Design of novel ceria-based nano-oxides for CO oxidation and other catalytic applications

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Carbon monoxide oxidation over various ceria-based solid solutions has been reviewed. The advantageous incorporation of various dopants in the ceria lattice (CeₓM₁₋ₓO₂; M = Zr and Hf, and CeₓM₁₋ₓO₂₋δ; M = La and Pr) to improve oxygen storage capacity and CO oxidation activity have been addressed. Nanosized doped ceria solid solutions are synthesized by a newly developed coprecipitation method from ultrahigh dilute aqueous solutions. To establish the thermal stability, the synthesized materials have been calcined at 773 and 1073 K and thoroughly characterized by various state-of-the-art techniques. The structural features have been investigated by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, UV-visible diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and BET surface area. X-ray diffraction and Raman Spectroscopic studies establish the formation of solid solutions and the TEM analysis specifies the nanosized nature of the mixed oxides. Further, the XPS and UV−vis DRS studies establish the existence of cerium in both 3+ and 4+ oxidation states and the presence of oxygen vacancies, respectively. Among various combinations, the ceria-hafnia solid solution exhibits the best oxygen storage capacity and excellent CO oxidation activity. As revealed by this model study, there is ample scope to design better materials for CO oxidation and related pollution abatement applications.

Keywords: Catalysts, Ceria, CO oxidation, Oxygen storage capacity, Solid solutions, Defective fluorite structure

Carbon monoxide is widely recognized pollutant, especially in effluent streams from three-way catalytic converters (including portable and back-up generators, lawn mowers, power washers, etc.), indoors and more recently in polymer electrolyte membrane fuel cells, etc. It is a toxic gas that causes oxygen deficiency (anoxemia) and exposures at 100 ppm or greater can be dangerous to human health. Generally, it is produced by the partial oxidation of organic matter due to the insufficient availability of oxygen for complete oxidation. These critical damages can be prevented by the oxidation of CO pollutant in the atmosphere into CO₂ as given in Eq. (1).

\[ \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2, \Delta G = -257.1 \text{ kJ mol}^{-1} \]  \(\text{(1)}\)

Several investigations have been focused on CO pollution abatement by using different catalytic materials due to the stringent environmental regulations being imposed around the world. Fortunately, noble metals are more suitable for CO oxidation because CO binds more strongly on the metal surfaces to progress the reaction. However, noble metals are characterized by various disadvantages such as high cost, limited availability, poor thermal stability and strong tendency to poisoning.

Metal oxides are alternate viable options that have been extensively investigated for CO oxidation owing to their low-price and less susceptibility to poisoning in comparison to pure metals. In particular, nanostructured metal oxides have attracted considerable interest compared to bulk owing to surface effect, small size influence, quantum size effect and so on, which opens up new opportunities for the development of materials with tailored properties. The small size leads to many distinct properties, which influences the lattice symmetry and the cell parameters. Amongst the various transition, non-transition and rare earth metal oxides, rare earth ceria (CeO₂) has gained much importance for various applications due to its multifunctional character.
For the control of environmental pollution, catalysts or sorbents that contain redox metal oxides are highly desired. Thus, ceria has attracted a lot of interest for CO oxidation and other applications that include three-way catalytic converters, solid oxide fuel cells, fluid catalytic cracking, water-gas-shift catalysis, photo catalysis, semiconductor devices, phosphors, sensors etc. due to its oxygen defect character, oxygen ion conductivity, oxygen storage/release capacity (OSC) and high mechanical strength, especially the oxygen ion conductivity and OSC associated with facile transformations between Ce$^{3+}$ and Ce$^{4+}$ oxidation states. This unique redox process can be triggered either by direct electron transfer from a metal particle (or molecule) adsorbed over the ceria surface, which would lead to partially positively charged (cationic) adsorbates, or, by oxygen release leaving an oxygen vacancy and two electrons localized on the Ce cations becoming Ce$^{3+}$. The former effect is particularly important when dealing with metals supported on ceria. The latter process is related to the ability of ceria to act as an oxygen buffer (referred to as oxygen storage/release component). Here, a crucial role is assigned to surface oxygen vacancies, which are likely to form more readily at the nanoscale. Nanosized ceria has been recognized to possess antioxidant properties and used in biomedical applications such as retinal degeneration and prevention from radiation induced cellular damage. However, the use of pure ceria in various fields is limited to low temperature applications. For high temperature functions, loss of OSC and lowering in oxygen ion conductivity are the major disadvantages owing to sintering which does not allow ceria to switch rapidly between 3+ and 4+ oxidation states. The OSC and oxygen ion conductivity are the eminent properties for many catalytic applications. In addition, the poor low-temperature performance does not enable ceria-only materials to meet the increasingly demanding standards required by legislation in the automotive pollution control devices. This has triggered the search for new catalyst compositions with improved properties. Therefore, a great deal of attention has been given to developing ceria-based materials with various dopants. However, the selection of an appropriate dopant and the synthesis of doped ceria solid solutions is a challenging task.

