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The Polymer-Protected Pd-Pt Bimetallic Clusters Having Catalytic Activity for Selective Hydrogenation of Diene. Preparation and EXAFS Investigation on the Structure

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The colloidal dispersions of the palladium-platinum bimetallic clusters were prepared by refluxing their salts in water/ethanol in the presence of poly(N-vinyl-2-pyrrolidone) under nitrogen. They work as catalysts for partial hydrogenation of diene. The highest activity was achieved by the bimetallic clusters with the molar ratio of Pd/Pt = 4/1, the EXAFS spectra and the TEM photographs of which strongly suggest the alloy formation with a core structure.

The activity and selectivity of metal catalysts can be dramatically improved by adding other components to the monometallic catalyst. Many interesting studies were made about the bimetallic catalysts on inorganic supports. The EXAFS (extended X-ray absorption fine structure) measurement is one of the best methods to provide the clear evidence for an alloy structure of the bimetallic clusters.[1-5] We have investigated on the preparation of colloidal dispersions of metal clusters protected by polymers and surfactants and on their application to the catalysts for selective hydrogenation and hydrogen evolution.[6-10]

The colloidal dispersions of palladium were prepared by reduction of palladium ions with refluxing alcohol in the presence of poly(N-vinyl-2-pyrrolidone) (PVP), and were applied to the catalyst with high activity and selectivity for the hydrogenation of dienes to monoenes.[7] In the previous letter,[11] we have reported the palladium-platinum bimetallic catalysts were prepared from $PdCl_2$, H_2PtCl_6 and PVP in refluxing water/ethanol under air. The catalytic activities for the partial hydrogenation of 1,3-cyclooctadiene depend on the composition of the bimetallic clusters and the highest activity was observed for those with the molar ratio of Pd/Pt = 4/1. The alloy formation was suggested indirectly by the UV-VIS spectra and the transmission electron micrographs of the bimetallic colloidal dispersions.

In the present letter we would like to describe the EXAFS analyses of the palladium-platinum bimetallic clusters at the molar ratio of Pd/Pt = 4/1. For this purpose we have prepared the colloidal dispersions of the bimetallic clusters under nitrogen to avoid the contamination by oxygen, and have checked the dependence of the catalytic activity on the metallic composition. The Pd/Pt = 4/1 bimetallic clusters prepared under nitrogen, which was shown to be the most active catalyst as well, have been clearly demonstrated by EXAFS measurements to have the bond between Pd and Pt forming a special core structure.

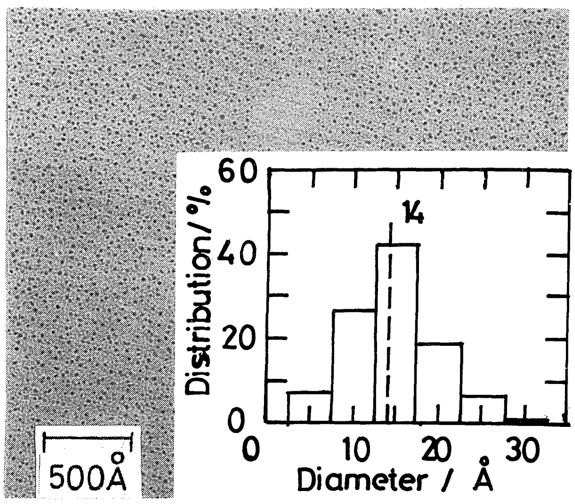

Fig. 1. TEM photograph and the size distribution histogram of the Pd/Pt = 4/1 bimetallic clusters prepared under nitrogen.

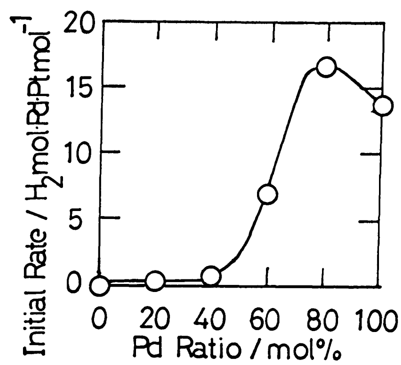

Fig. 2. Initial rate of catalytic hydrogenation of 1,3-cyclooctadiene (25 mM) at 30 ℃ over Pd/Pt bimetallic clusters (0.01 mM) prepared under N_2.

