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COLLOIDAL RHODIUM IN POLY(VINYLPYRROLIDONE) AS HYDROGENATION CATALYST FOR INTERNAL OLEFINS

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Refluxing of a methanol solution of rhodium(III) chloride and poly(vinylpyrrolidone) with sodium hydroxide gives a stable colloidal dispersion of rhodium particles of 8.8 Å in diameter. The colloidal dispersion exhibits a high catalytic activity for hydrogenation of internal olefins at 30°C under an atmospheric hydrogen pressure.

It has often been effective for the preparation of colloidal metals in aqueous medium to reduce the corresponding metal salts with an appropriate reductant like molecular hydrogen.[1] Organic solvents can also be used as a dispersion medium for non-aqueous colloidal dispersion to prevent hydrophobic metal particles from aggregation.[2] Previously[3] we reported that reduction of rhodium(III) chloride ($RhCl_3 \cdot 3H_2O$) with methanol in the presence of poly(vinyl alcohol) and water resulted in formation of a fine colloidal rhodium particles of 40 Å in diameter, which showed a high catalytic activity for hydrogenation of olefins. Now we wish to report the preparation of a novel colloidal rhodium by refluxing of a methanol solution of $RhCl_3 \cdot 3H_2O$ in the presence of poly(vinylpyrrolidone) and sodium hydroxide. The present colloidal dispersion in methanol consists of extremely fine rhodium particles of 8.8 Å in diameter and has the specific catalytic activity different from that in aqueous methanol.

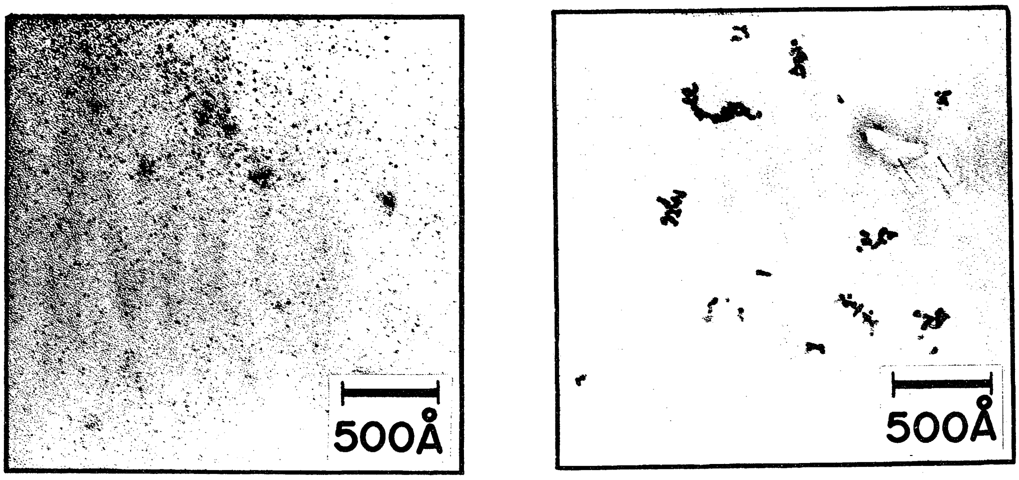
The preparative procedures are as follows. $RhCl_3 \cdot 3H_2O$ (Nippon Engelhald Ltd.; 8.8 mg, 0.033 mmol) and poly(vinylpyrrolidone) (degree of polymerization 3250, Tokyo Chemical Industry; 150 mg, 1.35 mmol as monomeric residue) were separately dissolved in two portions of methanol (22.5 ml for each). Both solutions were combined and refluxed. During the refluxing, no colloidal particles were formed since rhodium(III) chloride could not be reduced with boiling methanol in the absence of an additive.[4] After refluxing for 30 min, a methanol solution (5 ml) of sodium hydroxide (6.7 mg, 0.17 mmol) was added dropwise to the solution under reflux, resulting in rapid color change of the solution to dark brown, which corresponded to the formation of rhodium particles. After further refluxing for 10 min, a dark brown solution of colloidal rhodium, Colloidal dispersion **1**, was obtained. An another colloidal dispersion, **2**, was obtained by refluxing a solution of $RhCl_3 \cdot 3H_2O$ (8.8 mg) and poly(vinylpyrrolidone) (150 mg) in methanol (25 ml)-water (25 ml) for 4 hr according to a similar procedure to that reported previously.[3]

According to the mechanism proposed by Chatt,$^{5)}$ the reduction of $RhCl_3 \cdot 3H_2O$ with methanol proceeds through a methoxide complex formed from methanol and $RhCl_3 \cdot 3H_2O$ by proton elimination. It is expected effective for the proton elimination to add bases such as sodium hydroxide and water to the methanol.

Colloidal dispersion **1** had quite different characteristics in the size distribution and the dispersion state of rhodium particles as well as catalytic behavior from Colloidal dispersion **2**.

