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Preparation and Characterization of Bimetallic Pd–Cu Colloids by Thermal Decomposition of Their Acetate Compounds in Organic Solvents

Kunio Esumi,* Takafumi Tano, Kanjiro Torigoe, and Kenjiro Meguro

Department of Applied Chemistry, Institute of Colloid and Interface Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

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Bimetallic Pd–Cu/Cu_2O colloids are prepared by the thermal decomposition of their acetates dissolved in methyl isobutyl ketone and bromobenzene. In methyl isobutyl ketone, the average diameter of Pd–Cu_2O colloids decreases from about 130 to 50 nm with an increase of molar fraction of palladium acetate, while in bromobenzene the size of Pd–Cu colloids increases from about 8 to 15 nm. The composition of Pd–Cu or Pd–Cu_2O colloids is almost the same as that of the feed ratio of their acetates. The dispersion stability of these colloids is further addressed by measuring their ζ potentials.

Introduction

Colloidal particles are prepared by a variety of methods, which can be classified mainly into liquid- and vapor-phase processes.[1,2]

The liquid-phase process has been applied to many precious-metal systems,[3-6] and fine particles have also been obtained by using water/oil microemulsions.[7-9] However, most of this work has been limited to the use of aqueous solutions.

We have recently developed a new method to prepare precious metal particles by the thermal decomposition of their organometallic compounds in organic solvents.[10,11] In particular, monodispersed palladium particles have been obtained by the thermal decomposition of palladium acetate in methyl isobutyl ketone. The dispersion stability of these particles in methyl isobutyl ketone is quite high[11] due to the strong electrical repulsion between the particles.

In this study, we apply this new method to prepare bimetallic Pd–Cu particles in organic solvents. The Pd–Cu particles obtained are characterized by transmission electron microscopy and electron probe microanalysis (EPMA). Their surface properties are further studied by measuring their ζ potentials.

Experimental Section

Materials. Palladium acetate was donated by Tanaka Kikinzoku Kogyo Co., and copper(II) acetate was obtained from Wako Pure Chemical Ind. The organic solvents used were toluene, methyl isobutyl ketone, *o*-xylene, *p*-xylene, and bromobenzene. They were extrapure grades and used as received.

Preparation of Cu and Pd–Cu Colloids. To determine if the thermal decomposition of copper(II) acetate would occur, 2×10^{-5} mol of copper(II) acetate was dissolved in various organic solvents (40 mL) and their solutions were refluxed at their boiling points for 20 min. In the decomposition of palladium acetate, it has already been reported[11] that the critical thermal decomposition temperature of palladium acetate ranges between 110 and 116 °C in organic solvents.

Table I. Thermal Decomposition of Copper(II) Acetate in Various Organic Solvents

solvt	bp, °C	dipole moment, D	thermal dec	color	stability
toluene	110.6	0.37	*a*		
methyl isobutyl ketone	115.9	2.7[f]	*b*	yellow	*c*
p-xylene	138.4	0	*b*	yellow	*e*
o-xylene	144.4	0.44	*b*	yellow	*e*
bromobenzene	156.1	1.71	*b*	brown	*d*

[a] No colloid formation. [b] Colloid formation. [c] Very stable but precipitates within a few weeks. [d] Precipitates within a few days. [e] Precipitates immediately. [f] Dipole moment of methyl *n*-butyl ketone.

In the preparation of bimetallic Pd–Cu colloids, palladium acetate and copper(II) acetate in various proportions were dissolved in the organic solvents, and their solutions were refluxed as described above. The mixed ratios of palladium acetate and copper(II) acetate were as follows: 1:5, 2:4, 3:3, 4:2, and 5:1. The total concentration of the mixed acetates was 0.5 mmol dm^{-3}, and the refluxing time was 20 min.

