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# Nanoscopic Structure and Function of Polymer-Protected Metal Clusters

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**SUMMARY**: Colloidal dispersion of polymer-protected metal clusters were prepared by heat treatment of macromolecule-metal complexes, composed of water-soluble polymer and noble metal ions. The mixtures of two kinds of noble metal ions can provide polymer-protected bimetallic nanoclusters with a core/shell structure by the same procedure. In contrast, bimetallic clusters with the inverted core/shell structure are difficult to be prepared by the similar procedure. A sacrificial hydrogen strategy has been successfully proposed for the preparation of the inverted ones. When copper or nickel ions were used as one of the elements to prepare bimetallic clusters, rather random alloy structured nanoparticles were produced. The catalytic activity of these bimetallic clusters is, in general, higher than that of the corresponding monometallic ones.

## Introduction

Recently much attention has been paid to nanoscience and nanotechnology leading to nanodevices, because their developments are requested for the 21st century as an advanced information age. Polymer-protected metal clusters are expected to provide fundamental materials for nanoscience and nanotechnology.[1, 2)] Metal clusters can be prepared by both chemical and physical methods. The chemical method has an advantage for mass production. In the chemical method, metal ions are reduced by various kinds of reductants producing metal atoms, which aggregate to form metal clusters. Stabilizes are often used to stop the aggregation process at a certain stage and stabilize the metal clusters.

More than 20 years ago we developed an alcohol reduction method,[3, 4)] where alcohols were used as a mild reducing agent in the presence of water-soluble polymers. This method has advantages to produce metal clusters with rather uniform size easily. The size and shape of the metal clusters can be controlled by the reaction conditions. The metal clusters thus prepared work as active and selective catalysts. Here I would like to focus the control of

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nanoscopic structure and the relationship between structure and function, especially catalytic function of polymer-protected metal clusters. Among the metal clusters, bimetallic clusters are chosen as the object of the present topics.

## Nanoscopic Structure of Polymer-Protected Metal Clusters

The structure of polymer-protected metal clusters can be illustrated as Fig. 1, where the polymers were thought to adsorb physically on the surface of metal cluster particles. However, the detailed characterizations of the adsorbed polymer with IR[5] and XPS[6] have demonstrated that the polymers can coordinate to the metal forming rather strong chemical bonds. The polymer molecule can coordinate to the metal particle at multiple sites. Even though each coordination bond is weak, the multi-coordination results in the strong chemical adsorption of polymer molecule on the metal cluster surface.

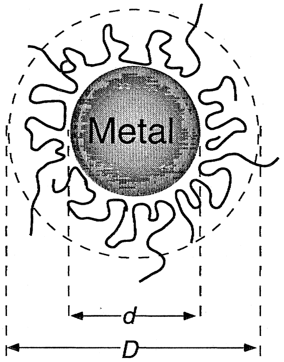

Fig. 1. Structure Model of Polymer-Protected Metal Cluster.

The size of the metal cluster (*d* in Fig. 1) can be easily measured with transmission electron microscopy (TEM). High resolution TEM can provide even the atomic distance in metal clusters. However, it is not easy to determine the entire size of polymer-protected metal cluster including the polymer envelope (*D* in Fig. 1). In the case of surfactant-protected metal clusters, a Taylor dispersion method can give a reasonable answer to the entire size.[7] If all the micelles contain a metal cluster in it, the scanning tunneling microscopy (STM) and/or atomic force microscopy (AEM) can be the method to give the entire size. However, these methods can not easily be applied to the polymer-protected metal clusters.

