Effects of Polymer Support on the Substrate Selectivity of Covalently Immobilized Ultrafine Rhodium Particles as a Catalyst for Olefin Hydrogenation

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ABSTRACT: Ultrafine rhodium particles prepared by alcohol reduction in the presence of a protective polymer were covalently immobilized onto a cross-linked polymer support by forming the amide bond between the primary amino group contained in the support and the methyl acrylate residue in the protective polymer of the particles. Catalytic activity of the immobilized particles was investigated in catalytic hydrogenation of olefins. The activity strongly depended on the substrates used in the reactions. The immobilized ultrafine rhodium particles preferentially hydrogenated hydrophilic substrates. In particular, the substrates containing a carboxyl group were hydrogenated by the immobilized catalyst more easily than by the dispersed catalyst of the ultrafine rhodium particles before the immobilization. The difference in the hydrogenation rates can be correlated with the solubility parameter of the substrates. Electrostatic interaction between the substrates and the polymer support leads to increased reaction rates.

Introduction

Extremely small metal particles of diameters from 10 to some hundreds angstroms exhibit many characteristics different from those of their bulk state. The unusual properties of ultrafine metal particles are under extensive investigations,[1] particularly concerning the high activity and high specificity in catalyses.[2-4]

The ultrafine particles of noble metals such as platinum, rhodium, and palladium can be easily prepared in dispersed forms by reduction of the corresponding metal ions in solutions in the presence of soluble protective polymers.[5-9] The protective polymers in solution are physically adsorbed on the surfaces of the metal particles. The adsorption is considered to be practically irreversible since simultaneous desorption of all polymer segments adsorbed on the surface would be unlikely. As a consequence, the protective polymers prevent aggregation of the particles by steric stabilization[10,11] and disperse them homogeneously in the liquid media.

A stable dispersion of ultrafine rhodium particles of a 40-Å average diameter was obtained by reflux of the rhodium chloride solution in water–methanol (1/1, v/v) with poly(vinyl alcohol).[5] The resulting rhodium particles showed high catalytic activity in the hydrogenation of olefins.[5,6] The alcohol reduction in methanol resulted in the formation of exceedingly small rhodium particles of a 9-Å average diameter by use of poly(*N*-vinyl-2-pyrrolidone) as a protective polymer with addition of a small amount of sodium hydroxide, and the 9-Å rhodium particles catalytically hydrogenated internal olefins more efficiently than terminal olefins.[7,8] Bimetallic alloy ultrafine particles, which exhibited improved catalyses, have also been prepared by the alcohol reduction from a mixed solution of the corresponding metal ions.[12,13]

In spite of their high catalytic power, there are some problems in the separation and the recovery of the ultrafine metal particles from the reaction mixtures. Applications of the ultrafine metal particles for practical catalyses strongly require immobilization of them onto some solid supports in a manner similar to that in applications of common homogeneous metal complex catalysts.

There are reports on immobilizations of ultrafine metal particles by the electrostatic attractive force between electrically charged ultrafine particles and ionic moieties on supports.[14] However, the electrostatic immobilization is thought to be unreliable for practical utilization since the electrostatic interaction might be canceled by altering ionic conditions of the dispersion media. Covalent immobilization achieved by a chemical reaction between ultrafine particles and supports could solve this problem. Nevertheless, there are no reports on the covalent immobilizations of ultrafine metal particles on supports to our knowledge.

When a suitable polymer support is chosen from a wide variety of the polymers derived from various organic reactions, the reaction field of the immobilized catalyst can be altered by the microenvironment of the polymer support, which may improve catalytic activity and selectivity. For example, rhodium complex catalysts immobilized on polystyrene resins were found to exhibit size selectivity for substrates in catalytic hydrogenation. This was ascribed to a sieve effect by the cross-linked reticular structure of the support resin,[15,16] and the selectivity was changed by changing the solvents for the reaction, owing to hydrophobicity of the polystyrene skeleton of the support.[17] Moreover, significantly higher optical yields than those by the homogeneous counterparts were attained in asymmetric syntheses by the catalysts immobilized on optically active supports such as proteins and synthetic polypeptides.[18,19] There are also a number of reports on the increases in selectivity and activity in polymer-immobilized catalysts.[20,21] In these cases the supports not only serve as carriers of catalytic sites to facilitate the separation of the catalysts but also contribute to the catalytic activity by support effects.

