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Novel synthesis, structure and catalysis of inverted core/shell structured Pd/Pt bimetallic nanoclusters

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Abstract. The catalytic properties of Pd-core/Pt-shell (inverted core/shell) structured bimetallic nanoclusters, synthesized by a successive addition method using sacrificial hydrogen, were investigated for hydrogenation of methyl acrylate. Partial deposition of Pt atoms on the surface of Pd nanoclusters can enhance the catalytic activity of the Pd atoms remaining in the surface of the inverted core/shell structured Pd/Pt bimetallic nanoclusters.

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1 Introduction

Recently, much attention has been paid to nanoscience and nanotechnology leading to nanodevices. Interests in the nanoscopic materials and their application to catalyses have greatly stimulated the research on metal nanoclusters [1–5]. Metal nanoclusters stabilized by organic molecules are now creating a new architecture of materials different from either conventional bulk materials or atoms, giving one of the smallest building blocks of matter. Most of the remarkable properties of metal nanoclusters are based on a high surface area and a quantum size effect.

Polymer-stabilized metal nanoclusters often act as an excellent homogeneous catalyst for many organic reactions. For example, palladium nanoclusters obtained by refluxing an alcohol/water solution of palladium ion in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) were used as an active catalyst for selective hydrogenation of cyclooctadienes [6]. PVP-stabilized noble metal nanoclusters were also effective catalysts for visible-light-induced hydrogen generation in the electron relay system of EDTA, tris(bipyridine)ruthenium(II), methyl viologen, and proton [7]. Poly(acrylic acid)-stabilized silver nanoclusters had higher catalytic activity than a commercial silver catalyst [8].

Multimetallic catalysts have widely been studied with a view to improve the quality of catalysts. Many investigations have focused on bimetallic catalysts to clarify the correlation of the catalytic behavior or the electronic structure with the alloy composition. Schmid *et al.* [9,10] reported a series of works on the preparation and catalytic properties of ligand-stabilized Au/Pd bimetallic nanoclusters by simultaneously dropping solutions of a metal and hydroxylamine to preformed metal nanoclusters. Au/Pd bimetallic nanoclusters were much more active than palladium monometallic nanoclusters as a catalyst for hydrogenation of hex-2-yne, although gold itself is well know to be inert to this reaction [10]. Simultaneous reduction of two kinds of noble metal ions by refluxing alcohol in the presence of PVP usually gave so-called core/shell structured bimetallic nanoclusters [11], in which atoms of the first element form a core and atoms of the second element cover the core to form a shell. This core/shell structure has been considered to be controlled by the order of redox potentials of both ions and of coordination ability of both atoms to PVP. In the case of a pair of palladium and platinum, Pt forms the core and Pd covers the core forming a shell, thus forming "Pt-core/Pd-shell" as a regular bimetallic structure.

In contrast the construction of a Pd-core/Pt-shell (inverted core/shell) structure is not so easy because Pd-core clusters can easily be solubilized by a redox reaction with the Pt ions later added with plans of covering the Pd-core with Pt atoms. We have succeeded in setting up a novel method using sacrificial hydrogen to control the core/shell structure [12]. This method was designed based on the following well-understood facts. Noble metals like Pd and Pt have the ability to adsorb hydrogen and split it to form metal hydride on the surface. Hydrogen atoms adsorbed on noble metals have a strong reducing ability, implying a low redox potential.

In this paper, we would like to report the details of characterization of PVP-stabilized Pd-core/Pt-shell bimetallic nanoclusters, and their catalytic properties for

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hydrogenation of methyl acrylate. To the best of our knowledge there is no report on catalytic studies of Pd-core/Pt-shell bimetallic nanoclusters. The catalytic properties of the inverted core/shell structured bimetallic nanoclusters can be explained by an electronic effect of adjacent Pt atoms on the surface Pd atoms.