The addition of different metal dopants into the ceria lattice leads to the formation of lattice defects in the crystal structure which enhance the OSC and oxygen ion conductivity. For example, the introduction of non–reducible tetravalent ions such as Zr$^{4+}$/Hf$^{4+}$ and trivalent ion such as La$^{3+}$ into the CeO$_2$ lattice are expected to create lattice defects due to the ionic radii difference between the Ce$^{4+}$ (0.097 nm) and Zr$^{4+}$ (0.084 nm) or Hf$^{4+}$ (0.083 nm) or La$^{3+}$ (0.110 nm), respectively. Apart from cerium, other rare earth elements like praseodymium also exhibit reducible character and show 3+ and 4+ oxidation states. Therefore, incorporation of variable valent cations into the ceria lattice is also expected to show interesting properties.

The present paper illustrates the design and development of doped ceria solid solutions with isovalent and variable valent cations and their comparison with well-proven ceria-zirconia solid solutions. The synthesis of designed nanosized ceria-hafnia (CH), ceria-zirconia (CZ), ceria-praseodymia (CP) and ceria-lanthana (CL) solid solutions has been achieved by a modified coprecipitation method from ultrahigh dilute solutions. The structural and redox properties have been investigated by various contemporary techniques namely, XRD, TEM, XPS, RS, UV-vis DRS and BET SA. The OSC and catalytic activity towards CO oxidation have also been evaluated.

Methodology
Catalyst preparation
Different synthetic strategies are available in the literature for the production of nanosized metal oxides. Among these, coprecipitation is the most viable method, easy in scalability and results in atomic scale mixing. Hence, the calcination temperature required for the formation of final product is low, which leads to lower particle size. Therefore, the described CL, CP, CH and CZ catalytic solid solutions were prepared by the modified coprecipitation method and the experimental details reported elsewhere. In brief, the desired amounts of respective precursors were dissolved separately in doubly–distilled water under vigorous stirring and mixed together. Upon complete mixing, the aqueous ammonium hydroxide solution was added drop–wise until the precipitation was complete ($\text{pH} \sim 8.5$). The obtained precipitates were washed, filtered and dried in the oven at 393 K for...
The dried samples were subsequently calcined at 773 K for 5 h at a heating rate of 5 K min\(^{-1}\) in air to obtain the final oxide materials. To understand the thermal behavior, the synthesized samples were subjected to additional calcination at 1073 K for 5 h. After cooling, the solid residues were ground until they were fine powders and stored in dry atmosphere. Pure cerium oxide (C) was also prepared for comparison purpose by adopting the same procedure.

**Catalyst characterization**

X–ray diffraction patterns presented herein were collected on a Rigaku Multiflex instrument using nickel–filtered Cu-K\(_\alpha\) (0.15418 nm) radiation 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 2–80°. The XRD phases present in the samples were identified with the help of Powder Diffraction File–International Center for Diffraction Data (PDF–ICDD). The average crystallite size of solid solution phases was calculated with the help of Scherrer equation by line broadening technique and the lattice parameter was calculated by a standard cubic indexation method using the intensity of most prominent peaks. The Raman spectra shown were recorded on a LabRam HR spectrometer (Horiba Jobin–Yvon) equipped with a CCD detector. The emission line at 514.53 nm from an Ar\(^+\)–Kr\(^+\) ion RM2018 laser (Spectra Physics) was focused on the sample under the microscope, with the diameter of the analyzed spot being ~1 µm. The power of the incident beam on the sample was typically 0.5 mW. Acquisition time was adjusted according to the intensity of Raman scattering. The wavenumber values reported from the spectra are accurate to within 1 cm\(^{-1}\). Surface areas were determined by BET method using N\(_2\) as the adsorbent, on a Micromeritics Gemini 2360 instrument. Prior to analysis, samples were oven dried at 393 K for 12 h and flushed with Argon gas for 2 h.

