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A Study on CeO_2/SiO_2 Composite Powder Synthesis Using Ultrasonic Spray Pyrolysis Method and Effect of Sensory Texture Improvement

Dong-Kyu Lee† · Jin-Hwa Lee

Department of Industrial Chemistry, College of Engineering, Chungbuk National University, Cheongju 361-763, Korea,

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Abstract : The spherical particles of CeO_2/SiO_2 composite powder with narrow-size distribution and pure phase particles were synthesized by ultrasonic spray pyrolysis method from aqueous cerium sulfate solution. The resulting composite powder was characterized by X-ray diffraction, scanning electron microscopy, transmittance electron microscopy, *in-vitro* sun protect factor, and BET surface area analysis. The concentration of cerium sulfate was tested to vary the particle size from $3.40X10^{-3}$ to $1.02X10^{-2}mol/cm^3$ to study concentration effect of starting material. The average particle size from the $3.40X10^{-3}mol/cm^3$ concentration was found to be slightly smaller than that from the $1.02\ X10^{-2}mol/cm^3$ concentration, because of the relation between the droplet size and the concentration of the starting material solution

Keywords : ultrasonic spray pyrolysis, composite powder, ceria, silica

1. Introduction

Ultrasonic spray pyrolysis is a useful method for the synthesis of high purity, homogeneous ceramic powder with specific chemical and phase composition, submicrometer and narrow particle size distributions, and relatively low sintering temperature. Using this technique, fine droplets may be formed from the feeding solution with the help of an ultrasonic generator that enables their transformation into the fine particles through the pyrolysis process[1-5]. This process consists of the ultrasonic generator of starting solution, sol, suspension, and the introduction of the generated aerosols into the furnace at elevated temperatures. During spray pyrolysis, aerosol droplets are transformed into microporous or dense particles by different processes, including solvent evaporation, precipitation of dissolved precursors, drying, pyrolysis of precipitated particles[5]. The advantage of this process is that all process mentioned above occur in one step as well as that each droplet/particle was reacted under same reaction conditions, and no subsequent milling is necessary. Also, nearly uniform size distribution may be achieved, because each of the liquid droplets acts as a small reactor, which provides the same particles and phase composition. By controlling the process

† 주저자 (e-mail : dklee@chungbuk.ac.kr)

parameters, such as pH, concentration, type of precursor and heating rate of droplets[6,7], it is possible to control the morphology, size distribution, homogeneity and phase composition of prepared particles. Especially, the average size distribution of the final particles can be determined from the size of sprayed droplets and its concentration in the starting solution. The size and morphology of the final produced particles may also be determined using the concentration and velocity of the droplet generated by ultrasonic device[8-11]. Cerium oxide is a major compound in the useful rare earth family and has been applied as one of practically used glass polishing materials, ultraviolet absorbents, and automotive exhaust promoters[12]. In recent years, ultrafine nanometer-sized particles have attracted much attention due to the physical and chemical properties. Fine particles of cerium oxide with very small size have great potential to develop new materials that are used as fine UV absorbent and high activity catalysts[12-17]. Especially, protection from the ultraviolet rays(UV) of sunlight is one of the interests because excessive exposure to UV damages human skin. Development of cosmetics with strong UV shielding ability is needed. Cerium oxide particles are used as UV shielding materials in cosmetics product because of their high optical transparency in the visible region and UV absorption ability[14]. However, when CeO_2 particles are used as UV absorption material in cosmetics, the surface of CeO_2 particle has to be modified with inert materials because CeO_2 exhibits photocatalytic properties. Many studies have reported the synthesis of silica and ceria having spherical shape by the spray pyrolysis method. The aim of this work was to adjust the conditions that could receive CeO_2/SiO_2 composite powder having a form of spherical shape. The spherical CeO_2/SiO_2 composite powder were prepared directly by using the ultrasonic spray pyrolysis from an aqueous cerium sulfate and silica suspension, and the effects of synthesis factors such as pyrolysis temperature, gas flow rate and starting material's concentration on the particle characteristics are investigated.

