Preparation of Colloidal Transition Metals in Polymers by Reduction with Alcohols or Ethers

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ABSTRACT

Colloidal dispersions of rhodium, palladium, osmium, iridium, and platinum are prepared by refluxing the methanol-water solutions of rhodium(III) chloride, palladium(II) chloride, osmium(VIII) oxide, sodium chloroiridate, and chloroplatinic acid, respectively, in the presence of poly(vinyl alcohol) as a protective colloid. The preparations of colloidal dispersions of rhodium are successful in the presence of vinyl polymer with polar group such as poly(vinyl alcohol), polyvinylpyrrolidone, or poly(methyl vinyl ether). Polyethyleneimine, gelatin, poly-(ethylene glycol), and dextran are ineffective as the protective colloid. Water-soluble primary alcohols such as methanol and ethanol, water-soluble secondary alcohols such as 2-propanol, and water-soluble diethers such as 1,4-dioxane are available as reductants for preparation of the colloidal dispersion of rhodium. The average diameters of metal particles in the colloidal dispersions of palladium, rhodium, platinum, iridium, and osmium in poly(vinyl alcohol) are determined by electron microscopy to be 53, 40, 27, 14, and < 10 Å, respectively. The particle size distribution in each colloidal dispersion is

sharp within 50 Å wide. The particles in the colloidal disper-
sions of both iridium and osmium are highly dispersed with no
aggregation, while in the colloidal dispersions of rhodium,
palladium, and platinum, there exist aggregates of 5-15, 5-30,
and 100-200 particles, respectively. Colloidal dispersions of
rhodium, palladium, osmium, and platinum are effective as
catalysts for hydrogenation of cyclohexene at 30.0°C under
atmospheric hydrogen pressure.

INTRODUCTION

Colloidal dispersions of transition metals have been prepared by
reduction of corresponding metal salts with molecular hydrogen [1],
hydrazine [2] in aqueous media.

It was previously [3, 4] reported that a colloidal dispersion of
rhodium was prepared by refluxing of the solution of rhodium(III)
chloride and poly(vinyl alcohol) in methanol-water. The size of
rhodium particle in the colloidal dispersion was sharply distributed
in the range from 30 Å to 70 Å and the average diameter of the
particle was 40 Å. It was suggested that the formation of colloidal
rhodium proceeded by three steps: coordination of poly(vinyl
alcohol) to rhodium(III) ion, reduction of rhodium(III) ion with
methanol and formation of the small particle of rhodium of 8 Å in
diameter, and growth to the large particle of rhodium of 40 Å in
diameter. The colloidal dispersion of rhodium was stable enough to
be stored under air for 20 days with no precipitation of metallic
rhodium. The colloidal dispersion was an effective catalyst for
hydrogenation of olefins at 30°C under an atmospheric hydrogen
pressure, having an activity 4.6 times as much as a commercial
rhodium catalyst supported on activated charcoal and 2.6 times as
much as the Nord's colloidal rhodium [1].

In the present study, this novel method is applied for preparation
of the colloidal dispersions of group VIII and Ib metals in various
water-soluble alcohols and ethers as a reductant. The dispersion
state of the resulting colloidal dispersions is examined by electron
microscopy. The catalytic activities of the colloidal dispersions
for hydrogenation of cyclohexene are also determined.

EXPERIMENTAL

Materials

Metal salts were commercial materials: $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$,
$NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$ (guaranteed reagent grade, Koso Chemi-
cal Co., Ltd.); $RuCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$ (Nippon Engelhald, Ltd.);

$PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, and $HAuCl_4 \cdot 4H_2O$ (guaranteed reagent grade, Kojima Chemical Co., Ltd.); $AgNO_3$ (guaranteed reagent grade, Kishida Chemical Co., Ltd.); OsO_4 (E. Merck A. G.); Na_2IrCl_6 (guaranteed reagent grade, Yoneyama Chemical Co., Ltd.).

Polymers were obtained commercially: poly(vinyl alcohol) (degree of polymerization 500, degree of saponification $> 98\%$, content of sodium acetate $< 2\%$, Nippon Synthetic Chemical Industry Co., Ltd.), poly(methyl vinyl ether) (degree of polymerization 570, Tokyo Chemical Industry Co., Ltd.), polyvinylpyrrolidone (K15, degree of polymerization 90; K30, degree of polymerization 360; K90, degree of polymerization 3250; extra pure grade, Tokyo Chemical Industry Co., Ltd.), polyethyleneimine (degree of polymerization about 1000, Tokyo Chemical Industry Co., Ltd.), poly(ethylene glycol) (degree of polymerization 450, Nippon Chromato Works, Ltd.), sodium poly-(R)-glutamate (degree of polymerization 300, Ajinomoto Co., Inc.), poly(acrylic acid) (degree of polymerization 3840, 25% aqueous solution, Wako Pure Chemical Industries, Ltd.), gelatin (Yoneyama Chemical Co., Ltd.), and gum arabic and dextran (degree of polymerization 330, Nakarai Chemicals, Ltd.).

Methanol, 2,2,2-trifluoroethanol, 2-methoxyethanol, 1,2-dimethoxyethane, 1,4-dioxane, and tetrahydrofuran were commercial guaranteed reagent grade materials. Ethanol, 1-propanol, 2-propanol, tert-butyl alcohol, 2-aminoethanol, ethylene glycol, and diethylene glycol dimethyl ether were commercial extra pure grade materials. These solvents were used without further purification.

Preparation of Colloidal Metal

A polymer (150 mg, 1.3-3.4 mmole as monomeric residue) as a protective colloid and a metal salt (0.033 mmole) were dissolved in a mixed solvent consisting of alcohol (25 ml) or ether (25 ml) and water (25 ml). Refluxing of the resulting solution under air on a boiling water bath or an oil bath for a definite period gave a homogeneous solution of colloidal dispersion of metal [4].

Electron Microscopy

The sample films, prepared by evaporation of a small amount of the colloidal dispersion of metal to dryness on a collodion film which was coated with a carbon layer and supported on copper grids, were mounted to an electron microscope, Hitachi Model H-500, operated at 125 kV. The magnification of the electron microscope was 200,000. Diameter of each of the metal particles, appearing in arbitrarily chosen areas of 8.0×10^6 Å^2, were determined from the enlarged

photographs, which corresponded to a magnification of 860,000. The particle size distribution and the average diameter of metal particles were obtained on the basis of these results [4].

Visible Spectroscopy

Visible spectra of the colloidal dispersions of rhodium were obtained on a Shimadzu Model MPS-50L spectrophotometer at room temperature using 1 cm quartz cell [4].