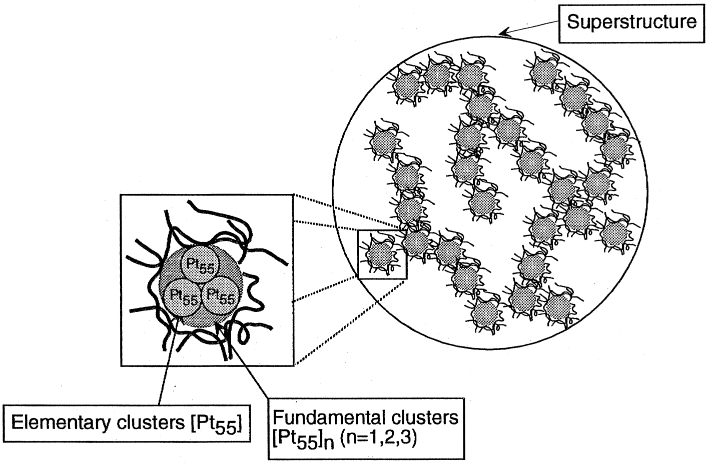

Fig. 2. Schematic Illustration of the Hierarchy of Self-Organization in Polymer-Protected Pt Cluster Dispersions.

Recently we have applied a small-angle X-ray scattering (SAXS) technique to the colloidal dispersion of polymer-protected Pt and Pt/Rh clusters. The SAXS results have demonstrated the regular structures in the colloidal dispersions. 8) Thus, the hierarchy in the regular structures in solution can be illustrated in Fig. 2 for example in the case of Pt. The superstructures illustrated in Fig. 2 could be constructed by physical crosslinkage among the polymers surrounding different metal cluster particles.

## Structure Control of Polymer-Protected Bimetallic Clusters

The polymer-protected bimetallic clusters, each particle of which involves both the elements, can be prepared by simultaneous or step-wise reduction of two kinds of metal ions in the presence of protecting polymers.2) The bimetallic clusters can have the various structures depending on preparation conditions, including core/shell, cluster-in-cluster, and random alloy. The simultaneous reduction cannot always result in the formation of bimetallic clusters. For example, simultaneous photoreduction of Au and Pt ions in the presence of surfactants result in the mixtures of Au and Pt monometallic clusters, while simultaneous alcohol reduction of Au and Pt ions in the presence of poly(*N*-vinyl-2-pyrrolidone)(PVP) produces the Au-core/Pt-shell bimetallic clusters.9) The step-wise alcohol reduction of Pd and then Au ions in the presence of PVP result in Au/Pd bimetallic clusters with cluster-in-cluster structures.10)

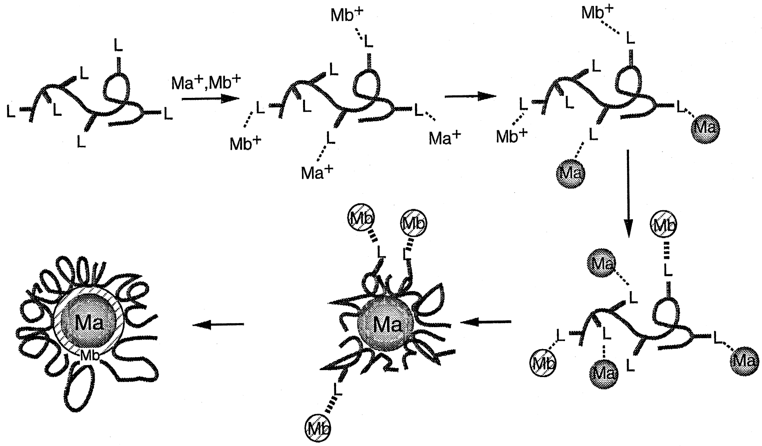

Fig. 3. Schematic Illustration of Formation Process of Core/shell-Structured Bimetallic Clusters.

The formation mechanism of core/shell-structured bimetallic clusters can be illustrated in Fig. 3. Thus, the redox potential of metal ions and the coordination ability of the protective polymer to metal atoms can control the structure. If the difference in both properties between the elements is not prompt, then the clear core/shell structure will not be produced but rather the bimetallic clusters with a cluster-in-cluster structure or a random structure will be formed, resulting at last in the formation of mixtures.