The UV–vis DRS measurements were performed over the wavelength range of 200–800 nm using a GBS–Cintra 10e UV–vis NIR spectrophotometer with an integration sphere diffuse reflectance attachment. Samples were diluted in KBr matrix by pelletization. The HREM studies were made on a JEM–2010 (JEOL) instrument equipped with a slow–scan CCD camera and at an accelerating voltage of 200 kV. Samples for TEM analysis were prepared by crushing the materials in an agate mortar and dispersing ultrasonically in ethyl alcohol. XPS analyses were performed using a Shimadzu (ESCA 3400) spectrometer. The X–ray source utilized was the Mg- K\(_\alpha\) (1253.6 eV) radiation. The analysis was done at room temperature and the pressures were typically on the order of less than 10\(^{-8}\) Pa. The charging of samples was corrected by setting the binding energy of the adventitious carbon\(^{23}\) (C 1s) at 284.6 eV. The samples were out-gassed overnight in a vacuum oven at 283 K before XPS measurements. All binding energies were measured within a precision of ±0.3 eV.

The OSC of the catalysts was measured by a thermogravimetry (TG) method employing a commercial Netzsch TG–DTA (Luxx, STA, 409 PC, Germany) analyzer under repeated thermal treatments in the temperature window of 573–1073 K. The OSC of the catalyst was measured in terms of the amount of oxygen released during cyclic heat treatments. The weight change during the thermal treatments was monitored by TG in flowing nitrogen or dry air. 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 in the steps of 5 K min\(^{-1}\). The weight loss of the sample during the second stage of heat treatment was used to measure the oxygen release properties.

**Catalytic activity**

The catalytic activity for CO oxidation was conducted at normal atmospheric pressure in a fixed-bed microreactor under the temperature ramp of 5 K min\(^{-1}\). Approximately 100 mg catalyst sample (250–355 µm sieve fraction) was diluted with quartz particles (1:1) of the same sieve fraction and placed in a quartz reactor (2 mm i.d., 6 mm o.d., 250 mm length) for the reaction. The temperature was measured using a thermocouple placed near the catalyst bed. The CO and CO\(_2\) gas concentrations were measured using an Uras 14 infrared analyzer module and the O\(_2\) concentration was measured using a Magnos 16 analyzer (Hartmann & Braun). Prior to the oxidation of CO, the catalysts were heated to 773 K in the 10.2 % O\(_2\)/Ar gas mixture, using a heating ramp of 10 K min\(^{-1}\), and kept at the final temperature for 1 h. The oxidized sample was then purged in argon. The CO/O\(_2\) reactant feed ratio was 1, and partial pressures of CO and O\(_2\) were in the range of 10 mbar.
Results and Discussion

