

Synthesis of CeO₂ Nanocrystalline Powder by Precipitation Method

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Abstract

Ceria (CeO₂) is an important rare earth oxide and has been widely investigated in the automotive exhaust purification, oxygen storage and release catalysis, and solid oxide fuel cell applications. In recent years, due to the excellent physical and chemical properties of nano-sized particles, which are significantly different from those of bulk particles, there is considerable interest in enhancing catalytic activity, sinterability, and other properties by decreasing the grain size into a nanometer range. In the present study, a simple precipitation procedure for the synthesizing of CeO₂ nanocrystalline powder (~13 nm) is presented. The structural evolutions and morphological characteristics of the nanopowder were investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM), thermo-gravimetry (TG), and Fourier transform infrared spectroscopy (FTIR). XRD results showed that face centered cubic CeO₂ particles with crystallite size in nanometer scale were formed. By increasing the calcination temperature from 100 to 300°C, the crystallite size decreases from 20 to 13.9 nm. By increasing the temperature more than 300°C, crystallite size of ceria increases. SEM studies showed the morphology of the prepared powder is sphere-like with a narrow size distribution.

Keywords: CeO₂, Precipitation, Powders, Nanoparticles

SYNTEZA NANOKRYSTALICZNEGO PROSZKU CeO₂ METODĄ STRĄCANIA

Tlenek ceru(IV) (CeO₂) jest ważnym tlenkiem ziem rzadkich i został szeroko zbadany w zastosowaniach obejmujących oczyszczanie spalin samochodowych, katalizę przechowywania i uwalniania tlenu oraz stałotlenkowe ogniwa paliwowe. W ostatnich latach, w związku z doskonałymi właściwościami fizycznymi i chemicznymi nanocząstek, znacznie różniącymi się od cząstek masywnych, istnieje znaczne zainteresowanie zwiększeniem aktywności katalitycznej, spiekalności i innych właściwości poprzez zmniejszenie rozmiaru ziarna do zakresu nanometrycznego. W prezentowanych badaniach pokazana jest prosta procedura strącania wykorzystana do syntezy nanokrystalicznego proszku CeO₂ (~13 nm). Ewolucja budowy i charakterystyka morfologiczna nanoproszku badana była z wykorzystaniem dyfraktometrii promieniowania X (XRD), skaningowej mikroskopii elektronowej (SEM), termogravimetrii (TG) i spektroskopii w podczerwieni z transformacją Fouriera (FTIR). Wyniki XRD pokazały, że wytworzono cząstki regularnego, centrowanego ściennie CeO₂ o nanometrycznym rozmiarze krystalitów. W wyniku zwiększenia temperatury kalcynacji ze 100 do 300°C rozmiar krystalitu zmniejsza się z 20 do 13.9 nm. W wyniku zwiększenia temperatury ponad 300°C rozmiar krystalitu tlenku ceru(IV) zwiększa się. Badania SEM ujawniły, że morfologia wytworzonych cząstek jest zbliżona do kulistej, a cząstki mają wąski rozkład wielkości.

Słowa kluczowe: CeO₂, strącanie, proszki, nanocząstki

1. Introduction

Ceria (CeO₂) is an important rare earth oxide and has been widely investigated in the automotive exhaust purification, oxygen storage and release catalysis, and solid oxide fuel cell applications. A remarkable property of CeO₂ is the number of effective redox Ce⁴⁺/Ce³⁺ sites and their ability to exchange oxygen [1, 2].

In the recent years, due to the excellent physical and chemical properties of nano-sized particles, which are significantly different from those of bulk particles, there is considerable interest in enhancing catalytic activity, sinterability, and other properties by decreasing the grain size into a nanometer range [3, 4].

CeO₂ nanopowders have been reported to be synthesized by different techniques, such as hydrothermal [5], mechanochemical [6], sonochemical [7], combustion synthesis [8], sol-gel [9], semi-batch reactor [10], microemulsion [11] and spray-pyrolysis [12].