The elemental ratios of Pd/Cu in Pd–Cu colloids were estimated from EPMA and absorption spectra. About 50 particles were analyzed for EPMA. The estimation was carried out as follows: after the decomposition of the mixed acetates, the suspension was centrifuged, and the concentrations of unreacted acetates in the supernatant were determined by using a UV–vis spectrophotometer (220A, Hitachi Co.). Here, the concentrations of respective acetates, which have absorption bands at 400 nm for palladium acetate in methyl isobutyl ketone and bromobenzene and at 690 nm for copper(II) acetate in the two solvents, were estimated from standard calibration. The differences in the initial and unreacted acetate concentrations were used to determine the elemental ratios of Pd/Cu in the Pd–Cu colloids.

The particle sizes were determined by transmission electron microscopy with a Hitachi H 800 microscope. The selected area electron diffraction patterns of the particles were also recorded. The X-ray diffraction measurements of the powder samples were carried out by a Geigerflex recording X-ray diffractometer Model RAD-B (Rigaku Denki Co., Ltd.). The thermal decomposition products of palladium acetate and copper(II) acetate in organic solvents were analyzed by gas chromatography (GA-7A, Shimadzu). Electrophoresis was used to determine the electrophoretic mobility required to calculate the ζ potential. The measurements were made in a glass–Teflon flat cell using the Laser Zee Meter Model 500 made by Pen Kem Co. The mobility values were converted to ζ potentials by using the Hückel equation. The

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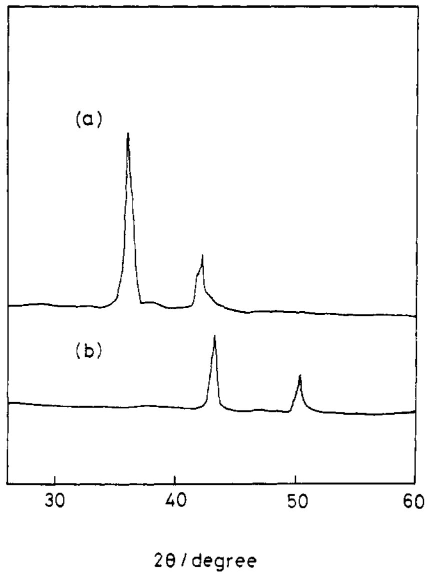

Figure 1. X-ray diffraction diagrams of Cu/Cu_2O samples: (a) powder samples prepared in methyl isobutyl ketone or *o*-xylene; (b) powder sample prepared in bromobenzene.

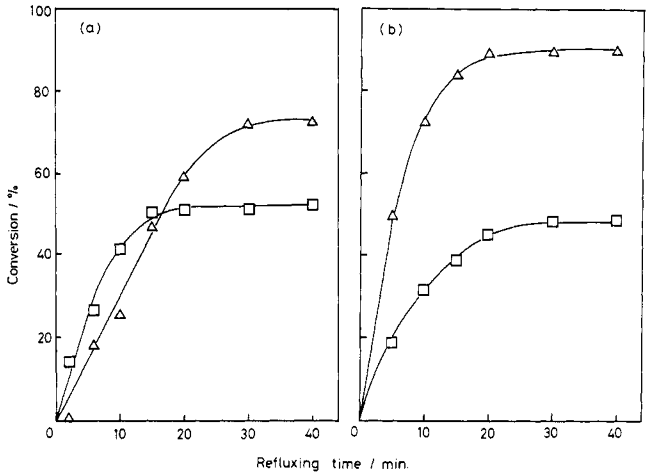

Figure 2. Change in conversion from respective acetates to Pd colloid (△) and Cu_2O/Cu colloid (□) in solvents with a refluxing time: (a) methyl isobutyl ketone; (b) bromobenzene. The concentrations of respective acetates are 0.5 mmol dm^{-3}.

stabilities of these colloids in the organic solvents were evaluated with the naked eye.