2. Experimental

Fig. 1 shows a schematic diagram of experimental apparatus. The ultrasonic spray pyrolysis system mainly consists of an ultrasonic generator, a reaction furnace, and precipitator. The starting material solution was ultrasonically pre-treated in an ultrasonic generator before spraying. The starting material solution was prepared by dissolving appropriate amounts of cerium sulfate ($Ce_2(SO_4)_3 \cdot H_2O$) in distilled water in order to obtain a $3.4X10^{-3}$, $5.1X10^{-3}$, $6.8X10^{-3}$, and $1.0 X10^{-2}$ mol/cm^3 solution. The aerosol based on this solution was made ultrasonically(mist generator 60Hz). Aerosol was introduced in a horizontal tubular reactor with air as a carrier gas(Air, flow rate 1.5cm^3/min). The laminar flow aerosol reactor used in the present study was a high-quality ceramic tube of 40mm inner diameter and about 600mm long.

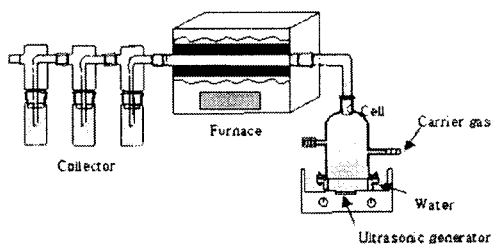

Fig. 1. Schematic diagram of the experimental apparatus.

The phase and crystallinity of prepared composite particles were characterizedby using X-ray diffractometer(XRD, Sintag Model XDS 2000) with CuKα radiation. The

particle morphology of prepared particles was determined in accordance to scanning electron microscopy(SEM, Hitachi S-2500C). Inner particle structure was examined by transmission electron microscopy(TEM, JEOL 2010 Carl Zeiss TEM109), and BET(ASAP2010, AutoporeIII 9420)was used for the determination of particle surface characteristics. To estimate the ability of composite powder to protect against UV rays, this was mixed with dispersant of emulsion type. Then sample was placed onto Trans-pore tape(3M). After 15min., the sun protection factor(SPF) was measured three time by sun protection factor analyzer system(SPF, Optometrics LLC SPF290).

3. Results and Discussion

The effects of reaction function on the morphology of CeO_2/SiO_2 particles were investigated. SEM analysis of the CeO_2/SiO_2 composite powder from a $3.4X10^{-3}$, $5.1X10^{-3}$, $6.8X10^{-3}$, and $1.0X10^{-2}$mol/cm^3 precursor solution revealed that CeO_2/SiO_2 composite particles had a spherical shape, as shown in Fig. 2. This phenomenon was caused to minimize sprayed droplet's free energy. The particles had a narrow particle size distribution in the micrometer range. It is obvious from Fig. 2 that the sprayed particles are spherical, smooth and nonagglomerated. As shown SEM photographic, particles consist of small solid spherical particles, particle fragments, irregular particles, and large particles with open and macroscopic surface pores. The fragments are formed by an abrupt evolution of the gases. The liquid

