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Influence of the heating method on the particle characteristics of copper oxide powders synthesized from copper nitrate aqueous solutions

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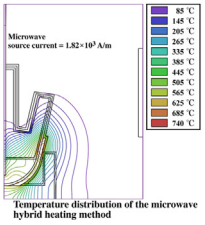
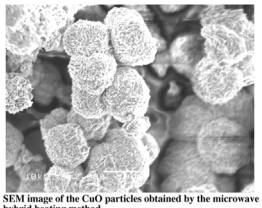
HIGHLIGHTS

- An increase in the heating rate decreases the median diameter of obtained CuO powder.
- Microwave hybrid heating method can produce the sharpest size distribution.
- Microwave hybrid heating has a higher energy efficiency than microwave heating.
- Microwave hybrid heating method achieves a uniform temperature distribution.

GRAPHICAL ABSTRACT



Temperature distribution of the microwave hybrid heating method


SEM image of the CuO particles obtained by the microwave hybrid heating method

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ABSTRACT

The influence of the heating method and rate on the morphology of CuO powders synthesized from $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solutions by denitration was investigated. The median diameter of the obtained powder was found to decrease as the heating rate increased, independent of the heating method. The microwave heating (MW) method remarkably reduced the particle size and enhanced the irregularity and disorder of the shape and surface of the particles, which were found to be more widely distributed. In contrast, the microwave hybrid heating (MHH) method (i.e., a combined usage of microwave and external heating) yielded the most spherical particles with the smoothest surface. It was also found that this heating method sharpened the particle size distribution and had higher energy efficiency than the MW method. Numerical simulations also indicated a difference in the energy efficiency between these two methods. The simulations also revealed that the MHH method could heat the whole reactor more uniformly with a lower microwave output. Moreover, the morphological difference of the powders obtained by these heating methods can be potentially explained by the difference in the simulated bulk temperature distribution and the intensity of the formed hot spot in the CuO particles caused by microwave irradiation.

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Nomenclature

C_p	specific heat capacity [J/(mol K)]
$\boldsymbol{E}$	electric field vector [V/m]
$\boldsymbol{H}$	magnetic field vector [A/m]
$\boldsymbol{j}_0$	current density [A/m^2]
j	imaginary unit
k	thermal conductivity [J/(s m K)]
p	time-averaged power density [W/m^3]
q	amount of heat generated per unit volume [W/m^3]
t	time [s]
T	temperature [K]
ω	angular velocity [rad/s]
ε	complex permittivity [F/m]
ε'	relative permittivity [-]
ε''	relative dielectric loss factor [-]
ε_0	vacuum permittivity [F/m]
μ	relative magnetic permeability [H/m]
μ'	real part of relative magnetic permeability [-]
μ''	imaginary part of relative magnetic permeability [-]
μ_0	vacuum permeability [H/m]
ρ	density [kg/m^3]

1. Introduction

Microwaves are widely used in various fields for many purposes including drying and heating processes (Chen et al., 2001; Kelen et al., 2006), ceramic sintering (Clark et al., 2000; Mondal et al., 2010; Fukui et al., 2013), organic (Min et al., 2010; Ma et al., 2011) and inorganic (Sithambaram et al., 2008; Tatlier et al., 2007; Fukui et al., 2006; Fukui et al., 2007; Fukui et al., 2012; Segawa et al., 2015) materials' syntheses, and nanoparticle synthesis (Mondal et al., 2015; Volanti et al., 2008). Microwave heating (MW) is one of the most promising heating methods for green sustainable industries. MW has a different heating mechanism from external conventional heating (CH) methods such as electric heating and infrared heating (IR). Specifically, a microwave generates heat from the interaction between its electromagnetic field and the dipole or charge of the object. Hence, a microwave can bring about the direct, rapid, internal, and selective heating of objects, and it may cause hot spots and superheating. These characteristics of MW can lead to a remarkable shortening of the required reaction time. They can also improve the yields and selectivity of products and the reaction rate (Sithambaram et al., 2008; Tatlier et al., 2007; Fukui et al., 2006; Fukui et al., 2007). Min et al. (2010) reported that MW produces different morphologies of CuO nanoparticles from those obtained using a CH method. Fukui et al. (2006, 2007) investigated zeolite synthesis from fly ash using MW. They revealed that MW reduces the particle size of the acquired zeolite particles and enhances the growth of a specific crystalline phase zeolite, i.e., phillipsite (Fukui et al., 2006). Hence, MW can affect the morphology and crystal structure of synthesized particles.

