Covalent Immobilization of Ultrafine Platinum Particles onto Crosslinked Polymer Support and Their Application to Catalysis

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

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Ultrafine particles of platinum were prepared as stable aqueous dispersions by a photoreduction method in the presence of soluble protective polymers. By use of the protective polymer with methyl acrylate residues as a reactive group, the polymer-protected ultrafine platinum particles were successfully immobilized onto crosslinked polymer supports with amino groups. The present immobilization was attributed to the formation of amide bonds by the reaction of methyl acrylate residues in the protective polymer with amino groups in the support, and the immobilization mechanism was investigated by the model reaction using protective polymer with *p*-nitrophenyl acrylate residues as a reactive group. The immobilized platinum particles obtained show high catalytic activity for hydrogenation of olefins and specific substrate selectivity due to a hydrophilic-hydrophobic interaction between the support and the substrate.

The ions of noble metals, such as gold, silver, platinum, and palladium, are easily reduced to the corresponding elemental metals in solutions by various reduction methods. By addition of soluble polymers before the reduction, stable dispersions of ultrafine metal particles protected by the polymers can be prepared.[1] These polymers, termed protective polymers or protective colloids, are adsorbed on the surface of metal particles by hydrophobic interactions, and prevent the aggregation of the particles by steric stabilization.[2,3] The adsorption of polymers on the surface of the fine particles is regarded as an irreversible process since the simultaneous desorption at all sites of multi-point adsorption of a long polymer chain is statistically difficult.[4] The interactions between the metal surface and the polymer chain are mainly to be attributed to essentially reversible physical adsorption.

Such ultrafine metal particles protected by polymers show high catalytic activity in various chemical reactions. Fine particles of rhodium and platinum protected by poly(vinyl alcohol) have high activity in hydrogenation of olefins under atmospheric pressure.[5] Noteworthy, rhodium particles of 9 Å average diameter catalyze hydrogenation of internal olefins more effectively than terminal olefins.[6] Ultrafine particles of palladium hydrogenate dienes to monoenes selectively without further hydrogenation.[7] The carbon–nitrogen triple bond of acrylonitrile is selectively hydrated by fine particles of copper protected by poly(*N*-vinyl-2-pyrrolidone), giving acrylamide in 100% yield without formation of any ethylene cyanohydrin.[8]

The dispersions of the polymer-protected fine metal particles are preferable to the conventional supported metal catalysts in the homogeneity of their particle sizes, the reproducibility in the preparation, and their activity and selectivity as catalysts. Nevertheless, the dispersed system has some difficulties in the separation of the products and the recovery of the catalysts from the reaction mixtures. The immobilization of the metal particles without reducing their activity, therefore, is of great importance for practical utilization of the catalysts. There have been some reports on immobilization of colloidal metal particles by use of Coulombic attractive force between charged colloidal particles and solid surfaces,[9] but there might be some problems. For example, electrical charges are neutralized at pH near the isoelectric point of the particles, and electrostatic interactions are drastically suppressed in organic media with low dielectric constants. Consequently, detachment of the particles from the support might occur by changing the environment of the electrostatically immobilized metal particles. In order to decrease these unfavorable probabilities it is required to make a strong linkage such as a covalent bond between the metal particle and the support. However, there has scarcely been any report on the immobilization of metal particles by covalent bondings.

Immobilization of homogeneous metal complexes has been widely investigated in the field of immobilized catalysts. Organic polymer supports have been widely used, since they can be easily functionalized by organic reactions. The formation of novel active sites by interactions between the metal complex and the polymer support,[10,11] and the increase in the catalytic selectivity by taking advantage of polymer effects[12–14] have been studied with great interest. Decrease of the activity of the metal complex catalysts caused by immobilization has been efficiently overcome by using a flexible spacer chain in pendant-like form.[15]

Protective polymers, which protect ultrafine metal particles from aggregation, can offer micro-environ-

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† Present address: The Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305.

†† Present address: Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162.

ment which is different from the bulk dispersion medium. Hence the modification of the protective polymers makes it possible to functionalize the fine metal particles. Thus a covalent immobilization of the fine metal particles can be achieved by bond formation between a functional group in the support and a reactive residue in the protective polymer. In this way the metal particles are immobilized onto the support in pendant-like form, minimizing the loss of activity of the fine metal particles due to the immobilization.

In the present paper, we introduce ester groups as reactive residues to the protective polymers by radical copolymerization. Covalent immobilizations of ultrafine platinum particles are successfully achieved by amide bond formation between the protective polymers and the support. Mechanisms of the immobilizations are investigated by following the formation of the releasing molecules during the immobilization reaction, together with a value of the ζ potential of the fine platinum particle. The catalytic activity of the immobilized platinum particles so obtained are examined in hydrogenation reactions of olefins. The selectivities for the substrates are discussed.[16)]

Experimental

Materials. Methyl acrylate and *N*-vinyl-2-pyrrolidone were purified by distillation of commercial guaranteed grade reagents under a nitrogen atmosphere. Acryloyl chloride was purified by vacuum distillation before use. A partially *N*-(2-aminoethyl) substituted polyacrylamide gel, Aminoethyl Bio-Gel P-150, was purchased from BIO·RAD Laboratories Co., Ltd. (California, U.S.A.) and used without further purification as the support for the immobilization. Other reagents were all of guaranteed grade and used as received.

