Nanosized Unsupported and Alumina-Supported Ceria-Zirconia and Ceria-Terbium Solid Solutions for CO Oxidation

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Abstract: Ceria-zirconia (CZ) and ceria-terbium (CT) and alumina-supported ceria-zirconia (CZA) and ceria-terbium (CTA) solid solutions were synthesized by coprecipitation and deposition precipitation methods, respectively. Structural characteristics and catalytic activity of the synthesized samples have been investigated using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), and Brunauer-Emmett-Teller (BET) surface area measurements. To evaluate the catalytic properties, total oxygen storage capacity and CO oxidation activity measurements were carried out. The XRD analyses revealed the formation of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ phase for CZ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ and $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ phases for CZA samples, respectively. While the formation of only $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-x}$ phase was noted for both CT and CTA samples. All the supported and unsupported samples adopted a fluorite-type structure and exhibited cell parameters with respect to Vegard's rule. The HRTEM results indicated well-dispersed particles of the size around 5 nm. The RS measurements suggested the presence of oxygen vacancies due to defective structure formation. The XPS studies revealed the presence of cerium in both Ce^{4+} and Ce^{3+} oxidation states in different proportions. It was found that CO oxidation for CTA occurs at very much lower temperature than CT, CZ, and CZA samples. Details of these findings by correlating with the structural characterization studies are consolidated.

Key words: ceria; zirconia; terbium; alumina-support; deposition coprecipitation; CO oxidation

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Emissions from vehicles and industrial plants are of great concern due to the damages they have forced on the environment, such as acid rain and photochemical smog [1]. Over the past several years, CeO_2 has come under intense scrutiny as a promoter in important industrial or environmentally friendly reactions, for example automotive exhaust gas purification, methane reforming processes, and water-gas shift reaction, etc. due to its structure and divergent properties [2]. In CeO_2 with fluorite type cubic structure, the $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ redox cycle is facile and oxygen mobility in the crystallographic structure is prompt. However, the major problem associated with pure CeO_2 is the loss of oxygen storage capacity (OSC) due to a reduction in surface area upon thermal treatment. The success of oxygen storage process based on ceria is due to ability to change of oxidation state during operation (i.e. CeO_2 to CeO_{2-x}) maintaining structural integrity, thus allowing oxygen uptake and release to occur smoothly [3]. Recently, much attention is devoted to nanocrystalline binary Ce-Ln-O (Ln = RE and transition metal ions) oxides, which show improved performance in comparison with their individual microcrystalline counterparts. It is known that by introducing different elements into

the CeO_2 lattice, stabilization of the structure against sintering along with enhanced reducibility is achieved as a result of the creation of structural defects in the lattice. Substitution of ceria induces distortion of the O^{2-} sublattice in the solid solutions which permit a higher mobility of lattice oxygen, thus the reduction occurs not only on the surface but also extends deep into the bulk. Especially, ceria nanostructures doped with Zr^{4+} , Ti^{4+} , Hf^{4+} , La^{3+} , $\text{Tb}^{3+/4+}$, and $\text{Pr}^{3+/4+}$ ions have been extensively investigated for various chemical reactions and proven to be superior in terms of both thermal/textural behaviours as well as catalytic activity (OSC and CO oxidation) compared with CeO_2 alone [4–9]. Particularly, the use of variable valence dopants has attracted lot of interest and it is thought that the addition of redox ions like Tb, Pr, etc. enhance the catalytic activity proceeding through an alternate route [10,11]. Based on the above fact, we have undertaken the present investigation. In this comprehensive study a systematic comparison has been attempted between ceria-zirconia and ceria-terbium solid solutions. Accordingly, we have prepared ceria-terbium mixed oxide and compared with widely established ceria-zirconia. Interestingly, the chemically inert and thermally stable sup-

ports over ceria-based mixed oxides, as a new generation of oxygen storage capacity systems, have been uniformly ascertained in many studies [12]. Recently, we have also shown that alumina-supported ceria-zirconia exhibit a strong influence on the thermal stability and redox behaviour of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions over other supports [13]. Motivated by these facts, alumina-supported ceria-terbium solid solutions were synthesized by means of deposition precipitation method and characterized using various techniques such as, Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction (XRD), Raman spectroscopy (RS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The synthesized materials are also examined by performing total oxygen storage capacity (TOSC) and CO oxidation activity. Combined with characterizations, a possible reason for the observed excellent CO activity for alumina-supported ceria-terbium has been discussed.

