

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

Formation and Catalytic Functionality of Synthetic Polymer-Noble Metal Colloid

Hidefumi Hirai^a

^a Department of Industrial Chemistry Faculty of Engineering, The University of Tokyo, Tokyo, Japan

To cite this Article Hirai, Hidefumi(1979) 'Formation and Catalytic Functionality of Synthetic Polymer-Noble Metal Colloid', Journal of Macromolecular Science, Part A, 13: 5, 633 – 649

To link to this Article: DOI: 10.1080/00222337908056678

URL: <http://dx.doi.org/10.1080/00222337908056678>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Formation and Catalytic Functionality of Synthetic Polymer-Noble Metal Colloid

HIDEFUMI HIRAI

Department of Industrial Chemistry
Faculty of Engineering
The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT

Colloidal dispersions of noble metals in synthetic polymers are prepared by reduction with alcohol. Reflux of a solution of rhodium(III) chloride and poly(vinyl alcohol) (PVA) in a methanol-water mixed solvent under argon or air for 4 hr gives a homogeneous solution of colloidal dispersion of rhodium (Rh-PVA-MeOH/H₂O). The particle size of metallic rhodium is distributed in a narrow range of 30-70 Å, and the average diameter is 40 Å. The formation of colloidal rhodium proceeds through three steps: coordination of poly(vinyl alcohol) to rhodium(III) ion, reduction with methanol to form small particles (8 Å in diameter), and growth of the small particle to large particle (40 Å in diameter). Polyvinylpyrrolidone (PVP) and poly(methyl vinyl ether) (PMVE) can be used in place of poly(vinyl alcohol) and result in colloidal dispersions, respectively, similar to Rh-PVA-MeOH/H₂O. Colloidal dispersions in nonaqueous solvent can be prepared by using ethanol instead of methanol-water (Rh-PVP-EtOH) and by using methanol instead of methanol-water, with addition of small amount of methanol solution of sodium hydroxide (Rh-PVP-MeOH/NaOH). The average diameters of rhodium particles in Rh-PVP-EtOH and Rh-PVP-MeOH/NaOH are 22 and 9 Å, respectively. The colloidal dispersions of palladium, silver,

osmium, iridium, platinum, and gold in aqueous or nonaqueous solvent are prepared by using polyvinylpyrrolidone. The colloidal dispersions are very stable even under air for 20 days. Those of rhodium, palladium, and platinum are effective catalysts for hydrogenation of olefins at 30°C under an atmospheric hydrogen pressure. The colloidal dispersion of palladium catalyzes highly selective hydrogenation of diene and dienolate to monoene and monoenoate, respectively.

INTRODUCTION

Synthetic polymers containing colloidal metal have the potential of functional polymers as catalyst, medicine, magnetic memory, electric semiconductor, etc..

In recent years the polymer-bound metal-complexes have been extensively studied [1]. The complex of poly(acrylic acid) with rhodium(III) chloride was found to catalyze the homogeneous hydrogenation of alkenes in methanol solution at 30°C under atmospheric hydrogen pressure [2]. The heterogeneous hydrogenation was made effective by using a complex of crosslinked poly(acrylic acid) [3]. Both complexes were activated for the hydrogenation catalyst by refluxing in a methanol-water solvent, resulting in a brownish-dark green product. The possibility of formation of rhodium metal on the activation was avoided by using the mild conditions of reduction, the coordination of polymer, and a small molar ratio of Rh(III)/monomeric residue of polymer. A styrene-divinylbenzene copolymer with iminodiacetic acid groups was made to chelate rhodium(III) and palladium(II) ions. After activation by refluxing in a methanol-water solvent, the rhodium chelate [4] and the palladium chelate [5] catalyzed the selective hydrogenation of terminal olefins and of conjugated dienes, respectively. Both the chelates were pale yellow-green. In these cases the formation of metal was suppressed by chelation. Recently, the formation of metallic rhodium active for hydrogenation was perceived in a phosphinated polystyrene-bound rhodium complex after aging under hydrogen [6] and in a phosphinated polyphenylsiloxane-bound rhodium complex after activation by hydrogen [7].

The present paper reports the preparation of colloidal dispersions of noble metals in synthetic polymers by reduction with alcohol. Some of the colloidal dispersions are stable and exhibit large catalytic activity and selectivity for hydrogenation. The process of the formation of colloidal dispersion is also discussed.