The sample films, prepared from Colloidal dispersions **1** and **2** by evaporating the solvent to dryness on collodion films 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. The electron micrographs of Colloidal dispersions **1** and **2** are illustrated in Figure 1. Figure 1a shows the homogeneous distribution of rhodium particles of about 9 Å diameter, which cannot be determined accurately from the electron micrograph because of the limit of resolution (3 Å). There cannot be found no aggregations of rhodium particles in Colloidal dispersion **1**. As shown in Figure 1b, Colloidal dispersion **2** consists of spherically or prolate-spheroidally shaped rhodium particles of 34.3 ± 1.1 Å diameter, which is determined directly from the enlarged photograph (× 860,000). Aggregations of 10 ~ 30 rhodium particles are also observed in Colloidal dispersion **2**.

Since the particle size of Colloidal dispersion **1** distributes in a quite different range from that of Colloidal dispersion **2**, the particles originating from **1** can be distinguished from those originating from **2** in the electron micrograph of the mixture of **1** and **2**. Thus the average diameter of rhodium particles in Colloidal dispersion **1** can be determined by using Colloidal dispersion **2** as a standard. Since the rhodium concentration in **1** is equal to that in **2**, the average particle diameter in **1** (d_1) is



a

b

Figure 1. Electron micrographs of colloidal rhodiums (× 200,000) : a, Colloidal dispersion **1** ; b, Colloidal dispersion **2**.

represented by the following equation

$$d_1 = \left(\frac{a}{b}\cdot\frac{n_2}{n_1}\right)^{\frac{1}{3}}\cdot d_2 \quad \text{-------------} \quad (1)$$

where a/b is a mixing volume ratio of **1** to **2**, n_1 and n_2 are the number of rhodium particles in unit volume of **1** and **2**, respectively, and d_2 is the average particle diameter in **2**. The value of n_2/n_1 was estimated to be 0.81 from the electron micrograph of the mixture of **1** and **2** (a/b = 1/50), and d_2 was directly determined to be 34.3 ± 1.1 Å from the electron micrograph. Using these values, d_1 was calculated to be 8.8 ± 0.6 Å from equation (1). The average particle diameter of 8.8 Å is nearly equal to three times as large as the atomic diameter of rhodium (2.69 Å). The 8.8 Å-particle is a limiting small particle containing one or two rhodium atom(s) in the center of the particle.

Both Colloidal dispersions **1** and **2** are effective catalysts for hydrogenation of olefins at 30°C under an atmospheric hydrogen pressure. The hydrogenation procedures were described in detail previously.[3)] Table 1 shows the catalytic activities of Colloidal dispersion **1** for hydrogenation of various olefins in comparison with those of Colloidal dispersion **2**. Both colloidal dispersions exhibit roughly the same catalytic activity for hydrogenation of terminal olefins. The most remarkable feature of Colloidal dispersion **1** as a catalyst is its much higher activity for hydrogenation of cyclic and internal olefins. The most striking case is for the hydrogenation of the C = C bond conjugated with a carbonyl group. When the Colloidal dispersion **1** is used, the ratio of the initial hydrogenation rate of mesityl oxide to that of methyl vinyl ketone is 4.0 : 1.0. By using Colloidal dispersion **2**, the

Table 1. Hydrogenation of terminal and internal olefins catalyzed by colloidal dispersions of rhodium

Substrate	Initial rate of hydrogen uptake (H_2 mol/Rh g-atom.sec)[a)]	
	1[b)]	**2**[b)]
1-Hexene	16.9	15.8
Cyclohexene	19.2	5.5
2-Hexene	12.8	4.1
Methyl vinyl ketone	7.9	3.7
Mesityl oxide	31.5	0.6
Methyl acrylate	20.7	11.2
Methyl methacrylate	27.6	5.8

a) Conditions : temperature 30.0°C, total pressure 1 atm, [Rh] = 0.01 mM, [substrate] = 25 mM, solvent = methanol (20 ml).

b) The average diameters of rhodium particles are 8.8 Å and 34.3 Å for Colloidal dispersions **1** and **2**, respectively.

ratio is reversed to be 1.0 : 6.2. The difference between the catalytic activities of **1** and **2** depending upon the structure of a substrate may be attributed to the size of rhodium particles. There is a far less steric hindrance of the substrate on the catalytic surface for Colloidal dispersion **1** because of extremely small size of rhodium particle.

The colloidal dispersions of both **1** and **2** in the presence of poly(vinylpyrrolidone) were so stable that no precipitate of rhodium metal appeared and the catalytic activities were unchanged during the course of standing in air for 9 days. In the absence of poly(vinylpyrrolidone), all the rhodium metal was deposited as a black precipitate during the refluxing either in a methanol / sodium hyroxide solution or a methanol / water solution.

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References and note

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