Synthesis of Silver and Copper Nanoparticles in a Water-in-Supercritical-Carbon Dioxide Microemulsion

Hiroyuki Ohde, Fred Hunt, and Chien M. Wai*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844

Received January 16, 2001. Revised Manuscript Received July 3, 2001

Nanometer-sized silver and copper metal particles can be synthesized by chemical reduction of Ag^+ and Cu^{2+} ions dissolved in the water core of a water in supercritical fluid carbon dioxide microemulsion. Sodium cyanoborohydride and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine are effective reducing agents for synthesizing these metal nanoparticles in the microemulsion. Formation of the metal nanoparticles was monitored spectroscopically using a high-pressure fiber-optic reactor equipped with a CCD array UV−vis spectrometer. Silver and copper nanoparticles synthesized in the microemulsion showed characteristic surface plasmon resonance absorption bands centered at 400 and 557 nm, respectively. Diffusion and distribution of the oxidized form of the reducing agent between the micellar core and supercritical CO_2 appeared to be the rate-determining step for the formation of the silver nanoparticles in this system.

Introduction

The catalytic potential of nanometer-sized transition metal particles is a subject of great interest to chemists in recent years. Numerous methods for preparation of metallic nanoparticles have been reported in the literature.[1−4] Using water-in-oil microemulsions as templates is one method of synthesizing nanopartices with narrow size distributions.[5,6] The average size of the nanoparticles synthesized by this method depends on the size of the microemulsion, which is determined by the water-to-surfactant ratio (*W*). One problem of using water-in-oil microemulsions for nanoparticle synthesis is the separation and removal of solvent from products. In recent years, supercritical carbon dioxide (SF CO_2) has been extensively studied as a solvent for chemical synthesis.[7,8] SF CO_2 offers several advantages over conventional organic solvents including (i) being one of the most environmentally friendly and low-cost solvents available, (ii) rapid separation of dissolved solute from the solvent by reduction of pressure, (iii) providing high diffusivity and thus accelerated reaction rates, (iv) tunable solvent strength through manipulation of the density and thus providing some control of the solubility of solutes. Nanoparticles synthesized in SF CO_2 may be used as catalysts for subsequent in situ chemical reactions in the fluid phase.

Silver and copper nanoparticles were synthesized in sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles in compressed propane and supercritical ethane solutions.[9] In a recent communication, a method for the synthesis of silver nanoparticles in SF CO_2 was described.[10] The method involved the formation of a water-in-supercritical-CO_2 microemulsion with silver nitrate dissolved in the aqueous core. This was followed by the introduction of a reducing agent to the fluid phase, causing reduction of Ag^+ to elemental Ag in the microemulsion. The reducing agent used in the previous study was sodium triacetoxyborohydride, $NaBH(OAc)_3$. A major difficulty of using $NaBH(OAc)_3$ as a reducing agent in supercritical CO_2 is its low solubility in the fluid phase. The solubility of $NaBH(OAc)_3$ in supercritical CO_2 is on the order of $<10^{-5}$ M (mol/L) at 40 °C and 200 atm. In the previous study, the introduction of $NaBH(OAc)_3$ was accomplished by dissolving the reducing agent in ethanol followed by injection of the ethanol solution into the supercritical CO_2 phase via an injector. Because of its small solubility, even in the ethanol-modified supercritical CO_2, the reducing agent often precipitated immediately after injection into the supercritical fluid reactor, causing plugging of tubing and connectors and making experimental conditions difficult to control.

We have recently evaluated a number of reducing agents for studying redox reactions in SF CO_2. The following two reducing agents, sodium cyanoborohydride ($NaBH_3CN$) and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), were found very effective for synthesizing metal nanoparticles in the water-in-supercritical-CO_2 microemulsion. Both of them are more soluble than $NaBH(OAc)_3$ in SF CO_2. $NaBH_3CN$ is stable in aqueous

---

(1) Petit, C.; Lixon, P.; Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 12974.
(2) Esumi, K.; Matsuhisa, K.; Torigoe, K. *Langmuir* **1995**, *11*, 3285.
(3) Henglein, A. *J. Phys. Chem. B.* **2000**, *104* (29), 6683.
(4) Okitsu, K.; Yue, A.; Tanabe, S.; Matsumoto, H. *Chem. Mater.* **2000**.
(5) Nagy, J. B. In *Handbook of Microemulsion Science and Technology*; Kumar, P., Mittal, K. L., Eds.; Marcel Dekker: New York, 1999; Chapter 17, p 499−546.
(6) Hirai, T.; Sato, H.; Komasawa, I. *Ind. Eng. Chem. Res.* **1994**, *33*, 3262.
(7) Wai, C. M.; Hunt, F.; Ji, M.; Chen. X. *J. Chem. Edu.* **1998**, *75*, 1641.
(8) Savage, P. E.; Gopalan, S.; Mizan, T. I.; Martino, C. J.; Brock, E. E. *AICHE J.* **1995**, *41*, 1723.
(9) Carson, J. P.; Khambaswadkar, K.; Roberts, C. B. *Chem. Mater.* **1999**, *11*, 198.
(10) Ji, M.; Chen, X.; Wai C. M.; Fulton, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2631.