Among the chemical processes, precipitation is simple in process, low in cost and saving in time in comparison to the another techniques.

In the present work, a CeO₂ nanopowder has been prepared via a simple precipitation method using CeCl₃·7H₂O and NH₃ as a precipitant agent. Morphology and phase analysis of resultant nanopowder and effect of thermal-treatment on synthesized nanopowder are investigated via SEM, TG, BET and FT-IR analysis.

2. Experimental

CeO₂ nanopowder was prepared by a precipitation method using CeCl₃·7H₂O (Merck, purity > 99.5 %) and NH₃ (Merck, purity > 99 %). At first, CeCl₃·7H₂O was dissolved in deionized water. Then, the mixture was stirred for 30 min and then NH₃ (0.5 M) was added to aqueous solution until the gel formed at a pH value of about 8.5 was reached. The resultant synthesis gel was then washed with boiling distilled water and dried at 80°C for 24 h. The dried gel (xerogel) was calcined for 2 h in a tube furnace at different temperatures.

The crystalline structure of the powders was determined by X-ray diffraction (Philips pw 3710) with CuK α radiation. The average crystallite size (*d*) of the powder was estimated from the Scherrer equation.

Thermogravimetric analysis (TG) was carried out in the range of 25-1000°C with a rate of 10°C·min⁻¹ (TGA, PL-STA-1640, Polymer laboratories, Stanton Redcraft, U.K.). N₂ adsorption-desorption isotherms were determined in a surface analyzer equipment (micrometrics, USA) at 77 K. The powder morphology was observed using a Phillips XL30 scanning electron microscope (Netherlands). Fourier transformation infrared spectroscopy analysis of dried gel and calcined powders were carried out in Bruker equipment (Vector-33 model, Germany) for studying the chemical groups of the dried gel and calcined powder.

3. Results and discussion

Fig. 1 illustrates the effect of temperature on the weight loss of the gel (TG curve). As it can be seen, the rate of weight loss is very high up to 200°C which is attributed to evaporation of absorbed water and dehydration of the dried gel. With removing the water and hydroxyl groups the rate of weight loss decreases dramatically with increasing the temperature. The weight loss after 200°C is attributed to the remaining volatile components, such as chloride components. The total weight loss of 10 % appears in the gel after heat treatment at 800°C. No significant weight loss occurs after 650°C that shows all volatile components leave the gel after this temperature.

The X-ray diffraction pattern of the gel before and after heat treatment for 2 h at a temperature range from 100 to 900°C are shown in Fig. 2. It is clear that the gel before heat treatment shows broad peaks of CeO₂ nanocrystals with pure cubic structure. By increasing the heat-treatment temperature

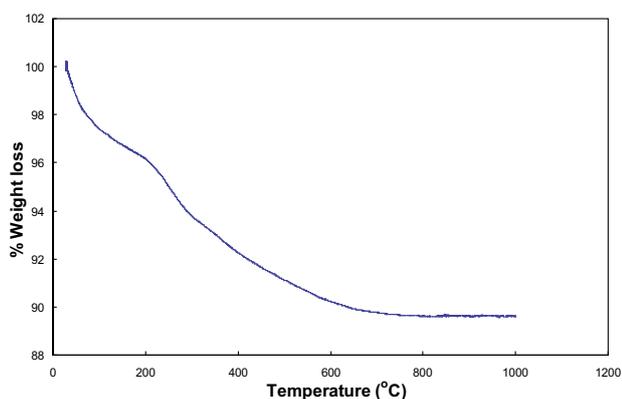


Fig. 1. TG curve of the dried gel.

to 900°C, the broadening of CeO₂ peaks decreases which shows growing of the CeO₂ nanocrystals. Although some researchers [14, 15] showed amorphous CeO₂ forms after synthesis via chemical routes but in the present study nanocrystalline CeO₂ is detected after synthesis of nanopowder without any heat-treatment. It seems that the activation energy for crystallization is low enough to cause the formation of CeO₂ nanocrystals at room temperature. It is known that there are Ce-O-Ce and Ce-OH-Ce bonds in the synthesized gel. With respect to TG curve (Fig. 1) the total weight loss is not very high (about 10 %) and it can be concluded that the amount of hydroxyl groups in the gel is also not very high.