Results and Discussion

Before the preparation of Pd-Cu colloids, the thermal decomposition behavior of copper(II) acetate alone in organic solvents was studied. The results for a 20 min of refluxing time are given in Table I. The copper(II) acetate did not decompose in toluene but did in methyl isobutyl ketone, *o*-xylene, and bromobenzene, thus indicating that the critical decomposition temperature of copper(II) acetate ranges between 110 and 116 °C. This temperature is almost the same as that of palladium acetate.[11] From the information in Table I and the X-ray diffraction patterns (Figure 1), we conclude that a copper metal colloid is obtained in bromobenzene, whereas in methyl isobutyl ketone and *o*-xylene, only a copper oxide (Cu_2O) colloid is obtained. However, the electron diffraction patterns of the samples were poorly resolved. At the present time, we cannot give satisfactory interpretation for formation of copper or copper oxide, depending on the kind of solvent. In methyl isobutyl ketone and bromobenzene, the conversion ratios from respective acetates to corresponding colloids were measured vs refluxing time (Figure 2). The conversion ratios increased with refluxing time and became constant after 20 min, except for palladium acetate in methyl isobutyl ketone. The conversion ratios to the Cu/Cu_2O colloids were almost the same for both solvents; however, the conversion ratios to the Pd colloid were greater in bromobenzene than in methyl isobutyl ketone. Above the critical thermal decomposition temperature of palladium acetate and copper(II) acetate, the primary reaction product was confirmed to be acetic acid.

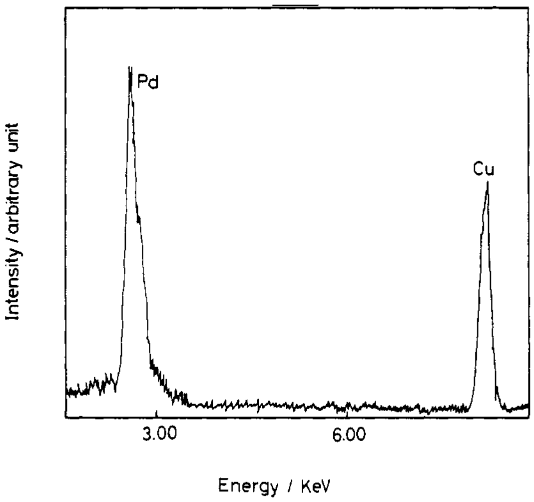

Figure 3. Electron probe microanalysis of one $Pd-Cu_2O$ colloidal particle prepared in methyl isobutyl ketone (Pd:Cu = 4:2).

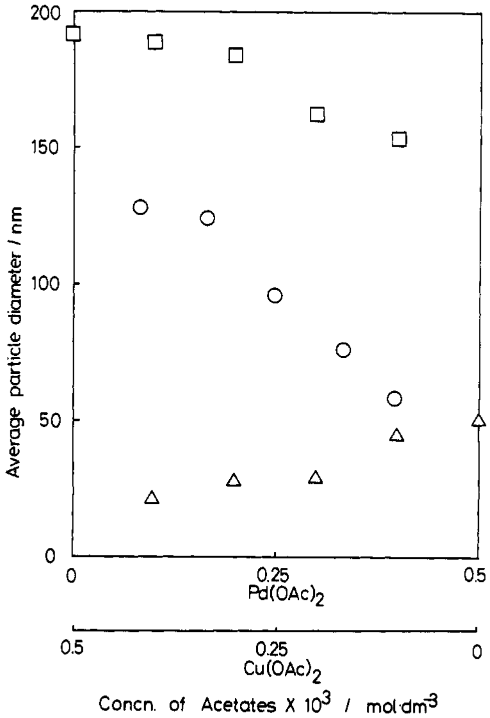

Figure 4. Influence of concentration of copper(II) acetate and palladium acetate on average diameters of $Pd-Cu_2O$ (○), Pd (△), and Cu_2O (□) colloids prepared in methyl isobutyl ketone.

