# Nanoscopic Naked Cu/Pd Powder as Air-Resistant Active Catalyst for Selective Hydration of Acrylonitrile to Acrylamide

## Yuan Wang, Hanfan Liu, and Naoki Toshima*

*Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China; Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan; and Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onoda-shi, Yamaguchi 756, Japan*

Nanoscopic naked Cu/Pd alloy powders, particle size in 1−5 nm, were prepared by a cold alloying process. The formation of nanoscopic bimetallic hydroxide colloids as precursors of the nanoscopic alloy powders was studied by means of TEM, XRD, and a titration method. These bimetallic alloy powders have provided the first example of Cu-based catalysts with high activity, selectivity, and stability against air for the selective hydration of acrylonitrile to acrylamide.

## Introduction

Study on the nanoscopic materials has become a challenging subject for chemists, physicists, and materials scientists. Metallic materials with small particle size (1−5 nm) are often prepared as colloids or large clusters by using a chemical process in the presence of protective ligands, surfactants, protective polymers, or inorganic supports, and usually from very dilute solutions.[1−9] Nanoscopic metal or alloy powders can also be prepared by a physical process called inert gas condensation technique,[10] in which very higher temperature must be used to evaporate metal. The inert gas condensation technique provides nanoscopic metal powders with average diameter of 5−10 nm and very clean surface. Studies on the physical properties of such powders have attracted much attention. Because the properties of nanoscopic metal and alloy materials are greatly dependent on their particle sizes,[1,11] it is reasonable to believe that a method able to decrease the particle size of naked metal or alloy to a range less than 5 nm is helpful for investigations on the properties of nanoscopic metallic materials. Little has been reported on naked metal or alloy powders of 1−5 nm prepared by using a chemical process, especially on that composed of a noble metal and a light transition metal, although many unusual processes generate metal or alloy in micron or submicron size.[12] On the other hand, bimetallic catalysts have become the subject of intensive efforts both in academia and industries, special properties of which are derived from an electronic ligand effect and a structural ensemble effect. For understanding the relationship between the structure and catalytic property of bimetallic catalysts, ligand-free nanoscopic alloy material should be favorable, although hurdles in preparation must be overcome, because the protective agent always causes limitation in the application of surface analytical techniques and may have some contribution to the catalytic properties.

We have succeeded in the preparation of poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Cu/Pd and Cu/Pt bimetallic colloids by using a cold alloying process (below 200 °C).[9] Here we report an unexpected finding that in the absence of PVP, naked Cu/Pd alloy powders in nanometer size can be obtained by using the cold alloying process, although the absence of protective colloids usually gives a big mass of precipitates by aggregation. The present cold alloying process can provide a convenient way with universal application to prepare other naked nanoscopic alloy materials composed of a noble metal and a light transition metal. The Cu/Pd alloy catalyst, thus prepared, works as a very effective catalyst for selective hydration of acrylonitrile to acrylamide and is characterized by air resistance, while Cu catalysts used for the hydration are usually airsensitive. Different from colloidal dispersions, the catalyst is easy to be separated from the reaction system after the reaction.

## Experimental Section

**Material and Equipment.** All reagents had at least a level of GR and were used without further purification. Transmission electron microscopy (TEM) photographs were taken by using a Hitachi H-7000 electron microscope. The particle size was measured from enlarged TEM photographs by using a magnifier with a magnifying power of 10 times. X-ray diffraction (XRD) patterns were recorded by a Rigaku Rint 2400 diffractometer at 40 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) data were measured on a JEOL JPS-90 SX photoelectron spectrometer.

**Preparation of Naked Nanoscopic Cu/Pd Bimetallic Powder.** In a typical preparation, $CuSO_4 \cdot 5H_2O$ (2 g, 8 mmol) was dissolved in 200 cm$^3$ of glycol at 80 °C. The temperature was then decreased to the range of 0−3 °C. Palladium acetate (0.599 g, 2.67 mmol, in 40 cm$^3$ of dioxane) was added to the solution, followed by adjusting the pH to about 10 by adding an aqueous solution of NaOH (1.0 mol dm$^{-3}$). A color change occurred from yellow to green in this process. Refluxing the obtained mixture at 198 °C for 3 h with a nitrogen flow passing through the reaction system to take away water and organic byproducts produced a black precipitate. The precipitate was filtered with a 0.2 $\mu$m membrane filter under nitrogen atmosphere and dried under vacuum. The isolated yield is about 96%.

