

Synthesis, Characterization, and Properties of Metallic Copper Nanoparticles

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Nanoscale particles of metallic copper clusters have been prepared by two methods, namely the thermal reduction and sonochemical reduction of copper(II) hydrazine carboxylate $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ complex in an aqueous medium. Both reduction processes take place under an argon atmosphere over a period of 2–3 h. The FT-IR, powder X-ray diffraction, and UV–visible studies support the reduction products of Cu^{2+} ions as metallic copper nanocrystallites. The powder X-ray analysis of the thermally derived products show the formation of pure metallic copper, while the sonochemical method yields a mixture of metallic copper and copper oxide (Cu_2O). The formation of Cu_2O along with the copper nanoparticles in the sonochemical process can be attributed to the partial oxidation of copper by in situ generated H_2O_2 under the sonochemical conditions. However, the presence of a mixture of an argon/hydrogen (95:5) atmosphere yields pure copper metallic nanoparticles, which could be due to the scavenging action of the hydrogen towards the OH^\bullet radicals that are produced in solution during ultrasonic irradiation. The synthesized copper nanoparticles exhibit a distinct absorption peak in the region of 550–650 nm. The transmission electron microscopy studies of the thermally derived copper show the presence of irregularly shaped particles (200–250 nm) having sharp edges and facets. On the other hand, the sonochemically derived copper powder shows the presence of porous aggregates (50–70 nm) that contain an irregular network of small nanoparticles. The copper nanoparticles are catalytically active toward an “Ullmann reaction”—that is, the condensation of aryl halides to an extent of 80–90% conversion. The time course of catalysis was studied for condensation of iodobenzene at 200 °C for a period of 1–5 h. The catalytic ability of copper nanoparticles produced by the thermal and sonochemical methods was compared with that of commercial copper powders.

1. Introduction

Nanoparticle research has witnessed tremendous growth due to the unusual chemical and physical properties which have been demonstrated to be an intermediate state of matter.^{1,2} The catalytic activity of the particles generally depends on their size, shape, and stabilizing agents, which are controlled by the preparation conditions.³ There are diverse approaches to the preparation of the nanoscale materials that have been reported in the literature.^{4–7} Some of these methods include controlled chemical reduction,⁴ electrochemical reduction,⁵ and metal vaporization.⁶ Re-

cently, sonochemical processing has been proven to be a useful technique for generating novel materials with unusual properties.⁷ The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles in liquid, which produces unusual chemical environments. The extreme conditions attained during bubble collapse have been exploited to prepare nanoscale metals,⁸ metal oxides,⁹ and nanocomposites.¹⁰

Although efforts have been made to study the change in the morphology (size and shape), nonlinear optical properties, and electrical conductivity of the copper nanoparticles under different preparation conditions, there are no reports in the literature regarding the sonochemical generation and catalytic activity of copper nanoparticles. The condensation of aromatic halides (except fluorine) catalyzed by copper, known as the “Ullmann reaction,” has gained tremendous laboratory and industrial interest due to its wide applicability in

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(1) Schmid, G. *Clusters and Colloids: From Theory to Applications*; VCH: Weinheim, 1994. Volokitin, Y.; Sinzig, J.; de-Jongh, L. J.; Schmid, G.; Vargaftik, M. N.; Moiseev, I. I. *Science* **1996**, *384*, 621.

(2) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511.

(3) Bonnemant, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Jousen, T.; Koppler, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*, 129. Ahmadi, S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.

(4) Pileni, M. P. *Langmuir* **1997**, *13*, 3266. Huang, H. H.; Yan, Y. Q.; Kek, Y. M.; Chew, C. H.; Xu, G. Q.; Ji, W.; Oh, P. S.; Tang, S. H. *Langmuir* **1997**, *13*, 172.

(5) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401. Bandyopadhyay, S.; Chakravorty, D. *J. Mater. Res.* **1997**, *12*, 2719.

(6) Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153. Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(7) Suslick, K. S. *Ultrasounds: Its Chemical, Physical and Biological Effects*; VCH: Weinheim, 1988.

(8) Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414. Kolytyn, Y.; Katabi, G.; Prozorov, R.; Gedanken, A. *J. Non-Cryst. Solids* **1996**, *201*, 159. Dhas, N. A.; Cohen, H.; Gedanken, A. *J. Phys. Chem. B* **1997**, *101*, 6834.

(9) Mulvaney, P.; Cooper, M.; Grieser, F.; Meisel, D. *J. Phys. Chem.* **1990**, *94*, 8339. Dhas, N. A.; Gedanken, A. *J. Phys. Chem. B* **1997**, *101*, 9495. Dhas, N. A.; Kolytyn, Y.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 3159.

