

## Study on the Catalytic Properties of Copper Oxide Nanoparticles Synthesized by Levitational Gas Condensation (LGC) Method

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The Cu oxide nano powders were synthesized by levitational gas condensation (LGC) method and their high heterogeneous catalytic effects of oxidation of 2,3,5-trimethyl-1,4-hydroquinone (TMHQ) and catalase activity were studied. The nano powders consist of mainly Cu<sub>2</sub>O. The catalytic effect which was clarified by the oxidation of TMHQ and the activity of catalase, was found to depend on the amount of Cu<sub>2</sub>O phase and the particle size.

**Keywords :** Cu oxide, Heterogeneous catalytic effect

### I. Introduction

Copper (Cu) oxides are widely applied in various organic syntheses such as reduction and oxidation processes, various condensation processes and syntheses of complex compounds etc. [1]. However, these processes are generally known to be nonselective and take place at relatively high temperature and pressure. In order to enhance selectivity, reactivity and catalytic ability of metals and their oxides, nanocrystalline materials as catalysts and reagents for organic syntheses have been actively investigated due to new properties of these catalysts and reagents caused by the active center on their surface [2-4]. The surface of nanocrystalline Cu oxide includes defect structure, resulting in non-stoichiometry [5]. Such materials in themselves have both advantages of homogeneous and heterogeneous catalysts. Application of nanomaterials as catalysts represents a new perspective and promising field in matrix catalysis and template synthesis.

The aim of this investigation is the development of effective catalytic and reaction systems on the base of nanocrystalline Cu oxides having high reactivity at ambient temperature. For the test of catalytic reaction, both the reaction of liquid-phase oxidation of 2,3,5-trimethyl-1,4-hydroquinone (TMHQ) and the catalase activity were chosen [6, 7]. The oxidation of TMHQ is an intermediate stage of hydroxylation of 2,3,6-trimethyl phenol in synthesis of tocopherol [6]. The catalase activity is informative parameter of catalytic properties of materials in red-ox

process. It is simulated by measuring the ability of catalase with the decomposition of hydrogen peroxide to isolation of molecular oxygen [8, 9].

### 2. Experimental Technique

High purity Cu oxide powders were synthesized by a LGC method as described in detail elsewhere [10]. Apparatus consists of high frequency induction generator of 5 kW, levitation and evaporation chamber, and oxygen concentration control unit. Pressure of mixed Ar and O<sub>2</sub> gas in a chamber was from 15 to 18 kPa. The starting material was Cu wire. For the comparison of catalytic properties of Cu oxides, the powders with various sizes were synthesized. The size control of powder was carried out by feeding velocity of Cu wire from 20 to 80 mm/min. The phase control of Cu, Cu<sub>2</sub>O and CuO was carried out by O<sub>2</sub> pressure. In Table I, the crystallite conditions of copper oxides were displayed.

Process of TMHQ oxidation was carried out in thermostatically controlled chamber, under agitation of mixed water and methanol solution (1 : 1 in volume) at 50 ± 0.2 °C. The rate of air supply was 6.2 l/h. Reaction was carried out at the contents of parent material (0.66 mmol) and nano powders (1 mmol).

Decomposition of hydrogen peroxide was carried out in thermostatically isolated chemical reactor (volume 10 ml). The solution of mixed water and methanol (1 : 1 in volume) was agitated with rate of stirring rod at 50 ± 0.2 °C. Reaction was carried out at the content of hydrogen peroxide (1.7 mmol) and nano powder (2 mg).

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**Table I.** The composition of nano copper oxides and the reaction yields of TMHQ oxidative dehydrogenation.

Sample (Size)	Conditions for synthesis: (Feeding speed, draft velocity, and pressure in chamber)	Phase composition, wt%			Catalytic yield (TMHQ)
		Cu	Cu <sub>2</sub> O	CuO	
a. (~20 nm)	Slow feeding (20~30 mm/min) 0.0 ≤ V <sub>O<sub>2</sub></sub> (l/min) ≤ 0.05, 15 kPa	78	22	-	No reaction
1. (35 nm)	Slow feeding (20~30 mm/min) 0.05 ≤ V <sub>O<sub>2</sub></sub> (l/min) ≤ 0.10, 17 kPa	20	62	28	active
2. (90 nm)	Fast feeding (60 mm/min) V <sub>O<sub>2</sub></sub> = 0.2 (l/min), 18 kPa	1	99	-	Initial
3. (35 nm)	Slow feeding (20~30 mm/min) V <sub>O<sub>2</sub></sub> = 0.2 (l/min), 17 kPa	-	100	-	Very active
4. (35 nm)	Slow feeding (20~30 mm/min) 0.1 ≤ V <sub>O<sub>2</sub></sub> (l/min) ≤ 0.15, 17 kPa	10	85	5	Very active