Apparatus. ^{1}H NMR spectra were obtained on a JEOL FX-90Q NMR spectrometer, and IR spectra were recorded by a JASCO type A-3 infrared recording spectrophotometer. UV-VIS absorption spectra were obtained on a Hitachi 340 recording spectrophotometer and a MCPD-110A rapid scanning multichannel photodiode array spectrometer from Otsuka Electronics Co. The ζ potential of the platinum particle was evaluated on the basis of the velocity of the boundary movement by electrophoresis in a U-tube with a potential gradient of 1.57 V cm^{-1}.[17)] Transmission electron micrographs were observed with a Hitachi HU-12A transmission electron microscope operated at an acceleration voltage of 100 kV. Molecular weights of the protective polymers were determined by gel permeation chromatography (GPC) with a Toyo Soda HLC-802UR high performance liquid chromatograph apparatus equipped with G7000H6+G5000H6 +G3000H8 columns using chloroform as a mobile phase and polystyrenes as standards. GPC experiments in aqueous phase were performed by a Toyo Soda HLC-803D high performance liquid chromatograph apparatus equipped with a G3000PW column with water as the mobile phase at a flow rate of 0.5 cm^3 min^{-1}.

Synthesis of Protective Polymer with Methyl Acrylate Residues (P(MA–VP)). Poly(methyl acrylate-*co*-*N*-vinyl-2-pyrrolidone) (P(MA–VP)) was prepared as follows. Methyl acrylate (0.8 cm^3, 9 mmol), *N*-vinyl-2-pyrrolidone (22 cm^3, 200 mmol) and benzoyl peroxide (0.05 g, 0.4 mmol) were dissolved in 16 cm^3 of ethanol and the solution refluxed for 4 h at 80 °C. The reaction mixture was poured into diethyl ether and the resulting white precipitate was purified by reprecipitation with chloroform and diethyl ether. The copolymer so obtained was soluble in water, methanol, ethanol, and chloroform, whereas acetone, dioxane, diethyl ether, and hydrocarbons were poor solvents. The copolymer was identified by IR and ^{1}H NMR spectroscopy. In the IR spectrum of the copolymer, the peaks at 1405 cm^{-1} and 980 cm^{-1} due to C–H bendings of vinyl group disappeared, although the peaks at 1680 and 1725 cm^{-1} remained. These were assigned to the carbonyl stretching of the pyrrolidone ring and the carboxymethyl group, respectively. ^{1}H NMR spectrum of the copolymer gave a peak due to methoxyl protons at δ=3.65 ppm and peaks due to pyrrolidone ring protons in the region from 2.0 to 3.4 ppm in δ. No peaks were observed in the region from 6 to 7 ppm in δ due to vinyl protons. The content of methyl acrylate residues of the copolymer was quantified as 35 mol% by estimation of the peak areas of the ^{1}H NMR spectrum. The number-averaged molecular weight of the copolymer so obtained was determined as ca.5800 from the GPC measurement.

Synthesis of Protective Polymer with *p*-Nitrophenyl Acrylate Residues (P(NPA–VP)). *p*-Nitrophenyl acrylate was synthesized from acryloyl chloride and *p*-nitrophenol in the presence of triethylamine,[18)] and identified by IR and ^{1}H NMR spectroscopy. *p*-Nitrophenyl acrylate (0.193 g, 1.0 mmol) and azobis(isobutylonitrile) (0.164 g, 1.0 mmol) were dissolved in 22 cm^3 of *N*-vinyl-2-pyrrolidone. The mixture was degassed twice by freeze-pump-thaw cycles and refluxed for 21 h at 70 °C under nitrogen. The reaction mixture was then poured into diethyl ether and poly(*p*-nitrophenyl acrylate-*co*-*N*-vinyl-2-pyrrolidone) (P(NPA–VP)) was obtained as a light-yellow solid after purification by reprecipitation with the chloroform–diethyl ether system. The copolymer so obtained was readily soluble in chloroform and ethanol, but the solubility in water was low, possibly due to the hydrophobic nitrophenyl groups. The IR spectrum of P(NPA–VP) retained the peaks at 3100, 1740, 1520, and 1350 cm^{-1} ascribed to the *p*-nitrophenyl ester group and the pyrrolidone ring, although no peaks from the vinyl group remained. The observed peaks at δ=7.2 and 8.3 ppm in the ^{1}H NMR spectrum of the copolymer were assigned to the protons of the para-disubstituted aromatic ring in the *p*-nitrophenyl residue, whereas no peaks were observed in the vinyl region. The content of *p*-nitrophenyl acrylate residues of the copolymer was 14 mol% on the basis of the peak areas of the ^{1}H NMR spectrum. The number-averaged molecular weight of P(NPA–VP) was estimated as ca.1600 from the GPC.

