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Colloidal Rhodium Dispersions Protected by Cyclodextrins

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Synopsis. Refluxing of an aqueous solution of rhodium(III) chloride and α- or β-cyclodextrin, followed by further refluxing in the presence of ethanol, gives a colloidal dispersion of rhodium particles of 28 Å in diameter. The colloidal dispersion exhibits effective catalyses in hydrogenation of olefins at 30 °C under an atmospheric pressure.

Interests in colloidal dispersions of metals have been rapidly increasing especially in this decade.[1,2]

Previously,[2–5] the present authors succeeded in the preparation of colloidal dispersions of noble metals by reducing their salts with alcohols such as ethanol and 1-propanol in the presence of various polymers. The polymers used were poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), and poly(methyl vinyl ketone). The resulting colloidal dispersions were characterized both by quite small particle sizes and by narrow distributions in particle sizes.

This paper describes the preparation of colloidal rhodium dispersions through the reduction of rhodium(III) chloride with ethanol using cyclodextrins, cyclic oligomers of 6—8 glucose units, as protective colloids. The catalytic activities of these colloidal dispersions in the hydrogenation of olefins will be shown.

Experimental

Colloidal rhodium dispersions were prepared as follows. First, 7.0 mg (2.7×10^{-5} mol) of rhodium(III) chloride trihydrate (Nippon Engelhard, Ltd.) and various amounts of α-, β-, or γ-cyclodextrin (Nakarai Chemical Co.) were dissolved in 30 ml of water, and the solution was refluxed for 30 min. Then, 10 ml of ethanol was added and the solution was further refluxed for 10 min, resulting in the formation of colloidal rhodium dispersion as a dark brown solution.

Sample films of colloidal dispersions for electron microscopy were prepared by evaporating the solvent to dryness on a collodion film coated with a carbon layer. Electron micrographs were measured by a Hitachi Model H 500 electron microscope operated at 125 kV at the magnification of 100000.

Hydrogenation of olefins catalyzed by colloidal rhodium dispersions was carried out at 30.0 °C under an atmospheric hydrogen pressure, and was followed by reading the uptake of hydrogen.

Results and Discussion

Homogeneous colloidal rhodium dispersion was obtained using α- or β-cyclodextrin. The minimal molar ratios of cyclodextrin to rhodium(III) chloride, required for the preparation of the colloidal dispersions, were 0.5 for α-cyclodextrin and 0.1 for β-cyclodextrin. These results were markedly in contrast with the rapid formation of black precipitates in the absence of cyclodextrin. The precipitation took place immediately after the refluxing of the water-ethanol mixture started.

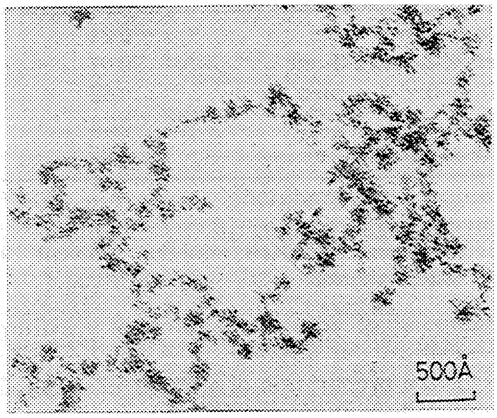

Fig. 1. Electron micrograph of colloidal rhodium dispersion prepared by using β-cyclodextrin equimolar to rhodium(III) chloride; ×100000.

When γ-cyclodextrin was used in place of α- or β-cyclodextrin, rapid precipitation took place and colloidal dispersion was not obtained, even at the molar ratio unity of γ-cyclodextrin to rhodium(III) chloride.

From these results, it is concluded that the protecting abilities of cyclodextrins are in the following order: β-cyclodextrin>α-cyclodextrin≫γ-cyclodextrin≈0.

Figure 1 shows the electron micrograph of rhodium colloidal dispersion prepared in the presence of β-cyclodextrin equimolar to rhodium(III) chloride. Highly dispersed fine rhodium particles are observed. The average diameter of the particles is 28 Å.

In aqueous solutions, apolar particles of rhodium metal should be bound to the apolar cavities of cyclodextrins. Since the particles are too large to be totally included in the cavity of α- or β-cyclodextrin, they sit on the top of the cavity. Thus, the surface of the rhodium particles is mostly covered with several cyclodextrin molecules, which prevent aggregation of particles.