(10) Dhas, N. A.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 3144.

the synthesis of symmetrical and unsymmetrical biaryls and polyaryls with different functional groups which are otherwise difficult to obtain.¹¹ The adsorption of aromatic halides on metal particles is strong because of the interaction of the delocalized π -electrons with the metal. The mechanism of the Ullmann condensation reaction is believed to be the nucleophilic attack of copper on an aromatic carbon carrying halogen substitution.

Metal hydrazine carboxylates, $M(N_2H_3COO)_2 \cdot 2H_2O$ ($M = Mg, Ca, Mn, Fe, Co, Ni, Cu$), have been used as precursors to fine particle oxide materials.^{12,13} The novelty of these precursors is due to their low-temperature ($<300^\circ C$) autocatalytic exothermic decomposition with the evolution of large amounts of gases to yield fine particles having high surface area oxides. Although a large amount of work has been carried out on these complexes to prepare simple and mixed metal oxides, no one has yet reported on the preparation of metallic nanoparticles. In this paper we report on the preparation of technologically important nanoscale copper metallic clusters by the thermal and ultrasound-assisted reduction of copper hydrazine carboxylate in water at near room temperature. We have also studied the effect of preparation conditions on the phase composition, morphology, and catalytic ability of copper nanoparticles toward the Ullmann reaction—that is, the condensation of iodobenzene to biphenyl in comparison to what occurs with commercial copper powder.

2. Experimental Section

Preparation of the Copper Hydrazine Carboxylate Precursor. The ligand hydrazine carboxylic acid, N_2H_3COOH , was prepared by saturating $N_2H_4 \cdot H_2O$ (99% Aldrich) with CO_2 gas. Copper hydrazine carboxylate (CHC) precursor was prepared by treating a saturated solution of cupric chloride with hydrazine carboxylic acid. The addition of solid N_2H_3COOH to a saturated solution containing Cu^{2+} ions facilitates the precipitation of $Cu(N_2H_3COO)_2 \cdot 2H_2O$, without the reduction of Cu^{2+} ions. The blue precipitate formed was filtered, washed with alcohol, and dried in a vacuum. The composition of the complex was fixed by chemical analysis as $Cu(N_2H_3COO)_2 \cdot 2H_2O$ [hydrazine 26.3%(obs), 26.7%(calc); Cu^{2+} 28.1%(obs), 27.4%(calc)]. The amount of Cu^{2+} was estimated iodometrically, using standard sodium thiosulfate. Hydrazine content was determined volumetrically, using 0.025 M KIO_3 under Andrew's conditions.¹⁴

The infrared absorption of CHC is similar to the reported spectrum of metal hydrazine carboxylate hydrates. In all complexes, the $N_2H_3COO^-$ group is known to act as a bidentate ligand and coordinates to the metal through N and O atoms, forming a five membered ring. The observed absorption frequencies at 3500 (ν_{OH}), 2980 (ν_{NH}), 1655 and 1495 (ν_{COO}), and 1010 cm^{-1} (ν_{NN}) are characteristic of the $Cu(N_2H_3COO)_2 \cdot 2H_2O$ complex.¹³

Synthesis of Copper Metallic Nanoparticles. (a) *Thermal Process.* The nanoparticles of copper in an aqueous medium were synthesized by the following method. In a typical experiment 300 mg of CHC was dissolved in 100 mL of distilled water. The reaction mixture was then refluxed at $\sim 80^\circ C$ for 3 h under an argon atmosphere. As the thermal

reduction proceeded, the blue solution turned to red, indicating the formation of metallic copper. The resulting reddish slurry was carefully transferred into a centrifuge tube, and the solid residue was recovered by centrifugation (9000 rpm for 20 min). It was further washed repeatedly with ethanol and dried in a vacuum. Dried samples were preserved in vials in an inert-atmosphere glovebox for further studies. The infrared (IR) spectrum of the resulting residue did not show any characteristic absorption of the CHC precursor.