EXPERIMENTAL

Preparation of Colloidal Dispersion

Metal-Polymer-Alcohol/H₂O. A synthetic polymer (150 mg, 1.3-3.4 mmole as monomeric residue) and a metal salt (0.033 mmole) were dissolved in an alcohol (25 ml)-water (25 ml) solvent. Refluxing the resulting solution under air or argon for a definite period gave a homogeneous solution of colloidal metal, that is, a colloidal dispersion.

Metal-Polymer-Alcohol. The colloidal dispersions in nonaqueous solvent were prepared by using normal alcohol except methanol or secondary alcohol instead of the alcohol-water solvent.

Metal-Polymer-MeOH/NaOH. A polymer and a metal salt were dissolved in methanol without water. After refluxing the resulting solution for 30 min, a methanol solution of sodium hydroxide (5 ml, 0.17 mmole) was added dropwise to the solution under reflux to result in a rapid formation of colloidal dispersion of the metal.

Electron Microscopy

The sample films prepared from the colloidal dispersion by evaporating the solvent to dryness on a collodion film coated with a carbon layer were observed by a Hitachi Model H 500 electron microscope operated at 125 kV at a magnification of 200,000.

Catalytic Functionality

Hydrogenation of olefins and diolefins was carried out in methanol solution at 30°C under an atmospheric hydrogen pressure by use of the colloidal dispersion as a homogeneous catalyst. The colloidal palladium in polyion complex was used as a heterogeneous catalyst. The progress of the hydrogenation was followed by hydrogen-uptake under an atmospheric pressure. The products were analyzed by glpc.

RESULTS

Formation of Colloidal Dispersion in Aqueous Solvent

Poly(vinyl alcohol) (PVA, degree of polymerization 500) and rhodium(III) chloride were dissolved in a methanol-water mixed

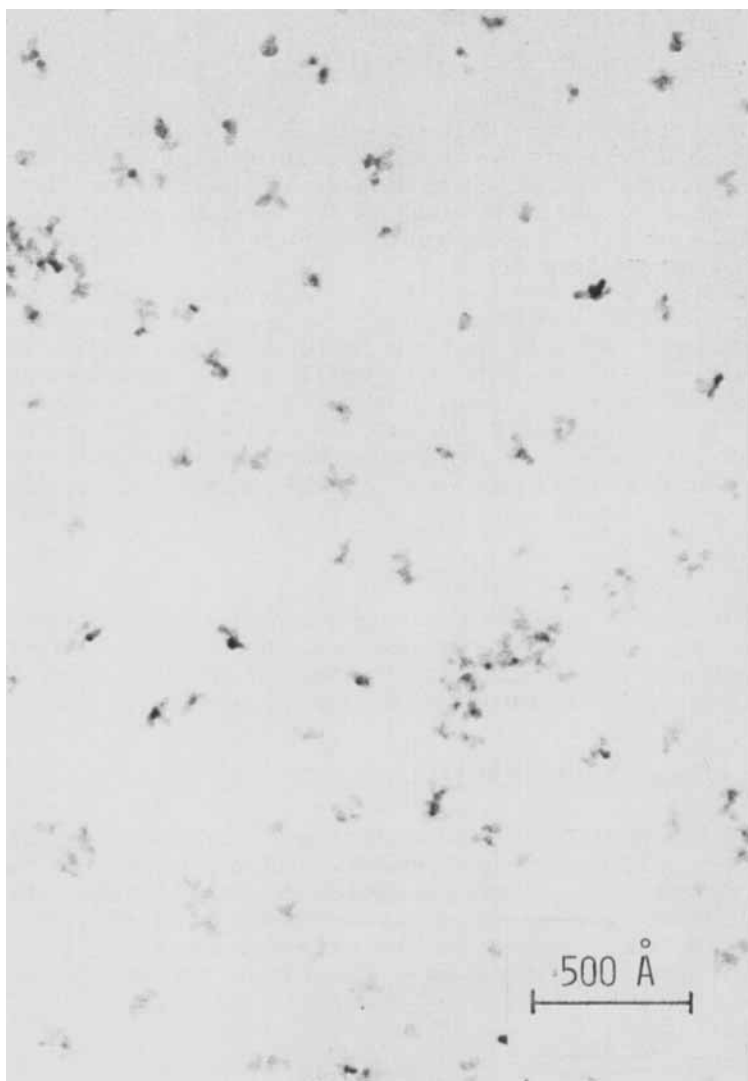


FIG. 1. Electron micrograph of colloidal dispersion Rh-PVA-MeOH/H₂O prepared by refluxing for 4 hr; $\times 200,000$.

