CHEMISTRY LETTERS, pp. 905-910, 1976. Published by the Chemical Society of Japan

# COLLOIDAL RHODIUM IN POLYVINYL ALCOHOL AS HYDROGENATION CATALYST OF OLEFINS

Hidefumi HIRAI, Yukimichi NAKAO, Naoki TOSHIMA,
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
and
Koichi ADACHI
Engineering Research Institute, Faculty of Engineering,
The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113

A colloidal rhodium has been prepared by reduction of rhodium(III) chloride with methanol in the presence of polyvinyl alcohol. The particle size distribution of the metallic rhodium is narrow ranging from 30 to 70 Å with a maximum at 35 Å. The colloidal dispersions in methanol-water solutions are effective for the hydrogenation of olefins at 30°C under an atmospheric hydrogen pressure.

Colloidal transition metals have been prepared by arc-discharge1) and reduction of corresponding metal salts with molecular hydrogen2) in the presence of natural polymers as protective colloid. The colloidal metals are a very effective catalyst for the hydrogenation of unsaturated compounds. Nord and co-workers prepared colloidal palladium,3) platinum,3) rhodium4) and iridium5) by reduction of the corresponding metal hydroxides with molecular hydrogen in aqueous solution using polyvinyl alcohol (PVA) as a protective colloid. We have succeeded in preparing of a colloidal rhodium of a smaller particle size within a narrower distribution by reduction of rhodium(III) chloride with alcohol in the presence of polyvinyl alcohol. This colloidal rhodium in polyvinyl alcohol has been found to be an effective catalyst for the hydrogenation of olefins in methanol at 30°C under an atmospheric hydrogen pressure.

Polyvinyl alcohol (degree of polymerization 500, Nippon Synthetic Chemical Industry Co., Ltd.; 151 mg, 1.00 mmol as monomeric residue) and $RhCl_3 \cdot 3H_2O$ (Nippon Engelhard Ltd.; 8.8 mg, 0.033 mmol) were dissolved in a methanol (25 ml)-water (25 ml) mixed solvent, resulting in a rose-pink solution. Refluxing of the solution in argon on a boiling water bath for 4 hr (solution temperature 79°C) gave a homogeneous dark brown solution of colloidal rhodium.

Formaldehyde was found to be formed in the refluxing solution. The amount of the resulting formaldehyde was determined by the chromotropic acid-sulfuric acid method.6) The formation of formaldehyde corresponded to the production of colloidal rhodium quantitatively. After refluxing for 16 hr the amount of formaldehyde reached a saturation value of 1.5 molar equivalent of $RhCl_3 \cdot 3H_2O$ added. The possibility that the resulting formaldehyde reduced the rhodium ion is rejected by the fact that formaldehyde can not reduce rhodium(III) chloride in water at 79°C.

$$2RhCl_3 \cdot 3H_2O + 3CH_3OH \longrightarrow 2Rh + 6HCl + 3HCHO + 6H_2O \qquad (1)$$

Similar colloidal rhodium dispersions were also obtained by the use of water-soluble primary alcohols such as ethanol and 1-propanol instead of methanol. In the absence of polyvinyl alcohol, rhodium(III) chloride was not reduced to the zero valence state in anhydrous methanol but to a black precipitate of rhodium metal in methanol-water. The presence of water in the refluxing solvent is indispensable for both dissolution of polyvinyl alcohol and reduction of rhodium(III) chloride to the zero valence state.

The film, prepared by evaporation of colloidal rhodium solution to dryness, was observed by a Hitachi Model HU-12A electron microscope at magnifications of 100,000 and 200,000 The illustrated in Figure 1 is the electron micrograph, which shows spherically or prolate- spheroidally shaped rhodium particles and the aggregation of less than 15 rhodium particles. Figure 2 shows the size distribution histgrams of rhodium particles appeared in an arbitrarily chosen area of $8.0 \times 10^6$ Å of the micrograph. The particle size is sharply distributed in the range between 30 and 70 Å, which comprises 94% of the particles. The average of the particle diameter is estimated to be 40 Å.

