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Influence of Reducing Atmosphere of Subcritical/Supercritical Mild Alcohols on the Synthesis of Copper Powder

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ABSTRACT: Copper powder with different size was synthesized using subcritical/supercritical mild alcohols without additional reductant. The interaction influence of the reducing atmosphere, including temperature, pressure, precursors, and alcohol types, was investigated. XRD and SEM were applied to analyze the composition and morphology of products synthesized. Results showed that the reducing atmosphere formed by critical conditions, precursors, and mild-alcohol types had a significant effect on the products. The reducing atmosphere could be enhanced obviously with higher temperature and pressure. CuO was easier to reduce than $Cu(NO_3)_2$ and $CuSO_4$ under the same conditions. Compared with ethanol, methanol could form a stronger reducing atmosphere at the same temperature and pressure. Supercritical methanol (250 °C, 9 MPa) with CuO as a precursor could provide the optimal reducing atmosphere for the synthesis of copper powder. In addition, it was proposed that mild alcohols should play an important role as capping agents as well as reducing agents under subcritical/supercritical conditions.

1. INTRODUCTION

Copper powder, with particle sizes between 1 nm and 10 μm, is applied in many areas, such as electrode material, conductive coatings, and efficient catalysts, because of its large specific surface area and high surface energy.[1,2] At present, several methods are used to prepare superfine copper powder, including hydrothermal and solvothermal,[3] thermal decomposition,[4] reverse micelle,[5] metal deposition[6] and liquid-phase reduction,[7−10] and so on. However, some restrictive problems exist in these methods. For example, the reducing agents used in liquid-phase reduction are either highly toxic or costly, hydrothermal methods require a long period of time, and the equipment for metal deposition is complicated and costly.

In recent years, supercritical fluids are widely developed for preparing superfine metal or metal oxide particles.[11−14] Preparations of copper superfine powders by using supercritical fluids are also reported by some literature. Aymonier et al. synthesized copper nanoparticles through the reduction of $Cu(hfac)_2 \cdot H_2O$ in supercritical CO_2/alcohol/H_2 mixtures, in which silica spheres were used as a model support.[15,16] Cason et al. prepared copper nanoparticles by reducing $Cu(AOT)_2$ using supercritical ethane, in which the reaction precursor $Cu(AOT)_2$ was difficult to obtain and was toxic.[17] Kim et al. reported the synthesis of copper nanoparticles in supercritical methanol with copper nitrate as a precursor, using supercritical methanol at higher temperatures (400 °C) and pressures (30 MPa).[18,19] Ziegler et al. synthesized copper nanocrystals with copper(II) nitrates hemipentahydrate and copper(II) acetate monohydrate in supercritical water with an additional capping ligand of 1-hexanethiol,[20] in which toxic and odor-reducing agents were needed.

In a word, superfine copper particles have been produced in some sc-fluids. Nevertheless, the precursors and additives used in these methods were seldom or toxic, which limited the development and application of these supercritical fluids in the preparation of pure copper. In these methods, the synthesis of subcritical/supercritical mild alcohols might be the most promising method for its characteristic simple, inexpensive, and moderate conditions. For this method, the reducing atmosphere of the system was the most critical factor for obtaining the zerovalent state of copper. Therefore, in this study, the constitution and reducing ability of the atmosphere of subcritical/supercritical methanol and ethanol were investigated with different conditions and inorganic precursors. Compared with organic precursors, copper oxide and inorganic copper salts had the advantages of being low cost and easily obtained. In addition, the total process could be made easier using moderate subcritical/supercritical conditions and the equipment requirements were also lower. The possible mechanism of the reaction, which occurred in a reducing atmosphere, was also provided in this paper.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Copper Powder. CuO, $Cu(NO_3)_2$, $CuSO_4$, and ethanol and methanol (each of analytical reagent (AR) grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PRC). All reagents were used without further purification.

