Surface & Coatings Technology 259 (2014) 302–309

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Fabrication of ceria particles using glycine nitrate spray pyrolysis

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ARTICLE INFO

Available online 18 April 2014

Keywords:
Ceria
Glycine nitrate
Chemical synthesis
Electron microscopy
Microstructure

ABSTRACT

Ceria-based materials are widely used in many industrial applications such as solid-oxide-fuel-cell electrolytes, catalyst supports and carbon monoxide reduction catalysts because of their superior properties. Morphologies of ceria particles have been well-correlated with their properties. Here we show that various morphologies of ceria particles can be achieved by using the mixed precursor solutions of cerium ammonium nitrate and glycine nitrate (GN) for the new method of glycine nitrate spray pyrolysis. Five precursor solutions with the GN concentrations of 0, 50, 60, 67 and 75 mol% have been investigated. The resultant particles show four distinct morphologies of sphere, hollow, flake and porous flake using scanning electron microscopy, transmission electron microscopy and nitrogen adsorption and desorption isotherms. Our results suggest that the morphological formation mechanisms are highly influenced by the factors of precursor solubilities, solvent evaporation rates and precursor thermal properties. In addition, we have demonstrated that the wall thickness of hollow particles can be achieved by selecting the suitable GN concentration range (50–67 mol%).

1. Introduction

Recently ceria particles have been used as solid-oxide-fuel-cell electrolytes [1], catalyst supports [2] and carbon monoxide (CO) reduction catalysts [3] because of their high ion conductivity, superior phase stability and reversible conversion of Ce(III) and Ce(IV) under oxygenation/deoxygenation cycles [3]. Among these applications, the ceria catalysts are attracted much attention in recent years. The catalytic properties of ceria are determined by their morphologies, sizes, shapes and surface areas [4,5]. Since the morphology plays an important role for controlling catalytic properties, many studies focus on various morphologies, such as solid [6], porous [7] and hollow [4]. In particular, ceria hollow-structured particles have several advantages over the solid particles of low density, large surface area and excellent loading capacity in sorption behaviors for catalysis [4]. For example, ceria hollow particles have much better removal capacities (22.4 mg/g for As(V) and 15.4 mg/g for Cr(VI)) than that of the commercial bulk ceria (0.3 mg/g for As(V) and 15.4 mg/g for Cr(VI)) due to the higher surface areas for the former (72 m^2/g for ceria hollow nanoparticles and 2 m^2/g for the bulk ceria) [4]. Therefore, ceria hollow particles have become one of the candidates for future catalysis applications.

A number of methods have been used to synthesize ceria hollow particles, including: thermal decomposition [4,8], hydrolysis [9], sol-gel [10] and spray pyrolysis (SP) [11,12]. In this study, SP has been chosen to fabricate the hollow particles because of its simple operation, continuous processing, production of high purity ceria powder and chemistry flexibility [13]. Our previous studies have shown that ceria hollow particles can be prepared by selecting suitable precursors such as cerium nitrate hydrates [11] or cerium acetates hydrate [12]. Furthermore, the formation of hollow structure when synthesized using the SP method is through the surface precipitation formation mechanism [14]. However, control of the detailed morphology of the hollow structures, i.e. the void size and shell thickness, has not been investigated. In this study, we attempt to establish a method to control the detailed hollow structures using the SP method.

Methods for fabricating hollow structures can be divided into two main strategies: template method and template-free method [4,8,15–18]. These methods are compared in Table 1. The template-free methods employ either the Ostwald ripening effect [4,8] or the Kirkendall effect [9] to form hollow structured ceria-based particles. Using the Ostwald ripening effect, although the homogenous particles can be obtained [4,8], its discontinuous processing can be challenging for mass production. The Kirkendall effect cannot be applied in the production of pure ceria hollow particles as it requires different diffusion rates of two elements to form a hollow structure for the ceria-based particles (e.g. $Ce_{1-x}Zr_xO_2$ [9]). On the other hand, the template techniques [15–18] require removal of hard (e.g. SiO_2) or soft templates (e.g. polystyrene) to form hollow structured particles. These template methods offer advantages over the template-free methods in their better control of the void sizes and size distributions. Among the template methods, the soft template method is preferred because hard template materials are generally removed by acid/base erosion, which may be harmful to the environment [4]. Therefore, a soft-template SP method for the production of ceria hollow particles is a preferred choice of synthesis method.