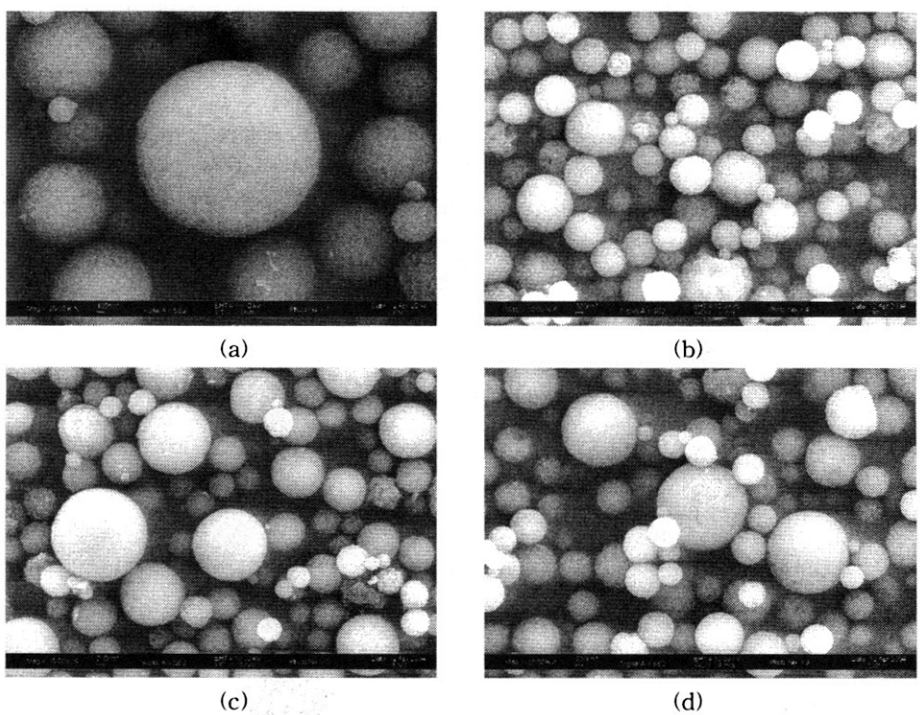

Fig. 2. SEM micrographs of CeO_2/SiO_2 composite particles by ultrasonic spray pyrolysis method with a starting material solution of (a) $3.4X10^{-3}$ mol/cm^3, (b) $5.1X10^{-3}$mol/cm^3, (c) $6.8X10^{-3}$mol/cm^3, (d) $1.0X10^{-2}$mol/cm^3

droplets passing the pyrolysis tube in a large temperature gradient undergo very rapid gelation and decomposition which occur first in the surface of the particle. These particles can be fractured when internal gas pressure is built up inside the particles. By comparing the powder $3.4X10^{-3}$ and $1.0X10^{-2}mol/cm^3$ starting material solutions, average particle size from the $3.4X10^{-3}mol/cm^3$ solution was found to be slightly smaller than that from the $1.0X10^{-2}mol/cm^3$ solution. This small difference can be explained by the relation between the droplet size and the concentration of the starting material solution.

To obtain a highly dense particle, the size and shape of particle are very important. Therefore, we conducted at various concentration to examine a shape of prepared particles. Fig. 3 shows the TEM photographs of CeO_2/SiO_2 particles prepared using ultrasonic spray pyrolysis method at different starting material solution concentration. Most of particle which was a little porous spherical second particle consist of dense spherical first particle. The prepared particles were shown as porous spherical shape, because the droplets were solidified in a pyrolysis process. This was due to gadually proceeded reaction from surface of the particle to the inside.

X-ray diffraction of the CeO_2/SiO_2 composite particles obtained in this study is showed in Fig. 4. The peaks corresponding to those of CeO_2 at 2θ=28.9, 33.3, 47.2 and 56.8°were observed. And, under the 2θvalue of 25°, the broad peak caused by amorphous silica was detected. We could know that at the various concentrations prepared particles had a same crystallization. As a result of XRD data, the higher cerium sulfate's concentration was increased, the higher cerium oxide's crystal peaks and lower amorphous silica's crystal peak were observed. Fig. 4. X-ray diffraction patterns of the CeO_2/SiO_2 composite particles by ultrasonic spray pyrolysis method with a starting material solution of (a) $3.4X10^{-3}$ mol/cm^3, (b)$5.1X10^{-3}$ mol/cm^3, (c) $6.8X10^{-3}$ mol/cm^3, (d)$1.0X10^{-2}$ mol/cm^3. The BET surface area of synthesized CeO_2/SiO_2 composite particles was 248-250m^2/g independent of precursor solution concentration. The result of *in-vitro* SPF test showed that the amount of CeO_2 was increased SPF value from 10.17 to 13.67. Table 1 showed formulation of pressed powder. Table 2 confirmed that the application sense of composited powder materials was deteriorated, but transparent effect was enhanced. CeO_2/SiO_2 composite

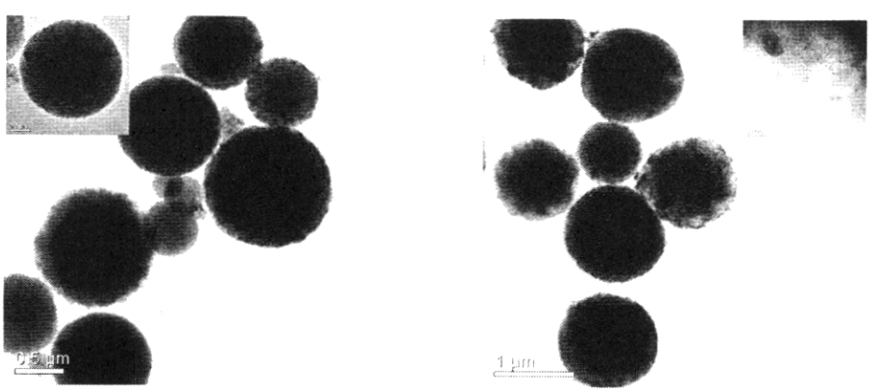

Fig. 3. TEM micrographs of CeO_2/SiO_2 composite particles by ultrasonic spray pyrolysis method with a starting material solution of (a)$3.4X10^{-3}$ mol/cm^3, (b)$6.8X10^{-3}$ mol/cm^3.

