Synthesis of CeO$_2$ nanoparticles by chemical precipitation and the effect of a surfactant on the distribution of particle sizes

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Nano-crystalline particles of CeO$_2$ have been synthesized by a low temperature chemical precipitation method. The precursor materials used in this research were cerium nitrate hexa hydrate (as a basic material), sodium hydroxide (as a precipitator material) and poly ethylene glycol or poly vinyl pyrollidone (as a surfactant material). In a typical experiment, an aqueous solution of the starting material containing Ce^{3+} ions was poured into an alkaline solution with the required percentage of surfactant. The resultant yellow colored precipitate [Ce(OH)$_4$] was washed with water / ethyl alcohol and then heat treated at 600 °C for 2 hours. The prepared CeO$_2$ nanoparticles were characterized by TG-DTA, XRD, FTIR, particle size analysis and SEM. From the results obtained, the effect of surfactants on the particle characteristics of CeO$_2$ is correlated and discussed.

Key words: CeO$_2$, chemical precipitation, surfactants, physical characterization.
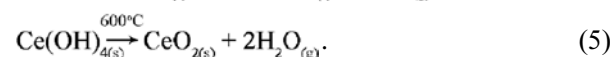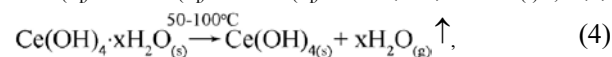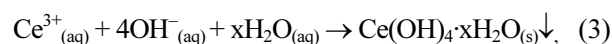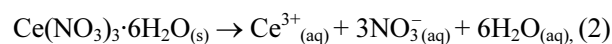
Introduction

It is well recognized that rare-earth oxides have applications in many fields. Among them, cerium oxide or ceria (CeO$_2$) finds enormous applications in catalysts/catalyst supports [1-2], oxygen ion conductors in solid oxide fuel cells [3-5], electrochemical oxygen pumps [6], UV absorbents [7], fluorescent materials [8] and amperometric oxygen ion monitors because of its high oxygen ion conductivity [9]. CeO$_2$ nanoparticles have been prepared by sol-gel processing [10-11], sonochemical synthesis [12], a thermal decomposition process [13], hydrothermal synthesis [14], a polymeric precursor route [15], etc. In many of the above processes, the main objective is the synthesis of phase pure CeO$_2$ based materials for various applications. The objective of this research is the synthesis of CeO$_2$ nanoparticles by the chemical precipitation process in the presence of sodium hydroxide, which is a very simple way and low in cost since the starting materials are few and inexpensive.

Experimental procedure

Preparation of pure CeO$_2$

High purity Ce(NO$_3$)$_3$·6H$_2$O, sodium hydroxide, poly ethylene glycol and poly vinyl pyrollidone were used in the preparation of CeO$_2$ nanoparticles. Initially, 0.01 M of Ce(NO$_3$)$_3$ (4.342 g of Ce(NO$_3$)$_3$ in 100 ml of water) and 0.04 M of sodium hydroxide (1.6 g of sodium hydroxide in 100 ml of water) were prepared. A surfactant namely poly

