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Magnetic and catalytic properties of copper ferrite nanopowders prepared by a microwave-induced combustion process

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Abstract

Copper ferrite nanopowders were successfully synthesized by a microwave-induced combustion process using copper nitrate, iron nitrate, and urea. The process only took a few minutes to obtain $CuFe_2O_4$ nanopowders. The resultant powders were investigated by XRD, SEM, VSM, and surface area measurement. The results revealed that the $CuFe_2O_4$ powders showed that the average particle size ranged from 300 to 600 nm. Also, it possessed a saturation magnetization of 21.16 emu/g, and an intrinsic coercive force of 600.84 Oe, whereas, upon annealing at 800 °C for 1 h. The $CuFe_2O_4$ powders specific surface area was 5.60 m^2/g. Moreover, these copper ferrite magnetic nanopowders also acted as a catalyst for the oxidation of 2,3,6-trimethylphenol to synthesize 2,3,5-trimethylhydrogenquinone and 2,3,5-trimethyl-1,4-benzoquinone for the first time. On the basis of experimental evidence, a rational reaction mechanism is proposed to explain the results satisfactorily.

Keywords: A. Powders: chemical preparation; C. Chemical properties; C. Magnetic properties; D. Ferrites; E. Biomedical applications

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1. Introduction

Nanopowders have many excellent properties, which are suitable for various applications such as components in recording tape, flexible disc recording media, magnetic fluids, biomedical material and as well as being a useful catalyst. The obtained magnetic copper ferrite powders have been reported [1–3]. Moreover, the basic properties of microstructure, predominate phase and magnetization were obtained from fine particles [4,5]. Recently, Fu and Lin reported on a microwave-induced combustion synthesis process to prepare nanopowders [6–8], in which the whole process takes only a few minutes to yield nanopowders. The combustion synthesis process is to dissolve metal nitrate and urea in water, and then to heat the solution in a microwave oven. The urea and metal nitrate decompose and yield flammable gases such as NH_3, N_2, and CO_2, respectively. After the solution reaches the point of spontaneous combustion, it begins burning and becomes a solid, which burns at a high temperature. The combustion does not finish until all the flammable substances are all burned out and it turns out to be a loose substance which shows voids, pores, and high friable formed by the escaping gases during the combustion reaction.

Because it functions as an anti-free radical, which provides the effect of preventing aging, apoplexy, heart disease, cardiovascular vessel disease and cancer, Vitamin E is one of the most important vitamins today. At present, the demand reaches several millions pounds every year [9]. The reason that Vitamin E is so expensive is that the initial reactant of Vitamin E is difficult to produce on a large scale. Therefore, many scientists devote themselves to study the way of how to achieve mass production, that is fast, effective and at a low cost for producing the initial reactant of Vitamin E, 2,3,5-trimethyl-1,4-benzoquinone in recent years. At present, in the aspect of industrial production and academic research, the majority use 2,3,6-trimethylphenol as the initial reactant for synthesizing TMBQ (2,3,5-trimethyl-1,4-benzoquinone). One example of the oxidation of 2,3,6-trimethylphenol by metal ion was carried out by Hoffman-La Roche AG [10], from which $CuCl_2$ (copper (II) chloride) is dissolved in a solvent of acetone/water to obtain a yield of 80–87%. Aihara and co-workers [11] also used $RuCl_3$ dissolved in solvent of methanol to obtain a yield of TMBQ