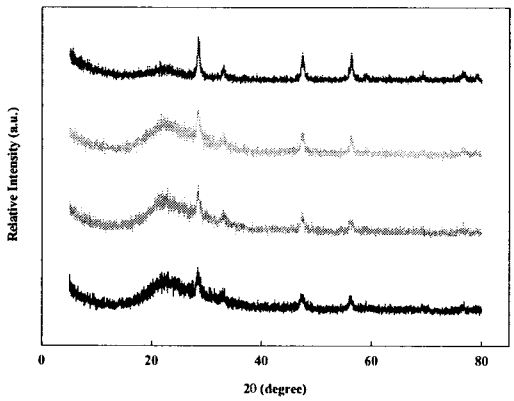

Fig. 4. X-ray diffraction patterns of the CeO_2/SiO_2 composite particles by ultrasonic spray pyrolysis method with a starting materialsolution of (a) $3.4X10^{-3}$ mol/cm^3, (b) $5.1X10^{-3}$ mol/cm^3, (c) $6.8X10^{-3}$ mol/cm^3, (d) $1.0 X10^{-2}$ mol/cm^3.

particleshad good transparent effect and spreadability. Using the press type cosmetics, it enhanced cosmetics sensory feeling effects. As CeO_2/SiO_2 composite particles had a spherical shape, it could makehighly sensory feeling, rolling effect and extensibility. In addition, it could give natural and transparent feeling, and could remarkably reduce unnatural coverage effect. From upper effects, this procedure not only overcame the default of cosmetics formulas limitation, which is about 6.00 %, but also had good product characteristics.

4. Conclusions

The CeO_2/SiO_2 composite particles were prepared by a simple ultrasonic generator and

Table 1. Formulations for Pressed Powder Foundation with Various Compositions

Materials	S/T	EX-1	EX-2	EX-3
Talc/Methicone/Dimethicone	Q. S. to 100			
Talc/Perfluoromethyl Isopropyl Ether	5.00	5.50	5.50	5.50
Aluminum Starch Octenyl Succinate	4.00	4.00	4.00	4.00
PTFE	3.50	3.50	3.50	3.50
Mica/TiO2/Mineral oil/Methicone	5.00	5.00	5.00	5.00
TiO_2	3.00	-	3.00	-
CeO_2	-	3.00	3.00	-
SiO_2	3.00	3.00	-	-
CeO_2-SiO_2 Composite Powder	-	-	-	6.00
IOY	0.48	0.48	0.48	0.48
IOR	0.24	0.24	0.24	0.24
IOB	0.03	0.03	0.03	0.03
Binder	5.70	5.70	5.70	5.70

Table 2. The Results of User Test

	S/T	EX-1	EX-2	EX-3
Sensory Feeling	3	3	2	5
Adhesion Feeling	4	3	5	4
Spreadabilty	3	4	2	5
Shinning	3	3	2	4
Coverage	4	4	5	3

< 5 : Exellent 4 : Good 3 : General 2 : Bad 1: Worst >

pyrolysis method using cerium sulfate solution as the source material. The flow rate, furnace temperature and the concentration of starting material were very important factors for the formation of CeO_2/SiO_2 composite particles. All of the condition of constant flow rate and furnace temperature, the particles were spherical and homogeneous, but the pure CeO_2 particles were synthesized, which was not to be coated by SiO_2. This technique has been shown to be a cheap and easy method to synthesize ultra-fine powder and binary and ternary oxides. According to *in-vitro* UV blocking test, the functional composite powder sample was higher than non-composited powder. When the composited powders were applied in pressed powder product, the covering effect of pressed powder product itself increased, and natural make-up effect and spreadability were also increased.

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