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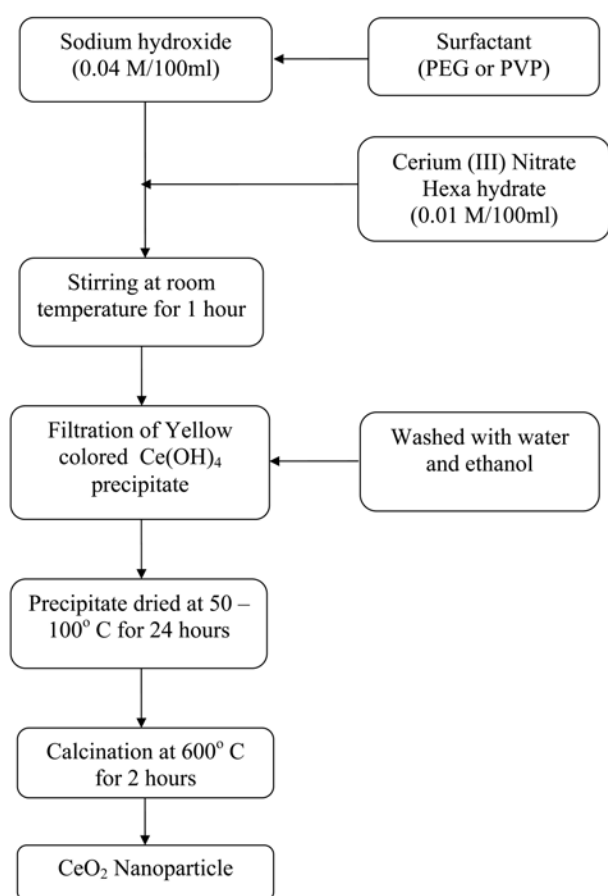 Fax: +091-422-2615615
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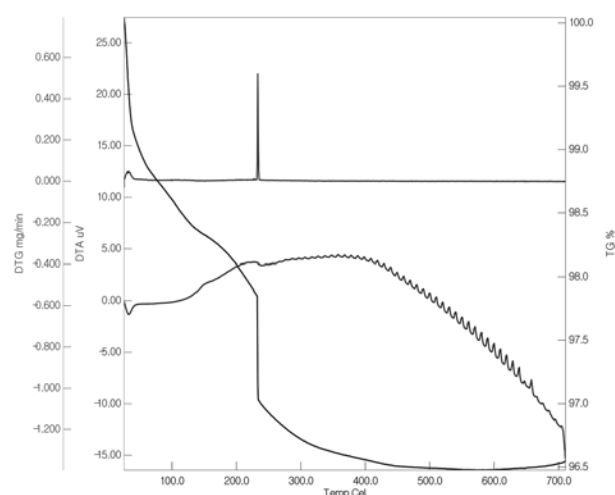ethylene glycol (1 ml or 2 ml PEG) or 10% poly vinyl pyrollidone (1 ml or 2 ml PVP) was added suitably to the sodium hydroxide solution. It has been reported that a surfactant plays a significant role in preventing agglomeration and getting finer particles [16]. Next, a Ce(NO$_3$)$_3$ solution was added drop wise into the solution of alkali and surfactant. They were mixed perfectly by a magnetic stirring apparatus (1000 rpm) at room temperature for 1 hour. The resultant yellow colored precipitate (Ce(OH)$_4$) was filtered, and then washed with deionized water and ethanol for 5-10 times and was dried at 50-100 °C for 24 hours. Then, the calcination was carried out at 300 °C, 450 °C and 600 °C for 2 hours each for four different samples. During calcination at a high temperature, the surfactant was removed and phase pure yellow coloured CeO$_2$ was formed. Fig. 1 shows a schematic illustration of the synthesis method. The main reactions occurring during the experimental procedure can be written briefly as follows:

$$4NaOH_{(s)} \rightarrow 4Na^+_{(aq)} + 4OH^-_{(aq)}, \tag{1}$$

$$Ce(NO_3)_3 \cdot 6H_2O_{(s)} \rightarrow Ce^{3+}_{(aq)} + 3NO^-_{3(aq)} + 6H_2O_{(aq)}, \tag{2}$$

$$Ce^{3+}_{(aq)} + 4OH^-_{(aq)} + xH_2O_{(aq)} \rightarrow Ce(OH)_4 \cdot xH_2O_{(s)}\downarrow, \tag{3}$$

$$Ce(OH)_4 \cdot xH_2O_{(s)} \xrightarrow{50\text{-}100°C} Ce(OH)_{4(s)} + xH_2O_{(g)}\uparrow, \tag{4}$$

$$Ce(OH)_{4(s)} \xrightarrow{600°C} CeO_{2(s)} + 2H_2O_{(g)}. \tag{5}$$

Characterization of the powder

Thermogravimetrical studies of the precursor material were performed with a SI EXSTAR 6000 TG/DTA 6300 instrument between 25 and 700 °C in a nitrogen atmosphere. The powder XRD studies were carried out using a Shimadzu XRD6000 X-ray diffractometer at a scan speed

Fig. 1. Schematic illustration of the synthesis of CeO$_2$ nanoparticles by a chemical precipitation process.

