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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Hirai, Hidefumi , Nakao, Yukimichi and Toshima, Naoki(1978) 'Preparation of Colloidal Rhodium in Poly(vinyl Alcohol) by Reduction with Methanol', Journal of Macromolecular Science, Part A, 12: 8, 1117 – 1141

To link to this Article: DOI: 10.1080/00222337808063179

URL: <http://dx.doi.org/10.1080/00222337808063179>

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Preparation of Colloidal Rhodium in Poly(vinyl Alcohol) by Reduction with Methanol

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ABSTRACT

Refluxing of a solution of poly(vinyl alcohol) and rhodium(III) chloride in methanol-water gives a colloidal dispersion of rhodium which is an effective catalyst for hydrogenation of cyclohexene in methanol at 30°C under atmospheric hydrogen pressure. Formaldehyde is produced quantitatively with the reduction of rhodium(III) chloride to metallic rhodium. The rhodium particles in the colloidal dispersion are found to consist of two kinds of particles, about 8 and 40 Å in diameter by electron microscopy. The sizes of the small (8 Å) and large (40 Å) particles are almost constant during the course of refluxing. The number of small particles, which is the great majority of particles at the early stage of refluxing, gradually decreases; concurrently the number of large particle increases on prolonged refluxing. An absorption peak appears at 260 nm at the early stage of refluxing. The presence of the 260 nm peak, which indicates the coordination of poly(vinyl alcohol) to rhodium(III) ion, is indispensable for the formation of a homogeneous colloidal dispersion of rhodium. The addition of ethylenediamine inhibits the formation of colloidal rhodium in refluxing. The catalytic activity of colloidal dispersion of rhodium is dependent upon the concentration of rhodium(III) chloride charged and is

independent of that of poly(vinyl alcohol). The formation mechanism of colloidal rhodium is discussed.

INTRODUCTION

Colloidal transition metals have been prepared by reduction of the corresponding metal salts [1-4] and by pulverization of metallic mass by using arc discharge [5]. The colloidal metals prepared by the former procedure are generally superior to those by the latter procedure with respect to small size and narrow size distribution of particles. In the preparation of colloidal metals in aqueous solution, natural polymers such as gelatin, dextrin, and sodium salt of lysalbinic acid, were added as a protective colloids to prevent coagulation and precipitation of metallic particles. Hernandez and Nord [6] obtained a stable colloidal dispersion of rhodium by using a synthetic high polymer, i. e., poly(vinyl alcohol), instead of a natural polymer. The role of polymer in the process of the formation of colloidal dispersion has not been clarified, although the action of polymer as a protective colloid toward metallic particles has been intensively studied and represented by various coefficients: gold number [1], protective value [7], etc.

In a previous communication [8], we reported a novel method for preparation of colloidal dispersion of rhodium by refluxing a solution of rhodium(III) chloride and poly(vinyl alcohol) in methanol-water. The particle size of rhodium in the colloidal dispersion was sharply distributed in the range between 30 and 70 Å, which comprised 94% of the particles. The average particle diameter was estimated to be 40 Å. The colloidal dispersion was effective for hydrogenation of cyclohexene at 30°C under 1 atm hydrogen pressure.

In the present study, the colloidal dispersions were investigated by electron microscopy and absorption spectroscopy. The effects of the refluxing time and of the addition of ethylenediamine on the formation of colloidal dispersion were examined. The catalytic activities of the resulting colloidal dispersions for hydrogenation of olefin were also investigated in detail.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) was obtained from Nippon Synthetic Chemical Industry Co., Ltd.; degree of polymerization 500, degree of saponification > 98%, content of sodium acetate < 2%. Rhodium(III) chloride

was obtained from Nippon Engelhard, Ltd., as a trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$). Commercial pure grade hydrogen (99.99999% purity) was passed through a column (Deoxo column, Nippon Engelhard, Ltd.,) before use to remove trace amounts of oxygen. Cyclohexene (G. R. grade) was obtained from Tokyo Chemical Industry Co., Ltd., and distilled in argon before use.

Preparation of Colloidal Dispersion of Rhodium

Poly(vinyl alcohol) (147 mg, 3.33 mmole as monomeric residue) and rhodium(III) chloride (8.8 mg, 0.033 mmole) were dissolved in a methanol (25 ml)-water (25 ml) mixed solvent to form a rose-pink solution. Refluxing the solution (solution temperature 79°C) under argon or air on a boiling water bath for 0.2 to 16 hr gave a homogeneous light brown to dark brown solution of colloidal rhodium, that is, a colloidal dispersion of rhodium.

Electron Microscopy

The sample films prepared by evaporation of a small amount of the colloidal dispersion of rhodium to dryness on a collodion film which was coated with a carbon layer and supported on copper grids were mounted in an electron microscope, Hitachi Model H-500, operated at 125 kV. The magnification of the electron microscope was 200,000. The diameter of each of the rhodium particles, in arbitrarily chosen areas of $8.0 \times 10^6 \text{ \AA}^2$, was determined from the enlarged photographs, which corresponds to a magnification of $\times 860,000$. The particle size distribution and the average diameter of rhodium particles were obtained on the basis of these results.

Absorption Spectroscopy

Absorption spectra of the colloidal dispersions of rhodium were obtained at room temperature on a Shimadzu Model MPS-50L spectrophotometer equipped with a 1 cm quartz cell.

Determination of the Oxidized Products of Methanol

The content of formaldehyde in the resulting colloidal dispersion of rhodium was determined by the chromotropic acid-sulfuric acid method [9]. The disodium salt of chromotropic acid (500 mg) was dissolved in 72% sulfuric acid (100 ml), resulting in a colorless chromotropic acid solution. The colloidal dispersion of rhodium

was cooled after refluxing for a fixed time and diluted with water to one tenth. The diluted solution (1.0 ml) was then heated with the chromotropic acid solution (5.0 ml) for 15 min on a boiling water bath, resulting in a purple solution. The concentration of formaldehyde was determined by an intensity of a peak at 575 nm in the visible spectrum of the solution. Identification of formaldehyde was also carried out by an alternative method involving the formation of the 2,4-dinitrophenylhydrazine adduct and a comparison of its IR spectrum with that in the literature [10].

Formic acid was transformed quantitatively into formaldehyde by reduction with magnesium-hydrochloric acid. The total amount of formaldehyde was determined by the chromotropic acid-sulfuric acid method. The difference in formaldehyde content between the colloidal dispersion treated with magnesium-hydrochloric acid and the original colloidal dispersion corresponded to the content of formic acid.

Carbon dioxide was expelled from the colloidal dispersion by bubbling through argon and then flushed to an aqueous solution of barium hydroxide to be fixed as a barium carbonate precipitate. The weight of barium carbonate gave the content of carbon dioxide.