In a typical synthetic procedure, 3 g (0.0375 mol) of CuO was loaded into a 50-mL autoclave, and then the air inside was exhausted under vacuum for 10 min after the autoclave was sealed. Twenty-five (25) grams (0.781 mol) of methanol was then discharged into the autoclave. The reaction was kept at 250 °C and 9 MPa for 10−60 min and then quenched to room temperature; ~10−15 min were required to reach the desired temperature. The formed product was treated

under ultrasonic for 10 min and then filtrated and washed three times with methanol. Copper powder was obtained after being dried under vacuum.

2.2. Sample Characterizations. The structure and purity of the products was identified by powder X-ray diffraction (XRD), which was carried out using Cu $K\alpha_1$ radiation on a D8 Avance X-ray generator (Bruker AXS Company, Germany). The X-ray intensity was measured over a diffraction angle from 20° 2θ to 80° 2θ with a step size of 2° 2θ min^{-1}. The morphologies of products were observed by scanning electron microscopy (SEM) (Model SM-6360LV, JEOL, Tokyo, Japan). The SEM images were obtained at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was also employed to analyze the morphology and microstructure of the products. The sample for TEM analysis was prepared by dispersing nanoparticles in ethanol and depositing them onto a carbon-coated copper TEM grid. X-ray photoelectron spectroscopy (XPS) (Mode ESCALAB250, Thermo VG) was employed to analysis the surface of the copper powders.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature and Pressure on the Reducing Atmosphere. The effect of temperature and pressure on the reducing atmosphere for preparing copper powder was investigated. CuO was used as the copper source, and the reaction time was 0.5 h. The XRD patterns of products are displayed in Figure 1. It can be seen that the products obtained
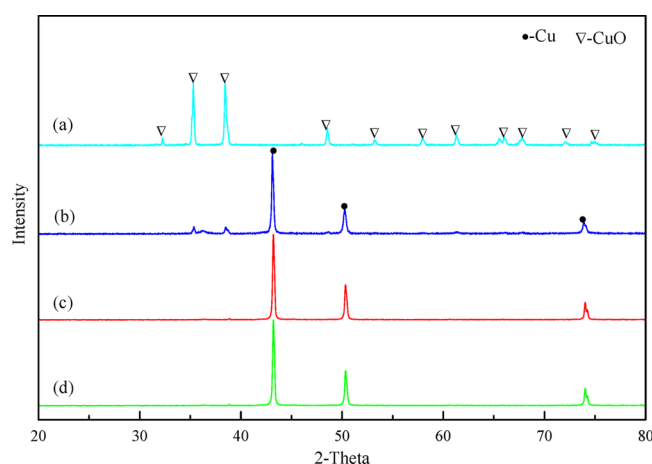

Figure 1. XRD patterns of the products prepared using CuO as the precursor at different temperatures and pressure for 0.5 h: (a) 150 °C, 5 MPa; (b) 200 °C, 7 MPa; (c) 250 °C, 9 MPa; and (d) 300 °C, 14 MPa.

under different atmospheres are distinct. Subcritical temperature (150 °C) and pressure (5 MPa) almost could not produce an effective reducing atmosphere and no reaction happened. XRD analysis showed that all diffraction peaks belonged to the precursor CuO (Figure 1a). Most of the CuO was reduced to pure copper when the subcritical temperature and pressure were 200 °C and 7 MPa, respectively, which was closer to the supercritical domain; however, a small amount of CuO still existed in the product system (Figure 1b). When the reaction was carried out under a supercritical methanol atmosphere (250 °C, 9 MPa and 300 °C, 14 MPa), CuO was completely reduced to pure metal. Only three diffraction peaks were observed, at 2θ = 43.53°, 50.65°, and 74.30°, which could be ascribed to the crystal planes of (111), (200), and (220) (see Figures 1c and 1d).

The above results indicated that the effects of temperature and pressure on the reducibility of atmosphere were significant.