(b) *Sonochemical Process.* Ultrasound irradiation of a slurry of CHC in an aqueous medium yields reddish nanoparticles of copper. On exposing a slurry of CHC complex in water to high-power (100 $W\ cm^{-2}$) ultrasound radiation, the blue colored slurry initially turns to red, which on further irradiation leads to the appearance of metallic luster. Typically, a slurry of CHC (300 mg) in distilled water (100 mL) was exposed to high-intensity ultrasound radiation for 3 h by employing a direct immersion titanium horn (Misonix XL sonicator; 1.13 cm diameter Ti horn, 20 kHz) for 2 h. The solutions to be irradiated were purged with argon gas and were kept under argon throughout the experiment. During the irradiation, the temperature of the reaction medium rose to $\sim 80^\circ C$, as measured using a iron-constantan thermocouple. The resulting reddish slurry was carefully transferred into a centrifuge tube, and the metal particle was recovered by centrifugation (9000 rpm for 20 min). The metallic particle thus obtained was washed thoroughly with ethanol and dried in a vacuum. Dried samples were preserved in vials in an inert-atmosphere glovebox for further studies.

The above experiment was also carried out under a mixture of an argon (95%) and hydrogen (5%) atmosphere. In both the thermal and sonochemical processes, the CHC complex was quantitatively converted into metallic copper nanoparticles.

Product Characterization. The X-ray diffraction patterns of the copper nanocrystallites were recorded by employing a Rigaku X-ray diffractometer (model 2028, $Cu\ K\alpha$). The lattice parameters were calculated with a least-squares fit, using the (111), (200), and (220) X-ray reflections. The UV-visible spectra of the copper nanoparticles were recorded in a Varian (model DMS 100S) spectrophotometer. The transmission electron micrographs (TEM) were obtained by employing JEOL-JEM 100SX microscopy. Samples for the TEM examination were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film and were allowed to dry in air.

Catalysis. Iodobenzene was obtained from Aldrich and was distilled before use. Copper powder was purchased from Fluka and used without further purification. The copper powders prepared by thermal and sonochemical methods were used for catalytic testing without further activation. In a typical reaction, 40 mg of copper and 80 mg of iodobenzene were heated in an oil bath maintained at $200^\circ C$. After the required time interval, the reaction system was cooled rapidly to room temperature, 0.5 mL of $CDCl_3$ was added, and then the organic compound was filtered through silica gel. The percentage of product formed was calculated based on the NMR integration of ortho protons of iodobenzene and biphenyl formed, which are distinctly separated in the 300 MHz (Bruker 300 MHz) NMR spectrum.¹⁵

3. Results and Discussion

Characterization. Powder X-ray. The formation of copper nanoparticles is confirmed by the powder X-ray diffraction (XRD). Figure 1 displays the XRD profile of the CHC complex and the products. The XRD pattern (Figure 1a) of the CHC quantitatively matches the earlier reported diffractogram.¹³ Figure 1b shows the XRD pattern of the copper formed by the thermal

(11) Ullmann, F. *Annalen*, **1904**, 332, 38. Forrest, J. J. *Chem. Soc.* **1960**, 566.

(12) Ravindranathan, P.; Patil, K. C. *Ceram. Bull.* **1987**, 66, 688. Ravindranathan, P.; Patil, K. C. *J. Mater. Sci.* **1987**, 22, 3261. Dhas, N. A.; Patil, K. C. *J. Solid State Chem.* **1993**, 102, 440.

(13) Manoharan, S. S.; Patil, K. C. *Proc. Ind. Acad. Sci.* **1989**, 101, 377.

(14) Vogel, A. I. A textbook of quantitative inorganic analysis; Longmans: London, pp 311, 358, 380, 1961.

(15) Iodobenzene: 7.73 δ , d, $J = 9$ Hz (2 H); 7.36 δ , m (1 H); 7.13 δ , t, $J = 8$ Hz (2 H). Diphenyl: 7.71 δ , d, $J = 9$ Hz (4 H); 7.47 δ , t, $J = 8$ Hz (4 H); 7.38 δ , m (2 H).

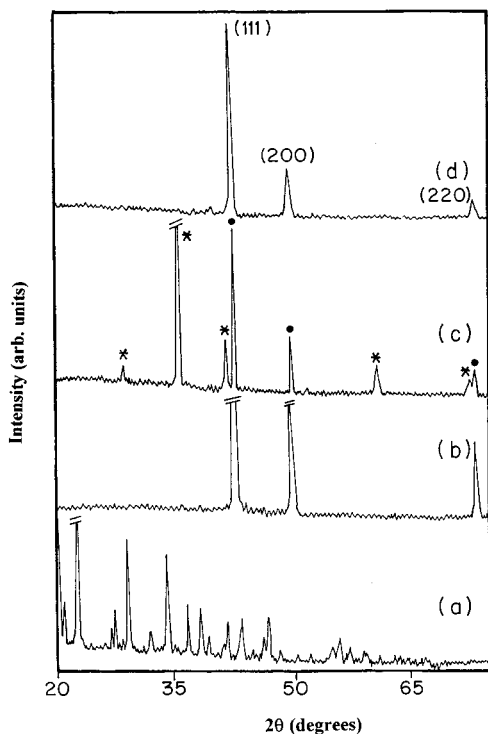


Figure 1. X-ray diffractograms: (a) CHC complex, (b) thermal reduction product of CHC, (c) sonochemical reduction product of CHC under argon atmosphere (* denotes Cu_2O , • denotes Cu), (d) sonochemical reduction product of CHC under a mixture of argon/hydrogen atmosphere.