Hydrogenation of Cyclohexene

The hydrogenation of cyclohexene was carried out in methanol (commercial G. R. grade) at 30.0°C under 1 atm hydrogen pressure. Into a flask where the atmosphere was previously replaced with hydrogen, methanol (18.7 ml) and the colloidal dispersion of rhodium (0.30 ml; Rh 2.0×10^{-7} mole) were poured in in that order. The solution was stirred in a 30.0°C thermostat under atmospheric hydrogen pressure for 1 hr for saturation with hydrogen. Then 1.0 ml of solution of cyclohexene (0.5 mmole) in methanol was added to the flask to begin the hydrogenation reaction, the total pressure being kept at 1 atm. The progress of the hydrogenation was followed by hydrogen uptake under atmospheric pressure. The initial rate of hydrogen uptake was determined by the initial slope of hydrogen uptake-time curves. The product was identified to as cyclohexane by GLPC with a 2 m column of β, β' -thiodipropionitrile at 55°C.

RESULTS

Formation of Colloidal Dispersion of Rhodium

A solution of poly(vinyl alcohol) and rhodium(III) chloride in methanol-water was heated to begin refluxing at a solution temperature of 79°C. The color of the solution turned from rose-pink to light

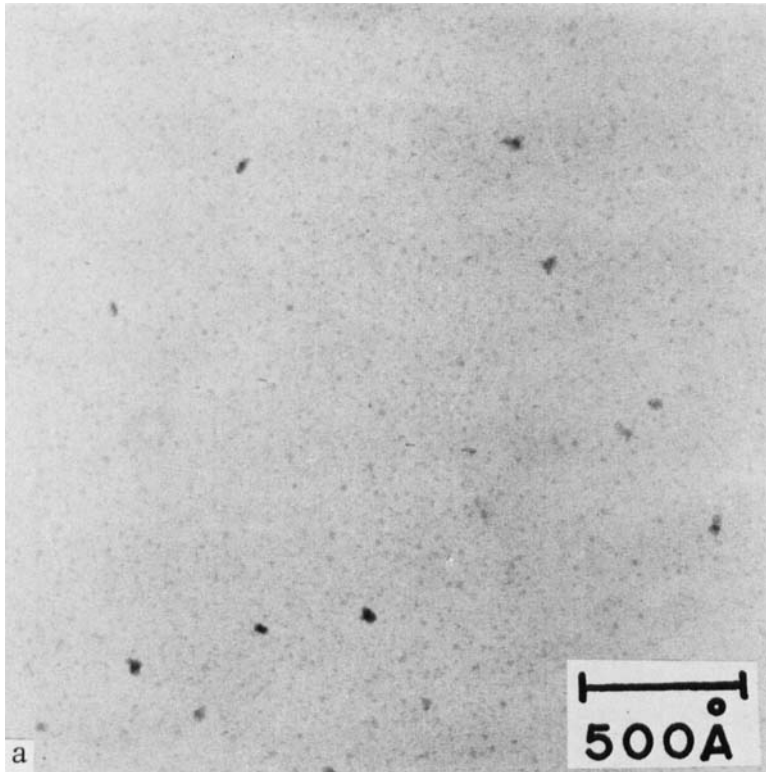


FIG. 1. Electron micrographs of colloidal rhodium in poly(vinyl alcohol)-methanol-water, prepared by refluxing for (a) 0.2 hr, (b) 4 hr, and (c) 16 hr; $\times 200,000$.

brown at the beginning of refluxing. Further refluxing of the solution caused gradual change in color to dark brown and gave a homogeneous dispersion of colloidal rhodium. Figure 1 shows electron micrographs of colloidal dispersions of rhodium prepared by refluxing for 0.2, 4, and 16 hr. All the rhodium particles in the electron micrographs can be classified into two groups: small and large particles. As stated later, the small particles and the large particles were determined to have mean diameters of 8 and 40 Å, respectively. As refluxing proceeds, the content of the small particles decreases, while that of the large particles increases.

When the colloidal dispersion prepared by refluxing for 0.2 hr

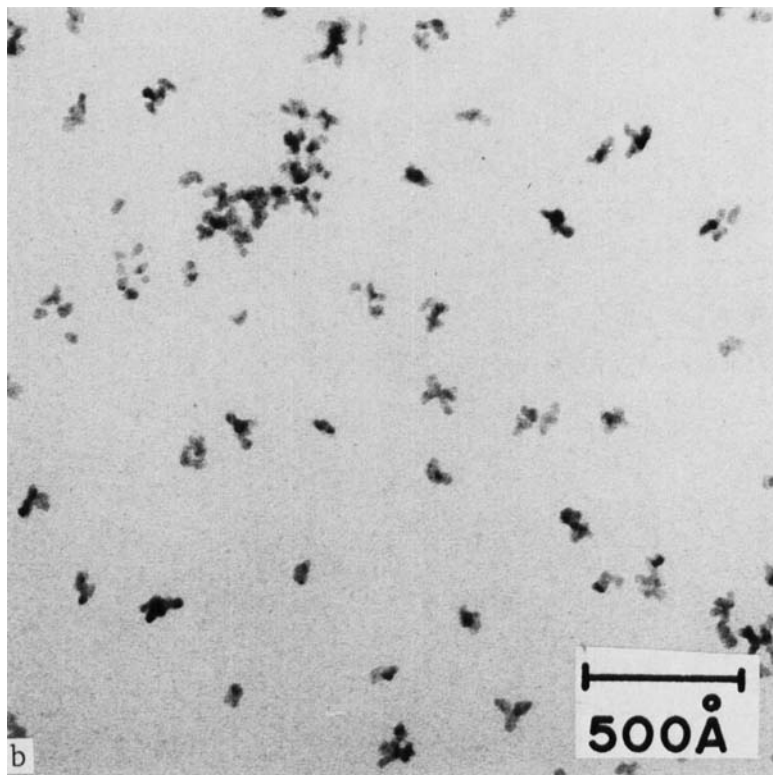


FIG. 1b.

was stirred for 30 min under hydrogen, the color of the colloidal dispersion turned from light brown to dark brown without precipitation. Figure 2 shows an electron micrograph of the colloidal dispersion prepared by refluxing for 0.2 hr followed by treatment with hydrogen at 1 atm pressure. In contrast to the colloidal dispersion before the hydrogen treatment (Fig. 1a), that after the hydrogen treatment (Fig. 2) does not contain the small particles (8 Å) but the extremely aggregated rhodium particles, of which the average diameter is estimated to be 40 Å. This value corresponds to the average diameter of dispersion of the large particle which appeared in the colloidal dispersion prepared by refluxing for a longer time without hydrogen treatment. The hydrogen treatment of the original solution of poly(vinyl alcohol) and rhodium(III)