Fig. 2. DTA/TGA spectrum obtained on the precursor material [Ce(OH)$_4$ + 2 .ml PEG]

Fig. 3. DTA/TGA spectrum obtained on the precursor material [Ce(OH)$_4$ + 2 ml 10% PVP].

of 5 degrees minute^{-1} using CuKα radiation. A Bruker IFS 66V FT-IR spectrometer was employed to record the FTIR spectra of CeO$_2$ powder in the range of 4000-400 cm^{-1}. The crystallite sizes of the ceramic powders were calculated by Scherrer's formula. The particle size of the powder was measured using Horiba Laser Scattering Particle Size Analyzer (LA-910) using triple distilled water as a medium. The surface morphology of the particles was studied by means of a JEOL Model JSM-6360 scanning electron microscope.
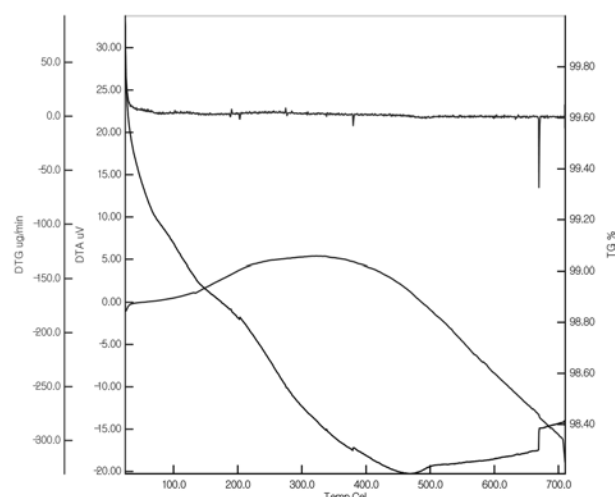
Results and Discussion

TGA/DTA studies

The TGA/DTA spectra obtained with the precursor materials [(Ce(OH)$_4$ + 2 ml PEG) and (Ce(OH)$_4$ + 2 ml 10% PVP)] are given in Figs. 2 & 3. The DTA peaks closely corresponding to the weight changes observed on the TGA curves. From Fig. 2, the total weight loss from 25 to 700 °C was found to be 3.47%. Also, the curve (Fig. 2) shows that the thermal decomposition of the precursor below 500 °C is in two well defined steps. The first step was from 100 to 210 °C which was characterized by an exothermic peak at 210 °C, attributed to the dehydration of hydroxide precursor as reported [17] and the second step was from 210 to

700 °C, attributed to the removal of organics in the form of oxides of carbon [18]. From Fig. 3, the total weight loss from 25 to 500 °C was 1.8%. This reduction in weight was attributed to the removal of water and oxides of carbon and nitrogen as reported in [19]. After 450 °C, it was found that the weight of the sample (0.2%) slowly increased upto 700 °C which may be attributed to the pure phase formation of CeO$_2$ [14]. The regular weight loss / gain in the powder was in accord with the exothermic / endothermic peaks found in the DTA curve (Fig. 3).

XRD studies

The XRD patterns of the CeO$_2$ powder prepared by the chemical precipitation method with surfactants namely 1 ml PEG, 2 ml PEG, 1 ml 10% PVP and 2 ml 10% PVP are shown in Fig. 4(a-d). The XRD patterns of the heat treated powders reveal the formation of well-crystallined single phase materials. No extra peaks corresponding to any other secondary phases are observed. The XRD patterns
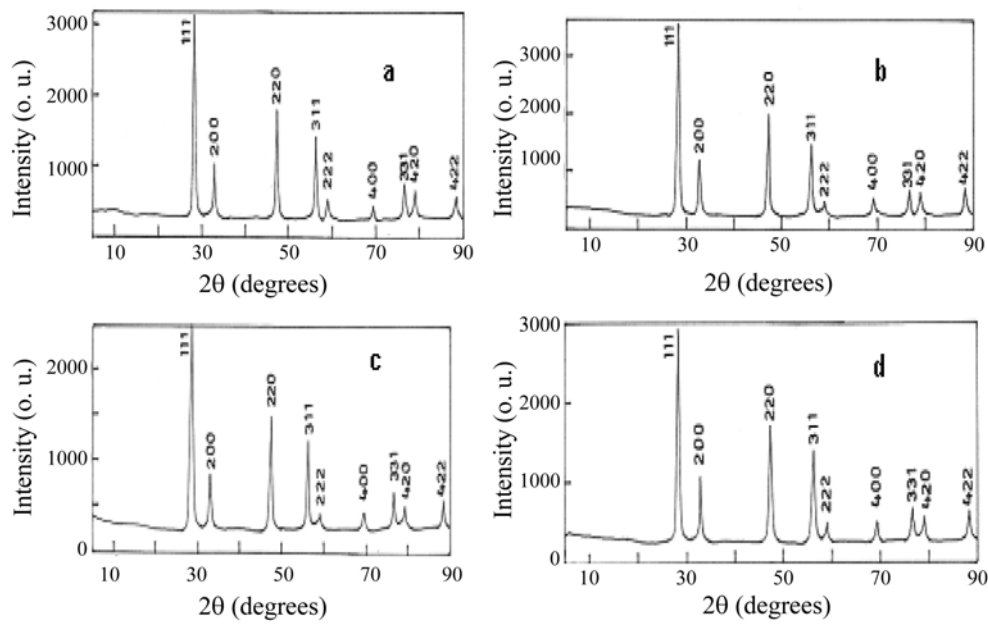
Fig. 4. XRD patterns obtained on calcined CeO_2 powder prepared by the chemical precipitation method with (a) 1 ml PEG , (b) 2 ml PEG (b), (c) 1 ml 10% PVP (d) 2 ml 10% PVP.