In most cases, however, the improvement in the activity and the selectivity is attributed to the exclusion of the substrates unadaptable to the microenvironment of the

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immobilized catalysts. An improvement in the catalyses by the activation of the catalyst due to substrate–support interactions has been rare. Recently, Nishikubo et al. reported the improved activity of polymeric photosensitizers containing a substrate-attracting group in photoisomerization reactions.[22-24] The results were ascribed to the effective concentration of the substrate around the sensitizer by electrostatic interaction between the substrate and the substrate-attracting group.

We have already reported the immobilization of the polymer-protected ultrafine platinum particles prepared by a photoreduction method onto an aminoethylated polyacrylamide gel.[25,26] The immobilization was responsible for formation of the amide bond by the chemical reaction between the methyl acrylate residue in the protective polymer and the primary amino group in the support gel. The mechanism of the immobilization was also confirmed by a model reaction using a protective polymer containing the *p*-nitrophenyl acrylate residue as a releasing group.[26]

In the present paper, polymer-protected rhodium ultrafine particles prepared by the alcohol reduction method are covalently immobilized onto the polymer support.[27] The immobilized ultrafine rhodium particles show high activity in catalytic hydrogenation of various olefins and high durability in repeated use of the catalyst. Moreover, the present immobilized catalyst exhibits a notable increase in selectivity and activity caused by substrate–support interactions.

Experimental Section

Materials. A protective copolymer of methyl acrylate and *N*-vinyl-2-pyrrolidone, P(MA–VP), was prepared by radical copolymerization.[26] The number-average molecular weight of the copolymer was ca. 5800 determined by gel permeation chromatography using polystyrene standards with $CHCl_3$ as a mobile phase. The content of the methyl acrylate residues in the protective polymer was estimated at 35 mol % on the basis of the ^1H NMR spectrum (in $CDCl_3$).

As a polymer support for the immobilization reaction, aminoethyl Bio-Gel P-150 (control no. 30156, aminoethyl capacity = 2.37 mequiv/dry gel·g, hydrated bed volume = 17.0 cm^3/dry gel·g) was purchased from Bio-Rad Laboratories (Richmond, CA). This support is a partly *N*-(2-aminoethyl)-substituted porous polyacrylamide gel in a beaded form. The original material before aminoethylation, Bio-Gel P-150, is a cross-linked polyacrylamide gel prepared by the copolymerization of acrylamide and *N,N'*-methylenebisacrylamide in a beaded form with diameters of 80–150 μm and with the exclusion limit molecular weight of 150 000 when swollen by water. This material (control no. 220701) was used as a polyacrylamide gel without the amino groups.

Poly(vinylpyrrolidone) K90 (PVP, average molecular weight of 360 000) from the Tokyo Kasei Chemical Co. was purified by reprecipitation from a chloroform–diethyl ether.

Five percent Rh–carbon was purchased from the Japan Engelhald Co. as a commercial catalyst of active carbon-supported metallic rhodium. Highly purified hydrogen (99.99999%) from the Nippon Oxygen Co., Ltd. was used for catalytic hydrogenation reactions. Other reagents were all of guaranteed grade and used without further purification.

Apparatus. UV–vis absorption spectra were recorded on a Hitachi 340 recording spectrophotometer. Transmission electron micrographs were observed with a Hitachi HU-12A transmission electron microscope operated at an acceleration voltage of 100 kV. Catalytic hydrogenation reactions of olefins were carried out under 1 atm of hydrogen at 30.0 °C.

Preparation of Ultrafine Rhodium Particles. Ultrafine rhodium particles were prepared by alcohol reduction.[27] Rhodium(III) chloride and the protective polymer, P(MA–VP), were dissolved in a water–ethanol (1/1, v/v) mixed solvent at the concentrations of $[RhCl_3] = 1.0 \times 10^{-3}$ mol/dm^3 and [P(MA–VP)] = 2.0 g/dm^3, and then the solution was refluxed for 1 h in an oil bath. A dark brown homogeneous dispersion was obtained. Under these conditions, the number of polymer residues per rhodium atom was 20. A sample for transmission electron microscopy was prepared by dropping the dispersion of the particles on a microgrid supported on a copper mesh and by subsequent drying in air.

