PREPARATION AND STRUCTURE OF Pd-Cu BIMETALLIC NANOPARTICLES BY ULTRASONIC IRRADIATION

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Abstract

We tried to prepare Pd-Cu bimetallic nanoparticles by use of ultrasonic cavitation in aqueous solution. In the processes of sonochemically reducing Pd(II) and Cu(II) ions, the Pd(II) ions remained in the solution were determined by spectrophotometer. To analyse the composition and structure of the prepared nanoparticles, X-ray analyses and microscopic analyses were done. These results indicated the formation of Pd-Cu bimetallic nanoparticles. In addition, the catalytic activities of products were estimated by hydrogenation of 4-pentenoic acid. The rate of hydrogenation decreased with increasing Cu ratio in the nanoparticles, suggesting the formation of Pd core and Cu shell bimetallic nanoparticles.

Introduction

It is known that nano-size metal particles have different functions from corresponding bulk-size metals. So the control of particle size and the complex consisted of more than one kind of metal are actively studied. We have found that sonochemically prepared metal particles such as Pd, Au, and Pt are of nanometer size with a fairly narrow distribution. These nanoparticles were odtained from reducing their metal ions in the aqueous solution with the special reduction system using ultrasound.

The formation of nanoparticles can be affected by the physicochemical effects of cavitation bubbles which are generated by ultrasonic irradiation in aqueous solution. The synthesis of bimetallic nanoparticles was also reported[1]. By selecting the combination of metal ions and a kind of surfactant contained in solution, the nanoparticles of alloy sonochemically obtained are divided into the random type and the core/shell type. Moreover, the mixture of unit particles may be obtained. We have investigated to prepare Pd-Cu bimetallic nanoparticles by reduction of Pd(II) and Cu(II) ions in aqueous solution using ultrasound. The reduction rate of Pd(II) ions was estimated spectroscopically, and the sonochemical products were analysed on their compositions and structures. Moreover, hydrogenation of 4-pentenoic acid was performed to evaluate the catalytic activities of the sonochemically prepared nanoparticles.

Experimental Section

Ultrasonic irradiation was carried out using a multiwave ultrasonic generator operated at 200kHz and a barium titanate oscillator of 65mm in diameter[2]. A cylindrical glass vessel(50mm inner diameter) with a total volume of 190ml was used for ultrasonic irradiation. The vessel had an arm with a silicon rubber septum that permits sample extraction without exposing the sample to air. The bottom of the vessel was planar and 1mm in thickness. The vessel was fixed at a constant position from the oscillator. During sonication, the vessel was closed and soaked in water bath which temperature was kept constant(about 25ºC). The irradiation setup is shown in Figure 1.

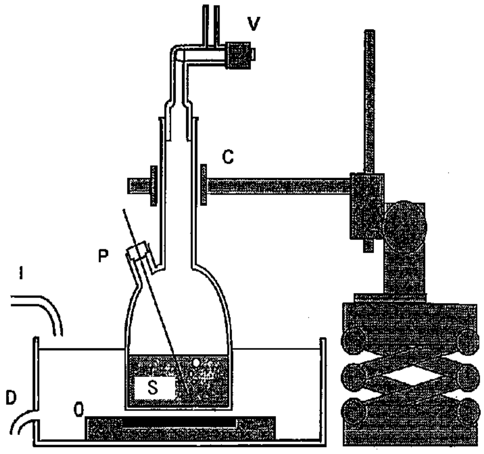

Figure 1 Ultrasonic irradiation setup (V:valve, C: clamp, P:septum, I:water inlet S:sample solution, O:oscillator, D: water outlet)

The sample solution(60ml) composed of 1.0mM $PdCl_2 \cdot 2NaCl \cdot 3H_2O$, 0.4mM poly(ethylene(40)glycol monostearate)(PEG(40)-MS), and 1.0-10mM Cu(II) ($(CH_3COO)_2Cu$ or $(HCOO)_2Cu$) in glass vessel were prepared. Before ultrasound irradiation, Ar-gas was injected into the vessel containing the sample solution at 50ml/min for 30minutes to remove air.