10.1021/cm010030g CCC: $20.00

solutions at least in the pH range 2−8.[11] The pH of water in equilibrium with CO_2 was measured to be around 2.8−2.9 in the temperature range 25−70 °C and pressure range 70−200 atm.[12] In another study, the pH of water in a water-in-supercritical-CO_2 microemulsion was reported to be around 3.5.[13] Thus, $NaBH_3CN$ should be stable in the aqueous core of the water-in-supercritical-CO_2 microemulsion. The oxidation potentials of these reducing agents in supercritical CO_2 are unknown. In organic solvents such as diglyme, the redox potential of $NaBH_4$ was reported ($E° = -0.6$ V vs NHE).[14] The oxidation potential of $NaBH_3CN$ is probably higher than that of $NaBH_4$. The standard redox potential of TMPD in DMF (*N*,*N*-dimethyl formamide) for the reaction $TMPD \rightarrow TMPD^{\bullet +} + e^-$ was reported to be $E° = 0.45$ V (vs NHE).[15] Our experiments indicate that these reducing agents are able to cause reduction of metal cations including Ag^+ and Cu^{2+} in the water-in-CO_2 microemulsion. This paper describes the synthesis of Ag and Cu nanoparticles in the water-in-supercritical-CO_2 microemulsion utilizing $NaBH_3CN$ or TMPD as a reducing agent and their subsequent characterization by spectroscopy. A high-pressure fiber-optic reactor connected to a CCD array UV−vis spectrometer was used to monitor the speed of formation of the metal nanoparticles in the microemulsion. The mechanism of formation of the metal particles in the microemulsion is also discussed.

Experimental Section

Chemicals. The reducing agents $NaBH_3CN$ and TMPD were obtained from Aldrich with purity >97%. The surfactants used in this study were sodium bis(2-ethylhexyl)sulfosuccinate (Aldrich, purity >98%) and a perfluoropolyether-phosphate obtained from Ausimont with a general structure of $CF_3O(OCF(CF_3)CF_2)_n(OCF_2)_mOCF_2CH_2OCH_2CH_2OPO(OH)_2$ and an average molecular weight of 870.[10] Other chemicals used in this study included silver nitrate (Aldrich), copper nitrate (Acros), and absolute ethanol (Aldrich). SFE grade CO_2 was obtained from Oxarc (Spokane, WA).

Apparatus and Procedure. A high-pressure view cell (15 mL in volume) with sapphire windows was used for the initial experiments to evaluate the conditions of formation of the water-in-supercritical-CO_2 microemulsion containing Ag^+ or Cu^{2+} in the aqueous core. The high-pressure view cell was described in a previous report.[10] The surfactant system consisted of a mixture of 12.8 mM AOT and 25.3 mM perfluoropolyether phosphate at a water-to-surfactant ratio W ($[H_2O]/[AOT]$) = 12. The concentration of metal ions in the water core was 0.1 M for Ag^+ and Cu^{2+}. In the whole reaction system, the concentration of the metal ions was 0.3×10^{-3} mol/L of SF CO_2. Typically, an optically transparent, water-in-supercritical-CO_2 microemulsion was visually observed after 30 min of stirring of the water−surfactant mixture in supercritical CO_2 at 38 °C and 200 atm in the high-pressure view cell.

The same concentrations and experimental conditions (38 °C and 200 atm) were then applied to a high-pressure fiber-optic reactor system.[16] The optical path length of the fiber optic reactor was 3 mm. The fiber-optic reactor was connected to a CCD array UV−vis spectrophotometer (Spectral Instruments model SI-440, Tucson, AZ) so that high-speed spectra could be obtained to monitor the reaction in supercritical CO_2. The spectrometer is capable of recording a full spectrum from 200 to 900 nm in 2 s. It can also measure the change in absorbance with time at a fixed specific wavelength. A blank measurement was taken before every reaction to provide a spectroscopic baseline.