obtained of the CeO_2 were compared with the standard data for CeO_2 (JCPDS card No. 34-0394). The lattice parameter (a) was calculated by the following lattice parameter formula:

$$a = \frac{d}{(h^2 + k^2 + l^2)^{1/2}} \qquad (6)$$

Where 'a' refers to the CeO_2 FCC lattice parameter, and h, k, l are the crystalline face indexes while 'd' is the crystalline face spacing. We observed that the all CeO_2 powders exhibited cubic (f.c.) cell geometry as reported in [20]. The unit cell volumes calculated for the ceria particles remained uniform. The theoretical density, T_d is calculated using the equation [21]:

$$T_d = ZM_c/V_cN_A \qquad (7)$$

where 'Z' is the number of chemical species in the unit cell, 'M_c' is the molar mass of a single chemical species corresponding to the chemical formula ($gmol^{-1}$), 'V_c' is the unit cell volume ($Å^3$) and 'N_A' is Avogadro's number (6.022×10^{23} mol^{-1}). These values were also agreed well with the reported data.

The broadening of X-ray diffraction peaks provides a convenient method for measuring small particle sizes. As the crystallite size decreases the width of the diffraction peak (or the size of the diffraction spot) increases. An approximate expression for the peak broadening is given by Scherrer's equation [22]:

$$x = z\frac{C\lambda}{\beta cos\theta} \qquad (8)$$

where 'x' is the crystallite size, 'C' is a numerical constant ($\sim$0.9), 'λ' is the wavelength of X-rays (for CuKα radiation, $\lambda = 1.5418$ Å), 'β' is the effective broadening taken as a full width at half maximum (FWHM) (in radians), 'θ' is the diffraction angle for the peak. The crystallite size of the particles, determined with Scherrer's formula, was found to be in the range of 11-23 nm . It was reported that the average crystallite size of pure CeO_2 prepared by thermal decomposition of cerous nitrate was found to be in the range of 18.8-22.1 nm [23]. Therefore, our values are also in accordance with the reported data. The crystallographic parameters obtained on the CeO_2 powder are given in Table 1.

Table 1. XRD data obtained on CeO_2 powder

| Sample	Surfactant	Crystal structure	Unit Cell parameter 'a' (Å)	Unit cell volume ($Å^3$)	Crystallite size (nm)	Theoretical density (g/cc)
CeO_2 (JCPDS No. 34-0394)	--	Cubic (F.C.)	5.4113	158.4581	--	7.22
CeO_2	PEG - 1 ml	Cubic (F.C.)	5.4308	160.1738	11.7928	7.1365
CeO_2	PEG - 2 ml	Cubic (F.C.)	5.4351	160.5545	15.7228	7.1196
CeO_2	10% PVP - 1 ml	Cubic (F.C.)	5.4380	160.8117	15.7219	7.1082
CeO_2	10% PVP - 2 ml	Cubic (F.C.)	5.4389	160.8915	23.58208	7.1047

FTIR studies

Figs. 5 and 6 show the FTIR spectra obtained on CeO_2 powder prepared by the chemical precipitation method with surfactants namely 2 ml PEG and 2 ml 10% PVP. FTIR measurements were done using the KBr method at RT. The spectra of each sample shows an absorption band at about 1380 cm^{-1} which is the characteristic vibration mode of CeO_2 [24]. The samples showed a peak at 2400 cm^{-1} which is due to the presence of dissolved or atmospheric CO_2 in the sample [25]. The peak which appeared at 3400 cm^{-1} is related to the O-H stretching vibration of H_2O in the sample [26]. The rest of the peaks were also similar with each other which indicates the formation of pure phase of CeO_2.