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(2,3,5-trimethyl-1,4-benzoquinone) 90%. Bodnar et al. [12] used the catalyst of $CuCl_2$ (copper (II) chloride) and $NH_4OH{\cdot}HClCo$ to obtain a yield of 72%. Jansen et al. [13] used a catalyst of heteropoly anion modified carbon ($PMO_9V_3O_{40}{}^{-6}$) dissolved in a solvent of acetone/water to obtain a yield of 60–80%. Tsai et al. [14] used the catalyst of Ag/Cu (II)/MCM-41 to obtain a yield of 87%. Meng et al. [15] also used catalyst of Ti- and V-containing mesoporous to obtain a yield of 70–80%. Kholdeeva et al. [16] also used amorphous TiO_2–SiO_2 to obtain a yield of 80–90%. The common points for those methods are that the metal ions are used as catalysts to obtain a high yield. However, those catalysts are expensive and difficult to prepare. On the other hand, the catalysts and products would be separated after reaction when they are dissolved in a solution. Recently, phase transfer catalysis (PTC) has been considered to be one of the most effective tools to overcome this difficulty in the synthesis of specialty chemicals [17]. Besides, the combination of oxidizing agent and copper ferrite is industrially important as the oxidation process is environmentally benign [18,19] for green chemistry.

In the present work, we have attempted a new method, a microwave-induced combustion synthesis process, to produce copper ferrite nanopowders. Then copper ferrite is used further as a catalyst for oxidation of 2,3,6-trimethylphenol (TMP) as described. The reaction of 2,3,6-trimethylphenol is by hydrogen peroxide in an acidic solution under copper ferrite catalytic condition.

2. Experimental procedures

2.1. Starting materials

Copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), urea ($CO(NH_2)_2$), 2,3,6-trimethylphenol (TMP), copper (II) chloride ($CuCl_2{\cdot}2H_2O$), hydrogenchloric acid (HCl), organic solvents (including dichloroethylane), hydrogen peroxide (H_2O_2, 35 wt% in water) and other reagents are all G.R. grade chemicals for synthesis.

2.2. Copper ferrite synthesis

The synthesis process involved the microwave-induced combustion of redox mixtures, in which metal nitrate acted as oxidizing reactant and urea as reducing agent. The initial composition of the solution containing strontium nitrate, ferric nitrate, and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concepts of propellant chemistry.

Stoichiometric amounts of copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), and urea ($CO(NH_2)_2$) dissolved in a minimum quantity of water were set in a crucible. The atomic ratio of Fe/Cu was set to be 2–12. The crucible containing the solution was introduced into a microwave-induced oven. After the solution reaches the point of spontaneous combustion, it began burning and released lots of heat, vaporized all the solution instantly and became a solid burning at the temperature over 800 °C. The entire combustion process produced copper ferrite powders in a microwave-induced oven takes only 1 h. A stoichiometric combustion reaction of metal nitrate with urea to form copper ferrite as follows:

$$3Cu(NO_3)_2 + 6Fe(NO_3)_3 + 20CO(NH_2)_2 \rightarrow 3CuFe_2O_4 + 20CO_2 + 32N_2 + 40H_2O$$

2.3. Characterization

A computer-interface X-ray powder diffractometer (XRD) with Cu Kα radiation (Rigaku D/Max-II) was used to identify the crystalline phase. BET surface area was experimentally measured by nitrogen adsorption employing a Micromeritics ASAP 2000 instrument and calculated using the five-point BET theory. Mean particle size (D_{BET}) is also calculated from the BET data according to $D_{BET} = 6/[\rho_{th} S_{BET}]$, where S_{BET} is the measured surface area and ρ_{th}, is the theoretical density of the compound. Particle morphological feature was imaged by scanning electron microscope (SEM, JEOL JEM 200CX) with an accelerating voltage of 15 kV.