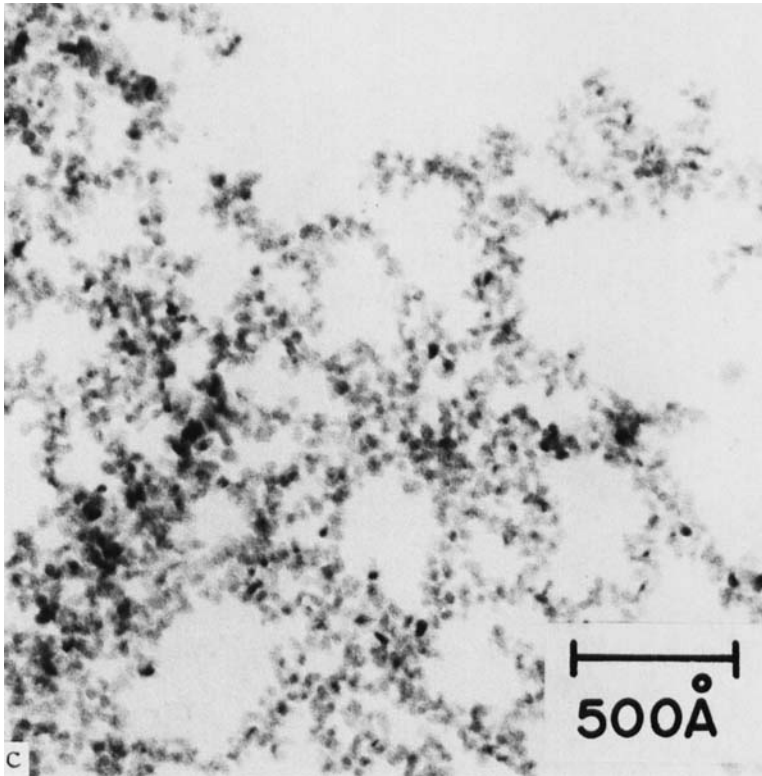


FIG. 1c.

chloride in methanol-water before refluxing, however, caused rapid precipitation of metallic rhodium.

Absorption Spectra of Colloidal Dispersion

Comparison of the UV spectrum of the colloidal dispersion prepared by refluxing for 0.2 hr (Fig. 3, solid line) with that of the original solution without refluxing (Fig. 3, dotted line) shows that an additional peak appears at 260 nm after refluxing. Refluxing of the aqueous solution of poly(vinyl alcohol) and rhodium(III) chloride for 1 hr at a solution temperature of 79°C under reduced pressure in the absence of methanol also gives an additional peak in the same region (Fig. 3, broken line). This fact indicates that methanol is not involved in the appearance of the peak at 260 nm.

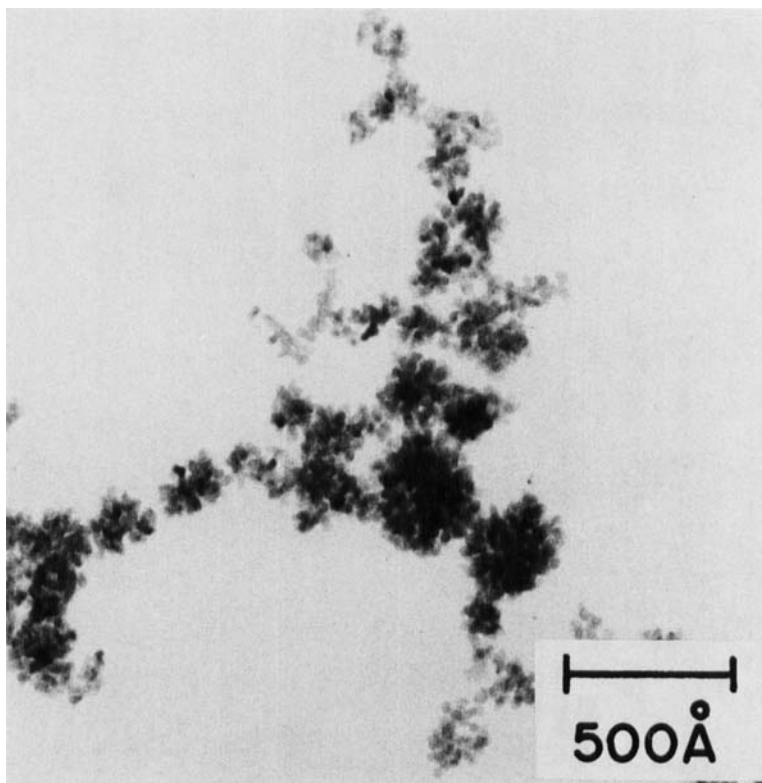


FIG. 2. Electron micrograph of colloidal rhodium prepared by refluxing for 0.2 hr followed by treatment with hydrogen; $\times 200,000$.

The visible spectra of the colloidal dispersions with different refluxing times are given in Fig. 4. All the optical density curves are monotonic without peaks. The longer the refluxing time, the more upward the optical density curves move parallel to each other. These facts indicate that the light scattering by rhodium particles is responsible for the increase in the optical density.

Large Particles

Figure 5 shows the size distribution of the large particles appeared in the electron micrograph of the colloidal dispersion of rhodium

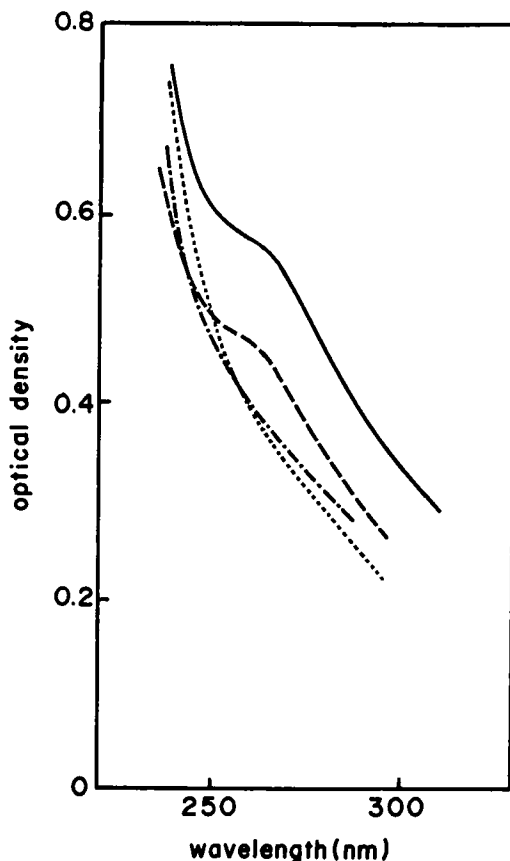


FIG. 3. UV spectra of the solutions of rhodium(III) chloride and poly(vinyl alcohol), $[Rh] = 0.22 \text{ mM}$, $[PVA] = 22.2 \text{ mM}$: (a) (—) solution in MeOH/H₂O (1/1) after refluxing for 0.2 hr; (b) (--) solution in MeOH/H₂O (1/1) immediately before the beginning of refluxing; (c) (- · -) solution in H₂O after refluxing at 79°C under reduced pressure for 1 hr; (d) (· - ·) solution prepared by refluxing of original solution (a) with ethylenediamine (0.22 mM) for 1 hr.