Particle size measurements

The particle size distribution of the CeO_2 powder prepared by the chemical precipitation method with surfactants namely 1 ml PEG, 2 ml PEG, 1 ml 10% PVP and 2 ml 10% PVP
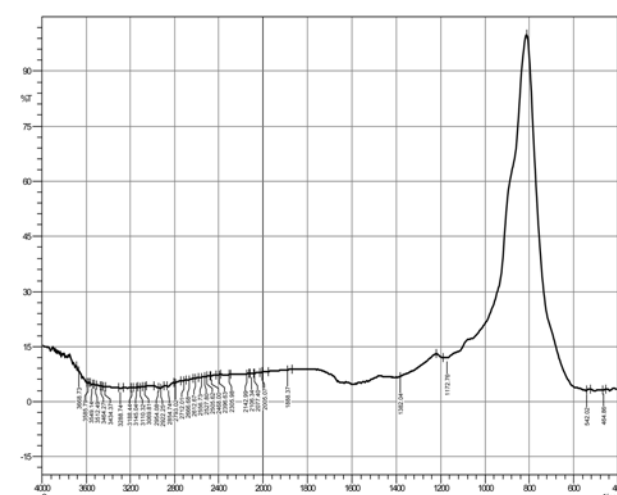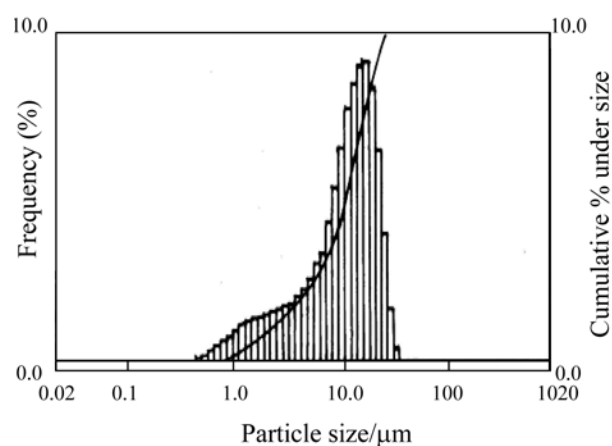
Fig. 5. FTIR spectrum obtained on calcined CeO_2 powder prepared by the chemical precipitation method (with 2 ml PEG).
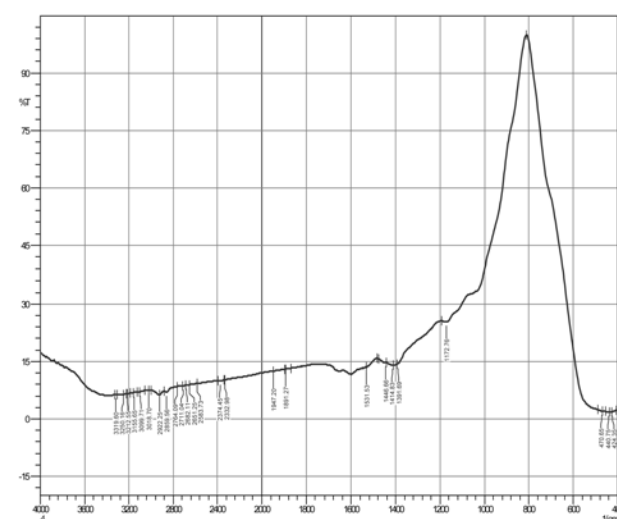
Fig. 6. FTIR spectrum obtained on calcined CeO_2 powder prepared by the chemical precipitation method (with 2 ml 10% PVP).

are shown in Figs. 7, 8, 9 and 10. The percentage frequency is on the left hand side of the plot indicated by the line. The % on the right hand side of the plot corresponds to the particle distribution (histogram) indicated by the bars. The particle characteristics of CeO_2 from particle size