2.4. Kinetics of synthesizing 2,3,5-trimethylquinone (TMBQ)

The reactor is a 125-mL four-necked Pyrex flask used for agitating the solution, insertion of the thermometer, taking samples, and feeding the reactants. A reflux condenser is attached to the port of the reactor to recover the organic solvent. The reactor is submerged into a water bath in which the temperature is controlled to ±0.1 °C. Hereafter are the steps of experiment. First, heat up the reactor to 60 degrees centigrade. Second, weigh precisely 2,3,6-trimethylphenol (TMP) and internal standard (biphenyl), and add 50 mL of organic solvent (dichloroethane, $C_2H_4Cl_2$) and 20 mL of water, and dissolve them completely. Third, put a proper amount of copper ferrite ($CuFe_2O_4$) and hydrochloric acid in the reactor following the catalytic reaction. Fourth, 20 mL of hydrogen peroxide (oxidant) is added into the above-mentioned solution. The solution is mixed thoroughly. Fifth, a sample was withdrawn at a certain time interval and analyzed by gas chromatograph (GC), and the conversion of 2,3,6-trimethylphenol (TMP) and the yield of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) were measured. During the reaction, a sample (0.2 mL) is diluted to 0.5 mL by the same organic solvent. The injection of the dilution sample into gas chromatography then proceeded for analysis. The conversion of 2,3,6-trimethylphenol (TMP), and the yield and the selectivity of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) are calculated from the spectrum of gas chromatography and the calibration curve of reactant and product.

The mixture was stirred mechanically by a two-blade paddle (5.5 cm) at 800 rpm. During the reaction, an aliquot sample of 0.2 mL was withdrawn from the solution at a chosen time. The sample was immediately introduced into the same organic solvent at 4 °C for dilution to retard the reaction, and then analyzed by gas chromatographic instrument (GC). The product TMBQ (2,3,5-trimethyl-1,4-benzoquinone) for identification was synthesized from the reaction of 2,3,5-trimethylhydrogenquinone (TMHQ) in a limited quantity and hydrogen peroxide in an organic solvent without containing catalyst. After completing the reaction, the solution was purified by vacuum evaporation to strip off the organic solvent and hydrogen peroxide. Then, TMBQ in solid form was re-dissolved into ethanol for re-crystallization, and a red crystal form of TMBQ was obtained at 4 °C. The contents of TMBQ and reactants were analyzed by GC instrument.

3. Results and discussion

3.1. Properties of copper ferrite nanopowders

Fig. 1 shows a scanning electron microscopy (SEM) morphology of the microwave-induced oven heated specimens with Fe/Cu ratio of 2. It clearly shows that the structures of the particles are crystal in form and finds that the particles stack on top of each other due to their magnetic attraction and exhibit a partially sintered microstructure. Also, the surface of the powder shows voids and pores formed by the escaping gas during the combustion reaction. The copper ferrite powder with a Fe/Cu ratio of 2 possesses a uniform particle size of about 400–800 nm, and the variation of the particle sizes are not sensitive to the copper ferrite powder with Fe/Cu 2–12.

Fig. 2 illustrates the X-ray diffraction patterns of the as received powder sample and as-received samples at different Fe:Cu ratio. It is evident that the annealed as received powder contain the copper ferrite. More Fe:Cu ratio lead will leads to a Fe_2O_3 type, a single phase spinel $CuFe_2O_4$ do not exist. This results is in agreement with an investigation [4], the reaction is proposed as:

$$2Fe(NO_3)_3 + 5CO(NH_2)_2 \rightarrow Fe_2O_3 + 5CO_2 + 8N_2 + 10H_2O$$

and

$$2Cu_{1-X}Fe_{2+X}O_4 \rightarrow 2(1-X)CuFeO_2 + (1 + 2X)Fe_2O_3 + (0.5-X)O_2$$

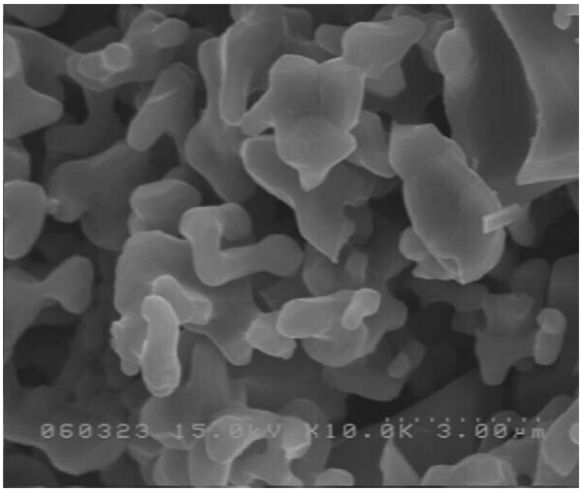

Fig. 1. SEM for the copper ferrite powder ($CuFe_2O_4$) annealed at 800 °C for 1 h.

