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POLYMER-PROTECTED BIMETALLIC CLUSTERS. PREPARATION AND APPLICATION TO CATALYSIS

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ABSTRACT

Colloidal dispersions of polymer-protected Pd/Pt and Pd/Au bimetallic clusters were prepared by reduction of an alcoholic solution of $PdCl_2$ and H_2PtCl_6 or $HAuCl_4$ in the presence of poly(*N*-vinyl-2-pyrrolidone). The reduction can be carried out by refluxing in alcohol or by irradiation with visible light. The dispersions of the bimetallic clusters obtained are stable for months at room temperature and have from dark brown to brownish red color. Transmission electron micrographs show that the bimetallic clusters are composed of well-dispersed ultrafine particles of uniform size, about 1.5 nm for Pd-Pd and 3.4 nm for Pd-Au in diameter. The catalytic activity of the bimetallic clusters depends on the metal composition. In the case of the partial hydrogenation of 1,3-cyclooctadiene, the activity went through a maximum when the alloy composition reached about 80% Pd and 20% Pt, or 60% Pd and 40% Au.

INTRODUCTION

We have reported that colloidal dispersions of noble metals protected by polymers can be prepared by reducing noble metal salts coordinated by aqueous polymers like poly(*N*-vinyl-2-pyrrolidone) under mild conditions as shown in Fig. 1 [1]. Refluxing the alcoholic solution (an alcohol-reduction method) [2, 3] or irradiation with visible light (a photoreduction method) [4, 5] can be used for mild reduction. The colloidal dispersions of noble metals thus obtained are composed of ultrafine particles with average diameters from 1 to 5 nm with narrow size distributions, and are stable for months at room temperature. They work as active catalysts for selective hydrogenation of internal olefins [6], selective partial hydrogenation of diene to monoene [7, 8], visible light-induced hydrogen generation from water [9, 10], and so on.

The activity and selectivity of a metal catalyst can be improved by adding the second and/or the third components to the catalyst. Many investigations on bimetallic heterogeneous catalysts aimed at correlating catalytic behavior and electronic structure with alloy composition. The alloy formation may be explained in terms of an ensemble effect and/or a ligand effect [11–13]. The bimetallic systems of large metal carbonyl clusters are also currently of considerable interest because of their catalytic activity and other unusual physical properties [14, 15].

The present paper concerns the preparation and characterization of colloidal dispersions of bimetallic clusters protected by polymers and their application to catalysis. A novel core structure will be proposed for the Pd/Pt (4/1) bimetallic cluster which shows maximum activity for selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctene.

EXPERIMENTS

Preparation of Bimetallic Clusters Protected by Polymers

An alcohol-reduction method [2, 3] and a photoreduction method [4, 5] were used for reduction of noble metal ions in solution. Ethanol solutions of palladium(II) chloride were prepared by stirring dispersions of

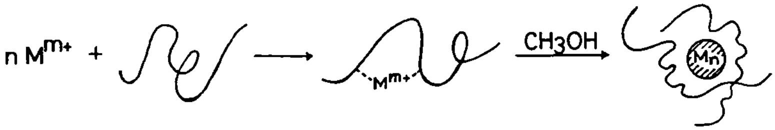


FIG. 1. Schematic presentation of the formation of the colloidal dispersions of noble metal clusters protected by polymers through the polymer–metal complexes.

$PdCl_2$ powder in ethanol for 48 h. Solutions of H_2PtCl_6 and $HAuCl_4$ were prepared by dissolving the corresponding crystal in water. Both solutions were mixed to produce a bimetallic ethanol/water (1/1) solution (50 cm^3) with a total metal concentration of 6.6×10^{-4} mol/dm^3 containing 151 mg poly(*N*-vinyl-2-pyrrolidone) (Tokyo Kasei Co., K30, MW = 40,000). The mixed solution was refluxed for 1 h for alcohol reduction. The degassed solution was irradiated with an Xe lamp (500 W, Ushio Co.) for 2 h for photoreduction.

