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Colloidal Dispersions of Palladium-Platinum Bimetallic Clusters Protected by Polymers. Preparation and Application to Catalysis

Naoki TOSHIMA,* Kakuta KUSHIHASHI, Tetsu YONEZAWA, and Hidefumi HIRAI+
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The colloidal dispersions of the palladium-platinum bimetallic clusters were prepared by refluxing the solution of $PdCl_2$ and H_2PtCl_6 in water/ethanol in the presence of poly(N-vinyl-2-pyrrolidone). The electronic absorption spectra and the transmission electron micrographs show the formation of an alloy in the clusters. The dispersions work as catalysts for the selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctene. The highest activity was achieved by the bimetallic clusters with a Pd/Pt molar ratio of 4/1.

The activity and selectivity of a metal catalyst can be improved, sometimes dramatically, by adding the second and/or the third components to the catalyst. Therefore, the role of additives has interested many researchers. The additive components may form alloys with the original metal, promoting the activity and/or selectivity of the catalyst. The effect of the additives on the improvement may be explained in terms of an ensemble effect and/or a ligand effect.1-8)

Colloidal dispersions of metal particles are often prepared by careful reduction of the metal ions in solutions. We have succeeded in preparing colloidal dispersions of noble metals by reduction of the corresponding metal ions with refluxing alcohol in the presence of aqueous polymers such as poly(N-vinyl-2-pyrrolidone).9) We applied them to the catalyses of the selective hydrogenation of olefins,10) the selective partial hydrogenation of dienes to monoenes,11) the visible light-induced hydrogen generation from water,12) etc.

There are many investigations of bimetallic catalysts on inorganic supports, but little attention has been paid to the colloidal dispersions of the bimetallic cluster particles. In this paper we describe the preparation of the colloidal dispersions of the palladium-platinum bimetallic clusters by the alcohol-reduction method.9) These bimetallic clusters were then applied to the catalysis of the selective artial hydrogenation of 1,3-cyclooctadiene to cyclooctene. Their catalytic activities were found to depend on the composition of the bimetallic clusters, and the highest activity was achieved with the Pt/Pd molar ratio of 4/1.

The preparation of colloidal dispersions of the Pd-Pt bimetallic clusters was as follows: The ethanol solution of palladium(II) chloride (1.32 mmol dm^{-3}) was

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+Present address: Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162.

prepared by stirring the dispersions of $PdCl_2$ (14.0 mg, 0.079 mmol) powder in ethanol (60 cm^3) for 48 h. The obtained solution was mixed together with an aqueous solution of hexachloroplatinic(IV) acid (1.32 mmol dm^{-3}), water and ethanol to make a series of water/ethanol (1/1 v/v) mixture solutions (50 cm^3) of designed Pd/Pt molar ratio. Each solution was put into a flask (100 ml) with poly(N-vinyl-2-pyrrolidone) (PVP, 151 mg, Tokyo Kasei Co., K30, Mw=40,000) and heated for 1 h to reflux under air, resulting in sudden change of the color to make a series of clear dark brown solutions.

A series of the electronic spectra of these colloidal solutions thus obtained were measured. The spectra of the bimetallic colloidal dispersions were found not only to differ from that of the monometallic colloidal dispersion of Pd or Pt, or of their mixtures, but also to have a characteristic pattern as shown in Fig. 1: The absorbance in shorter wavelength gradually decreases with the increase of the Pd/Pt ratio, while in longer wavelength it remains almost constant.

The transmission electron micrographs of the colloidal dispersions were obtained with a Hitachi model HU-12A or H-7000 electron microscope, as shown in Fig. 2. The photographs clearly demonstrate that the bimetallic clusters are composed of ultrafine particles of almost uniform size, although the palladium or platinum particles are more widely distributed in size than the bimetallic ones. These results on the electron micrographs as well as the absorption spectra strongly suggest that the present bimetallic system is not the mixture of the monometallic particles but is composed of Pd-Pt alloy particles.

The bimetallic colloidal dispersions thus obtained were applied as catalysts to the partial hydrogenation of 1,3-cyclooctadiene in ethanol at 30°C under 1 atm of hydrogen. The activities were measured by the initial rate of hydrogen uptake.