The preparation of Pd-Cu colloids was carried out in these two organic solvents, methyl isobutyl ketone and bromobenzene. The elemental ratios of Pd/Cu in $Pd-Cu_2O$ colloids prepared in methyl isobutyl ketone are tabulated in Table II. The result of a typical EPMA analysis of a $Pd-Cu_2O$ particle is shown in Figure 3. By measuring X-ray photon counts vs energy, one can tell which elements are present and in what amounts. Figure 3 shows that both Pd and Cu are present in each particle; therefore the possibility that the samples consist of a mixture of pure Pd particles and pure Cu_2O particles was ruled out. A similar microanalysis of Pd-Au colloid particles was carried out by Michel and Schwartz,[5] who re-

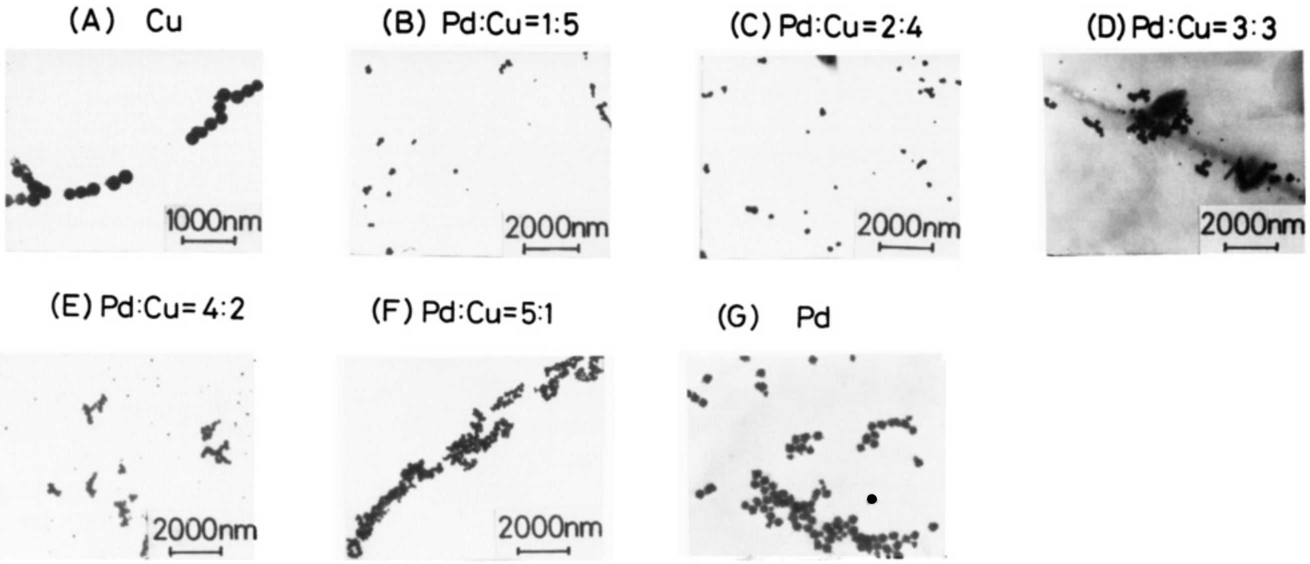

Figure 5. Electron micrographs of Pd–Cu_2O colloids prepared in methyl isobutyl ketone: (A) Cu_2O colloid, (B) 1:5, (C) 2:4, (D) 3:3, (E) 4:2, (F) 5:1, (G) Pd colloid. These ratios indicate the mixed ratios of palladium acetate:copper(II) acetate.

Table II. Elemental Ratio of Pd–Cu_2O Colloid Obtained in Methyl Isobutyl Ketone

	init ratio		composn ratio			
			from abs spectra		from EPMA	
	Pd	Cu	Pd	Cu	Pd	Cu
1:5	0.17	0.83	0.18	0.82	0.15	0.85
2:4	0.33	0.67	0.30	0.70	0.30	0.70
3:3	0.50	0.50	0.59	0.41	0.51	0.49
4:2	0.67	0.33	0.70	0.30	0.66	0.34
5:1	0.83	0.17	0.82	0.18	0.78	0.22