**Hydration of Acrylonitrile to Acrylamide.** To an aqueous dispersion (25 cm$^3$) of Cu/Pd bimetallic powder (0.2 g), acrylonitrile (0.3 cm$^3$) was added at 78 °C under nitrogen for the reaction. The products were analyzed by a gas chromatography.[9]

**Hydrogenation of *cis,cis*-1,3-Cyclooctadiene.** The bimetallic powder (Pd content, 0.132 mmol) and 20 cm$^3$ of ethanol were added into a flask, the atmosphere of which was replaced in advance with hydrogen at atmospheric pressure. The

---
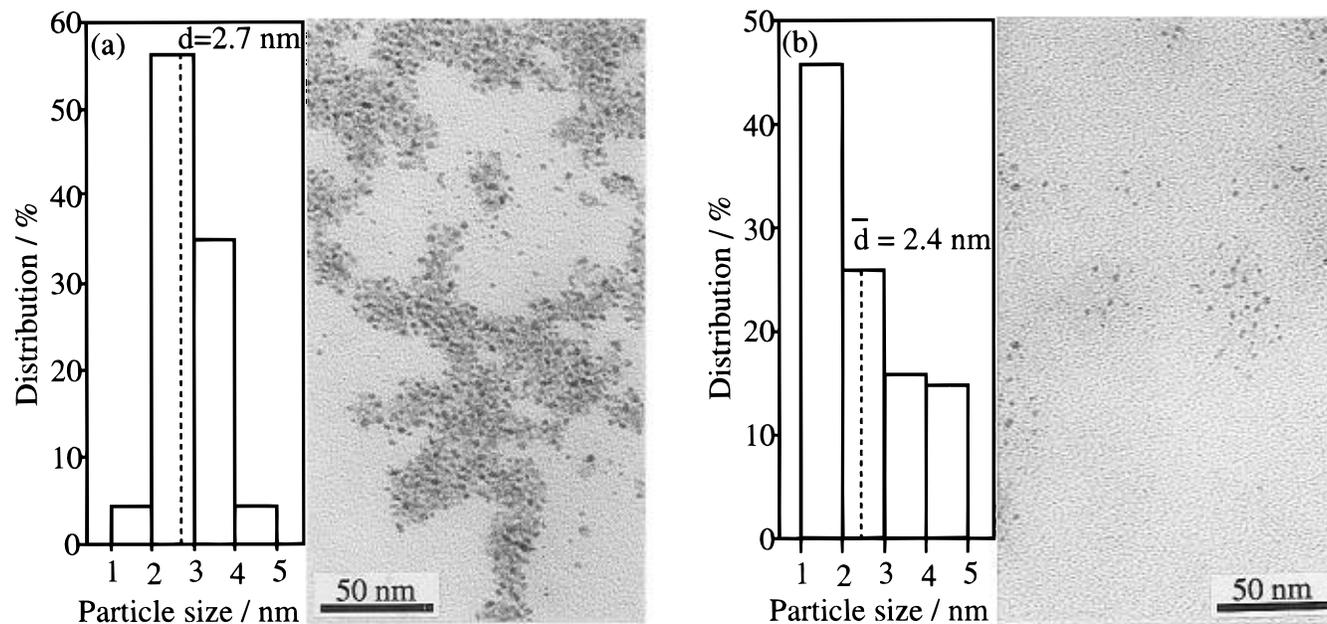
**Figure 1.** Transmission electron micrographs and size distributions of nanoscopic Cu/Pd bimetallic powders: (a) Cu/Pd (3/1), (b) Cu/Pd (2/1).

mixtures were stirred for 1 h at 30 °C to activate the catalyst. Then, to the mixture, an ethanol solution (1 cm³) containing 0.58 mmol of *cis,cis*-1,3-cyclooctadiene was added keeping the total pressure at 1 atm. The progress of the hydrogenation was followed by hydrogen uptake under atmospheric pressure.

