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Effect of precursor characteristics on zirconia and ceria particle morphology in spray pyrolysis

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Abstract

Ultrasonic spray pyrolysis of acetate-based precursors with precisely measured precursor drop size was employed to produce ZrO_2 and CeO_2 particles. A bimodal size distribution of the product particles indicates a significant influence of the gas-to-particle conversion mechanism in addition to the conventionally accepted one-particle-per-drop mechanism. Due to the differences in solubility of the precursors, ZrO_2 particles are spherical in shape and smooth on their surfaces while the CeO_2 particles are bowl-like in shape with uneven surfaces. Spherical and monodispersed particles with a peak diameter <100 nm can be obtained by reducing the precursor concentrations to 0.01 wt.% in both the different precursor system.

Keywords: A. Powders: Chemical preparation; A. Precursors: organic; D. CeO_2; D. ZrO_2; Spray pyrolysis; Microstructure

1. Introduction

Spray pyrolysis has been widely used to produce fine powders because it is an inexpensive and continuous, ambient pressure process. This process is more economical than other processes (such as sol–gel and chemical vapor deposition) that involve multiple steps or that must be carried out under vacuum. Furthermore, spray pyrolysis offers numerous possibilities for controlled synthesis of advanced ceramic powders and films because of its chemical flexibility [1,2]. For example, yttria-stabilized zirconia (YSZ) has been the most commonly used solid electrolyte in solid oxide fuel cells due to its oxygen conductivity at the classical operating temperature (1000 °C) and its desirable chemical stability in both reducing and oxidizing atmospheres [3,4]. Addition of ceria to YSZ further increases the oxygen conductivity and reduces the operating temperature [5,6]. In addition, cerium oxide (ceria, CeO_2) has generated considerable interest because of its applications in gas sensors [7], catalytic supports in automotive exhaust system [8–10] and electrolyte in solid-oxide fuel cell [4,11]. Such spherical fine ZrO_2 ceramic powders with a narrow size distribution are highly desirable because they result in high reactivity and high packing density and, thus, enhancing the densification of powders with uniform microstructure at low sintering temperature [3].

Precursor drops undergo three major steps during the course of spray pyrolysis: (1) drop size shrinkage due to evaporation, (2) conversion of precursor into oxides, and (3) solid particle formation. The particle formation may involve two mechanisms: intraparticle reaction (conventional one-particle-per-drop mechanism) and gas-to-particle conversion [12]. In the one-particle-per-drop mechanism, each droplet is regarded as a micro reactor and converts into one solid particle when it travels through the tubular reactor. In contrast, gas-to-particle conversion occurs when the precursor is volatile and is transported across the particle-gas interface [12,13]. The vapor of the product materials, after being formed by chemical reaction in the gas phase, may either condense on the particles or nucleate to form new particles. Zhang et al. [14] demonstrated the influence of zirconium precursor saturation

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concentrations on zirconia particle morphology in spray pyrolysis using a conventional ultrasonic nebulizer. They established two criteria for synthesis of solid spherical particles [14,15]: (1) the initial relative solution saturation (C_0/C_s, where C_0 and C_s are precursor concentration and precursor saturation concentration, respectively) must be ~0.01 or less; (2) the precipitated salt must not undergo plastic deformation or melting during heating.

In this work, precursor drop size was measured precisely and acetate-based zirconium and cerium precursors with drastically different solubilities were employed to determine particle morphology of the resulting YSZ and CeO_2 product powders. We found that bimodal particle size distributions were produced, suggesting that both one-particle-per-drop and gas-to-particle conversion mechanisms were involved in spray pyrolysis. We also found very different particle morphology for the two precursors used. The experimental results are consistent with the aforementioned first criterion. Dense spherical particles were produced when the initial relative solution saturations were less than ~0.01. In contrast, hollow [16] or bowl-like particles were formed as in the case of precursor cerium acetate (CeA).