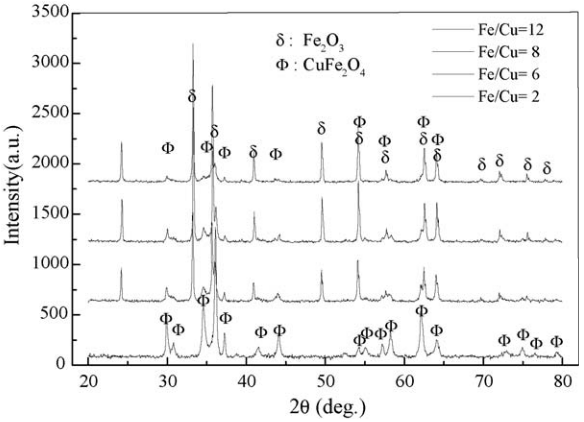

Fig. 2. XRD patterns for copper ferrite prepared by microwave-induced combustion process at various Fe/Cu ratios.

When the atomic ratio of Fe:Cu was larger than 2, a Fe_2O_3 mixture begins to form. During the TMP oxidization, the only oxidizing catalyst was $CuFe_2O_4$. The formation of Fe_2O_3 did not increase the reaction rate and also reduced magnetic strength of the copper ferrites.

The magnetization measurements for the as-received specimen and the varying composition ratio were carried out using a vibrating-sample magnetometer (VSM) at room temperature with an applied magnetic field of 12 kOe to reach saturation values. Fig. 3 shows the magnetic properties curves of microwave oven heated specimen with different Fe:Cu ratios. This indicates that the copper ferrite is a soft, magnetic material, which reveals minimal hysteresis. The copper ferrite with Fe:Cu ratio of 2–12 possesses a saturation magnetization of 21.16–5.04 emu/g, and an intrinsic coercive force of 600.84–267.25 Oe. In short as the Fe:Cu ratio increases, there is a reduction in magnetic strength due to the formation of Fe_2O_3. So that, the value of the magnetization measured at Fe:Cu ratio of 2 is larger than the Fe/Cu ratio of 12.

Fig. 4 illustrates the effect of the different Fe:Cu ratio on the pore volume. From these results, it is clear that the Fe:Cu ratio of 12 obtained a higher pore volume. The specific surface areas

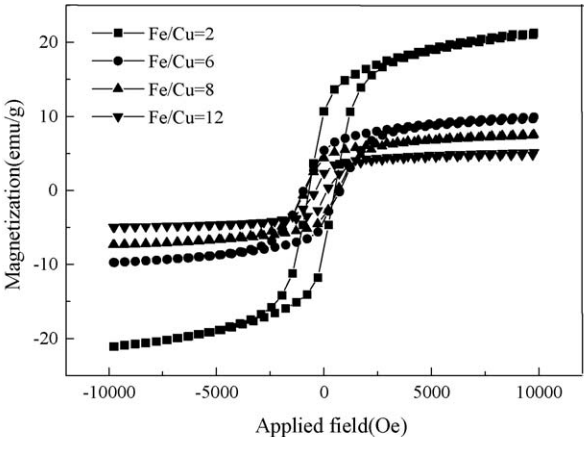

Fig. 3. Magnetization curve at various Fe/Cu ratios.

