Effect of cobalt doping on structural, optical and redox properties cerium oxide nanoparticles

Anees A. Ansari, J. Labis, M. Alam, Shahid M. Ramay, N. Ahmad & Asif Mahmood

To cite this article: Anees A. Ansari, J. Labis, M. Alam, Shahid M. Ramay, N. Ahmad & Asif Mahmood (2016) Effect of cobalt doping on structural, optical and redox properties cerium oxide nanoparticles, Phase Transitions, 89:3, 261-272, DOI: 10.1080/01411594.2015.1116532

To link to this article: https://doi.org/10.1080/01411594.2015.1116532

Published online: 11 Dec 2015.

Submit your article to this journal

Article views: 391

View related articles

View Crossmark data

Citing articles: 10 View citing articles
Effect of cobalt doping on structural, optical and redox properties of cerium oxide nanoparticles

Anees A. Ansari a*, J. Labisa, M. Alam b, Shahid M. Ramay c, N. Ahmad b and Asif Mahmood d

aKing Abdullah Institute for Nanotechnology, King Saud University, Riyadh, Saudi Arabia; bResearch Center, College of Sciences, King Saud University, Riyadh, Saudi Arabia; cDepartment of Physics, King Saud University, Riyadh, Saudi Arabia; dDepartment of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia

(Received 13 May 2015; accepted 2 November 2015)

Cobalt-doped ceria nanoparticles were synthesized using the polyol method under coprecipitation hydrolysis. The structural, morphological, optical and redox properties were observed to investigate the influence of different concentration of cobalt ion doping on the prepared CeO2 nanomaterials in terms of X-ray diffraction, field-emission transmission electron microscopy, thermogravimetric analysis, Fourier-transform infrared spectroscopy, UV/vis absorption spectroscopy and temperature program reduction techniques. The optical band gap energy was calculated from the optical absorption spectra for doped ceria nanoparticles, which have been found to be 2.68, 2.77, and 2.82 eV for the 2, 4, and 7 mol% Co ion-doped CeO2 nanoparticles, respectively. As observed, the band gap energies increases as the doping Co ion concentrations increased, which could be due to significant increased oxygen vacancies with Co doping. The synergistic interaction between Co and CeO2 was the main factor responsible for high catalytic activity of cobalt-doped CeO2 model catalysts.

Keywords: structural ceramic materials; chemical synthesis; X-ray diffraction; redox properties

1. Introduction

In recent years, research interest on CeO2 and doped CeO2 nanoparticles are increasing, due to that possession, many attractive properties make them highly promising materials for diverse applications, such as solid electrolytes or anode materials in solid oxide fuel cells, automotive three-way catalysts, a water-gas shift catalyst, ultraviolet absorbers, oxygen sensors, and catalysts for dehydrogenation of higher alcohols.[1–10] However, the most relevant use of CeO2-based compounds is in automotive pollution control, as promotors of the so-called three-way catalyst.[1,6] Almost all vehicles nowadays are equipped with catalytic converters, which invariably contain some CeO2-containing oxide as catalyst promoter. The wide use of these systems as catalyst components promoted renewed interest with regards to these materials in the form of nano-sized, high surface area powders. The possibility of producing redox nanomaterials with tunable redox capability to activate simple reactants has recently been explored.[1,3–5] Nano-structured materials which provide novel properties appear to be a cutting edge frontier in designing catalysts and catalyst promoters for specific catalytic reactions.[3–8]

