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Designing the morphology of ceria particles by precursor complexes

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Abstract

Ceria-based materials are widely used as catalysts, catalyst supports and electrolytes in many industrial applications. The morphological requirements of ceria particles vary depending on their applications. Here we show that complex morphologies of ceria particles can be achieved by using precursor complexes in the spray pyrolysis (SP) method. Three precursor complexes have been investigated: the complex of cerium acetate hydrate (CeA) and cerium nitrate hydrate (CeN); CeA and cerium ammonium nitrate (CeAN); and CeN and CeAN. Our results suggest that the morphological formation mechanism is highly correlated with the factors of precursor solubilities, solvent evaporation rates and precursor melting temperatures.

Keywords: A. Powders: chemical preparation; B. Microstructure—final; B. Electron microscopy; D. CeO_2

1. Introduction

Ceria is known for industrial materials because of its superior properties of ion conductivity [1], thermal stability [2] and oxygen storage capacity [3], leading to the widespread use of ceria-based particles as components in applications such as solid oxide fuel cell (SOFC) electrolytes [1], catalyst supports [4] and carbon monoxide (CO) reduction catalysts [3]. In order to achieve optimal performance, the morphology requirements of ceria particles vary depending on their applications [1,3,4]. For example, SOFC electrolytes must be dense, and therefore solid ceria particles with minimum porosity are desirable [1]. For catalyst support applications, ceria particles with a porous structure provides greater, therefore leading to higher reaction efficiency [4]. When used as catalysts for CO oxidation, the hollow ceria structures offer the advantages of providing greater gas adsorption [3]. Furthermore, Du et al. [5] have recently reported that rod-shaped ceria particles with a high proportion of (100) and (110) surfaces are catalytically more active compared to spherical ceria particles with a high proportion of (111) surfaces. In addition, those authors also found that the ceria rods have higher ratio of Ce^{3+} (10.8%) compared to that (6.9%) of the spherical ceria particles. These examples illustrate that the morphology plays a significant role in governing the useful properties of ceria particles.

A number of methods have been used to synthesize ceria particles, including the sol–gel method [6,7], micro-emulsion [8], precipitation [9,10] and spray pyrolysis (SP) [11–15]. Here we have chosen the SP process because of its simple operation, continuous processing, production of high purity powder and chemistry flexibility [16]. Table 1 summarizes the previous reports of the four particle morphologies of solid, hollow, concaved and multiporous particles and their corresponding precursor solution (salt and solvent) used in the synthesis [11–15]. These reports establish that there is a strong correlation between particle morphology and the single salt precursor [11–15]. However, studies using precursor complexes are (multiple salt systems) are scarce. In order to obtain more complex morphologies for a wider range of industrial applications, it is important to develop the SP methods and the relevant formation mechanisms using precursor complexes.

In this study, three precursor complexes were applied to produce various morphologies, namely a mixture of cerium acetate hydrate (CeA) and cerium nitrate hydrate (CeN), a mixture of CeA and cerium ammonium nitrate (CeAN)

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Table 1
Previous experimental results of various morphological ceria particles synthesized by SP.

Morphology	Salt	Solution	Particle size, (nm)	References
Solid	$(NH_4)_2Ce(NO_3)_6$	DI water	~30 to 600	Shih et al. [11]
Hollow	$Ce(NO_3)_3 \cdot 6H_2O$	DI water	~70 to 750	Kang et al. [12]
Hollow	$Ce(C_2H_3O_2)_3 \cdot 1.5H_2O$	DI water	~100 to 300	Shih et al. [13]
Concaved	$Ce(C_2H_3O_2)_3 \cdot 1.5H_2O$	DI water	~350 to 780	Chen et al. [14]
Multiporous	$Ce(NO_3)_3 \cdot 6H_2O$	DI water	~30 to 900	Shih et al. [15]

and a mixture of CeN and CeAN. The decomposition behaviors of the three salts were examined by the thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The geometries and the crystallographic structures of the ceria particles were examined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Also, the surface morphologies and surface areas of the particles were analyzed by scanning electron microscopy (SEM) and nitrogen adsorption and desorption isotherms (BET method), respectively. Our result shows that the different complex precursors lead to new complex morphologies of ceria particles via different SP formation mechanisms.

2. Experimental procedures

The ceria powders from the precursor complexes, including (i) 50 mol% CeA ($Ce(C_2H_3O_2)_3 \cdot 1.5H_2O$, 99.9%, Alfa Aesar, Johnson Matthey Co.) and 50 mol% CeN ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%, Alfa Aesar, Johnson Matthey Co.) (CeA+CeN), (ii) 50 mol% CeA and 50 mol% CeAN ($(NH_4)_2Ce(NO_3)_6$, 99.5%, Alfa Aesar, Johnson Matthey Co.) (CeA+CeAN) and (iii) 50 mol% CeN and 50 mol% CeAN (CeN+CeAN), were prepared using a laboratory-scale SP electrostatic deposition system. Initially, three cerium precursors were dissolved separately in de-ionized water to form three 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 particles were then collected by a cylindrical electrostatic collector with an applied high-voltage potential of −16 kV.

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

TEM specimens of the ceria particles from the precursors complexes of CeA+CeN, CeA+CeAN and CeN+CeAN were prepared by dispersing the particles in acetone using an ultrasonic bath for around 5 min, and then depositing a drop of suspension onto holey carbon film grids. The solvent on the 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 morphology and the crystallographic structure of the ceria powders. The morphologies of three ceria powders were obtained from numerous TEM micrographs, and more than 150 particles were examined to obtain the particle diameter distributions. The crystallographic structures of three particles are characterized by SAED from random selected particles with an aperture size of 800 nm.

Since projection images from TEM only reveal two-dimensional morphologies [13], surface morphologies were taken using field-emission scanning electron microscopy (FESEM, JSM-6500F, JEOL, Japan) to compare with the TEM images for three-dimensional morphologies.

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 samples were degassed at 150 °C for 3 h before measurements. The average values and standard deviations of the specific surface areas from three repeated measurements were obtained.

3. Results and discussion

Fig. 1 shows the TGA and DTA analyses for the single salt systems of CeA, CeN and CeAN. Firstly, the four weight-loss stages for CeA (Fig. 1(a), obtained from TGA data with the temperature ranges of ~50 to ~110 °C, ~110 to ~160 °C, ~160 to ~280 °C and ~280 to ~800 °C are attributed to formation of $Ce(C_2H_3O_2)_3 \cdot H_2O$ (97% of CeA), $Ce(C_2H_3O_2)_3$ (92% of CeA), $Ce_2O_2CO_3$ (64% of CeA) [17] and CeO_2 (53% of CeA), which are in agreement with the calculated weight-loss values of 97%, 92%, 63% and 50%; the endothermic peak of 158 °C and the exothermic peaks of 201 °C and 250 °C shown in the DTA data suggest dehydration and the formation of cerium complexes of oxyacetate ($Ce(OH)(CH_3COO)$) and dioxocarbonate ($Ce_2O_2CO_3$) [17,18], respectively. For CeN, TGA shows that only two weight-loss stages of ~50 to ~230 °C and ~230 to ~800 °C are associated with dehydration of CeN ($Ce(NO_3)_3$) and the formation of CeO_2 [19] as shown in Fig. 1(b). The DTA diagram shows that the first two endothermic peaks are attributed to dehydration of CeN and the last endothermic peak is attributed to the decomposition of $Ce(NO_3)_3$ to CeO_2; the experimental weight percentages of these two stages are 74% and 41%, which are close to the expected values of 75% and 43%. Finally, for CeAN, the two major stages of decomposition are related to