prepared by refluxing for 4 hr. In this histogram the small particles are omitted because of their small content (less than 1 wt %). The size of the large particles is sharply distributed in the range from 30 Å to 70 Å, which includes 94% of the total particles. The average diameter is determined to be 40 Å from this histogram. The size

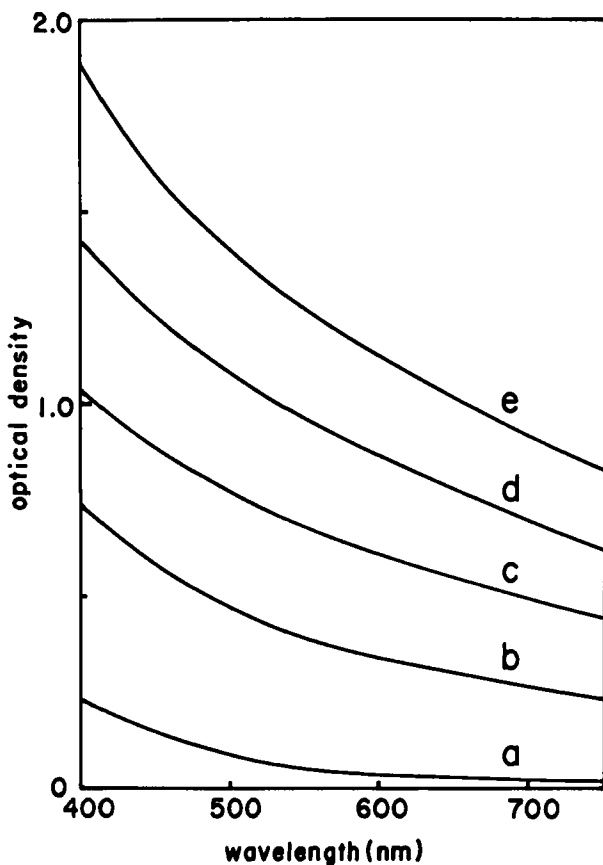


FIG. 4. Visible spectra of colloidal dispersions of rhodium prepared by refluxing for (a), 0.2 hr, (b) 1.0 hr, (c) 2.0 hr, (d) 4.0 hr, and (e) 16 hr.

distribution histograms of the large particles in the colloidal dispersions prepared by refluxing for 0.2 and 16 hr were obtained as well. The dependence of the average diameter of the large particles on the refluxing time for preparation is shown in Fig. 6. The value of the diameter goes up to 38 Å in the early stage and changes slightly on further refluxing.

According to the Rayleigh Law, the intensity of the light scattering caused by fine particles is proportional to both the number of particles

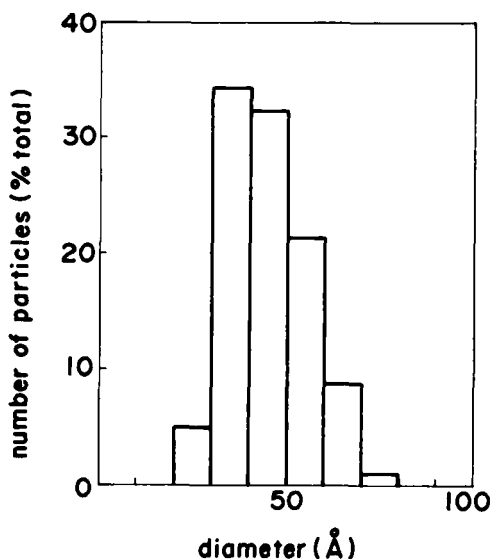


FIG. 5. Particle size distribution of colloidal rhodium in poly(vinyl alcohol) prepared by refluxing for 4 hr.

and the square of the volume of the particle. The ratio of the number of small particles (8 Å) to that of large particles (40 Å) is estimated to be 100, and the ratio of the volume is $(8/40)^3$ in the case of the colloidal dispersion prepared by refluxing for 0.2 hr, which represents the case of the largest ratio in number. From these values, the contribution of the small particles to the light scattering is estimated to be less than 1% of the total scattering. Consequently, the light scattering of the colloidal dispersion prepared by refluxing for more than 0.2 hr can be entirely attributed to that of the large particles. Since the diameter of the large particles is nearly constant during the course of refluxing (Fig. 6), the optical density of the colloidal dispersion must be proportional to the number of large particles. Figure 7 gives the relationship between the proportion of large particles and the refluxing time. The former is estimated by the optical densities of the colloidal dispersions at 750 nm. In this region of wavelength, the absorption due to ionic rhodium species is negligible. The number of large particles increases linearly with the refluxing time during the initial 2 hr and reaches at a saturated value after more than 10 hr.

The electron diffraction of the large particles in the colloidal dispersion prepared by refluxing for 16 hr was also studied, giving

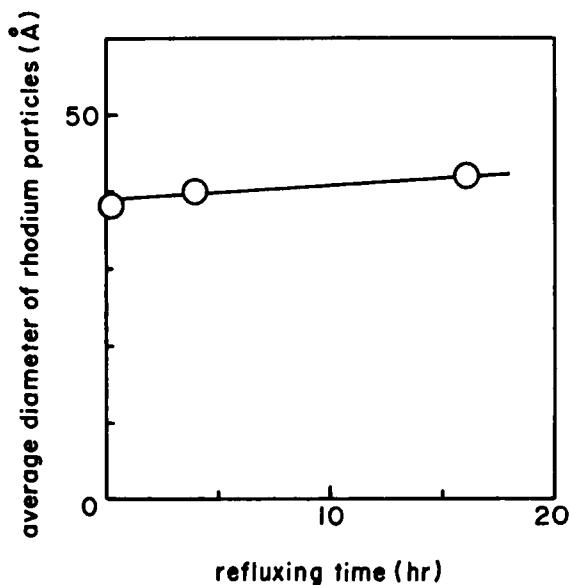


FIG. 6. Dependence of the average diameter of rhodium particles upon the refluxing time.

four Debye rings, of which the relative diameters were in the ratios 1.00:1.14:1.61:1.87. These values are consistent with the theoretical for the crystal structure of a face-centered cubic lattice, 1.00:1.16:1.66:1.94.