1 Experimental

1.1 Catalyst preparation

Ceria-zirconia (CZ, 50:50 molar ratio based on oxides) and ceria-terbium (CT, 80:20 molar ratio based on oxides), and alumina-supported ceria-zirconia (CZA, 100:50:50 molar ratio based on oxides) and ceria-terbium (CTA, 100:80:20 molar ratio based on oxides) samples were prepared by coprecipitation and deposition precipitation methods, respectively, by using dilute aqueous NH_3 solution as a precipitating agent. For mixed oxides preparation, required amounts of ammonium cerium(IV) nitrate (GR, Loba Chemie) and zirconium nitrate (AR, Fluka) or terbium(III) nitrate (AR, Aldrich) were dissolved separately, each in 500 ml of deionized water then mixed together and stirred continuously for 1 h. Aqueous NH_3 solution was added dropwise at a flow rate of 30 ml/min, to the mixture solution until pH ~ 8.5 , under vigorous stirring. For supported samples, desired quantity of powdered $\gamma\text{-Al}_2\text{O}_3$ (Harshaw) having a specific surface area of $127 \text{ m}^2/\text{g}$ was first dispersed in about 2000 ml of deionized water and stirred for 2 h. Required amounts of ammonium cerium(IV) nitrate and zirconium nitrate or terbium(III) nitrate were dissolved separately in 500 ml deionized water and mixed together. Then under stirring condition, the mixture solution was added thoroughly to the above solution and the whole mixture was diluted to 4000 ml with deionized water. The stirring was continued for another 1 h. Aqueous NH_3 solution was added dropwise at a flow rate of 30 ml/min to the mixture until pH ~ 8.5 under vigorous stirring. The obtained precipitates were filtered off, washed several times with deionized water, and oven-dried at 393 K for 12 h, then subsequently calcined at

773 K for 5 h in air atmosphere. After cooling, the solid residues were ground with a ceramic mortar and pestle until fine powders were obtained.

1.2 Catalyst characterization

The XRD data were acquired on a Rigaku Multiflex instrument equipped with nickel-filtered $\text{Cu } K_\alpha$ (0.15418 nm) radiation source and a scintillation counter detector. The step size and the time per step were, respectively, fixed at 0.02° and 1 s in the range of 12° – 80° . The mean crystallite size of the solid solution phases was estimated with the help of Scherrer equation from line broadening, and the lattice parameter was calculated by a standard cubic indexation method using the intensity of the most prominent peak (111). The RS were obtained at room temperature using a LabRam HR800UV Raman spectrometer (Horiba Jobin-Yvon) fitted with a confocal microscope and liquid-nitrogen cooled charge-coupled device (CCD) detector. Samples were excited either with 325 nm of a He-Cd laser (Melles Griot) which was focused on the sample under the microscope with the diameter of the analyzed spot being $\sim 1 \mu\text{m}$. The acquisition time was adjusted according to the intensity of Raman scattering. The wavenumber values reported from the spectra are accurate to within 1 cm^{-1} .

Specific surface areas of the samples were determined by a single point BET analysis of the nitrogen adsorption isotherms at liquid N_2 temperature (77 K) over a Gemini 2360 instrument via a thermal conductivity detector. Prior to the experiment, samples were degassed at 393 K for 2 h to remove any surface adsorbed residual moisture. Surface area is obtained by using the desorption data. The high resolution transmission electron microscopy (HRTEM) studies were made on a JEM-2010 instrument (JEOL) equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. Samples for HRTEM were prepared by crushing the materials in an agate mortar and dispersing them ultrasonically in ethyl alcohol. After dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film and allowed to dry. The specimen was examined under vacuum at room temperature.