Therefore, there are a lot of Ce-O-Ce bonds in the gel and if the thermodynamic conditions are available, crystalline ceria is formed. The evolution of crystallite size of the CeO₂ powder during calcination has been investigated, and the results obtained from X-ray line-broadening of the (111) peak are summarized in Fig. 3. As it can be seen, crystallite size decreases from 20 to 13.9 nm with increasing the calcination temperature from 100 to 300°C. On the other hand, with increasing the temperature by more than 300°C increasing of crystallite size is caused. The decrease of crystallite size in the first step of calcinations (between 100 and 300°C) may be due to rapid decomposition of the gel particles accompanied by the appearance of considerable stresses, which leads to an intense decomposition of the particles. Increasing of crystallite size after 500°C is attributed to a typical effect of temperature on crystal growth. For instance, Li *et al.* [13] reported that the crystallite size of CeO₂ shows exponential dependence on the calcination temperature, indicating that crystallite growth is diffusion related.

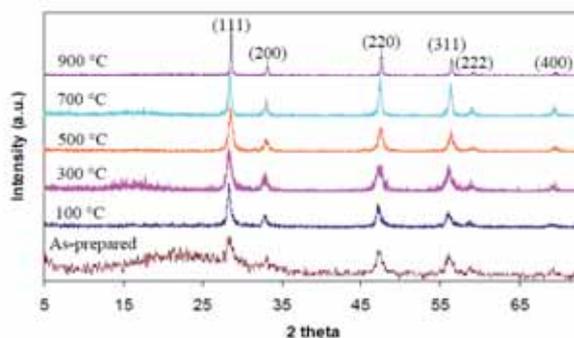


Fig. 2. XRD patterns of as-prepared and heat treated samples at various temperatures for 2 h.

The effect of the calcination temperature on the surface area is shown in Fig. 4. The surface area increases up to 300°C and reaches to 41 m²/g, then it decreases when the temperature becomes higher. The increase of BET is parallel to the decrease of CeO₂ crystallite size up to 300°C. In addition, removing of volatile component causes changing the textural properties of nanopowders and increasing the surface area in each particle. Nevertheless, as the calcination temperature increases from 300 to 700°C, the surface area of CeO₂ decreases due to the higher size particles formed and the subsequent loss of microporosity and increasing the pores volume on the surface of particles.

Fig. 5 presents the SEM images of the powder heat treated at different temperatures. As it can be seen, grain size of powders decreases with increasing the calcination

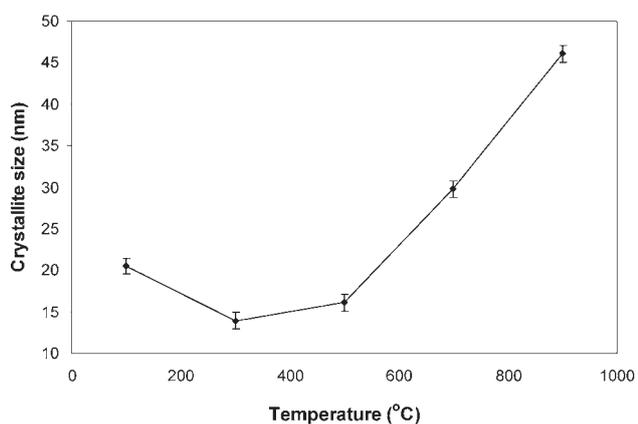


Fig. 3. Effect of calcination temperature on crystallite size of CeO₂.