Immobilization of Ultrafine Rhodium Particles on Polymer Support. Three grams of the dry support, the polyacrylamide gel containing the primary amino groups, was swollen with 102 cm^3 of water before addition of 60 cm^3 of the dark brown dispersion of the rhodium ultrafine particles protected by P(MA–VP). After 3 days of stirring the suspension was allowed to settle. The support had turned dark brown in contrast with the colorless supernatant. The filtered support was washed with water several times and then with methanol to displace water in the support. Drying it in vacuo at 50 °C gave the immobilized catalyst of the ultrafine rhodium particles.

Catalytic Hydrogenation of Olefins. Hydrogenation reactions of various olefins catalyzed by the immobilized ultrafine rhodium particles were carried out as follows:

A recation vessel containing 0.1 g of the immobilized rhodium catalyst (the amount of rhodium metal = 2×10^{-6} mol) and a Teflon rotor was filled with hydrogen. Into the vessel was injected with a syringe 19 cm^3 of a water–ethanol (1/1, v/v) mixed solvent, and the mixture was agitated with a magnetic stirrer at 30.0 °C under 1 atm of hydrogen. After a steady volume of the gas phase was attained, the reaction was initiated by addition of 1 cm^3 of a 1.0 mol/dm^3 ethanol solution of the substrate to the vigorously agitated mixture (the final volume of the liquid phase was 20 cm^3) and the hydrogen uptake was monitored by a gas burette during the reaction.

The activity of active carbon-supported metallic rhodium catalyst was measured by the same procedure using 0.05 or 0.10 g of 5% Rh–carbon as the catalyst. In the experiments for the dispersion of the ultrafine rhodium particles as the catalyst 1 cm^3 of the dispersion (the amount of rhodium metal = 1×10^{-6} mol) and 18 cm^3 of the solvent were used. The initial rates of hydrogenation as a measure of the catalytic activity were calculated from the slope of the least-squares regression lines fitted to the data of the hydrogen uptake assuming pseudo-first-order kinetics.

Results and Discussion

Preparation of Ultrafine Rhodium Particles. Ultrafine particles of rhodium were previously reported by the present authors to be prepared by reflux of the alcoholic solution of rhodium chloride in the presence of protective polymers.[6] Poly(vinyl alcohol), poly(ethylene glycol), poly(*N*-vinyl-2-pyrrolidone), and some other polymers were used, and a particularly stable dispersion of the ultrafine rhodium particles was obtained by using poly(*N*-vinyl-2-pyrrolidone).

The d–d transition absorption of rhodium(III) ions in the region of 300–400 nm in the UV–vis spectrum of the initial solution completely disappeared after reflux with a water–ethanol (1/1, v/v) mixed solvent. A strong broad structureless absorption appeared from the near-UV region through the longer end of the visible region as shown in Figure 1. Such a shape of the spectrum is a common characteristic of dispersions of ultrafine particles of rhodium, palladium, and platinum.[12,13] The dispersion of the ultrafine rhodium particles thus obtained was homogeneous and dark brown and stable for several years even under air.

The transmission electron micrograph of the dispersed ultrafine particles of rhodium is shown in Figure 2 together with a histogram of the particle size distribution. The particles are well dispersed and almost monodisperse without marked aggregation. The number-average diameter of the particles and the standard deviation are 37.5 and 11.2 Å, respectively.

Immobilization of Ultrafine Rhodium Particles on Polymer Support. The support used for the immobi-

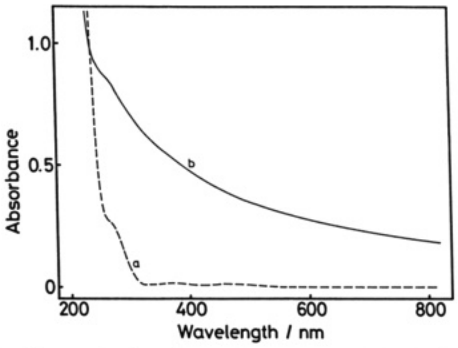


Figure 1. Change in the absorption spectra of the $RhCl_3$ solution by reflux in aqueous ethanol in the presence of P(MA–VP) as a protective polymer before (a) and after (b) the alcohol reduction.