Hydrogenation of Cyclohexene

Methanol (18.7 ml) and a colloidal dispersion of metal (0.30 ml) were poured in that order into a flask where the atmosphere was previously replaced with hydrogen. The solution was stirred in a 30.0°C thermostat at an atmospheric pressure for 1 hr to be saturated with hydrogen. Then a methanol solution (1.0 ml) containing 0.5 mmole of cyclohexene was added to the flask keeping total pressure at 1 atm. The progress of the hydrogenation was followed by hydrogen uptake under atmospheric pressure [4].

RESULTS

Colloidal Dispersions of Groups VIII and Ib Metals

Twelve salts of group VIII metals and group Ib metals were examined for the preparation of colloidal dispersions of the metals by refluxing of the methanol-water solution of the metal salts for 4 hr in the presence of poly(vinyl alcohol). The results are summarized in Table 1.

Homogeneous dark brown solutions of the colloidal dispersions were obtained in the cases of rhodium(III) chloride, palladium(II) chloride, osmium(VIII) oxide, sodium chloroiridate, and chloroplatinic acid. Chloroauric acid gave no colloidal dispersion but yielded a reddish brown precipitate which gradually changed into metallic gold. Silver nitrate and ruthenium(III) chloride also gave no colloidal dispersion but the precipitates of the corresponding metals. The salts of metals in the first transition series, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$, were not reduced to the zero-valent state by refluxing of the methanol-water solution, resulting no colloidal dispersion. The colloidal dispersions of rhodium, palladium, osmium, and platinum exhibited catalytic activity for

TABLE 1. Colloidal Dispersions of Transition Metals Prepared by Reduction with Methanol in the Presence of Poly(vinyl Alcohol)

Starting metal salt	Colloidal dispersion		
	Formation	Particle size $(Å)^a$	Catalytic activity $(H_2$ mole/metal g-atom $\cdot$ sec$)^b$
$RuCl_3 \cdot 3H_2O$	No[c]		
$RhCl_3 \cdot 3H_2O$	Yes[d]	40	3.9
$PdCl_2 \cdot 2H_2O$	Yes[d]	53	0.3
$AgNO_3$	No[e]		
OsO_4	Yes[d]	< 10	0.6
Na_2IrCl_6	Yes[d]	14	0
$H_2PtCl_6 \cdot 6H_2O$	Yes[d]	27	0.2
$HAuCl_4 \cdot 4H_2O$	No[f]		

[a]Average diameter of the metal particles in colloidal dispersion.
[b]Conditions for hydrogenation of cyclohexene: temperature 30.0°C, total pressure 1 atm, [metal] = 0.01 mM, [cyclohexene] = 25 mM, solvent = methanol (19.85 ml)-water (0.15 ml).
[c]A black precipitate was deposited.
[d]A homogeneous dark brown solution.
[e]A yellow precipitate was deposited.
[f]A reddish brown precipitate was deposited.

hydrogenation of cyclohexene at 30.0°C under atmospheric hydrogen pressure. That of iridium was not effective as a hydrogenation catalyst. The colloidal dispersion of rhodium exhibited an exceedingly high catalytic activity.