The proposed structures of the present colloidal particles are consistent with the larger protecting ability of β-cyclodextrin than that of α-cyclodextrin, since almost all of the guest compounds previously investigated showed stronger binding with β-cyclodextrin than with α-cyclodextrin.[6] Minimal protecting ability of γ-cyclodextrin is associated with less apolar property of the cavity. The order for the three kinds of cyclodextrins in the protecting abilities is also identical with the decreasing order in their solubilities in water.

The above arguments are supported by the fact that dextran (degree of polymerization, 360), which has no cavities, shows no measurable protecting ability at the molar ratio 7 to rhodium(III) chloride. Here, a glucose residue of dextran is taken as a unit. Furthermore, both poly(ethylene oxide) and poly(*N*-vinylpyrrolidone)(degree of polymerization, 110 and 90, respectively) exhibit no effective protection at the residual molar ratio unity with respect to rhodium(III) chloride.

TABLE 1. CATALYTIC ACTIVITIES OF COLLOIDAL DISPERSION OF RHODIUM PREPARED BY USING β-CYCLODEXTRIN IN THE HYDROGENATION OF OLEFINS[a)]

Substrate	Initial rate of hydrogen uptake (H_2 mol/Rh g-atoms·s)
3-Buten-2-one	0.24
3-Methyl-3-buten-2-one	0.07
3,4-Dimethyl-3-penten-2-one	0.32
Acrylonitrile	0.22
Methacrylonitrile	0.06

a) Hydrogenation conditions: temperature, 30.0 °C; total pressure, 1 atm; [Rh]=[β-cyclodextrin]=4×10^{-5} mol·dm^{-3}; [substrate]=2.5×10^{-2} mol·dm^{-3}; solvent, 19.5: 0.5 (v/v) water-ethanol.

The refluxing of aqueous solution of rhodium(III) chloride prior to the addition of ethanol is definitely required for the preparation of a homogeneous colloidal dispersion. When rhodium(III) chloride was directly dissolved in the 3:1 water–ethanol mixture and the solution was refluxed for 10 min, considerable amounts of precipitates were formed together with a homogeneous dark brown colloidal dispersion.

On refluxing an aqueous solution of rhodium(III) chloride and β-cyclodextrin for 30 min, the absorbance in the 200—350 nm region decreased and a shoulder appeared at 260 nm. These changes are attributable to complex formation of rhodium(III) chloride with β-cyclodextrin. Rhodium ions in the complexes were then reduced by the ethanol added, and the resulting colloidal dispersion showed a monotonic absorption without peaks.[4)]

As shown in Table 1, the rhodium colloidal dispersion prepared with β-cyclodextrin effectively catalyzed hydrogenation of water-soluble olefins at 30.0 °C under an atmospheric hydrogen pressure.

Methyl substitutions in the substrate at the β-position with respect to the carbonyl group enhance catalytic hydrogenation. The hydrogenation of 3,4-dimethyl-3-penten-2-one is about 4.6 times as fast as that of 3-methyl-3-buten-2-one. In contrast, methyl substitution at the α-position with respect to the carbonyl or cyano group suppresses the reaction. The rates for 3-methyl-3-buten-2-one and methacrylonitrile are 3 fold smaller than the values for the corresponding substrates without a methyl group at the α-position.

These results indicate the inclusion complex formation of the substrates with one of the β-cyclodextrins, located on the surface of the rhodium particles, prior to the catalytic functions of the particles. In order to make the catalyses effective, the penetration of the substrate in the cavity should be from the side involving the C–C double bond rather than from the side involving the polar groups. The alkyl substitution at the β-position enhances the inclusion of the substrate into the apolar cavity from the side involving the C–C double bond due to increase in the apolar character of this side. On the other hand, alkyl substitution at the α-position decreases the polar character in the side involving the polar group, resulting in the suppression of the inclusion from the side involving the C–C double bond.

The participation of β-cyclodextrin, located on the surface of rhodium particles, in the catalyses is further supported by the fact that the hydrogenation of 3-buten-2-one is almost totally inhibited by the addition of 10^{-2} mol dm^{-3} of cyclohexanol. In contrast, methanol exhibits no effect on the hydrogenation at the same concentration. The inhibition by cyclohexanol, which forms inclusion complex with β-cyclodextrin, is attributable to its competition with the substrate for the cavity of β-cyclodextrin.

In conclusion, complex formation of rhodium(III) chloride with α- or β-cyclodextrin, followed by the reduction of them with ethanol, gives a colloidal rhodium dispersion. The dispersion exhibits specific catalyses in the hydrogenation of olefins.

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