Characterization of the Bimetallic Clusters

Electronic spectra of colloidal dispersions of metal clusters were measured with a Hitachi model 340 spectrophotometer. Transmission electron micrographs were taken with a Hitachi model HU-12A and H-7000 electron microscope.

Hydrogenation of 1,3-Cyclooctadiene Catalyzed by Colloidal Dispersions of the Bimetallic Clusters

The catalytic activity of the metal clusters was measured by the initial rate of hydrogen uptake in the hydrogenation of 1,3-cyclooctadiene (25 $mmol/dm^3$) in ethanol at 30°C under 1 atm of hydrogen while keeping the total concentration of noble metal at 0.01 $mmol/dm^3$. The product distribution was measured with a GLPC (capillary column OV-1) in the course of the hydrogenation.

RESULTS AND DISCUSSION

Preparation of Bimetallic Clusters Protected by Polymers

General methods for the preparation of colloidal dispersions of the noble metal clusters protected by polymers were applied to the present preparation of bimetallic clusters protected by polymers. For example, Pd/Pt bimetallic clusters were prepared by refluxing an alcohol/water (1/1) solution of $PdCl_2$ and H_2PtCl_6 in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) under air or nitrogen.

$$PdCl_2 + C_2H_5OH \rightarrow Pd + 2HCl + CH_3CHO \quad (1)$$

$$H_2PtCl_6 + 2C_2H_5OH \rightarrow Pt + 6HCl + 2CH_3CHO \quad (2)$$

The colloidal dispersions of Pd/Pt bimetallic clusters protected by polymer have a brown color and are stable for months at room temperature. The addition of a small amount of sodium hydroxide during preparation seems to accelerate the reduction of noble metal ions, resulting in the production of rather smaller particles of metal clusters [2, 16]. The sodium hydroxide probably reacts to form the alkoxide ion which is a more potent reducing agent than ethanol. This alcohol-reduction method can also be used to prepare Pd/Au bimetallic clusters. Although refluxing a pure auric acid ($HAuCl_4$) solution in ethanol/water (1/1) in the presence of PVP cannot reduce gold(III) ions to zero-valent gold, the coexistence of $PdCl_2$ does produce Pd/Au bimetallic clusters. The alcohol-reduction method can also be applied to the preparation of Pd/Rh and Ru/Co bimetallic clusters protected by PVP, the details of which will not be described here.

The photoreduction method can also be used for the preparation of bimetallic clusters. For example, visible light irradiation of $PdCl_2$ and/or $HAuCl_4$ in ethanol/water (1/1) in the presence of PVP gave brown to red solutions of Pd and/or Au clusters.

$$PdCl_2 \xrightarrow{h\nu} Pd + Cl_2 \tag{3}$$

$$HAuCl_4 \xrightarrow{h\nu} Au + HCl + \frac{3}{2} Cl_2 \tag{4}$$

The chlorine gas produced can probably react with water or ethanol to produce hydrochloric acid and hypochlorous acid, or hydrochloric acid and acetaldehyde.

$$Cl_2 + H_2O \rightarrow HCl + HClO \tag{5}$$

$$Cl_2 + C_2H_5OH \rightarrow 2HCl + CH_3CHO \tag{6}$$

Thus, the presence of ethanol can accelerate the photoreduction of noble metal ions.

Electronic Spectrum of Colloidal Dispersions of the Bimetallic Clusters

The electronic spectra of the bimetallic clusters thus prepared were measured. Generally, the resulting colloidal dispersions of metal clusters have no peaks in the spectra. However, the spectrum of the dispersions of bimetallic clusters is different from that of the mixed solution of the two kinds of monometallic clusters. The examples are shown in Fig. 2 for the case of Pd/Pt bimetallic clusters protected by PVP. The spectra of the Pd/Pt bimetallic colloidal dispersions were found not only to differ from that of the monometallic dispersions of Pd or Pt, or their mixtures, but also to have a characteristic pattern: The absorbance at shorter wavelengths gradually decreases with an increase of the Pd/Pt ratio, while at longer wavelengths it remains almost constant.