Electron micrographs of the colloidal metals are illustrated in Fig. 1. No aggregates of metal particles were found in the colloidal dispersions of osmium and iridium. Aggregations of 5-15 particles occur in the colloidal dispersion of rhodium and aggregations of 5-30 particles in that of palladium. A few aggregates of 100-200 particles appear in the field of the colloidal dispersion of platinum. Figure 2 shows the size distribution histograms of metal particles appear in the enlarged electron micrographs of the colloidal metals. In the colloidal dispersion of osmium, all the particles are smaller than
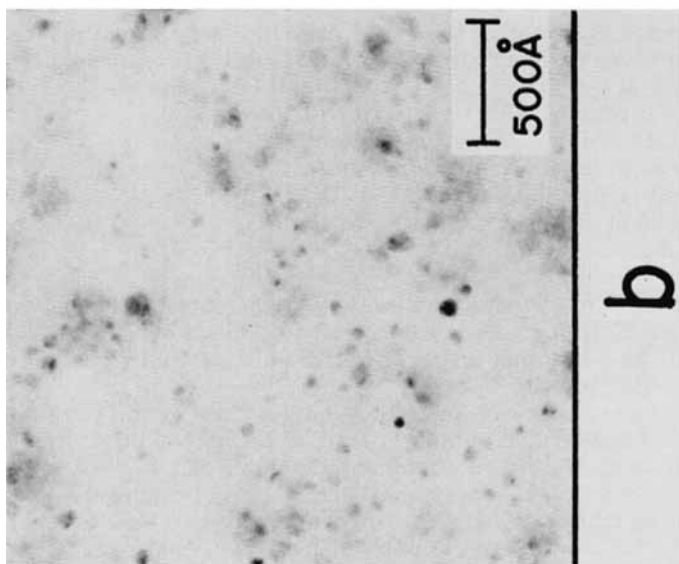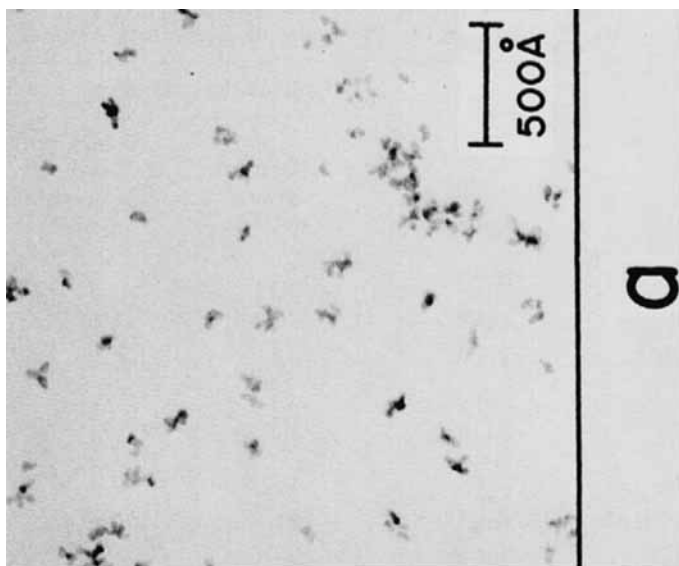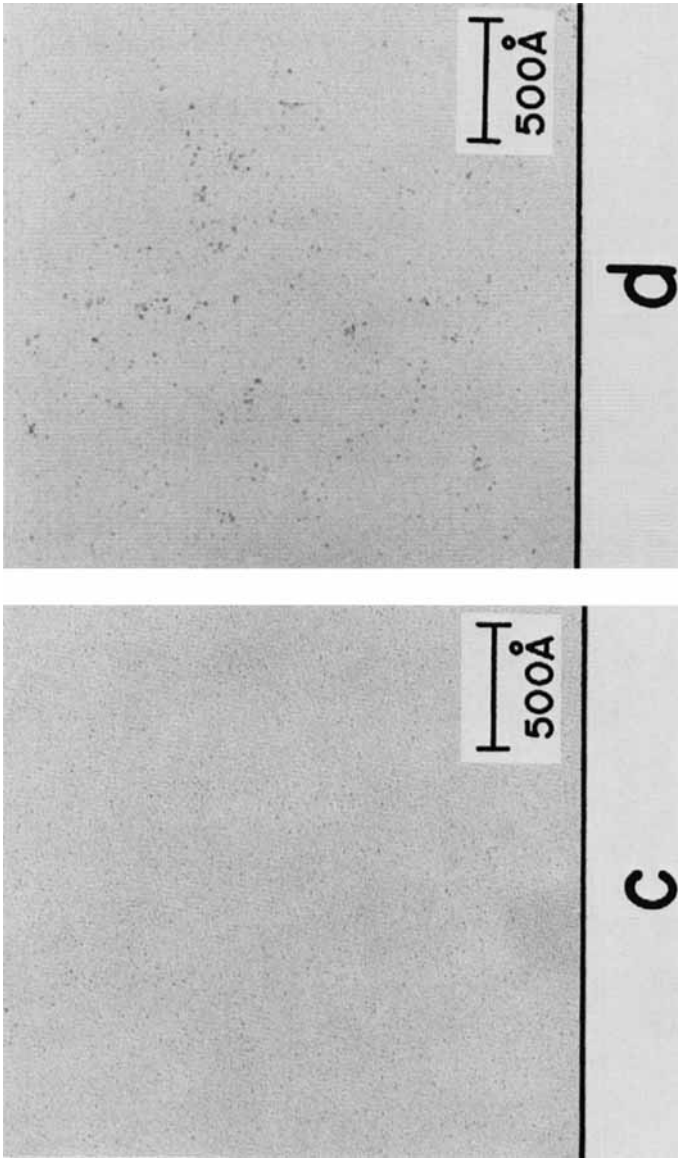
Figure 1 (continued)
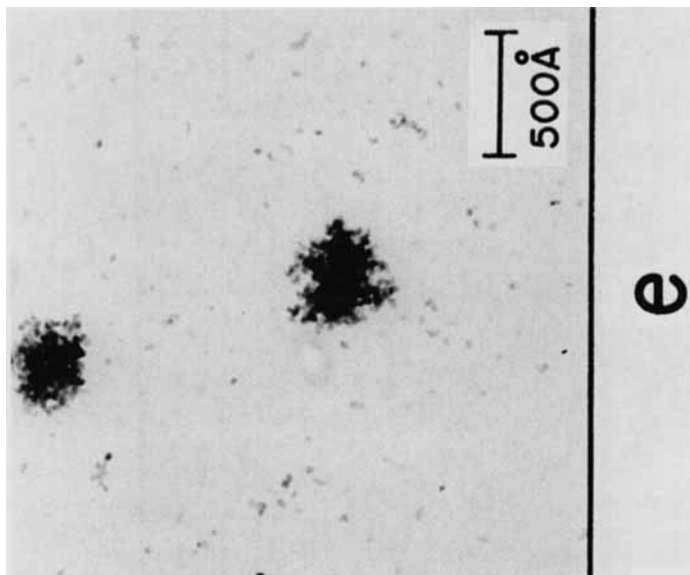
FIG. 1. Electron micrographs of colloidal metal in poly(vinyl alcohol) prepared by reduction with methanol: (a) colloidal rhodium; (b) colloidal palladium; (c) colloidal osmium; (d) colloidal iridium; (e) colloidal platinum.
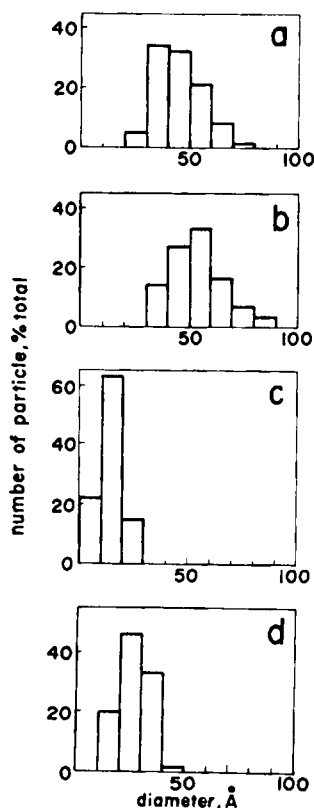
FIG. 2. Size distributions of metal particle in the colloidal dispersions of (a) rhodium, (b) palladium, (c) iridium, and (d) platinum.

10 Å in diameter. As shown in Table 1, the average diameters of metal particles estimated on the basis of the size distribution histograms depend on the kinds of metal, decreasing in the order; palladium > rhodium > platinum > iridium > osmium.

Polymers as Protective Colloids

Availabilities of ten polymers as protective colloids for the colloidal dispersion of rhodium were examined by refluxing of the methanol-water solution of rhodium(III) chloride and the polymer of interest. Table 2 summarizes the results. Homogeneous dark brown

TABLE 2. Colloidal Dispersions of Rhodium Prepared by Using
Various Polymers as a Protective Colloid

Polymer	Degree of polym- erization	Colloidal dispersion	
		Particle size $(\text{Å})^a$	Catalytic activity (H_2 mole/Rh g-atom · sec)[b]
Poly(vinyl alcohol)	500	40	3.1
Poly(methyl vinyl ether)	570	43	9.6
Polyvinylpyrrolidone K15	90	30	3.1
Polyvinylpyrrolidone K30	360	34	5.5
Polyvinylpyrrolidone K90	3250	35	5.5

[a]Average diameter of rhodium particles in colloidal dispersion.
[b]Conditions for hydrogenation of cyclohexene: temperature 30.0°C,
total pressure 1 atm, [Rh] = 0.01 mM, [cyclohexene] = 25 mM,
solvent = methanol (19.85 ml)-water (0.15 ml).

solutions of the colloidal dispersions of rhodium were obtained at a
complete conversion of the charged rhodium(III) chloride by using
either poly(vinyl alcohol), poly(methyl vinyl ether) or polyvinyl-
pyrrolidone. On the other hand, only a small conversion of rhodium
ion into colloidal rhodium was attained by using sodium poly-(R)-
glutamate or sodium polyacrylate. The amount of rhodium particles
in these colloidal dispersions were determined by the optical density
to be less than 2% of the charged amount of rhodium. The optical
density of the colloidal dispersions at 750 nm is proportional to the
concentration of colloidal particle on the basis of the fact that the
particle size of colloidal rhodium prepared by using poly(vinyl
alcohol) is constant during the refluxing longer than 0.2 hr [4]. The
residual part of rhodium(III) in the charged rhodium(III) chloride
seemed to remain in the solution as rhodium ions.