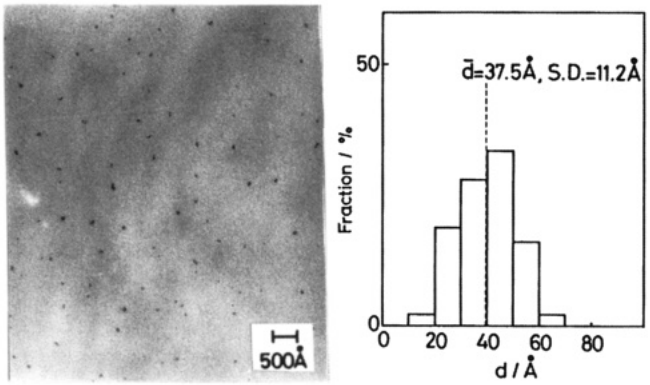
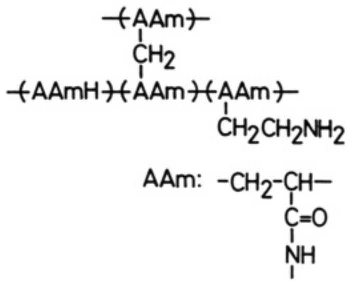


Figure 2. Transmission electron micrograph of the ultrafine rhodium particles prepared by alcohol reduction in the presence of P(MA–VP). The particle size distribution and an average diameter are also shown.

Chart I



lization in this study is a partly *N*-(2-aminoethyl)-substituted cross-linked polyacrylamide gel (Chart I). The support is a white powder when dry and a colorless translucent slurry when mixed with water. When stirring is discontinued after sufficient swelling with water of a volume twice that of the hydrated bed volume of the gel, the colorless slurry of the support settles down to the lower layer within 5–10 min. After addition of the dark brown dispersion of the ultrafine rhodium particles protected by P(MA–VP) followed by stirring for a few days, the support turned dark brown and the upper liquid phase changed to colorless. Transfer of a dark brown from the liquid phase to the support is ascribed to the immobilization of the ultrafine rhodium particles in the dispersion onto the support.

The present immobilization is stable to repeated washing with water, methanol, ethanol, etc., resulting in no release of the particles from the support. The immobilized particles are also stable to a pH change of the system in the pH range from 2 to 13. Moreover, the immobilization goes to completion by the same procedure even at high ionic strength in a 0.1 M NaCl solution. The stability of the immobilized particles suggests formation of a firm linkage between the particle and the support and can rule out physical adsorption or electrostatic adsorption as the mechanism of the immobilization.

Scheme I

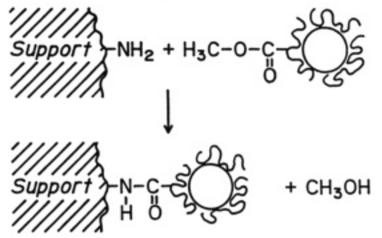


Table I
Catalytic Activity of Immobilized Ultrafine Rhodium Particles in Hydrogenation of Olefins

	initial hydrogenation rate[a]		
substrate	immobilized ultrafine particles (r_i)	5% Rh–carbon (r_c)	r_i/r_c
ethyl vinyl ether	610	7.7	79
cyclohexene	150	7.0	21
cyclopentene	230	44	5.2
1-hexene	190	38	5.0
acrylic acid	120	16	7.5
mesityl oxide	30	12	2.5

[a] In mmol of H_2/mol of Rh·s; at 30.0 °C under 1 atm of hydrogen in ethanol–water (1/1).

When a polyacrylamide gel without the amino groups was used instead of the support containing the amino groups, neither coloring the gel nor decoloring of the liquid phase occurred by addition of the dispersion of the ultrafine rhodium particles protected by P(MA–VP). No immobilization of ultrafine rhodium particles protected by the homopolymer PVP was observed even with the aminoethylated polyacrylamide gel as the support. These results clearly indicate that the present immobilization requires both the amino group in the support and the methyl acrylate residue in the protective polymer, leading to the conclusion that the formation of an amide bond by the reaction of the methyl acrylate residue and the amino group would cause the immobilization (Scheme I).

The immobilization mechanism of ultrafine platinum particles protected by P(MA–VP) has been investigated in detail by performing a model reaction, making use of a protective polymer with the *p*-nitrophenyl acrylate residue instead of the methyl ester.[26] The results have confirmed formation of the amide bond between the protective polymer and the support. The same mechanism can be applied to the present immobilization of the rhodium particles. The significantly lower reactivity of the methyl ester than that of the *p*-nitrophenyl ester may reflect on the fact that the immobilization needed a few days for completion whereas the model reaction finished within at most several hours.[28] Besides, if electrostatic interactions are responsible for the immobilization, the immobilization should be much faster.