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http://dx.doi.org/10.1016/j.surfcoat.2014.04.016
0257-8972/

Table 1
Previous experimental results of the hollow ceria particles.

Hollow formation mechanism	Precursors	Synthesis	Morphology	Particle size (nm)	Surface area (m^2/g)	References
Ostwald ripening	$Ce(NO_3)_3{\cdot}6H_2O$ and N_2H_4O	Microwave-assisted thermal decomposition	Porous hollow	~200	~70	Cao et al. [4]
Ostwald ripening	$Ce(NO_3)_3{\cdot}6H_2O$, $C_4H_8N_2O_3$ and $KBrO_3$	Thermal decomposition	Hollow	~1000–2000	~35	Yang et al. [8]
Kirkendall effect	Ce(III) and Zr(IV) precursors and $C_2H_6O_2$	Hydrolysis	Porous hollow	~100	~140–180	Liang et al. [9]
Hard Template (SiO_2)	$Ce(NO_3)_3{\cdot}6H_2O$ and SiO_2 gel	Thermal decomposition	Hollow	~300–400	~35	Guo et al. [15]
Hard template (SiO_2)	$Ce(NO_3)_3{\cdot}6H_2O$, $SiC_8H_{20}O_4$, NH_4OH and $C_2H_6O_2$	Thermal decomposition	Porous hollow	~250	~120	Strandwitz and Stucky [16]
Soft template (polystyrene)	$Ce(NO_3)_3{\cdot}6H_2O$ and $(C_8H_8)_n$	Thermal decomposition	Hollow	~500	N. A.	Yamaguchi et al. [17]
Soft template (polystyrene)	$Ce(NO_3)_3{\cdot}6H_2O$ and $(C_8H_8)_n$, $C_{10}H_{10}$, $K_2S_2O_8$, $C_4H_6O_2$ and $(CH_2)_6H_4$	Thermal decomposition	Hollow	~200	~65	Chen and Lu [18,29]

In this study, soft templates, low-molecular weighted glycine nitrate (GN), has been selected to replace the common templates of polystyrene. The main reason is that SP calcination rate is very rapid (e.g. ~100 °C/s [19]), polystyrene (high-molecular weighted) may decompose incompletely to cause carbon contamination [20]. The precursor solutions containing five different GN molar concentrations (GN/(GN + cerium ammonium nitrate (CeAN))) were applied to produce ceria particles with various morphologies. The decomposition behaviors of CeAN and GN were examined by thermogravimetric analysis (TGA). The crystallographic phases of the ceria powders were examined by X-ray diffraction (XRD). The surface morphologies and geometries were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Specific surface areas were characterized using nitrogen adsorption and desorption isotherms (BET method). Based on the result, the hollow structured ceria particles can be successfully produced with controlled morphology and thickness using glycine nitrate spray pyrolysis (GNSP) method.