Supercritical conditions of methanol could enhance atmosphere reducibility markedly for reducing CuO to pure metal thoroughly. Some literature reported that supercritical methanol could release free hydroxyl ions (OH$^-$),[13] which had strong reducibility.[21] However, there was no or fewer OH$^-$ when alcohol was in the subcritical domain. Thus, copper oxide could not be reduced completely to copper under the atmosphere produced by a subcritical domain. It also revealed that higher temperature and pressure were beneficial to the dissociation of OH$^-$ from MeOH and a stronger reducing atmosphere.[22]

3.2. Effect of Copper Precursors on the Reducing Atmosphere and the Required Time. Figures 2 and 3 were
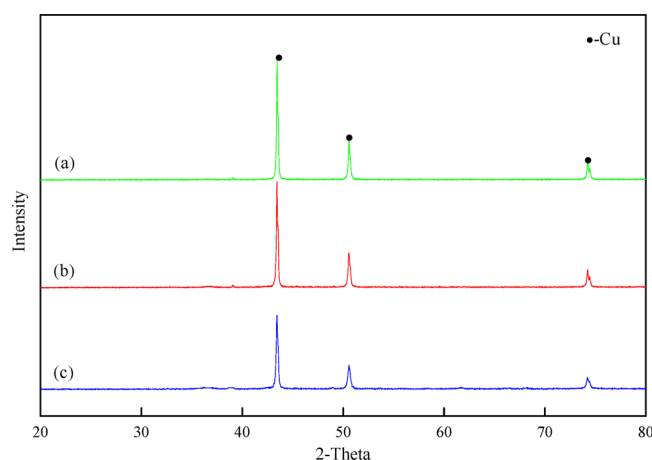

Figure 2. XRD patterns of the samples prepared using CuO as precursor for (a) 0.25 h, (b) 0.5 h, and (c) 1.0 h at 250 °C and 9 MPa.

the XRD patterns and SEM images of samples obtained under the atmosphere formed by supercritical MeOH at 250 °C and 9 MPa with different times (0.25, 0.5, and 1.0 h), in which CuO was used as the precursor. Figure 2 showed that 0.25 h was enough for complete reaction in the supercritical reducing atmosphere, and no longer time was needed. The SEM images in Figure 3 revealed the morphology of products obtained with different time was distinct. Spherical shape and particles 300−400 nm in diameter were formed after 0.25 h (Figure 3a). With the increasing of reaction time, well-regulated morphology of products disappeared and particles aggregated gradually (see Figures 3b and 3c). It indicated that morphology and dispersion of Cu particles would change dramatically with the length of retention time in the reducing atmosphere. Therefore, suitable reaction time was the key factor to synthesize fine copper particles, which was much smaller than the raw CuO powder (see Figure 3d).

