화염분무열분해법에 의한 염화아연 수용액으로부터 산화아연 나노입자의 생성

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Formation of Zinc Oxide Nanoparticles from Zinc Nitrate Solution by Flame Spray Pyrolysis

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Introduction

Particles smaller than several tens of nanometer in primary particle diameter are considered as nanoparticles. One of the valuable characteristics of nanoparticles is their high surface area per unit volume, resulting in higher activity as a catalyst and greater sensitivity as a sensor. Titanium dioxide (TiO_2) nanoparticles, for example, are used as a photocatalyst, in cosmetics for high absorption of ultraviolet light, in toners and coating materials, etc [1]. Ceramic nanoparticles such as TiO_2 and SiO_2 are routinely produced by the gas-to-particle conversion in flame reactors because this method provides good control of particle size, particle crystal structure and purity [2].

Spray pyrolysis, liquid droplet-to-particle conversion process, is well known valuable process to form mixed-metal oxide nanophase particles with high purity, controlled stoichiometry and crystallinity [3,4]. However, the use of spray pyrolysis is sometimes too limiting and, in some cases, incorrectly describes the critical thermal process during spray pyrolysis. For example, pyrolysis (i.e., thermal decomposition) does not adequately capture the various oxidation, nitridation, or reduction-based thermal processes that will be increasingly important applications of spray pyrolysis processes. It has also been difficult to obtain nanoparticles by the spray pyrolysis because the droplets of liquid precursors were large in diameter and high in concentration.

Flame spray pyrolysis, spray pyrolysis assisted with flame, was suggested that could be effective to produce particles from single to multi component at enough high temperature of the flame for the complete thermal decomposition such as oxidation chemistry. However, there have been relatively few studies on the synthesis of particles by the flame spray pyrolysis [5, 6].

Despite of interesting and important results obtained by previous researchers, the flame spray pyrolysis needs to be further investigated to characterize the formation, growth and phase transformation of nanoparticles mainly because of its complex environment. There are many variables such as flame configuration, precursor concentration, droplet diameter, gas composition and gas flow rate, affecting flame characteristics as well as the formation, aggregation, sintering, phase composition and crystallinity of particles.

In the present study, ZnO nanoparticles are synthesized by the flame spray pyrolysis, and their formation process is discussed. The employed reactor consists of an ultrasonic atomizer and a diffusion flame burner. Molar concentration of $Zn(NO)_3$ and flow rates of combustion gases such as oxygen, hydrogen and air are manipulated, as key experimental variables, to control particle size, size distribution and crystal structure.

Experiments

A schematic of the experimental apparatus for the generation of ZnO nanoparticles is shown in Fig. 1. The experimental apparatus consists of an ultrasonic atomizer of aerosol precursor, a burner for diffusion flame, and a particle collector. In the present study, the diffusion flame, that exhibits strong gradients in concentration and temperature during particle formation and growth, was utilized to synthesize the composite nanoparticles. A diffusion flame burner composed of five concentric stainless tubes was prepared. Configuration of the flame was $(Ar+Zn(NO)_3)/Ar/H_2/(O_2+air)/air$. An aqueous solution of $Zn(NO)_3$ was first atomized with an ultrasonic vibrator (1.7 MHz), and the atomized $Zn(NO)_3$ was subsequently carried into the central tube of the burner by introducing dry argon (Ar) gas (99.999%). Hydrogen (H_2) was used as a fuel while oxygen (O_2) and air were used as oxidants. A Pt-Rh R type thermocouple of 0.5 mm in diameter (Omega Engineering) was used to measure flame temperatures of the burner. The measurements were performed three times for each condition, and mean values were chosen as the flame temperatures in the axial and radial direction of the flame in the absence of the precursor. ZnO nanoparticles generated from the flame were collected, at the location 150 mm above the burner surface, with a cold glass tube maintained at 12 ^{o}C by flowing cooling water inside. The particles in the hot stream were deposited on the surface of the cold glass tube due to thermophoresis [5]. The particle morphology and size were characterized by transmission electron microscopy (TEM, Philips Model CM12). The average particle diameter was determined by counting more than 200 particles from TEM pictures. The specific surface area of the powders was measured by nitrogen adsorption at –196 ^{o}C using the BET equation (Micrometrics Model ASAP 2400). Assuming spherical particles, the average particle size d_p was calculated from measured specific surface area A and particle density ρ_p by $d_p = 6/(\rho_p \bullet A)$, and calculated particle sizes and observed ones were compared. X-ray diffractometer (XRD, Rigaku Co. Model RTP 300 RC) was used to obtain X-ray diffraction patterns of powders.