Effect of Addition of Ethylenediamine

Ethylenediamine was found to inhibit the formation of the colloidal dispersion of rhodium in the refluxing stage. Figure 8 shows the relationship between the number of large particles (40 Å) estimated by the optical density of the colloidal dispersion and the amount of ethylenediamine added to the original solution of poly(vinyl alcohol) and rhodium(III) chloride. The formation of the large particle was almost entirely inhibited when equimolar ethylenediamine with rhodium(III) chloride charged was added. The added ethylenediamine also inhibited the formation of formaldehyde, as described later. The resulting solution was ineffective for the catalytic hydrogenation of cyclohexene. These facts indicate that the added ethylenediamine inhibits not only the formation of the large particles (40 Å) but also

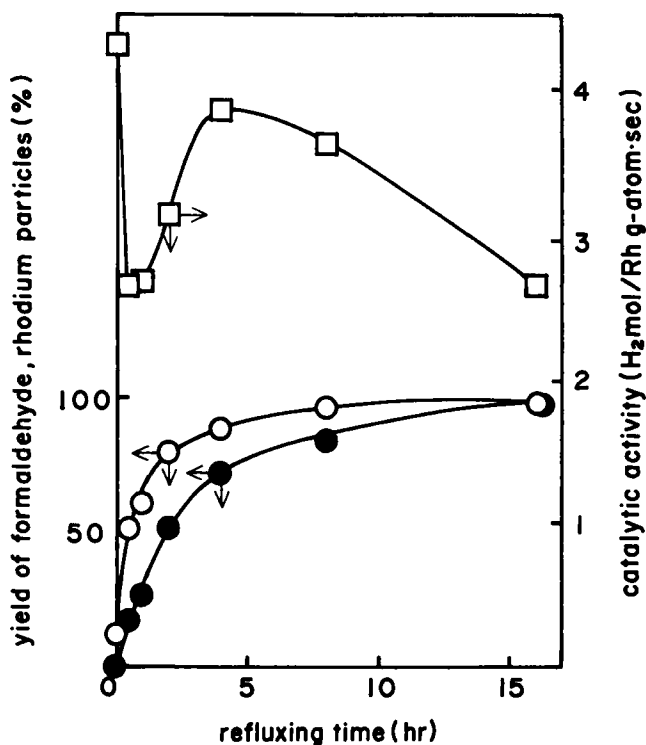


FIG. 7. Dependence on reflux time of yields of (○) formaldehyde and (●) rhodium particle and (□) of catalytic activity for hydrogenation of cyclohexene.

that of the small particles (8 Å). In contrast to the case of ethylenediamine, addition of triethylamine influenced the formation of rhodium particles slightly, even when 100 molar equivalents of triethylamine to rhodium(III) chloride was added. When the colloidal dispersion prepared by refluxing for 0.2 hr was refluxed in the presence of ethylenediamine, the peak at 260 nm in the UV spectrum disappeared as shown in Fig. 3, and the optical density at 750 nm of the visible spectrum increased by a factor of 1.72. These facts indicate that ethylenediamine eliminated the species responsible for the peak at 260 nm but had no effect on the conversion of the small particles to the large particles.

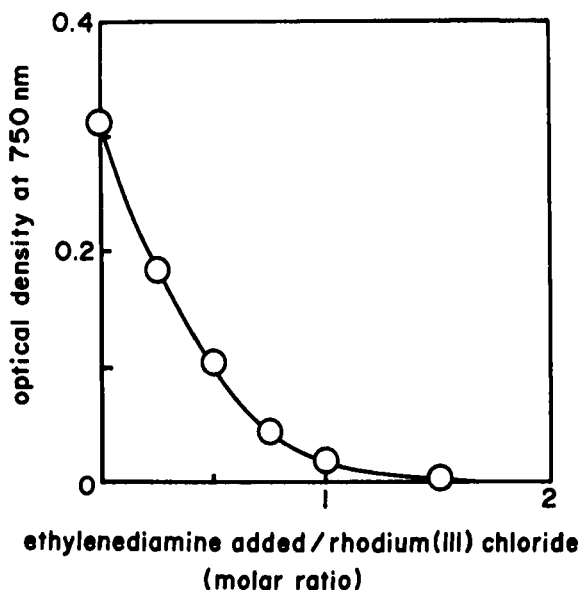


FIG. 8. Inhibition of colloidal rhodium formation by addition of ethylenediamine; cell length = 1 cm, refluxing time = 1 hr.

Small Particles

The size of the small particles could not be determined accurately by electron microscopic measurement because of the limitation of resolution (3 Å). The diameter of the small particle was determined by the technique of addition of ethylenediamine as follows. When the colloidal dispersion of rhodium prepared by refluxing for 0.2 hr was further refluxed in the presence of ethylenediamine, the peak at 260 nm in the UV spectrum disappeared as shown in Fig. 3, and the optical density at 750 nm of visible spectrum increased by a factor of 1.72. During the refluxing, no small particles were produced from rhodium(III) chloride, because the formation of both the large particle and the small particle was inhibited by the addition of ethylenediamine to the original solution of poly(vinyl alcohol) and rhodium(III) chloride in methanol-water. As described previously, the small particles contribute very little to the light scattering which is responsible for the increase in the optical density at 750 nm. Since the diameter of the large particles is nearly constant, the optical density of the colloidal dispersion is proportional to the

number of large particles. Accordingly, the increment of 0.72 part in the optical density may be correlated to the conversion of the small particles in the original dispersion to the large particles (40 Å). The original ratio of the number of small particles to that of large particles (40 Å) in the colloidal dispersion prepared by refluxing for 0.2 hr was estimated to be 100 from the electron micrograph. These facts indicate that 100 small particles correspond to 0.72 large (40 Å) particle. The diameter d of the small particle may be represented as follows:

$$100d^3 = 0.72(40)^3 \quad (1)$$

From Eq. (1) we determine the diameter of the small particle to be 7.7 Å. This value falls in the range obtained by a direct measurement from the electron micrograph.

Electron diffraction measurement of the small particle included in the colloidal dispersion prepared by refluxing for 0.2 hr was unsuccessful because of the much lower density of the small particles in the electron microscope field.

Oxidation of Methanol during Refluxing

Formaldehyde was found to form during the course of refluxing for the preparation of colloidal dispersion of rhodium. Figure 7 shows the formaldehyde formation during refluxing under argon. The amount of formaldehyde formed reaches at a limiting value of 1.5 molar equivalent to that of rhodium(III) chloride charged. Refluxing of the original solution under air gave about three times as much formaldehyde as refluxing under argon. The colloidal dispersions of rhodium prepared under air, however, was quite similar to those prepared under argon with respect to the diameter of the rhodium particle, the dispersion state, and the activity.

Further oxidization products of methanol, that is, formic acid and carbon dioxide, were confirmed to be absent. Formaldehyde was unable to reduce rhodium(III) chloride in an aqueous solution at 79°C. Because the concentration of formaldehyde in the colloidal dispersions was extremely low (less than 30 ppm), all the formaldehyde must be in the form of methylene glycol [11]. This is the reason why formaldehyde can remain quantitatively in the colloidal dispersion even under refluxing in spite of its low boiling point (-20°C).