process. The peak positions are consistent with metallic copper. All possible peaks of copper are observed, which indicates the polycrystalline nature of the product. The X-ray reflections are indexed on the basis of the fcc structure of copper with the space group of $Fm\bar{3}m$ (ASTM card no. 4-0836, X-ray diffraction files for inorganic materials). The calculated lattice constant, $a = 3.6147 \text{ \AA}$, is in good agreement with the literature value (3.6150 \AA).

The XRD pattern of the sonochemically derived solid product under an argon atmosphere showed additional peaks, apart from the one which corresponds to metallic copper (Figure 1c). The additional peaks are assigned to Cu_2O , in comparison with those described in the literature (ASTM card no. 34-1354). The formation of Cu_2O indicates that the sonochemical reaction mechanism is different from that of the conventional thermal process under similar experimental conditions. However, the ultrasound irradiation under a mixture of an argon and hydrogen atmosphere yields pure copper nanoparticles (Figure 1d). The formation of nanocrystalline copper under sonochemical conditions is rather surprising, since, in general, it yields amorphous materials.⁸ However, the formation of nanocrystallites can be correlated to the nature (volatility, solubility, etc.) of the starting material (see below).

UV-Visible. Figure 2 shows the absorption spectrum of the copper nanoparticles prepared by both the thermal and sonochemical processes. The sonochemically prepared copper nanoparticles display an absorption peak at around 570 nm. This peak can be assigned to the absorption of nanoparticles of copper.¹⁶ A modest blue shift ($\sim 20\text{--}30 \text{ nm}$) of the absorption edge relative to that of the bulk copper powder ($\sim 600 \text{ nm}$) is observed.

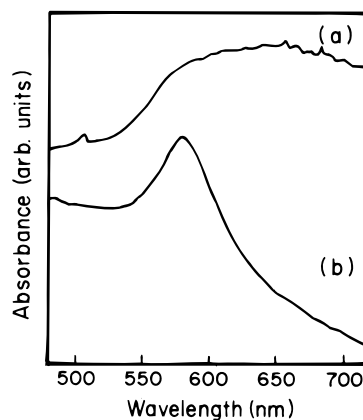


Figure 2. UV-visible spectra of copper prepared by (a) the thermal process and (b) the sonochemical process.

This observation alludes to the size effect of the copper nanocrystallites. On the other hand, the thermally prepared copper nanoparticles display a broad absorption from 550 to 700 nm. The broadness of the absorption peak probably stems from the wide size distribution.

Microstructure. Figures 3 and 4 reveal the TEM microstructure of the thermally and sonochemically derived copper nanoparticles, respectively. The micrograph of thermally derived nanoparticles of copper shows (Figure 3) the presence of dense agglomerates. The particles have an irregular shape, and their distribution, likewise, is not uniform (200–300 nm). This is probably due to the partial solubility of the CHC complex in the water under the given experimental conditions. At a higher magnification (Figure 3b), the micrograph shows that the particles have well-defined sharp faces and corners. The microstructure also shows the existence of dislocations within the crystallites.

The sonochemically derived powder shows the presence of porous nanoparticles that are aggregated irregularly (Figure 4), which makes the measurement of exact particle size difficult. However, the particles are smaller ($\sim 50 \text{ nm}$) than those obtained by the thermal process. At a higher magnification, the porous network of small nanoparticles can be seen (Figure 4b). The formation of such an irregular porous network as a result of the sonochemical effect has also been observed for other systems.^{8,9} The formation of a large network of $(\text{Cu}^0)_n$ could be due to the interparticle collision between the copper nanoparticles associated with the sonochemical cavitation effects.⁷

Mechanism of Sonochemical Reduction. The chemical reactions driven by intense ultrasonic waves that are strong enough to produce cavitation are oxidation, reduction, dissolution, and decomposition.^{7,17–20} Other reactions, such as promotion of polymerization, have also been reported to be induced by ultrasound. It has been known that three different regions are formed