The XPS analysis was performed using a ESCA 3400 spectrometer (Shimadzu). The X-ray source utilized was $\text{Mg } K_\alpha$ (1253.6 eV) radiation. The analysis was done at room temperature and pressures were typically in the order of less than $1 \times 10^{-8} \text{ Pa}$ to avoid large amount of noise in the spectra from contaminants. Charging of the samples was minimized by referencing the spectra to the C 1s line at $E_b = 284.6 \text{ eV}$. Samples were outgassed overnight in a vacuum oven before XPS measurements.

1.3 Catalyst evaluation

A thermogravimetric method, essentially similar to that described previously elsewhere, was used to determine the TOSC by the oxygen release characteristics of the samples in the temperature region 573–1073 K [14]. The change in the weight of the sample was monitored by thermogravimetry (TG) under cyclic heat treatments in flowing nitrogen or dry air. A commercial Netzsch TG-DTA analyzer (Sta 409 PC Luxx, Germany) was employed for this purpose. The heat cycle consisted of heating the sample to 1073 K, cooling to 423 K, and again heating to 1073 K. All heating and cooling rates were maintained at 5 K/min. The weight loss of the sample during the second heating cycle was used to measure the oxygen release properties [14].

The catalytic activity of the sample for oxidation of CO was conducted at normal pressure (one atmosphere) in the temperature range 300–773 K in a fixed bed microreactor under the temperature ramp of 5 K/min. Approximately 100 mg catalyst sample (250–355 μm sieve fraction) was diluted with quartz particles of the same sieve fraction and was placed in a quartz reactor and its ends plugged with ceramic wool. Reaction temperature was monitored using a thermocouple placed in the hollow part of the reactor. The following gases and gas mixtures were used (supplied by air liqueur): 9.98% CO (99.997%) and 10.2% O₂ (> 99.995%) with argon (> 99.999%) as balance. The total flow rates maintained by three mass flow controllers were in the range of 50–60 ml/min (milliliters normalized to 273.15 K and 1×10^5 Pa). The CO and CO₂ gas concentrations were measured using an Uras 14 infrared analyzer module, and the O₂ concentration was measured using a Magnos 16 analyzer (Hartmann&Braun). Prior to oxidation of CO, the catalyst was heated to 773 K in the 10.2% O₂-89.8% Ar gas mixture, using a heating ramp of 10 K/min, and kept at the final temperature for 1 h. The oxidized sample was then purged in argon to avoid gas phase reaction and cooled to the desired starting temperature. The CO/O₂ reactant feed ratio was 1, and partial pressures of CO and O₂ were in the range of 1×10^3 Pa.

2 Results and discussion

2.1 XRD result

The XRD patterns of CZ, CT, CZA, and CTA samples calcined at 773 K are shown in Fig. 1. For comparison purpose, XRD profile of pure cerium oxide calcined at 773 K and $\gamma\text{-Al}_2\text{O}_3$ are included in the figure. The diffraction peaks of the samples could be indexed to (111), (200), (220), (311), (222), (400), and (331) crystal faces corresponding to a characteristic fluorite type structure of ceria. All XRD features clearly indicated the formation of solid solution between ceria and dopant ion (Zr or Tb) and correspond to

Fig. 1. Powder XRD patterns of ceria (C), CZ, CT, CZA, and CTA samples calcined at 773 K and $\gamma\text{-Al}_2\text{O}_3$.

solely fluorite type lattice. Interestingly, there are no diffraction peaks corresponding to alumina in the supported samples, indicating amorphous nature of the support. The XRD analysis revealed that in the case of CZ solid solution, the observed phase composition corresponds to $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (PDF-ICDD 28-0271) instead of the expected $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ composition, which indicates that all the Zr cations are not completely incorporated into the CeO_2 lattice and there could be the presence of some amount of amorphous ZrO_2 at the grain boundaries of CZ particles. While in the case of CZA solid solution, the observed phase composition was $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (PDF-ICDD38-1439) and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (PDF-ICDD38-1436) indicating that alumina support facilitated the incorporation of more Zr atoms into the ceria lattice. In the case of Tb doping, an identical composition $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ was observed in both CT and CTA solid solutions [15].