In the case of Pd/Au bimetallic clusters, an interesting behavior was observed in a series of the electronic spectra as shown in Fig. 3: The electronic spectra of the Pd/Au bimetallic clusters have peaks around 510 nm when Pd/Au = 1/4 and 2/3, while no peaks are found at Pd/Au = 3/2 and 4/1. Since the colloidal dispersions of gold have a red color and the dispersions of the gold clusters prepared by the photoirradiation of auric acid in ethanol gave a peak at 530 nm, the mixtures of both Pd and Au clusters have a peak even at a high Pd/Au ratio like 4/1. The lack of a peak in the electronic spectra of the Pd/Au (Pd/Au = 4/1 and 3/2) bimetallic clusters clearly indicates alloy formation between palladium and gold.

Transmission Electron Micrographs of the Bimetallic Clusters

Transmission electron microscopy is a useful method to characterize the metal clusters protected by polymers. The average diameter and the size distribution are important information for the metal clusters. In

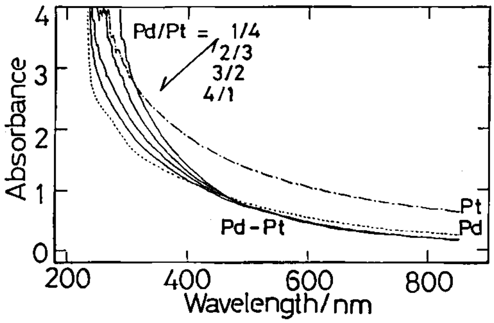


FIG. 2. A series of UV-VIS spectra of the bimetallic colloidal dispersions of Pd/Pt (ratio = 4/1, 3/2, 2/3, 1/4), and the spectra of Pd (···) and Pt (-·-) dispersions.

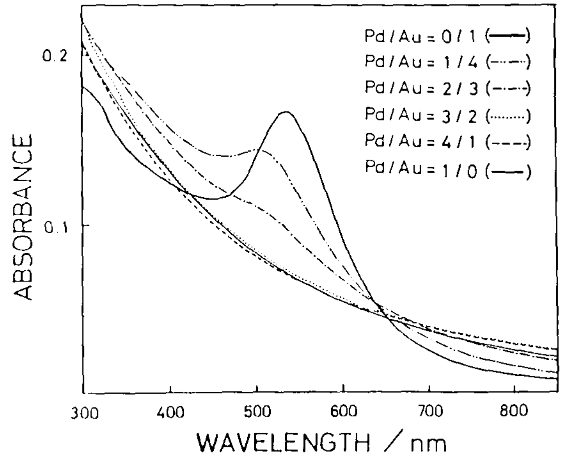
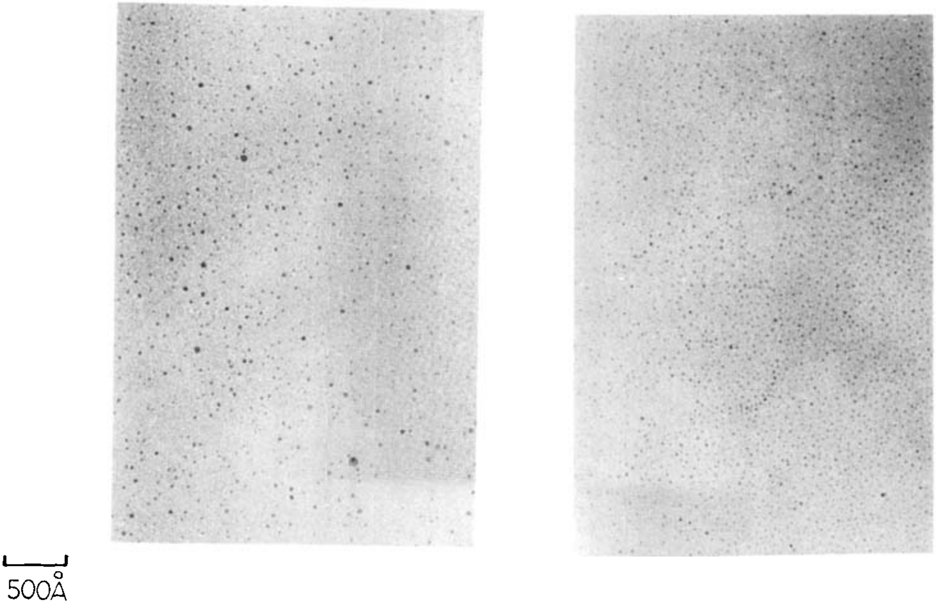


