Novel Approach for the Preparation of Metal Containing Mesoporous Silica Using Solubilization of Fatty Acid Salt

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We have prepared copper-containing mesoporous silica (Cu/MS) using solubilization of copper oleate in nonionic surfactant aggregates. The amount of copper loading in calcined Cu/MS corresponded to the amount of copper oleate solubilized in surfactant aggregates of the mixed solution.

Mesoporous silicas (MSs) have attracted attention because of their high surface areas and uniform pore dimensions since they were first reported.[1–3] The MSs are promising materials for catalyst supports and adsorbents involving relatively large organic molecules because the pore diameter of MSs (2–50-nm diameter) is larger than that of zeolites. The siliceous MSs have a chemically inert framework due to amorphous nature of the pore wall, therefore, transition metals containing mesoporous silicas have been synthesized by many researchers in order to increase active sites for catalytic reactions.[4,5] The various methods of introduction for the transition metals to MSs have been proposed, such as impregnation method, template-ion-exchange method, direct synthesis (one-pot synthesis) method, and post-synthesis (grafting) method. In this paper, we report a novel method of preparation for metal containing mesoporous silica using solubilization of fatty acid salt. Solubilization of organic compounds, such as mesitylene, 1,3,5-trimethylbenzene, *n*-alkanes, amines, and so on, has been used in the synthesis of MSs in order to expand their pore sizes.[3,6–9] We attempted to prepare copper containing MS using nonionic surfactant aggregates with solubilized copper oleate as structure-directing agent.

MS was prepared using nonionic surfactant, alkyl polyethylene-oxide alcohol [$CH_3(CH_2)_{15}(OCH_2CH_2)_8OH$, denoted to $C_{16}EO_8$], as structure-directing agent.[10] $C_{16}EO_8$ aqueous solution (5.9 wt %, 50 mL) and copper oleate ($Cu(C_{17}H_{33}COO)_2$, 0.164 g) were mixed at ambient temperature at 310 K for 10 days, producing bluish solution without turbidity. The pH of this solution was adjusted to 4 or 8 by addition of sodium hydroxide. Tetraethoxysilane (TEOS) was added to the solution and the mixed suspension was stirred at ambient temperature for 24 h. The solid product was filtered, washed with distilled water, and dried at ambient temperature for 24 h. The product (denoted to Cu/MS) was finally calcined at 873 K for 4 h in air. The molar ratio of the final gel mixture was 9.5 $C_{16}EO_8$:0.5 copper oleate:95 TEOS.

Figure 1 shows photographs of mixed aqueous solutions of $C_{16}EO_8$ and copper oleate at pH 4 and 8. The mixed aqueous solutions of $C_{16}EO_8$ and copper oleate were transparently blue without formation of any precipitate.

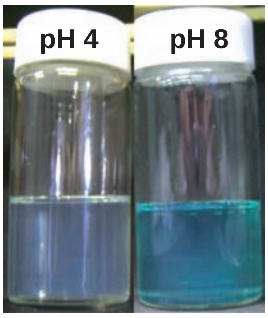

Figure 1. Photographs of mixed aqueous solutions of $C_{16}EO_8$ and copper oleate at pH 4 and 8.

The trapping efficiency of the copper oleate molecules was estimated by the dialysis in order to reveal that the copper oleate was solubilized in $C_{16}EO_8$ surfactant aggregates without ionic dissociation of Cu^{2+} and oleic anion. The mixed aqueous solutions of $C_{16}EO_8$ and copper oleate at pH 4 and 8 were put into a regenerated cellulose tube (14000 molecular weight cutoff, Viskase). Unsolubilized copper oleate molecules and Cu^{2+} ions in the tube were transferred into external 1 L of distilled water, which was changed with fresh distilled water five times during 12 h. After the dialysis, the copper concentration of copper oleate solubilized in surfactant aggregates was estimated by the inductively coupled plasma (ICP) measurement. The trapping efficiencies of the copper oleate molecules solubilized in surfactant aggregates at pH 4 and 8 were 0.97 and 38%, respectively. This result revealed that a part of copper oleate molecules was solubilized in $C_{16}EO_8$ surfactant aggregates without ionic dissociation of Cu^{2+} and oleic anion at pH 8. On the other hand, at lower pH than 4, most of oleate ions in the mixed solution might exist as acid form ($C_{17}H_{33}COOH$) to release Cu^{2+} because a lot of H^+ ions shift the following chemical equilibrium to the right; $Cu(C_{17}H_{33}COO)_2 + 2H^+ \rightleftarrows 2C_{17}H_{33}COOH + Cu^{2+}$.

The Cu amounts for the calcined Cu/MSs determined by X-ray fluorescence technique are listed in Table 1. In the case of pH 4 and 8 for the mixed solution in the synthesis process (these

Table 1. Amount of copper in surfactant aggregates of the mixed solution and copper loading in calcined Cu/MS

pH of the mixed solution	Trapping efficiency of copper oleate[a]/%	Amount of copper loading in calcined Cu/MS[b]/wt %
4	0.97	0.040
8	38	1.3

[a]The trapping efficiencies of copper oleate solubilized in surfactant aggregates were estimated by the dialysis. [b]The values were determined by X-ray fluorescence technique.