The diffraction peaks became broad after the incorporation of Zr or Tb cations into the ceria lattice which further broadened when deposited on the alumina support. This observation indicated that the crystallite size of the ceria is becoming smaller and smaller by the incorporation of dopant and in turn deposition on to the support. The average crystallite sizes and lattice parameters of all the mixed oxides are presented in Table 1. From the table it is also clear that the change in the lattice parameter is obvious following the Vegard's rule due to incorporation of dopant ions with indifferent ionic radius with reference to the cerium ion [16]. The calculated lattice parameter value for CZ solid solution revealed incorporation of smaller zirconium cations (Zr^{4+}) into the ceria lattice having smaller cell dimension than ceria. The lattice parameters obtained for the CT solid solution are larger than expected if the whole terbium is present as Tb^{4+} , hence, a part of terbium must be present as

Table 1 BET surface area, crystallite size, and lattice parameter of the C, CZ, CT, CZA, and CTA samples calcined at 773 K

Sample	Surface area (m ² /g)	Crystallite size (nm)	Cell parameter (nm)	TOSC ^a
C	41	7.3	0.541	0.04
CZ	84	4.5	0.535	0.16
CT	85	5.5	0.537	0.18
CZA	146	4.0	0.529	0.42
CTA	148	3.7	0.538	0.36
γ -Al ₂ O ₃	127	—	—	0.00

^aTOSC = Weight loss $\times$ 10/32.

Tb³⁺. The lattice parameters of the CZA sample is slightly smaller than that of the CZ this could be due to the incorporation of more amount of Zr into the ceria lattice. The lattice parameter of the CTA sample is slightly larger than that of the unsupported ceria-terbia of the same chemical composition (0.537 nm). This indicates the presence of small excess amount of trivalent cations in the lattice of the resultant supported oxide, either namely Ce³⁺ and Tb³⁺ or both, having cationic radii of 0.114 and 0.104 nm, respectively. Being these trivalent cations are bigger than the tetravalent Ce⁴⁺ (cationic radius of 0.097 nm), they can compensate for the contraction of the ceria lattice due to the presence of smaller Tb⁴⁺ (cationic radius of 0.088 nm). In the case of Al₂O₃-supported samples, the formation of CeAlO₃ is also not observed. It could be inferred from XRD results that the deposition coprecipitation adopted in the present study may be a good method to obtain highly dispersed ceria-zirconia and ceria-titania mixed oxides over the supports without the formation of inert compounds.

2.2 RS result

The RS is widely used to investigate the oxygen lattice vibration in fluorite-type oxides. In the present study, RS are collected by using ultraviolet wavelength excitation (325 nm) which enables selective detection of the crystal structure surface region. Therefore, we conclude that the bands are attributed to relative contribution of the oxygen vacancies from the surface region [17]. The UV Raman spectra of CZ, CT, CZA, and CTA are shown in Fig. 2. The UV Raman of pure ceria is also included in the figure as a reference. For the space group Fm3m, the only Raman active mode (F_{2g}) is centered at around 460 cm⁻¹ could be attributed to the F_{2g} Raman-active mode characteristic of the fluorite cubic type lattice, which can be viewed as a symmetric breathing mode of the oxygen atoms around cerium ions. The band at this region is due to symmetric O–Ce–O stretching mode [18]. This band is sensitive to any disorder in the oxygen sublattice and the presence of this band indicates that all samples exhibit a global cubic fluorite type

Fig. 2. UV Raman spectra of the C, CZ, CT, CZA, and CTA samples calcined at 773 K.

structure in line with XRD results. The intensity of the Raman band depends on several factors including grain size, morphology, etc. [19]. No Raman lines due to ZrO₂ and Tb₄O₇ were observed corroborating with the XRD results indicating the formation of solid solution. The presence of a prominent broad band at ~600 cm⁻¹ could be attributed to a non-degenerate Raman inactive longitudinal optical (LO) mode of ceria, which arises due to relaxation of symmetry rules. Interestingly, the peak at ~600 cm⁻¹ for supported and unsupported CT samples is relatively more pronounced compared to supported and unsupported CZ, respectively which could attributed to presence of more number of reducible sites (Ce³⁺/Tb³⁺) located near surface region. Within the CT and CTA, the CTA has shown a high intense band compared to CT. These sites may facilitate the adsorption and desorption of gaseous oxygen and thereby could offer better activity for oxidation reaction. The nature of this band may be due to the resonance enhancement of the Raman scattering cross section under UV excitation. The absence of any other Raman features provided one more inference that alumina is not forming any compound with cerium, zirconium and terbium oxides.