To ensure the formation of a homogeneous microemulsion in the fiber-optic reactor, the stirring time was set at 1 h. After that, stirring was stopped and $NaBH_3CN$ in an ethanol solution was injected into the reactor via an attached stainless steel cell (0.7 mL in volume) at a pressure of 250 atm. The final concentration of $NaBH_3CN$ in the supercritical fluid system was 1×10^{-3} M and the fluid phase contained 0.5% ethanol. In the case of TMPD, it was injected into the system without ethanol because of its high solubility in supercritical CO_2. In any case, the reducing agent introduced into the system was below its saturation concentration in the fluid phase. A schematic diagram of the high-pressure reaction system used for this study is shown in Figure 1. The supercritical fluid experiments were performed in a hood due to possible leaks and spill of chemicals from the high-pressure reaction system.

Results and Discussion

The Reducing Agents. The solubility of $NaBH_3CN$ in SF CO_2 is still small, on the order of 10^{-4} M at 40 °C and 200 atm. Therefore, an ethanol solution of $NaBH_3CN$ was injected into the SF CO_2 system to make the final composition of the fluid phase containing 0.5% ethanol. The solubility of $NaBH_3CN$ in this 0.5% ethanol-modified SF CO_2 is about 10^{-2} M at 40 °C and 200 atm. Precise control of the reducing agent concentration in the SF CO_2 reaction system can be accomplished using this method. Under the specified conditions, $NaBH_3CN$ can effectively cause reduction of Ag^+ and Cu^{2+} in the microemulsion system, leading to the formation of nanometer-sized metal particles. TMPD is very soluble in SF CO_2, with a solubility estimated to be >0.5 M at 40 °C and 200 atm in CO_2. Therefore, no ethanol or other modifier is needed when TMPD is used as a reducing agent for the SF CO_2 experiments. In aqueous solutions, the oxidized form $TMPD^{\bullet +}$ is purple blue in color and absorbs strongly in the visible range from 500 to 650 nm with two prominent peaks at 563 and 607 nm. $TMPD^{\bullet +}$ is stable in water but decomposes readily in supercritical CO_2.

The Microemulsion. According to our experiments, the AOT microemulsion is not soluble in CO_2. The perfluoropolyether phosphate probably serves as a co-surfactant to make the microemulsion soluble in SF CO_2.[10] Without AOT, the PFPE-PO_4 surfactant alone is probably unable to form a stable microemulsion phase with a water core. The experimental W value (ratio of H_2O/PFPE-PO_4) for the formation of an optically transparent phase for PFPE-PO_4 at 40 °C and 200 atm in CO_2 was about 6. After correction for the solubility of water in the SF CO_2, the real W value for the water/PFPE-PO_4 surfactant assembly was less than 3. This W value appears too small for the formation of a microemulsion with a water core. The headgroup of the surfactant probably could be solvated by three water molecules without forming a microemulsion. Using a

---

[11] Sullivan, E. A.; Wade, R. C. U.S. Patent 70−20075; *Chem. Abstr. 76*, 116980.

[12] Toews, K. L.; Shroll, R. M.; Wai, C. M. *Anal. Chem.* **1995**, *67*, 4040.

[13] Niemeyer, E. D.; Bright, F. V. *J. Phys. Chem.* **1998**, *102*, 1474.

[14] Connelly N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (b) Connelly, N. G.; Payne, J. D.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 295.

[15] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, John Wiley and Sons: New York, 1980.

[16] Hunt, F.; Ohde, H.; Wai, C. M. *Rev. Sci. Instr.* **1999**, *70*, 4661.