Preparation of Ultrafine Platinum Particles. Ultrafine platinum particles were prepared as aqueous dispersions by a photoreduction method.[19)] Potassium tetrachloroplatinate (II) and the copolymer P(MA–VP) were dissolved in a water–ethanol (1/1, v/v) mixed solvent at concentrations of 1.0×10^{-3} mol dm^{-3} and 2 g dm^{-3}, respectively. The number of residues of the protective polymer per platinum atom was 20. The solution in a Pyrex Schlenk tube was degassed twice by freeze-pump-thaw cycles and then irradiated by a 500 W ultra high-pressure mercury lamp (Ushio Electric Co., Ltd.) for 2 h at room temperature. A dark brown homogeneous dispersion was obtained. When P(NPA–VP) was used as a protective polymer, ultrafine platinum particles were prepared by the same procedure at concentrations of [Pt]=1.0×10^{-4} mol dm^{-3} and [P(NPA–VP)]=0.25 g dm^{-3}. Under these conditions, the ratio of polymer residues to a platinum atom was 25.

Immobilization of Platinum Particles Protected by P(MA–VP) onto Polymer Support. A polyacrylamide gel with 2-aminoethyl groups was used as a support for immobilization. One gram of the support was sufficiently swollen by 53 cm^3 of water, and to this mixture was added 20 cm^3 of the dark brown aqueous dipersion of the ultrafine platinum particles. After stirring this mixture for several hours the dark brown colored support was separated by filtration and washed repeatedly with water and then with methanol. The resulting support was dried in vacuo to obtain the immobilized catalyst.

Reaction of Protective Polymer with *p*-Nitrophenyl Acrylate Residues with 2-Aminoethyl Polyacrylamide Gel. The model reactions of immobilization by the use of the protective polymer containing *p*-nitrophenyl ester residues instead of methyl ester were carried out in buffer solutions at pH 8.3, 9.3, and 10.3. The ionic strengths of the buffer solutions were adjusted to 0.5 mol dm^{-3} by addition of potassium chloride in all cases. A half gram of 2-aminoethyl polyacrylamide gel (2-aminoethyl content, 0.87 milliequivalent) was sufficiently swollen by 11 cm^3 of the buffer solution at the prescribed pH. The pH values of the supernatants were the same as those of the initial buffer solutions. The reaction was initiated by addition of 5 cm^3 of the dispersion of ultrafine platinum particles which were protected by a copolymer with *p*-nitrophenyl acrylate residues, P(NPA–VP). Aliquots of the reaction mixture were sampled after appropriate intervals and the filtrates of the samples were measured spectrographically.

Measurement of Catalytic Activities of the Ultrafine Platinum Particles for Olefin Hydrogenation. Catalytic hydrogenation reactions of various olefins under atmospheric pressure were carried out as follows: To 0.1 g of the immobilized platinum catalyst (amount of platinum, 2×10^{-6} mol), 19 cm^3 of a water–ethanol (1/1, v/v) mixed solvent was added and the mixture was stirred at 30.0 °C under hydrogen at atmospheric pressure until a steady volume of the gas phase was attained. Then the reaction was started by addition of 1 cm^3 of the ethanol solution of the substrate to give a total volume of 20 cm^3. The hydrogen uptake was followed by a gas burette to determine the initial rate of hydrogenation. In the case of the reaction using the dispersion of ultrafine platinum particles as a catalyst, 1 cm^3 of the dispersion (amount of platinum, 1×10^{-6} mol) and 18 cm^3 of the solvent was used.

Results and Discussion

Preparation of the Dispersions of Ultrafine Platinum Particles. Ultrafine particles of platinum were prepared by photoreduction using a copolymer with methyl acrylate residues, P(MA–VP), as a protective polymer. The dispersions obtained showed a dark brown color and were stable for more than several months. Absorption spectra of the dispersion are illustrated in Fig. 1. The dispersions of platinum particles obtained after the photoreduction show broad absorption spectra without structure from the visible region to the near UV. The absorption peaks due to $PtCl_4^{2-}$ completely disappeared on photoreduction, showing completion of the reduction of the platinum ions. The transmission electron micrograph was observed by dropping the obtained dispersion on a micro grid supported on a copper mesh. The resulting electron micrograph with size distribution is shown in Fig. 2. The platinum particles were small with considerably narrow size distribution at an average dimeter of ca. 19 Å.