### Results and Discussion

**Preparation and Characterization of Nanoscopic Cu/Pd Alloy Powders.** The polyol process technology developed by Fievet and co-workers[12b] provided a convenient way to prepare metal powder in micron or submicron size. In the polyol process, powdering metal oxides of Cu, Ni, Co, or noble metal were reduced to prepare fine metal powders in micron or submicron range by refluxing polyol at about 200 °C. In order to decrease the size of metal particles and search for an available method to obtain nanoscopic bimetallic alloy powder containing a noble metal and a light transition metal, we modify the polyol process by dissolving the corresponding metal salts in a polyol and adjusting the pH value to about 10−11. In this process, nanoscopic bimetallic hydroxide colloids are produced (vide infra). The nanoscopic bimetallic hydroxide particles are then reduced to prepare nanoscopic alloy powders by refluxing polyol with a nitrogen flow passing through the reaction system to take away water and organic byproducts.

Figure 1 shows the TEM images and size distributions of Cu/Pd (3/1) and Cu/Pd (2/1) bimetallic powders. The TEM samples were prepared by dispersing the powders into water containing poly(*N*-vinyl-2-pyrrolidone). Particle sizes of the bimetallic powders distribute in the range of 1−5 nm in the both cases and the average diameter is 2.7 and 2.4 nm, respectively. The unusual ultrafine characteristic is believed to be due to, as one of benefits, the formation of bimetallic hydroxide colloid as the precursor. Particles of the Cu/Pd (2/1) hydroxide colloid, measured by TEM, are distributed in size within the range of 1−4 nm with an average diameter of 1.9 nm (Figure 2). Thus, it can be speculated that in the present reduction process, each colloidal particle of the bimetallic hydroxide is reduced to form a bimetallic cluster, and several of the former bimetallic clusters aggregate together to form a particle of the nanoscopic bimetallic powder. This is different from the usual reduction and aggregation process for preparing metal and alloy particles from metal ions in solution, in which
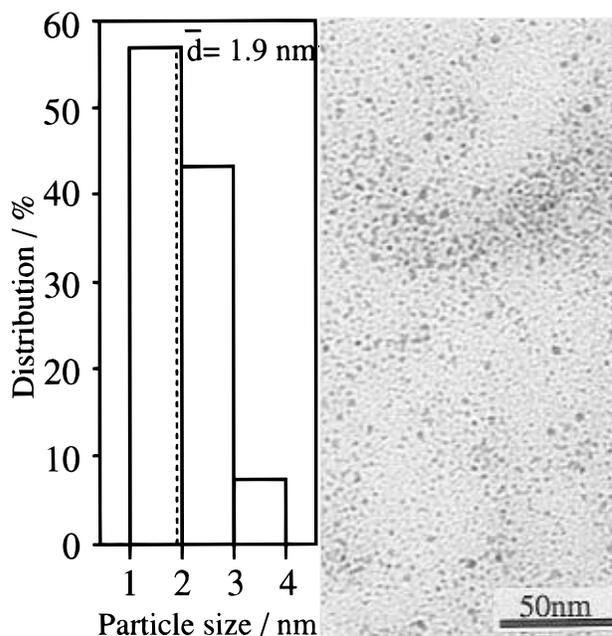


**Figure 2.** TEM micrograph and size distribution of Cu/Pd (2/1) hydroxide colloid.

the particle size is controlled by the ratio of speeds of crystal nucleus formation and the growth of crystal grains, and the structure of formed bimetallic particles strongly depends on the redox potential of each metal element.

The formation of copper hydroxide colloid in water solution has been well studied.[13] The reaction process of $CuSO_4 \cdot 5H_2O$ and $Pd(OAc)_2$ with NaOH in glycol was followed by titration of the corresponding glycol solutions of the metal salts with an aqueous solution of NaOH as shown in Figure 3. From Figure 3, it can be clearly seen that the pH values of the solutions dramatically increase when the ratio of $OH^-$ to $M^{2+}$ reaching the value near 2, and both $CuSO_4 \cdot 5H_2O$ and $Pd(OAc)_2$ can react with NaOH at the pH lower than 6. Because the practical operation for the preparation of Cu/Pd bimetallic hydroxide colloid in this work was conducted by adding excess amount of aqueous solution of NaOH to the glycol solution of $CuSO_4 \cdot 5H_2O$ and $Pd(OAc)_2$, and the pH at beginning of this operation was higher than 6, in the practical