Fig. 7. Particle size pattern obtained on calcined CeO_2 powder prepared by chemical precipitation with 1 ml PEG.
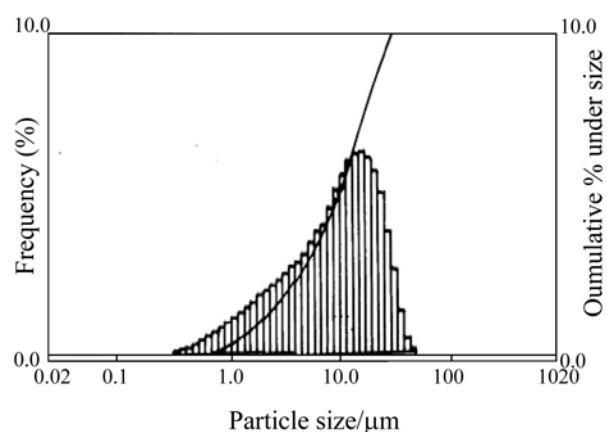
Fig. 8. Particle size pattern obtained on calcined CeO_2 powder prepared by chemical precipitation with 2 ml PEG.
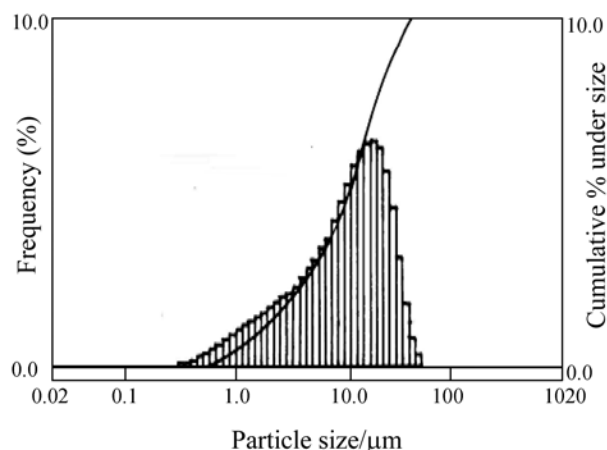
Fig. 9. Particle size pattern obtained on calcined CeO_2 powder prepared by chemical precipitation with 10% 1 ml PVP.

analysis are presented in Table 2, where the median particle diameter represents the particle diameter equal to 50% of the cumulative distribution and the mean particle diameter represents the arithmetically averaged value of the frequency distribution. From the curve (Fig. 7), it was observed that the particle size of the powder was in the range of 0.510-39.23 µm. Also, it was found that 53% of particles are less than 13 µm in size. From the curve (Fig. 8), it was found that the particle size of the powder was in the range of 0.339-51.47 µm. More than 60% of particles are less than 13 µm in size. From the curve (Fig. 9), it was found that the particles are present between 0.339-58.95 µm. Also, it was found that more than 50 % particles are less than 11 µm in size. From the curve (Fig. 10), it was found that the particles are present between 0.339-59.95 µm. Also, it was clearly found that 70% of particles are very much less in particle size, i.e., 17.38 µm. From the particle characteristics, it was concluded that all particles are having micron meter size particles also along with nano sized particles.

### Scanning electron microscopic studies

SEM images of the CeO_2 powder prepared by the chemical precipitation method with surfactants namely 1 ml PEG, 2 ml PEG, 1 ml 10% PVP and 2 ml 10% PVP are shown in Figs. 11, 12, 13 and 14. From the SEM images, it was found that all the CeO_2 particles are porous. The pore size of the powder is in the range 10-50 µm. Also, the samples were quite agglomerated. Fig. 11 exhibits a flake-like morphology and the grain sizes were found to be between 42-56 nm. Fig. 12 has a layer-like morphology with grain sizes between 38-50 nm. Fig. 13 has a porous