2.3 HRTEM and BET surface area

In order to substantiate the observations made from XRD and Raman measurements and to uncover the information on the nanometer sizes of the investigated oxide samples, HRTEM analyses were undertaken and the representative micrographs are shown in Fig. 3. As can be noted from these micrographs, the particle size of all the samples are observed to be in the range of 5–8 nm. In all the images, small and well faceted mixed oxide particles deposited on the surface of larger surface area support are clearly visible. The mixed oxide crystals seem to be well distributed on the

support, i.e., homogeneous in nature. HRTEM micrographs provide a better perception of the size and dispersion of these mixed oxide particles. As observed, the mixed oxide particles are agglomerated in nature. Plain faces representing the support could not be seen suggesting the amorphous nature of it. This observation is supported by the XRD results as well. The shapes of the particles are more or less cuboctahedral. There is observed some sort of amorphous region in the case of CTA sample. Table 1 lists the information about the specific surfaces of various catalysts along with $\gamma\text{-Al}_2\text{O}_3$ obtained from N_2 physisorption measurements. The CZ and CT samples prepared under identical conditions by adopting the same preparation technique exhibited surface areas of 84 and 85 m^2/g , respectively. When these are dispersed over the alumina support, the surface area is increased. This observation further revealed the ability of alumina support to stabilize the CZ and CT against sintering.

Fig. 3. HRTEM images of the CZ (a), CT (b), CZA (c), and CTA (d) samples calcined at 773 K.

2.4 XPS result

The Ce 3d core level spectra of different samples are presented in the Fig. 4. As can be seen from figure the $3d_{3/2}$ and $3d_{5/2}$ (represented as U and V, respectively) contributions. The peak at ~ 916.6 eV (U''') is mainly correspond to the Ce^{4+} state. The U''' peak is the most convenient feature to follow the progressive reduction of Ce, since it does not overlap with others. The peaks of Ce^{3+} (V^0 , U^0) are generally noticed at around 881 and 898 eV, respectively. Here, it can be seen that the latter peak is overlapping with V''' . The satellites to these features (V' and U') occur at 885.9 and 904.2 eV, respectively. It can be observed that the shoulder

Fig. 4. XPS spectra of the CZ, CT, CZA, and CTA samples calcined at 773 K.

above 881 eV is made up of a mixture of V and V^0 features and the usual good separation between V and V'' (characteristic of only Ce^{4+} state) is prevented by a significant intensity of V' indicating the presence of Ce^{3+} in the sample. The presence of the Ce^{4+} state is supported by a considerable intensity of the U''' peak. Thus, on the surface of the samples, the concentrations of both Ce^{4+} and Ce^{3+} are quite comparable. A progressive reduction of Ce^{4+} into Ce^{3+} oxidation state results with a decrease in the U''' intensity and an increase in V' and U' at the expense of V'' and U'' for supported samples compared with unsupported samples [15]. Particularly, CTA has shown significant intensity ratio ($\text{Ce}^{3+}/\text{Ce}^{4+}$) among the investigated samples conferring its high reducibility.

2.5 OSC result

The OSC of all the samples are given in the Table 1. It is known that fluorite-type structure plays an important role for the OSC. In general terms, from pure ceria $\rightarrow$ ceria solid solutions $\rightarrow$ supported ceria solid solutions the OSC is increased [10,13]. Specificity of mixed oxides for oxygen storage was shown to be due to the participation of bulk oxygen. Hence, another important point, which can be drawn from the obtained results, is that the oxygen storage takes place not only at the surface but also in the bulk. In the present investigation the CZ and CT solid solutions exhibited higher OSC compared with pure ceria that could be due to the bulk oxygen availability in the solid solutions. Among these solid solutions, the CT has shown significantly high OSC compared with CZ which could be due to the redox nature of Tb and therefore more amount of oxygen contributed to OSC. Further, the supported solid solutions exhibited almost 8–10 times higher OSC than that obtained for pure ceria sample, since the $\gamma\text{-Al}_2\text{O}_3$ support

showed no OSC activity within the experimental conditions. The increase in the OSC of the supported sample may be due to an increased dispersion of the mixed oxide over the support with significant increase in the surface area. Within CZA and CTA samples, the CZA has shown higher OSC, this could be due to the more amount of Zr incorporation (from XRD) into the ceria lattice after depositing it on to the alumina support that consequently enhances the reducible cerium ions (Ce^{4+}).