Nanoscopic Naked Cu/Pd Powder

*J. Phys. Chem., Vol. 100, No. 50, 1996* **19535**
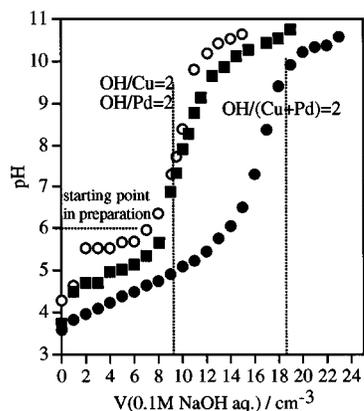


**Figure 3.** Titration curve of metal salts. Solvent, glycol (150 cm³) containing dioxane (10 cm³); aqueous solution of NaOH (0.1 mol dm⁻³); temperature, 0−3 °C. ○, Copper sulfate (0.46 mmol); ■, palladium acetate (0.46 mmol); ●, mixture of copper sulfate (0.46 mmol) and palladium acetate (0.46 mmol).

process, copper and palladium hydroxide species should form at the same time without selectivity. Aggregation of these metal hydroxide species will produce colloidal particles homogeneously composed of $Cu^{2+}$, $Pd^{2+}$, and $OH^-$ ions that we called as Cu/Pd bimetallic hydroxide colloid. The colloidal particles of copper hydroxide and Cu/Pd bimetallic hydroxide were separated from the colloidal solutions and dried under vacuum. XRD measurements for the nanoscopic metal and bimetallic hydroxide revealed that the diffraction pattern of the Cu/Pd bimetallic hydroxide colloidal particles has no strong diffraction peak and does not contain the signals in the diffraction pattern of the copper hydroxide colloidal particles, proving that the Cu/Pd bimetallic hydroxide colloid is not a simple mixture of copper hydroxide and palladium hydroxide or oxide colloids.

In the present process, both $Cu^{2+}$ and $Pd^{2+}$ ions can be completely reduced to the state of zero valence, as verified by the measurements of XPS, Auger spectra, IR, atomic absorption spectroscopy (AAS), and XRD. XPS measurements were carried out for a Cu/Pd (2/1) bimetallic powder. The sample was transferred into the machine under nitrogen atmosphere and measured under vacuum at $2.7 \times 10^{-6}$ Pa. Figure 4 shows the XPS spectra of the bimetallic Cu/Pd (2/1) powder and the binding energies of Cu and Pd in the bimetallic powder are listed in Table 1. Table 1 reveals that the $3d_{5/2}$ binding energy of Pd in the Cu/Pd bimetallic powder and that in a palladium powder prepared by the similar method have a value of 335.4 and 335.5 eV, respectively, indicating a metallic state of Pd in both cases. Copper species in copper powder prepared by a similar method and that in the Cu/Pd bimetallic powder have a $2p_{3/2}$ binding energy of 932.7 and 932.6 eV, respectively, both with 1.6 eV of half-width, suggesting that the valence states of Cu are less than 2 in both cases, which is confirmed by the absence of the shake-up line in the Cu 2p photoelectron region of $Cu^{2+}$ compounds.[14,15] It is well-known that the $L_3M_{45}M_{45}$ Auger line of Cu is suitable for distinguishing $Cu^+$ from $Cu^0$ species. Cu atoms in the Cu powder have been proved to be in a zero-valent metallic state by this technique.[9] The observed Auger line $CuL_3M_{45}M_{45}$ of Cu species in the Cu powder has a value of 918.8 eV (kinetic energy) with a modified Auger parameter of 1851.3 eV, which agree well with those reported for Cu metal, 918.2 and 1851.6 eV, respectively, but are quite different from those for $Cu_2O$, 916.0 and 1849.1 eV.[15] Unfortunately, the signal of this line in the Cu/Pd bimetallic powder cannot be clearly observed due to the existence of the strong peak of Pd 3d electron at the same region.
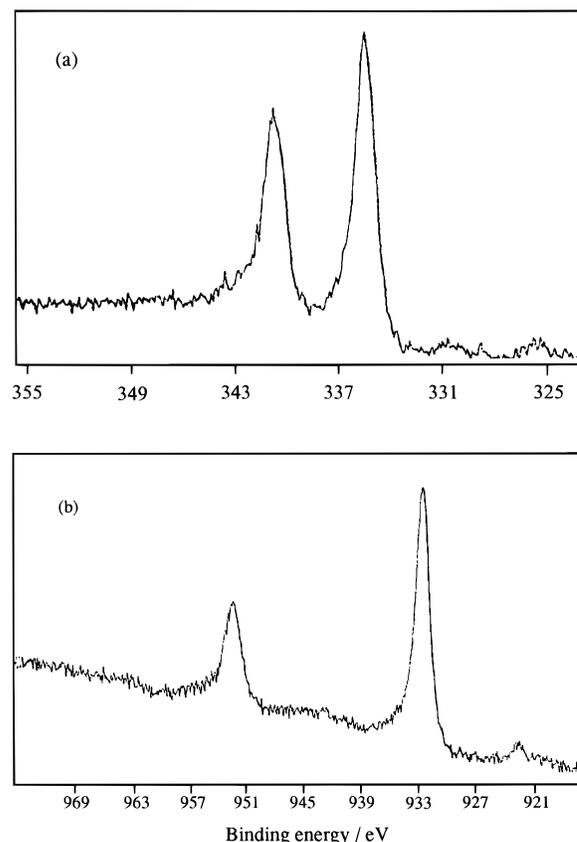