Catalytic Activity of Immobilized Ultrafine Rhodium Particles in the Hydrogenation of Olefins. The immobilized ultrafine rhodium particles thus obtained have a high catalytic activity in hydrogenation of various olefins as shown in Table I. As substrates, ethyl vinyl ether, cyclohexene, cyclopentene, 1-hexene, acrylic acid, and mesityl oxide (4-methyl-3-penten-2-one) were used. The rates of hydrogen uptake in catalytic hydrogenation reactions of olefins are first-order in the substrates. Figure 3 presents examples of the first-order plots in the hydrogenation of acrylic acid.

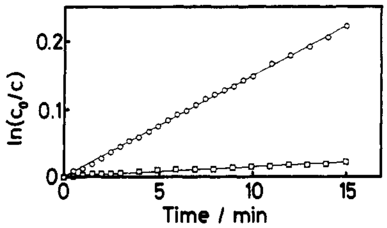


Figure 3. First-order kinetic plots in hydrogenation reactions of acrylic acid catalyzed by the immobilized (○) and dispersed (□) ultrafine rhodium particles.

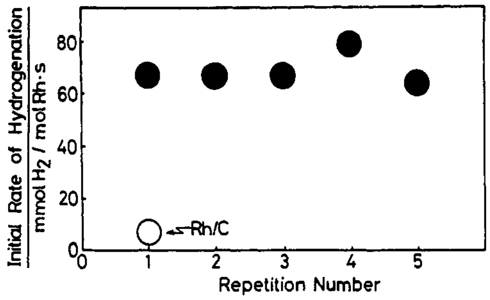


Figure 4. Catalytic activities of the immobilized ultrafine rhodium particles repeatedly used in hydrogenation of cyclohexene (recovered by decantation).

The initial rates of hydrogenation catalyzed by the immobilized ultrafine rhodium particles, r_i, are from several fold up to severeal 10-fold higher than those of the active carbon-supported commercial rhodium metal catalyst, r_c, as indicated in Table I. The support used for the immobilization, the aminoethylated polyacrylamide gel, swells most efficiently in water but shows almost no swelling in ethanol. In the mixed solvent water–ethanol (1/1, v/v) used in the present hydrogenation, the support appears to swell to the same extent as in water, and, thus, a decrease in the activity of the immobilized catalyst, which could be caused by unfavorable shrinkage of the reticular structure of the gel, seems to be negligible under the present conditions.

The immobilized ultrafine rhodium particles can be separated easily from the reaction mixtures by filtration or decantation and are stable throughout the catalytic reactions as well as during the recovery procedures. The durability of the immobilized rhodium particles repeatedly used in hydrogenation of cyclohexene is presented in Figure 4, in which the catalyst was separated by decantation, washed with water and then with methanol, and used again. The immobilized catalyst retains 98% of the initial activity even in the fifth run. These results demonstrate that the linkage responsible for the immobilization is sufficiently firm and that a decrease in the intrinsic activity of the ultrafine rhodium particles by, for example, aggregation of the particles, must be negligible. Aggregation of the ultrafine particles can be efficiently prevented if the particles are discretely immobilized on the support and prevented from contacting each other. This may be the most important contribution to the high durability of the immobilized ultrafine particles.

On the other hand, it has been found that the rhodium particles appear to decrease more or less in their activity by the immobilization compared with the original dispersed particles except in the hydrogenation of acrylic acid. Moreover, an extent of the decrease notably varies with the substrates as listed in Table I. Although decreases in catalytic activities by immobilizations of catalytic species are commonly observed, the extent of the decreases is usually not dependent so much upon the kind of the substrates with similar size if the decreases are simply imputed to the increases in the steric hindrance and/or the consequent decreases in diffusion rates of the substances. The strong dependence observed here, therefore, could not be explained without considering interactions between the substrate and the support. Further details have been investigated on the effects of the support by use of a wide variety of substrates listed in Table II and are discussed in the following session.

