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Synthesis of ceria nanoparticles by flame electrospray pyrolysis

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Abstract

A flame electrospray pyrolysis is presented for synthesizing CeO_2 nanoparticles with a dense morphology, high crystallinity and nanometer size. Hydrated cerium nitrate precursor dissolved in an ethanol/diethylene glycol butyl ether mixture was injected into a CH_4/air premixed flame using an electrospray method. The number size distributions of the as-prepared particles were trimodal. It is suggested that the particles for the fine mode were formed by a Rayleigh disintegration of the charged precursor droplets during the droplet evaporation. The particles for the coarse and middle modes are surmised to come from primary and secondary droplets, respectively, which were formed simultaneously during the atomization processes. The CeO_2 nanoparticles for the coarse mode were nonspherical and composed of few crystallites. The nanoparticles for the fine and middle modes were nearly spherical and nonagglomerated. The as-prepared CeO_2 nanoparticles showed highly crystallinity.

Keywords: Flame; Electrospray; Spray pyrolysis; Ceria nanoparticle

1. Introduction

Interest in nanoparticles has expanded rapidly, because they exhibit unique and improved material properties different from the bulk. Nanoparticles have been synthesized using several techniques: sol–gel, spray pyrolysis, chemical vapor condensation, high-energy ball milling, and pulsed laser ablation. Of the emerging methods available for the production of metal oxide powders, spray pyrolysis has been widely used to prepare continuously spherical, high-purity, multicomponent products, because of its low cost and versatility. Various functional materials, such as metals, metal oxides, and mixed metal oxides, have been produced as powders or films by spray pyrolysis (Messing, Zhang, & Jayanthi, 1993). One of the advantages of this process is the ease of the precursor injection into the reaction zone. A vapor precursor feeding system, such as the bubbling method, is complicated when the evaporation temperatures of the precursors are high or when the vapor pressures differ with each other.

In this technique, precursor solutions are first atomized into droplets, which are subsequently pyrolyzed to produce solid particles, usually in the hot reaction zone. Therefore, the atomizer determines the quality of the resulting particles. Generally, in the spray pyrolysis technique, three types of atomizer are used to spray the precursor into droplets: ultrasonic, mechanical, and electrospray (Messing et al., 1993).

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Electrospray pyrolysis has attracted attention because it can produce submicron, highly charged droplets. Electrospray refers to a process in which a liquid jet breaks up into droplets under the influence of electrical forces (Ciach, Geerse, & Marijnissen, 2004). The charge on the droplets eventually minimizes the coagulation process, which is a severe problem for powder production via aerosol routes (Nakaso, Han, Ahn, Choi, & Okuyama, 2003). In particular, electrospraying in the cone-jet mode can generate droplets with a very narrow size distribution (Ciach et al., 2004). Therefore, electrospray is a promising technique for precursor atomization in powder production and film formation using the spray method. Although the low flow rate of electrospray is the main disadvantage, several investigations to increase the flow rates of electrospray have been recently reported for scale-up process (Duby, Deng, Kim, Gomez, & Gomez, 2006).

Most studies of electrospray pyrolysis have used a hot-walled furnace as the energy source for the chemical reaction to produce functional particles. Similarly, Nakaso et al. (2003) reported the electrospray assisted chemical vapour deposition method to synthesize nonagglomerated and unipolarly charged nanoparticles using a furnace reactor. They injected a volatile precursor solution directly into a high-temperature furnace using an electrospray method and were able to produce fewer agglomerated particles than those produced by the conventional vapour-feeding method. The production of ceramic particles using an inorganic precursor by furnace electrospray pyrolysis has been reported (Lenggoro, Okuyama, Fernández de la Mora, & Tohge, 2000; Okuyama, Lenggoro, Tagami, Tamaki, & Tohge, 1997; Park & Burlitch, 1996; Rulison & Flagan, 1994a; van Erven, Moerman, & Marijnissen, 2005). A problem of the furnace electrospray pyrolysis method is the loss of particles by deposition onto walls. The droplets generated by an electrospray carry a high electric charge close to the Rayleigh charge limit. The associated large electrical dispersion effect causes a considerable penetration loss by deposition onto the walls and a drastic decrease of the overall particle throughput efficiency. This problem has been resolved by neutralizing the droplets immediately after atomization through a source of ions with the opposite polarity (Lenggoro et al., 2000; Rulison & Flagan, 1994a; van Erven et al., 2005).

Flame offers several advantages over a furnace reactor, including a higher operating temperature, faster heating and cooling rates, more economical operation, and easier scale-up (Brewster & Kodas, 1997). Moreover, particle loss could be significantly reduced because the reaction zone is open to air. However, the electrospraying nozzle should be located far enough from the flame zone to maintain a stable spray for two reasons: (i) electrospray cannot operate under high temperatures and (ii) it cannot operate in the presence of relatively large concentrations of chemi-ions in the combustion region, which results in a lower electric breakdown threshold than the minimum field necessary to establish a stable spray (Gomez & Chen, 1994).

Flame electrospray pyrolysis has been reported for the synthesis of highly crystalline Fe_2O_3 and Fe_2O_3/SiO_2 nanoparticles (Ahn, Ahn, Jeon, & Choa, 2004a, 2004b), although very few studies it terminated have been undertaken on the flame electrospray pyrolysis. Little is known about the mechanism of aerosol generation using flame electrospray pyrolysis, including the key variables. In this study, the feasibility of synthesizing cerium oxide nanoparticles using the newly designed flame electrospray pyrolysis method is investigated systematically by controlling the operation parameters, such as the flow rate of the spray solutions and the electric field.

2. Experiment

Fig. 1 shows the experimental setup for flame electrospray pyrolysis, which comprises (i) an electrospray source to generate the droplets from the solutions, (ii) a premixed methane/air flame where the solution droplets decompose to form nanoparticles, and (iii) sampling and measuring the nanoparticles.

Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.99%, Sigma-Aldrich, USA) was used as the source of Ce. A 0.01 M $Ce(NO_3)_3 \cdot 6H_2O$ solution was prepared by dissolving the inorganic precursor in a mixture of 99 vol% ethanol ($\geqslant$99.9%, Merck, Germany) and 1 vol% diethylene glycol butyl ether ($CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$, $\geqslant$99%, Sigma-Aldrich, USA). Ethanol was chosen as the solvent for its good solubility of the solute and its low surface tension. The diethylene glycol butyl ether was used to suppress the liquid evaporation; the boiling point of diethylene glycol butyl ether is ca. 230 °C while that of ethanol is ca. 78 °C. The electrospray nozzle used a stainless steel capillary (U1148, Upchurch, USA) with outer and inner diameters of 0.787 and 0.46 mm, respectively. The solution was fed into the capillary using a syringe pump (220, KD Scientific, USA). The liquid flow rate was maintained within 0.2–0.5 ml/h to ensure a stable electrospray. The capillary was connected to a 2.5 ml gas-tight syringe (Hamilton, USA) using Teflon tubing. A potential difference of several kilovolts was applied between the capillary and a grounded ring electrode (5 mm I.D.) through a high-voltage positive-polarity DC power supply (Korea Switching, Korea). The capillary was vertically placed at the center of the honeycomb to spray upward and it terminated 1 mm above the ceramic honeycomb. The ring