Table III. Elemental Ratio of Pd–Cu Colloid Obtained in Bromobenzene

	init ratio		composn ratio			
			from abs spectra		from EPMA	
	PD	Cu	Pd	Cu	Pd	Cu
1:5	0.17	0.83	0.29	0.71	0.32	0.68
2:4	0.33	0.67	0.40	0.60	0.43	0.57
3:3	0.50	0.50	0.73	0.27	0.72	0.28
4:2	0.67	0.33	0.79	0.21	0.80	0.20
5:1	0.83	0.17	0.93	0.07	0.91	0.09

ported that the composition of these colloids can be determined by analytical electron microscopy. As shown in Tables II and III, the elemental ratio of Pd/Cu estimated from EPMA agreed well with that from the absorption spectra. Furthermore, the mixed ratios of palladium acetate and copper(II) acetate are comparable to those of Pd–Cu_2O/Pd–Cu colloids. Thus, the conversions to Pd–Cu_2O/Pd–Cu colloids are proportional to the feed ratios of the mixed acetates. In this study, the conversions from their acetates to the Pd–Cu_2O/Pd–Cu colloids range between 50 and 60%. Figure 4 shows the average particle diameters of Pd–Cu_2O, Pd, and Cu_2O colloids prepared in methyl isobutyl ketone. The average diameters of the Pd–Cu_2O colloids decreased gradually from 130 to 50 nm with an increase of the molar ratio of palladium acetate in the mixed acetates. As a comparison, the concentration than that of the Pd colloid. As the ratio of palladium acetate to copper(II) acetate increases, the rate of nucleation and growth of the Cu_2O colloid is inhibited due to the incorporation of Pd, and the particle size of the Pd–Cu_2O colloids becomes smaller.

effect on particle size of pure Pd and Cu_2O colloids was studied; the average diameter of pure Pd and Cu_2O colloids increased with an increase of corresponding acetate. The

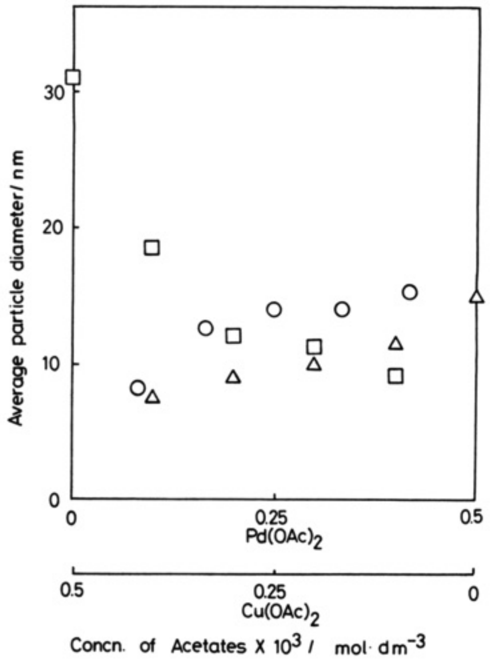

Figure 6. Influence of concentration of copper(II) acetate and palladium acetate on average diameters of Pd–Cu (○), Pd (△), and Cu (□) colloids prepared in bromobenzene.

average diameters of the Pd and Cu_2O colloids ranged between 10 and 50 nm and between 150 and 190 nm, respectively. The change in the average diameter of the Pd–Cu_2O colloids is similar to that of the Cu_2O colloids, suggesting that the formation of Pd–Cu_2O colloids in methyl isobutyl ketone is mainly controlled by the nucleation of the Cu_2O colloid.