2 Experiments

2.1 Preparation

Poly(*N*-vinyl-2-pyrrolidone) (PVP, average molecular weight 40,000, 45 mmol as monomeric residue) and palladium(II) acetate (1.21 mmol in 100 mL of dioxane) were dissolved in 600 mL of ethylene glycol in a 1,500-mL flask. The pH of mixtures was adjusted to 8 by adding an aqueous solution of NaOH (0.1 $\mathrm{mol\,L^{-1}}$) under stirring. The colloidal solution of Pd(II) hydroxide in ethylene glycol was stirred at 160 °C for 3 h for preparation of Pd nanoclusters with a nitrogen flow passing through the reaction system. The PVP-stabilized Pd nanoclusters in glycol were washed in an ultrafilter equipped with a membrane with water and ethanol under nitrogen, and were used as the cores for preparation of Pd-core/Pt-shell bimetallic nanoclusters.

The Pd-core nanoclusters (0.2 mmol of Pd) were dispersed in 150 mL mixtures of water, ethylene glycol and ethanol (1:1:1) in a 250-mL flask equipped with a dropping funnel which was charged with a degassed aqueous solution of potassium tetrachloroplatinate(II) (0.4 mmol in 100 mL of water). The reaction flask was connected with a hydrogen balloon and the dropping funnel as well. Air in the reaction flask was first replaced by hydrogen, and the Pd nanoclusters were treated with hydrogen under stirring for 2 h. The aqueous solution of potassium tetrachloroplatinate(II) was added into the reaction system drop by drop within about 6 h, and the reaction was continued for 8 h. The PVP-stabilized Pd-core/Pt-shell bimetallic nanoclusters, thus produced, were washed with water and methanol on the ultrafilter, and dried under vacuum at 40 °C.

2.2 Characterization

PVP-stabilized Pd-core/Pt-shell bimetallic nanoclusters were dispersed in dichloromethane. The dispersed solution was degassed by three freeze-thaw cycles, and filled with a CO gas. Infrared (IR) spectra were measured on a JEOL JIR-Winspec50 FTIR spectrophotometer. Pd-core/Pt-shell bimetallic nanoclusters employed here were characterized by transmission electron microscopy (TEM) at 100 kV on a Hitachi H-7000 electron microscope. Samples for TEM were prepared by placing a drop of the colloidal dispersion of nanoclusters onto a carbon-coated copper microgrid for high resolution TEM, followed by naturally evaporating the solvent. The mean diameter was calculated by counting the diameters of 200 particles with a magnifier (10 times) on the TEM photograph of 100,000 magnifications. X-ray photoelectron spectroscopy (XPS) data were measured with a Kratos AXIS-HS spectrometer (Mg target, 12 kV, 5 mA).

2.3 Catalysis

The catalytic activities of Pd-core/Pt-shell bimetallic nanoclusters were evaluated by the rate of hydrogenation of methyl acrylate. Ethanol dispersions of bimetallic nanoclusters (0.3 mL, 2.0×10 $\mathrm{L^{-4}}$ mmol of total metal) and ethanol (18.7 mL) were placed in a flask, the atmosphere of which was replaced in advance with hydrogen at an atmospheric pressure. The mixtures were kept at 30 °C for 2 h under stirring to activate the catalyst. Then, the ethanol solution (1 mL) containing 0.5 mmol of methyl acrylate was added to the mixtures keeping the total pressure at 1 atm. The reaction was traced by hydrogen uptake, with the initial slope of which the catalytic activities were determined.

3 Results and discussion

3.1 Characterization of Pd-core/Pt-shell bimetallic nanoclusters

Colloidal dispersions of Pd-core/Pt-shell (inverted core/shell) structured bimetallic nanoclusters were prepared by covering Pd-core nanoclusters with Pt atoms successively produced by sacrificial hydrogen adsorbed on the Pd nanoclusters. Fig. 1 depicts the relationship between the average particle diameter and the metal composition of Pd-core/Pt-shell bimetallic nanoclusters. Particle sizes of Pd-core/Pt-shell bimetallic nanoclusters are gradually increasing with increasing Pt content, since all Pd-core/Pt-shell bimetallic nanoclusters are prepared by using the same Pd monometallic nanoclusters as the core. The bimetallic nanoclusters are well separated from each other without heavy aggregation although some aggregates of two or three particles can be observed at a relatively high molar ratio of Pt, *e.g.*, at 67 mol% of Pt. This phenomenon may be caused by the relatively low PVP/metal ratio at the high total metal concentration and by the surface property of Pt particles. In fact the aggregation tendency was observed in the case of PVP-stabilized Pt monometallic nanoclusters [13].