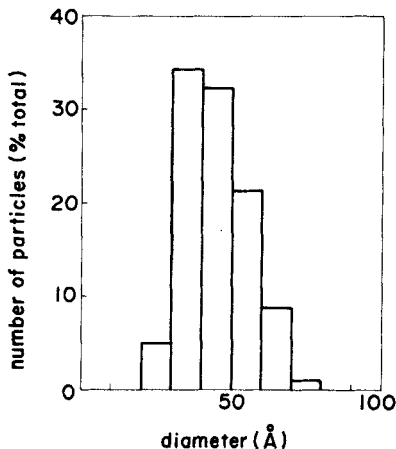


FIG. 2. Particle size distribution of colloidal rhodium in Rh-PVA-MeOH/H₂O prepared by refluxing for 4 hr.

solvent to form a rose-pink solution. Refluxing of the solution caused a color change to light brown at the initial stage. Further refluxing gave a homogeneous dark brown solution, that is, a colloidal dispersion of rhodium (Rh-PVA-MeOH/H₂O) [8].

Figure 1 illustrates the electron micrograph of the colloidal dispersion of rhodium prepared by refluxing for 4 hr. The size distribution of the colloidal rhodium is shown in Fig. 2. The size of rhodium particles is sharply distributed in the range from 30 to 70 Å, where 94% of the whole particles are included. The average diameter is determined to be 40 Å from this histogram [8].

The colloidal dispersion prepared by refluxing for a shorter time than 0.2 hr consisted almost entirely of small particles, about 8 Å in diameter. The number of the small particles decreased with the increasing number of the large particles of about 40 Å in diameter on further refluxing. All the rhodium particles in the electron micrographs can be classified into two groups of small particles (8 Å) and large particles (40 Å). The average diameter of rhodium particles, except those smaller than 10 Å, went rapidly up to 38 Å in the early stage and was almost constant during the course of refluxing, as shown in Fig. 3.

The electron diffraction of the colloidal dispersion indicated that the crystal structure of the large particle was a face-centered cubic lattice [9]. The addition of ethylenediamine to the refluxing solution inhibited the formation of the small particles and did not affect the

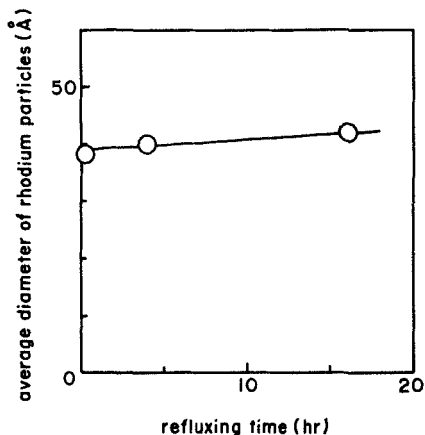
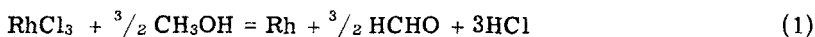


FIG. 3. Dependence of the average diameter of rhodium particles, except those smaller than 10 Å, in Rh-PVA-MeOH/H₂O upon the refluxing time.

conversion of the small particles to the large particles. The average diameter of the small particles was determined to be 7.7 Å by calculation from the results of electron micrograph, the optical density of the colloidal dispersion at 750 nm, and the addition of ethylenediamine [9].

The oxidation product from methanol in the refluxing solution was confirmed to be formaldehyde, all of which was in the form of methylene glycol. The amount of formaldehyde was determined by the chromotropic acid-sulfuric acid method [9]. The formation of formaldehyde corresponds to the formation of colloidal rhodium quantitatively, as shown in Fig. 4. The amount of formaldehyde reached a saturation value of 1.5 molar equivalent of the charged rhodium(III) chloride.