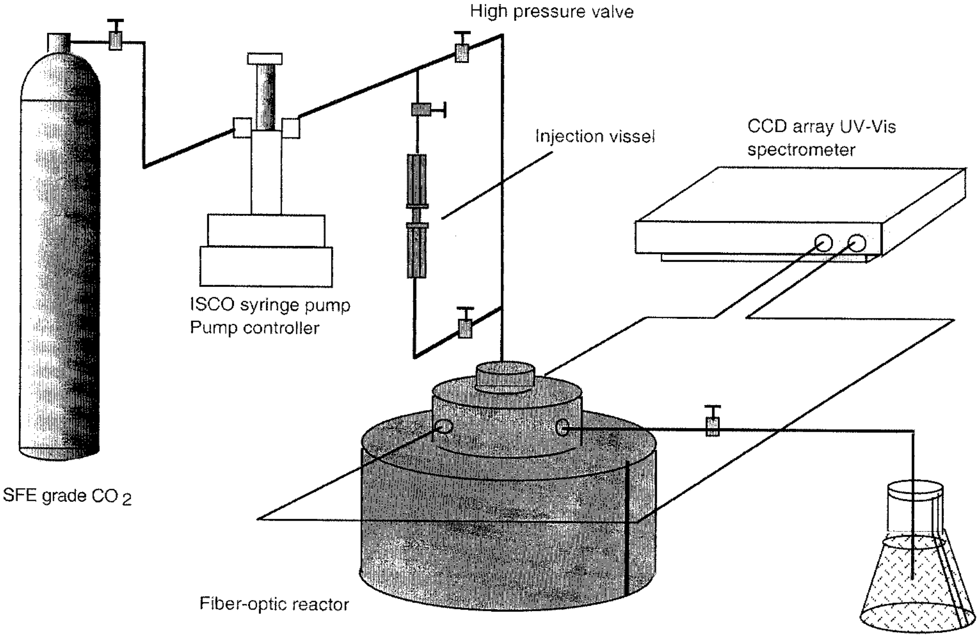

Figure 1. High-pressure fiber-optic reaction system for studying the formation of Nanometer-sized metal particles in a water in supercritical fluid CO_2 microemulsion.

mixture of AOT and PFPE-PO_4 with the concentrations specified in the Experimental Section, a stable water-in-CO_2 microemulsion with H_2O/AOT ratio of up to 34 could be formed at 40 °C and 200 atm. The *W* value of the microemulsion was not affected by the presence of 0.1 M of silver nitrate or copper nitrate in the water core. For these reasons, we chose to use a mixture of AOT and PFPE-PO_4 for making the water-in-CO_2 microemulsion for this metal nanoparticle synthesis study.

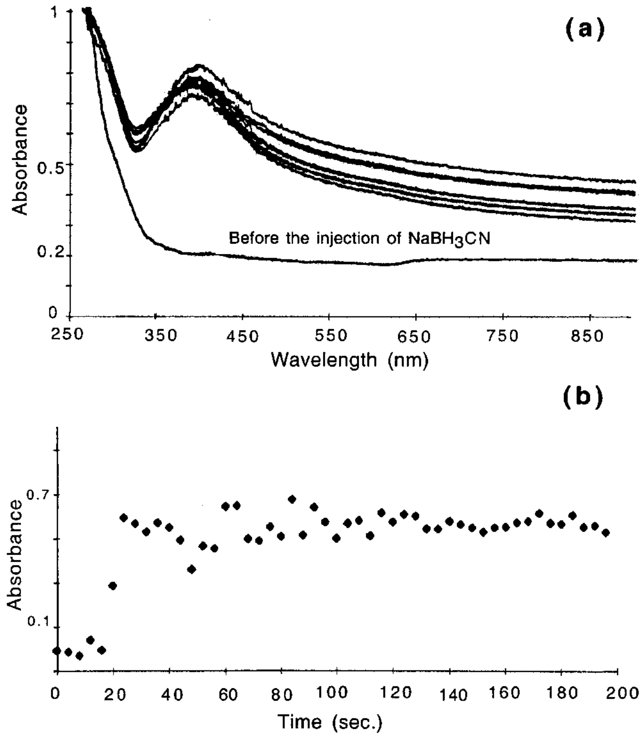

Figure 2. (a) UV/vis spectra of the Ag nanoparticles prepared by reacting $NaBH_3CN$ with silver nitrate in the water-in-supercritical-CO_2 microemulsion. (b) Change of the 400-nm peak intensity with time (taken at 4-s intervals).

Formation of Silver Nanoparticles. Figure 2a shows the UV−vis spectra of the silver nanoparticles formed by the reaction of $NaBH_3CN$ dissolved in SF CO_2 with the Ag^+ ($AgNO_3$) in the water core of the microemulsion. The spectra shown in Figure 2a were taken at 4-s intervals after the injection of the reducing agent. Silver nanoparticle is yellow in color with its characteristic peak, originated from the surface plasmon resonance absorption, centered at 400 nm.[1] The observed spectra are characteristic of silver nanoparticles with sizes around 4 nm in diameter.[10] Figure 2b shows the rate of increase of the absorbance of the 400-nm peak with time. The reducing agent was injected at the fourth data point that caused a temporary disturbance of the optic system. After that, the absorbance of the 400-nm peak increased very rapidly and reached a saturation value after approximately 25 s. The reducing agent apparently can penetrate through the liquid membrane of the microemulsion, effectively causing reduction of silver and formation of silver nanoparticles. The synthesized silver nanoparticles can be collected by different methods. Ji et al. used the RESS (rapid expansion of supercritical solution) method[17] to collect the silver nanoparticles synthesized in the water-in-CO_2 microemulsion using $NaBH(OAc)_3$ as the reducing agent. The TEM pictures of the collected silver nanoparticles showed an average size of approximately 5−15 nm, larger than the calculated size based on the spectroscopic information. The results suggested that the RESS method might cause aggregation of the particles during expansion, resulting in a wider size distribution. In this study, we used an in situ deposition method by reducing the pressure of the system to the cloud point of the microemulsion, so that the silver nanoparticles in the microemulsion would precipitate on a solid surface. Figure 3 shows a TEM micrograph of the silver nanoparticles collected on a carbon-coated copper grid using this internal deposition method. The

