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Formation of metallic silver and copper in non-aqueous media by ultrasonic radiation

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ABSTRACT

Concentrated suspensions of silver and copper salts in silicone oil were heated to 200 °C and irradiated with ultrasonic energy for different time durations. Characterization of the products was done using X-ray powder diffraction. In most cases, metallic Ag or Cu were obtained, together with their oxide forms Ag_2O and Cu_2O. The salts, used as precursors, do not dissolve in silicone oil but rather form a heterogeneous system, and we assume that local heating, caused by the acoustic cavitation, enhanced their thermal decomposition and the formation of metallic particles. It was found that the presence of silver particles enhances the formation of metallic copper. This phenomenon was observed in the experiment with the acetate salts mixture.

1. Introduction

Irradiation of liquids with powerful ultrasonic energy creates acoustic cavitation which involves the formation, growth and implosive collapse of acoustic bubbles. The collapse of the gas bubbles is associated with short-lived conditions of extremely high temperatures (ca. 5500 K) and pressures (2000 atm) which can enhance the rates of chemical reactions. Moreover, in certain solvents, the ultrasonic energy can create free radicals that participate in chemical reactions. According to the literature, sonochemical reactions can take place at two sites of the gas bubbles: (a) in the interior of the bubble (in the gas phase), and (b) in the liquid shell that surrounds the bubble. However, in the case of volatile materials, the interior of the bubbles was proposed to be the principal site of the sonochemical reactions. In addition, during sonication the species present in the bulk solution can react with radicals that are formed inside or on the surface of the collapsing bubble [1]. The collapse of the bubbles generates transient shockwaves with local pressures of several hundreds of atmospheres. Such a mechanical effect leads to the mixing of the reactants, enhances their dissolution, and accelerates the reaction rates [2].

The chemical effects of ultrasonic irradiation in different media have been studied. In an aqueous medium, the high-intensity ultrasonic energy forms Ḣ and OḢ radicals by homolytic cleavage of the water molecules. These primary radicals react rapidly with other radicals or with chemical species in solution. For example, hydrogen peroxide is usually formed as a consequence of the reduction of Ḣ and oxidation of OḢ radicals [1]. In non-aqueous media, such as liquid alkanes, sonolysis causes random C–C bond cleavage. The terminal radicals that are formed can react in various routes: a) elimination of ethylene to form shorter-chain radicals; b) elimination of H atoms to form 1-alkenes; or c) abstraction of H atoms to form shorter alkenes and secondary radicals. In the case of alkanes, the sonolysis also generates large amounts of H_2, CH_4 and C_2H_2 that are similar to the products obtained in high-temperature pyrolysis experiments (≈1200 °C) [3].

Recently, we reported that prolonged sonication (~1–2 h) of PEG-400 or certain organic solvents can generate carbon dots (C-dots) and carbon film [4,5]. This is in accordance with a literature report that describes different carbon nanostructures obtained by prolonged sonication [6]. C-dots were used as reducing agents for obtaining silver nanoparticles from Ag^+ [7]. Sonication was also reported to be a useful method for modifying silicon-backbone polymers, but the use of silicone oil as a medium for chemical reactions was less investigated [8].

Thermal decompositions of silver and copper salts were reported in the literature. Logvinenko et al. [11] studied the thermal decomposition of silver acetate under inert atmosphere, which yielded metallic silver and other products (CO, CO_2, H_2O and CH_3COOH). They suggested that the metal formation occurs via intramolecular reduction that follows the complex decomposition process that starts at 270 °C. Nakano et al.

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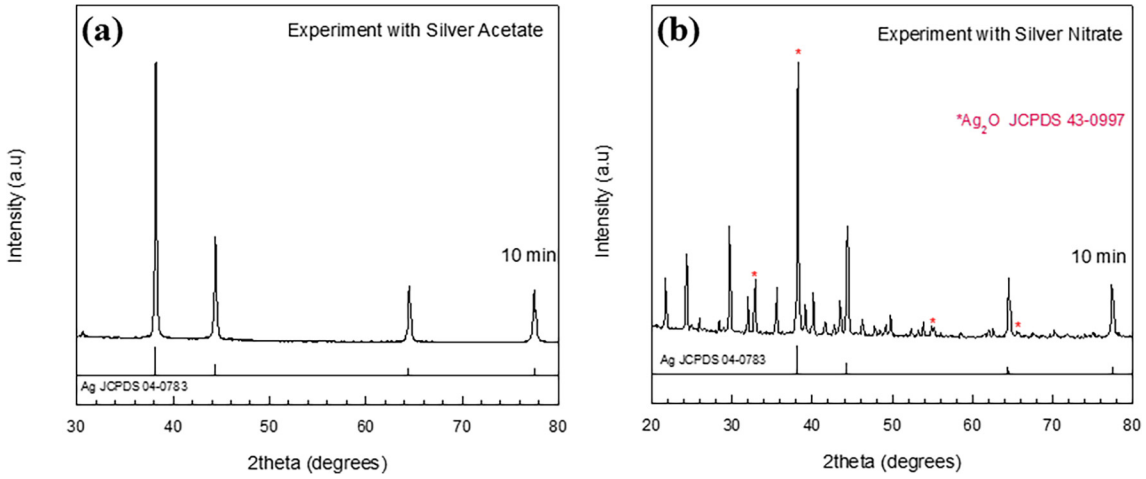

Fig. 1. X-ray powder diffraction patterns of the samples obtained after 10 min sonications of suspensions of (a) silver acetate and (b) silver nitrate in silicone oil heated to 200 °C. The Bragg peaks for metallic silver are marked.