**Figure 4.** XPS spectra of Pd and Cu in Cu/Pd (2/1) bimetallic powder: (a) Pd 3d band, (b) Cu 2p band.

**TABLE 1: XPS Data of Nanoscopic Cu/Pd (2/1) Alloy Powder**

| sample | BE (eV) | | ref |
| | Cu $2p_{3/2}$ | Pd $3d_{5/2}$ | |
| --- | --- | --- | --- |
| Cu | 933.1 | | 15 |
| $Cu_2O$ | 933.1 | | 15 |
| CuO | 934.0 | | 15 |
| Pd | | 335.5 | 15 |
| PdO | | 336.4 | 15 |
| Cu/Pd(2/1) | 932.6 | 335.5 | this work |
| Pd | | 335.4 | this work |
| Cu | 932.8 | | this work |
| $C_{1s}$ (graphite) | $284.2 \pm 0.2$ | | |

The IR spectra of Cu metal and its oxides have been well studied,[16] which provide an effective method to distinguish Cu metal from its oxides. The IR spectrum of the Cu/Pd (3/1) powder does not have any absorption peak in the range from 500 to 650 cm⁻¹, while the spectrum of $Cu_2O$ with the same amount of Cu has a very strong absorption peak at about 627 cm⁻¹. The XPS and IR characterization results rule out the possibility that there exists copper oxide in the nanoscopic Cu/Pd powder.

The metal composition of the bimetallic powder was measured by atomic absorption spectroscopy. The bimetallic powder prepared with a charged Cu/Pd ratio of 3 had a metal composition of 99.8% with a Cu/Pd ratio of 3.04.

X-ray diffraction measurements were carried out in order to investigate the alloy structure of the bimetallic powder. Figure 5 shows the XRD diffraction diagrams of nanoscopic Cu/Pd bimetallic powders at various ratios of Cu to Pd, and that of Pd and Cu powder prepared by the same method. In pattern a (Figure 5), the following peaks assignable to Cu at the positions of 43.36° (43.3°), 50.46° (50.3°), 74.16° (73.8°), and 89.96°, and in pattern e (Figure 5) the peaks assignable to Pd at the positions at 39.96° (40.0°), 46.48° (46.4°), 68.00° (67.8°),