---

(17) Matson, D. W.; Fulton, J. L.; Petersen, R. C.; Smith, R. D. *Ind. Eng. Chem. Res.* **1987**, *26*, 2298.

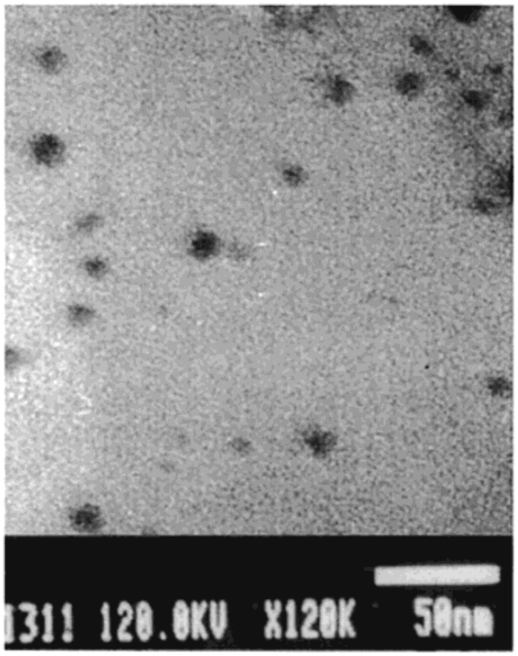

Figure 3. TEM micrograph of the Ag nanoparticles collected on a carbon-coated copper grid using the internal deposition method.

particle size of the silver nanoparticles collected by this method appears similar to that collected by the RESS method, i.e., about 5−15 nm in diameter. It is not clear whether the surfactants were coated on the surface of the nanoparticles or not, because our TEM micrograph was not able to distinguish the surfactants from the metal nanoparticles. On the basis of the TEM micrograph, aggregation of the nanoparticles apparently took place during the internal deposition process. One potential method of preventing aggregation of nanoparticles is by utilization of chemical stabilizers. For example, a recent report by Shah et al. indicated that perfluorodecanethiol could stabilize silver nanoparticles for dispersion in supercritical CO_2.[18] Ligands containing thio, sulfide, and amino functional groups that have good affinity for metal surfaces were used by Lin et al. to modify the surface of gold nanoparticles synthesized in a water-in-toluene microemulsion.[19] The ligand stabilization approach may provide a method of collecting nanoparticles synthesized in supercritical CO_2 using the microemulsion as a template.

Sodium borohydride was also tested for the reduction of silver in SF CO_2. The solubility of $NaBH_4$ in SF CO_2 is very small ($<10^{-4}$ M in the presence of 5% EtOH). Using the same procedure described above for the $NaBH_3CN$ experiments, the formation of silver nanoparticles with $NaBH_4$ was observed, but the intensity of the 400-nm absorption peak was much lower than that observed for the case of $NaBH_3CN$. Some precipitate was found in the injection vessel and in the reactor after the experiment apparently caused by the precipitation of the reducing agent during injection. It was reported in the literature that $NaBH_4$ could react with CO_2 in a pressure tube at 125 °C.[20] In our system at 38 °C, reaction between $NaBH_4$ and CO_2 was unlikely, but the low solubility of $NaBH_4$ was probably a major factor limiting its use as an effective reducing agent for studying redox reactions in supercritical CO_2. When NaH_3CN was used as a reducing agent in the water-in-supercritical-CO_2 microemulsion system, no precipitation was observed.