Among alcohols other than methanol, the water-soluble primary alcohols such as ethanol and the water-soluble secondary alcohols such as 2-propanol were available for preparation of colloidal

dispersion of rhodium in place of methanol. The colloidal dispersion prepared by using these alcohols were similar to those prepared by using methanol. The use of tert-butyl alcohol, however, gave no colloidal dispersion of rhodium, because a tertiary alcohol had no activity for reduction of rhodium(III) ion. In the preparation of the colloidal dispersion of rhodium by using methanol, the presence of water was indispensable for both the dissolution of poly(vinyl alcohol) and the reduction of rhodium(III) chloride.

Catalytic Hydrogenation

The colloidal dispersion of rhodium was found to be an effective catalyst for hydrogenation of cyclohexene at 30.0°C under 1 atm hydrogen pressure [8]. The hydrogenation produced cyclohexane smoothly, and the hydrogen uptake ceased at the equimolar amount with cyclohexene charged. During the reaction, the reaction mixture was homogeneous without precipitation of metallic rhodium. As shown in Fig. 7, the catalytic activity of the colloidal dispersion for hydrogenation of cyclohexene varies with the refluxing time for preparation. The catalytic activity increases markedly in the earliest stage of refluxing for shorter time than 1 min, and then decreases rapidly, and, after passing successively through a minimum at 0.5 hr and a maximum point at 4 hr refluxing, gradually diminishes again. The activity at the beginning of refluxing differs to some extent, depending on the batches of preparation.

When both the charged concentration (0.67 mM) of rhodium(III) chloride and the refluxing time (2 hr) are fixed, the catalytic activity of the colloidal dispersion is nearly constant in the range of poly(vinyl alcohol) concentration from 13.3 to 113 mM as shown in Fig. 9. In the case of fixed concentration of poly(vinyl alcohol) (66.7 mM), the catalytic activity has the maximum value at 0.67 mM of the charged concentration of rhodium(III) chloride as shown in Fig. 10. When the charged concentration of rhodium(III) chloride is higher than 0.67 mM, the catalytic activity was rather low under the same conditions but could be enhanced by shortening the refluxing time (see Table 1). When the rhodium(III) chloride concentration was lower than 0.67 mM, the catalytic activity could be also enhanced by prolonging the refluxing time (Table 1). When the original solution of rhodium(III) chloride (0.67 mM) with poly(vinyl alcohol) was refluxed for only 1 min, then immediately diluted to 0.33 mM with methanol-water and further refluxed for 2 hr, the resulting colloidal dispersion of rhodium exhibited the same activity as those prepared at a concentration of 0.67 mM during the refluxing (Table 1). These facts indicate that the catalytic activity of colloidal dispersion is dependent only upon the charged concentration of rhodium(III) chloride and is independent of the total concentration of rhodium(III) species in further refluxing.

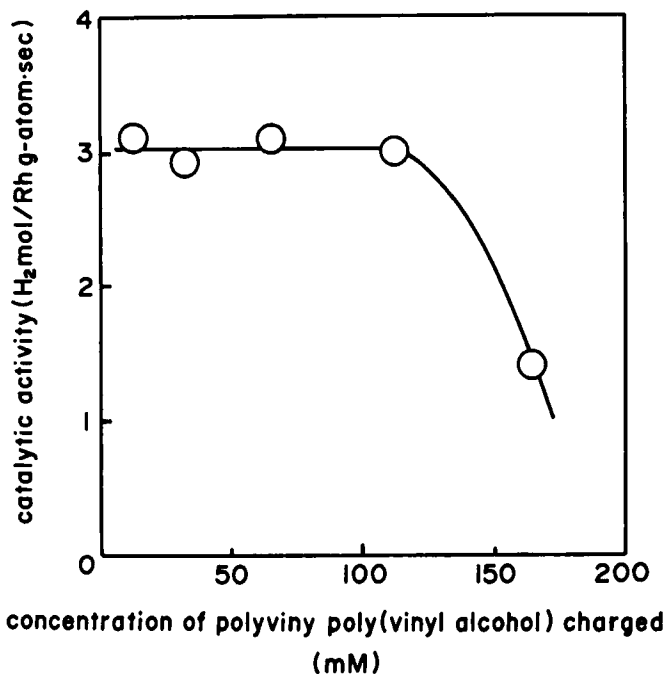


FIG. 9. Dependence of catalytic activity of colloidal dispersion of rhodium for hydrogenation of cyclohexene upon concentration of poly(vinyl alcohol) charged; concentration of rhodium(III) chloride charged, 0.67 mM.

DISCUSSION

Formation of Colloidal Rhodium

In the early stage of the refluxing of the solution of poly(vinyl alcohol) and rhodium(III) chloride in methanol-water, an absorption peak appeared at 260 nm in the UV spectrum (Fig. 3). The same peak also appeared even in the absence of methanol. This fact implies that the peak is independent of the reduction process of rhodium(III). The addition of ethylenediamine diminished the optical density of this peak (Fig. 3). An absorption band at 260 nm was reported to appear on coordination of poly(vinyl alcohol) to copper(II) ion [12]. These facts indicate that the coordination of poly(vinyl alcohol) to rhodium(III) ion is responsible for the appearance of the peak at 260 nm. It

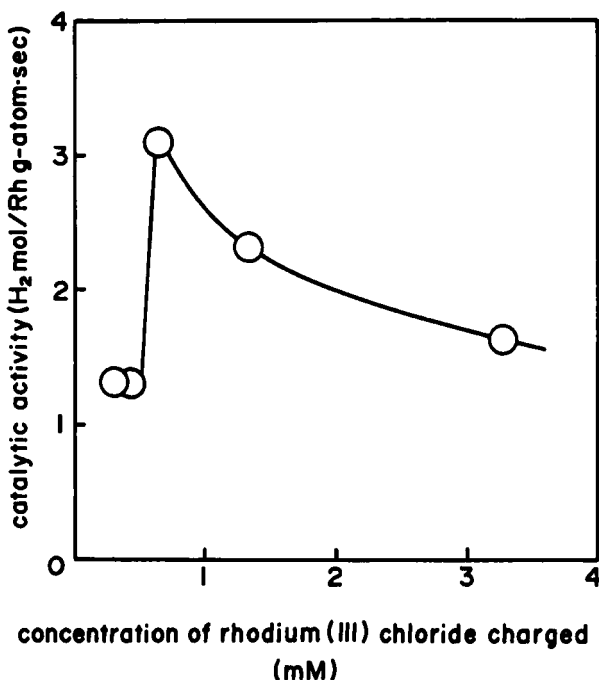


FIG. 10. Dependence of catalytic activity of colloidal dispersion of rhodium for hydrogenation of cyclohexene upon concentration of rhodium(III) chloride charged; concentration of poly(vinyl alcohol) charged, 66.7 mM.

was confirmed that the peak at 260 nm was not related to charge transfer from chloride ligand to central rhodium(III) ion. The charge-transfer band appeared at 230 nm in the original solution before heating and gradually diminished without shift in wavelength with rising solution temperature, resulting in a complete disappearance before the beginning of refluxing.