The unsuccessful examples can be classified into two cases. In
the first case, with polyethyleneimine, gelatin, or gum arabic, no
reduction of rhodium(III) ion to the zero-valent state occurred. In
the second case, with poly(ethylene glycol) or dextran, metallic
rhodium formed by reduction deposited as a black precipitate.

The colloidal dispersion of rhodium obtained by using poly(vinyl
alcohol), poly(methyl vinyl ether) or polyvinylpyrrolidone exhibited
a catalytic activity for hydrogenation of cyclohexene at 30°C under

an atmospheric hydrogen pressure. As shown in Table 2, the catalytic activity depended on the kind of polymer used, decreasing in the order; poly(methyl vinyl ether) > polyvinylpyrrolidone > poly(vinyl alcohol). That of rhodium obtained by using polyvinylpyrrolidone seems to increase with the increasing degree of polymerization of polyvinylpyrrolidone, reaching a constant value at degrees of polymerization higher than 360.

The colloidal dispersion of rhodium prepared by using poly(vinyl alcohol), poly(methyl vinyl ether), or polyvinylpyrrolidone gave a homogeneous film on evaporation to dryness. The resulting film could be dissolved with the original solvent to yield the colloidal dispersion of rhodium again. The resulting colloidal dispersion showed the same catalytic activity as the original colloidal dispersion.

The electron micrographs of the colloidal rhodiums obtained by using poly(methyl vinyl ether) and polyvinylpyrrolidones of different degrees of polymerization are shown in Fig. 3. Both the colloidal dispersion prepared by using poly(methyl vinyl ether) and that prepared by using polyvinylpyrrolidone K90, contains the aggregates of rhodium particles to the same extent as that prepared by using poly(vinyl alcohol) does (Fig. 1). The electron micrographs (Fig. 3, b, c, and d) of the colloidal dispersions obtained by using polyvinylpyrrolidones K15, K30, and K90 indicate that the lower the degree of polymerization of polyvinylpyrrolidone, the smaller the number of rhodium particle constituting the aggregates. The size distribution histograms of rhodium particles (Fig. 4) in the enlarged electron micrographs of the colloidal dispersions prepared by using poly-(methyl vinyl ether), and polyvinylpyrrolidones K15, K30, and K90 indicate that the particle size of rhodium in each colloidal dispersion is sharply distributed in the range of about 30 Å wide, comprising 94% of the total particles. The average diameters of rhodium particles are only slightly different from each other in the range from 30 to 43 Å, depending on the polymers used as shown in Table 2, whereas the kind of metal salt used as a starting material markedly affected the particle size of the colloidal metal as shown in Table 1.

No colloidal rhodium was produced when the aqueous solution of rhodium(III) chloride and a polymer, such as poly(vinyl alcohol), poly(methyl vinyl ether) and polyvinylpyrrolidone was heated at 79°C in the absence of methanol. This indicates that the polymers do not act as a reductant toward rhodium(III) chloride. In the case of poly(methyl vinyl ether), tert-butyl alcohol which had no ability to reduce rhodium(III) chloride was used to make a mixed solvent of tert-butyl alcohol (25 ml)-water (25 ml) for dissolution of poly(methyl vinyl ether).
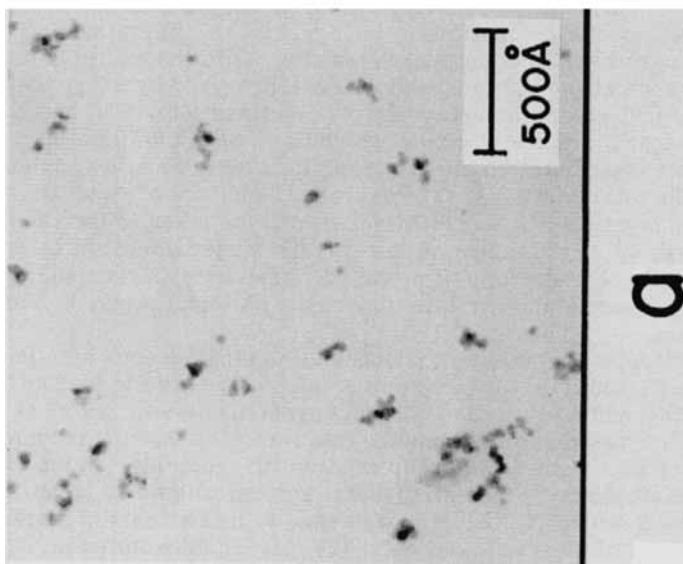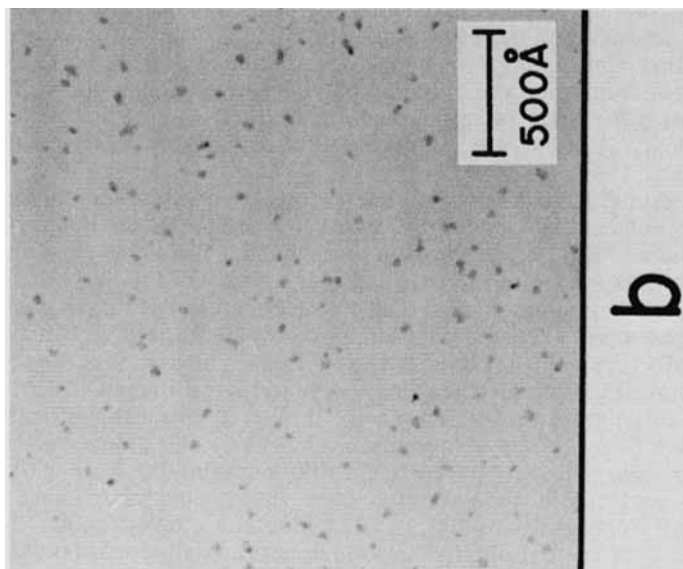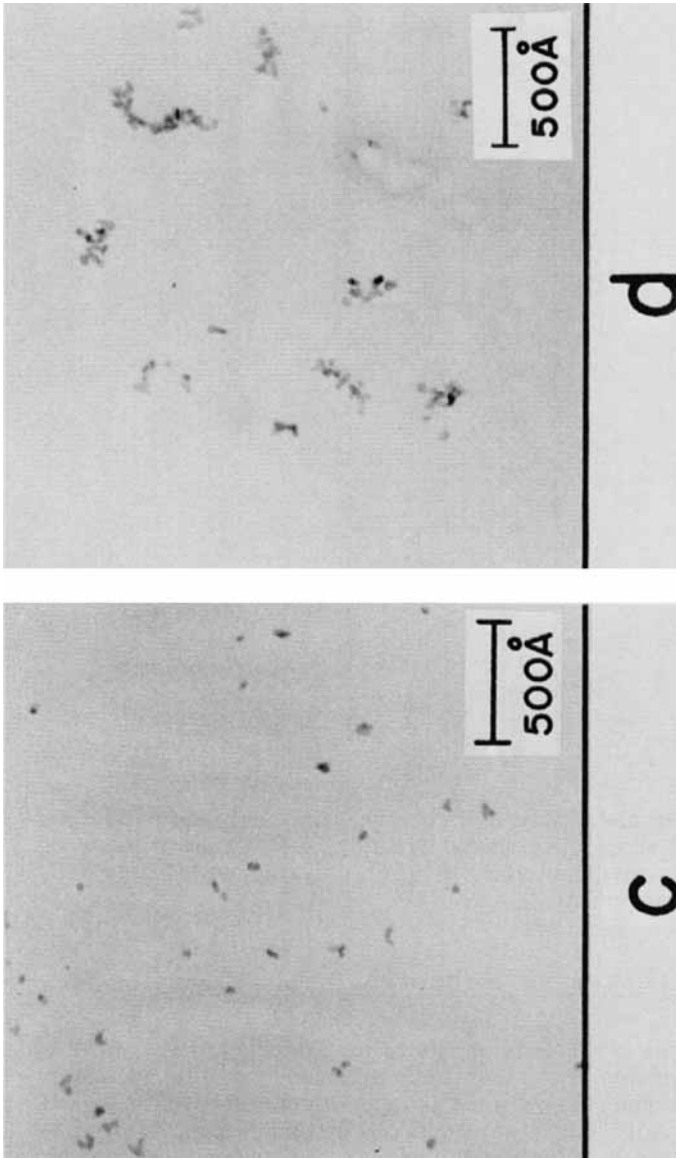
FIG. 3. Electron micrographs of colloidal rhodium prepared by using (a) poly(methyl vinyl ether), (b) polyvinylpyrrolidone K15, (c) polyvinylpyrrolidone K30, and (d) polyvinylpyrrolidone K90.
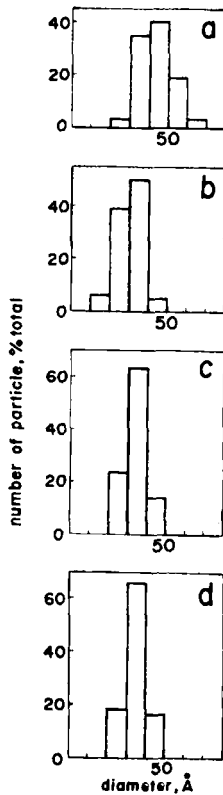
FIG. 4. Size distributions of rhodium particle in the colloidal dispersions of rhodium prepared by using (a) poly(methyl vinyl ether), (b) polyvinylpyrrolidone K15, (c) polyvinylpyrrolidone K30, and (d) polyvinylpyrrolidone K90.

