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IMMOBILIZATION OF COLLOIDAL PLATINUM PARTICLES ONTO POLYACRYLAMIDE GEL HAVING AMINO GROUPS AND THEIR CATALYSES IN HYDROGENATIONS OF OLEFINS

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Colloidal platinum dispersions, prepared by photo-reduction of tetrachloroplatinate(II) ion in the presence of a copolymer of N-vinyl-2-pyrrolidone and acrylamide, are treated with polyacrylamide gel having amino groups, resulting in stable immobilization of colloidal particles onto the gel. The immobilized catalysts exhibit high activities in hydrogenations of olefins at 30 °C under 1 atm.

Colloidal dispersions of metals are prepared by reducing the corresponding metal salts in the presence of appropriate protective polymers.1) The dispersions show high and selective catalyses in hydrogenations of olefins,1) partial hydrogenations of dienes to monoenes,2) and hydrations of unsaturated nitriles to unsaturated amides.3) The protective polymers take important roles both in the preparation of the dispersions and in the catalytic functions.

These results indicate that the immobilization of polymer-protected colloidal metal particles onto some supports can provide still more efficient catalysts, which have high and selective catalytic activities and in addition can be easily recovered from reaction mixtures.

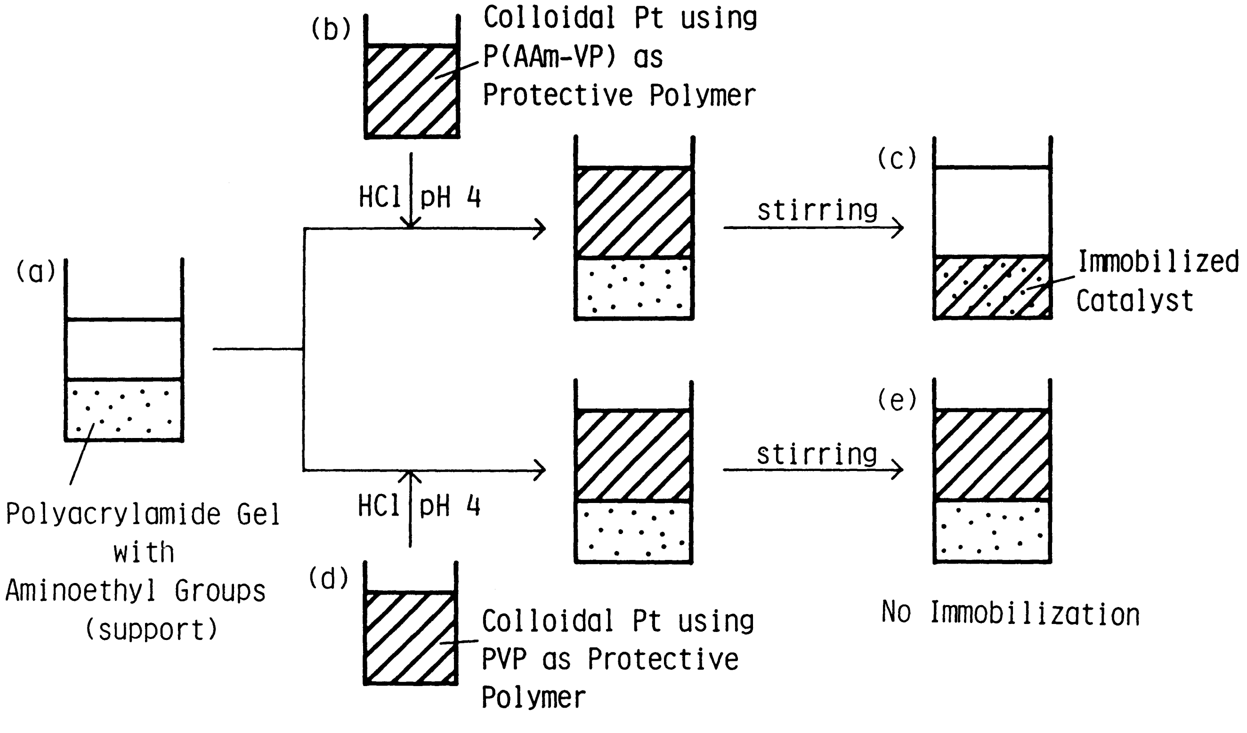
Nakao and Kaeriyama4,5) immobilized fine particles of noble metals, prepared without the use of protective polymers, using electrostatic interactions between the particles and supports. However, there have been few reports on the immobilization of polymer-protected colloidal metal particles to supports.

The present paper reports that the immobilization of colloidal platinum particles onto a polyacrylamide gel having aminoethyl groups, which takes advantage of reactions between protective polymers and the gel as support, and is stable in a wide range of pH. The activities of the resulting immobilized catalysts in the hydrogenations of olefins are shown.