2. Experimental methods

2.1. Materials preparation and product characterization

The precursors used for generation of yttria-stabilized zirconia (YSZ) particles in this study were zirconium hydroxyl acetate (ZHA)/yttria acetate hydrate (YAH) in Y_2O_3/ZrO_2 molar ratios of 3/97. The chemical formula of ZHA and YAH are $Zr(OH)_{4-x}(CH_3COO)_x$ (where $x = 1.36$, Aldrich Chem. Co., Inc.) and $(CH_3CO_2)_3Y{\cdot}xH_2O$ (Aldrich Chem. Co., Inc.), respectively, and the chemicals are reagent grade with >99% purity. Cerium acetate (CeA) was used as the precursor for production of CeO_2 particles. The chemical formula of CeA is $Ce(C_2H_3O_2)_3{\cdot}1.5H_2O$ (99.9%, Alfa Aesar, A Johnson Matthey Co.). The respective molecular weights of ZHA, YAH, and CeA reported by the manufacturers are 216, 266, and 344. The concentration of precursor solutions, YAH/ZHA and CeA in deionized water, ranged from 0.01 to 1.0 wt%. While the solubility of CeA in water is taken from the manufacturer's MSDS data, the solubility of ZHA in water is experimentally measured by heating the ZHA solution in a constant temperature bath until the ZHA precipitates, and then weighing the remaining solution. The solubility was subsequently calculated.

Characterization of the as-received precursors was carried out by thermogravimetric analysis (TGA, Perkin-Elmer Model TGA-7) under gaseous nitrogen flow for removal of product gases. The heating rate was set at 40 °C/min. The phase identification of product particles was performed by X-ray diffractometry (Philips X'pert PW3040, Philips Co., Netherlands) with Cu Kα radiation. In order to confirm the lattice structure of the doped ZrO_2, pure silicon powder was used as a standard in the XRD measurement. Moreover, the phase identification of hydrolyzed CeA was carried out on the powder precipitated from the CeA aqueous solution at approximately 80 °C. The morphology of spray pyrolyzed particles was examined using field emission scanning electron microscopy (SEM, Model 1530, Leo, Germany). Finally, the particle size distribution was determined by number counting over 500 particles from the SEM micrographs.

2.2. Spray pyrolysis system

A schematic diagram of the bench-scale spray pyrolysis system is shown in Fig. 1. Major components of the system are: (1) a three-zone furnace 130 cm in length (Linberg Model Blue M), (2) a 3 in. tubular quartz reactor (7.6 cm in i.d. and 170 cm in length) located in the furnace, (3) a conventional ultrasonic nebulizer with a resonant frequency of 1.65 MHz (King Ultrasonics Co., Ltd., Taipei, Taiwan) for generation of sprays (precursor drops), and (4) precision flow meters and controllers (MKS Model 1179, Andover, MA). As shown in this figure, the upward airflow of 20 L/min first carries the atomized precursor

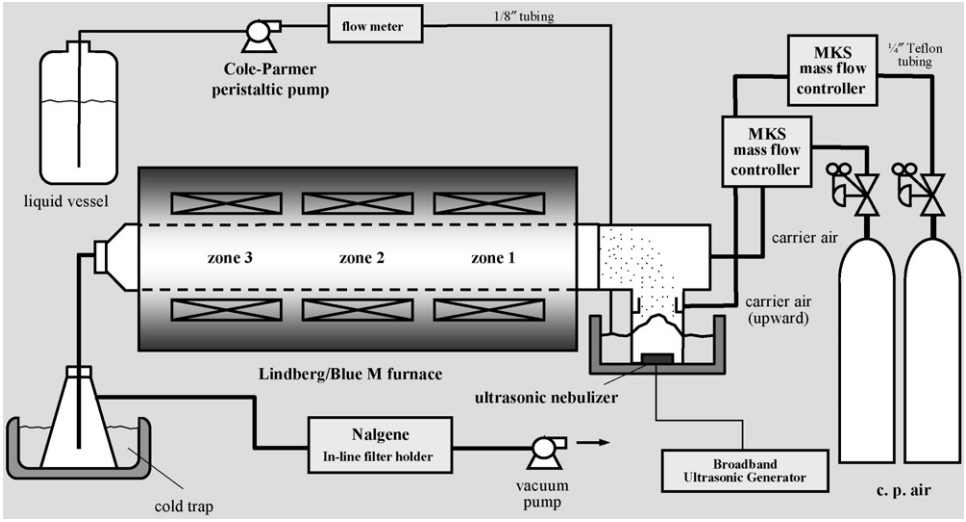

Fig. 1. Schematic diagram of spray pyrolysis system of conventional ultrasonic nebulizer.