FIG. 3. A series of UV-VIS spectra of the bimetallic colloidal dispersions of Pd/Au (ratio = 1/4, 2/3, 3/2, 4/1), and the spectra of Au (——) and Pd (—) dispersions.

(a&b)



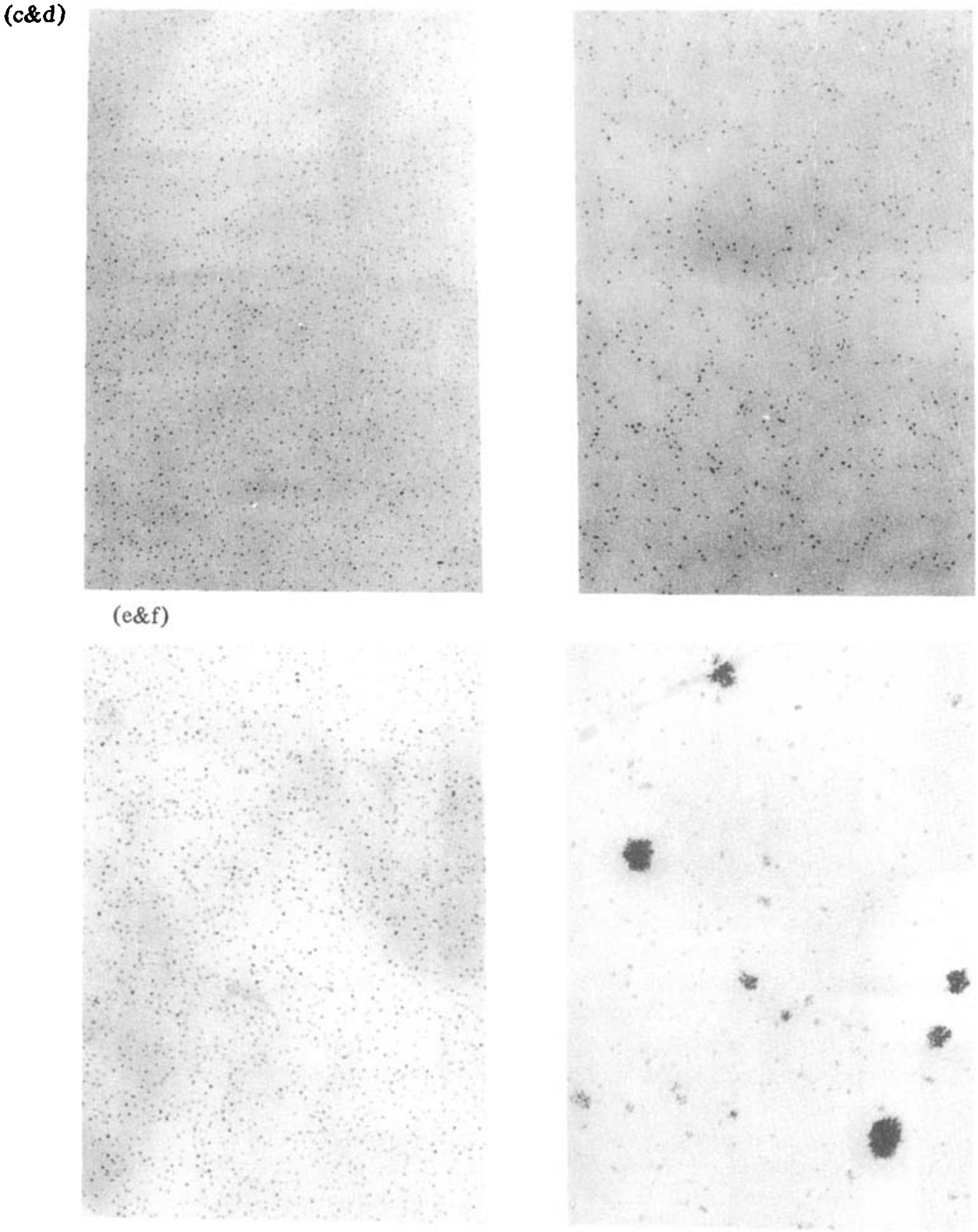


FIG. 4. Electron micrographs of (a) Pd monometallic, (b) Pd/Pt (4/1) bimetallic, (c) Pd/Pt (3/2) bimetallic, (d) Pd/Pt (2/3) bimetallic, (e) Pd/Pt (1/4) bimetallic, and (f) Pt monometallic clusters protected by poly(*N*-vinyl-2-pyrrolidone).

general, the particles of the noble metal clusters prepared by mild reduction conditions are small in size (1-3 nm) and narrow in size distribution, i.e., uniform and homogeneous.

In the present system we found that the bimetallic clusters are more uniform or homogeneous than the monometallic ones. Figure 4 shows examples for the case of Pd/Pt bimetallic clusters. As shown in Figs. 4(a) and 4(f), the monometallic clusters of Pd and Pt are small in size, but show aggregation of the small particles and/or crystal growth to form rather large particles to a certain extent. On the contrary, the size of the bimetallic clusters is small and neither aggregation nor growth is observed. Moreover, excellent uniformity is observed for each Pd/Pt bimetallic cluster of different Pd/Pt ratios (cf. Figs. 4b, 4c, 4d, and 4e for Pd/Pt = 4/1, 3/2, 2/3, and 1/4, respectively). An example of the narrow size distribution is shown in Fig. 5 for the Pd/Pt (4/1) bimetallic clusters.

The same tendency was observed in the case of Pd/Au bimetallic clusters protected by PVP. The gold clusters prepared by the photoreduction method are very large in size, 10-50 nm in diameter, while the palladium clusters prepared by the same method are 1-2 nm in diameter. In contrast, when Pd/Au bimetallic clusters were prepared by the simultaneous photoreduction of both Pd and Au ions, electron micrographs revealed almost uniform particles of 3.4 nm average diameter.