The amount of Pd(II) ions remained in the solution after each irradiation time was determined by a colorimetric method[1] and then the reduction rate of Pd(II) ions was estimated. The addition of saturated NaI solution (1/10 of the exposed sample in volume) to the sample solution resulted in the formation of Pd(II)-iodide complex with large absorbance at λ=408nm and the aggregation of Pd particles. Then the aggregated particles containing Pd were removed by filtration.

Samples for electron microscopes were prepared by drying droplets of dispertion colloid on a carbon-supported copper mesh in a vacuum. The images of the products and the element mapping analysis were carried out with a field emission-scanning electron microscope(FE-SEM). The FE-SEM was equipped with a energy-dispersive X-ray spectroscopic analyser(EDS).

The hydrogenation was carried out by using the conventional vacuum line equipped with a digital manometer. The round glass vessel which had a silicon rubber septum for injection of 4-pentenoic acid was used for the hydrogenation. A colloidal dispersion(30ml) containing 3ml of the extracted sample after ultrasound irradiation and 27ml of water was kept to attain the equilibrium state under 101.3kPa(1atm) of hydrogen for 60minutes at room temprature. Then, the hydrogen in the vacuum line was extracted. After hydrogen gas of 101.3kPa was introduced into the vaccum line of reaction system again, 200μl of 4-pentenoic acid was injected into the vessel containing the prepared sample. The experiment was carried out at 25±1°C stirring the sample in the reaction vessel at 101.3kPa of hydrogen.

Results and Discussion

Figure 2 shows the change in the concentration of Pd(II) ions in the sample solutions with 1.0mM or 8.0mM of $(CH_3COO)_2Cu$ during ultrasonic irradiation. The solid lines in Figure 2 show the parts of linear decrease in concentration of Pd(II) ions. Then, the reduction rate of Pd(II) was estimated from the linear change of Pd(II). Thus, the concentration of $(CH_3COO)_2Cu$ or $(HCOO)_2Cu$ included in the starting solution was changed from 1.0mM to 10mM, and the works as above were done. Figure 3 shows the change in the reduction rate of Pd(II) ions as a function of Cu(II) concentration for $(CH_3COO)_2Cu$ or $(HCOO)_2Cu$. The reduction rate of Pd(II) speedily decreased as the concentration of Cu(II) increased. Then the reduction rate of Pd(II) ions became constant at a Cu(II) concentration of more than 3.0mM for $(CH_3COO)_2Cu$ and of more than 4.0mM for $(HCOO)_2Cu$.

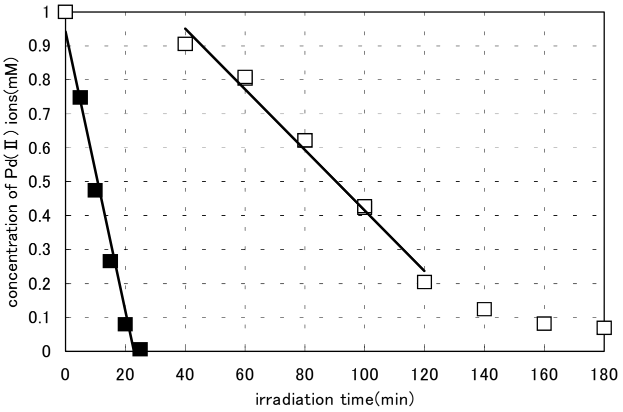

Figure 2 Change in concentration of Pd(II) ions under ultrasonic irradiation (■: 1.0mM $(CH_3COO)_2Cu$, □: 8.0mM $(CH_3COO)_2Cu$ with 1.0mM $PdCl_2$ and 0.4mM PEG(40)-MS)

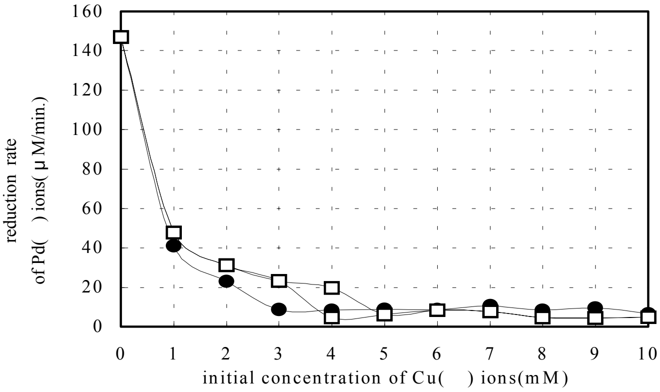

Figure 3 Effect of the initial concentration of Cu(II) ions on the reduction rate of Pd(II) ions under ultrasonic irradiation in the sample solution containing $(CH_3COO)_2Cu$(●) or $(HCOO)_2Cu$(□) with 1.0mM $PdCl_2$ and 0.4mM PEG(40)-MS by control of initial concentration of Cu(II)