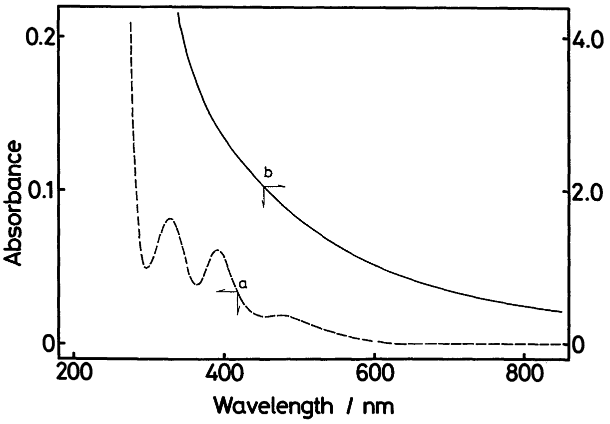


Fig. 1. UV-VIS absorption spectrum of colloidal dispersion of ultrafine platinum particles before (a) and after (b) photoreduction.

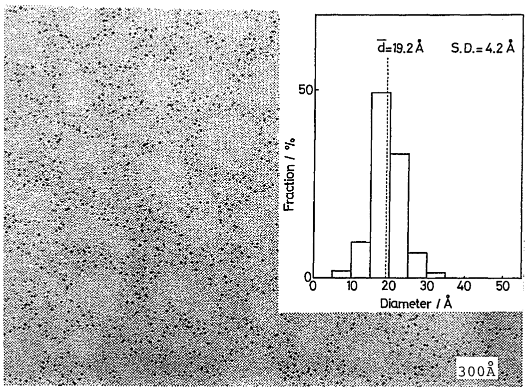


Fig. 2. Transmission electron micrograph of ultrafine platinum particles prepared by photoreduction in the presence of P(MA–VP). Particles size distribution and average diameter are also shown.

Although a solution of the protective polymer alone showed the peak at elution volume of 12 cm^3, the peak of the protective polymer disappeared for the dispersion of the polymer-protected ultrafine platinum particles in the aqueous GPC measurements. This result suggests that, at least under the conditions of the present GPC experiments, the protective polymer remains adsorbed on the surface of the platinum particles without any desorption. Since the platinum particles protected by the polymer are required to permeate through the porous gel packed in the GPC column under high head pressure around 15 kgf cm^{-2} (1470 kPa) in the GPC experiments, the adsorption of the protective polymer on the surfaces of the metal particle is considered to be fairly strong. This is consistent with a practical irreversibility of polymer adsorption on the solid surface at the liquid–solid interface.[4]

Immobilization of the Ultrafine Platinum Particles to the Polymer Support. The main chain of the polymer protecting the metal particles in solution is considered to consist of sequences of segments termed "trains", "loops", and "tails".[20] The "trains" are in direct contact with the surface of the metal particle, and "loops" and "tails" are the middle and the free ends of the polymer chains, respectively, both extending into the bulk solution. In the protective polymers, the reactive residues which can practically react with the support are likely to be those in "loops" and "tails". Even after the "loops" and "tails" have been linked to the support, the "trains" are considered to interact with the metal surface. Consequently, it is expected that the ultrafine metal particles will be immobilized onto the support with the surrounding protective polymers in a pendant-like form as illustrated in Fig. 3.

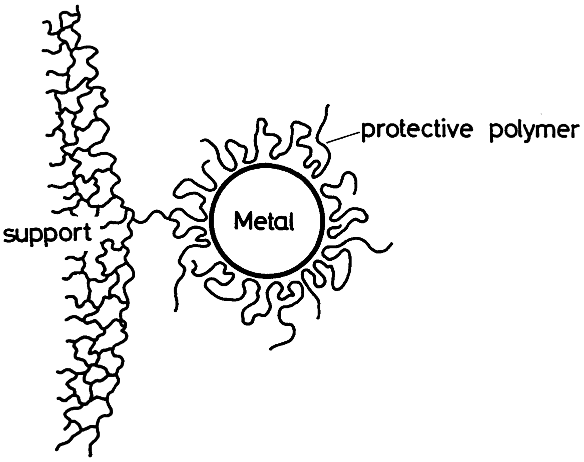


Fig. 3. Schematic illustration for covalent immobilization of ultrafine metal particles protected by polymers.

The support used for the immobilization is a crosslinked acrylamide gel in which some amide groups are 2-aminoethylated (the 2-aminoethyl content is 1.74 milli-equivalent per gram of the dry gel). The support, a white fine powder in the dry state, becomes a colorless translucent slurry when swollen by water. After swelling 1.0 g of the support by 53 cm^3 of water, a translucent slurry of the support settled down to the lower layer and the upper layer was transparent as an aqueous supernatant. To this mixture, was added 20 cm^3 of the dark brown dispersion of ultrafine platinum particles protected by P(MA–VP), and the mixture was stirred for several hours. When the resulting mixture was stilled for a while, the dark brown support settled down to the lower layer and the liquid phase turned colorless. This color change clearly demonstrates the immobilization of the platinum particles in the dispersion onto the support. The appearance of these procedures is schematically shown in Fig. 4.