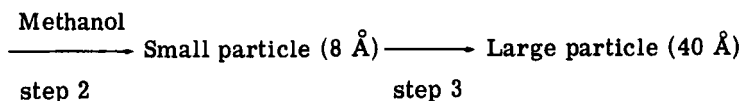
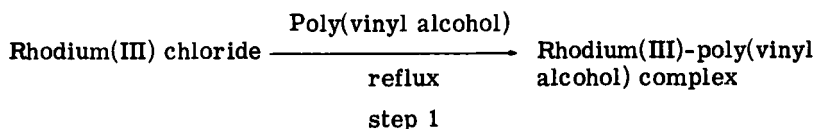
The small particle (8 Å) was a metal atom cluster which appeared at first on reduction of rhodium(III) ion. The conversion of the small particles (8 Å) to large particles (40 Å) is confirmed by the facts that the small particles constituted the great majority of particles produced in the early refluxing period and that the number of small particles gradually decreased with increasing number of the large particle on continuance of refluxing. Consequently, the following scheme can be proposed for the process of colloidal rhodium formation:

TABLE 1. Catalytic Activity of Colloidal Dispersion of Rhodium Prepared under Various Conditions

Charged concentration (mM)		Refluxing time (hr)	Catalytic activity (H ₂ mole/Rh g-atom-sec) ^a
Rhodium(III) chloride	Poly(vinyl alcohol)		
0.67	33.3	2	2.9
0.67	66.7	2	3.1
1.33	66.7	2	2.3
1.33	66.7	0.5	3.9
0.33	66.7	2	1.3
0.33	66.7	6	1.8
0.33	33.3	2	1.2
0.67	66.7	2 ^b	3.0

^aFor the hydrogenation of cyclohexene; temp 30°C, total pressure 1 atm, [cyclohexene] = 25 mM, [rhodium] = 0.01 mM, solvent = methanol/water (130/1) (20 ml).

^bConcentrations of rhodium(III) chloride and poly(vinyl alcohol) are 0.67 and 66.7 mM, respectively, in the early refluxing for 1 min, and 0.33 and 33.3 mM, respectively, in the subsequent refluxing for 2 hr.



Coordination of Poly(vinyl alcohol) to Rhodium(III) Ion (Step 1)

Poly(vinyl alcohol) can be hardly coordinated to rhodium(III) ion in the original solution of rhodium(III) chloride and poly(vinyl alcohol) in methanol-water, because the pH value of the original solution immediately before reflux is 4.5. The original solution just before the beginning of refluxing had no absorption peak in the range of

220-330 nm and gave black precipitates of metallic rhodium upon contact with molecular hydrogen. Immediately after refluxing, the solution exhibited an absorption peak at 260 nm and produced a homogeneous colloidal dispersion of rhodium upon contact with molecular hydrogen. Accordingly, the appearance of an absorption peak at 260 nm which indicates the coordination of poly(vinyl alcohol) to rhodium(III) ion is indispensable for the formation of a homogeneous colloidal dispersion of rhodium. The catalytic activity of the colloidal dispersion of rhodium for hydrogenation was dependent upon the concentration of rhodium(III) species at the beginning of reflux and was not influenced by the concentration of rhodium(III) species in the subsequent reduction process in refluxing. From these facts, it is conceivable that almost all the rhodium(III) ions coordinate poly(vinyl alcohol) at a charged molar ratio of the monomeric residue to rhodium larger than 50 (or 100) in 1 min refluxing, and that the colloidal rhodium is preferentially produced by reduction of the rhodium(III) ion in the coordination state.

Formation of Small Particles (8 Å) (Step 2)

This step consists of two steps, the reduction of rhodium(III) ion to the zero-valent state and the aggregation of zero-valent rhodium atoms to the small particle (8 Å). In the first step, methanol was converted to formaldehyde, which was not effective for reduction and so remained without change. Refluxing of the solution of rhodium(III) chloride and poly(vinyl alcohol) in methanol-water under argon gave just 1.5 molar equivalent of formaldehyde to rhodium(III) chloride charged. Tert-butyl alcohol, having no α -hydrogen, was ineffective for the reduction of rhodium(III) chloride. On the basis of these results, the following stoichiometry can be proposed;



where coordinated poly(vinyl alcohol) is ignored. Refluxing of the solution under air gave more formaldehyde than estimated from Eq. (2). The formation of extra formaldehyde may be attributed to the autoxidation of methanol catalyzed by colloidal rhodium formed [13]. It has been reported that various transition metal ions are reduced to a low valent state [14-16], that is, hydride complexes [17] or a metallic state [18] with alcohols which are converted to corresponding carbonyl compounds. Chatt and co-workers [17] proposed a mechanism via an alkoxido complex for formation of the hydrido-carbonyl-ruthenium(II) complex from ruthenium(II)-tertiary phosphine complex and ethanol. Accordingly, the mechanism of reduction of rhodium(III) chloride with methanol can be proposed as follows. First methanol coordinates to rhodium(III) ion as an

oxonium complex prior to the formation of an alkoxido complex. The oxonium complex then loses a proton and changes to an alkoxido complex. In this step, a base is required for the elimination of protons. Dissolution of rhodium(III) chloride in water results an acidic solution. This indicates that the aquo ligand, which is originally coordinated to the rhodium(III) ion, is partly converted to a hydroxido ligand. The resulting hydroxido ligand may act as the base which is concerned with the elimination of protons from the oxonium complex. The fact that rhodium(III) chloride was not reduced by refluxing in anhydrous methanol indicates the indispensability of water for the reduction of rhodium(III) ion with methanol. Considering that the hydrido ligand originates from coordinated water, the indispensability of water is understandable.

Besides the hydroxido ligand, sodium acetate included in poly(vinyl alcohol) (1-2%) also has a chance of acting as a base in the elimination of protons. The contaminant sodium acetate, the content of which was determined by IR spectra, can be removed by washing with methanol. The colloidal rhodium prepared by using poly(vinyl alcohol) free from sodium acetate had the same particle size and the same catalytic activity as those of rhodium prepared by using the original poly(vinyl alcohol) without washing. As illustrated in Fig. 9, the catalytic activity of the colloidal dispersion was constant over a broad range of poly(vinyl alcohol) concentration. These two experimental results lead to the notion that sodium acetate does not concern with the reduction of rhodium(III) ion.