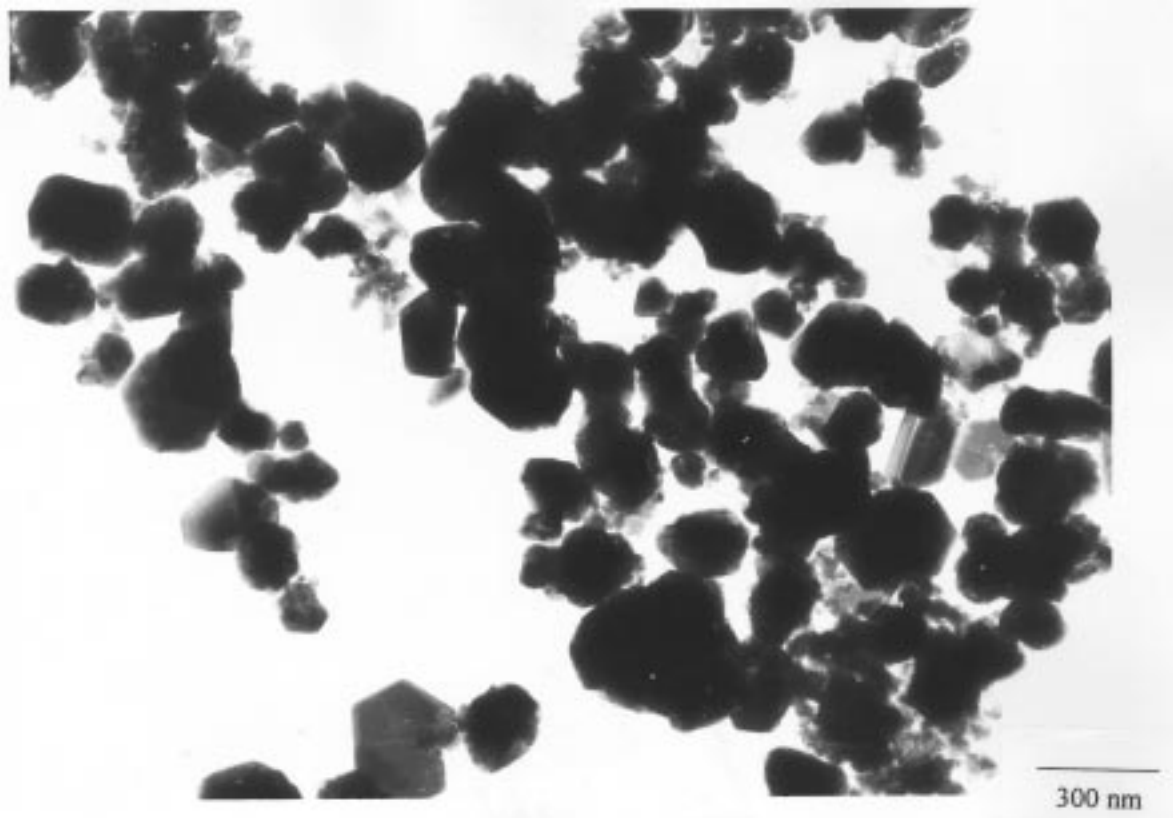
(16) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.

(17) Alegria, A. E.; Lion, Y.; Kondo, T.; Riesz, P. *J. Phys. Chem.* **1989**, *93*, 4908.