The immobilization was strong enough to permit repeated washing with solvents such as water, methanol, and ethanol. No release of the immobilized particles from the support was observed. No detachment of the immobilized particles was detected on altering the pH of the system within the range from 2 to 13. Moreover, the immobilization was completed even at high ionic strength in a 0.1 mol dm^{-3} NaCl solution. From these results, both physical adsorption and electrostatic adsorption can be ruled out as the nature of the present immobilization. As planned, a firm linkage between the protective polymer and the support is believed to be formed.

By the use of a polyacrylamide gel without any 2-aminoethyl group as a support instead of with the 2-aminoethyl group, no immobilization of platinum

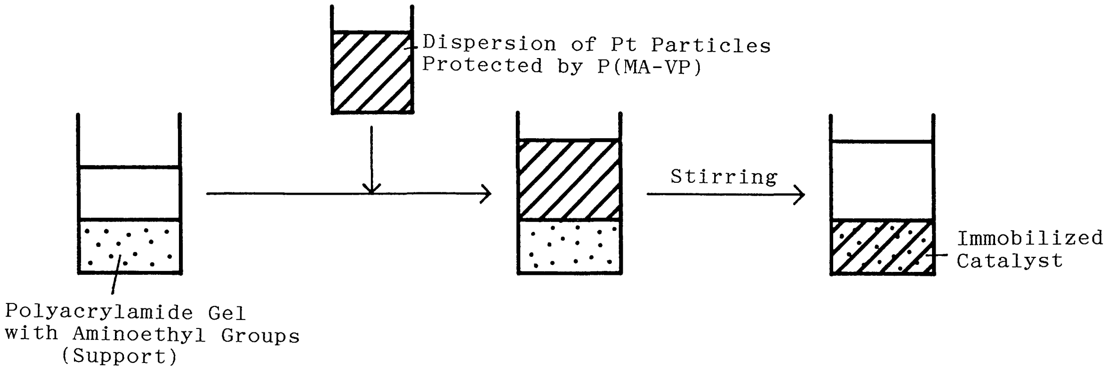
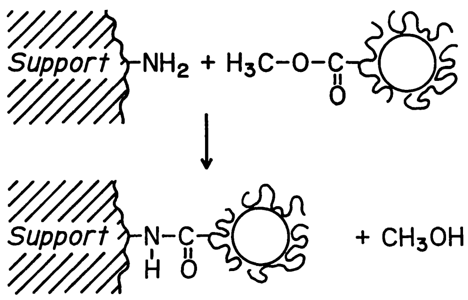
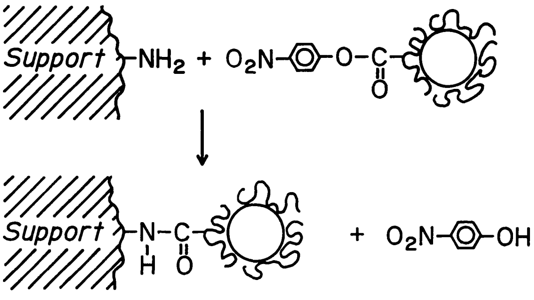


Fig. 4. Schematic diagram for immobilization of ultrafine platinum particles onto polyacrylamide gel having amino groups.



Scheme 1.



Scheme 2.

particles protected by P(MA–VP) occurred. On the other hand, no platinum particles protected by poly(*N*-vinyl-2-pyrrolidone) without a methyl acrylate residue were immobilized onto the 2-aminoethyl polyacrylamide gel. It is obvious from these facts that both the 2-aminoethyl groups in the support and the methyl acrylate residues in the protective polymer are required to achieve the immobilization.

The above results strongly suggest the formation of an amide bond by the chemical reaction between the methyl acrylate residue in the protective polymer and the amino group in the support, as shown in Scheme 1, in the similar way to the aminolysis of an ester. To confirm this conjecture, a model reaction was performed by use of a protective polymer with *p*-nitrophenyl ester residues instead of methyl acrylate, and the reaction mechanism of the immobilization was investigated.

Immobilization Mechanism. Assuming the amide bond formation occurs by aminolysis of the methyl ester residues in the protective polymers, the immobilization reaction must be accompanied by an evolution of methanol as shown in Scheme 1. Nevertheless, the methanol evolved could not be detected by a gas chromatograph in the preliminary experiments because of the enormous amount of accompanying ethanol. If the immobilization was achieved by using a protective polymer with *p*-nitrophenyl ester as the reactive residue, instead of methyl ester, *p*-nitrophenol must have been evolved[21] during the immobilization reaction as is shown in Scheme 2. *p*-Nitrophenol is a chromophore with a pK_a value of 7.1, and, in basic conditions, has strong absorption maximum at λ=400 nm with ε=18,200 as *p*-nitrophenolate.[22] The amide bond formation in the immobilization thereby can be examined by following the absorption spectrum of the released *p*-nitrophenolate anion in the liquid phase.

