Synthesis and Catalysis of Colloidal Dispersions of Pd/Ni Bimetallic Clusters

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Pd/Ni bimetallic clusters have been successfully prepared for the first time by a polyol reduction method, in which a mixed solution of Pd and Ni salts were reduced at high temperature by ethylene glycol. The bimetallic clusters are proved by TEM, XRD and preliminary EXAFS analysis to have an alloy structure. The bimetallic clusters show much higher catalytic activity for hydrogenation of nitrobenzene to aniline under mild conditions than the monometallic Pd or Ni clusters.

Nanoscopic metal particles, i.e., metal clusters are of great importance in respect to their specific properties being different from bulk metals.[1] The dispersions of noble metal clusters, both mono-[2,3] and bi-[4-9]metallic ones, can easily be obtained by the reduction of noble metal ions in water in the presence of water-soluble polymers, such as poly(N-vinyl-2-pyrrolidone) (PVP), under mild reaction conditions, for example, only refluxing with alcohol. Clusters and colloids of less noble metals are much more difficult to be generated. In recent publications we have reported the synthesis and characterization of PVP-protected Pd/Cu clusters by using a modified polyol reduction method at high temperature.[10,11] However, the study of more attractive nickel-containing bimetallic clusters has been hampered by the even lower redox potential of nickel (E^0 (Ni^{2+}/Ni^0) = -0.257 V) than that of copper (E^0 (Cu^{2+}/Cu^0) = 0.342 V). The generation of nickel fine particles by a chemical method has been proved to be very difficult. For example, the reduction of nickel salts by using such a strong reductant as borohydrides was reported giving only nickel boride particles instead of nickel particles,[12] although the similar method can give copper colloids.[13] In the present study, we have audaciously and successively expanded the uses of the above mentioned polyol reduction method into the preparation of PVP-protected Pd/Ni bimetallic clusters. To the best of our knowledge, this is the first report of Pd/Ni clusters in the 1-2 nm size range. It was also found that they have remarkably high catalytic activity under mild reaction conditions for the hydrogenation of nitrobenzene to aniline, one of the important industrial processes.

The PVP-protected Pd/Ni bimetallic colloidal dispersions were prepared by following procedure: PVP (K-30, MW: 40000, 4.006 g) and nickel sulfate ($NiSO_4 \cdot 7H_2O$) were dissolved in 600 cm^3 of glycol at 80 ℃. To this solution, the dioxane solution of palladium(II) acetate was added at 0-5 ℃, followed by adjusting the reading of pH meter to 9-11 by dropwise addition of NaOH (1 mol dm^{-3}). The total amount of the two metal ions was always kept constant at 2.5 mmol. The solutions were stirred and refluxed under nitrogen flow at 198 ℃ for 2 h, resulting in the well-dispersed and stable dark-brown colloidal dispersion of the bimetallic clusters. PVP-protected Pd and Ni colloidal dispersions were also obtained by the similar procedure.

Transmission electron micrograph of the obtained dispersions revealed fine particles with uniform size and narrow size distribution when the Pd mole content is within the range of 20-80%, while aggregation phenomenon was rarely observed. Figure 1 shows the transmission electron micrograph of the Pd/Ni(1/1) bimetallic clusters. The particles mainly distribute within the range from 1.6 to 2.0 nm in diameter with average diameter of 1.89 nm. This observation suggests the formation of alloy structure.

The X-ray diffraction patterns of the PVP-protected monometallic and Pd/Ni bimetallic clusters are depicted in Figure 2. The diffraction pattern of Pd/Ni bimetallic clusters is clearly different from that of monometallic clusters, and different from the physical mixture of PVP-protected Pd or Ni clusters as well. These differences clearly demonstrate that the obtained Pd/Ni bimetallic clusters have an alloy structure and are different from a simple physical mixture of the correspond monometallic clusters.

Extended X-ray absorption fine structure (EXAFS), a powerful characterization method for the decision of alloy structure, at the National Laboratory for High Energy Physics (KEK) was also used for the structural analysis of the Pd/Ni bimetallic clusters. Figure 3 shows the k^3-weighted Fourier-transformed EXAFS spectra at Pd K-edge of the Pd foil, Pd/Ni(1/1) foil and the colloidal dispersions of the Pd/Ni bimetallic clusters with Pd/Ni ratios at 3/2, 1/1 and 2/3. The main peak at 2.5 Å for Pd foil can be assigned to a Pd-Pd bond. In the case of Pd/Ni(1/1) foil, the main peak shifted to the place at about 2.1 Å, while only a small shoulder peak at 2.5 Å was observed. This new peak at 2.1 Å can be attributed to a Pd-Ni bond. In a series of EXAFS spectra of Pd/Ni (3/2, 1/1, and 2/3) bimetallic clusters, the height of the main peak at 2.5 Å decreases with decreasing Pd/Ni ratio, almost splitting into two peaks at ca. 2.5 and 2.1 Å. These preliminary results can support the concept that both Pd-Pd and Pd-Ni bonds exist at the same time within each particle of Pd/Ni bimetallic clusters. This concept could be consistent with the results obtained by x-ray diffraction experiments.