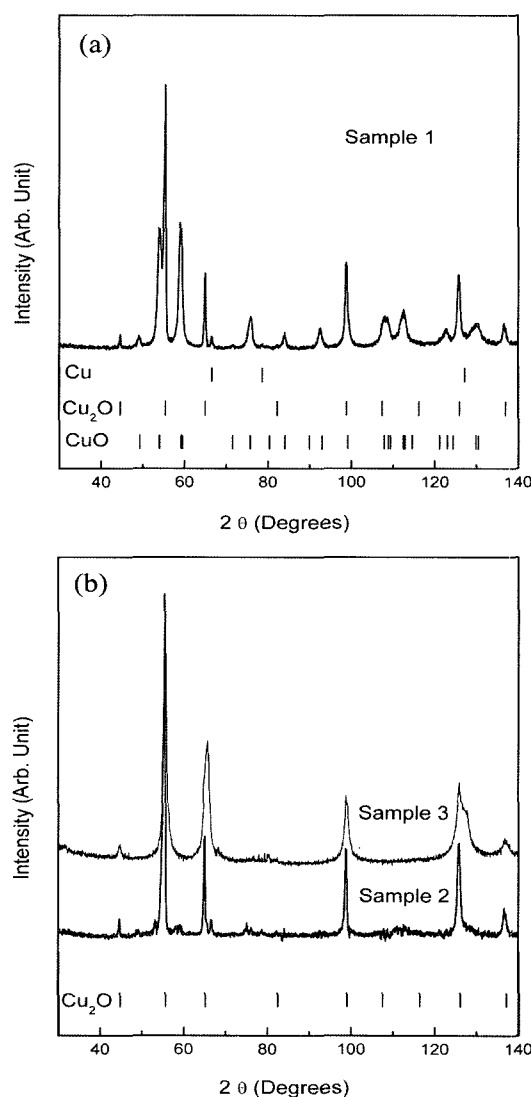
The size and the specific surface area of the as-prepared sample were characterized by TEM (Transmission Electron Microscope) and BET surface area analyzer. The oxide phase and crystal structure were analyzed by XRD.

### 3. Results and Discussion

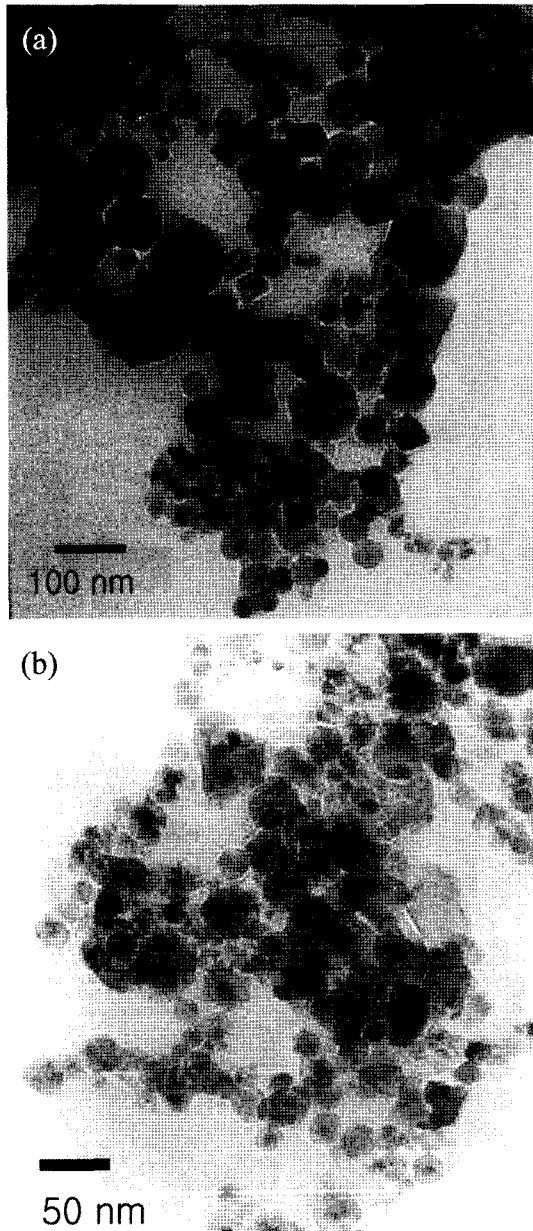
In Table I, the nanocrystal samples of copper oxides with different phase composition used for different reactions are given. The controlling of the feeding speed of metal wire and a gas atmosphere in chamber plays a role of determining Cu oxide phase and size of particles. Table I displays size and phase of Cu oxides synthesized by LGC method under various conditions [10].