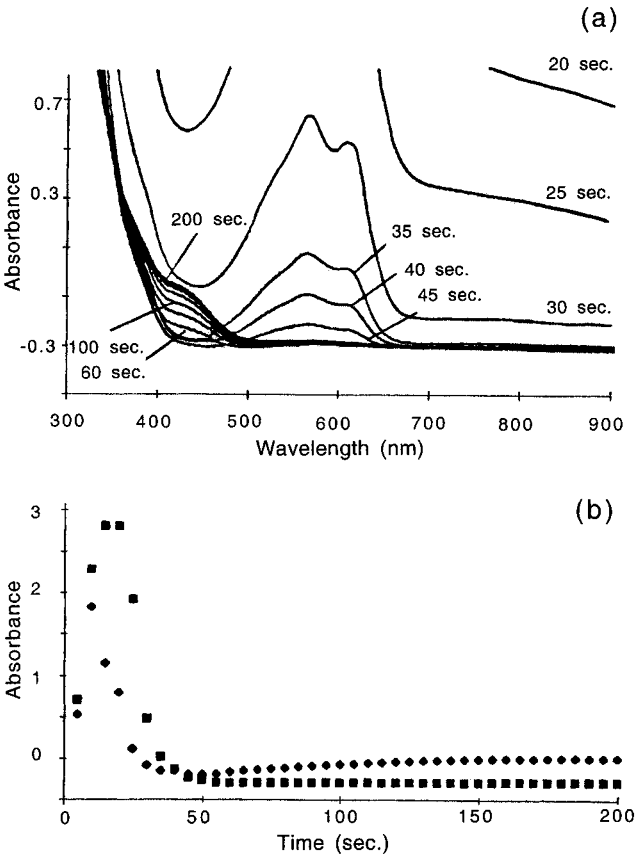

Figure 4. (a) UV/vis spectra of the Ag nanoparticles prepared by reacting TMPD with silver nitrate in the water-in-supercritical-CO_2 microemulsion. (b) Change of the 400-nm (Ag nanoparticle, ◆) and the 563-nm (TMPD$^{\bullet+}$, ■) peak intensities with time using TMPD as a reducing agent.

Figure 4a shows the formation of Ag nanoparticles in the microemulsion using TMPD as the reducing agent. The strong absorbance of TMPD$^{\bullet+}$ in supercritical CO_2 with peaks around 563 and 607 nm appeared immediately after the injection, indicating that a redox reaction involving TMPD was occurring very rapidly in the system. The absorption peak of Ag nanoparticles around 400 nm was masked initially by the huge background absorption of the TMPD$^{\bullet+}$ but became visible after about 50 s. Figure 4b shows the change in absorbance at 400 and 563 nm with time. The jump in absorbance at 400 nm after the injection of TMPD was due to the huge background absorption of the TMPD$^{\bullet+}$ produced in the SF CO_2 phase. The absorption of TMPD$^{\bullet+}$ started to decrease rapidly after about 20 s and continued to decrease slowly throughout the experiment. The drop in the 400-nm peak intensity followed that of the TMPD$^{\bullet+}$ peak until after about 50 s and then started to increase. This increase was obviously due to the absorption of the Ag nanoparticles as shown in Figure

---

(18) Shah, P. S.; Holmes, J. D.; Doty, R. C.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 4245.

(19) Lin, X. M.; Sorensen, C. M.; Klabunde, K. J. *Chem. Mater.* **1999**, *11*, 198.

(20) Wiberg, E.; Amberger, E. *Hydrides of the Elements of Main Groups I−IV*, Elsevier Publishing Co., Amsterdam, 1971; p 128.

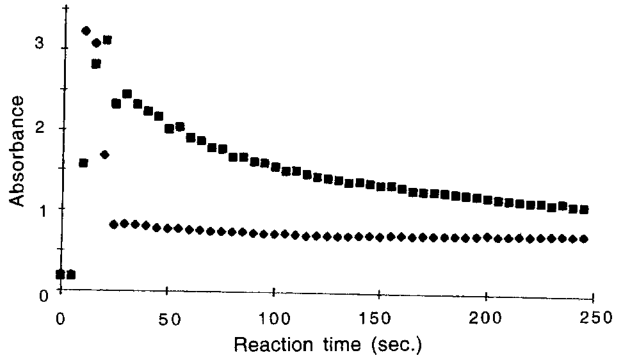

Figure 5. Change of the 400-nm Ag nanoparticle (◆) and the 563-nm TMPD$^{•+}$ (■) absorbance with time using TMPD as a reducing agent in 5% ethanol-modified SF CO_2. The conditions for the preparation of Ag nanoparticle were the same as that in Figure 2, except ethanol was used as a modifier.

