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Effect of surfactants and digestion time on nano crystalline cerium oxide characteristics synthesized by differential precipitation

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Abstract

Nanocrystalline ceria has been synthesized by differential precipitation method in presence of poly-vinyl-pyrolidone (PVP) and polyethylene glycol (PEG) as surfactants. Sodium carbonate (Na_2CO_3) was used as an precipitation agent. The precipitate was digested for 4–12 h, dried at 80 °C for 24 h and, then calcinated at 400 °C for 4 h. The nanocrystalline ceria was characterized by thermo gravimetric analysis (TGA), X-ray diffraction (XRD), N_2 adsorption/desorption (BET) and scanning electron microscopy (SEM). The digestion time, type and amount of surfactant materials were optimized to provide nanocrystalline ceria with high surface area. The results revealed that the surfactant agent increases the surface area due to decrease of crystalline size. Furthermore, PEG surfactant resulted in formation of smaller particles compared to PVP. Moreover, increasing the digestion time to 8 h, improves the samples pore volume and surface area. The nanocrystalline ceria was synthesized with surface area of 102.8 m^2/g and crystalline size of 8 nm in presence of surfactant.

Keywords: Ceria; Precipitation

1. Introduction

Ceria is an oxide of the rare earth cerium but this substance has numerous applications such as solid oxide fuel cells [1], optical devices [2], solar protector [3], oxygen gas sensor [4], and as catalyst support in the reaction of hydrogenation [5], and water gas shift [6]. However, performance of ceria in above uses is strongly influenced by the physical properties of ceria particles [7]. Easier reducibility of ceria as well as high oxygen storage capacity and mobility of surface oxygen will make ceria as a good choice for catalyst support [8].

Synthesis of ceria by hydrothermal, polymeric precursor, organometallic decomposition, and flux method mainly need high temperature and pressure whereas the precipitation method produces nano crystalline ceria at atmospheric pressure and room temperature [9]. There are various ways to carry out the precipitation process. In the simplest way, precipitation agent will be added to metal salt solution in the beaker (and vice versa). Disadvantages of this method is composition variations, pH and temperature during the precipitation. Consequently, inhomogeneous product is formed [10]. In this research, to adjust the pH and to form the homogeneous product with high purity, two solutions were placed in two separate burets and were added to beaker containing distilled water in the constant ratio, simultaneously. This method was called differential precipitation.

Universally, cerium (III) nitrate and different precipitation agents, including ammonia [7–11], sodium hydroxide [12] and urea [13] were used for synthesizing of ceria. Use of high amount of precipitation agent and high temperature for precipitation of cerium cations are the main defects for these agents. [14]. In this research, in order to resolve these problems Na_2CO_3 has been used as a precipitation agent. Na_2CO_3 leads to precipitate cerium (III) carbonate at room temperature, prevents additional hydrolysis and pH is fixed in range of 6.5–7 during the precipitation. In addition, PVP/PEG was used as surfactant to improve physical properties. Surfactants led to increase in surface area by decreasing crystalline size [15].

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The aim of this research is to synthesize nano crystalline ceria with high surface area via the differential precipitation method by use of PVP and PEG as surfactants. This research has been focused principally on effects of surfactant and digestion time on the crystalline size, surface area, pore volume and morphology of the ceria powders.

2. Experimental

2.1. Materials

The materials used in this research were cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%, LOBA Chemie) and sodium carbonate (Na_2CO_3,99%, LOBA Chemie) as a metal salt and precipitation agent materials, respectively. In addition to, polyvinylpyrrolidone (PVP) or poly ethylene glycol (PEG) are surfactant materials.

2.2. Preparation of nanocrystalline ceria

0.06 M solution of Ce (III) nitrate and 0.08 M of Na_2CO_3 solution were prepared by dissolving an appropriate amount of Ce $(NO_3)_3 \cdot 6H_2O$ and Na_2CO_3 in distilled water, respectively.