2.6 CO oxidation activity

The catalytic activities of CZ, CT, CZA, and CTA were tested for CO oxidation. The activity measurements were performed at normal atmospheric pressure and the conversion of CO was evaluated as earlier reports [15]. The conversion of CO as a function of reaction temperature is presented in Fig. 5. It is evident from figure that both supported and unsupported CT samples exhibited better activity in terms of total conversion as well as light-off temperature (temperature at 50% conversion). Both CTA and CT samples exhibited maximum conversion at approximately 730 and 773 K with light-off temperatures around 604 and 621 K, respectively, whereas CZ and CZA samples have shown light-off temperatures above 650 K, and maximum CO conversion beyond 750 K. The catalytic efficiency order was found to be $\text{CZ} < \text{CZA} < \text{CT} < \text{CTA}$. This shows the superiority of the CTA sample over other samples. It is known from the literature that OSC plays a major role but in the present case, the OSC is not in the same order with activity [13]. From the table, CZA has shown high OSC nevertheless CT and CTA have shown high activity. During the oxidation of CO, the rapid transformation of adsorbed CO in to CO_2 strongly depends on the rate of uptake/release of lattice oxygen. In fact, the oxygen uptake/release depends not only on total OSC but also on the number of redox sites

Fig. 5. Conversion of CO versus temperature for CZ (1), CT (2), CZA (3), and CTA (4) samples calcined at 773 K.

and rate of redox cycles as well [20]. The number of redox sites are unaltered (both $\text{Ce}^{3+/4+}$ and $\text{Tb}^{3+/4+}$ ions act as redox sites) for CT and CTA sample whereas for CZA ($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ confirmed from XRD) these are decreased. Moreover, in the Zr doped ceria oxygen vacancies are trapped by the high electronegative Zr ions, hence oxygen transfer rate decreased [21]. All these parameters together make CZA less active than CTA even less than CT. The high activity of CTA over other samples is also correlated with the combination of facts which include (i) small crystallite size, high surface area and (ii) more reducibility as supported by XRD, HRTEM, and XPS. Thus, the combined use of XRD, RS, XPS, and HRTEM techniques provided interesting information regarding the influence of support on the CO oxidation activity of highly dispersed ceria-terbium solid solution. From the obtained results it is obvious that the CTA sample has the promising characteristics to be used as a catalyst for CO oxidation.

3 Conclusions

Ceria-zirconia and ceria-terbium solid solutions dispersed over Al_2O_3 support possessing high specific surface area and good thermal stability were synthesized by a deposition coprecipitation method. The X-ray diffraction analysis revealed the crystal faces corresponding to a fluorite-type structure of investigated samples and there is no indication of formation of other compounds such as CeAlO_3 for supported samples. Raman spectroscopy studies suggest formation of oxygen vacancies, and lattice defects in various samples, which are important from the catalytic point of view. The high resolution transmission electron microscopy studies revealed the nanocrystalline nature of the dispersed ceria-terbium and ceria-zirconia solid solutions. The catalytic activity of the synthesized samples for CO oxidation was found to follow the order alumina-supported ceria-terbium > ceria-terbium > alumina-supported ceria-zirconia > ceria-zirconia. In terms of conversion as well as light-off temperatures (50% conversion), the alumina-supported ceria-terbium is remarkably better than all other samples. The substantially high activity could be due to the formation of solid solution and more defect sites in its crystal lattice, better dispersion of the active phase over the support, more number of redox sites and high rate of redox cycles. Thus, alumina-supported ceria-terbium could be a promising catalyst for use in the TWC formulations.

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