Alcohol or Ether as Reductant

Availabilities of alcohols or ethers for the preparation of the colloidal dispersion of rhodium were examined by refluxing of the solution of rhodium(III) chloride and poly(vinyl alcohol) in a mixed solvent of alcohol (25 ml)-water (25 ml) or ether (25 ml)-water (25 ml). Table 3 summarizes the results. When tert-butyl alcohol or 2-aminoethanol was used, rhodium(III) chloride was not reduced to the zero valent state yielding no colloidal dispersion of rhodium. Refluxing of the solution of rhodium(III) chloride in ethylene glycol

TABLE 3. Colloidal Dispersions of Rhodium Prepared by Reduction with Various Water-Soluble Alcohols and Ethers in the Presence of Poly(vinyl Alcohol)[a]

		Colloidal dispersion	
Alcohol or ether	Refluxing temp. (°C)	Formation	Catalytic activity (H_2 mole/Rh g-atom · sec)[b]
Methanol	79	Yes	3.1
Ethanol	83	Yes	3.4
1-Propanol	88	Yes	2.6
2-Propanol	83	Yes	3.4
Tert-butyl alcohol	81	No	0
2,2,2-Trifluoroethanol	82	Yes	0.8
2-Aminoethanol	108	No	0
Ethylene glycol	92[c]	Yes	1.7
2-Methoxyethanol	100	Yes	3.5
1,2-Dimethoxyethane	83	Yes	3.5
Diethylene glycol dimethyl ether	100	Yes	3.1
1,4-Dioxane	100	Yes	1.9
Tetrahydrofuran	69	No	0

[a]Refluxing time: 2 hr.
[b]Conditions for hydrogenation of cyclohexene: temperature 30.0°C, total pressure 1 atm, [Rh] = 0.01 mM, [cyclohexene] = 25 mM, solvent comprised of methanol (19.7 ml) and alcohol or ether (0.15 ml)-water (0.15 ml) used in the preparation.
[c]No refluxing; since refluxing of the solution at 105°C gave a black precipitate.

(25 ml)-water (25 ml) at 105°C gave a black precipitate of metallic rhodium, while keeping the solution temperature at 92°C without refluxing gave a homogeneous colloidal dispersion of rhodium. By using the rest of the alcohols listed in Table 3, normal dark brown solutions of the colloidal dispersions of rhodium were obtained.

By using water-soluble 1,4-diethers such as 1,2-dimethoxyethane, the colloidal dispersions of rhodium were formed, while by using tetra-hydrofuran, a monoether, rhodium(III) chloride was not reduced and no colloidal dispersion of rhodium was formed. As shown in Table 3, each of the colloidal dispersions of rhodium obtained by using six alcohols and four ethers exhibits the high catalytic activity for hydrogenation of cyclohexene ranging narrowly from 1.7 to 3.6 H_2 mole/Rh g-atom · sec except for that in the case of 2,2,2-trifluoro-ethanol.

The colloidal dispersions of rhodium thus obtained were stable enough to be stored under air except for the case of 1,4-dioxane, where the dispersion was rather unstable, giving a precipitate of metallic rhodium after standing under air for a week. The electron micrographs of the typical colloidal dispersions of rhodium prepared by using ethanol and 1,4-dioxane are shown in Fig. 5. The colloidal rhodium obtained by using ethanol is quite similar to that prepared by using methanol, while that obtained by using 1,4-dioxane differs from that prepared by using methanol with respect to aggregation of rhodium particles.

The formations of colloidal rhodium in methanol-water [4], ethanol-water, 1-propanol-water and 2-propanol-water were followed by the measurement of optical densities at 750 nm. As shown in Fig. 6, the rate of the increase of optical density corresponding to the rate of the formation of colloidal rhodium decreases depending upon the kind of alcohol mixed with water in the order; ethanol > 1-propanol > methanol > 2-propanol. In each of the cases the optical density approaches a saturated value of about 0.8. This result indicates that the particle sizes in the final colloidal dispersions are nearly equal to each other, since the charged concentrations and amounts of rhodium are the same.