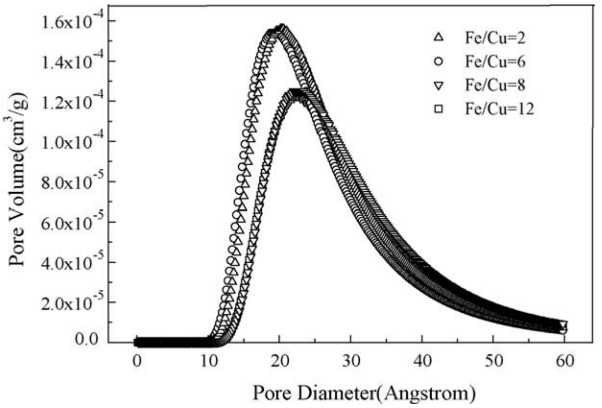

Fig. 4. Pore diameter distribution curves for various Fe/Cu ratios.

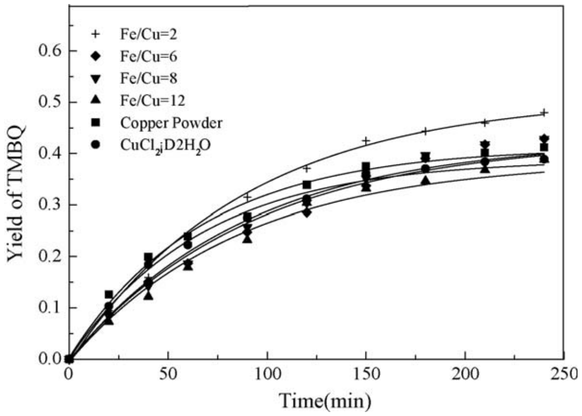

Fig. 5. Effect of kind of various Fe/Cu ratios on the yield of 2,3,5-trimethyl-1,4-benzoquinone; 2,3,6-trimethylphenol: 1.200 g, H_2O_2 = 20 mL, HCl = 5 mL, $C_2H_4Cl_2/H_2O$ = 50 mL/20 mL, 800 rpm, 60 °C.

were calculated by means of BET method (S_{BET}). The copper ferrite with Fe/Cu ratio of 2–12 is about 5.60–4.27 m^2/g. The copper ferrite with Fe:Cu ratio of 2 samples present high specific surface areas and pore volumes. The addition of urea into copper ferrite during combustion promoted porosity in the end product. The results indicated that when Fe:Cu = 2, relatively larger pores formed in a distribution that appeared to be homogenous. It possesses more copper active sites, so the oxidation reaction is enhanced.

3.2. Kinetics of synthesizing 2,3,5-trimethylquinone (TMBQ)

Fig. 5 also shows the influence of kinds of Fe:Cu ratio on yield of 2,3,5-trimethyl-1,4-benzoquinone; wherein the yield in 240 min is about 45% when the concentration of copper ferrite, copper powder and $CuCl_2$ (copper (II) chloride) is higher than 0.400 g. 2,3,6-Trimethylphenol will form 4-chloro-2,3,6-trimethlyphenol (CITMP) when chlorine ion presents, and form 2,3,5-trimethyl-1,4-benzoquinone in further reaction. Wherein, the conversion of 2,3,6-trimethylphenol (TMP) tends to become flat after 40 min under high concentration of hydrochloric acid and copper ferrite, and the reaction forms the maximum amount of dimer intermediate (D or DQ). For further reaction, thereafter the dimer reduces gradually and the amount of 2,3,5-trimethyl-1,4- benzoquinone (TMBQ) increases with the increase in the reaction time. Catalysts generally reduce the energy of activation so that the product might be formed at a higher yield of TMBQ. The mechanism of catalyzing oxidation reaction of 2,3,6-trimethylphenol by copper catalyst is: copper ion first reacts with 2,3,6-trimethylphenol, wherein the hydroxyl group (–OH) on the 2,3,6-trimethylphenol is attacked by the copper ion, causing departure of hydrogen ions and the formation of free radical on –O. Thereafter, the free radical on oxygen atom transfers to the carbon atom opposite to oxygen atom on the ring of benzene, and reacts with oxidant to form 2,3,5-trimethyl-1,4-benzoquinone. However, the carbon atom attacked by the copper ion is opposite to the hydroxyl group (–OH), resulting in the destruction of ring of benzene and the formation of a free radical on the carbon atom of the ring of benzene.