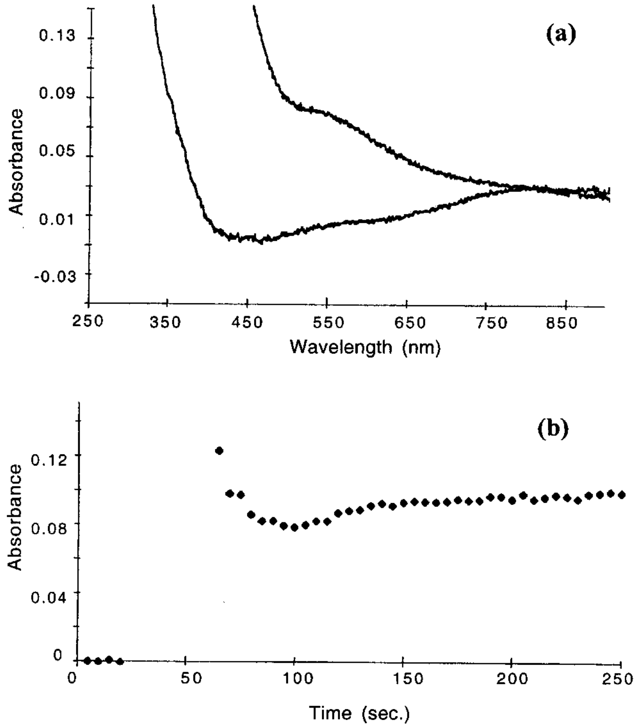

Figure 6. (a) UV/vis spectra of the Cu nanoparticles prepared by the reaction of copper nitrate in the water-in-supercritical-CO_2 microemulsion with TMPD in SF CO_2 taken at 0 s (bottom spectrum) and at 180 s (top spectrum) of the experiment. (b) Change of the 557-nm Cu nanoparticle absorbance with time.

4a. An important observation from Figure 4b is that the rate of formation of Ag nanoparticles using TMPD as a reducing agent appears slower than that observed in the case of $NaBH_3CN$ shown in Figure 2b. The distribution of the size of the Ag nanoparticles using TMPD or $NaBH_3CN$ as a reducing agent is about the same based on our TEM micrographs.

The large absorption peaks at 563 and 607 nm coincided with the absorption peaks of TMPD$^{•+}$ in water. Our interpretation of the formation of Ag nanoparticle in the water-in-CO_2 microemulsion based on the experimental observation is given as follows. First, TMPD diffused from the fluid phase into the microemulsion, followed by the reduction of Ag^+ to elemental Ag with the formation of TMPD$^{•+}$. The TMPD$^{•+}$ produced in the water core of the microemulsion migrated to the supercritical CO_2 phase and underwent decomposition, as indicated by the rapid decrease of its absorption intensity shown in Figure 4b. The absorption of Ag nanoparticles at 400 nm began to increase after the TMPD$^{•+}$ absorption was reduced to the near background level in about 50 s. The presence of TMPD$^{•+}$ probably would cause hindrance to the formation of Ag nanoparticles in the water core. Therefore, aggregation of the elemental Ag to form silver nanoparticles exhibiting characteristic surface plasmon resonance absorption at 400 nm was delayed until TMPD$^{•+}$ was nearly depleted in the water core. After that, the intensity of the 400-nm peak continued to increase and reached a saturation value after 200 s. The redox reaction between Ag^+ ion and the reducing agent appears to involve several processes, including the diffusion of the reducing agent from the fluid phase to the water core, redox reaction occurring in the water core, and distribution of oxidized form of the reducing agent between the water core and the fluid phase. An estimation of the energetics of the redox reaction is difficult to perform on the basis of the limited knowledge available at the present time for these processes.

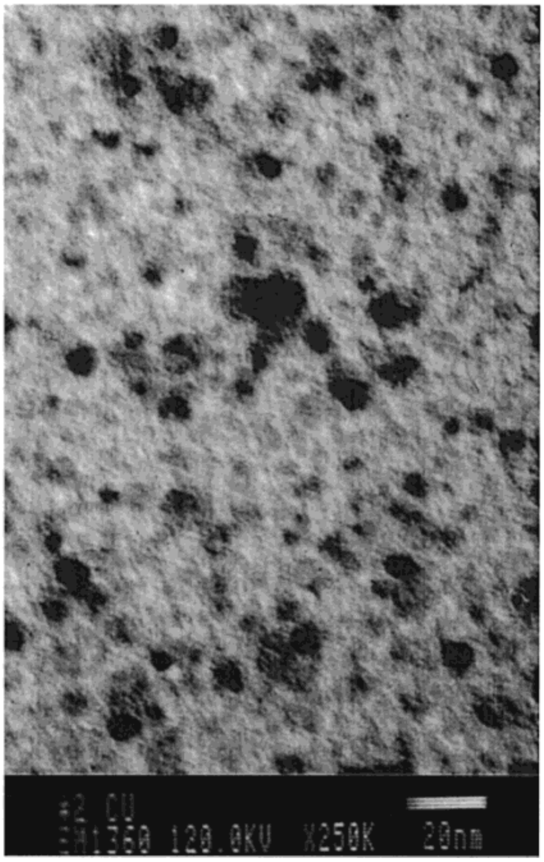

Figure 7. TEM micrograph of the copper nanoparticle collected by the RESS method. $NaBH_3CN$ was used as the reducing agent for the reduction of Cu^{2+}.