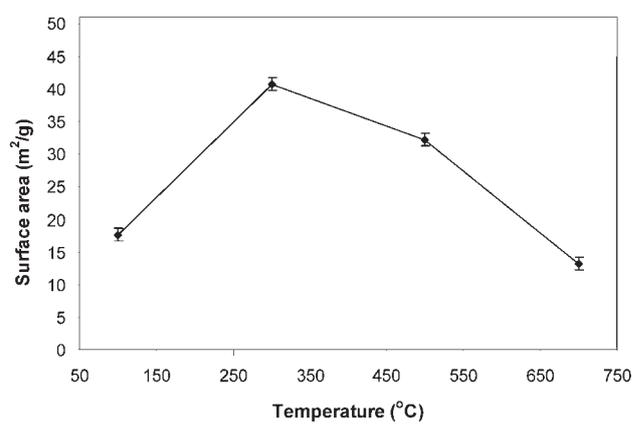
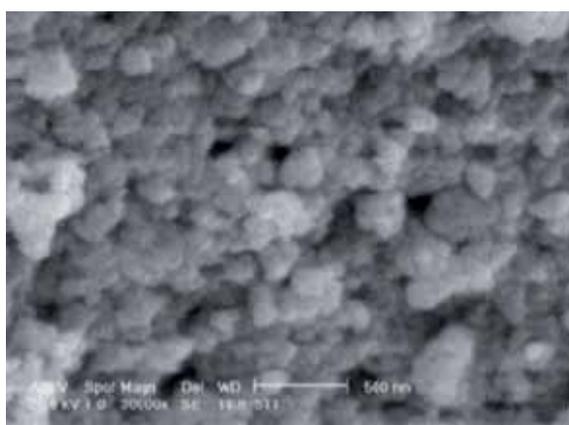
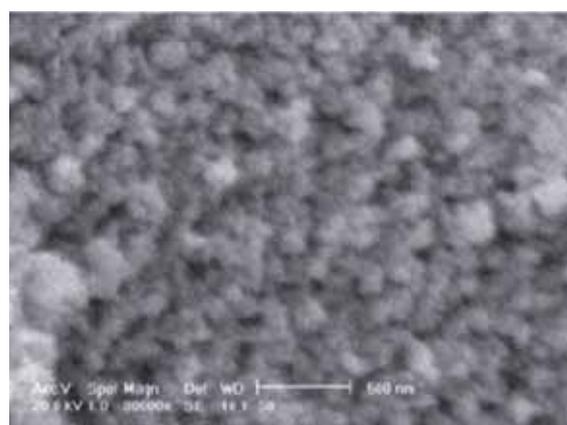


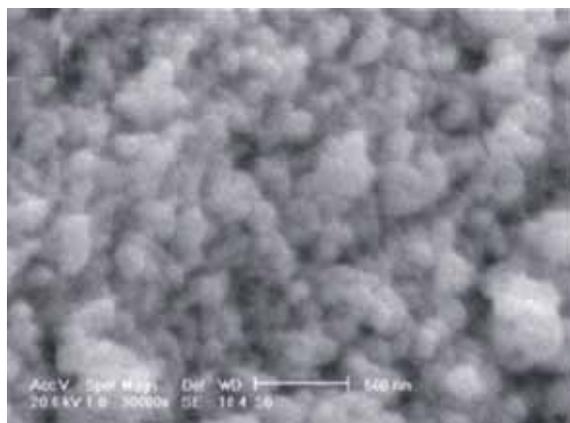
Fig. 4. Effect of calcination temperature on surface area.



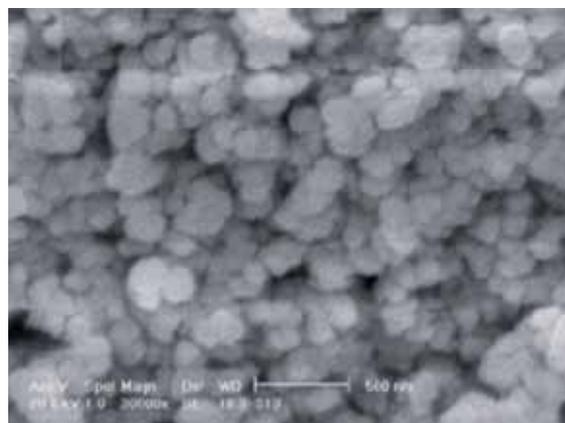
a)