In addition to CuO, two most common copper salts Cu(NO$_3$)$_2$ and CuSO$_4$ were also applied for studying the effect of precursors on the atmosphere. The results are shown in Figures 4 and 5. XRD analysis showed that types of precursors would influence the reducing ability of atmosphere markedly. For Cu(NO$_3$)$_2$, no copper but Cu$_2$O and CuO were produced after reacting 0.25 h under supercritical methanol (250 °C, 9 MPa) (Figure 4a). When increasing the reaction time to 0.5 or 1.0 h, copper began to appear in the products (see Figures 4b and 4c). For CuSO$_4$, a large amount of copper could be obtained after only 0.25 h. Comparing Figures 2, 4, and 5, it could be seen that different reducing atmospheres were needed by different precursors. It was worth noting that pure copper
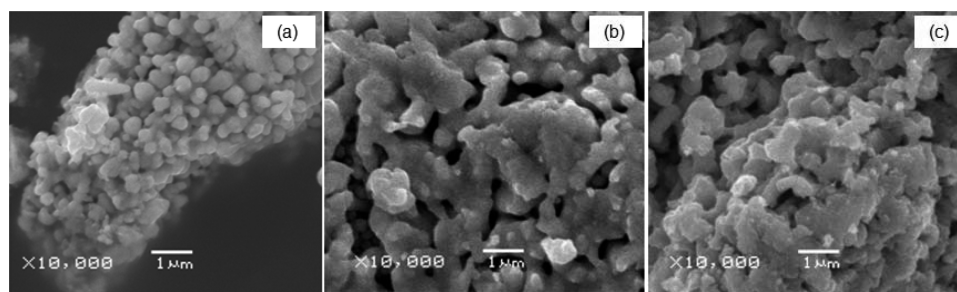
Figure 3. SEM images of the powders synthesized using CuO as precursor for (a) 0.25 h, (b) 0.5 h, and (c) 1.0 h at 250 °C and 9 MPa.
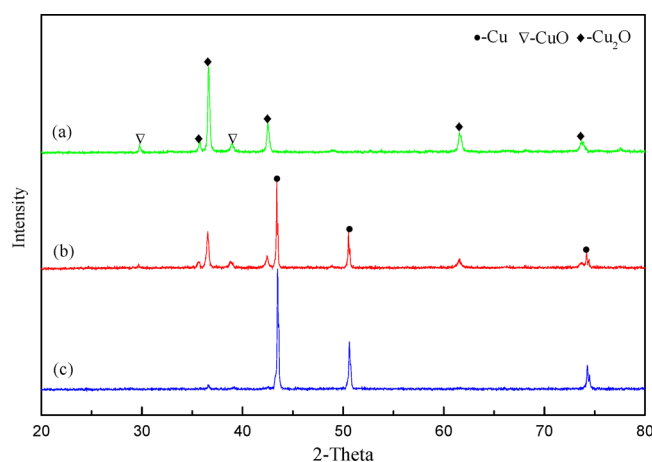

Figure 4. XRD patterns of the samples prepared using $Cu(NO_3)_2$ as the precursor for (a) 0.25 h, (b) 0.5 h, and (c) 1.0 h, at 250 °C and 9 MPa.
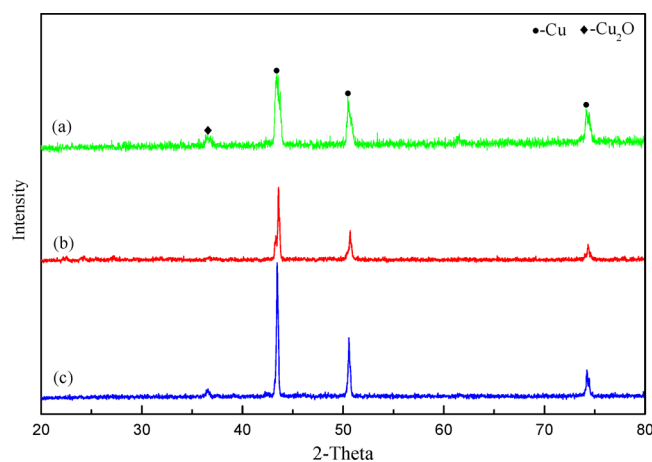

Figure 6. XRD patterns of the samples prepared using different precursors for 5 min at 300 °C and 14 MPa: (a) $Cu(NO_3)_2$, (b) $CuSO_4$, and (c) CuO.

Figure 5. XRD patterns of the samples prepared using $CuSO_4$ as precursor for (a) 0.25 h, (b) 0.5 h, and (c) 1.0 h, at 250 °C and 9 MPa.