**19536** *J. Phys. Chem., Vol. 100, No. 50, 1996*

Wang et al.
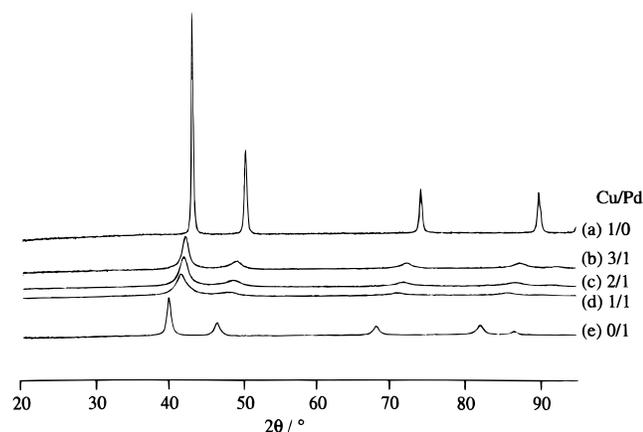


**Figure 5.** X-ray diffractograms of ultrafine powders: (a) Cu, (b) Cu/Pd (3/1), (c) Cu/Pd (2/1), (d) Cu/Pd (1/1), and (e) Pd.

**TABLE 2: X-ray Diffraction Lines of Cu/Pd Nanoscopic Alloy Powder**

| | $d$(0.1 nm) at various $hkl$ values | | | |
|---|---|---|---|---|
| compd | 111 | 200 | 311 | ref |
| Cu | 2.09x | 1.815 | 1.090 | 17 |
| Pd | 2.25x | 1.954 | 1.383 | 17 |
| Cu₃Pd | 2.13x | 1.869 | 1.12x | 17 |
| Cu₂O | 2.47x | 2.144 | | 17 |
| CuO | 2.32x | | | 17 |
| Cu/Pd (3/1) | 2.135 | 1.857 | 1.117 | this work |
| Cu | 2.085 | 1.807 | 1.090 | this work |
| Pd | 2.254 | 1.952 | 1.377 | this work |

81.92°, and 86.48° can be observed, where the numbers in parentheses are cited from literature.[17] The pattern b of Cu/Pd powder at Cu/Pd ratio of 3 exhibits diffraction lines at $2\theta$: 42.30°, 49.00°, 72.04°, and 87.19°, agreeing well with that of a Cu₃Pd phase (see Table 2). It is well-known that copper and palladium are miscible over their entire composition range. For the disordered fcc phase of Cu/Pd, the lattice constant increases monotonically with increasing content of palladium.[18] Such a kind of shift in the position of the X-ray diffraction lines can be observed in the present bimetallic powder system as shown in Figures 5 and 6. No diffraction line for Cu, Pd, CuO, Cu₂O, and PdO exists in the X-ray diffraction patterns of the bimetallic powders. From these results, it can be concluded that the structure of the nanoscopic bimetallic particles is a Cu/Pd alloy or solid solution.

## Catalytic Properties

Hydration of acrylonitrile to acrylamide, an important industrial process, has been the subject of many patents and academic publications.[19] Copper-based catalysts exhibit high activity and selectivity to acrylamide accompanied by a serious problem of high sensitivity to air. Copper oxide and MnO₂ have been found to have good selectivity for the formation of acrylamide and high stability to air,[20] but their activities are too low for the industrial application. The catalytic properties of the present nanoscopic Cu/Pd bimetallic powder for the hydration reaction were examined. The results are listed in Table 3. The average catalytic activity within 2 h of the bimetallic catalyst (Cu/Pd = 2) is about 21 times higher than that of the Cu powder prepared by the same method. When the reaction continued for 4 h over the Cu/Pd (Cu/Pd = 2) powder catalyst, the yield of acrylamide increased up to 95%. No cyanohydrin was detected during the reaction, suggesting a nearly 100% selectivity. The average catalytic activity, up to a yield of 84%, of the bimetallic powder Cu/Pd (2/1) (1.1 mol amide·mol Cu⁻¹·h⁻¹) is close to that (1.3
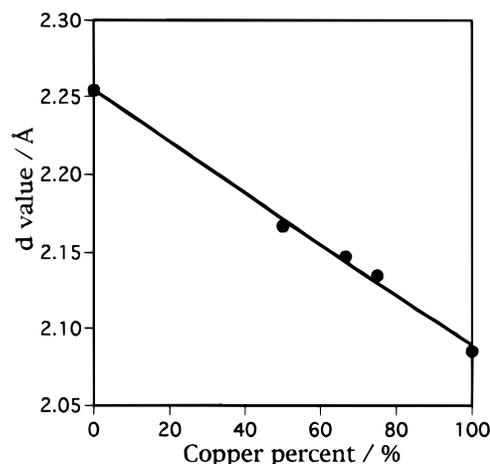