The original solution just before the beginning of reflux had no absorption peak in the range of 240-290 nm and gave a black precipitate of metallic rhodium upon contact with atmospheric hydrogen. After the refluxing for 0.2 hr, the solution exhibited an absorption peak at 260 nm and produced a homogeneous colloidal dispersion of rhodium upon contact with atmospheric hydrogen. The absorption peak at 260 nm disappeared on the addition of ethylenediamine

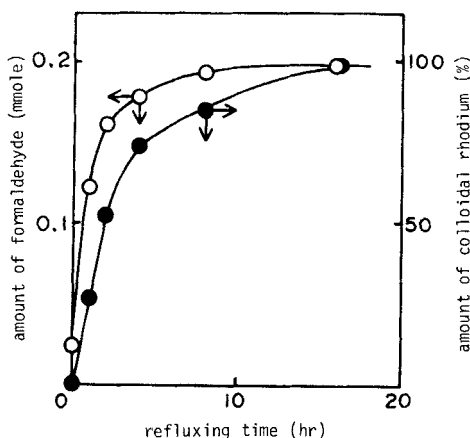


FIG. 4. Dependences of yields of (○) formaldehyde and (●) rhodium particle upon refluxing time. Rh-PVA-MeOH/H₂O; under nitrogen atmosphere; RhCl₃, 0.133 mmole.

equimolar with the charged rhodium(III) chloride to the original solution. The absorption peak at 260 nm can be ascribed to the coordination of poly(vinyl alcohol) to rhodium(III) ion [9].

Similar colloidal dispersions of rhodium in methanol-water were prepared by using polyvinylpyrrolidone (PVP, degree of polymerization 3250) and poly(methyl vinyl ether) (PMVE, degree of polymerization 570), respectively, instead of poly(vinyl alcohol). The average diameters of rhodium particles in the colloidal dispersions, Rh-PVP-MeOH/H₂O and Rh-PMVE-MeOH/H₂O, are shown in Table 1.

Water-soluble primary alcohols such as ethanol and 1-propanol and water-soluble secondary alcohols such as 2-propanol were available for preparation of colloidal dispersion of rhodium in poly(vinyl alcohol) in place of methanol. When a tertiary alcohol such as tert-butanol was used instead of methanol, the reduction of rhodium(III) ion did not occur, yielding no colloidal dispersion.

Formation of Colloidal Dispersion in Nonaqueous Solvent

The colloidal dispersions in nonaqueous solution were prepared by using a normal alcohol, other than methanol, and a secondary alcohol, respectively, instead of the methanol-water mixed solvent. The electron micrograph (Fig. 5) of the colloidal dispersion Rh-PVP-EtOH illustrates the well dispersed state of rhodium particles. The

TABLE 1. Particle Size and Catalytic Activity of Colloidal Dispersion of Rhodium

Colloid	Particle size (Å) ^a	Catalytic activity (H ₂ mole/Rh g-atom-sec) ^b	
		1-Hexene	Cyclohexene
Rh-PVA-MeOH/H ₂ O	40	15.2	3.1
Rh-PMVE-MeOH/H ₂ O	43	22.5	9.6
Rh-PVP-MeOH/H ₂ O	34	15.8	5.5
Rh-PVP-EtOH	22	14.5	10.3
Rh-PVP-1-PrOH	24		9.3
Rh-PVP-MeOH/NaOH	9	16.9	19.2

^a Average diameter of rhodium particles in colloidal dispersion.

^b For hydrogenations of 1-hexene and cyclohexene under the conditions: 30°C, total pressure 1 atm, [Rh] = 0.01 mM, [Substrate] = 25 mM, solvent methanol 20 ml.

average diameters of the rhodium particles in Rh-PVP-EtOH and Rh-PVP-1-propanol were 22 and 24 Å, respectively.

When methanol was used without water as a nonaqueous solvent, no colloidal metal was formed by refluxing the solution of a polymer and a metal salt in methanol. The addition of a methanol solution of sodium hydroxide to the refluxing solution enabled the rapid formation of a dark brown solution, the colloidal dispersion Rh-PVP-MeOH/NaOH [10]. The electron micrograph revealed that the particle size of Rh-PVP-MeOH/NaOH was extremely small, 9 Å in diameter, as shown in Fig. 6. The average diameter was determined to be 8.8 ± 0.6 Å by calculation from the results of electron microscopy by using the colloidal dispersion Rh-PVP-MeOH/H₂O (34.3 ± 1.1 Å) as a standard [10].

Formation of Colloidal Dispersions of Various Metals

The formation of colloidal dispersions of groups VIII and Ib metals from the corresponding salts was attempted by using the three procedures described above. The results are summarized in Table 2. All of the resulting colloidal dispersion, except those of silver and gold, were dark brown solutions.