Nord and co-workers [19] reported that poly(vinyl alcohol) acted as a reductant to palladium(II) hydroxide in the preparation of colloidal palladium. The IR spectrum of poly(vinyl alcohol), however, remained unchanged during the course of the preparation of the colloidal dispersion of rhodium. Furthermore, heating of the aqueous solution of rhodium(III) chloride and poly(vinyl alcohol) in the absence of methanol gave no colloidal rhodium. Consequently, poly(vinyl alcohol) does not act as a reductant in preparation of the colloidal rhodium.

The diameter of the small particle was estimated to be 8 \AA by using addition of ethylenediamine which coordinated strongly to rhodium(III) ion, resulting in dissociation of poly(vinyl alcohol) in the coordination state. The number of rhodium atoms involved in a small particle (8 \AA) can be estimated to be 20 on the basis of the density of rhodium metal (12.4 g/cm^3). The diameter, 8 \AA , is just equal to six times the length of the bond radius of rhodium metal (1.34 \AA), that is, the total length of three rhodium atoms aligned in a straight line. The crystal structure of rhodium metal was a face-centered cubic lattice, where the coordination number was 12. In the course of the particle formation from rhodium atoms, a particle of diameter shorter than 8 \AA may be unstable, because all the constituting rhodium atoms are located on the surface of particles lacking the central rhodium atoms which bind the surface rhodium atoms.

The possible size of the smallest particle, therefore, can be estimated as 8 Å in diameter, corresponding to the sum of the diameters of three rhodium atoms, which can contain one rhodium atom in the center of the particle. From the estimate above, the formation process of the small particle (8 Å) is proposed as follows. The rhodium(III) ions in the complex with poly(vinyl alcohol) are reduced with methanol to the zero valent state. The resulting rhodium(0) atoms aggregate together to a particle 8 Å in diameter which includes 20 rhodium atoms. At this stage, poly(vinyl alcohol) may cover all the surface of the small particle of rhodium (8 Å), preventing it from further aggregation. The poly(vinyl alcohol) molecule (DP 500) presumably takes a thread-ball shape. The diameter of the thread ball can be estimated on the basis of Hosono and Sakurada's data [20] to be about 100 Å. Accordingly, the small particle of rhodium (8 Å) can gather only a few poly(vinyl alcohol) molecules on its surface. The attractive force may be ascribed to a hydrophobic interaction between the surface of metallic rhodium and the hydrophobic part of poly(vinyl alcohol).

Conversion of Small Particles (8 Å) to Large Particles (40 Å) (Step 3)

The narrow size distribution observed in the large particles indicates that a particle of 40 Å diameter is much more stable. The large particles (40 Å) are the rhodium crystallites with a face-centered cubic lattice. On the other hand, the small particles (8 Å) are the agglomerates of rhodium atoms, which can dissociate into rhodium atoms to be arranged as crystallites growing up to the large particles (40 Å). The stability of the large particle (40 Å) may be associated with the presence of poly(vinyl alcohol) molecules on its surface. Checking by use of steric model indicates that a large particle (40 Å) can be just covered by six poly(vinyl alcohol) molecules of 100 Å diameter.

Colloidal Dispersion of Rhodium as Hydrogenation Catalyst

In the earliest stage (within 1 min) of refluxing, the colloidal dispersion exhibited a remarkably large catalytic activity for hydrogenation as shown in Fig. 7. The colloidal rhodium, however, would not yet be formed in sufficient amount at this stage. This fact could be interpreted by the presence of the secondary colloidal rhodium resulting from the reduction of rhodium(III)-poly(vinyl alcohol) complex with molecular hydrogen. Compared with the case of colloidal rhodium prepared by reduction with methanol, the colloidal rhodium prepared by reduction with hydrogen showed a rather widely varied

catalytic activity, while the average diameters of rhodium particles in both systems were equal to each other, about 40 Å. These results indicate that the diameter of the rhodium particle is independent of the reductant used, supporting the mechanism for the formation of the large particle (40 Å) described above. The gradual decrease of the catalytic activity of colloidal rhodium during refluxing for longer than 8 hr can be attributed to the decrease of the effective catalytic surface caused by the aggregation of rhodium particles as shown in Fig. 1. With the progress of refluxing the number of rhodium particles increases, while particles formed gradually aggregate. Thus the catalytic activity of the colloidal dispersion of rhodium maximizes at 4 hr refluxing. The higher the concentration of rhodium (III) chloride charged, the shorter the optimum refluxing time tends to be.

The catalytic activity of the colloidal dispersion of rhodium for hydrogenation is higher than that of any other rhodium catalyst [8]. This high activity would be due to the wider surface area of the catalyst. Nord and co-workers [19] investigated the average size of the colloidal palladium prepared by reduction with molecular hydrogen in alkaline solution. They reported that the average diameter of colloidal palladium which was originally 700 Å decreased to 90 Å after removal of large particles by ultracentrifugation. In contrast to the Nord's colloidal palladium, the colloidal rhodium comprises much smaller particles, the average diameter of which is 40 Å with a narrow distribution in the range from 30 to 70 Å.

Although at the boiling point (79°C) the catalytic activity of colloidal dispersion of rhodium gradually decreased because of the aggregation of rhodium particles, under rather mild conditions, that is, at room temperature, the state of dispersion of the rhodium particles in the colloidal dispersion was so stable even under air that the colloidal solution could be stored for 20 days without any change in dispersion state [8]. Furthermore, the colloidal rhodium solution prepared by redissolution of a polymer film which was obtained by evaporation of the solvent from the colloidal dispersion to dryness had the identical dispersion state of rhodium particles and a similar catalytic activity to that of the original colloidal dispersion. The remarkable stability of the colloidal dispersion of rhodium is due to the action of poly(vinyl alcohol) as a protective colloid.

CONCLUSIONS

A colloidal dispersion of rhodium of 40 Å diameter is prepared by refluxing of a solution of poly(vinyl alcohol) and rhodium(III) chloride in methanol-water.

Rhodium(III) chloride is transformed into a large rhodium particle (40 Å) via the rhodium(III)-poly(vinyl alcohol) complex and the small particle (8 Å).

With the reduction of rhodium(III) chloride to rhodium(0), methanol is oxidized to formaldehyde.

Poly(vinyl alcohol) was effective for regulation of the particle size as well as for stabilization of the colloidal dispersion.

The colloidal dispersion is an effective catalyst for hydrogenation of cyclohexene at 30.0°C under atmospheric hydrogen pressure.

ACKNOWLEDGMENTS

The authors would like to express their grateful acknowledgment to Mr. Koichi Adachi for his help in the electron microscopic measurement. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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Accepted by editor May 2, 1978

Received for publication June 6, 1978