Figures 7g, 7h, and 7i show that the average size was 24.0, 285.8, and 358.9 nm for the copper particles obtained from CuO, $Cu(NO_3)_2$, and $CuSO_4$, respectively. The above results revealed that precursors could influence not only the reducing ability of the atmosphere but also the morphology and size of the products obviously. CuO had the apparent advantages of being able to prepare uniform and smaller-sized copper particles, while the copper salts produced powder with larger particle size, which might be caused by the effect of the anion (NO_3^- and SO_4^{2-}). BET results showed that surface area size of three copper particles were 23.8, 5.6, and 2.4 m^2/g, respectively. Therefore, comparing with $Cu(NO_3)_2$ and $CuSO_4$, CuO was preferred to be precursor for Cu synthesis by supercritical MeOH.

The results also indicated that the reaction mechanisms in the process were different for cupric oxide and inorganic copper salts. For $Cu(NO_3)_2$ and $CuSO_4$, Cu^{2+} in system was combined with OH^- to produce $Cu(OH)_2$ first, which was then decomposed into cupric oxide by dehydration. NO_3^- released from $Cu(NO_3)_2$ possessed strong oxidizability, which could weaken the reducing atmosphere of the system significantly. Therefore, a longer time was needed to obtain pure copper from $Cu(NO_3)_2$ than from $CuSO_4$ as the precursor.

In order to analyze the elements composition on the surface of copper powder, XPS characterization was carried out. As shown in Figure 8a, the XPS survey spectra possess four peaks centered at 284.2, 531.9, 930.9, and 950.9 eV, corresponding to C 1s, O 1s, Cu $2p_{3/2}$, and Cu $2p_{1/2}$, respectively. XPS of C 1s ranging from 281 to 291 eV was shown as Figure 8b, which exhibited three peaks by curve fitting of the C 1s spectrum, in