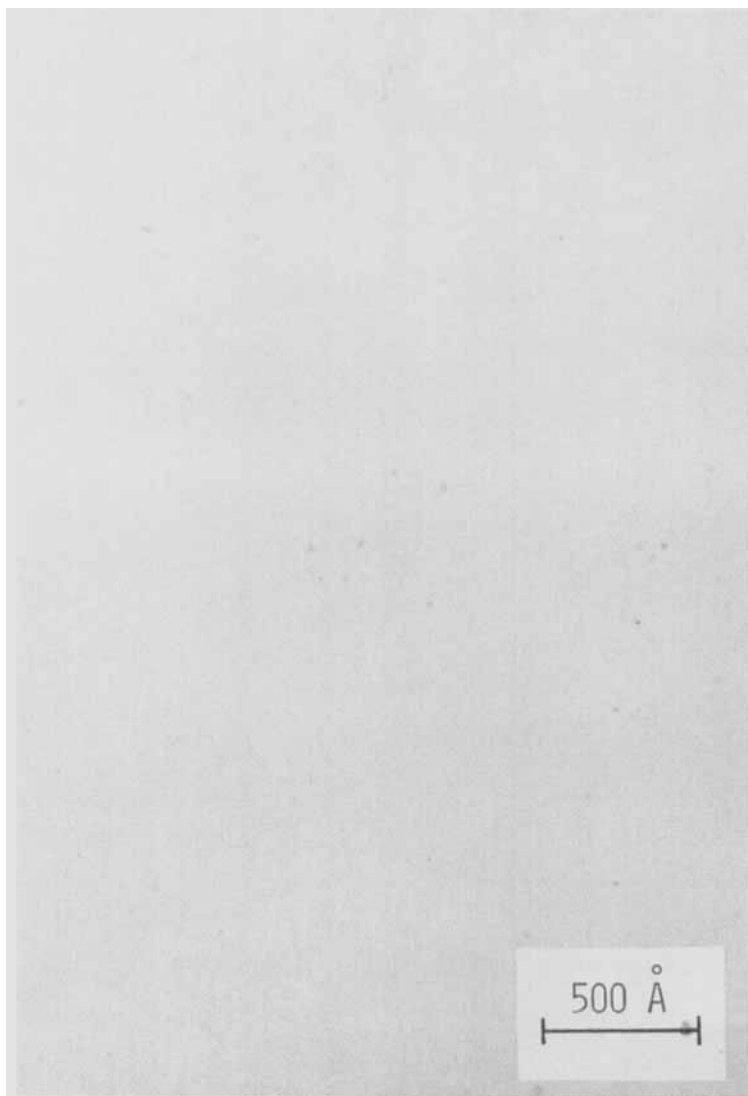


FIG. 5. Electron micrograph of colloidal dispersion Rh-PVP-EtOH prepared by refluxing 30 min; $\times 200,000$.



FIG. 6. Electron micrograph of colloidal dispersion Rh-PVP-MeOH/NaOH prepared by refluxing for 10 min; $\times 200,000$.

TABLE 2. Formation of Colloidal Dispersions of Groups VIII and Ib Metals from Corresponding Salts

Metal salts	Colloidal dispersion		
	PVA-MeOH/H ₂ O ^a	PVP-EtOH ^b	PVP-MeOH/NaOH ^c
RuCl ₃ ·3H ₂ O	No	No	No
RhCl ₃ ·3H ₂ O	Yes	Yes	Yes
PdCl ₂ ·2H ₂ O	Yes	Yes	Yes
AgNO ₃	No	Yes	Yes
OsO ₄	Yes	Yes	Yes
Na ₂ IrCl ₆	Yes	Yes	Yes
H ₂ PtCl ₆ ·6H ₂ O	Yes	No	Yes
HAuCl ₄ ·4H ₂ O	No	No	Yes

^aRefluxing for 4 hr.

^bRefluxing for 30 min.

^cRefluxing for 10 min.

The colloidal dispersions Ag-PVP-EtOH and Ag-PVP-MeOH/NaOH were light yellow solutions and Au-PVP-MeOH/NaOH was a red solution. The salts of the first transition metals gave no colloidal dispersion.

Colloidal Palladium in Polyion Complex

An orange-colored solution of PdCl₂·2H₂O (0.5 mmole), poly(acrylic acid) (PAA, degree of polymerization 2600, 40 mmole) and sodium hydroxide (40 mmole) in methanol (100 ml)-water (100 ml) was refluxed under nitrogen for 6 hr.