Calculation of parameters of the crystalline lattice, phase composition, quantitative analysis and evaluation of blocks of coherent scattering (BCS) were carried out. In Fig. 1 diffraction patterns of powders with different BCS (30 and 100 nm) are shown. The positions of Bragg peaks of phases presenting in samples are shown in Fig. 1(a). It represents Cu oxides (sample 1) with size of 35 nm prepared under low O<sub>2</sub> pressure ranges from 0.05 to 0.1. The main peaks corresponded to typical cuprite (Cu<sub>2</sub>O), and small amount of copper (Cu) and tenorite (CuO) was found. Parameters of monoclinic tenorite (space group C2/c) are equal to  $a = 4.6837$ ,  $b = 3.4226$ ,  $c = 5.1288$  Å, and  $\beta = 99.54^\circ$  [11]. Smaller parameter values of tenorite correspond to samples exposed to air for a long time. In a sample 2 with size of 90 nm (Fig. 1(b)), the width of main peaks corresponding to typical cuprite (Cu<sub>2</sub>O) was sharpened. In a sample 3 with size of 35 nm (Fig. 1(b)), the weak wide main peaks corresponded to typical cuprite (Cu<sub>2</sub>O). Cuprite crystalline lattice parameter in samples was  $a = 4.268$  Å (table parameter value  $a = 4.270$  Å [11]).

The microstructure and phase composition of nano



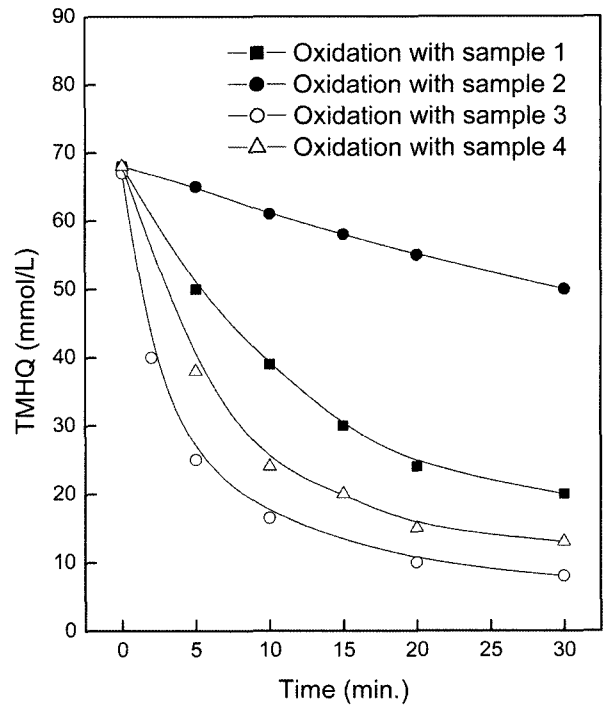
**Fig. 1.** X-ray diffraction pattern of nano powder (a) sample 1 (Cu 20 %, Cu<sub>2</sub>O 62 %, CuO 18 %) with size of 35 nm, (b) sample 2 (Cu<sub>2</sub>O 99 %) with size of 90 nm, and sample 3 (Cu<sub>2</sub>O 99 %) with size of 35 nm.



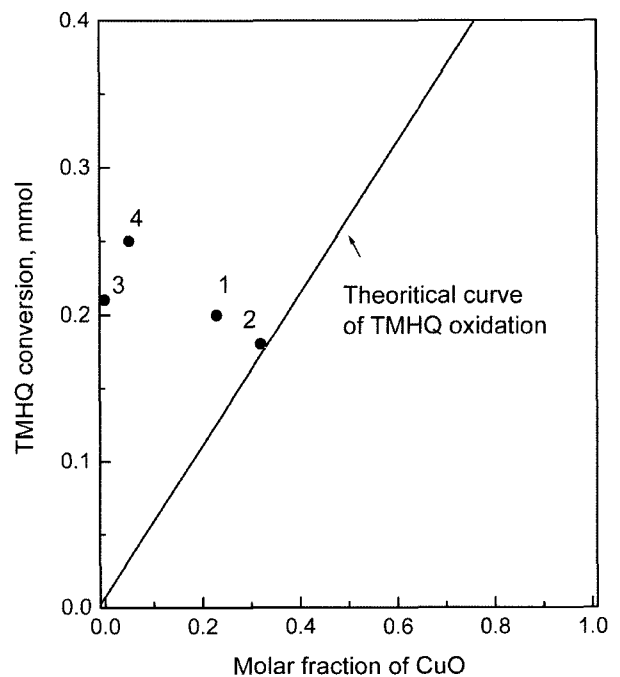
**Fig. 2.** TEM images of  $\text{Cu}_2\text{O}$  nano particles (a) sample 2 ( $\text{Cu}_2\text{O}$  99 %) with size of 90 nm, and (b) sample 3 ( $\text{Cu}_2\text{O}$  99 %) with size of 35 nm.

powders were studied with TEM measurement. The spherical shaped Cu oxides sample 2 and 3 were manufactured and their sizes were 90 and 35 nm, respectively (Fig. 2).