The reactions were carried out at pH 8.3, 9.3, and 10.3, in both the presence and absence of the support. The absorption spectra of filtrates of the reaction mixtures were recorded against the reaction time. The absorption by the platinum particles was compensated by deduction of absorbance at 550 nm from the values at 400 nm, and the time course of the net values obtained was analyzed.

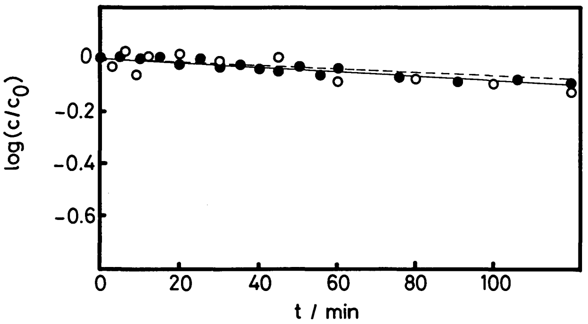


Fig. 5. Change of *p*-nitrophenol concentration during the aminolysis of *p*-nitrophenyl acrylate residues in P(NPA–VP) as the protective polymer of ultrafine platinum particles at pH 8.3 in the presence (○) and the absence (●) of the support with amino groups.

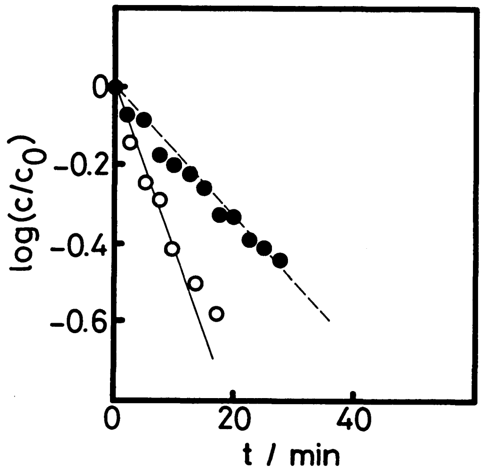


Fig. 6. Change of *p*-nitrophenol concentration during the aminolysis of *p*-nitrophenyl acrylate residues in P(NPA–VP) as the protective polymer of ultrafine platinum particles at pH 10.3 in the presence (○) and the absence (●) of the support with amino groups.

Because the concentration of hydroxide ions in an aqueous phase is steady and the amount of the amino groups in the support (0.87 milli-equivalent) is in large excess to that of the *p*-nitrophenyl ester residues in the protective polymer (1.75×10^{-3} mmol), pseudo first-order kinetics can be assumed for the ester residues. As plotted in Figs.5 and 6, logarithms of the concentrations of the remaining ester residues in the protective polymer linearly decrease with the reaction time, confirming the validity of the pseudo first-order assumption. Apparent pseudo first-order rate constants k_{obs} were calculated from the slopes of the straight lines fitted to the data at each pH by least-squares regressions. The results are summarized in Table 1. Since the values of k_{obs} contain contributions from the spontaneous hydrolysis of P(NPA–VP) at the corresponding pH, the differences between k_{obs} in the presence and absence of the support at each pH are ascribed to net esterlysis by the amino groups in the support. The value of k_{obs} at pH 10.3 for the P(NPA–VP) involving the ultrafine platinum particles in the presence of the support is obviously larger than the value in the absence of the support, which confirms the attack of the amino groups on the *p*-nitrophenyl acrylate residues resulting in the formation of the amide bond between the support and the protective polymers with release of *p*-nitrophenol. At pH 8.3, on the other hand, the value of k_{obs} in the presence of the support is small and almost the same as in the absence of the support. These facts indicate that the release of *p*-nitrophenol at pH 8.3 is not due to reaction with the amino groups in the support but mostly to the reaction with water, spontaneous hydrolysis.

The amino group in the support is considered to have a pK_a value about 10 estimated from the values for alkylamines, for example $pK_a=10.63$ for ethylamine,[23] so that half of the amino groups and almost all of them must be protonated at pH 10.3 and 8.3, respectively. The absence of the release of *p*-nitrophenol by the reaction with the amino groups at pH 8.3 is imputed to a loss of nucleophilicity of the amino group on protonation. This is inconsistent with the occurrence of the immobilization at pH 8.3. The protonated amino group acquires a positive charge at the same time with the loss of nucleophilicity so that electrostatic attractive force may play a major role in the immobilization at pH 8.3 if the ultrafine platinum particles are charged negatively as is generally reported for inorganic colloidal particles.[24] From the electrophoretic experiments, the ζ potential of the platinum particle was evaluated as -10 mV, in agreement with the previous reports for the sign of the charge.[24] In the immobilization at pH 8.3, the platinum particles are thus assumed to be adsorbed electrostatically on the positively charged amino groups in the support. If this is the case, the detachment of the platinum particles from the support is expected at higher pH area where the amino group is deprotonated and loses the positive charge. Actually, no release of the platinum particles was detected on increase of the pH from 8.3 to 10 or 12. Instead both the coloring of the liquid phase by release of *p*-nitrophenol and flocculation of the support were observed. This finding is ascribed to the gain of nucleophilicity of the amino group and at the same time the charge neutralization and the consequent amide bond formation by the amino group with the copolymer protecting the platinum particles before their release.