*Corresponding author. Email: amustaqueemahmad@ksu.edu.sa

© 2015 Taylor & Francis
Nowadays, it has been a continuous search for metal ions doping that promote the ionic conductivity of CeO$_2$ nanoparticles at moderate temperature. A range of potential dopant materials has been employed to promote the ionic conductivity of the synthesized CeO$_2$ nanopowder.[1–5] Radovic et al. employed the hydrothermal method for the preparation of iron-doped CeO$_2$ nanoparticles to investigate the effect of iron doping on optical properties of nanomaterial.[11] Some researchers have shown that iron-containing nanocrystalline CeO$_2$ is an active and stable catalyst in low- and high-temperature redox reactions.[12,13] Copper-doped ceria has been employed to enhance the catalytic activity over the wide range of temperature.[14] Some rare earth metal ions have been doped in CeO$_2$ lattice to enhance the ionic conductivity of the materials and investigate their applications for solid oxide fuel cells.[3,4,15] Fu et al. doped low contents of Au in CeO$_2$ nanoparticles to enhance the catalytic activity of the materials.[16] Some other groups have synthesized noble metal-supported CeO$_2$ for their applications in the three-way automotive catalyst that enhance low-temperature water gas shift reaction.[5,17] The reducibility and catalytic activity of CeO$_2$ was significantly enhanced by the presence of a small amount of transition metals, outside the platinum group. Platinum was the first metal demonstrated to have a considerable effect on CeO$_2$ reducibility.[5] However, the cost of noble metal ions are high and is the main drawback for their use in developing catalytic materials. In this study, we considered cobalt ion as an ionic conductivity promoter because it is the neighborhood of the above-mentioned two elements. Moreover, based on the effect of severely under sized dopant ions reported by Chen and Chen [18], the Co$^{2+}$ ion may have the tendency to enhance grain boundary mobility of CeO$_2$, since its ionic size is much smaller than that of the matrix ion (i.e. Ce$^{4+}$). To our knowledge, there are only a very few literature reports concerning the redox behavior of CeO$_2$ with Co as an additive.[19–21] Furthermore, Co was reported as an effective dopant for the densification of SnO$_2$.[22,23] Varela et al.[22] and Cerri et al.[23] reported that the addition of 0.5–2 mol% CoO into SnO$_2$ promotes the densification of this oxide up to ~99.0% of the theoretical density; and the sintering of Co-doped SnO$_2$ seems to be controlled by solid state diffusion because of the absence of experimental evidence for an eutectic liquid in this system. They deduced that Co$^{2+}$ ions incorporating into SnO$_2$ crystallites have acted as an acceptor leading to the addition of oxygen vacancies into SnO$_2$, thus enhancing the densification rate of this oxide.

In this paper, we report the synthesis of different concentrations of Co-doped CeO$_2$ nanoparticles by the complexing hydrothermal co-precipitation method. The synthesized doped CeO$_2$ nanoparticles were analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), field-emission transmission electron microscopy (FE-TEM), energy dispersive X-ray analysis (EDX), UV/vis absorption spectra, optical band gap energy, Fourier transform infrared (FTIR) spectroscopy and temperature-programmed reduction (TPR) measurements. In addition, the morphological structure, optical properties, and thermal stability of the synthesized nanophosphors were also systematically studied in this article.

2. Experimental

2.1. Materials and methods

Cerium nitrate (99.99%, BDH Chemicals Ltd, England), cobalt nitrate (E-Merck, Germany) ethylene glycol, C$_2$H$_5$OH, and NH$_4$OH were used as starting materials without
any further purification. The ultrapure deionized water was used for the preparation of solutions. The ultrapure deionized water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). All other chemicals used were of reagent grade.