The reaction of interaction TMHQ with air oxygen in solution  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  results in formation of 2,3,5-trimethyl-1,4-quinone (TMQ) practically the only product (selectivity on TMQ > 99.5 %) [9] TMQ formed during reaction reacts with parent material forming a molecular complex - quinhydrone. Kinetic curves of TMHQ oxidation at the presence of nanocrystalline particles of Cu oxides (sample



**Fig. 3.** Kinetic curves of TMHQ oxidation in presence of nano samples of Cu oxide with average size ranfes from 35 nm to 90 nm synthesized by LGC method.



**Fig. 4.** Dependance of TMHQ conversion as a function of composition of nano powders.

1, 2, 3, and 4) have the following shape given in Fig. 3. Samples containing mainly pure Cu (Cu 78 %,  $\text{Cu}_2\text{O}$  -

22 %, sample a) in the structure do not show catalytic reactivity. Catalyst activity depends on the oxide powder. In Fig. 4 the dependence of TMHQ conversion from composition of nanopowders is shown. According to the position of points relative to line, it is possible to divide nano Cu oxide powders synthesized by LGC method into two types.

The powder (sample 2) with size of 90 nm prepared by LGC method is located on a theoretical straight line. It contains mainly Cu<sub>2</sub>O phase. The powder (1, 3 and 4) with small size showed active catalytic effect. The samples of 3 and 4 show more active reaction than sample 1. These samples contain small CuO quantity, not exceeding 0.15 mole fraction. The results of oxidation of TMHQ were represented on the Table. The catalytic yield of sample 1 comparing with sample 3 and 4 was relatively low. The properties of these three samples showed same range of particle sizes and different ratio of Cu and Cu oxide phase. The yield of oxidation of TMHQ depends on the particle size and amount of Cu<sub>2</sub>O phase. Obviously, the oxidation of parent material occurs substantially under action of oxygen fixed and activated in a matrix of nano powders.

The catalase activity is one of methods to recognize the interplaying catalytic properties in the coordination compounds. The catalytic activity of Co, Mn, Fe, Cu hydroxides was estimated by such method. The work is aimed to solve the scientific problem related to investigation of chemical intoxication mechanisms of water phenol solutions and its derivatives during their cleaning according to given technique. The data in the Table II show results of catalase activity for nano Cu oxide with different size and phases prepared by LGC method.

The freshly prepared Cu<sub>2</sub>O powder with size of 90 nm (sample 2) shows higher catalase activity than the sample containing large amount of CuO (sample 1). The reaction of sample 3 with size of 35 nm containing mainly Cu<sub>2</sub>O showed much higher activity than sample 2 with size of 90 nm and same oxide phase. The size of particles is the most significant factor. The particle size affects surface state. The specific surface areas of samples 1, 2, and 3 were 34, 17, and 38 m<sup>2</sup>/g, respectively. The specific surface area is related with manufacturing method. The LGC

**Table II.** Catalase activity of copper oxides nano samples.

Sample, composition (size)	H <sub>2</sub> O <sub>2</sub> Conversion % molar
a. Cu 78 %, Cu <sub>2</sub> O 22 % (20 nm)	10.2
1. Cu 20 %, Cu <sub>2</sub> O 62 %, CuO 18 % (35 nm)	50.3
2. Cu <sub>2</sub> O 99 % (90 nm)	62.1
3. Cu <sub>2</sub> O 100 % (35 nm)	99.8
4. Cu 10 %, Cu <sub>2</sub> O 85 %, CuO 5 % (35 nm)	82.3

method contributes to prepare nano scaled powder with high specific surface area.

## 4. Conclusion

The Cu oxide nano powders were synthesized by levitational gas condensation (LGC) and their heterogeneous catalytic properties were investigated. The results of catalytic tests indicated high activities of Cu oxides powder synthesized by levitational gas condensation (LGC). The catalytic effect which was clarified by oxidation of TMHQ and catalase depended on the amount of cuprite phase, the particle size and surface effect.

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