Hydrogenation of nitrobenzene catalyzed by PVP-protected Pd/Ni bimetallic colloids was carried out in ethanol at 30 ℃ under 1 atm of hydrogen. Products were analyzed with gas

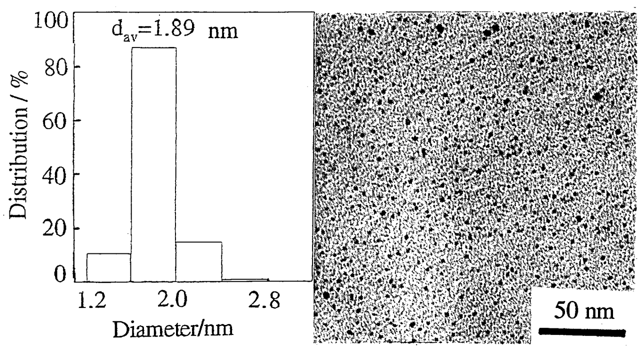

Figure 1. Transmission electron micrograph of PVP-protected Pd/Ni(1/1) clusters.

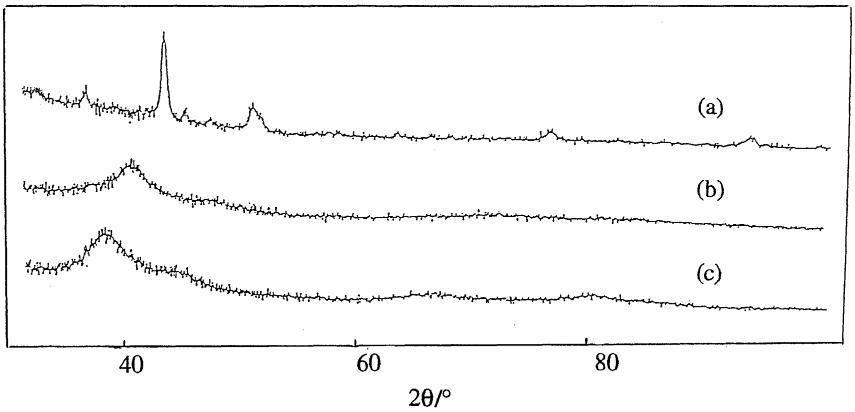

Figure 2. X-ray diffraction patterns of PVP-protected (a) Ni, (b) Pd/Ni(1/1), and (c) Pd clusters.

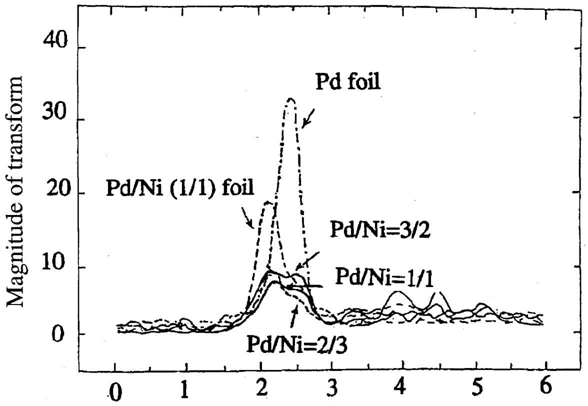

Figure 3. Fourier-transformed EXAFS spectra at Pd K-edge of the Pd foil, Pd/Ni(1/1) foil, and the colloidal dispersions of the pd/Ni bimetallic clusters at Pd/Ni ratio=3/2, 1/1, and 2/3.

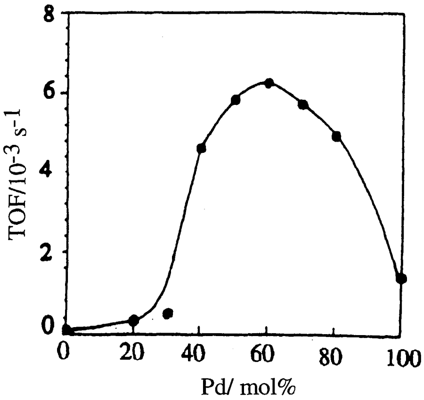

Figure 4. The relationship between the metal composition and the catalytic activity of the colloidal dispersions of Pd/Ni bimetallic clusters for the hydrogenation of nitrobenzene. [Nitrobenzene]=4.7×10^{-2}mol.dm^{-3}, [catalyst]=1.0×10^{-2}mol.dm^{-3}, p (H_2)=1 atm in ethanol at 30℃.

chromatography (PEG 20, 140 ℃) and infrared spectra, being proved to be aniline. The plot of catalytic activity (expressed by turnover frequency) versus the Pd/Ni ratio is shown in Figure 4, which reveals that Pd/Ni clusters with Pd ratios range from 40 to 80% show much higher catalytic activity than both Ni and Pd monometallic clusters, and that Pd/Ni(3/2) colloid shows the highest catalytic activity, ca. 4.2 times the value of monometallic Pd clusters in the present experiments. This plot also clearly demonstrates that the colloidal dispersions of bimetallic Pd/Ni clusters are not mixtures of the two monometallic clusters, but each cluster particle contains both Pd and Ni atoms, forming a kind of alloy structure. The interaction between Pd and Ni in a cluster particle could affect the catalytic activity. Further studies related to this preliminary successful result, including the structural consideration of metal clusters with respect to their catalytic activity by detailed EXAFS analysis and the evaluation of ferromagnetic properties, are in progress.

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