2.2. Preparation of Co ion-doped cerium oxide nanoparticles

In a typical reaction, 0.2M Ce(NO$_3$)$_3$·6H$_2$O (0.98, 0.96, and 0.93 mol%) was dissolved in 50 ml ethylene glycol and heated on a hot plate up to 80 °C. Separately, 0.02M cobalt nitrate (0.02, 0.04, and 0.07 mol%) dissolved in ethylene glycol was added drop-wise in the foregoing reaction and the whole solution mixture was kept on a hot plate with magnetic stirring at 80 °C to obtain a homogenous mixture. Later, homogenously mixed solution was transferred in a 250 ml flask fitted with reflux condenser and hydrolyzed for 24 h. An amount of ammonia was added to the hydrolyzed solution and the precipitate was obtained. The obtained gray-colored precipitate was centrifuged and washed several times with distilled water to remove the excess amount of ammonium and nitrate ions, the obtained product was dried at 100 °C. The prepared samples were annealed at 400 °C in air for 2 h. We examined the systematic changes in the color of the cerium hydroxide precipitate. The color of the prepared cerium hydroxide precipitate was changed gradually from gray to yellow after being exposed to air. This may be due to the oxidation of peroxide Ce(OH)$_3$OOH to Ce(OH)$_4$ by oxygen. This procedure was repeated for synthesis and purification of different Co-doped CeO$_2$ concentrations.

2.3. Characterization

The crystallinity of the powder samples were examined by XRD at room temperature with the use of Rigaku-Dmax 2500 diffractometer equipped with Cu K$_\alpha$ (λ = 1.54056 Å) radiations as the X-ray source. TGA was performed with TGA/DTA, Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland. The size and morphology of the samples were inspected using a FE-TEM equipped with the EDX (FETEM, JEM-2100F, JEOL, Japan) operated at an accelerating voltage of 200 kV. EDX analysis was used to confirm the presence of the elements. The samples for TEM were prepared by depositing a drop of the colloidal ethanol solution of the powder sample onto a carbon-coated copper grid. The FTIR spectra were recorded on a Perkin-Elmer 580B IR spectrometer using a KBr pellet technique in the range 4000–400 cm$^{-1}$. The UV/vis absorption spectra were measured in the Perkin-Elmer Lambda-40 spectrophotometer in the range 200–600 nm, with the sample contained in 1 cm$^3$ stoppered quartz cell of 1 cm path length. TPR by H$_2$ (H$_2$-TPR) was performed with the Thermo-Finnigan TPDRO 1100 instrument with a thermal conductivity detector. Before detection, the gas was purified by a solid trap containing CaO + NaOH materials in order to remove the H$_2$O and CO$_2$. The quartz tube reactor was loaded with 50 mg sample in powder form and heated from room temperature to 900 °C in 5% H$_2$/N$_2$ mixture with a flow rate of 20 ml min$^{-1}$. By replacing the 5% H$_2$/N$_2$ with 5% CO/He, the CO-TPR tests were also carried out. After the sample was reduced by 5% H$_2$/N$_2$ from room temperature to 500 °C and held for 10 min, temperature-programmed oxidation tests were performed from room temperature into 900 °C in 6% O$_2$/He flow at a rate of 20 ml min$^{-1}$. All measurements were performed at room temperature.
3. Results and discussion

