion, which are characterized both by small average diameter (50 Å) and by narrow size distribution, have been successfully immobilized onto the polyacrylamide gel having amino groups without significant aggregation.

In conclusion, colloidal rhodium particles protected by a copolymer of methyl acrylate and N-vinyl-2-pyrrolidone are firmly immobilized onto a polyacrylamide gel having amino groups at pH 4-9. The resultant catalysts have large activities in the hydrogenation of olefins, and are repeatedly used without measurable decrease in the activities.

References

1) H. Hirai, J. Macromol. Sci. -Chem., A13, 633 (1979).

2) H. Hirai, H. Chawanya, and N. Toshima, Bull. Chem. Soc. Jpn., 58, 682 (1985).

3) H. Hirai, H. Wakabayashi, and M. Komiyama, Bull. Chem. Soc. Jpn., 59, 545 (1986).

4) H. Hirai, M. Ohtaki, and M. Komiyama, Chem. Lett., 1986, 269.

5) M. L. Bender, R. Bergeron, and M. Komiyama, "The Bioorganic Chemistry of Enzymatic Catalysis," John-Wiley & Sons, New York (1984), Chap. 5.

(Received October 4, 1986)