Effects of Addition of Acids and Bases

The effect of the addition of an acid or a base to the methanol-water solution of rhodium(III) chloride and poly(vinyl alcohol) on the formation of colloidal dispersion by refluxing was investigated. The results are listed in Table 4. Refluxing the solution with sodium hydroxide gave colloidal dispersion which exhibited 2.7 times the catalytic activity for hydrogenation as much as those obtained without an additive. This colloidal dispersion, however, was rather unstable to give a considerable amount of the precipitate of metallic rhodium after standing at room temperature for a day. In contrast, refluxing the solution of rhodium(III) chloride and poly(vinyl alcohol) with additional hydrochloric acid gave a stable colloidal dispersion of rhodium with a small amount of the precipitate of metallic rhodium.
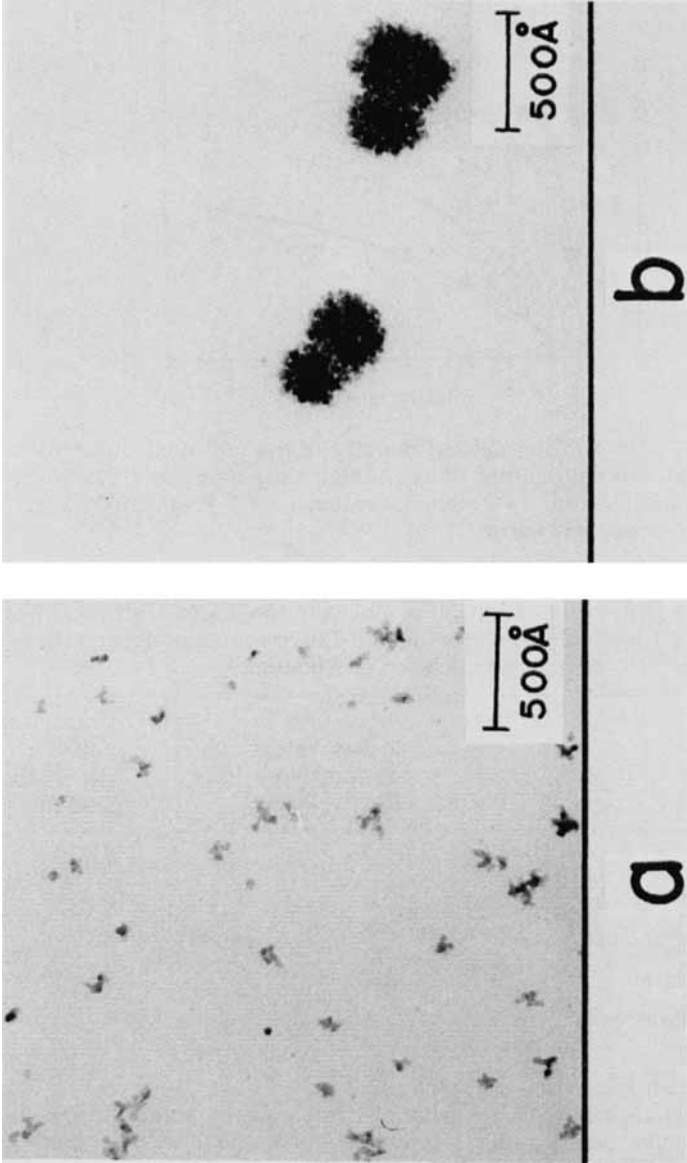
FIG. 5. Electron micrographs of colloidal rhodium in poly(vinyl alcohol) prepared by reduction with (a) ethanol and (b) 1,4-dioxane.
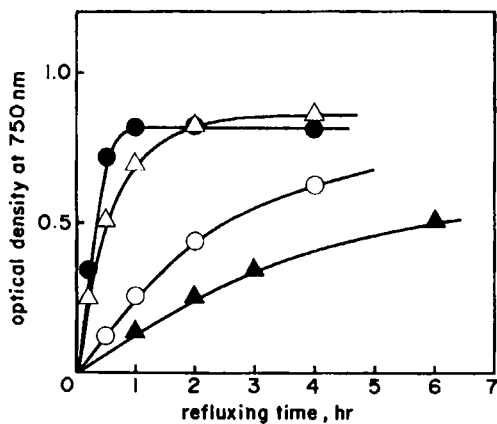
FIG. 6. Plots of the optical density of the colloidal dispersion of rhodium at 750 nm against the refluxing time using various solvents: (○) methanol-water, (●) ethanol-water, (△) 1-propanol-water, and (▲) 2-propanol-water.

TABLE 4. Effects of Addition of Acids or Bases to Methanol-Water Solution of Rhodium(III) Chloride and Poly(vinyl Alcohol) on the . Formation of Colloidal Dispersion of Rhodium[a]

Additive	Molar ratio of additive/ $RhCl_3 \cdot 3H_2O$	Catalytic activity (H_2 mole/Rh g-atom · sec)[b]
None	0	3.1
Sodium hydroxide[c]	5	8.4
Hydrochloric acid[d]	5	2.1
Triethylamine	100	2.7
Ethylenediamine[e]	1.5	0

[a]The solutions were refluxed for 2 hr.

[b]Conditions for hydrogenation of cyclohexene: temperature 30.0°C, total pressure 1 atm, [Rh] = 0.01 mM, | cyclohexene] = 25 mM, solvent comprised of methanol (19.85 ml) and water (0.15 ml).

[c]After standing under air for a day, a black precipitate of metallic rhodium was deposited.

[d]A small amount of metallic rhodium was deposited during the refluxing.

[e]No reduction of rhodium(III) chloride to zero valent state occurred.

The resulting colloidal dispersion exhibited a rather low activity, which was probably ascribed to a lower concentration of colloidal rhodium. The addition of triethylamine of 100 times the molar quantity of rhodium(III) chloride gave substantially no effect both on the formation of and on the catalytic activity of the colloidal dispersion of rhodium. In contrast, the addition of ethylenediamine even at 1.5 times the molar quantity of rhodium(III) chloride suppressed the reduction of rhodium(III) species to the zero valent state yielding no colloidal dispersion of rhodium.