XRD patterns of CZ, CH, CP and CL solid solutions along with pure CeO$_2$ calcined at 773 and 1073 K are presented in Fig. 1a and 1b, respectively, together with the lattice parameter (LP) and crystallite size (D) values. It may be noted from Fig. 1 that all XRD patterns revealed the presence of standard cubic fluorite-type phase of CeO$_2$ and the absence of La$_2$O$_3$, Pr$_6$O$_{11}$, ZrO$_2$ and HfO$_2$ individual oxide peaks. The XRD results further confirmed the formation of respective solid solutions with the composition Ce$_{0.75}$Zr$_{0.25}$O$_2$, Ce$_{0.8}$Hf$_{0.2}$O$_2$, Ce$_{0.8}$Pr$_{0.2}$O$_{2-δ}$ and Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ for 773 K calcined samples. Further, a small shift in the peak positions is observed towards higher or lower 2θ angles, relative to the pure ceria, depending on the ionic radius of the doped cations in agreement with the formation of solid solutions. Generally, it was observed that on doping of CeO$_2$ with smaller radius M$^{n+}$ cation than Ce$^{4+}$ (0.097 nm), such as Zr$^{4+}$ (0.084 nm) and Hf$^{4+}$ (0.083 nm), the peak positions are slightly shifted towards higher 20 angles than that of pure CeO$_2$. On the other hand, doping of CeO$_2$ with larger radius M$^{n+}$ than Ce$^{4+}$, such as Pr$^{3+}$ (0.113 nm) and La$^{3+}$ (0.110 nm), leads to the peak positions towards lower 2θ values. The lattice parameter values of all samples as shown in the Fig. 1 are well matched with the values reported in the literature. It is observed from these values that in the case of doped CeO$_2$ samples with smaller radius cations (Zr$^{4+}$ and Hf$^{4+}$), the lattice parameter for 773 K calcined samples is decreased compared to pure ceria, while for larger radius cations (Pr$^{3+}$ and La$^{3+}$) doped samples, the lattice parameter values are increased. Thus the changes in the lattice parameter values suggest the formation of CL, CP, CH and CZ solid solutions by replacing the Ce$^{4+}$ with the doped cations. Interestingly, the calculated lattice parameter value (0.5527 nm) of CP solid solution is significantly greater than the expected value for the incorporation of Pr$^{3+}$. It should be noted that the radius of Pr$^{4+}$ (0.096 nm) is close to that of Ce$^{4+}$ (0.097 nm), while the radius of Pr$^{3+}$ (0.113 nm) is much larger than that of Ce$^{4+}$, which indicate that both Pr$^{3+}$ and Pr$^{4+}$ ions are present in the CP solid solution respectively. In addition to this, the lattice parameter of CP solid solution is close to that of pure CeO$_2$, suggesting a large number of Pr$^{4+}$ ions in the CP solid solution along with a small portion of Pr$^{3+}$ ions. Hence, the average ionic radius of Pr$^{n+}$ (n = 3–4) ion is similar to that of the ionic radius of Ce$^{4+}$ ion. Upon increasing the calcination temperature, the lattice parameter is decreased for CZ solid solution, while for CH, CP and CL solid solutions, the lattice parameter remained the same as in the case of 773 K calcined samples. From these observations, it is evident that the CZ solid solution undergoes a phase separation and the CH, CP and CL solid solutions remained in a single phase with increase of calcination temperature. As known from the literature, phase segregation leads to a decrease in the activity as well as stability of the catalysts. Thus, the results suggest that the CZ solid solution is somewhat less

Fig. 1—Powder XRD patterns of CeO$_2$ (C), Ce$_{0.75}$Zr$_{0.25}$O$_2$ (CZ), Ce$_{0.8}$Hf$_{0.2}$O$_2$ (CH), Ce$_{0.8}$Pr$_{0.2}$O$_{2-δ}$ (CP) and Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ (CL) calcined solid solutions. [(a) 773 K; (b) 1073 K].
stable and active than that of CH, CP and CL solid solutions in the explored temperature range of 773–1073 K. In general, the diffraction peaks of all samples calcined at 773 K are broader and lower in intensity. However, at 1073 K the peaks became narrower and higher in intensity. These results illustrate that the crystallite size increases upon increasing the calcination temperature due to sintering. Interestingly, the Ce$_{0.75}$Zr$_{0.25}$O$_2$ phase is manifested in the case of CZ solid solution calcined at 773 K instead of Ce$_{0.5}$Zr$_{0.5}$O$_2$ due to incomplete incorporation of Zr$^{4+}$ cations into the CeO$_2$ lattice while the remaining amount of ZrO$_2$ is present in an amorphous state at the grain boundaries of CZ particles. Further, a slight shift in the diffraction peaks is noted in the case of 1073 K calcined samples due to more incorporation of Zr$^{4+}$ ions into the CeO$_2$ lattice with the formation of Ce$_{0.6}$Zr$_{0.4}$O$_2$ cubic phase.