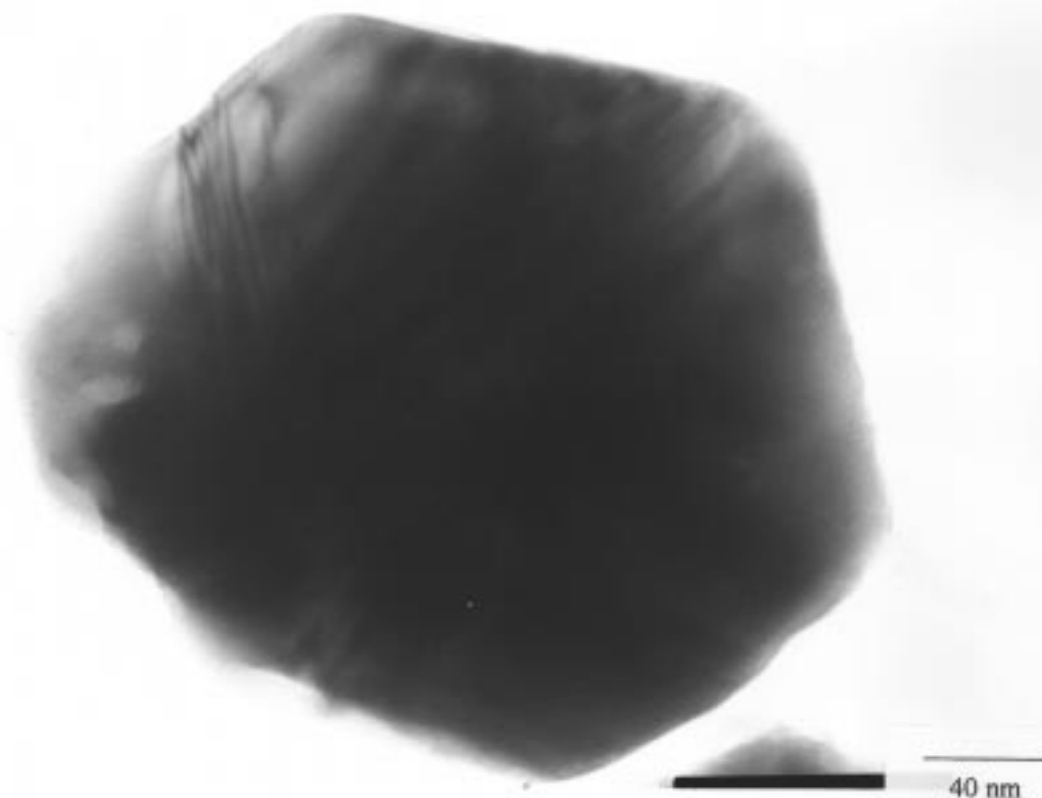
(18) Gutierrez, M.; Henglein, A. *J. Phys. Chem.* **1988**, *92*, 2978.

(19) Sostaric, J. Z.; Mulvaney, P.; Grieser, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2843.

(20) Gutierrez, M.; Henglein, A.; Dohrmann, J. *J. Phys. Chem.* **1987**, *91*, 6687.



(a)



(b)

Figure 3. TEM micrograph of copper nanoparticles prepared by the thermal process at two different magnifications: (a) bar = 300 nm, (b) bar = 40 nm.