3.1. Crystallographic morphology

The crystal structure and phase purity of the Co-doped CeO$_2$ nanostructures in Figure 1 are analyzed by XRD. The principal reflections as seen in the diffraction patterns can be ascribed to fluorite CeO$_2$. All reflection peaks correspond to the (111), (200), (220), (311), and (222) planes, which are well indexed and identified to the pure CeO$_2$ nano-product (space group: $Fm\bar{3}m$), has the cubic fluorite phase (JCPDS card 12-0797). The broad and sharp reflection peaks suggest that the prepared products are well crystallized and very small in sizes. The intensities and positions of the diffraction peaks are in good agreement with the literature data. No Co$_3$O$_4$ and other salts can be observed by XRD over the entire doping range. The absence of impurity peaks indicates good incorporation of Co into the lattice sites of CeO$_2$ or the amount is too small to be detected by XRD. Furthermore, the structure of the as-generated Co-doped CeO$_2$ could have remained the same upon doping. This means the formation of homogeneous Co-Ce-O solid solutions.[27,28] The calculated lattice parameter for the as-prepared 2%, 4%, and 7% Co-doped CeO$_2$ products are found to be (1) 5.4089 Å, (2) 5.4086 Å, (3) 5.407 Å, respectively, which are slightly lower than its bulk counterpart (5.411 Å). The calculated average grain size as estimated from the Debye–Scherrer formula using the half width of diffraction peak of (111) plane, 15.4 nm for 2, 13.39 nm for 4, and 12.6 nm for 7 mol% Co-doped CeO$_2$. Yet, the gradual decrease in the peak intensity and the slight increase in the peak width with the introduction of Co indicate that the grain size is minimal after Co doped into CeO$_2$ lattice. On the other hand, the diffraction peaks of Co-Ce-O shift slightly to higher angle by comparison with pure sample, resulting from the CeO$_2$ lattice contraction and the generation of the lattice distortion in the doped nanoparticles, which is attributed to the substitution of the smaller divalent Co ion$[r(Co^{2+}) = 0.65 \text{ nm}]$ for Ce$^{4+} [r(Ce^{4+}) = 0.97 \text{ nm}].[27,29]$ It is observed that CeO$_2$ and Co-doped CeO$_2$ nanoparticles experience considerable lattice deformation, which is in good agreement with earlier reports.[27,19–21] Those reports indicated that doping caused a change in the Ce–O bond length (lattice distortion) and on the overall lattice parameter.[29–33]
The size and morphology of the prepared Co-doped CeO$_2$ nanoparticles were analyzed by the TEM images. Figure 2 clearly shows the typical image of Co-doped CeO$_2$ nanoparticles. TEM image reveals that hydrothermal-co-precipitated nanoproducts consist of well crystalline and highly agglomerated nanoparticles in spherical morphology with sizes ranging from 12.6 to 15.4 nm. The results were in good agreement with the XRD data. EDX analysis confirmed the formation of single-phase Co-doped CeO$_2$ nanoparticles (Figure 3). The presence of Co in the 2%, 4%, and 7% Co-doped CeO$_2$ nanoparticles was indicated by the EDX spectrum. No Co phase was detected by the XRD, confirming that Co was doped into the CeO$_2$ lattice. An increase in the Co dopant concentration enhances the presence of Co (weight %) as confirmed by the EDX spectrum.

3.2. Thermogravimetric analysis

TGA was performed to determine the thermal stability and desorption temperature of various species between the temperature range of $\sim$25 °C–800 °C under nitrogen atmosphere at a heating rate of 10 °C/min (Figure 4). The thermograms of Co-doped CeO$_2$ nanoparticles are all similar in shape and show degradation of their constituents into two decomposition steps. There is a $\sim$2%–3.5% weight loss up to 200 °C (Figure 4(a) and
Figure 3. EDX analysis of the as-prepared cobalt-doped cerium oxide nanoparticles.

Figure 4. Thermo-gravimetric analysis of cobalt-doped cerium oxide nanoparticles.
4(b)), whereas nanoparticles (Figure 4(c)) shows 3.5% weight loss. This is slightly higher than that of Figure 4(a) and 4(b) doped nanoparticles. It mainly resulted from the removal of chemisorbed water and the release of organic residues that are trapped inside the pores. The second stage decomposition is observed between 200 °C and 800 °C (weight loss 4%–4.5%), which is likely due to the burning and elimination of surface OH groups. It is known that there are two types of surface OH groups, terminal Ce–OH and bridge Ce–(OH)–Ce.[34] Dissociation temperature of these surface OH groups differs from each other depending upon the chemical surroundings. Thus, the decrease in weight occurs in a rather wide range of temperature. No peaks corresponding to further crystallization are found on the DTA curve, indicating that the samples are crystalline. This is further confirmed by XRD. After heating at 800 °C, no obvious weight loss is observed.