[12] heated silver acetate under N_2 atmosphere and detected the structural changes by XRD at different temperatures. They observed that the formation of metallic silver started between 150 and 175 °C and was completed between 200 and 250 °C, being affected by parameters such as the heating rate and gas flow rate. Thermal decomposition of copper acetate monohydrate under ambient atmosphere was studied by Lin et al. [10]. After the dehydration step at around 150 °C, decomposition of this salt was detected at around 270 °C. Identification of the products by XRD showed the presence of CuO, Cu_2O and Cu.

The goal of this work was to study the reactions occurring when ultrasonic energy is applied to high-concentrated suspensions of Ag and Cu salts in silicone oil, and in particular to explore the prospective formation of metallic particles. Three sets of experiments were done, in which suspensions of acetate, nitrate and sulfate salts of silver and copper in silicone oil were irradiated with ultrasonic energy. In the first and second sets of experiments, sonications of single-component suspensions were performed, while the third set involved sonication of a mixture of salts. Formation of metal oxides and free metals was observed, as a function of the different types of salts and durations of sonication.

2. Experimental

2.1. Materials

Silver acetate (anhydrous 99%, Alfa Ésar), silver nitrate (anhydrous 99.9%, Merck), copper (II) acetate monohydrate (ACS reagent ≥98%, Sigma Aldrich), copper (II) nitrate (hemipentahydrate, ≥98%, Sigma Aldrich), copper (II) sulfate (pentahydrate, 98%, Sigma Aldrich), and silicone oil (density 0.97 g/mL at 25 °C, boiling point 250 °C, viscosity 10 cS) were used as received.

2.2. Procedure

A test tube containing a suspension of 38 mg/mL of silver or copper (II) salts or a 1:1 wt ratio mixture of silver and copper salts in 12 mL of silicone oil was heated under Ar flow at 200 °C in an oil bath. The tip of the ultrasonic rod (10 mm in diameter) was dipped in the silicone oil, ca. 2 cm above the salt grains. The suspension was irradiated with ultrasonic energy at 20 kHz and 60% amplitude for different durations of time, using an ultrasonic transducer (Sonics and Materials Inc., USA, model VCX 750, frequency 20 kHz, voltage 230 V AC). After sonication, the suspension was cooled to room temperature under Ar flow. The solid particles were separated by centrifugation and washed five times with n-hexane to remove all the silicone oil from the solid material. The samples were dried overnight under vacuum at room temperature.

2.3. Characterization

X-ray powder diffraction (XRD) was done using a Bruker D8 diffractometer equipped with a scintillation counter and monochromatic sources. The Bragg–Brentano geometry was adopted using CuKα radiation (λ = 1.541 Å) at a setting of 40 kV and 40 mA. The phases were identified using the joint committee on powder diffraction standards (JCPDS) database (International Center for Diffraction Data). Images of the particles were obtained by environmental scanning electron microscopy (ESEM) using a FEI QUANTA 200F instrument. Thermogravimetric analysis (TGA) was performed using a TGA/SDTA851e Mettler Toledo instrument operating up to 900 °C, at a scan-rate of 10 K/min under air or N_2 flow.

3. Results

3.1. Sonication of silver salts in silicone oil

3.1.1. Silver acetate

0.45 g of silver acetate was mixed with 12 mL of silicone oil (38 mg/mL), and the mixture was heated to 200 °C for 30 min in an oil bath. Silver acetate is insoluble in silicone oil, and only a certain fraction of it was suspended while most of the salt remained as a precipitate. Irradiation with ultrasonic energy produced no audible sound during the first two minutes, perhaps due to the high viscosity of the suspension in which no gas bubbles could be formed and therefore cavitation could not occur [9] or because of the presence of the solid salt grains that interfered with the formation of the gas bubbles until they were fully suspended. As cavitation started, a thicker suspension was formed, and its color changed over time from light grey to dark grey. After 10 min of sonication, the suspension was cooled to ambient temperature, and the solid was separated from the silicone oil by centrifugation, washed several times with n-hexane, and dried overnight. XRD analysis of the powder (Fig. 1a) gave a pattern that includes the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections for the silver cubic phase (JCPDS file No. 04-0783), indicating the conversion of Ag(I) to metallic silver.

In order to verify the role of sonication in the reduction of ionic silver, a similar heterogeneous solid-liquid system of silver acetate in silicone oil was heated to 200 °C for 50 min without applying ultrasonic energy. No metallic silver was formed in this case, leaving only the unreacted salt in the silicone oil. TGA characterization of silver acetate showed a single step of weight loss of 34–35% in the temperature range of 185–297 °C, which corresponds to the loss of acetate ion (theoretical

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