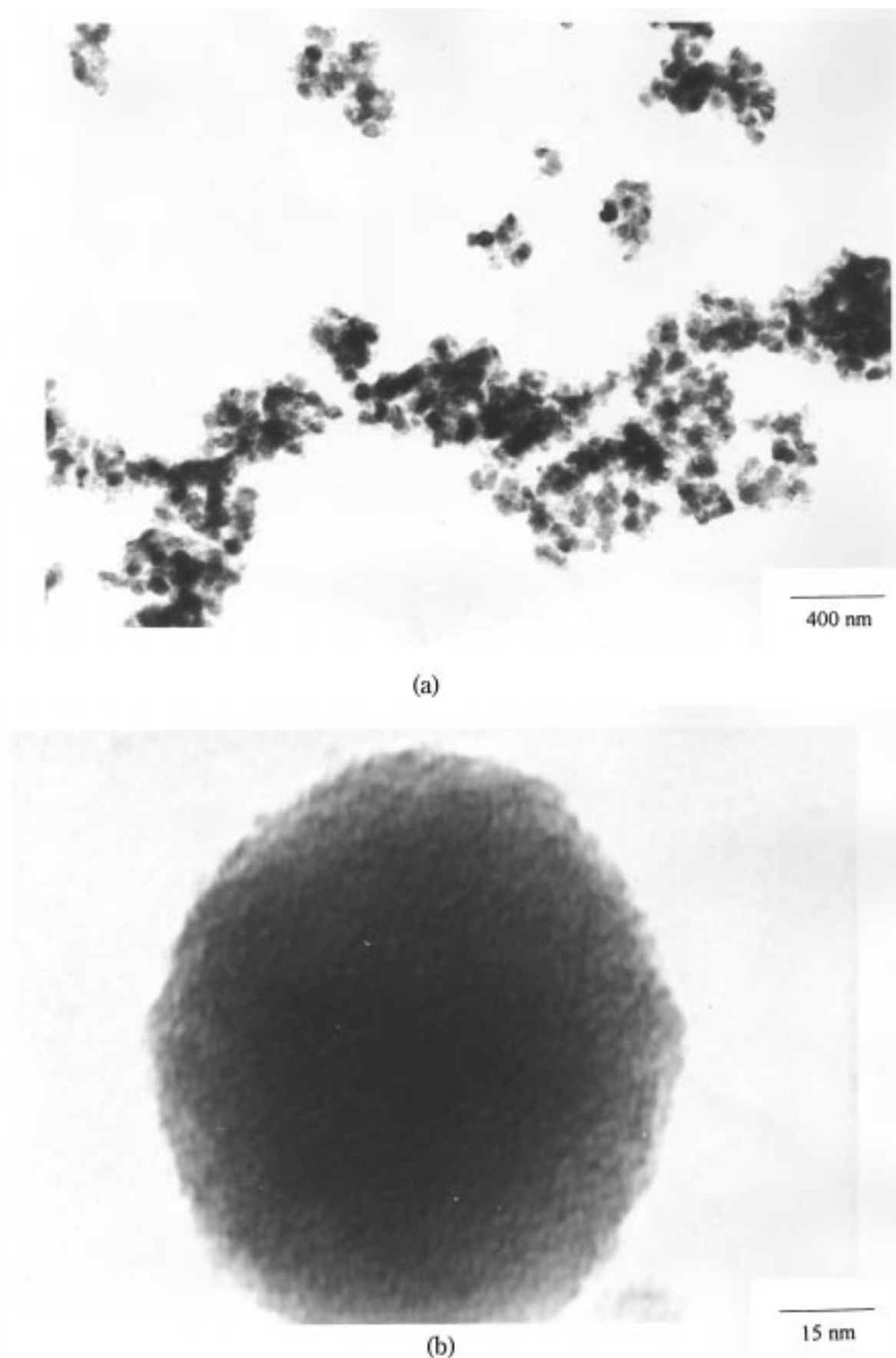


Figure 4. TEM micrograph of copper nanoparticles prepared by the sonochemical process at two different magnifications: (a) bar = 400 nm, (b) bar = 15 nm.

during the aqueous sonochemical process: (1) the inner environment (gas phase) of the collapsing bubble, where

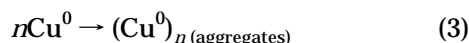
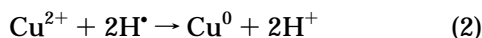
elevated temperatures (several thousands of degrees) and pressures (hundreds of atmospheres) are produced,

which causes water to vaporize and further to pyrolyze into H^\bullet and OH^\bullet radicals; (2) the interfacial region between the cavitation bubbles and the bulk solution where the temperature is lower than in the gas-phase region, but still high enough to induce a sonochemical reaction; and (3) the bulk solution, which is at ambient temperatures and is where the reaction between reactant molecules and OH^\bullet or H^\bullet radicals takes place. Among the above-mentioned three regions, it appears that the interfacial zone and the bulk solution are the major areas where the sonochemical reduction takes place. Due to the low vapor pressure of the CHC complex, only a negligible amount of the Cu^{2+} ion is expected to be present inside the cavity or bubble for a sonochemical reaction. It is generally observed that the sonochemical decomposition of volatile precursor occurs inside the bubble, yielding amorphous materials, due to the very high quenching rate (10^8 K/s) experienced by the products. On the other hand, the sonochemical reactions that occur in the interfacial or bulk regions yield nanocrystalline materials. Therefore, the non-volatile nature of the CHC complex and the formation of nanocrystalline products excludes the reduction of Cu^{2+} ions inside the bubble. Hence, it is reasonable to assume that the sonochemical reduction of Cu^{2+} ions would have occurred in both the interfacial region and in the bulk solution, not in the gas-phase region.

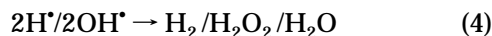
The mechanism of the reduction process must take into consideration radical species generated from water molecules by the absorption of ultrasound. The likely reaction steps and explanation for the sonochemical reduction process are summarized below.



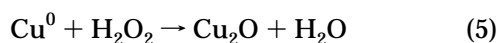
The H^\bullet radicals formed in eq 1 can act as a reducing species and trigger the $Cu^{2+} \rightarrow Cu^0$ reduction.



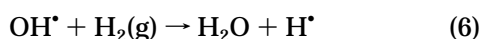
The possible pathway for the formation of Cu_2O could be due to the partial oxidation of Cu^0 by the secondary species formed by the recombination of the H^\bullet and OH^\bullet radicals. In the absence of any additives or scavengers, the H^\bullet and OH^\bullet radicals readily recombine to give the products as shown in eq 4.²⁰



The oxidant H_2O_2 thus generated can initiate the oxidization of copper metallic clusters into copper(I) oxide.



However, in the presence of an argon and hydrogen atmosphere, the formation of H_2O_2 can be arrested due to the scavenging of OH^\bullet radicals by the hydrogen,²⁰ thereby yielding pure copper nanoparticles.