DISCUSSION

Reduction of Metal Ion to Colloidal Metal

In order to prepare the active small metal particles from the metal ion, it may be necessary to reduce the metal ion to zero-valent state in a special field. The formation of the colloidal dispersion of rhodium by the present method proceeds through the coordination of poly(vinyl alcohol) to rhodium(III) ion and the reduction of rhodium(III) ion with methanol accompanied by the formation of formaldehyde [4]. The proposed scheme of the reduction is as follows. In the first step, methanol coordinates to rhodium(III) ion as an oxonium-complex. The resulting oxonium-complex loses a proton, giving a methoxido-complex, which changes to a hydrido-complex with the formation of formaldehyde. Chatt and co-workers [5] reported that ruthenium(II) complex was converted to a hydrido-complex by ethanol via an ethoxido-complex with the formation of acetaldehyde. The resulting hydrido-rhodium(III) complex releases an additional proton giving a low valent rhodium ion, which is reduced to the zero-valent state through disproportionation. Among the intermediate complexes, the oxonium-complex seems to be the most stable one. Consequently, proton elimination from the oxonium-complex may be the rate-determining step. Iron(III), cobalt(II), nickel(II), and copper(II) ions were not reduced to the zero-valent states with methanol. The standard electrode potentials of the metal ions of the first transition series $(Fe^{3+}, -0.036 \text{ V}; Co^{2+}, -0.277 \text{ V}; Ni^{2+}, -0.250 \text{ V}; Cu^{2+}, +0.344 \text{ V})$ are much more negative than those of the second and third transition series $(Rh^{3+}, +0.8 \text{ V}; Pd^{2+}, +0.83 \text{ V}; Ag^{+}, +0.799 \text{ V}; Au^{3+}, +1.42 \text{ V})$ [6, 7]. The lower reactivity of the metal ions in the first transition series can be related to their more negative oxidation-reduction potentials.
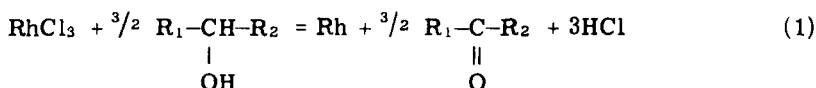
Roles of Polymer

As described in the previous paper [4], poly(vinyl alcohol) acts both as a ligand to rhodium(III) ions during the reduction, and as a protective colloid against aggregation of the rhodium particles. Poly(methyl vinyl ether) and polyvinylpyrrolidone also gave the colloidal dispersions of rhodium as well as poly(vinyl alcohol). On the other hand, poly(ethylene glycol) and dextran gave no colloidal dispersion of rhodium but black precipitates of metallic rhodium. This may be attributed to rather low ability of polymers in the latter group for protection of colloidal rhodium. Polyethyleneimine, gelatin, and gum arabic gave neither colloidal dispersion of rhodium nor precipitates of metallic rhodium. The polymers in this group may so strongly coordinate to rhodium(III) ion that the reduction of rhodium(III) ion may be inhibited. Available polymers, poly(vinyl alcohol), poly(methyl vinyl ether) and polyvinylpyrrolidone, seem to have both an appropriate ability for coordination to rhodium(III) ion and a high ability for protection of colloidal rhodium from aggregation. These polymers have a common structure of a poly-vinyl skeleton with polar groups. They may act as a protective colloid in the manner where the hydrophobic parts of main chains are in contact with the surface of the rhodium particles and the hydro-philic polar groups direct outside giving the hydrophilicity to the colloidal particles of rhodium.

Poly(vinyl alcohol) is effective as a protective colloid for prepara-tion of the colloidal dispersions of palladium, osmium, iridium, and platinum as well as for that of rhodium. On reduction of the salts of gold, ruthenium, and silver with methanol, metallic precipitates deposited even in the presence of poly(vinyl alcohol). The precipita-tions of the metals in these cases may be attributed to the rather low ability of poly(vinyl alcohol) for protection of the metal particles of gold, ruthenium and silver. It was reported that the protective ability of the polymer in the colloidal dispersion of gold was quite different from that in the colloidal dispersion of Congo Rubine [8].

As shown in Fig. 3 (b, c and d), decreasing the degree of polym-erization of polyvinylpyrrolidone used resulted in the depression of the aggregation of rhodium particles in the colloidal dispersion. Similar effects of the degree of polymerization of polyvinylpyrrolidone on the protective ability for colloidal silver particles were reported [9]. A polyvinylpyrrolidone molecule of low degree of polymerization is considered to exist in nearly linear conformation and to cover effectively the metallic surface of colloidal particles [10]. The increase of the total number of terminal groups with the decrease of the degree of polymerization may be also responsible for the high protective ability of polyvinylpyrrolidone.

Reducing Abilities of Alcohols or Ethers

Formation of formaldehyde of 1.5 molar equivalent to rhodium(III) chloride has been confirmed in the preparation of the colloidal dispersion of rhodium by refluxing the methanol-water solution of poly(vinyl alcohol) and rhodium(III) chloride [4]. It was also confirmed by GLPC analysis that acetaldehyde and acetone were produced by using ethanol and 2-propanol, respectively, instead of methanol in the preparation of the colloidal dispersion of rhodium. Other primary and secondary alcohols will also produce the corresponding carbonyl compound with reduction of rhodium(III) chloride. The equation (1) can be proposed for the reduction of rhodium(III) chloride with the primary and secondary alcohols with α-hydrogen atom:

$$\text{RhCl}_3 + {}^3/_2 \ \text{R}_1-\underset{\overset{|}{\text{OH}}}{\text{CH}}-\text{R}_2 = \text{Rh} + {}^3/_2 \ \text{R}_1-\underset{\overset{\|}{\text{O}}}{\text{C}}-\text{R}_2 + 3\text{HCl} \qquad (1)$$

where R_1 and R_2 are hydrogen atom or alkyl group. Tert-butyl alcohol without an α-hydrogen atom was ineffective for the reduction of rhodium(III) chloride.

As illustrated in Fig. 6, the rate of the formation of colloidal rhodium in methanol-water at 79°C is much lower than that in ethanol-water at 83°C. In spite of the nearly equal refluxing temperature (Table 3), 2,2,2-trifluoroethanol is much less effective for the reduction of rhodium(III) chloride than methanol. The differences in the reducing abilities of alcohols are presumably caused by the I effect of the substituents (+I effect for methyl group and -I effect for trifluoromethyl group). Dobson and Robinson [11] reported that ethanol was dehydrogenated to acetaldehyde in the presence of a ruthenium complex catalyst, whereas methanol was not dehydrogenated in the same conditions. The higher reactivity of ethanol than methanol in the catalytic dehydrogenation is also associated with the +I effect of methyl group. 2-Aminoethanol is expected to coordinate strongly to rhodium(III) ion through chelation, which may be the reason for its inhibition of the reduction of rhodium(III) ion. Colloidal rhodium was produced more slowly in 2-propanol than in 1-propanol. Two methyl groups of 2-propanol may sterically depress the formation of the oxonium-complex of rhodium(III) ion.