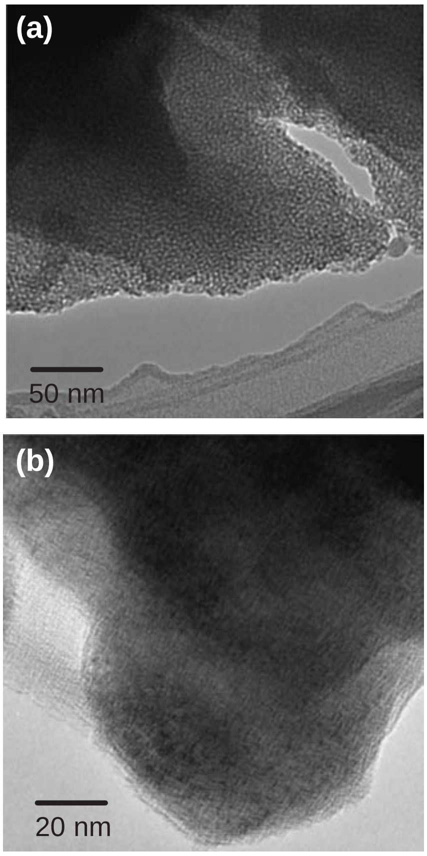

Figure 2. TEM images of calcined Cu/MSs in the case of pH (a) 4 and (b) 8 for the mixed solution.

calcined products were denoted to Cu/MS(pH 4) and Cu/MS(pH 8)), the loadings of copper in calcined Cu/MSs were 0.040 and 1.3 wt %, respectively. The amount of copper loading in calcined Cu/MS corresponded to the amount of copper oleate solubilized in surfactant aggregates of the mixed solution. This result indicated that copper species solubilized in surfactant aggregates were supported in the channels of the calcined Cu/MS and that unsolubilized copper species were not loaded on the calcined Cu/MS.

X-ray photoelectron spectroscopy (XPS) analysis for both calcined Cu/MSs was done to measure valence of copper species in Cu/MSs. No peaks for copper species were observed in the spectrum of Cu/MS(pH 4) because the loading of copper was very small. In the case of Cu/MS(pH 8), the Cu $2p_{1/2}$ peak was observed at 933.9 eV, which was due to CuO.[11] Cu is seemed to be present in the +2 oxidation state in this synthesis process. No X-ray diffraction (XRD) peaks due to copper particles were observed in the both calcined Cu/MSs, indicating that copper species were highly dispersed in the MS channels.

Figure 2 shows transmission electron microscopy (TEM) images[12] for Cu/MSs prepared by using solubilization of copper oleate at pH 4 and 8. Copper particles were not observed in any TEM images of both Cu/MSs, in agreement of XRD measurements, therefore copper species were highly dispersed in the Cu/MSs. The *meso*-architecture of the Cu/MSs was not so periodic but mesopores were observed. These TEM images with worm-hole structure of the porous framework agreed with the TEM image of calcined MSU-1 in the literature,[10] where nonionic surfactant was used as structure-directing agent. XRD patterns of the calcined Cu/MSs showed 100 reflections at low angle with d spacing of 4.5 nm, characteristic of mesostructured compounds. The breadth of the reflection is consistent with that of the worm-hole channel pore.[10] N_2 adsorption-desorption isotherms at 77 K for the calcined CuMSs were measured and the pore size distribution was calculated from the Barrett–Joyner–Halenda method. The BET surface area of calcined Cu/MS(pH 4) was 1198 $m^2\,g^{-1}$, and the average pore size was 2.4 nm. The result of N_2 adsorption isotherms revealed that Cu/MS(pH 8) (BET surface area = 100 $m^2\,g^{-1}$) had much less surface area than Cu/MS(pH 4). This result can be explained by a fact that a reaction rate of hydrolysis and polycondensation for TEOS molecules at pH 8 was much slower than that at pH 4.

We can conclude that we succeeded in preparing copper containing MS using copper oleate solubilized in nonionic surfactant aggregates for the first time. Numerous attempts have been made to synthesize transition-metals-containing mesoporous silicas by mixing the transition-metal complexes or salt in synthesis gels. The great advantages of synthesis method in this study are not only that copper atoms cannot be buried inside the wall of silica framework because copper oleate are located in templates of surfactant aggregates but also that copper atoms are dispersed in the channels of MS, as revealed by TEM and XRD measurements, because copper oleate should be surrounded by nonionic surfactants without a domain of copper oleate molecules in the solubilization. This method will be applied to synthesis of another-metal-containing mesoporous silica materials using the corresponding fatty acid salt within the limits of solubilization for the fatty acid salts in surfactant aggregates.

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12 Transmission electron microscopy (TEM) images were measured using a Hitachi H-7650 electron microscope with a cold field-emission gun operated at 120 kV.

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