In 5% ethanol-modified supercritical CO_2 phase, we noticed that the absorption of TMPD$^{•+}$ would not decrease as rapidly as that observed in the same system with neat CO_2. The migration of TMPD$^{•+}$ to the supercritical phase and its subsequent decomposition apparently was retarded by the presence of ethanol in supercritical CO_2. As shown in Figure 5, the absorption of Ag nanoparticles was not observed at 400 nm in the ethanol-modified supercritical CO_2 system. This observation appears consistent with the suggestion that $TMPD^{\bullet+}$ would hinder the formation of the Ag nanoparticle in the microemulsion.

The results observed from the TMPD experiments indicate that the migration and distribution of the oxidized form of the reducing agent (i.e. $TMPD^{\bullet+}$) is likely to be the rate-determining step for the formation of silver nanoparticles in this system. When $NaBH_3CN$ was used as the reducing agent, formation of Ag nanoparticles was virtually completed in about 25 s, which was considerably faster than that observed in the TMPD case (ca. 200 s). Since oxidized products of $NaBH_3CN$ are much smaller compared with $TMPD^{\bullet+}$, it probably would diffuse faster and also would not create a steric hindrance for the formation of Ag nanoparticles in the water core.

Formation of Copper Nanoparticles. Figure 6a shows the absorption spectra of Cu nanoparticles produced by the reduction of Cu^{2+} in the water core of the microemulsion using TMPD as a reducing agent. The concentrations of $Cu(NO_3)_2$ and TMPD in the SF CO_2 phase were 0.3×10^{-3} and 1×10^{-3} M, respectively. Cupric ion (Cu^{2+}) has a broad absorption band centered around 800 nm. After the injection of TMPD, the broad Cu^{2+} absorption band began to decrease and strong absorption of $TMPD^{\bullet+}$ at 563 and 607 nm immediately appeared. The strong $TMPD^{\bullet+}$ absorption in the beginning masked the absorption of copper nanoparticle, which has a characteristic surface plasmon resonance absorption band centered around 557 nm.[21] Figure 6a shows the absorption of Cu nanoparticles recorded 3 min after the injection of the reducing agent TMPD. Visual observation of the Cu nanoparticles in the microemulsion was also made using a high-pressure view cell with sapphire windows. The copper nanoparticles formed by this method showed a light red color in supercritical CO_2. Figure 6b shows the change in absorbance of the 557-nm peak with time. The spectra were taken at 5-s intervals and the injection of the reducing agent took place at the fourth data point. As explained previously in the Ag nanoparticle case, a rapid initial increase in absorption at 557 nm after the injection was due to the increase in background caused by the strong absorption of $TMPD^{\bullet+}$. The absorption at 557 nm dropped to a minimum in about 100 s and started to increase gradually due to the formation of the Cu nanoparticles in the water core of the microemulsion.

When $NaBH_3CN$ was used as the reducing agent, the rate of formation of Cu nanoparticles was faster than that observed for the TMPD case. The formation of Cu nanoparticles was virtually complete after about 30 s, similar to that observed for the formation of silver nanoparticles in the microemulsion using $NaCH_3CN$ as the reducing agent. The Cu nanoparticles were collected on a carbon-coated copper grid using the RESS method described in the literature.[17] Figure 7 shows a TEM micrograph of the collected Cu nanoparticles. The size of the Cu nanoparticles was in the range 5−15 nm.

Conclusions

This study has demonstrated that with a CO_2-soluble reducing agent, such as $NaBH_3CN$ or TMPD, reduction of Ag^+ and Cu^{2+} in the water-in-supercritical-CO_2 microemulsion and subsequent formation of metal nanoparticles can take place effectively. The reaction is rapid based on the in situ spectroscopic measurements, suggesting that the microemulsion is dynamic in nature. The water-in-CO_2 microemulsion may provide a nanoreaction system for synthesizing a variety of nanoparticles in supercritical CO_2 using ionic species or water-soluble compounds as starting materials dissolved in the water core of the microemulsion.

Acknowledgment. This research was supported by a DEPSCoR grant from Army Research Office (ARO).

CM010030G

---

[21] Lisiecki, I.; Pileni, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 3887.