A copolymer of N-vinyl-2-pyrrolidone and acrylamide (P(AAm-VP)) was prepared by radical copolymerization in water at 80 °C using benzoyl peroxide as initiator. The acrylamide residue content in the copolymer was 37 mol%, as determined by ^{1}H-NMR spectroscopy. Polyacrylamide gel having aminoethyl residues was obtained from Bio-Rad laboratories; the aminoethyl residue 1.74 milli-equivalent per 1 g of dry gel.

Colloidal dispersions of platinum were prepared as follows; potassium tetrachloroplatinate(II) (22.8 mg) and the N-vinyl-2-pyrrolidone-acrylamide copolymer (0.11 g) were dissolved in 55 cm^3 of water-ethanol mixture (1:1 in volume), and the solution was degassed twice by freeze-thaw method. Then the solution was irradiated with a 500W super-high-pressure mercury lamp (Ushio Electric Inc., type 501C) at room temperature for 2 h. The colloidal dispersions were obtained as homogeneous dark brown solutions. Transmission electron microscopies showed that the average diameter of platinum particles in the dispersions was 30 Å.

Procedures of the immobilization of the colloidal platinum particles onto the polyacrylamide gel having aminoethyl groups are depicted in Scheme 1. One gram of the gel (aminoethyl residue 1.74 milli-equivalent) was first sufficiently swollen in 53 cm^3 of water. To this mixture ((a) in Scheme 1), 20 cm^3 of dark brown colloidal platinum dispersion ((b), Pt content 0.02 mmol; the acrylamide residue in the protective polymer 0.148 milli-equivalent) was added, after pH of the dispersion was adjusted to 4 with hydrochloric acid. After being stirred for 15 min, the mixture was allowed to stand for 5 min. By this procedure almost all the colloidal platinum particles were successfully immobilized to the gel, producing an immobilized catalyst as dark brown gel (c). The supernatant was almost perfectly transparent, showing absence of colloidal particles in the liquid phase any more.



Scheme 1.

The immobilization was stable in a wide range of pH (2-13), and no release of the colloidal particles from the immobilized catalysts was detected even when the catalysts were repeatedly washed with water. These results rule out a possibility of immobilization by simple electrostatic force. The aminoethyl residues in the gel should be in their neutral forms above pH 10 and thus no electrostatic attraction can operate there.

The immobilization at pH 7 was considerably slower than that at pH 4, and about 20 h were required for all the colloidal particles to be immobilized effectively.

When a homopolymer of N-vinyl-2-pyrrolidone (PVP), which was purchased from Tokyo Kasei Kogyo Co., Ltd. and had viscosity-averaged degree of polymerization 3240, was used as protective polymer ((d) in Scheme 1) in place of the copolymer of N-vinyl-2-pyrrolidone and acrylamide, the immobilization of colloidal particles did not proceed at all at pH 4 (e). The immobilization of colloidal particles to an acrylamide gel without aminoethyl groups was not successful either. Thus, both the amino residues in the gel and the acrylamide residues in the protective polymer are definitely required for the stable immobilization of the colloidal particles. Probably, the immobilization is associated with formation of amide bonds, since productions of ammonia on the immobilization is detected using color development with sodium hypochlorite and 1-naphthol.[6)]

Table 1 shows the results of catalytic hydrogenation of olefins by the colloidal platinum particles immobilized to the polyacrylamide gel having aminoethyl groups. The hydrogenations were carried out in water-ethanol mixture (1:1 in volume) at 30 °C under 1 atm of hydrogen and were followed with the uptake of hydrogen determined by a gas burette.

Table 1. Initial Rates of Hydrogenation of Olefins Catalyzed by Colloidal Platinum Particles

Substrate	Initial hydrogenation rate[a)]			r_i/r_c
	Immobilized colloidal particles (r_i)	Colloidal dispersion	50% platinum carbon (r_c)	
Ethyl vinyl ether	160	340	1.6	100
Acrylamide	100	180	1.3	76.9
1-Hexene	110	330	3.2	34.4
Cyclohexene	36	240	2.1	17.1
Mesityl oxide	22	210	2.0	11.0
Acrylonitrile	22	45	-	-

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

The catalytic rates (r_i) per platinum atom on the immobilized catalyst in the hydrogenations of olefins are 10 to 100 times as large as the values (r_c) for commercially obtained platinum carbon catalyst (Pt content 50%). The ratios (r_i/r_c) for the hydrogenations of ethyl vinyl ether, acrylamide, and 1-hexene are 100, 77, and 34, respectively.

The large catalytic activity of the present immobilized catalyst is ascribed to the fact that colloidal platinum particles, which have large surface area due to their small sizes (average diameter 30 Å) and are effectively separated from each other without aggregation in the dispersion, are immobilized to the support without losing their catalytic activities significantly. Slight decrease (1.8-9.5 fold) in the catalytic activities on the immobilization, compared with the values for the homogeneous dispersions, are associated with enhancement in steric hindrance.

The present immobilized catalysts were easily separated from reaction mixtures by decantation or filtration, and the recovered catalysts showed almost the same catalytic activities as the values listed in Table 1.

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