## Synthesis of Inverted Core/Shell Structured-Bimetallic Clusters

Since the core/shell structure can be produced by the above mechanism according to the difference in the properties of two elements, it is not so easy to produce the clusters with inverted core/shell structure, where the elements forming the core and shell in the usual core/shell structured clusters are inverted. The stepwise preparation procedure can not be applied to the synthesis of inverted core/shell-structured clusters, because the redox reaction between core metal clusters and additional metal ions occurs due to the redox potential difference.

Thus, we have recently developed a novel method to produce inverted core/shell-structured bimetallic clusters by using sacrificial hydrogen.[11)] The reaction process is illustrated in Fig. 4. The advantage of this method is based on the fasts that the reducing ability of hydride (hydrogen adsorbed on the surface of metal clusters) is higher than that of hydrogen dissolved in the solvent, and that atoms of the second metal are produced just on the surface of cluster particles of the first metal.

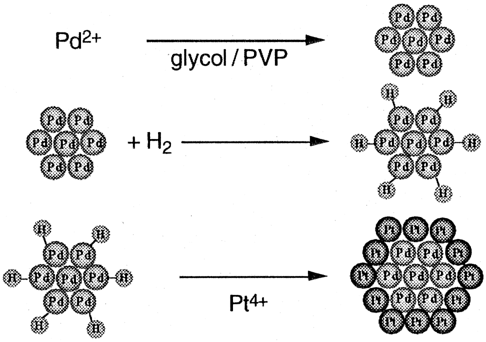

Fig. 4. Synthesis of Inverted Core/Shell-Structured Bimetallic Clusters by Succession Reduction Using Sacrificial Hydrogen.

## Catalysis of Bimetallic Clusters

Catalysis has been extensively studied and is one of the most interesting properties for bimetallic clusters. Surprisingly the catalytic activity of bimetallic clusters is almost always higher than that of the corresponding monometallic clusters. Here some examples are shown.

The first example is the case of Pt-core/Pd-shell-structured bimetallic clusters which have been prepared by the simultaneous reduction of Pt and Pd ions by alcohol in the presence of PVP.[12, 13)] The catalytic activity of the bimetallic clusters for the partial hydrogenation of 1,3-cyclooctadiene to cyclooctene depends on the composition of the clusters. Since Pt clusters have no activity and Pd clusters high activity, the Pd/Pt bimetallic clusters were through to have the activities just between the corresponding monometallic clusters. However, the catalytic activity of Pd/Pt bimetallic clusters increases from that of Pt clusters by increasing the content of Pd and has the maximum at Pd/Pt mole ratio of 4/1. The Pd/Pt(4/1) bimetallic clusters have more than twice activity of the Pd monometallic clusters. At this mole ratio (4/1), the bimetallic cluster is found to have a complete core/shell structure. That is, 13 Pt atoms forms a core, and 42 Pd atoms surrounds the core with one atomic layer forming the shell. Thus, all the Pd atoms, which are catalytically active, are located on the surface, and are neighbored by Pt atom(s), which are located at the center of the cluster particle forming a core. The high catalytic activity can be explained by the electronic effect of neighboring Pt on the surface Pd. If the catalytic activity is normalized by dividing the reaction rate by the number of surface Pd atoms, then the normalized catalytic activity is theoretically expected to be constant at all the range of Pd contents as shown in a broken line of Fig. 5. However, the observed normalized activity, shown in solid line in Fig. 5, is different from the expected one. This difference may suggest that some aggregation of the Pd atoms in the surface layer is required for the active catalysis for the hydrogenation.

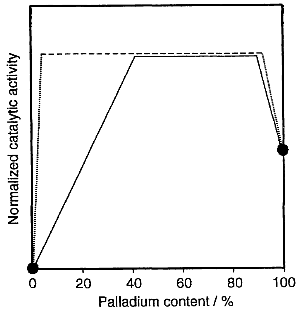

Fig. 5. Expected (broken line) and Observed (solid line) Catalytic Activity of Pt-Core/Pd-Shell-Structured Bimetallic Clusters.