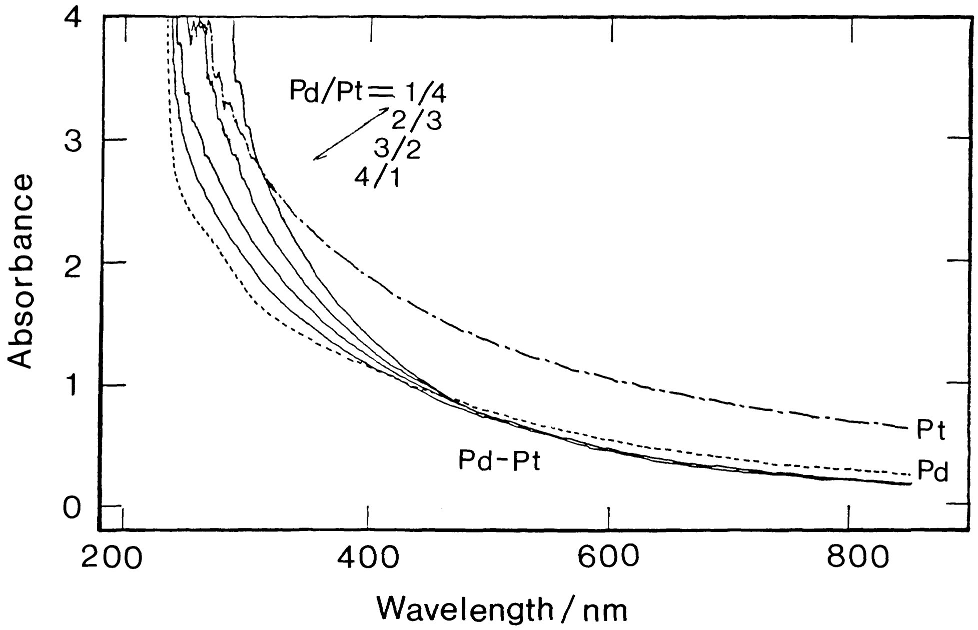

Fig. 1. The series of the UV-VIS spectra of bimetallic colloidal dispersions of Pd/Pt ratio = 4/1, 3/2, 2/3, 1/4, and the spectra of Pd(-------) and Pt(-—·—).