The tendency to uniform size of the Pd/Pt and Pd/Au bimetallic clusters is considered to be evidence for alloy formation in the bimetallic clusters.

Catalysis of the Bimetallic Clusters Protected by Polymers

The dispersions of the Pd/Pt and Pd/Au bimetallic clusters protected by PVP can work as active catalysts for the selective partial hydrogenation of 1,3-cyclooctadiene in ethanol at 30°C under 1 atm of hydrogen. The dependence of the catalytic activity upon the metal composition of the bimetallic clusters was investigated for the Pd/Pt and Pd/Au bimetallic clusters prepared by the different methods.

Colloidal dispersions of the Pd/Pt bimetallic clusters protected by PVP were prepared by the simultaneous reduction of Pd(II) and Pt(IV) ions in the presence of PVP with an alcohol-reduction method under air. They were used as catalysts for the hydrogenation of 1,3-cyclooctadiene. The dependence of the activity on the metal composition is shown in Fig. 6. The dispersions of the Pt monometallic clusters prepared by the same

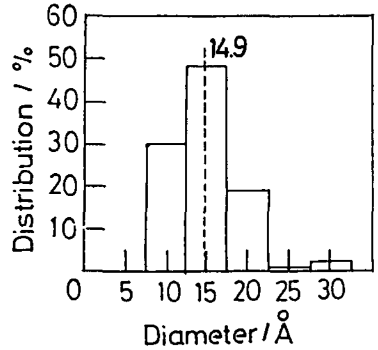


FIG. 5. Particle size distribution of the Pd/Pt (4/1) bimetallic clusters. The dashed line indicates the average diameter.

method as above have almost no activity as catalysts. However, the coexistence of Pd in the clusters increases the catalytic activity, and the maximum activity is achieved by Pd/Pt (4/1) bimetallic clusters which show about twice the activity of Pd monometallic clusters prepared by the same method. The corresponding mixtures of dispersions of both Pd and Pt monometallic clusters did not produce such high activities.