Figure 5 shows the electron micrographs of the Pd–Cu_2O colloids prepared in methyl isobutyl ketone, indicating that they have a relatively large particle size distribution, whereas Pd and Cu_2O colloids show monodispersed sizes. These changes in the particle size may be derived from a different decomposition rate between palladium acetate and copper(II) acetate in methyl isobutyl ketone, i.e., the rate of nucleation and growth of the Cu_2O colloid is greater

On the other hand, when Pd–Cu colloids were prepared in bromobenzene, their average diameters were significantly different from those in methyl isobutyl ketone (Figure 6). It is apparent that the average diameters of Pd, Cu, and Pd–Cu colloids prepared in bromobenzene are

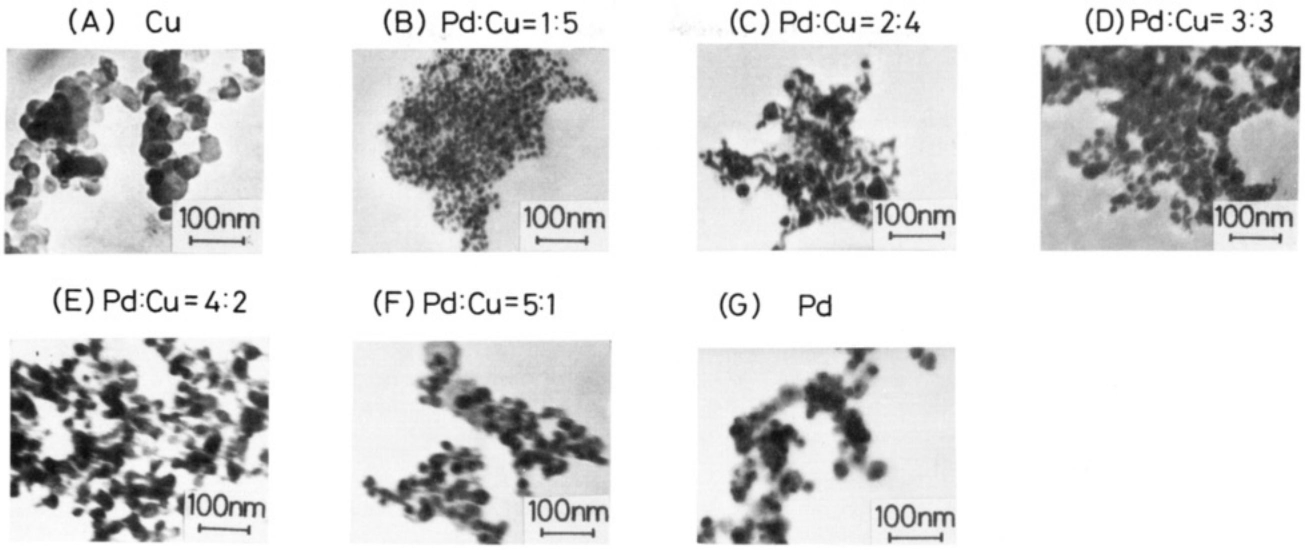

Figure 7. Electron micrographs of Pd–Cu colloids prepared in bromobenzene: (A) Cu colloid, (B) 1:5, (C) 2:4, (D) 3:3, (E) 4:2, (F) 5:1, (G) Pd colloid. These ratios indicate the mixed ratios of palladium acetate:copper(II) acetate.

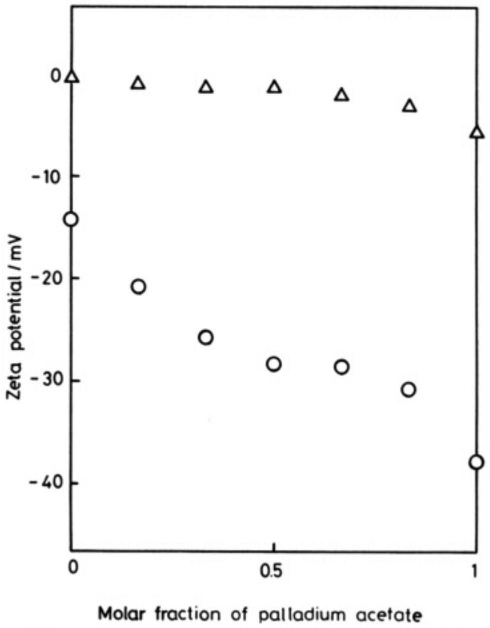

Figure 8. Change in ζ potentials of Pd–Cu_2O/Pd–Cu colloids prepared in organic solvents with a mixed ratio of copper(II) acetate and palladium acetate: (O) methyl isobutyl ketone; (Δ) bromobenzene.