Results and Discussion

The concentration of $Zn(NO)_3$ in the flame was varied from 3.76×10^{-6} to 1.13×10^{-5} mol/l by changing the molar concentration of aqueous solution of $Zn(NO)_3$, holding the gas flow rate as follows; 1st : 2 l/min of Ar, 2nd : 1 l/min of Ar, 3rd : 6 l/min of H_2, 4th : 4 l/min of O_2 and 6 l/min of air, and 5th : 15 l/min of air. As $Zn(NO)_3$ concentration increased, the specific surface area decreased from 58 to 45 m^2/g. Figure 2 shows the TEM pictures of ZnO nanoparticles made by flame spray pyrolysis. The average diameter from the TEM pictures was about 10 nm at the concentration of 3.76×10^{-6} mol/l and increased to about 15nm by increasing the concentration to 1.13×10^{-5} mol/l. Size distributions of ZnO nanoparticles were quite uniform and the geometric standard deviations were nearly constant about 1.5 as the concentration increased. From the analysis of X-ray diffraction pattern, as shown in Figure 3, the clear crystallinity of the ZnO nanoparticles was found.

The flow rates of combustion gases affect the flame temperature that plays a very important role in the determination of the particle size and crystal structure during the flame spray pyrolysis for the synthesis of ZnO nanoparticles. For the control of the flame temperature, the flow rates of combustion gases such as hydrogen, oxygen and air were varied in this study.

Hydrogen flow rate varied from 4 to 7 l/min at the fixed condition (Fig. 2a). With the increase in hydrogen flow rate the maximum flame temperature was increased from 1450 to 1650℃, and then the average particle diameter also increased from 8 to 19 nm. As oxygen flow rate at the 4th tube of the burner varied from 6 to 2 l/min, the average particle diameter decreased from 18 to 11 nm.

The total gas flow rate was changed from 34 to 49 l/min by increasing only the air flow rate in the 5th tube of the burner while fixing the $Zn(NO)_3$ feed rate at 3.84×10^{-4} mol/min, Ar at 1 l/min in the 2nd tube, H_2 at 6 l/min in the 3rd tube, O_2 and air at 10 l/min in the 4th tube and air at 15 l/min in the 5th tube. As the air flow rate in the 5th tube increased 15 to 30 l/min, the flame temperature and the $Zn(NO)_3$ concentration in the flame decreased from 1,540 to 1,330 ^{o}C and from 1.13×10^{-5} to 7.84 x

10^{-6} mol/l, respectively, resulting in the lower coagulation rate of small particles. Thus, the average particle diameter decreased from 17 to 10 nm with an additional effect of shorter residence time.

The stages on the formation of nanoparticles during the flame spray pyrolysis were not discussed in the previous studies. It is suggested in this study as follows; a large droplet of precursor (5 μm in diameter) generated by the ultrasonic atomizer explodes by the contact with the flame of high temperature at the burner surface; it is divided into many very smaller droplets; and then, the smaller droplet undergo the stages, as spray pyrolysis, such as evaporation of solvent (H_2O), precipitation of solute ($Zn(NO)_3$) and drying, thermal decomposition, and coalescence. However, the size of particles after the coalescence stage depends on the initial concentration of aqueous solution of precursor but still very small, only several nanometers, as to be considered as primary particles or nuclei. Such primary particles can grow into larger particles by the aggregation accompanied with sintering among them, similar to the particle growth process in the gas phase reaction, as described in Figure 9. Therefore, the particles can grow up to several tens of nanometer in diameter as the aerosol precursor concentration increased at a fixed flame temperature with a constant gas flow rate. Thus, large particles were generated at the higher precursor concentration as shown in Figure 2. The detailed experimental study to prove the suggestion on the formation of nanoparticles and synthesis of various composite nanoparticles by the flame spray pyrolysis will be future subjects of our study.