**Figure 6.** Plot of $d$(111) value of nanoscopic bimetallic Cu/Pd powder vs Cu/Pd ratio.

**TABLE 3: Hydration of Acrylonitrile to Acrylamide Catalyzed by Cu/Pd and Cu Powder Catalysts[a]**

| catalyst | repeated no.[b] | amount of catalyst (g) | acrylonitrile (M) | time (h) | yield (%) | selectivity (%) |
|---|---|---|---|---|---|---|
| Cu/Pd | 1 | 0.200 | 0.18 | 2 | 84 | >99.6 |
| | 2 | 0.195 | 0.18 | 2 | 85 | >99.6 |
| | 3 | 0.190 | 0.18 | 2 | 83 | >99.6 |
| Cu | 1 | 0.109 | 0.18 | 4 | 8 | 97 |
| | 2 | 0.090 | 0.18 | 4 | 2 | |

[a] Reaction was conducted at 79 °C in water (25 cm³) under nitrogen. [b] Catalysts were recovered and washed under air for the repeated use.

mol amide·mol Cu⁻¹·h⁻¹) of the PVP-protected Cu/Pd (2/1) bimetallic colloid.[9] The present nanoscopic powdering catalysts can be easily separated from the reaction system by filtration, while the PVP-protected bimetallic colloidal catalyst cannot be separated by the simple filtration. There exists a net weak attractive interaction between the naked metal particles, which gives rise to loosely bound aggregators. This net attractive interaction is so weak that primary metal particles can be dispersed again in the presence of PVP as proved by the TEM measurements. The bimetallic catalyst recovered and washed under air maintains its activity and selectivity almost completely, showing a good stability against oxygen, while the catalytic activity of the Cu powder recovered under air is about only $^1/_3$ of that of the original Cu powder catalyst (see Table 3). To the best of our knowledge, this is the first published example of a highly active and selective catalyst with good stability against air for this process. We have not yet found a satisfactory explanation for the good stability against air of the present Cu/Pd catalyst. There is a possibility that the Pd atoms in the surface of the Cu/Pd powder prevent the Cu atoms from deep oxidation, and the coordination of the C=C double bond of acrylonitrile to the Pd atom of the Cu/Pd particle makes the CN bond close to the Cu species in the surface of the bimetallic powder, thus facilitating the hydration catalyzed by the Cu species.

The existence of Pd atoms on the surface of the bimetallic powder is confirmed by its good catalytic properties for selective hydrogenation of *cis*,*cis*-1,3-cyclooctadiene. The activity and selectivity strongly depend on the ratio of Cu/Pd as shown in Figure 7. The catalytic properties of the bimetallic powder for the hydration and hydrogenation reactions do demonstrate again the formation of the bimetallic structure.

## Conclusion

A cold alloying process for preparing naked nanoscopic Cu/Pd bimetallic powder (1−5 nm) is described in this paper, which

Nanoscopic Naked Cu/Pd Powder

*J. Phys. Chem., Vol. 100, No. 50, 1996* **19537**
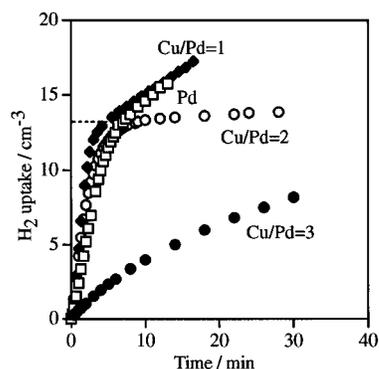


**Figure 7.** Time courses of hydrogenation of 1,3-cyclooctadiene catalyzed by the ultrafine powder catalysts: Cu/Pd (1/1) (◆), Cu/Pd (2/1) (○), Cu/Pd (3/1) (●), and Pd (□). Reaction conditions were as follows: temperature, 30 °C; $H_2$ pressure, 1 atm; solvent, 21 cm³ of ethanol; Pd content, 0.131 mmol; COD, 0.58 mmol.

is different from the usual reduction and aggregation process for the preparation of metal particles from metal ions in solution but is characterized by formation of bimetallic hydroxide colloid before the reduction process. The bimetallic powder has been characterized by XRD, IR, AAS, XPS, and its catalytic properties. Both Cu and Pd are reduced to a valence state of zero in the present process and the structure of the bimetallic Cu/Pd powder is Cu/Pd alloy or solid solution. Catalytic properties of the bimetallic powder for selective hydration of acrylonitrile to acrylamide and for selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctaene have been studied. In the hydration reaction, the bimetallic powder catalyst exhibits good stability against air and high activity as well as high selectivity for the formation of acrylamide. In the hydrogenation reaction, both the activity and selectivity are strongly dependent on the Cu/Pd ratio.