3.3. Optical properties

Figure 5 shows the FTIR spectra of prepared Co-doped CeO₂ nanoparticles. An infrared broad band along with weak intensity bands located at ~3433, 1623, 1331, and 1066 cm⁻¹ are observed, which can be ascribed to ν(O–H) stretching vibration and δ(OH) bending vibrations, respectively, of the physically adsorbed water molecules on the nanoparticle surface (Figure 5(a)–5(c)).[34,35] The residual water or hydroxyl groups are also detected from the TGA analysis. An intense band located at around 500–400 cm⁻¹ is attributed to Ce–O stretching vibration modes and thus reveal the formation of the Ce–O–Co network within the nanoparticles.[35]

Figure 6 shows the optical absorption spectra of the Co-doped CeO₂ nanoparticles. A strong absorption band emerges at the UV range of 270–400 nm, which originate from the charge transfer between the O²⁻ 2p and Ce 4f states.[34–36] The spectral profile indicates a charge-transfer transition of Ce⁴⁺ overlaps with the 4f¹→5d¹ transition of Ce³⁺. No absorption is detected above 500 nm in wavelength. It is evident from the spectra that the adsorption edge shifted toward longer wavelength (red-shift) with increasing Co-dopant concentration that is contrast with the bulk CeO₂ powder data.

![Figure 5. FTIR spectra of cobalt-doped cerium oxide nanoparticles.](image_url)
The plots of $a(h\nu)^2$ vs. photon energy of different Co ion-doped CeO$_2$ nanoparticles are shown in Figure 7. The optical band gap value can be determined by fitting the absorption data to the direct transition equation by extrapolating the linear portions of the curves to zero absorption

$$a(h\nu) = E_D(h\nu - E_g)^{1/2},$$

where $a$ is the optical absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the direct band gap, and $E_D$ is a constant.[28,36] The correlated band gap energies are 2.68, 2.77, and 2.82 eV for the 2, 4, and 7 mol% Co ion-doped CeO$_2$ nanoparticles, respectively. Figure 7 shows that an increase in the dopant concentration results in an increase of the optical band gap energy. The lowest band gap value is seen in the case of the 2 mol% Co-doped CeO$_2$ nanoparticles. The reason for the enhanced performance in the case of doped CeO$_2$ is due to the fact that the addition of Co ions results in the formation of interstitial...
sites, which in turn create new energy levels (impurity energy levels) between the valence and conduction bands.[28,36] The impurity energy levels allow for intrinsic band gap excitation under the visible light region. This implies that the higher energy state of 3d-electrons from Co-cation dopants can be excited to the conduction band of CeO$_2$.[37] thereby enhancing its catalytic performance. Similar values are within the range reported in the literature.[38] Saranya et al. observed Co-doped CeO$_2$ (2.84 eV) compared with that of pure CeO$_2$ (3.13 eV) nanoparticle.[39] Yue and Zhang reported that doping CeO$_2$ with Co could reduce the band gap of CeO$_2$ more effectively than do other transition-metal dopants.[40] Masui et al. reported the band gaps of 4.1 and 2.6 nm CeO$_2$ nanoparticle prepared using reverse micelles to be 3.38 and 3.44 eV, respectively.[41] Doping with Co ions creates oxygen vacancies and favors the formation of Ce$^{3+}$ from Ce$^{4+}$. This increases the amount of Ce$^{3+}$ states, resulting in the formation of localized energy states that are closer to the conduction band[42] thereby decreasing the band gap.