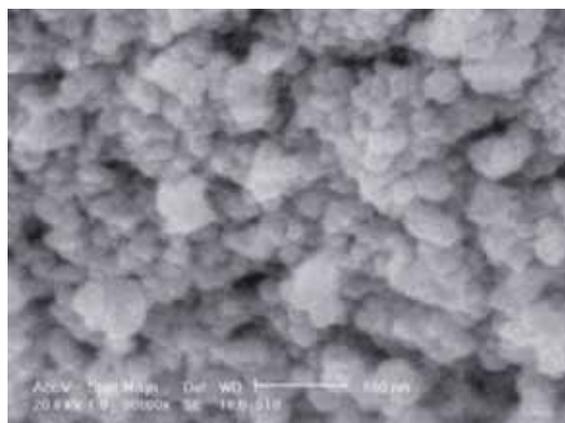
b)



c)



d)



e)

Fig. 5. SEM images of the powders heat treated at different temperatures: a) 100°C, b) 300°C, c) 500°C, d) 700°C, e) 900°C.

temperature up to 300°C due to removing of volatile component and gel decomposition (Figs. 5a and 5b).

Then by increasing the temperature more than 300°C, grain size of powders increases due to the effect of temperature and crystal growth (Figs. 5b, 5c and 5d). It is clear that SEM studies on the changing grain size with temperature are in good agreement with the changing of the crystallites size which is obtained by Scherrer equation (Fig. 3). Figs. 5d and 5e show that the particles began to sinter and agglomerate together with increasing calcination temperature. This shows that the synthesized powder is very sinter-active so that it starts to sinter at low temperatures and it can be used as raw material for fabrication of bulk ceria. For sintering of the crystalline materials at medium temperatures, the surface diffusion mechanism and the surface area reduction can be correlated to the sintering time, t , and temperature, T , by [16]

$$\frac{\Delta S}{S} = k \cdot \left[\gamma \cdot t \cdot \exp\left(\frac{-E}{R \cdot T}\right) / T \right]^{1/3.5}, \quad (1)$$

where S is the surface area, γ is the specific surface area, E is the activation energy for surface diffusion, and k is a constant. By increasing the temperature after 500°C, surface diffusion is activated and causes to sinter and agglomerate of the ceria grains with each other, therefore it causes the surface area to reduce with the higher rate after 500°C (Fig. 4).

In addition, SEM micrographs show that most of the particles are spherical in shape. Considering that CeO₂ has been synthesized by wet soft chemistry, the uniform size and shape are achieved. Cabus-Llaurado *et al.* [14] synthesized a CeO₂ nanopowder by the precipitation method using CeCl₃·7H₂O and (NH₄)₂CO₃ as precipitant agent and showed, synthesized nanopowders have a layered structure with high surface area. Therefore it can be concluded that the precipitant agent may have strong effect on morphology of the resultant powder. In addition, Chen *et al.* [17] found that calcination atmosphere plays an important role on the size and shape of resulting particles in the precipitation method.

Fig. 6 shows the FTIR spectra of the CeO₂ nanopowder heat-treated at various temperatures for 2h. The absorption broad peak at 3000-3600 cm⁻¹ and absorption peak at around 1620 cm⁻¹ may be attributed to the O-H vibration of water. The two absorption peaks become weaker by increasing the heat-treatment temperature. It should be mentioned that the two remaining absorption peaks in the specimens heat treated at 500°C and 700°C could result from moisture absorption during testing.