Summary

Zinc oxide (ZnO) nanoparticles were synthesized by the oxidation of zinc nitrate ($Zn(NO)_3$) in a spray flame reactor. A diffusion flame burner with an ultrasonic atomizer was install on the employed reactor. Molar concentration of $Zn(NO)_3$ and flow rates of combustion gases such as oxygen, hydrogen and air were chosen as key experimental variables for the control of the particle size. Polyhedral crystalline ZnO nanoparticles ranged from 8 to 25 nm in average particle diameter were produced by through all the experiments. Formation of nanoparticles from droplet of the precursor through the flame spray pyrolysis was suggested. The average particle diameter increased as concentration of the reactant increased. The average particle diameter also increased as the maximum flame temperature increased by increasing flow rates of hydrogen and oxygen. When the total gas flow rate increased by increasing the air flow rate, however, the maximum flame temperature decreased, resulting in smaller particles in average diameter.

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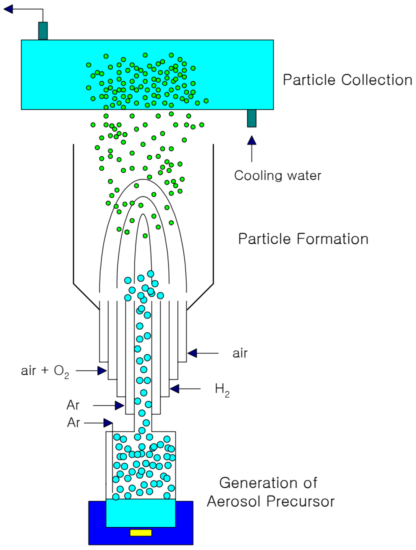

Fig. 1. A Schematic of the apparatus for the synthesis of ZnO nanoparticles.

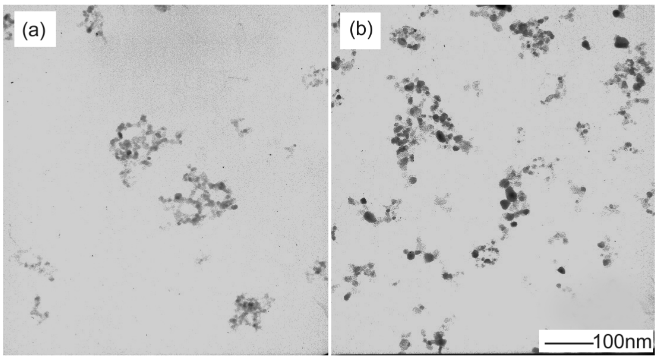

Fig. 2. TEM micrographs of ZnO nanoparticles (a: 3.76 x 10^{-6}, b: 1.13. x 10^{-5} mol/l).

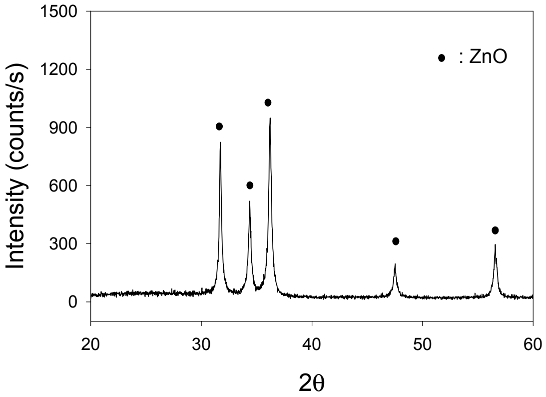

Fig. 3. X-ray diffraction pattern of the product particles.