The resulting solution of colloidal dispersion of palladium (Pd-PAA-MeOH/H₂O) was added to an aqueous solution (100 ml) of polyethyleneimine (PEI, degree of polymerization 1100, 40 mmole). Thereafter, the pH of the solution was adjusted to 4 by adding 1 N HCl aqueous solution, resulting in precipitation of a polyion complex containing colloidal palladium [11].

This gray precipitate was the colloidal palladium in polyion complex composed of poly(acrylic acid) and polyethyleneimine, Pd-PAA-PEI. The average diameter of the palladium particles in Pd-PAA-MeOH/H₂O was 60 Å.

Catalytic Functionality of Colloidal Dispersion

The catalytic functionality of the colloidal dispersion was examined on the catalytic activity for hydrogenation of olefins and on the catalytic selectivity for hydrogenation of cyclo diene and dienoate to cyclomonoene and monoenoate, respectively.

The colloidal dispersions of rhodium, palladium, and platinum were effective as catalyst for hydrogenation of olefin. Those of osmium and iridium were effective only as Os-PVA-MeOH/H₂O and Ir-PVP-EtOH, respectively.

The catalytic activity of the colloidal dispersion of rhodium was higher than that of any other rhodium catalyst. For example, the activity of Rh-PVA-MeOH/H₂O for hydrogenation of 1-hexene, as shown in Table 1, is 2.6 times that of Nord's colloidal rhodium in poly(vinyl alcohol) [12] and 4.6 times that of a commercial catalyst of rhodium on charcoal on the basis of the activity per 1 g-atom rhodium.

Table 3 collects the initial rates of hydrogen uptake on the hydrogenations of various olefins and diolefins using three type of colloidal dispersions of rhodium. Either of three colloidal dispersions exhibits roughly the same catalytic activity for hydrogenation of terminal olefins. The catalytic activities for internal and cyclic olefin, especially for conjugated olefinic bond decrease in the following order:



Hydrogenations of cyclopentadiene, 1,3- or 1,5-cyclooctadiene, and methyl linoleate by use of colloidal dispersion of palladium yielded cyclopentene, cyclooctene, and methyl monoenoate, respectively, at high selectivity. The results are summarized in Table 4. The catalytic selectivity is expressed as molar fraction of monoene or monoenoate in the reaction mixture when the hydrogen uptake goes up to the amount equimolar with the charged diene or dienoate.

The catalytic activity of the colloidal palladium for conjugated diene is larger than that for nonconjugated diene.

The colloidal dispersion, Pd-PVP-MeOH/NaOH, exhibits a large catalytic activity and a high selectivity. The colloidal palladium in polyion complex, Pd-PAA-PEI, displays a high selectivity and a smaller catalytic activity. The commercial catalyst of palladium on charcoal Pd-C shows a medium activity and a lower selectivity.

The average diameters of the palladium particles in Pd-PVP-MeOH/NaOH and Pd-PVP-MeOH/H₂O were 25 Å and 65 Å, respectively.

TABLE 3. Catalytic Activity of Colloidal Dispersions of Rhodium for Hydrogenation of Olefins and Diolefins

Substrate	Catalytic activity (H ₂ mole/Rh g-atom-sec) ^a		
	Rh-PVP-MeOH/H ₂ O	Rh-PVP EtOH	Rh-PVP-MeOH/NaOH
1-Hexene	15.8	14.5	16.9
Cyclohexene	5.5	10.3	19.2
2-Hexene	4.1	9.5	12.8
Styrene	1.9	2.5	3.2
Methyl vinyl ketone	3.7	4.3	7.9
Mesityl oxide	0.6	4.7	31.5
Methyl acrylate	11.2	17.7	20.7
Methyl methacrylate	5.8	15.1	27.6
Acrylonitrile	0.5	0.8	0.9
Cyclooctene	0.6	1.1	1.2
1,3-Cyclooctadiene	3.7	9.8	17.5
1,5-Cyclooctadiene	2.6	3.7	3.7
1-Hexyne	0.1	0.1	0.2

^aHydrogenation conditions: 30°C; total pressure, 1 atm; [Rh] = 0.01 mM; [Substrate] = 25 mM; solvent, methanol (20 ml).