Table II
Catalytic Activities of Ultrafine Rhodium Particles in Hydrogenation of Olefins

	initial hydrogenation rate[a]			
substrate	immobilized ultrafine particles (r_i)	dispersed ultrafine particles (r_d)	r_i/r_d	δ_{sub},[b] $cal^{1/2} \cdot cm^{-3/2}$
1-pentene	150	1470	0.10	7.2[c]
1-hexene	190	1290	0.15	7.4
cyclopentene	230	1110	0.21	8.3[c]
cyclohexene	150	720	0.21	8.5[c]
mesityl oxide	30	230	0.13	9.0
2-methyl-2- pentene	13	67	0.19	7.5[c]
allyl alcohol	79	130	0.61	11.8
ethyl vinyl ether	610	1180	0.52	7.7[c]
3-buten-1-ol	140	310	0.45	10.1[c]
allylamine	200	450	0.44	9.3[c]
methyl vinyl ketone	330	770	0.43	9.5[c]
methyl acrylate	290	1090	0.27	8.9
acrylic acid	120	33	3.6	12.0
3-butenoic acid	130	31	4.2	11.1[c]

[a] In mmol of H_2/mol of Rh·s; at 30.0 °C under 1 atm of hydrogen in ethanol–water (1/1). [b] Solubility parameter values after ref 29 unless otherwise noted. [c] Calculated value.

Environmental Effect of Polymer Support on Substrate Selectivity of Immobilized Ultrafine Rhodium Particles. The influence of the support on the activity of the immobilized ultrafine rhodium particles was investigated for normal terminal, internal, and cyclic alkenes and also for other unsaturated compounds such as alcohols, ketones, ethers, esters, and carboxylic acids as the substrates. The results are summarized in Table II together with the activity of the dispersed rhodium particles before the immobilization, r_d. The ratios of the catalytic activity of the immobilized rhodium particles to that of the dispersed ones, given as r_i/r_d in Table II, are measures of the change in activity caused by the immobilization. In terms of molecular size of the substrates, 1-pentene, for example, would be able to diffuse through the reticular structure of the support more easily than the larger cyclohexene.[15] However, the value of r_i/r_d is smaller for 1-pentene, implying that the decrease in the catalytic activity by the immobilization cannot be solely ascribed to the decrease in the diffusion rates of the substrates.

Ethyl vinyl ether, allyl alcohol, and 3-buten-1-ol have rather large values of r_i/r_d, although the unsaturated hydrocarbons such as 1-pentene and cyclohexene yield considerably small values as shown in Table II. The substrates of the former group are considered to be hydrophilic whereas the latter ones are hydrophobic. As mentioned before, the rates of the catalytic hydrogenation are first-order in substrate concentration, and the support is the aminoethylated polyacrylamide gel with the highly hydrophilic acrylamide skeleton. Both facts suggest that the ratio r_i/r_d may reflect the local concentration of the substrate in the hydrophilic polymer support. The support would favor hydrophilic substrates. The data in Table II show that r_i/r_d can be approximately correlated with the solubility parameter δ[29] of the substrates.

High miscibility between the substrate and the support will give a small difference in their δ values, δ_{sub} and δ_{gel},

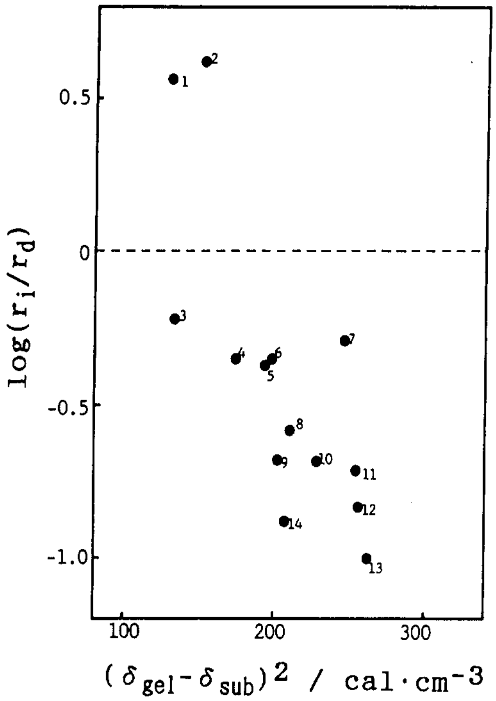


Figure 5. Relationship between the log (r_i/r_d) value for the catalytic hydrogenation rate and the solubility parameter of the substrate, δ_{sub}. The δ_{gel} value is assumed to be the same as that of water, 23.4 $cal^{1/2}\cdot cm^{-3/2}$. Substrates: 1, acrylic acid; 2, 3-butenoic acid; 3, allyl alcohol; 4, 3-buten-1-ol; 5, methyl vinyl ketone; 6, allylamine; 7, ethyl vinyl ether; 8, methyl acrylate; 9, cyclohexene; 10, cyclopentene; 11, 2-methyl-2-pentene; 12, 1-hexene; 13, 1-pentene; 14, mesityl oxide.