powder was synthesized by reacting 5 min under a more intense reducing atmosphere of 300 °C and 14 MPa for any one of the three precursors in Figure 6. The SEM and TEM images, as well as the size distributions of Cu particles obtained at 300 °C and 14 MPa with different precursors are also present in Figure 7. Figure 7a showed that uniform spherical-shaped particles 20−50 nm in diameter could be obtained, using CuO as material, which was consistent with the TEM result in Figure 7d, while the products prepared with $Cu(NO_3)_2$ and $CuSO_4$ as precursors possessed larger particle size (∼200−600 nm) and aggregated markedly (see Figures 7b, 7c, 7e, and 7f).
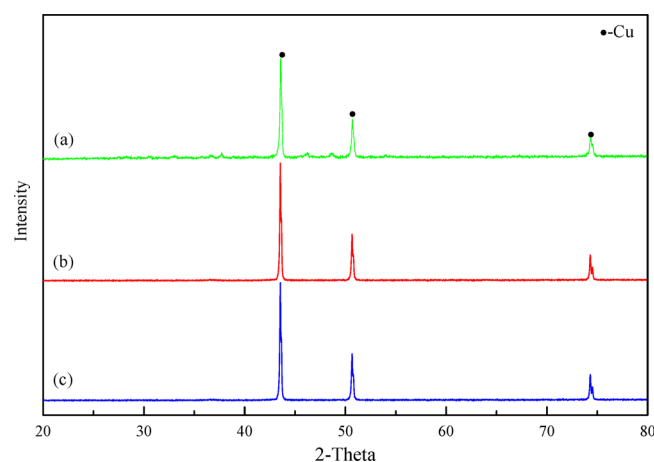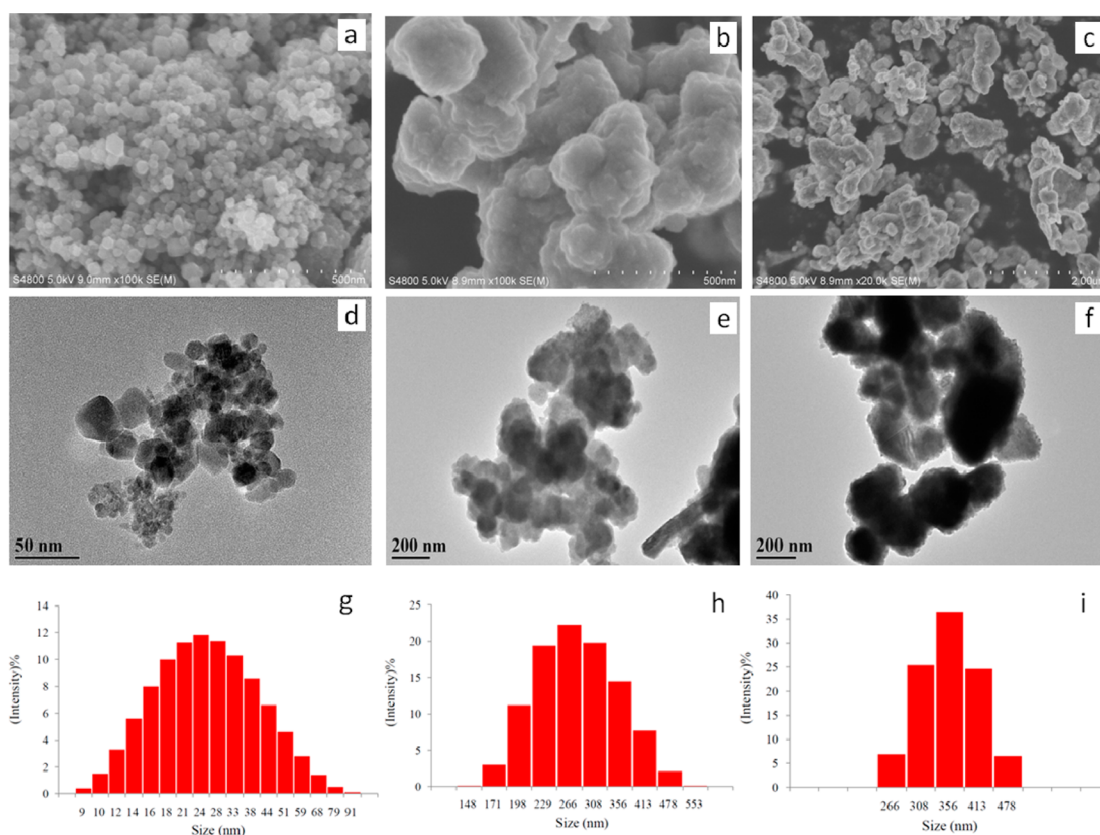
Figure 7. SEM images, TEM images, and size distributions of the products prepared using different precursors for 5 min at 300 °C and 14 MPa: (a, d, g) CuO, (b, e, h) $Cu(NO_3)_2$, and (c, f, i) $CuSO_4$.
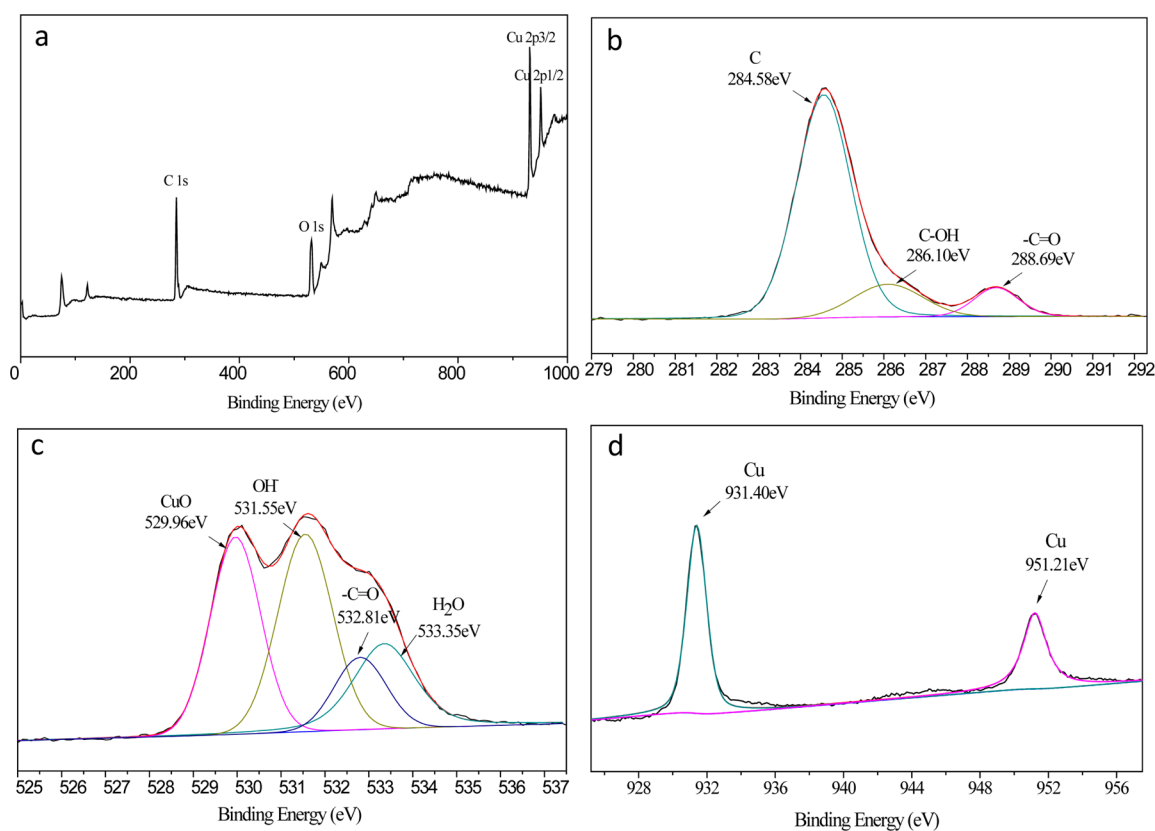

