

Surface Modification of Copper Nanoparticles with Organosiloxanes in Supercritical Water

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ABSTRACT

Surface modified copper particles were synthesized in sub- and supercritical water at 29-30 MPa using both batch and flow reactor systems. A copper (II) acetate aqueous solution is a starting material for the synthesis, and organosilicon compounds with epoxy groups were used as a surface modifier. Particles synthesized in the presence of the surface modifier by the flow system at around 400 °C were dispersed in chloroform. Reduction of copper oxide was observed without reducing agent by the synthesis using a batch reactor. These results suggest that the modifier has a reducing ability in supercritical water at 400°C.

INTRODUCTION

Effective heat release from electronic devices will be a critical issue for successful device design in the future. As polymeric materials containing nanosize thermal conductive fillers are one of the possible candidates for this purpose, the technology development focusing on nanocomposite materials is globally ongoing. In order to avoid the aggregation and to obtain high dispersion of nanoparticles in polymer, surface modification of metal nanoparticles is important. Particularly for a Si-based nanohybrid synthesis, Si-based modifiers should be expected to have high affinity with organosiloxane polymers. Supercritical hydrothermal synthesis is a method to produce metal oxide crystals from metal salt aqueous solutions using supercritical water [1]. Recently, synthesis of organic-inorganic hybrid nanoparticles in supercritical water has also been proposed [2-4]. Ziegler *et al.* reported that organic monolayer-stabilized copper nanoparticles can be formed using alkanethiols as capping ligands in supercritical water [3]. On the other hand, Ogawa *et al.* reported that polyorganosiloxanes can be successfully synthesized from an alkoxysilane by hydrolysis and subsequent polycondensation reactions in hot compressed water [5]. In this study, in-situ surface modification of copper and copper oxide nanoparticles with organosilicon compounds was examined in sub- and supercritical water.

EXPERIMENTAL

Materials

A copper (II) acetate monohydrate ((CH₃COO)₂Cu·H₂O, Wako Pure Chemical Industries, Ltd.) aqueous solution was used as a starting material while 1,3-bis(2-(3,4-epoxycyclohexyl)ethyl)-tetramethyldisiloxane (ESO, Dow Corning Toray Co., Ltd.) was

used as a surface modifier (Fig. 1). The modifier was diluted with methanol (Kanto Chemical Co., Inc.) by 0.5 mol/L for the flow system. In all the experiments, distilled water was used. Copper (II) oxide (CuO, average particle size 48 nm, C. I. Kasei Co., Ltd.) powder was also used to examine the reducing ability of ESO.

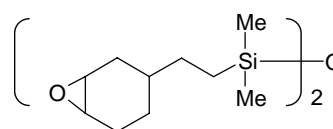


Fig. 1 Chemical structure of ESO

Procedure

Two types of reaction system were used in this study: a continuous flow reaction system and a batch reaction system. The experimental apparatus for the flow reaction system is shown in Fig. 2. A copper (II) acetate aqueous solution (0.1 mol/L under ambient condition) and a modifier solution were fed with high pressure pumps 1 and 2, respectively. The solutions were mixed at a mixing point with preheated water fed with pump 3, and the resulting mixture was rapidly heated up to reaction temperature. To prevent the particle formation before the mixing point, the feed line of metal salt solution was cooled by an external cooling jacket. The mixing ratio of copper (II) acetate aqueous solution to the preheated water was set at 1:4 in volume under ambient conditions. The reactor was made of SUS 316 tube. The temperature at the mixing point was calculated on the basis of an enthalpy balance of pure water. The temperature on the outer wall of the reactor measured by thermocouple was used for calculation of residence time. At the exit of the reactor, particle suspension in hot water was cooled by a heat exchanger with external cooling water flow. After the cooler, a collecting section made of 1/2 inch SUS316 tube was equipped to collect large particles by sedimentation whereas smaller particles were recovered as the suspension in a container located after a back pressure regulator. The internal pressure was controlled by the regulator. For the batch reaction, 400 mg CuO particles, 400 mg ESO and a proper amount of water were loaded in a SUS316 reactor with 10 mL inner volume and heated by a salt bath above 300°C. Approximately 3 minutes were required to reach the given temperature, and the reaction time (10min.) includes the heating up time. After the reaction, the reactor was quenched in a water bath.