Figure 4a)-c) show the FE-SEM images of the nano-particles obtained from the sample solutions as follows:a)1.0mM $PdCl_2$ and 0.4mM PEG(40)-MS (sonicated for 10min), b)1.0mM $PdCl_2$, 1.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 20min), c) 1.0mM $PdCl_2$, 8.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 180min)

Figure 4a) shows the dispersion state of Pd nanoparticles. In Figure 4b), particles of about 100nm aggregates, but the particles of smaller size seem to be composed than 100nm. As seen in Figure 4c), a mass with irregular shapes is formed over the entire image, probably, due to the very slow reduction rate of Pd(II) as shown in Figure 3.

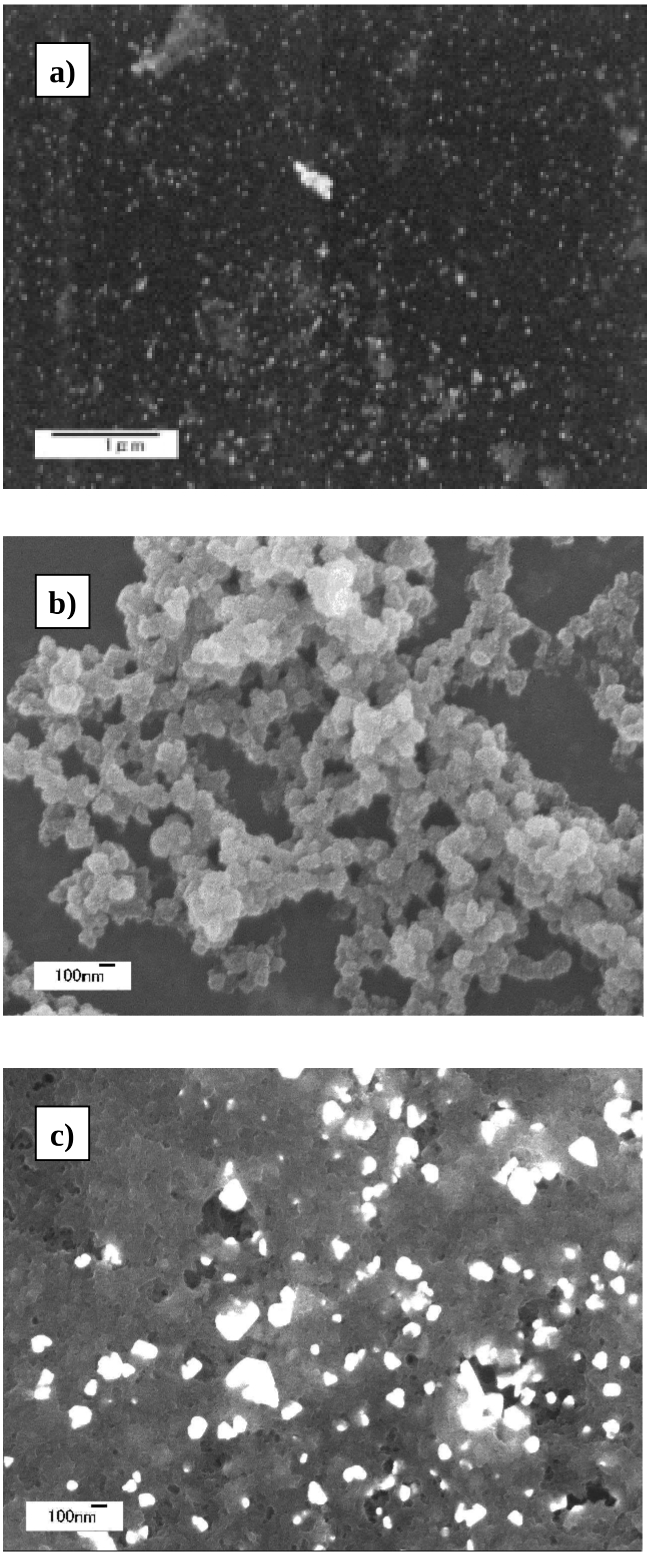

Figure 4 FE-SEM images of the products : **a)**1.0mM $PdCl_2$ and 0.4mM PEG(40)-MS (sonicated for 10min), **b)**1.0mM $PdCl_2$, 1.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 20min), **c)** 1.0mM $PdCl_2$, 8.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 180min)

The element mapping analysis was carried out for the products from irradiation by using EDS. The composition of the product obtained from the solution containing 1.0mM $PdCl_2$, 1.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 20 min) was almost composed of Pd, and only Cu was detected for the composition of the sample containing 1.0mM $PdCl_2$, 8.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 180 min) had the surface consisted of Cu mostly.

Figure 5 shows the time variation of hydrogen pressure(initial pressure:101.3kPa) for three different sample(□:1.0mM $PdCl_2$, 0.4mM PEG(40)-MS (sonicated for 10min),■:1.0mM $PdCl_2$, 1.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 20min), ▲:1.0mM $PdCl_2$, 8.