Several kinds of core/shell-structured bimetallic clusters of noble metals as well as monometallic clusters have been prepared by the same method as the case of Pd/Pt bimetallic clusters, and been examined for the catalysis for visible-light-induced hydrogenation in the system of EDTA/tris(bipyridine) ruthenium(II) dichloride/methyl viologen/metal cluster.[14] The colloidal dispersions of Pt clusters had been known as the best catalyst for the above hydrogen generation.[15, 16] The bimetallic clusters involving Pt, however, are found more active than the Pt monometallic clusters, and the Pt/Ru bimetallic cluster is observed to be much more active than those examined before. In addition, the hydrogen generation rates of bimetallic and monometallic clusters of noble metals are nearly proportional to the electron transfer rates from methyl viologen cation radical to the metal cluster at a steady state. The high catalytic activity of the core/shell-structured bimetallic clusters is attributed to the electron localization due to the contact of two different elements, as illustrated in Fig. 6. The electron deficient surface atoms can more easily accept electron from methyl viologen cation radicals than the neutral surface atoms of monometallic clusters.

Inverted core/shell-structured bimetallic clusters are also applied to the catalysis for hydrogenation of olefine.[17] When the Pd core particle is covered by Pt atoms, the number of surface Pd atoms decreases, resulting in reduction of the catalytic activity. In fact, if the surface Pd atoms are completely covered by Pt atoms, then the catalytic activity almost disappears. In contrast, when only the small amount of Pt atoms deposit on the surface of the Pd cluster particle, the normalized catalytic activity of the surface Pd atom rather increases from that of monometallic Pd clusters. Thus, even the surface Pt atoms depositing on the Pd clusters can increase the catalytic activity of the remaining surface Pd atoms by the contact with Pt atoms, as discussed in the case of core/shell-structured bimetallic clusters (cf. Fig. 7).

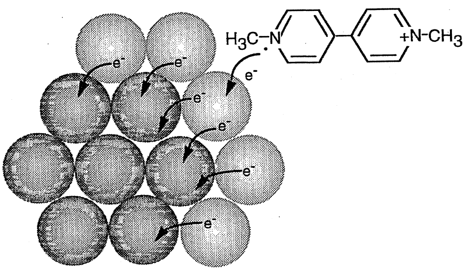

Fig. 6. Electronic Promotion Effect of Core Metal on the Electron Transfer Rate from Methyl Viologen Cation Radical to Surface Metal.

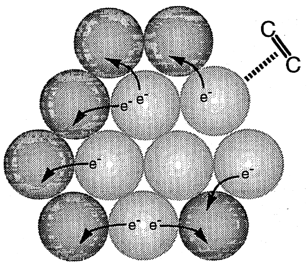

Fig. 7. Electronic Promotion Effect of Neighboring Metal on the Catalytic Activity of Surface Metal for Hydrogenation of Olefin.

In the case of bimetallic clusters having a random alloy structure, the catalytic activity increases by including the additional element. The examples are shown for selective hydration of acrylonitrile to acrylamide by Cu/Pd bimetallic clusters (Surface Cu atoms work as the catalyst.),[18, 19] partial hydrogenation of diene to monoene by Cu/Pd bimetallic clusters (Surface Pd atoms work as a catalyst.),[18, 19] and hydrogenation of olefin by Ni/Pd bimetallic clusters (Surface Pd atoms works as a catalyst.) [20, 21] as well.

## Conclusions

In the chemistry of polymer-protected metal clusters, the polymers play important roles for not only stabilizing the cluster but also controlling the structure and function. The catalytic function of the polymer-protected metal clusters depends on their nanoscopic structures, which include that of surrounding polymers and metal clusters. Especially the nanoscopic or atomic structures of the bimetallic cluster are very important for understanding catalytic function of polymer-protected bimetallic clusters.

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