Similar results were obtained for dispersions of Pd/Pt bimetallic clusters prepared by refluxing in alcohol/water under nitrogen and refluxing in alcohol/water containing a small amount of sodium hydroxide. The dependence of catalytic activity upon metal composition are plotted for both cases in Figs. 7 and 8. Even though the precise shapes of the curves

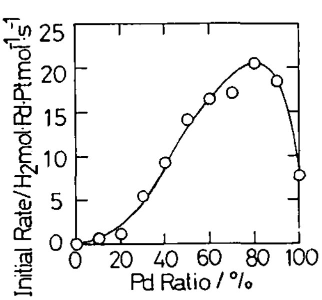


FIG. 6. Dependence of catalytic activity on the metal composition of the Pd/Pt bimetallic clusters prepared by refluxing in ethanol/water under air.

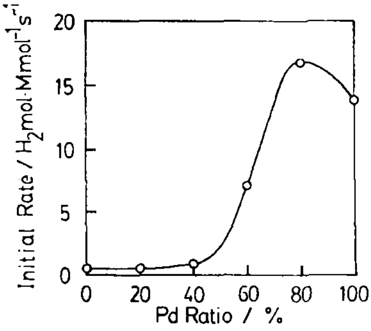


FIG. 7. Dependence of catalytic activity on the metal composition of the Pd/Pt bimetallic clusters prepared by refluxing in ethanol/water under nitrogen.

differ, maximum activities were achieved at a Pd/Pt = 4/1 ratio in both cases, which is the same as the case of Pd/Pt bimetallic clusters prepared under air as shown in Fig. 6. The significance of 80% Pd in the bimetallic particle will be discussed later.

Pd/Au bimetallic clusters prepared by the photoreduction method also show catalytic activity for the selective hydrogenation of 1,3-cyclooctadiene. The activity depends on the metal composition as well. The results are shown in Fig. 9, in which the maximum activity is given by the bimetallic clusters at a molar ratio of Pd/Au = 3/2.

Both Pd/Pt (4/1) and Pd/Au (3/2) bimetallic clusters reveal a high selectivity of above 99% for the production of cyclooctene with the complete consumption of 1,3-cyclooctadiene.

Possible Structure of the Pd/Pt (4/1) Bimetallic Clusters

It is interesting that, in the case of the Pd/Pt bimetallic system, the highest catalytic activity is achieved by bimetallic clusters of Pd/Pt = 4/1. This behavior is independent of the preparation method. Furthermore, all the Pd/Pt bimetallic clusters are about 1.4 nm in diameter. These results suggest a common structure for Pd/Pt bimetallic clusters and a special model for those of Pd/Pt = 4/1.

The bulk metals of Pd and Pt are known to have a face-centered cubic lattice and nearly the same atomic radii. If the data on the bulk metal can be applied to the metal cluster, the cluster of 1.4 nm diameter will be a

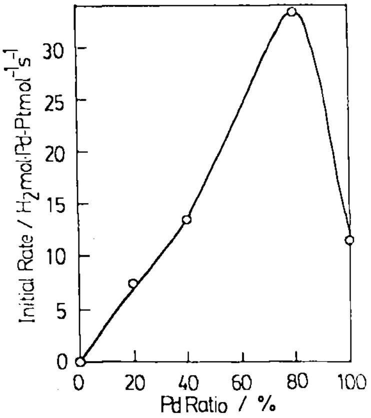


FIG. 8. Dependence of catalytic activity on the metal composition of the Pd/Pt bimetallic clusters prepared by refluxing in ethanol/water containing a small amount of sodium hydroxide under air.