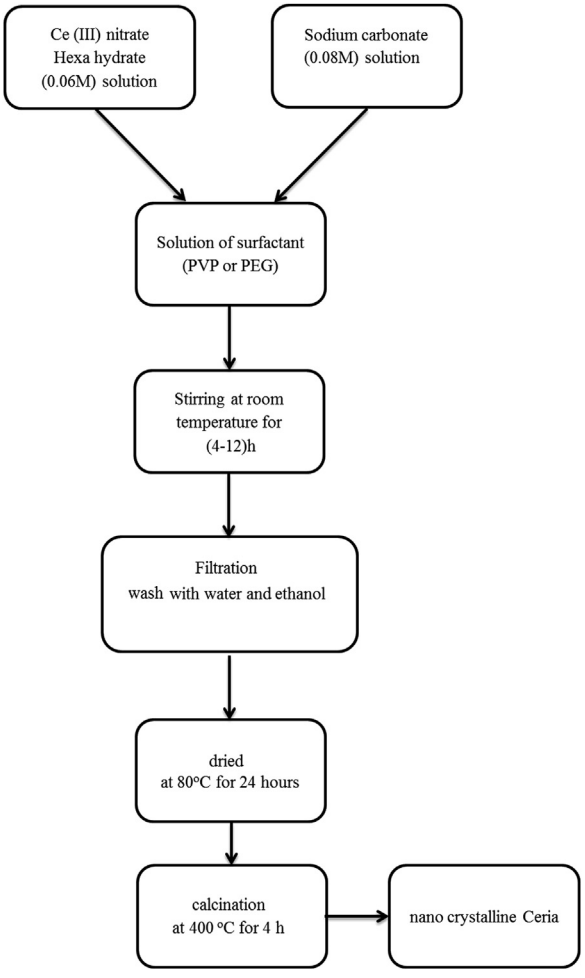

Fig. 1. Schematic illustration of nano crystalline CeO_2 prepared by the differential precipitation method.

Table 1
Description of the synthesized samples by a differential precipitation method.

Sample	Type of surfactants	Amount of surfactant (wt%)	Digestion time (h)
Ceria 1	—	0	4
Ceria 2	PVP	1	4
Ceria 3	PVP	0.5	4
Ceria 4	PVP	0.3	4
Ceria 5	PEG	0.5	4
Ceria 6	PEG	0.3	4
Ceria 7	PEG	0.5	8
Ceria 8	PEG	0.5	12

Appropriate amount of surfactant (0, 0.3, 0.5, 1 Wt%) is dissolved in distilled water. Aqueous solutions of metal and precipitation agent were placed in two burets and simultaneously added to surfactant solution (PVP or PEG) to precipitate a cerium (III) carbonate ($Ce_2(CO_3)_3 \cdot 8H_2O$). The precipitates digested for 4–12 h at room temperature, then filtered with a mixture of distilled water and ethanol for 5–10 times and thereafter dried at 80 °C for 24 h. The calcination process was carried out at 400 °C for 4 h to make nano crystalline ceria. These samples were synthesized by different surfactants and digestion times (Fig. 1). Table 1 shows the samples synthesized at different conditions.

2.3. Characterization

Thermo gravimetric analysis (TGA) for dried cerium (III) carbonate carried out by PL-STA-1640 Thermo-gravimetry Analyzer in air. Air temperature was increased from room temperature to 600 °C with a rate of 5 °C/min.

The XRD patterns were recorded on diffractometer X-ray (P Analytical X'Pert-Pro) using a CuKα monochromatized radiation source and a Ni filter in the range $2\theta = 20°–80°$. The crystalline sizes of samples were given by Scherrer's equation:

$$d_{XRD} = \frac{0.9\,\lambda}{\mathrm{FWHM}.\cos\,\theta} \quad (1)$$

Where 'd_{XRD}' is the crystalline size, 'λ' for Cu Kα radiation is 1.5418 Å, FWHM (in Rad.) is the full width at half maximum of the characteristic peak of sample and θ is the diffraction angle.

The N_2 adsorption–desorption analysis (BET) was carried out at boiling temperature of nitrogen (−196 °C) using an automated gas adsorption analyzer (Tristar 3020, Micrometrics).

CeO_2 powders morphologies were observed via scanning electron microscopy (SEM) (EM2500), operating with a voltage of 25 kV.

3. Results and discussion

3.1. TGA curve

TGA curve for dried cerium (III) carbonate is shown in Fig. 2. Gradual weight loss about 9% at temperatures lower than 250 °C is allocated to the loss of physical adsorbed water and water in the crystalline structure. The main weight loss of

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