With the colloidal rhodium-polyvinyl alcohol catalyst (Rh-PVA), hydrogenation of various olefins were carried out in methanol at 30°C under an atmospheric hydrogen pressure.7) The catalytic activity of Rh-PVA varies with the refluxing time in preparation. The Rh-PVA catalyst used in following hydrogenations was prepared by refluxing for 4 hr, having a maximum activity. The progress of the hydrogenation was

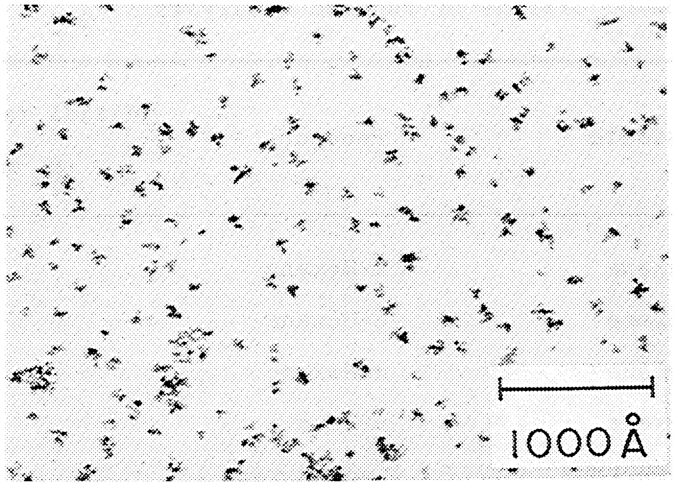

Fig.1. Electron Micrograph of Rh-PVA (×100,000).

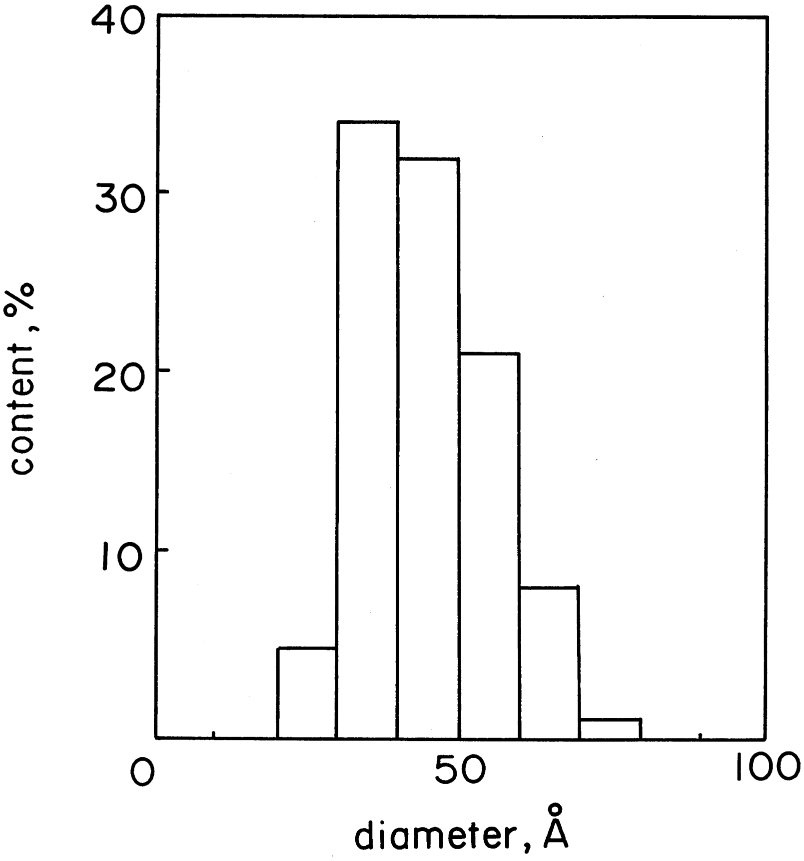

Fig.2. Size Distribution of Rhodium Particles in Rh-PVA.

Table 1. Hydrogenation of olefins by rhodium catalysts[a)]

| Catalyst | Substrate | Product | Initial rate of hydrogenation ($H_2$ mol/Rh g-atom.sec) |
|---|---|---|---|
| Rh-PVA[b)] | 1-Hexene | n-Hexane | 15.2 |
| Rh-PVA[c)] | 1-Hexene | n-Hexane | 12.6 |
| Nord's Rh-PVA[d)] | 1-Hexene | n-Hexane | 5.9 |
| Rh/C(5%)[e)] | 1-Hexene | n-Hexane | 3.6 |
| Rh-PVA | Cyclohexene | Cyclohexane | 3.1 |
| Rh-PVA | 2-Hexene | n-Hexane | 1.6 |
| Rh-PVA | Styrene | Ethylbenzene | 1.6 |
| Rh-PVA | Mesityl oxide | Methyl isobutyl ketone | 3.6 |
| Rh-PVA | Methyl vinyl ketone | Methyl ethyl ketone | 6.7 |

a) Temp. 30.0°C, total press. 1 atm., [Rh]=0.01 mM, [Substrate]=25 mM, solvent [methanol/water(130/1)]=20 ml.