Some diethers including 1,4-dioxane were available as a reductant for the preparation of the colloidal dispersion of rhodium as well as alcohols, while monoethers such as tetrahydrofuran were not. Nishiguchi and co-workers [12] reported that α-hydrogen transfer from 1,4-dioxane to an appropriate hydrogen acceptor such as olefins resulted in the formation of 1,4-dioxene in the presence of a

complex catalyst such as tris(triphenylphosphine)chlororhodium(I) through a hydrido-rhodium(III) complex. This suggests that the reduction of rhodium(III) ion with 1,4-dioxane in the present study proceeds in a similar manner to that with alcohols through a hydrido-rhodium(III) complex.

It was confirmed that poly(vinyl alcohol), poly(methyl vinyl ether) and polyvinylpyrrolidone did not act as a reductant to rhodium(III) chloride. The polymer concentrations are much less (0.3%), compared with that of the alcohol or ether used as a reductant.

States of Colloidal Dispersions of Metal

The electron micrographs given in Fig. 1 show both the particle size and the dispersion state of colloidal metal. In the preparation of the colloidal dispersion of rhodium in poly(vinyl alcohol), rhodium particles 8 Å in diameter appeared prior to the formation of the final particles 40 Å in diameter [4]. Desorption of the poly(vinyl alcohol) molecule from the surface of the 8 Å particle seems to stimulate growth to the 40 Å particle. Colloidal particles of palladium and platinum may be produced through a similar path to that of rhodium. Both the colloidal dispersions of palladium and platinum were stable enough to be stored under air at room temperature. A marked aggregation appeared in the colloidal dispersion of platinum is probably attributed to the much faster rate of the formation of platinum particles and their frequent collision in the course of refluxing for a given period. The average diameter of colloidal palladium is largest among the five colloidal metals listed in Table 1. Reversible interconversion between palladium(II) and palladium(0) was well known to occur smoothly [13]. The interconversion presumably stimulates the growth of the colloidal particles of palladium.

Catalytic Activity of Colloidal Dispersion of Metal for Hydrogenation

As shown in Table 1, the catalytic activity of colloidal dispersion of metal for hydrogenation of cyclohexene decrease in the order; rhodium $\gg$ osmium $>$ palladium $>$ platinum $>$ iridium = 0. This order is consistent with that of the catalytic activity of metal film for hydrogenation of ethylene reported by Beeck [14] (rhodium $>$ palladium $>$ platinum; osmium and iridium were lacking), although the catalytic activity of the colloidal dispersion was exceedingly higher than that of the film of the corresponding metal. The high activity of rhodium metal can be attributed to the lattice constant, as proposed by Beeck [15].

The colloidal dispersion of rhodium prepared by using poly(methyl vinyl ether) is the most effective catalyst for hydrogenation in spite of the largest diameter of the colloidal rhodium (Table 2). The difference of catalytic activity caused by the kind of polymers may be interpreted on the basis of the diffusion rate of the substrate in the polymer layer which covers the catalytic surface.

Effect of Additives

The presence of sodium hydroxide in the refluxing solution of rhodium(III) chloride and poly(vinyl alcohol) resulted in both acceleration of the formation rate of colloidal rhodium and a marked increase of the catalytic activity of the colloidal dispersion for hydrogenation. On the other hand, the catalytic activity of the colloidal dispersion of rhodium, which was prepared without an additive, was scarcely influenced by the addition of the same amount of sodium hydroxide to the reaction mixture for hydrogenation. It is presumed that sodium hydroxide in the refluxing solution accelerates both the coordination of poly(vinyl alcohol) to rhodium(III) ion and the reduction of rhodium(III) ion with methanol, resulting in the formation of much smaller colloidal rhodium. In addition, sodium hydroxide caused unstabilization of the dispersion state of colloidal rhodium, since the sodium ion has a tendency to neutralize the surface charge of colloidal rhodium.

In contrast to the case of sodium hydroxide, the addition of hydrochloric acid in the preparation of colloidal rhodium had only small effect on either the catalytic activity or the stability of the resulting colloidal dispersion. Ethylenediamine had quite a different influence from triethylamine. The former strongly inhibited the formation of colloidal rhodium, whereas the latter scarcely did. Ethylenediamine are presumed to coordinate strongly to rhodium(III) ion through chelation, retarding the coordination of methanol to rhodium(III) ion. Polyethyleneimine probably inhibits the reduction of rhodium(III) ion in a similar manner to ethylenediamine.

CONCLUSION

Colloidal dispersions of metals of group VIII and Ib can be prepared by refluxing the alcohol (or ether)-water solution of the corresponding metal salts and a polymer.

Water-soluble primary and secondary alcohols and water-soluble 1,4-diether reduce the metal ions to the colloidal metal.

Vinyl polymers having a polar group protect colloidal metals from aggregation, resulting in formation of stable colloidal dispersion of metal.

The compounds used as polymers, alcohols, or additives having more than two carboxylic groups or amino groups coordinate so strongly to the metal ion through chelation that the colloidal dispersion cannot be formed by the reduction of the metal ion with alcohol or ether.

ACKNOWLEDGMENTS

REFERENCES

[1] L. Hernandez and F. F. Nord, J. Colloid Sci., 3, 363 (1948).
[2] C. Paal and C. Amberger, Ber., 37, 124 (1904).
[3] H. Hirai, Y. Nakao, N. Toshima and K. Adachi, Chem. Letters, 1976, 905.
[4] H. Hirai, Y. Nakao and N. Toshima, J. Macromol. Sci.–Chem., A12, 1117 (1978).
[5] J. Chatt, B. L. Shaw and A. E. Field, J. Chem. Soc., 1964, 3466.
[6] N. A. Lange ed., Handbook of Chemistry, 10th ed., McGraw-Hill, New York, 1961.
[7] W. M. Latimer, The Oxidation States of the Elements and their Potentials in Aqueous Solutions, Prentice-Hall Inc., New York, 1952.
[8] H. B. Williams and L. T. Chang, J. Phys. Colloid Chem., 55, 719 (1951).
[9] B. Jirgensons, Makromol. Chem., 6, 30 (1951).
[10] B. Jirgensons and M. E. Straumanis, A Short Textbook of Colloid Chemistry, 2nd ed., Pergamon Press, London, 1962.
[11] A. Dobson and S. T. Robinson, Inorg. Chem., 16, 137 (1977).
[12] T. Nishiguchi, K. Tachi and K. Fukuzumi, J. Am. Chem. Soc., 94, 8916 (1972).
[13] J. Smidt, Chem. Ind., 1962, 54.
[14] O. Beeck, Rev. Modern Phys., 17, 61 (1945).
[15] O. Beeck, Discussions Faraday Soc., 8, 118 (1950).