Table 2. Particulate properties obtained on CeO_2 powder

| Sample	Surfactant	Mean particle diameter (µm)	Median particle diameter (µm)
CeO_2	PEG - 1 ml	12.8	12.4
CeO_2	PEG - 2 ml	9.9	11.9
CeO_2	10% PVP - 1 ml	11.0	12.9
CeO_2	10% PVP - 2 ml	11.0	12.9
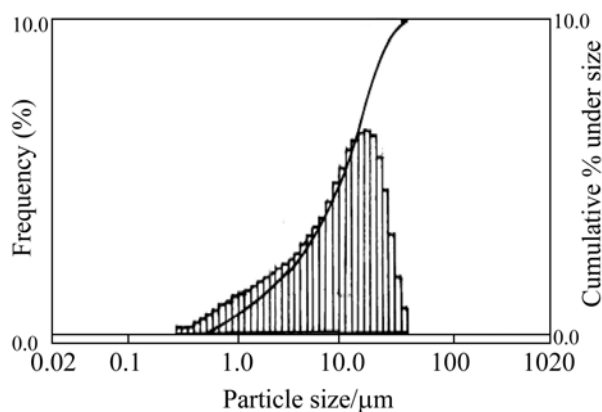
Fig. 10. Particle size pattern obtained on calcined CeO_2 powder prepared by chemical precipitation with 10% 2 ml PVP.
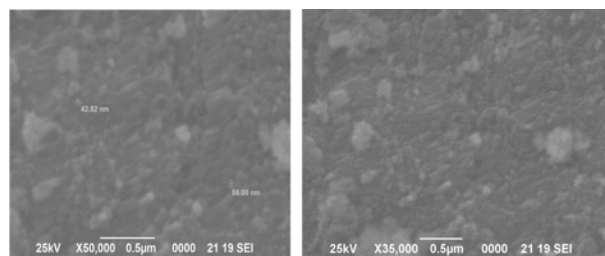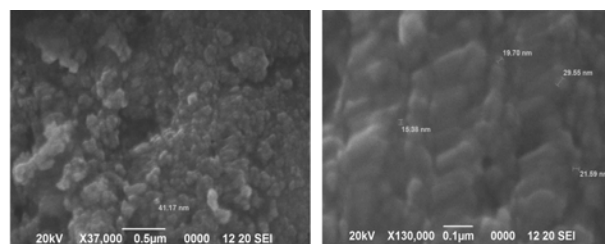

Fig. 11. SEM image obtained on calcined CeO_2 powder prepared by chemical precipitation with 1 ml PEG.
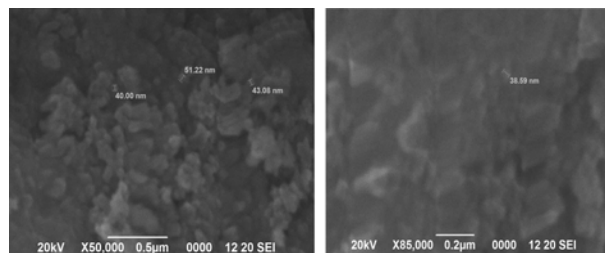
Fig. 12. SEM image obtained on calcined CeO_2 powder prepared by chemical precipitation with 2 ml PEG.
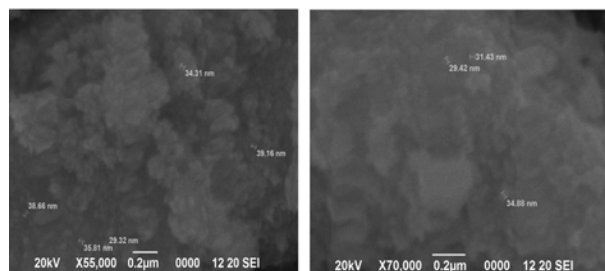
Fig. 13. SEM image obtained on calcined CeO_2 powder prepared by chemical precipitation with 10% 1 ml PVP.

Fig. 14. SEM image obtained on calcined CeO_2 powder prepared by chemical precipitation with 10% 2 ml PVP.

structure and the grain sizes were less than 35 nm. Fig. 14 demonstrates a fine circular morphology with a small grain size. The grain size was less than 30 nm. From the SEM data, it was seen that the CeO_2 particles have very fine particle characteristics with 2 ml of 10% PVP.

Conclusions

Chemical precipitation of CeO_2 nano particles using cerium nitrate hexa hydrate, sodium hydroxide and surfactants (PEG and PVP) have been considered. From the TGA/DTA results, it is clear that the all organics present

in the precursor were released around 500 °C. The XRD data obtained on CeO$_2$ powder is in good agreement with the standard reported data. From the FTIR data, it is shown that all samples exhibited characteristic peaks for CeO$_2$. The particulate properties obtained on CeO$_2$ powder suggest that the particles are present from nano to micrometer size. The SEM images exhibit that 2 ml 10% PVP (surfactant) serves better when compared with the other compositions of surfactant in reducing the particle size of CeO$_2$. Also, it serves as a good surfactant in controlling the agglomeration of CeO$_2$ particles during the calcination process.

Acknowledgement

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