respectively. Logarithms of r_i/r_d, which is a measure of the change in the catalytic activity of the ultrafine rhodium particles caused by the immobilization onto the support, are plotted against $(\delta_{gel} - \delta_{sub})^2$ in Figure 5. A fairly good relationship is observed between them in the negative region of the ordinate, indicating that the low miscibility between the substrate and the support causes a large decrease in the activity. These results agree with the qualitative observation that the decreases in the activity by the immobilization of the catalyst are large for the hydrophobic substrates. It is therefore concluded that an environmental effect by the polymer support considerably contributes to the substrate selectivity through the hydrophilic–hydrophobic interaction between the substrate and the hydrophilic environment of the support matrix.

In hydrogenation of acrylic acid and 3-butenoic acid, the immobilized ultrafine rhodium particles have been revealed to exhibit remarkably higher catalytic activity than that of the homogeneous dispersion of the particles as seen in Table II, with striking r_i/r_d values much larger than 1. These results mean that the activity of the immobilized catalyst can be sufficiently improved to overcome the decrease in the activity caused by the steric hindrance of the support. This phenomenon occurs only for acid substrates. A large number of free amino groups must remain in the support without undergoing the immobilization reaction since the initial amount of the amino group in the support (2.37×10^{-3} mol equiv) was in large excess to that of the methyl acrylate residue in the protective polymer (1.37×10^{-4} mol). It is therefore presumed that the local concentration of the substrate such as acrylic acid and 3-butenoic acid around the immobilized catalyst could be increased by the electrostatic interaction between the free amino group in the support and the carboxyl group in the substrate. Enormous deviation of plots for these two substrates from others seen in Figure 5 can imply a specific interaction between the substrates and the support since the solubility parameter governs only the heat of mixing without any assumption on special interactions such as electrostatic or hydrogen bonding.

The results discussed above lead to the conclusion that the hydrophilic–hydrophobic interaction and the electrostatic interaction caused by the polymer matrix of the support enable selective concentration of the substrates around the immobilized rhodium particles and hence improve the activity and the selectivity of the immobilized catalyst.

Concluding Remarks

The immobilized ultrafine rhodium particles were successfully prepared by making use of the formation of covalent bonds between the protective polymer of the particles and the polymer support. In the catalytic hydrogenation reactions by the immobilized ultrafine rhodium particles, the environmental effect of the polymer support, which was ascribed to the hydrophilic–hydrophobic interaction between the hydrophilic skeleton of the polymer support and the substrates, decreased the local concentratioon of the hydrophobic substrates in the reaction field. The immobilized catalyst thereby preferentially hydrogenated the hydrophilic substrates. Further, the effect due to Coulomb's attractive force by free amino groups in the support efficiently concentrated the substrates containing the carboxyl group. These substrate–support interactions governed by the microenvironment of the polymer support did induce the novel selectivity in the catalysis of polymer-protected ultrafine rhodium particles.

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(27) Preliminary results of this work have been published as communications: (a) Komiyama, M.; Ohtaki, M.; Hirai, H. *Chem. Lett.* **1987**, 149. (b) Komiyama, M.; Ohtaki, M.; Hirai, H. *J. Coord. Chem.* **1988**, *18*, 185.

(28) A rate constant for the aminolysis of *p*-nitrophenyl isobutylate by butylamine in dioxane was 0.013 $M^{-1}\,s^{-1}$ (Su, C.-P.; Morawetz, H. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 185), whereas ethylaminolysis of methyl acetate with an ethylene glycol catalyst gave (3.08 ± 0.03) × 10^{-6} (Arnett, E. M.; Miller, J. G.; Day, A. R. *J. Am. Chem. Soc.* **1950**, *72*, 5635). This comparison should be qualitative since the conditions were not completely the same.

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Registry No. P(MA–VP), 27155-03-9; rhodium, 7440-16-6; ethyl vinyl ether, 109-92-2; cyclohexene, 110-83-8; cyclopentene, 142-29-0; 1-hexene, 592-41-6; acrylic acid, 79-10-7; mesityl oxide, 141-79-7; 1-pentene, 109-67-1; 2-methyl-2-pentene, 625-27-4; allyl alcohol, 107-18-6; 3-buten-1-ol, 627-27-0; allylamine, 107-11-9; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; 3-butenoic acid, 625-38-7.