The preformed metal cores of the first element are often oxidized by the metal ions of the second element added for making the shell, when the metal ions of the second element have a higher redox potential than those of the first element. X-ray photoelectron spectroscopy of the evaporated sample of Pd-core/Pt-shell bimetallic nanoclusters was measured in order to determine the valency of both elements. Palladium species of the bimetallic nanoclusters had a $3d_{5/2}$ binding energy of 335 eV. This is consistent with a metallic state of Pd [14], indicating the 0-valency of Pd in Pd-core/Pt-shell bimetallic nanoclusters. Platinum species had a $4f_{7/2}$ binding energy of 71 eV, showing the 0-valency of Pt.

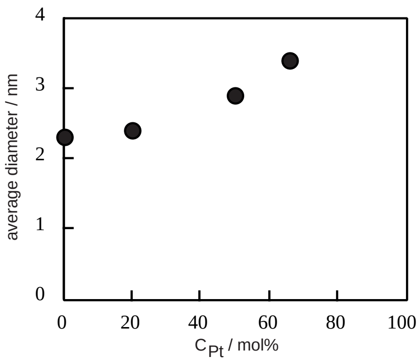

Fig. 1. Average diameter of Pd-core/Pt-shell bimetallic nanoclusters as a function of the platinum content.

An FT-IR spectrum of adsorbed CO (IR-CO) is useful for exploring the surface metal composition of bimetallic nanoclusters. Pd and Pt nanoclusters have been studied by this method [15,16]. Bradley *et al.* [17] studied the structure of Cu-Pd bimetallic nanoclusters by the IR-CO method as well as X-ray absorption spectroscopy. Fig. 2 shows IR spectra of CO adsorbed on Pd-core/Pt-shell bimetallic nanoclusters investigated here as well as those of monometallic Pd and Pt nanoclusters. Monometallic Pd nanoclusters (Fig. 2a) have a strong absorption band at 1941 cm^{-1}, assignable to a bridging adsorption band of CO adsorbed on the Pd surface, and a weak band at 2052 cm^{-1}, assignable to a linear adsorption band of CO adsorbed on the Pd surface. In contrast monometallic Pt nanoclusters (Fig. 2b) have a strong band at 2062 cm^{-1}, assignable to CO adsorbed in linear type on the Pt surface, and a very weak and broad band centered at about 1860 cm^{-1}, assignable to CO on a bridging site on the Pt surface. Fig. 2c shows the IR-CO spectrum of Pd-core/Pt-shell (1/1) bimetallic nanoclusters prepared by depositing Pt on the Pd core. Only the spectral feature of CO adsorbed on the Pt monometallic nanoclusters, *i.e.*, a strong band at 2068 cm^{-1} and a very weak broad band at 1892 cm^{-1}, can be observed, while that derived from CO adsorbed on Pd at 1941 cm^{-1} (Fig. 2a) completely disappeared, proving that the Pd core was completely covered by a Pt shell. In contrast, physical mixtures of Pd and Pt monometallic nanoclusters with a Pd/Pt ratio of 1/1 show spectral features of CO adsorbed on the Pd and Pt monometallic nanoclusters, respectively (Fig. 2d).