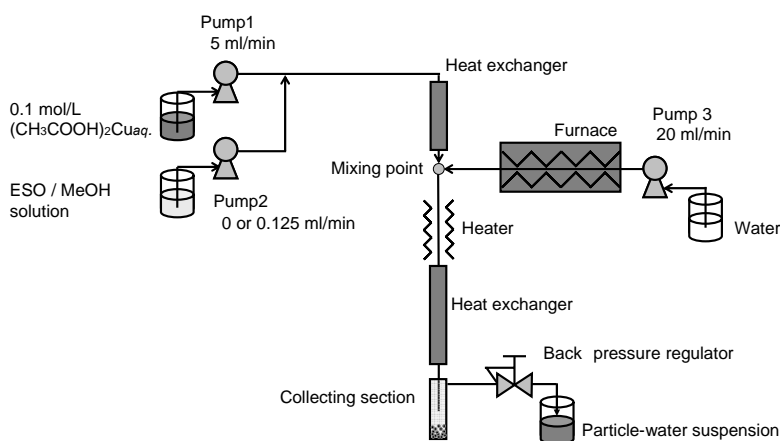


Fig. 2 Schematic diagram of experimental apparatus for a continuous flow system

Analysis

Particle separated from the particle-water suspension by centrifugation were washed twice with water and more than 3 times with methanol to remove the remaining compounds.

After washing, particles were dried at 80°C in a vacuum oven more than 3 hours. Morphology of the particles was observed by a transmission electron microscopy (TEM) analysis. Identification of the products was made by powder X-ray diffractometry (XRD) using CuK α radiation.

RESULTS

Hydrothermal synthesis and surface modification using a flow reactor

Experimental conditions using a continuous flow reactor are summarized in Table 1.

Table 1 Experimental conditions for a continuous flow reaction

Run No.	Temperature		Pressure	Flow rate			Residence time
	MP	Reactor		Pump1	Pump2	Pump3	
	°C	°C	MPa	mL/min	mL/min	mL/min	s
F1	405	400	30	5	-	20	3.6
F2	407	396	30	5	0.125	20	4.2

The [Cu²⁺]/[ESO] molar ratio at the mixing point was 4/1. Particles obtained through the back pressure regulator were brown while particles recovered from the collecting section were reddish brown for both runs. Figure 3 shows the TEM image of the product obtained through the back pressure regulator. Cubic particles with the size ranging from 20 nm to 1 μ m were formed when the modifier was present. Dispersibility of the particles obtained through the back pressure regulator was examined in a binary solvent system comprising chloroform and water as shown in Fig. 4. The particles synthesized in the presence of the modifier were dispersed in a chloroform phase, whereas those in the absence of the modifier were dispersed in a water phase. This result suggests that the surface property of the particles was changed by the in-situ modification with ESO.

Control of oxidation state of Cu

A series of experiments was conducted using a batch reactor to examine the effect of synthetic conditions on the oxidation state of Cu. The [CuO]/[ESO] molar ratio was about 5/1. The XRD patterns of unreacted CuO powder and particles after the batch reaction with and without ESO as a modifier at 300°C, 30 MPa and 400°C, 29 MPa are shown in Fig. 5. The XRD patterns

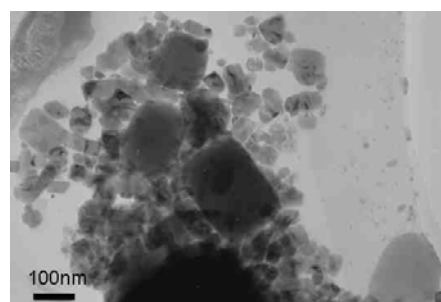


Fig. 3 TEM image of products synthesized in the presence of ESO (Run F2)