Raman spectra of various solid solutions along with pure ceria calcined at 773 and 1073 K are shown in Fig. 2a. The Raman bands reflect both the surface and bulk information due to the weak absorption of samples in the visible range. Generally, Raman spectra provide information about the M–O bond arrangement and lattice defects, predominantly in the case of ceria-based solid solutions. Characteristic peaks of cubic fluorite-structure (~465 cm$^{-1}$) along with lattice defect peaks (550–620 cm$^{-1}$) are seen in Fig. 2a. Interestingly, no bands pertaining to individual oxides are observed indicating the formation of solid solutions in agreement with XRD results. The observed strong band at ~465 cm$^{-1}$ is generally designated with the $F_{2g}$ mode, characteristic of cubic fluorite structure which can be viewed as symmetric breathing mode of the oxygen atoms around cerium ions. When ceria is doped with other metal ions, a change in the $F_{2g}$ peak shape and position could be observed, which is attributed to several factors such as phonon confinement, strain, inhomogeneity of the size distribution, defects and variations in phonon relaxation with the particle size. The shift in the $F_{2g}$ band is also due to change in the M–O vibration for doped ceria which further depends on the ionic radius of dopant ion. Hence, the $F_{2g}$ mode of CH and CZ solid solutions is shifted to higher wavenumbers, while for CL and CP solid solutions the $F_{2g}$ mode is shifted to lower wavenumbers. The intensity of $F_{2g}$ peak is sensitive to the calcination temperature. As can be noted from the figure, the intensity of $F_{2g}$ mode was enhanced on increasing the...
calcination temperature, revealing better crystallization as supported by the XRD studies. In addition to the \( F_{2g} \) band, some other bands around 550–620 cm\(^{-1} \) are also seen (Fig. 2b). The lattice defects in ceria-based solid solutions are of mainly two types, namely, oxygen vacancy defects and \( \text{MO}_{8^-} \)-type complex defects. These shoulder type of bands arise due to the change in the valence state and/or difference in the ionic radius of the dopant to that of \( \text{Ce}^{4+} \) ion\(^{25} \). For CL sample, a broad band ranging from 550 to 600 cm\(^{-1} \) is observed, probably due to mixed contribution from oxygen vacancy defect and \( \text{MO}_{8^-} \)-type complex (\( M = \text{La} \)). The band at about 620 cm\(^{-1} \) for both CH and CZ solid solutions is mainly because of \( \text{MO}_{8^-} \)-type complex (\( M = \text{Hf} \) and \( \text{Zr} \)) defect. The observation of band at about 573 cm\(^{-1} \) in CP solid solution could be due to different oxidation states and not due to the ionic radius of the dopant because the average ionic radius of Pr cations is similar to that of \( \text{Ce}^{4+} \) ion intune with XRD results\(^{25} \). The high intense band for CP sample in this region may also be due to color change by Pr doping, which increases optical absorption\(^{29} \).

The oxygen–metal ion charge transfer bands in ceria–based solid solutions have been studied by UV–vis DRS. The UV–vis DRS spectra of the C, CL, CP, CH and CZ solid solutions calcined at 773 K are shown in Fig. 3. All the samples exhibited three absorption maxima in the wavelength range 250–340 nm. The former two are charge transfer bands (\( \text{O}^2- \rightarrow \text{Ce}^{3+} (\sim 255 \text{ nm}) \) and \( \text{O}^2- \rightarrow \text{Ce}^{4+} (\sim 287 \text{ nm}) \)) and the latter band is interband transition (IBT, \( \sim 340 \text{ nm} \))\(^{31} \). Above 400 nm, the absorption intensity pertaining to C, CL, CH and CZ samples decreases, whereas, the CP solid solution is strongly absorbed in the visible range of 400–650 nm due to a \( \text{Pr}^{3+} \) ion transition, in concurrence with the high intense defect peak in Raman spectra. The \( \text{O}^2- \rightarrow \text{Ce}^{3+} \) transitions give information about the defect sites as observed from Raman spectra. The particular component is highly pronounced and well resolved when \( \text{Hf}^{4+} \) ion is doped into the ceria lattice.

The HREM images obtained for all the samples calcined at 773 and 1073 K are presented in Fig. 4. The average particle size is found to be 4–8 nm when
calcined at 773 K, while the size of the particles is increased to two folds (7–17 nm) when the samples were calcined at 1073 K. These observations are well matched with the average crystalline size values obtained from X-ray line broadening by Scherrer equation as depicted in Fig. 1, and also the surface area measurements shown in Table 1. For all the samples, a gradual decrease in the surface area is observed with increase in calcination temperature due to agglomeration of the particles, which is also clearly reflected in the HREM images.