3.2 Catalysis of Pd-core/Pt-shell bimetallic nanoclusters

A colloidal dispersion of Pd nanoclusters acts as an effective catalyst for hydrogenation of olefins. The Pd/Pt (4/1) bimetallic nanoclusters with a regular core/shell (Pt-core/Pd-shell) structure have much higher catalytic activity than Pd monometallic nanoclusters [11]. Thus, the next question is how the catalytic activity of Pd-core/Pt-shell (inverted core/shell) structured bimetallic nanocluster is. Fig. 3 depicts the relationship between the metal composition and the catalytic activity of Pd-core/Pt-shell bimetallic nanoclusters for hydrogenation of methyl acrylate. Since Pt have low activity and Pd have high activity for hydrogenation as described above, Pd-core/Pt-shell bimetallic nanoclusters were thought to have the activities just between the two corresponding monometallic nanoclusters. However, the catalytic activities of Pd-core/Pt-shell bimetallic nanoclusters are lower than those expected at the molar ratio of less than 50 mol% of Pd, and are higher than those expected at the molar ratio more than 50% of Pd. The increment of catalytic activity from the linear correlation can be explained by an electronic effect of the neighboring Pt on the surface Pd. When the Pd core particles is mostly covered by Pt atoms, the number of surface Pd atoms decreases, resulting in decrease of the catalytic activity. In contrast, when only the small amount of Pt atoms deposit on the surface of the Pd nanocluster particle, catalytic activities of the Pd atoms still remaining on the surface of particles increase by an electronic effect of the neighboring Pt which has been deposited on the surface of particles.

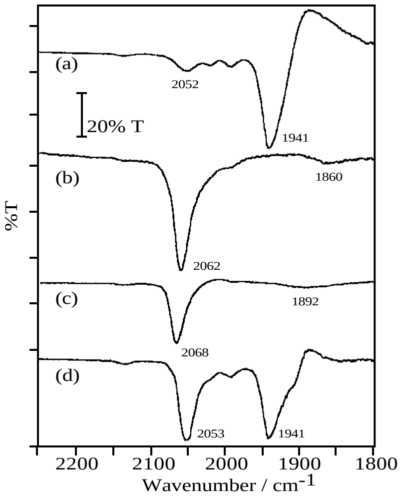

Fig. 2. Fourier transform infrared spectra of CO adsorbed on PVP-stabilized nanoclusters: (a) Pd, (b) Pt, (c) Pd-core/Pt-shell (1/1), and (d) physical mixture of Pd and Pt.

To examine the effect of the surface structure on catalyses, catalytic activities were normalized by division by the number of surface Pd atoms, which was estimated by the atomic ratio of Pd based on XPS data and the average diameter of particles measured by TEM. Thus, the catalytic activity of a Pd atom on the surface was calculated by dividing the total catalytic activity (R) by the number of surface Pd atoms. The number of surface Pd atoms can be calculated on the basis of both the degree of dispersion (D) of Pd-core/Pt-shell bimetallic nanoclusters and the ratio of Pd in the surface layer (C_{sPd}) determined by surface intensities ratios between Pd and Pt based on XPS data. The degree of dispersion can be calculated by

$$D = 1 - \frac{(d - 2.76 \times 2)^3}{d^3} \tag{1}$$

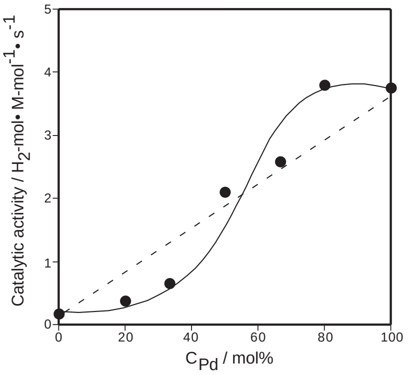

Fig. 3. Relationship between catalytic activity and metal composition of PVP-stabilized Pd-core/Pt-shell bimetallic nanoclusters for hydrogenation of methyl acrylate.

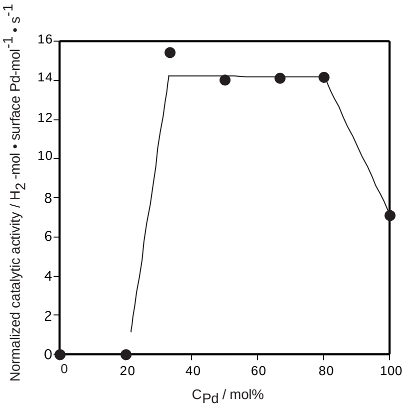

Fig. 4. Normalized catalytic activity as a function of metal composition of PVP-stabilized Pd-core/Pt-shell bimetallic nanoclusters.