3.4. TPR studies
The H$_2$-TPR characterization is performed to investigate reducibility features of the as-prepared Co ion-doped CeO$_2$ catalysts, and the results are shown in Figure 8. In our experimental results, we observed two reduction peaks in pure CeO$_2$, one at about 122 °C and the other at 402 °C, which attributed to the reduction of surface capping oxygen and bulk oxygen species, respectively.[43] In our experimental case, the reduction temperatures are much lower than the reported temperature of ~500 °C and ~800 °C.[44] As the Co metal ion introduce into the CeO$_2$ lattice, the observed reduction peaks shift to lower temperature. It indicates that Co ion greatly promotes the surface reduction, as observed the sharp reduction peak at 305 °C in 2 mol% Co-doped CeO$_2$ nanoparticles, possibly due to the hydrogen spillover effect. Similarly, the degree of promotion increases as the doping concentrations of Co ion increases. Concerning the reduction pattern of CeO$_2$, two main reduction peaks can be observed, one at 112 °C and the other at 305 °C, due to the two-step reduction of Co$_3$O$_4$ involving CoO intermediate.[43] The second peak observed at 274 °C for the 7 mol% Co-doped CeO$_2$ is much lower as compared to pure CeO$_2$, which is at 403 °C. It assumes that this peak consumes much more H$_2$ for the

![Figure 8. H$_2$-TPR profiles of cobalt-doped cerium oxide nanoparticles.](image-url)
reduction on the Co-doped CeO₂ catalyst compared to pure CeO₂ nanoparticles. It clearly indicates that Co ions interact with the ceria nanoparticles within the surface lattice and these surface Co ions promote the reduction of the CeO₂ surface. However, the H₂ consumption of the 7 mol% Co-doped CeO₂ is lower than that of 4 mol% Co-doped CeO₂. This is probably because the dispersion of Co particles on the surface partly blocks the reduction of the ceria. The broad peak associated with the reduction of the bulk CeO₂ is significantly shifted for the 7 mol% Co-doped sample and the 4 mol% Co-doped sample. However, the peak area for three samples are different and show that the Co doping have significant influence on the reduction of bulk CeO₂. Comparing the relative intensity of the second peak for three samples, it is quite clear that the amount of reducible Co is higher in the 7 mol% Co-doped CeO₂ sample than in the 2 mol% Co-doped CeO₂ nanoparticles. It is obvious that the Ce₀.₉₃Co₀.₀₇O₂ nanoparticles show high redox properties at low temperature among Co-doped CeO₂ nanoparticles with various cobalt contents. As we know, CeO₂ can uptake and release oxygen via the transformation between Ce³⁺ and Ce⁴⁺. As we discussed previously, after Co doping, the Ce₁₋ₓCoₓO₂ solid solution might form partially. Therefore, Co-doped CeO₂ nanoparticles can easily uptake and release oxygen via the transition of Co²⁺/Co³⁺ and Ce³⁺/Ce⁴⁺, and at the meantime, surface oxygen can participate in CO oxidation. So, beyond doubt, the catalytic redox activity of Co-doped CeO₂ nanoparticles is very important for the CO oxidation. Consequently, the Ce₀.₉₃Co₀.₀₇O₂ nanoparticles may exhibit an excellent catalytic performance at the lowest temperature as a result of the highest redox properties, which will also be confirmed by the catalytic activity evaluation.[45,46] This is further consistent with the EDX results showing that Co is distributed uniformly within the lattice of the Co-doped sample.

4. Conclusions
Nanocrystalline cobalt ion-doped CeO₂ particles with an average size 12.6–15.4 nm and narrow size distribution have been directly synthesized by a polyol-assisted co-precipitation process, which is confirmed by powder XRD, EDX, and optical absorption studies. It was found by XRD and optical absorption that an increase doping concentration of Co alters the crystallinity of the materials due to an increase in the oxygen vacancies inside the CeO₂ lattice. The band gap energies were also affected after increasing the doping contents of Co ion in CeO₂ lattice. TPR measurements revealed that enhanced doping concentration of Co ion enhanced redox properties and high doping content in CeO₂ promote to reduce at low temperature due to the doping effect. The simple preparation approach holds promises in the future large-scale synthesis of cobalt-doped CeO₂ nanoparticles for applications in solid electrolytes, electrochemical biosensor, and electrochromic devices.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
The authors extend their sincere appreciations to the Deanship of Scientific Research at King Saud University for its funding this Prolific Research group (PRG-1436-26).
References