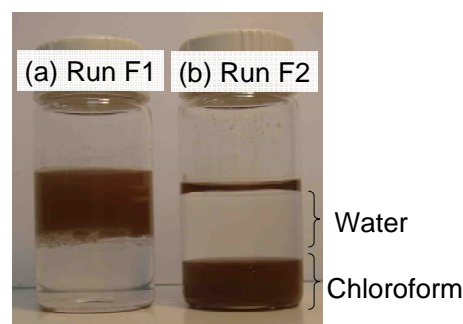


Fig. 4 Dispersibility of particles synthesized (a) without ESO (Run F1) and (b) with ESO (Run F2)

of particles after the treatment of water without ESO at both 300°C (Fig.5 b) and 400°C (Fig.5 c) were the same as that of the unreacted CuO (Fig.5 a). However, after the reaction in the presence of ESO at 300°C (Fig.5 e), intensity of the peaks assignable to CuO was decreased while peaks due to copper(I) oxide (Cu₂O) were observed. Only the peaks assignable to metallic copper (Cu) were observed by the reaction with ESO at 400°C. These results suggest that ESO has a reducing ability to CuO in sub- and supercritical water, and the ability is more significant at 400 °C. This reducing ability may be caused by the ring-opening reaction of epoxy group. At higher temperature, reducing gas such as CO was formed by the decomposition of ESO, and the gas generation could promote the reduction of CuO into Cu.

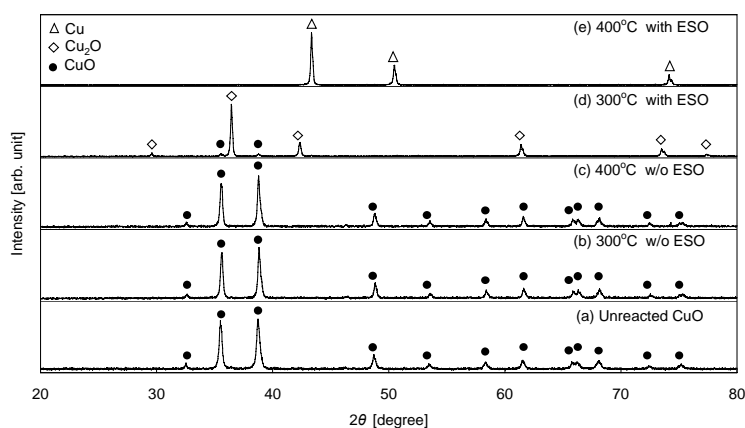


Fig. 5 XRD patterns of the particles from batch reactions (a) unreacted CuO, (b) without ESO at 300 °C, (c) without ESO at 400 °C, (d) with ESO at 300 °C, (e) with ESO at 400 °C

CONCLUSION

Hydrothermal synthesis of nanoparticles from a copper (II) acetate aqueous solution with and without ESO were conducted using a continuous flow reactor in supercritical water. Particles produced with ESO were well dispersed in chloroform, suggesting that the surface modified particles were synthesized. Furthermore, CuO nanoparticles were reduced to Cu at 400°C and 29 MPa in the presence of ESO by 10 minutes batch reaction. These results suggest that surface modified copper particles can be produced in supercritical water.

ACKNOWLEDGMENT

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REFERENCES :

- [1] Adsciri, K., Kanazawa, K., Arai, K., J. Am. Ceram. Soc., Vol. 75, **1992**, p. 1019
- [2] Adschiri, T., Chem. Lett., Vol. 36, **2007**, p. 1188
- [3] Ziegler, K. J., Doty, R. C., Johnston, K. P., Korgel, B. A., J. Am. Chem. Soc., Vol.123, **2001**, p. 7797
- [4] Rangappa, D., Ohara, S., Umetsu, M., Naka, T., Adschiri, T., J. Supercrit. Fluids, Vol. 44, **2008**, p. 441
- [5] Ogawa, T., Watanabe, J., Oshima, Y., J. Supercrit. Fluids, Vol. 45, **2008**, p. 80