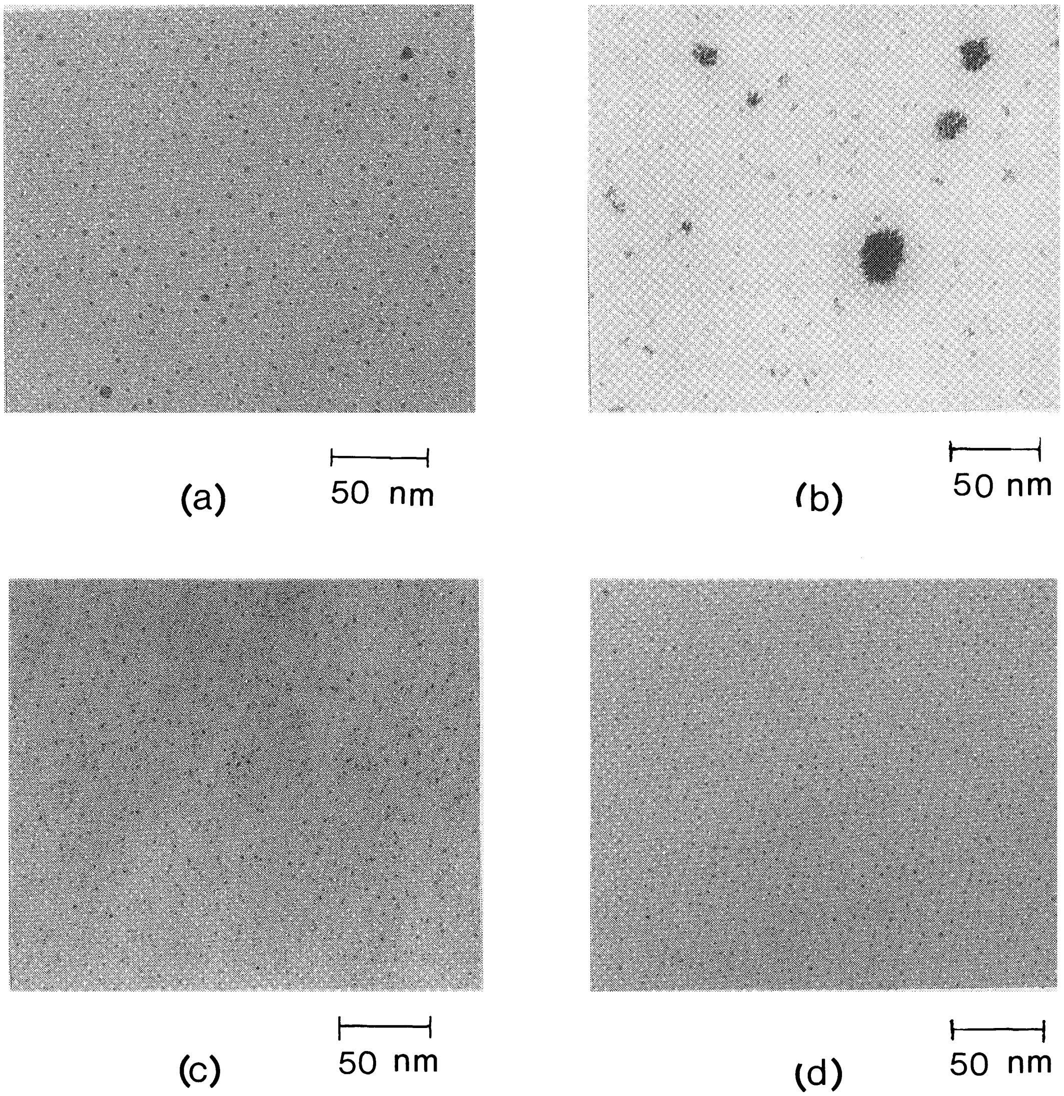

Fig. 2. TEM photographs showing ultrafine particles of colloidal dispersions of (a) Pd, (b) Pt, (c) bimetallic Pd/Pt =1/1, and (d) =4/1.

The catalytic activities of the bimetallic clusters of various Pd/Pt ratios are plotted against the metal composition in Fig. 3. The maximum activity, achieved by the composition of Pd/Pt = 4/1, is about three times of that of the palladium clusters prepared by the same method, when the total molar amounts of the noble metals are kept constant for comparison. This high activity observed in the bimetallic clusters was never observed in the mixtures of the palladium and the platinum clusters. Thus, these results do again demonstrate the formation of the alloy in this bimetallic system.

The product distribution was traced with a GLPC in the hydrogenation of 1,3-cyclooctadiene using the bimetallic catalyst of Pd/Pt = 4/1. The selectivity for the cyclooctene formation at the complete conversion of 1,3-cyclooctadiene was more than 99%, which is at the same level as with the palladium cluster catalyst.$^{9)}$

In conclusion, colloidal dispersions of various composition of bimetallic clusters protected by polymers were obtained by the simultaneous reduction of $PdCl_2$ and H_2PtCl_6 in refluxing alcohol, and found to be composed of ultrafine particles of Pd-Pt alloys. They work as the catalyst for the selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctene, and the highest activity was achieved by the Pd/Pt = 4/1 bimetallic clusters, which is about three times higher than by the palladium clusters.

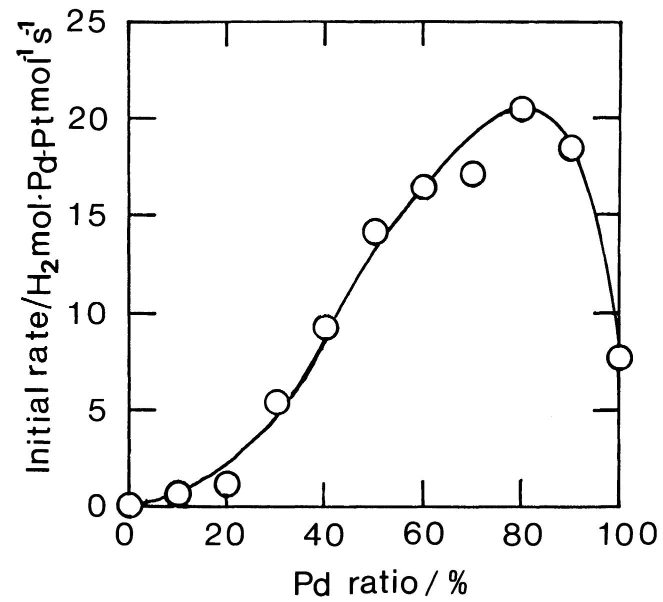

Fig. 3. The dependence of the catalytic activity of the Pd-Pt bimetallic clusters on its metal composition in partial hydrogenation of 1,3-cyclooctadiene.

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