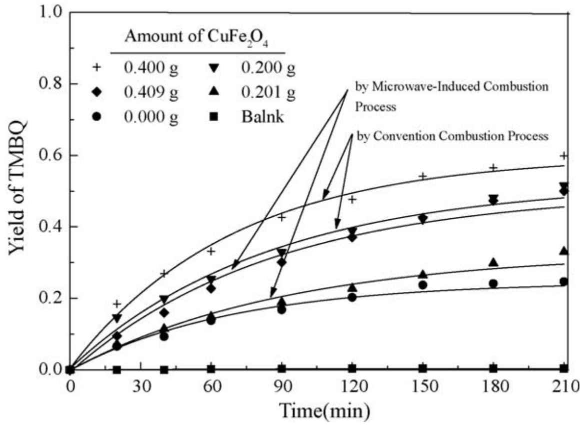

Fig. 6. Effect of conventional combustion and microwave-induced combustion process on the yield of 2,3,5-trimethyl-1,4-benzoquinone; 2,3,6-trimethylphenol: 1.200 g, H_2O_2 = 20 mL, HCl = 5 mL, $C_2H_4Cl_2/H_2O$ = 50 mL/20 mL, 800 rpm, 60 °C.

The main reaction may be shown as:

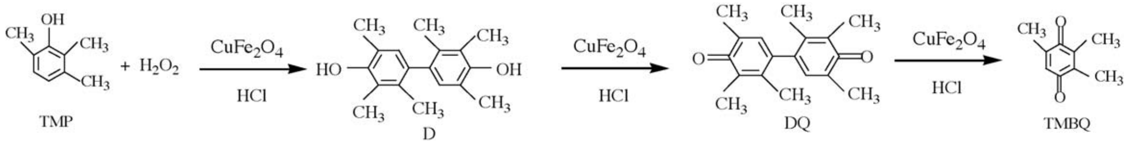

Fig. 6 shows the comparison of conventional high temperature combustion and microwave-induced combustion, it was found that copper ferrite prepared by the former method possessed a significantly better catalytic effect during TMP oxidization. 2,3,6-Trimethylphenol (TMP) forms 4-chloro-2,3,6-trimethlyphenol (CITMP) when chlorine ions are present, and forms 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) in further reaction. This was because the conventional method uses higher temperatures during calcination at 1000 °C and 8 h, hence allowing better formation of crystalline $CuFe_2O_4$. However, the microwave-induced method is a faster and cheaper alternative to prepare the catalyst.

4. Conclusions

In this study, the preparation of copper ferrite nano-particles using copper nitrate, iron nitrate and urea as starting materials have been synthesized successfully by a microwave-induced combustion process. The synthesis of a pure $CuFe_2O_4$ is prevented at Fe:Cu ratio of 2–12. The particle size, magnetism and structure were also determined. The synthesized copper ferrite powders with various Fe:Cu ratio where the particle size ranged from 300 to 600 nm. Moreover, the copper ferrite with Fe/Cu ratio of 2–12 possessed a saturation magnetization of 21.16–5.04 emu/g and an intrinsic coercive force of 600.84–267.25 Oe. In short as the Fe:Cu ratio increases, there is a reduction in magnetic strength due to the formation of Fe_2O_3. According to the experimental results, it shows that it is very helpful to the catalytic reaction to add copper ferrite nanopowders, wherein copper ion reacts with 2,3,6-trimethylphenol first, then the –OH on the 2,3,6-trimethylphenol is attacked by copper ion and the free radical on –O forms, and reacts with oxidant to form 2,3,5-trimethyl-1,4-benzoquinone.

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