## References and Notes

(1) Schmid, G., Ed. *Clusters and Colloids*; VCH: Weinheim, Germany, 1994; *Chem. Rev.* **1992**, *92*, 1709.
(2) Klabunde, K. J.; Tan, B. J. *Chem. Mater.* **1991**, *3*, 30.
(3) Bradley, J. S.; Will, E. W.; Klein, C.; Chaudret, B.; Duteil, A. *Chem. Mater.* **1993**, *5*, 2540.
(4) Bönnemann, H.; Brijoux, W.; Brinkmann, K.; Binjus, E.; Fretzen, R.; Joussen, T.; Korall, B. *J. Mol. Catal.* **1992**, *74*, 323.
(5) Hirai, H.; Nakao, Y.; Toshima, N. *J. Macromol. Sci., Chem.* **1979**, *A13*, 727.
(6) Toshima, N.; Yonezawa, T.; Kushihashi, K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2537.
(7) Wang, Y.; Liu, H. *Polym. Bull.* **1991**, *25*, 139.
(8) Esumi, E.; Tano, T.; Torigoe, K.; Meguro, K. *Chem. Mater.* **1990**, *2*, 564.
(9) Toshima, N.; Wang, Y. *Chem. Lett.* **1993**, 1611. Toshima, N.; Wang, Y. *Langmuir* **1994**, *10*, 4574.
(10) (a) Granqvist, C. G.; Buhrman, R. A. *J. Appl. Phys.* **1976**, *47*, 2200. (b) Zhu, X.; Birringer, R.; Herr, U.; Gleiter, H. *Phys. Rev.* **1987**, *B35*, 9085.
(11) Hirai, H.; Toshima, N. *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press Inc.: Boca Raton, FL, 1996; Vol. 2/C, p 1310.
(12) For example: (a) Bönnemann, H.; Brujoux, W.; Joussen, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 273. (b) Fievet, F.; Lagier, J. P.; Blin, B. *Solid State Ionics* **1989**, *32/33*, 198. (c) Fievet, F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, *14*, 29. (d) Matijević, E. *Faraday Discuss. Chem.* **1991**, *92*, 229. (e) Matijetić, E. *Chem. Mater.* **1993**, *5*, 412.
(13) Yokoi, H.; Kawate, S.; Iwaizumi, M. *J. Am. Chem. Soc.* **1986**, *108*, 3358.
(14) Haber, J.; Machej, T.; Ungier, L.; Ziolkowski, J. *J. Solid State Chem.* **1987**, *25*, 207.
(15) Briggs, D., Seach, M. P., Eds. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; John Wiley & Sons: New York, 1983.
(16) Bentley, F. F.; Smithson, L. D.; Rozek, A. L. *Infrared Spectra and Characteristic Frequencies 7000−3000 cm⁻¹*; John Wiley & Sons: New York, 1968; p 103.
(17) Powder Diffraction File Hanawalt Search Manual: Inorganic Phase, Set, 1−42, Internation Centre for Diffraction Data, PA, 1992.
(18) Pearson, W. B. *A Handbook of Lattice Spacings and Structures of Metal and Alloys*; Pergamon: London, 1976.
(19) For example see: (a) Hayashi, H.; Nishi, H.; Watanabe, Y.; Okazaki, T. *J. Catal.* **1981**, *69*, 44. (b) Funabiki, T.; Yamashita, H.; Yase, M.; Omatsu, T.; Yoshida, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2133.
(20) Miura, H.; Sugiyama, K.; Kawakami, S.; Aoyama, T.; Matsuda, T. *Chem. Lett.* **1982**, 183.

JP961877G