The colloidal dispersions of the Pd-Pt bimetallic clusters were prepared by the same way as described in the previous letter[11] except under nitrogen instead of air. All the dispersions are clear dark brown and do not form precipitates under nitrogen for more than a year. The transmission electron micrographs of the clusters were obtained with a Hitachi model H-7000 electron microscope. The photograph of the Pd/Pt = 4/1 bimetallic clusters are shown in Fig. 1, which clearly demonstrates that the bimetallic clusters have an almost uniform size. The diameter of each of the particles was determined from the enlarged photographs. The particle size distribution histogram and the average diameter, shown in Fig. 1, were obtained on the basis of the measurements of the three hundred particles. The catalytic activities of the dispersions were measured for the partial hydrogenation of 1,3-

Table 1. Coordination numbers around the Pd and Pt atoms of the Pd/Pt = 4/1 bimetallic cluster determined from EXAFS data

Absorbing metal	Scattering metal	Interatomic distance r/Å	Coordination number N		
			Observed	Pt core	Random
Pd	Pd	2.74±0.03	4.4±0.4	4.6	6.0
Pd	Pt	2.73±0.03	2.3±0.2	2.0	1.9
Pt	Pt	2.73±0.03	5.5±0.5	5.5	1.9
Pt	Pd	2.72±0.03	3.1±0.7	6.5	6.0

cyclooctadiene by the same way as in the previous letter.[11] Figure 2 shows the dependence of the activities upon the metal compositions. The maximum activity was achieved by the bimetallic clusters with the composition of Pd/Pt = 4/1, which is the same as those prepared under air. The maximum activity is about 1.4 times of that of the monometallic palladium clusters.

The product compositions during the reaction were analyzed by a gas chromatography with a capillary column (Ohkura GC-701, Column: Gasukuro-Kogyo Squalene 0.28mmϕ × 30m). At 100% conversion of 1,3-cyclooctadiene over the Pd/Pt = 4/1 bimetallic cluster catalyst prepared under nitrogen, the yield of cyclooctene was 96.9%, which is considerably large but less than the value for the Pd/Pt = 4/1 bimetallic cluster catalyst prepared under air (99.6%) or for the monometallic Pd cluster catalyst (99.9%).[7] The EXAFS data showed the presence of Pd-O-Pd bonds on the surface of the clusters prepared under air, but not for those prepared under nitrogen.

In order to study the structure of the Pd/Pt = 4/1 bimetallic cluster, the EXAFS spectra were measured with BL-10B line at the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF). For EXAFS measurements 1.0 dm^3 of the cluster dispersions were concentrated by evaporation under reduced pressure and the concentrated dispersions were kept under nitrogen in the cells having polyimide film (KAPTON-H) windows. The light pass length of 50 and 10 mm were used for Pd K edge and Pt L_3 edge measurement, respectively. The spectra data were analyzed by using EXAFS2 program at the Research Center for Spectrochemistry of the University of Tokyo. The theoretically derived phase shift and amplitude functions were used according to the literature.[12,13] The model compounds used in the present work were Pd and Pt foil, and Pt-Pd alloy foil (Pt:Pd=9:1).

The average diameter of Pd/Pt = 4/1 bimetallic clusters obtained by the electron micrograph was 14 Å. The bulk metals of Pd and Pt are known to take a face centered cubic structure. These data suggest a 3 layer structure with 55 atoms. The coordination numbers around the Pd atom calculated from the EXAFS spectra are 4.4±0.4 and 2.3±0.2 for Pd and Pt, respectively, and those around the Pt atom are 5.5±0.5 and 3.1±0.7 for Pt and Pd, respectively, as shown in Table 1.[14] These numbers are quite different from those calculated for the random model, where 42 palladium atoms and 13 platinum atoms are located completely at random. If the 42 palladium atoms are on the surface of the clusters and the 13 platinum atoms are in the core (Pt core model as shown in Fig. 3), the Pd/Pt ratio is almost 4/1, and the coordination numbers calculated are quite consistent with the observed values as shown in Table 1. On the basis of these results the Pt core model can be taken as a model for Pd/Pt = 4/1 clusters.

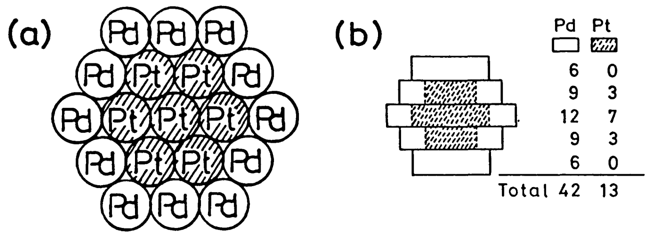

Fig. 3. (a) Illustration of the cross section of a Pt core model for the Pd/Pt = 4/1 bimetallic cluster and (b) the perspective drawing from the side of the same model.

In conclusion, the Pd/Pt = 4/1 bimetallic clusters protected by the aqueous polymer showed the highest activity as the catalyst for partial hydrogenation of 1,3-cyclooctadiene to cyclooctene among the Pd-Pt bimetallic cluster dispersions prepared under nitrogen. The size and the coordination numbers obtained by the TEM photographs and the EXAFS spectra, respectively, have indicated that the Pd/Pt = 4/1 bimetallic clusters have a special alloy structure as the Pt core model shown in Fig. 3.

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