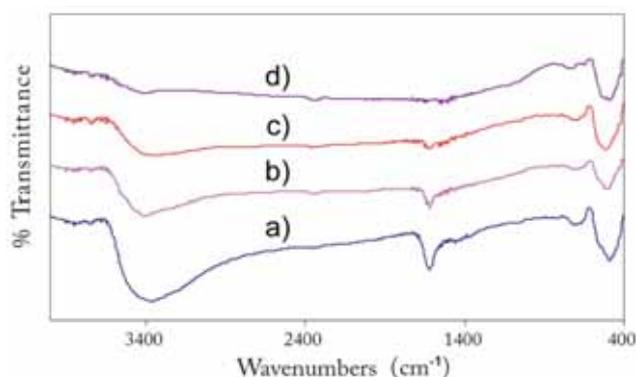


Fig. 6. IR spectra of CeO₂ gel at various temperatures: a) 100°C, b) 300°C, c) 500°C, d) 700°C.

The broad band below 700 cm⁻¹ is due to the envelope of the phonon band of the metal oxide network. Therefore it can be concluded that, by increasing the temperature, hydroxyl groups are decomposed in the gel and only Ce-O bands remain. This transformation is according to following equations:



4. Conclusions

In the present study a CeO₂ nanopowder synthesized by the simple precipitation method. The findings can be summarized as follows:

The crystallite size decreases from 20 to 13.9 nm with increasing the calcination temperature from 100 to 300°C, while increasing temperature more than 300°C causes increasing of crystallite size. The morphology of the prepared powder is sphere-like with a narrow size distribution.

The total weight loss of 10 % appears in the specimens after heat treatment due to removing of volatile components.

The surface area increases up to 300°C and reaches to 41 m²/g, then it decreases when the temperature becomes higher due to increasing the particle size and changing the textural properties of particles. The rate of surface area reduction increases after 500°C, due to sintering and agglomeration of the grains.

References

- [1] Gu L., Meng G.: *Mater. Res. Bull.*, 42, (2007), 1323-1331.
- [2] Angel G. D. Padilla J. M., Cuauhtemoc I., Navarrete J.: *J. Mol. Catal. A*, 281, (2008), 173-178.
- [3] Meyers M.A., Mishra A., Benson D.J.: *Prog. Mater. Sci.*, 51, (2006), 427-556.
- [4] Hassanzadeh-Tabrizi S. A., Taheri-Nassaj E., Sarpoolaky H.: *J. Alloys Compd.*, 456, (2008), 282-285.
- [5] Zhou Y.C., Rahaman M.N.: *J. Mater. Res.*, 8, (1993), 1680-1686.
- [6] Li Y. X., Chen W. F., Zhou X. Z.: *Mater. Lett.*, 59, (2005), 48-52.
- [7] Yu J. C., Zhang L., Lin J.: *Colloid Interface Sci.*, 260, (2003), 240-243.
- [8] Chen W., Li F., Yu J.: *Mater. Lett.*, 60, (2006), 57-62.
- [9] Alifanti M., Baps B., Blangenois N.: *Chem. Mater.* 15, (2003), 395-403.
- [10] Zhou X. D., Huebner W., Anderson H. U.: *Chem. Mater.*, 15, (2003), 378-382.
- [11] Lee J. S., Choi S. C.: *Mater. Lett.*, 59, (2005), 395-398.
- [12] Yoshioka T., Dosaka K., Sato T.: *J. Mater. Sci. Lett.*, 11, (1992), 51-55.
- [13] Li J. G., Ikegami T., Lee J. H., Mori T.: *Acta Mater.*, 49, (2001), 419-426.
- [14] Cabus-Llaurado M. C., Cesteros Y., Medina F., Salagre P., Sueiras J. E.: *Micropor. Mesopor. Mater.*, 100, (2007), 167-172.
- [15] Hasannejad H., Shahrabi T. Sabour-Rouhaghdam A., Aliofkhaezrai M., Saebnoori E.: *Appl. Surf. Sci.*, 254, (2008), 5683-5690.
- [16] German R. M.: *Simulation of Diffusion Controlled Sphere-Sphere Sintering*, Elsevier, Amsterdam, 1977, 18-25.
- [17] Chen H., Chang H.: *Solid State Commun.*, 133, (2005), 593-598.

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