where d is the diameter of the particle (Å) and the number 2.76 is the radius of platinum in Å. The normalized catalytic activity (R_{sPd}) is then calculated by equation (2)

$$R_{\mathrm{sPd}} = R/D \times C_{\mathrm{sPd}}. \tag{2}$$

Fig. 4 exhibits the relationship between the metal composition of bimetallic nanoclusters and the normalized catalytic activity. The activity of a surface Pd atom (normalized activity) is almost constant for Pd-core/Pt-shell bimetallic nanoclusters between 30 and 80 mol% of Pd, and is higher than that of Pd monometallic nanoclusters. This could be attributed to the enhancement of the catalytic activity of surface Pd atoms by an electronic effect by the neighboring Pt. The similar increment of catalytic activity of the surface Pd atom by the neighboring Pt has been observed in Pt-core/Pd-shell (regular core/shell) structured bimetallic nanoclusters as described before [11]. Thus, even the surface Pt atoms depositing on the Pd nanoclusters can increase the catalytic activity of the remaining surface Pd atoms by contact with Pt atoms.

4 Conclusion

Polymer-stabilized Pd-core/Pt-shell (inverted core/ shell) structured bimetallic nanoclusters were synthesized by addition of Pt ions into the dispersion of Pd-core hydrides prepared by treatment of Pd-core nanoclusters with molecular hydrogen. Structures of Pd-core/Pt-shell bimetallic nanoclusters have been confirmed by FT-IR spectra of adsorbed CO molecules. The IR-CO method has shown that Pd-core/Pt-shell bimetallic nanoclusters are not mixtures of monometallic Pd and Pt nanoclusters, but consist of a single particle containing both elements. In Pd-core/Pt-shell (1/1) bimetallic nanoclusters the Pd-core was partially covered by a Pt shell. The catalytic properties of Pd-core/Pt-shell bimetallic nanoclusters were investigated for hydrogenation of methyl acrylate under mild conditions. The presence of Pt atoms on the surface of Pd particle in the inverted core/shell structured Pd/Pt bimetallic nanoclusters can enhance the catalytic activity of Pd atoms on the surface.

References

1. G. Schmid, in *Clusters and Colloids* (VCH Publishers, Weinheim, 1994).
2. J.H. Fendler, in *Nanoparticles and Nanostructured Films* (WILEY-VCH, Weinheim, 1998).
3. H. Bönnemann, W. Brijoux, in *Advanced Catalysts and Nanostructured Materials* (Academic Press, New York, 1996).
4. H. Hirai, N. Toshima, in *Polymeric Materials Encyclopedia* (CRC Press, Boca Raton, 1996), p. 1310.
5. N. Toshima, T. Yonezawa, New J. Chem. **22**, 1179 (1998).
6. H. Hirai, H. Chawanya, N. Toshima, Bull. Chem. Soc. Jpn. **58**, 682 (1985).
7. N. Toshima, K. Hirakawa, Polym. J. **31**, 1127 (1999).
8. Y. Shiraishi, N. Toshima, Coll. Surf. A **169**, 59 (2000).
9. G. Schmid, A. Lehnert, J.O. Halm, J.O. Bovin, Angew. Chem., Int. Ed. Engl. **30**, 874 (1991).
10. G. Schmid, H. West, J.O. Halm, J.O. Bovin, C. Grenthe, Chem. Eur. J. **2**, 1099 (1996).
11. N. Toshima, T. Yonezawa, K. Kushiashi, J. Chem. Soc., Faraday Trans. **89**, 2537 (1993).
12. Y. Wang, N. Toshima, J. Phys. Chem. B **101**, 5301 (1997).
13. Y. Shiraishi, M. Nakayama, E. Takagi, T. Tominaga, N. Toshima, Inorg. Chim. Acta **300-302**, 964 (2000).
14. C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, MN, 1978).
15. M.R. Mucalo, R.P. Cooney, J. Chem. Soc., Faraday Trans. **87**, 1221 (1991).
16. L.N. Lewis, N. Lewis, J. Am. Chem. Soc. **108**, 7228 (1986).
17. J.S. Bradley, G.H. Via, L. Bonnevio, E.W. Hill, Chem. Mater. **8**, 1895 (1996).