2. Experimental procedure

The ceria powders from the five precursors: (i) 0 mol% GN ($C_2H_5NO_2$, 98%, Acros Organics, US) and 100 mol% CeAN ($(NH_4)_2Ce(NO_3)_6$, 99.5%, Alfa Aesar, Johnson Matthey Co., US)), (ii) 50 mol% CeAN and 50 mol% GN ($(CeAN)_{50}(GN)_{50}$), (iii) 40 mol% CeAN and 60 mol% GN ($(CeAN)_{40}(GN)_{60}$), (iv) 33 mol% CeAN and 67 mol% GN ($(CeAN)_{33}(GN)_{67}$) and (v) 25 mol% CeAN and 75 mol% GN ($(CeAN)_{25}(GN)_{75}$), were prepared using a laboratory-scale SP electrostatic deposition system. Firstly, CeAN and GN were dissolved separately in de-ionized water to form five precursor solutions (1 wt.%). In the SP process the precursor solution was first atomized into small droplets while an air flow with a controlled flow rate carried the droplets into the heated tubular reactor with three heating zones of 250, 650 and 350 °C. In the reactor the droplets undergo solvent evaporation, solute precipitation and precursor decomposition to convert into oxide particles. The resulting charged particles were then collected by a cylindrical electrostatic collector with an applied high-voltage potential of −16 kV.

The precursors of CeAN and GN were characterized by the thermal analyses of TGA (TG-DTA 8120, Rigaku, USA) under an ambient airflow to remove decomposition products. The heating rate was 10 °C/min.

X-ray diffractometer (D2 Phaser, Bruker, German), with Ni-filtered Cu-Kα radiation, was used to characterize the crystallographic structures of the particles from the precursor solutions of CeAN, $(CeAN)_{50}(GN)_{50}$, $(CeAN)_{40}(GN)_{60}$, $(CeAN)_{33}(GN)_{67}$ and $(CeAN)_{25}(GN)_{75}$. Quantification of crystallite size and strain was using the following procedure. In order to obtain the precise values, XRD peak broadening effect was estimated using the following equation [21]

$$\beta_{hkl} = \left[(\beta_{hkl})^2_{measured} - \beta^2_{instrumental}\right]^{1/2} \quad (1)$$

where β_{hkl} instrumental corrected integral breadth of the reflection located at 2θ, $\beta_{instrumental}$ is contributed by XRD instrument, which was measured by a silicon standard peak (111).

Also, Scherer formula and the equation for strain induced broadening were given below

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta} \quad (2)$$

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \quad (3)$$

where D is the crystallite size, k is the shape factor (0.9), λ is the wavelength of Cu Kα radiation, and ε is the strain, which induced XRD peak broadening.

By combining Eqs. (2) and (3), Williamson and Hall proposed a method of deconvoluting size and strain broadening by looking at the peak width as a diffraction angle 2θ as follow [25].

$$\beta_{hkl} = \frac{K\lambda}{D\cos\theta} + 4\varepsilon\tan\theta. \quad (4)$$

In addition, TEM specimens of these five ceria powders were prepared by dispersing the particles in acetone using an ultrasonic bath for around 5 min, and then depositing a drop of suspension onto lacy carbon film grids. The solvent on the lacy carbon grids was evaporated at room temperature. The field emission gun-transmission electron microscope (Tecnai G2 F20, FEI, USA), operated at 200 keV, was used to examine the two-dimensional particle morphologies. Since projection images from TEM only reveal two-dimensional morphologies [12], surface morphologies were taken using field-emission scanning electron microscopy (FESEM, JSM-6500 F, JEOL, Japan) to compare with the TEM images for three-dimensional morphologies. Therefore, the 3-D morphologies of five ceria powders were obtained from numerous TEM and SEM micrographs, and more than 250 particles were examined to obtain the particle diameter distributions. In addition, in order to obtain porosity values of hollow particles, wall thicknesses and pore diameters of more than twenty ceria particles for each powder have been calculated using the corresponding TEM images.

The specific surface areas of the ceria powders were measured using the BET method (ASAP 2010, Micromeritics, USA) from nitrogen adsorption and desorption isotherm data obtained at −196 °C on a constant-volume adsorption apparatus. The as-prepared ceria powders were degassed at 150 °C for 3 h before measurements. The average values and standard deviations of the specific surface areas were obtained from a number of repeated measurements.

3. Results and discussion

Fig. 1 shows the TGA analysis for CeAN and GN. Firstly, the two main decomposition stages for CeAN are related to the formation of $Ce(NO_3)_4$