Table 1. Apparent Pseudo First-Order Rate Constants for Aminolysis of *p*-Nitrophenyl Ester Residue in P(NPA–VP)

System	$k_{\mathrm{obs}}\times10^6/\mathrm{s}^{-1}$		
	pH 8.3	pH 9.3	pH 10.3
Pt/P(NPA–VP)[a]+Support	3.1	24	160
Pt/P(NPA–VP)[a] only	2.4	7.4	67

a) Pt ultrafine particles protected by P(NPA–VP).

From the results mentioned above, it is corroborated that, in the pH range where the amino groups have nucleophilicity, amide bonds are formed by chemical reactions between the ester residues in the protective polymers and the amino groups in the support, and the polymer-protected ultrafine platinum particles are covalently immobilized onto the support.

Catalytic Activities of the Immobilized Ultrafine Platinum Particles. The immobilized ultrafine platinum particles obtained were subjected to catalytic hydrogenation reaction of olefins under atmospheric pressure at 30 °C. Initial rates of the hydrogenation of various olefins catalyzed by the immobilized platinum

Table 2. Catalytic Activities of Ultrafine Platinum Particles for Hydrogenation of Olefins

Substrate	Initial hydrogenation rate[a]				
	Immobilized ultrafine particles (r_i)	Colloidal dispersion (r_d)	50% platinum carbon (r_c)	r_i/r_c	r_i/r_d
Ethyl vinyl ether	160	340	1.6	100	0.47
Acrylamide	100	180	1.3	77	0.56
1-Hexene	110	330	3.2	34	0.33
Cyclohexene	36	240	2.1	17	0.15
Mesityl oxide	22	210	2.0	11	0.10
Acrylonitrile	22	45	0.0	—	0.49

a) H_2-mmol Pt-mol^{-1} s^{-1} at 30.0 °C under 1 atm of hydrogen in ethanol/water (1:1). See text for details.

particles and the commercial platinum carbon catalyst are shown in Table 2. Ethyl vinyl ether, acrylamide, 1-hexene, cyclohexene, mesityl oxide (4-methyl-3-penten-2-one), and acrylonitrile were used as substrates. The immobilized platinum particles show remarkably high catalytic activities which are 11, 34, and 100 times as large as the commercial platinum carbon catalyst for mesityl oxide, 1-hexene, and ethyl vinyl ether, respectively. The commercial platinum carbon catalyst has little activity for hydrogenation of acrylonitrile. These results indicate that the catalytic activities of the ultrafine platinum particles are not seriously damaged through the immobilization procedure.

The catalytic activities of the dispersions of platinum particles before immobilization vary by a factor up to 2 for all except acrylonitrile, whereas the activities of the immobilized platinum particles range over a factor of 7 between ethyl vinyl ether and mesityl oxide at the maximum. This situation is attributed to the fact that the decrease of the activities by the immobilization depends on the substrates, i.e., the decreases are small for ethyl vinyl ether, acrylamide, and acrylonitrile, and large for 1-hexene, cyclohexene, and mesityl oxide. The ratio of the activities of the immobilized platinum particles to those of the dispersions of the particles before the immobilization, r_i/r_d, was calculated as a measure of the change of activities by the immobilization. The ratios are around 0.5 for acrylamide, acrylonitrile, and ethyl vinyl ether, 0.33 for 1-hexene and about 0.1 for cyclohexene and mesityl oxide as indicated in Table 2.

The change of the value of r_i/r_d is influenced by the presence of the support. The support for the immobilization has an acrylamide skeleton with strong hydrophilicity so that the effective concentraions of hydrophobic substrates can decrease around the active sites of the immobilized catalyst. The values of r_i/r_d and solubilities in water (w% in water)[25] of the substrates as a qualitative measure of their hydrophilicity are summarized in Table 3. The values of r_i/r_d exhibit a similar tendency in the order to the solubilities in water except for cyclohexene and mesityl oxide. Cyclohexene is an internal olefin with larger steric hindrance for hydrogenation than the terminal olefins on account of two methylene groups adjacent to the carbon–carbon double bond. The steric hindrance for mesityl oxide is also extremely large because of two methyl groups and one carbonyl group next to the double bond. It is considered that the steric hindrance for these substrates will be emphasized by the bulky support in the vicinity of the catalytic active sites, which results in a large decrease of the catalytic activity by the immobilization of the platinum particles onto the support. The decrease of the catalytic activity of the ultrafine platinum particles by the immobilization is thus considered to depend on the change of effective concentration of substrates around the catalyst owing to the hydrophilic–hydrophobic interaction with the strongly hydrophilic support and further to the increasing steric hindrance by the support for the highly sterically hindered olefins.