smaller than those in methyl isobutyl ketone. The change in the average diameter of the Pd–Cu colloids prepared in bromobenzene is also very similar to that of the Pd colloid. Figure 7 shows the electron micrographs of the various colloids prepared in bromobenzene. The fact that the average diameter of Pd–Cu colloids prepared in bromobenzene is smaller than that in methyl isobutyl ketone may be explained by a different nucleation rate: the nucleation rate in bromobenzene, having a higher boiling point than methyl isobutyl ketone, is much faster than that in methyl isobutyl ketone, resulting in a larger number of nuclei in bromobenzene and smaller particle sizes. Table III shows that the elemental ratios of Pd/Cu in Pd–Cu colloids are larger than those of the mixed acetates, indicating that the colloids are enriched in Pd relative to the feed mixture. These results are supported by the data in Figure 2, which shows that in bromobenzene, the conversion from palladium acetate to palladium is higher than that from copper(II) acetate to copper.

To evaluate the dispersion stability of Pd–Cu_2O/Pd–Cu colloids, the dispersion state of the colloid was observed with the naked eye. The colloids prepared in bromobenzene precipitated within a few days, while those prepared in methyl isobutyl ketone were stable for a few weeks. In addition, the ζ potential of Pd–Cu_2O/Pd–Cu colloids was measured (Figure 8). In bromobenzene, the ζ potential of Pd–Cu colloids was very small and was not affected by the molar ratio; the ζ potential of Pd–Cu_2O colloids in methyl isobutyl ketone changed markedly from −15 to −35 mV with an increase in the molar ratio of palladium acetate. It is apparent that the stabler Pd–Cu_2O colloids are associated with the lower ζ potentials, thus suggesting that electrical repulsion forces play an important role in obtaining a stable dispersion of Pd–Cu_2O/Pd–Cu colloids. The difference in the ζ potential of Pd–Cu_2O/Pd–Cu colloids in both methyl isobutyl ketone and bromobenzene may be correlated with the dipole moments of the solvents: methyl isobutyl ketone with a higher dipole moment than bromobenzene would interact more strongly with the colloids. Furthermore, since the donor number[12] of methyl isobutyl ketone is considered to be greater than that of bromobenzene, the former solvent will donate an electron more easily than the latter solvent, resulting in a larger negative ζ potential in the former solvent. However, a more in-depth study is needed to develop a precise mechanism for the origin of the ζ potential of Pd–Cu colloids in organic solvents.

Conclusions

The thermal decomposition of mixed palladium acetate and copper(II) acetate in organic solvents with a boiling point of more than 110 °C produces bimetallic Pd–Cu_2O/Pd–Cu colloids. The average diameter and the dispersion stability of these colloids are dependent on the organic solvents used. In methyl isobutyl ketone, the particle size of Pd–Cu_2O colloids is mainly affected by the molar ratio of copper(II) acetate, while in bromobenzene the particle size of Pd–Cu colloids is affected by the molar ratio of palladium acetate. The average diameter of Pd–Cu_2O colloids obtained in methyl isobutyl ketone is considerably larger than that of Pd–Cu colloids in bromobenzene. The dispersion stability of the Pd–Cu_2O colloids in methyl isobutyl ketone is higher than that of the Pd–Cu colloids in bromobenzene, probably due to stronger electrical repulsion forces.

Registry No. Pd, 7440-05-3; Cu, 7440-50-8; Cu_2O, 1317-39-1; palladium acetate, 3375-31-3; copper(II) acetate, 598-54-9; methyl isobutyl ketone, 108-10-1; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; bromobenzene, 108-86-1.

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