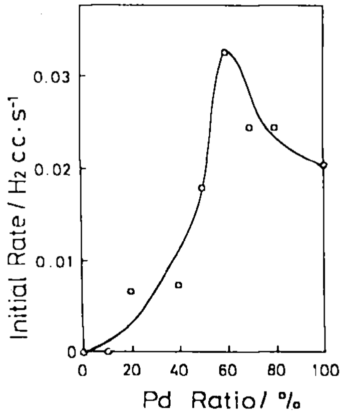


FIG. 9. Dependence of catalytic activity on the metal composition of the Pd/Au bimetallic clusters prepared by photoreduction in ethanol/water.

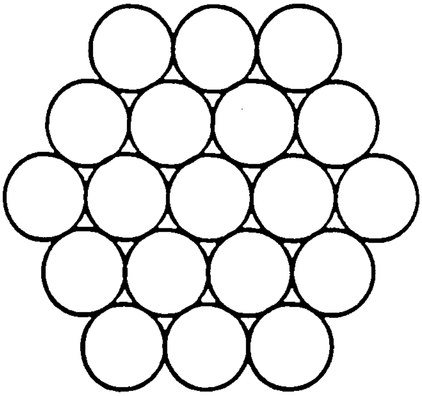


FIG. 10. The largest cross-section of an ideal model structure of a noble metal cluster of 1.4 nm diameter.

particle with a three-layered structure composed of 55 atoms, the largest cross-section of which is shown in Fig. 10.

On the other hand, there are many reports about metal carbonyl clusters, the structures of which have been investigated energetically. These reports suggest structures to be considered for the present bimetallic clusters. It can be empirically said for the bimetallic carbonyl clusters that the heavier metals are located near the center of the carbonyl cluster and

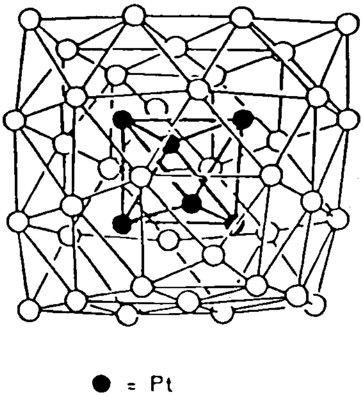


FIG. 11. Metallic skeleton of $[Ni_{38}Pt_6(Co)_{48}H]^{5-}$ cluster according to Heaton [17].

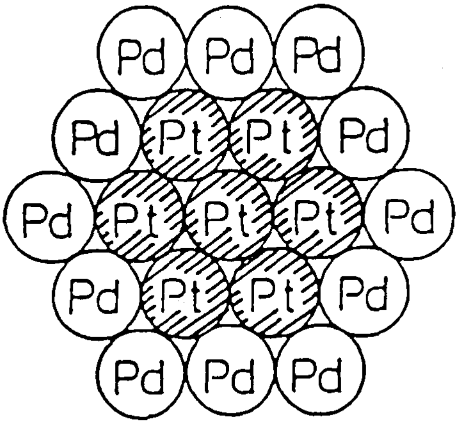


FIG. 12. The largest cross-section of a core model as a possible structure for the Pd/Pt (4/1) bimetallic cluster.

the lighter metals are near the surface. For example, the structure of $[Ni_{38}Pt_6(Co)_{48}H]^{5-}$ was reported by Heaton et al. [17] to be as shown in Fig. 11.

Based on the above consideration, we present the structure shown in Fig. 12 for Pd/Pt (4/1) bimetallic clusters. In this model, 13 Pt atoms are located at the center of the cluster and 42 Pd atoms surround the Pt core. This core model structure is supported by preliminary results on Pd/Pt (4/1) bimetallic clusters found by using the EXAFS (extend x-ray absorption fine structure) technique. Details of the EXAFS results as well as application of the concept of sequential potential field [18] to the present system will be reported elsewhere.

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