Figure 8. (a) XPS spectra of Cu powder; curve fitting of (b) C 1s, (c) O 1s, and (d) Cu 2p.

which the peak at 288.69 eV was related to $-C=O$. The peaks at 286.10 and 284.58 eV were related to $C-OH$ of MeOH and carbon, respectively. The O 1s peak was also split into four peaks, as shown in Figure 8c, which indicated that there were residual of CuO (529.96 eV), OH^- (531.55 eV) released from MeOH, $-C=O$ (532.81 eV, C1) and H_2O (533.35 eV) on the surface of the product. Both of $-C=O$ groups (288.69 and 532.81 eV) indicated that HCHO was produced by oxidation of MeOH in the process. In addition, it worth noting that the three peaks at 288.69, 531.55, and 532.81 eV explained the capping role of MeOH in the process. Figure 8d showed the two peaks (931.40 and 951.21 eV) of elemental copper.

3.3. Effect of Types of Mild Alcohols on the Reducing Atmosphere. There was a great difference in the properties of different supercritical mild alcohols. In addition to methanol, ethanol was also applied to form reducing atmosphere in this study. Figure 9 showed the XRD patterns of products prepared
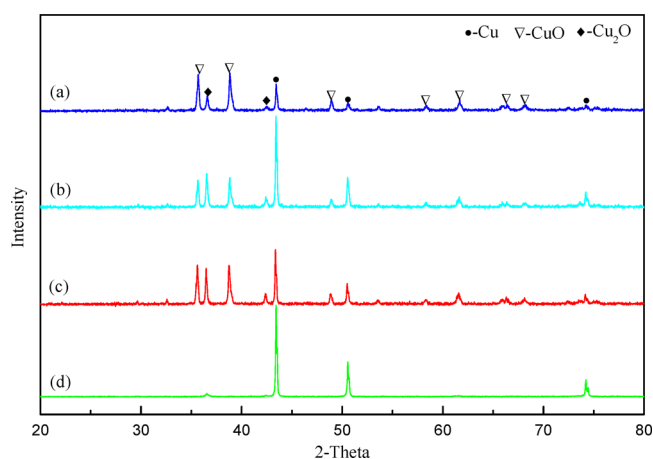