The colloidal dispersions were very stable, with no coagulation and no precipitation of metals during the hydrogenation. For example, Rh-PVA-MeOH/H₂O was resistant to air, retaining a catalytic activity at 83% of initial activity after standing in air for 20 days. The catalytic activity of Rh-PVP-MeOH/NaOH was unchanged during the course of standing in air for 9 days. The colloidal dispersion gave a homogeneous film on evaporation of the solvent to dryness. The resulting film could be dissolved with the original solvent to yield the colloidal dispersion again. The resulting colloidal dispersion exhibited the identical dispersion state and the similar catalytic activity to the original colloidal dispersion.

TABLE 4. Selective Hydrogenation of Dienes by Colloidal Palladium Catalyst^a

Substrate	Catalyst	Catalytic activity (H ₂ mole/Rh g-atom-sec)	Selectivity (%) ^b
Cyclopentadiene	PVP-MeOH/NaOH ^c	8.8	97
	PAA-PEI ^d	0.09	98
1,3-Cyclooctadiene	PVP-MeOH/NaOH ^c	35.	100
	PAA-PEI ^d	0.13	99
1,5-Cyclooctadiene	PVP-MeOH/NaOH ^c	1.8	99
	PAA-PEI ^d	0.009	94
Methyl linoleate	PVP-MeOH/NaOH ^c	6.1	95
	PVP-MeOH/H ₂ O ^e	1.8	92
	Pd-C ^f	1.9	71

^aConditions: 30°C, total pressure, 1 atm; solvent, MeOH.

^bMolar fraction of monoene or monoenoate in the reaction mixture at the one molar equivalent hydrogen uptake.

^cPd-PVP-MeOH/NaOH: Pd = 0.0002 mmole; [Pd] = 0.01 mM; [Substrate] = 25 mM; solvent, 20 ml.

^dPd-PAA-PEI: Pd = 0.125 mmole; [Substrate] = 200 mM, solvent, 50 ml.

^ePd-PVP-MeOH/H₂O: Pd = 0.002 mmole; [Pd] = 0.1 mM; [Substrate] = 25 mM; solvent, 20 ml.

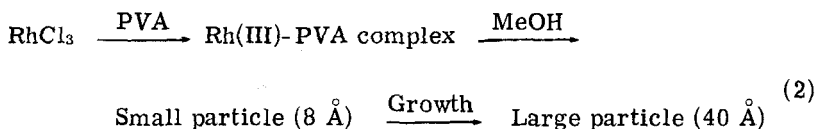
^fPd-charcoal: Pd = 0.001 mmole; [Substrate] = 25 mM, solvent, 20 ml.

DISCUSSION

Formation of Colloidal Dispersion

For the process of formation of the colloidal dispersion of rhodium, the experimental results indicate the scheme shown in Eq. (2).

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.



Alcohol also coordinates to the rhodium(III) ion as an oxonium 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 proton. This base is hydroxido ion derived from the water for metal-polymer-alcohol/H₂O and hydroxido ion derived from sodium hydroxide for metal-polymer-alcohol/NaOH. The basicity of alcohol for proton was reported [13] in the following order: 1-PrOH > EtOH ≫ MeOH. Consequently, it is reasonable that ethanol or 1-propanol itself acts as a base for metal-polymer-EtOH or 1-PrOH.

The resulting alkoxido complex is converted into a hydrido complex with the formation of aldehyde. The hydrido rhodium(III) complex releases an additional proton with the conversion into a low valent rhodium complex, which gives a zero valent rhodium through disproportionation.

The zero valent rhodium aggregates to form the small particle (8 Å). The value of diameter, 8 Å is equal to three times the diameter of rhodium atom (2.68 Å). The small particle (8 Å) corresponds to a Rh₁₃ cluster whose central atom takes a coordination number of twelve. This estimation is supported by the fact that the large particle (40 Å) is made up by a face-centered cubic lattice, where the coordination number is twelve.

The small particles (8 Å) are converted to the crystallites of the large particles (40 Å). This process probably includes the rearrangements of rhodium atoms in the small particle (8 Å) for nucleation and for growth to crystallite. The stabilization of the large particle (40 Å) may be associated with the fact that the surface of 40 Å particle can be just covered by six poly(vinyl alcohol) molecules (DP 500) of 100 Å diameter.

The protective action of polyvinylpyrrolidone is superior to those of other synthetic polymers [14]. The rhodium particles (9 Å) in the colloidal dispersion Rh-PVP-MeOH/NaOH are much more stabilized both by the protective action of polyvinylpyrrolidone and by the nonaqueous solvent of methanol, compared with the small particle (8 Å) in Rh-PVA-MeOH/H₂O.