b) Just after preparation.

c) After standing in air for 20 days.

d) Colloidal rhodium prepared by Nord's method,[4)] solvent[methanol/water(3/1)]=20 ml.

e) Rhodium on charcoal(5%), commercial catalyst(Nippon Engelhard Ltd.), solvent [methanol]=20 ml.

followed by hydrogen-uptake under an atmospheric pressure. Products and initial rate of hydrogen uptake are shown in Table 1. For all of the olefins listed in Table 1, the hydrogen uptakes ceased at the equimolar amount with the C=C bond of substrate, where the products were identified by glpc with a 2 m column of β,β'-thiodipropionitrile.

The colloidal dispersion was very stable with no coagulation and no precipitation of metallic rhodium during the hydrogenation. The Rh-PVA catalyst is resistant to air, keeping the catalytic activity at 83% of initial activity after standing in air for 20 days (see Table 1). The product analysis indicated that the C=C bonds of substrates were hydrogenated selectively and that the coexisting C=O bond or benzene ring were not hydrogenated. As shown in Table 1, the activity of Rh-PVA is 2.6 times that of Nord's colloidal rhodium catalyst and 4.6 times that of a commercial catalyst of rhodium on charcoal on the basis of the activity per 1 g-atom rhodium. The rate of hydrogenation depends upon the structures of substrates, decreasing in the order; terminal olefin > cyclic olefin > internal olefin. The relative catalytic activities of the colloidal dispersion prepared by use of methanol, ethanol and 1-propanol were 1.0 : 1.1 : 0.8.

Among rhodium species, a hexachlororhodate species was known to be reduced to the metal precipitate by 2-propanol in the presence of a small amount of water.8) A rhodium trichloride species, however, can not be reduced to the zero valence state by alcohol in the absence of water: refluxing of the solution of $RhCl_3 \cdot 3H_2O$ and sodium acetate in ethanol-acetic acid gave a rhodium(II) complex $[Rh_2(OCOMe)_4]$9); refluxing of the solution of $RhCl_3 \cdot 3H_2O$ and cyclooctadiene in ethanol yielded a rhodium(I) complex $[Rh_2Cl_2(C_8H_{12})_2]$.10) The reduction of rhodium(III) chloride to colloidal rhodium, the zero valence state, may be associated with the coordination of water which promotes the reduction of the rhodium(I) species to the zero valence state.

The features of the Rh-PVA catalyst may be ascribed to the small particle size (35 Å) of metallic rhodium with a narrow distribution(30-70 Å). Nord and co-workers11) reported that the average particle diameter of metallic palladium prepared by molecular hydrogen reduction was 700 Å and decreased to 90 Å after removal of large particles by ultra-centrifugation. This implies that the initial distribution of particle size was much wider than that of Rh-PVA in the present study.

The authors wish to thank Mr. Shigehide Takagi for his help in the preliminary electron microscope experiments. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References and note

1) G. Bredig, Z. Angew. Chem., 11, 951 (1898).
2) C. Paal and C. Amberger, Ber., 37, 124 (1904); A. Skita, ibid., 42, 1627 (1909).
3) L. D. Rampino and F. F. Nord, J. Amer. Chem. Soc., 63, 2745 (1941).
4) L. Hernandez and F. F. Nord, J. Colloid Sci., 3, 363 (1948).

5) W. P. Dunworth and F. F. Nord, J. Amer. Chem. Soc., 72, 4197 (1950).

6) W. Horwitz, Ed., "Official Methods of Analysis", 8th ed., Association of Official Agricultural Chemists, George Benta Publishing Co., Mensha, Wis., 1955, p492.

7) Into a flask in which the atmosphere was previously replaced with hydrogen, methanol (18.7 ml) and the colloidal rhodium solution (0.30 ml) are poured in this order. The solution was stirred in a 30.0°C thermostat at an atmospheric pressure for 1 hr to saturate with hydrogen. Then the methanol solution of substrate (1 ml), containing 0.5 mmol of substrate, was added into the flask keeping total pressure at 1 atm to begin hydrogenation reaction.

8) H. B. Chairman, J. Chem. Soc. B., 1967, 629.

9) B. C. Y. Hui, W. K. Teo and G. L. Rempel, Inorg. Chem., 12, 757 (1973).

10) J. Chatt and L. M. Venanzi, J. Chem. Soc., 1957, 4735.

11) L. D. Rampino, K. E. Kavanagh and F. F. Nord, Proc. Nat. Acad. Sci. U. S., 29, 246 (1943).

(Received July 5, 1976)