Figure 9. XRD patterns of the samples prepared in supercritical ethanol using CuO as the precursor at 250 °C, 7 MPa for (a) 0.25 h, (b) 0.5 h, and (c) 1.0 h, and (d) at 300 °C, 12 MPa for 5 min.

in supercritical ethanol using CuO as precursor under different atmospheres. Figures 9a−c revealed that the products consist of Cu, Cu_2O, and CuO, no matter how long the reaction lasted within 1.0 h at 250 °C and 7 MPa. However, only 5 min was needed to obtain pure copper at 300 °C and 12 MPa (Figure 9d). The above results indicated supercritical MeOH could form stronger reducing atmosphere than EtOH at the same temperature and pressure.

3.4. Proposed Reaction Mechanism. On the basis of XRD, SEM, TEM, and XPS results, the reaction mechanism available during the synthesis of copper in the reducing atmosphere of supercritical methanol was elucidated and described in Figure 10. MeOH was decomposed into free OH^- and CH_3^+ first when it reached the supercritical domain. The covalent bond of CuO was then destroyed by CH_3^+ and OH^- at higher temperature and pressure. $Cu^{2+}(-O-CH_3^+)OH^-$ appeared to be the intermediate as a result of the combination between methyl cation and oxygen atom which possessed strong electronegativity. This revealed that the supercritical methanol also played the role of solvent in addition to reducing agent, which was consistent with the literature.[23,24] Electron transfer from the O atom to the Cu atom happened in the intermediate, and then zerovalent copper, hydroxyl, and methoxy radicals were formed. Subsequent electron transfer in methoxy radicals produced formaldehyde and a hydrogen radical, which would react with the hydroxyl radical to produce H_2O.

4. CONCLUSIONS

In summary, a reducing atmosphere formed by subcritical/supercritical mild alcohols had been applied to prepare copper powder. Results showed that the composition and morphology of products obtained depended mainly on the reducing atmosphere, which was influenced by temperature, pressure, metal precursors, and types of mild alcohol. Supercritical (higher temperature and pressure) mild alcohols could provide a stronger reducing atmosphere than subcritical mild alcohols. CuO was easier to reduce to pure copper than $Cu(NO_3)_2$ and $CuSO_4$ under the same atmosphere. The atmosphere formed by methanol possessed stronger reducibility than ethanol. In the synthesis process, methanol played an important role as a capping agent as well as a reducing agent under supercritical conditions.

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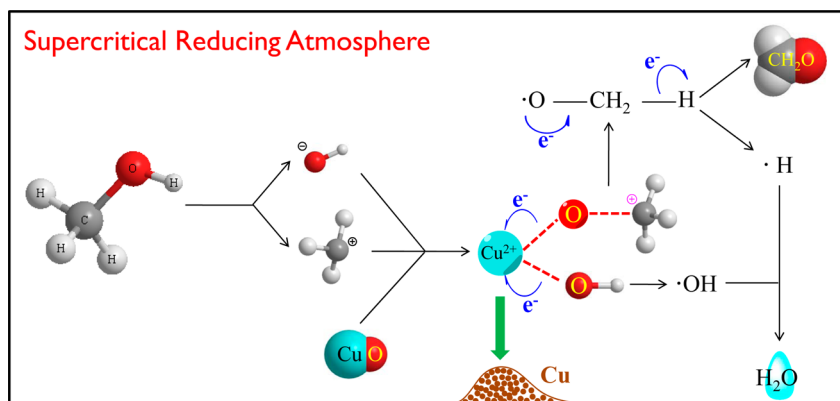The authors declare no competing financial interest.

Figure 10. Schematic diagram of reaction mechanism under the reductive supercritical mild-alcohol synthesis.

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