The standard electrode potentials of the first transition metals of group VIII and Ib are significantly more negative than those of the second and the third transition metals of the same groups [15]. This is the reason why the salts of the first transition metals gave no colloidal dispersion by using alcohol as a reductant.

Catalytic Functionality of Colloidal Dispersion

The high catalytic activity of the colloidal dispersion is due to wider surface area of the catalyst containing small metal particles. There is small deference in the catalytic activities for terminal olefin among the colloidal dispersions of rhodium (see Tables 1 and 3). For internal and cyclic olefins, the catalytic activity of Rh-PVP-MeOH/H₂O is small remarkably and that of Rh-PVP-MeOH/NaOH is large significantly. There is far less steric hindrance of the substrate on the catalytic surface in the small metallic particle. The latter exhibits a particularly large activity for conjugated diene and conjugated carbonyl compound, as shown in Table 3. This feature can be associated with the characteristics of a metallic particle smaller than 20 Å in diameter. The order of the catalytic activity also corresponds to that of the size of rhodium particles in the catalyst.

The colloidal dispersion Rh-PMVE-MeOH/H₂O is the most effective catalyst for hydrogenation of 1-hexene, in spite of the largest size of rhodium particle as shown in Table 1. This fact indicates the diffusion rate of substrate in the polymer layer covering the surface of rhodium particle depends on the kind of polymer.

The selective hydrogenations under mild conditions of cyclopentadiene, cyclooctadiene, and methyl linoleate to cyclopentene, cyclooctene and methyl monoenoate, respectively, has been achieved by using the colloidal dispersion of palladium. The large catalytic activity and the high selectivity of Pd-PVP-MeOH/NaOH are ascribed to the small particle size of palladium (average diameter 25 Å). The selectivity of Pd-PVP-MeOH/NaOH is also due to the polyvinylpyrrolidone covering the surface of the particle.

The colloidal palladium in polyion complex Pd-PAA-PEI exhibits a high selectivity. The polyethyleneimine bound to poly(acrylic acid) covers the palladium particle (average diameter 60 Å) resulting both the high selectivity and the low catalytic activity caused by suppression of the diffusion of substrate.

Methyl linoleate is a nonconjugated dienoate. The hydrogenation of methyl linoleate by use of the colloidal palladium proceeds probably both through that of conjugated dienoate derived by isomerization and through the direct hydrogenation of the isolate olefinic bond.

The synthetic polymer in the colloidal dispersion plays an important role in two ways. The coordination of the polymer to the metal ion suppresses the reduction rate of the metal ion, and the protective action of the polymer prevents the small particles of metal from coagulating. Consequently, the synthetic polymer is indispensable for the formation of a homogeneous dispersion of small particles as well as for the stabilization of a homogeneous dispersion state of the small particles.

ACKNOWLEDGMENT

This research was partly supported by the Takeda Science Foundation.

REFERENCES

- [1] R. H. Grubbs, Chem. Technol., 1977, 512.
- [2] Y. Nakamura and H. Hirai, Chem. Letters, 1974, 645.
- [3] Y. Nakamura and H. Hirai, Chem. Letters, 1974, 809.
- [4] Y. Nakamura and H. Hirai, Chem. Letters, 1975, 823.
- [5] Y. Nakamura and H. Hirai, Chem. Letters, 1976, 165.
- [6] A. Guyot, Ch. Graillat, and M. Bartholin, J. Mol. Catal., 3, 39 (1977/78).
- [7] M. Bartholin, J. Conan and A. Guyot, J. Mol. Catal., 2, 307 (1977).
- [8] H. Hirai, Y. Nakao, N. Toshima, and K. Adachi, Chem. Letters, 1976, 905.
- [9] H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. Sci.-Chem., A12, 1117 (1978).
- [10] H. Hirai, Y. Nakao, and N. Toshima, Chem. Letters, 1978, 545.
- [11] Y. Nakamura and H. Hirai, Chem. Letters, 1976, 1197.
- [12] L. Hernandez and F. F. Nord, J. Colloid Sci., 3, 363 (1948).
- [13] L. S. Levitt and B. W. Levitt, Tetrahedron, 27, 3777 (1971).
- [14] B. Jirgensons, Makromol. Chem., 6, 30 (1951).
- [15] N. A. Lange, Ed. Handbook of Chemistry, 10th ed., McGraw-Hill, New York, 1961.