Therefore, the argon and hydrogen mixtures produce

Scheme 1

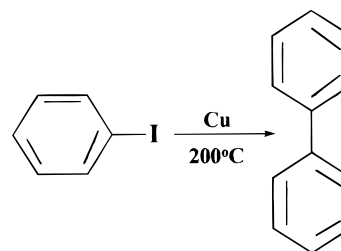


Table 1. Catalytic Yield of the Biphenyl in the Ullmann Reaction at 200 °C for 5 h for the Copper Catalyst Having Different Particle Sizes

source of copper catalyst	particle size (nm)	yield (%)
sonochemical	50–70	88
thermal	200–250	79
commercial	500–600	43

even more H^\bullet radicals than normal, according to eq 6, thereby enhancing the reduction of Cu^{2+} ions under the sonochemical conditions. The above mechanism involves radicals, which explains the formation of a mixture of products under the argon atmosphere and pure copper nanoparticles in the argon/hydrogen environment.

Catalytic Activity. The condensation of iodobenzene to biphenyl (Scheme 1) was chosen as the model reaction for catalytic study, due to its significance in organic synthesis.

The total yields of biphenyl in the condensation of iodobenzene for different copper powders are summarized in Table 1. The particle size of the different copper powders was included in the table for comparison. The commercial copper shows a 43% conversion of iodobenzene to biphenyl for 5 h under our experimental conditions. The thermally prepared copper powder shows a better conversion (79%) compared to that of the commercial one. The sonochemically prepared copper nanoclusters show a maximum conversion of about 88%. The higher catalytic activity toward the condensation of iodobenzene could be due to the higher catalytic surface area of small and porous nanoparticles. The poor catalytic ability of the commercial copper powders is a direct result of dense aggregates of larger sized particles.

Figure 5 compares the activity of sonochemically and thermally prepared copper nanoclusters along with the commercial copper powder. It is very clear that both thermally and sonochemically generated copper powders show a higher conversion rate than does the commercial one. From the plot it can be seen that the maximum conversion is attained at about 3 h in the case of thermally and sonochemically generated copper powder. However, in the case of commercial copper powder, it is almost linear for up to 5 h. The catalytic behavior of copper nanoparticles thus prepared provides a better yield and reduced reaction time in the conversion of iodobenzene to biphenyl. Further study of copper catalyzed organic reactions using copper nanoparticles leads to interesting practical applications.

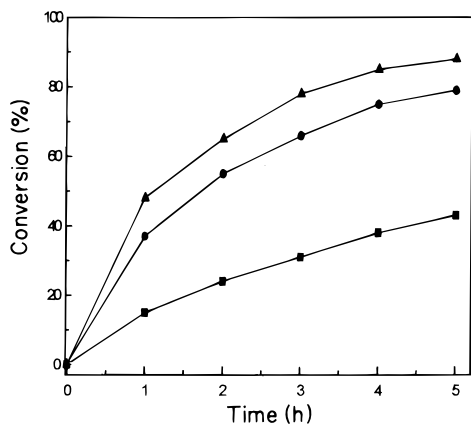


Figure 5. Catalytic activity of different copper nanoclusters toward the iodobenzene condensation as a function of time (■, commercial copper powder; ●, prepared by the thermal process; ▲, prepared by the sonochemical process).

4. Conclusion

Nanoparticles of copper clusters have been obtained by the thermal and the sonochemical reduction of the copper hydrazine carboxylate complex. The powder XRD shows the formation of Cu_2O , in addition to copper nanoparticles, during the sonochemical process in an argon atmosphere, indicating the generation and participation of radicals that are formed by the sonolysis of water. Ultrasonic irradiation of CHC under a mixture of argon and hydrogen atmosphere yielded pure copper metallic clusters, which explains the scavenging

action of hydrogen toward the OH^\bullet radicals. A possible mechanism involving the participation of H^\bullet and OH^\bullet radicals has been proposed for the sonochemical reduction of Cu^{2+} ions to metallic copper nanoparticles. It is apparent that the chemical mechanism of the formation of nanoparticles under sonochemical conditions is different from that under thermal conditions. The TEM studies revealed that the thermally derived nanoparticles are dense, with sharp faces, while the sonochemical process yields porous nanoparticles. The copper powders prepared by the thermal and sonochemical reduction of copper hydrazine carboxylate precursor are capable of enhancing the rate of the Ullmann reaction, and the catalytic activity of these copper powders is superior to that of the commercial powders. This method promises the preparation of other technologically important simple and binary alloys of transition metallic clusters.

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