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 180min)). The catalytic activity in the products from the sample solution containing Cu(II) decreases remarkably in compare to that of Pd nanoparticles with high catalytic activity for the hydrogenation of 4-pentenoic acid. The product obtained from the sample solution containing only Cu(II) ions had no catalytic activity in hydrogenation. From the result obtained, it was suggested that the structure of nanoparticles obtained from the sample solution containing Pd(II) and Cu(II) was Pd core/Cu shell type.

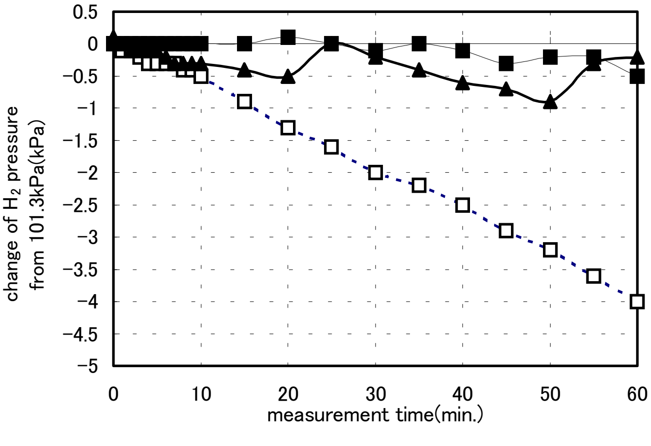

Figure 5 The catalytic activities for hydrogenation of 4-pentenoic acid (□:1.0mM $PdCl_2$, 0.4mM PEG(40)-MS (sonicated for 10min),■:1.0mM $PdCl_2$, 1.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 20min), ▲:1.0mM $PdCl_2$, 8.0mM $(CH_3COO)_2Cu$, and 0.4mM PEG(40)-MS (sonicated for 180min))

Conclusion

1. The reduction rate of 1mM Pd(II) ions decreased remarkably with increasing Cu(II) concentration and then levelled off independent of Cu(II) concentration.

2. From FE-SEM images, the morphology of the product formed at a small concentration of Cu(II) was the aggregation of particles of less than 100nm in size, that at a high concentration of Cu(II) was the mass with irregular shapes.
3. From the result of EDS, the product obtained from the solution containing 1.0mM Cu(II) consisted of almost Cu, and only Cu was detected for the product obtained from the sample solution containing 8.0mM Cu(II).
4. From the result of catalytic activity, the structure of nanoparticles obtained from the sample solution containing Pd(II) and Cu(II) was Pd core/Cu shell.

References

[1] Y. Mizukoshi, T. Fujimoto, Y. Nagata, R. Oshima, and Y. Maeda, "J. Phys. Chem. B," vol. 104, pp. 6028-6032, 2000

[2] K. Okitsu, H. Bandow, Y. Maeda, and Y. Nagata, Chem. Mater., vol 8, pp.315-317, 1996.