A nuclear fuel powder, which is a mixture of uranium oxide and plutonium oxide (called mixed oxide or MOX fuel powder), is synthesized directly by the denitration of the mixed aqueous solutions of uranium nitrate and plutonium nitrate extracted from spent nuclear fuel. As the MW method has been applied to this recycling process in Japan (Koizumi et al., 1983; Oshima, 1989; Kato et al., 2004; Asakura et al., 2007), we previously clarified the mechanism for the direct denitration of the metallic oxide powder from a metallic nitrate aqueous solution using MW (Fukui et al., 2012). The properties of the fuel pellet obtained by sintering of the MOX powder depend on factors such as its particle morphology and size (Asakura et al., 2007). Furthermore, an improvement in the energy efficiency of the heating in this process and accurate control of the characteristics of the MOX fuel powder using various heating devices is required. It has also been reported that the microwave hybrid heating (MHH) method, which is a combination of the use of a microwave and an external electric heating source, can produce much higher efficiency and increase the heating rate considerably (Wu et al., 2012).

Accordingly, in this study, CuO powders synthesized from $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solutions by denitration using various heating sources and rates are investigated by investigating the morphology of the products. The effects of the heating methods, i.e., MW, IR, conventional electric heating, and MHH, on the morphology of metallic oxide powders denitrated from metallic nitrate aqueous solutions are revealed. Moreover, the microwave energy efficiency, electromagnetic field, and temperature distribution in the reactor are also examined using numerical simulations.

2. Materials and methods

2.1. Denitration experiments

Commercially supplied high-purity copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) reagent (Sigma-Aldrich) was used as a raw material, which was completely dissolved in distilled water. This 5.5 mol/L aqueous solution was heated up to 350°C with different heating equipments at various heating rates to decompose it into CuO powder by denitration. After reaching 350°C, the temperature was kept constant for 5 min. Here, the heating rate is defined as the average increasing rate of the temperature in the range of 180–320°C. It has been reported that the denitration from $Cu(NO_3)_2 \cdot 3H_2O$ to CuO by MW proceeds with the following reaction sequence as the temperature increases, independent of the heating method.

$$Cu(NO_3)_2 \cdot 3H_2O \rightarrow Cu(NO_3)_2 \cdot 2.5H_2O \rightarrow Cu_3(NO_3)(OH)_3 \rightarrow CuO$$

It has also been indicated that the intermediates decompose to CuO mainly in the same temperature range (Fukui et al., 2012).

The schematic representations of the heating apparatus used in the experiments are shown in Fig. 1. The experimental setup for the MW method is given in Fig. 1(a) (Fukui et al., 2012; Segawa et al., 2015). The MW equipment (Shikoku–keisoku, μ-Reactor) consists of a magnetron, a proportional–integral–derivative (PID) controller, a stainless steel cavity, and a K-type thermocouple (used for temperature measurement). The microwave, which has a 2.45-GHz frequency generated by the magnetron, irradiated 15.0 mL of the aqueous solution of the starting material in a three-necked glass flask reactor (100 mL in volume) set in the cavity. At first, the output of the microwave was fixed until the temperature attained the above-mentioned preset temperature (350°C); then, the output was adjusted to keep the temperature constant using the PID controller. The heating rate was varied by changing the initial output. The water vapor and nitrogen oxide gas generated in the reaction were removed from the reactor by feeding air at a constant flow rate of 100 mL/min. These gases were captured by a condenser or distilled water in a gas washing bottle.

The experimental setup for the MHH method is illustrated in Fig. 1(b) (Fukui et al., 2006, 2007). An electric heater and an adiabator were added to the MW equipment, as shown in Fig. 1(a). An electric heater with a constant 80 W output was installed around the lower part of the reactor, and the adiabator covered by aluminum foil, which was made of porous silica and alumina, was set over the electric heater. Both the microwave and electric heater heated the