Table 3. Relationship between r_i/r_d and Solubility of Substrates in Water

Substrate	r_i/r_d	Solubility/%[a]
Acrylamide	0.56	68.3
Acrylonitrile	0.49	7.35
Ethyl vinyl ether	0.47	0.9
1-Hexene	0.33	0.00697
Cyclohexene	0.15	0.0213
Mesityl oxide	0.10	2.89

a) Ref. 25.

The immobilized catalyst of ultrafine platinum particles is easily separated from the reaction mixtures by filtration or decantation. No release of the particles occurs during these separating operations. The recovered catalyst can be used repeatedly, and shows almost same activity as the initial one. These facts suggest that the immobilization of the metal particles is firm and that the agglutination of the ultrafine metal particles is prevented during the reactions and recovery of the catalyst. These can be regarded as the advantages of the present immobilization method, in which the metal particles are well dispersed and separately immobilized on the support.

Conclusion

For practical utilization of the peculiar catalytic activities of the ultrafine metal particles, immobilization of the particles onto some supports without serious damage to the activity is required. The immobilization by chemical reaction between the polymers protecting the metal particles and the polymer support provides a powerful response to this request.

In the present study, the ultrafine platinum particles were successfully immobilized onto the polymer support by covalent bonds formed by the reaction between the protective polymer with methyl acrylate residues and the support with amino groups. The model reaction using the protective polymer with *p*-nitrophenyl ester residues was performed to investigate the mechanism of the immobilization. It was confirmed that the immobilization was achieved by the formation of amide bonds from aminolysis of ester residues in the protective polymer attacked by amino groups in the support in the range of pH where the amino group retains its nucleophilicity. The immobilized catalyst showed both high activity for hydrogenation of olefins and specific selectivities attributed to the hydrophilic–hydrophobic interactions between the olefins and the support. It is concluded that the present immobilization of the metal particles is stable and that the immobilized catalyst is durable for recovery and repeated use with no significant loss of activity.

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References

1) H. Hirai, Y. Nakao, and N. Toshima, *J. Macromol. Sci., Chem.*, **A13**, 727 (1979); H. Hirai and N. Toshima, in "Tailored Metal Catalysts," ed by Y. Iwasawa, D. Reidel Publishing Company, Netherlands (1986), pp. 87—140.

2) W. Heller and T. L. Pugh, *J. Polym. Sci.*, **47**, 203 (1960).

3) D. H. Napper, *J. Colloid Interface Sci.*, **58**, 390 (1977).

4) J. M. H. M. Scheutjens and G. J. Fleer, *Adv. Colloid Interface Sci.*, **16**, 341 (1982).

5) H. Hirai, *J. Macromol. Sci., Chem.*, **A13**, 633 (1979).

6) H. Hirai, Y. Nakao, and N. Toshima, *Chem. Lett.*, **1978**, 545.

7) H. Hirai, H. Chawanya, and N. Toshima, *Reactive Polym.*, **3**, 127 (1985).

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

9) For example, Y. Nakao, and K. Kaeriyama, *J. Colloid Interface Sci.*, **131**, 186 (1989).

10) P. Perkins and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **101**, 3985 (1979).

11) M. Barteri, B. Pispia, and M. V. Primiceri, *Biopolymers*, **18**, 3119 (1979).

12) R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, **93**, 3062 (1971).

13) G. Innorta, A. Modeffi, F. Scagnolari, and A. Foffani, *J. Organomet. Chem.*, **185**, 403 (1980).

14) F. R. Hartley, S. G. Murray, and P. N. Nicholson, *J. Mol. Catal.*, **16**, 363 (1982).

15) J. M. Brown and H. Molinari, *Tetrahedron Lett.*, **1979**, 2933.

16) Preliminary results of this work have been published as communications; H. Hirai, M. Ohtaki, and M. Komiyama, *Chem. Lett.*, **1986**, 269; H. Hirai, M. Ohtaki, and M. Komiyama, *Chem. Lett.*, **1987**, 149.

17) A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

18) C.-P. Su and H. Morawetz, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 185 (1977).

19) N. Toshima, T. Takahashi, and H. Hirai, *Chem. Lett.*, **1985**, 1245.

20) T. F. Tadros, in "Polymer Colloids," ed by R. Buscall, T. Corner, and J. F. Stageman, Elsevier, Essex (1985), Chap. 4.

21) C.-P. Su and H. Morawetz, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1059 (1978).

22) A. Eigel, H. Bunemann, and N. Dattagupta, *Makromol. Chem.*, **175**, 1847 (1974).

23) "Kagaku Binran Kisohen," 3rd ed, ed by Chemical Society of Japan, Maruzen, Tokyo (1984), p. II-339. (A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York (1974, 1975, 1977), Vol. 1—3.)

24) B. Jirgensons and M. E. Straumanis, "A Short Textbook of Colloid Chemistry," 2nd ed, Pergamon, New York (1962).

25) J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Techniques of Chemistry," Vol. 2, "Organic Solvents," 4th ed, John Wiley & Sons, New York (1986).