The valence/oxidation state of the elements and the surface composition of various solid solutions calcined at 773 K have been examined by photoelectron spectroscopy. The XPS profiles of Ce 3d for various samples are shown in Fig. 5. The electron binding energy values agree well with the reported results\textsuperscript{32,33}. As shown in the figure, the Ce 3d core level spectra is composed of ten components, in which u and v refer to the Ce 3d\textsubscript{3/2} and Ce 3d\textsubscript{5/2}, respectively. The u, v, u\textsubscript{o} and v\textsubscript{o} peaks are assigned as main signals, while the remaining all are referred to as satellites. Among these, u, u\textsuperscript{′}, u\textsuperscript{′′}, v, v\textsuperscript{′}, and v\textsuperscript{′′}, and u\textsubscript{o}, u\textsuperscript{′}, v\textsubscript{o} and v\textsuperscript{′} peaks correspond to the Ce\textsuperscript{4+} and Ce\textsuperscript{3+}, respectively. Hence, Ce ions are present in both 4+ and 3+ oxidation states. It may be noticed from the figure that the intensity of the v\textsuperscript{′} signal increases in the order: CZ < CP < CL < CH, with the simultaneous decrease in the intensity of the u\textsuperscript{′′} signal. Therefore, these results indicate an enhancement of Ce\textsuperscript{3+} concentration in the same order.

The O 1s core level spectra of CL, CP, CH and CZ sample calcined at 773 K are shown in Fig. 6. The O 1s peak contains mainly two constituent peaks, generally observed at \textasciitilde530.3 ± 0.3 and 533.0 ± 0.3 eV,

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SA (m\textsuperscript{2}g\textsuperscript{−1})</th>
<th>OSC (\textmu mol of O\textsubscript{2}/g ceria)</th>
</tr>
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<tbody>
<tr>
<td>C 773</td>
<td>41</td>
<td>40</td>
</tr>
<tr>
<td>C 1073</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>CZ 773</td>
<td>84</td>
<td>167</td>
</tr>
<tr>
<td>CZ 1073</td>
<td>36</td>
<td>–</td>
</tr>
<tr>
<td>CH 773</td>
<td>78</td>
<td>248</td>
</tr>
<tr>
<td>CH 1073</td>
<td>26</td>
<td>–</td>
</tr>
<tr>
<td>CP 773</td>
<td>72</td>
<td>210</td>
</tr>
<tr>
<td>CP 1073</td>
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<td>–</td>
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<td>225</td>
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<tr>
<td>CL 1073</td>
<td>40</td>
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respectively. The former peak is attributed to lattice oxygen while the latter corresponds to the surface hydroxyl and carbonate groups\textsuperscript{28}. The La 3d, Pr 3d, Hf 4f and Zr 3d core level spectra of CL, CP, CH and CZ solid solutions respectively are depicted in Fig. 7. The peaks observed at ~834.3 and 838.6, and 851 and 855.5 eV for La 3d correspond to 3d\textsubscript{5/2} and 3d\textsubscript{3/2}, respectively. This splitting pattern in core level spectra of La 3d arises due to the spin orbit interaction and charge transfer from ligand (O 2p) to the metal (La 4f). Splitting energy observed from the spectra is ~4.25 eV, which is also supported by earlier reports\textsuperscript{22}. Because of the complex nature of Pr 3d\textsubscript{3/2} sublevel due to the multiplet effects, we have studied the Pr 3d\textsubscript{3/2} region to understand the oxidation states of Pr. The Pr 3d\textsubscript{3/2} spectra exhibited two peaks at about 929.7 and 934.5 eV assigned to Pr\textsuperscript{3+} and Pr\textsuperscript{4+}, respectively, in line with previous results\textsuperscript{21}. This evidences the information from XRD results that similar to Ce, the Pr ion also exhibits redox property (3+ and 4+). The two characteristic peaks are observed at about 17.2 and 18.6 eV for CH sample, which correspond to Hf 4f\textsubscript{7/2} and Hf 4f\textsubscript{5/2}, respectively. The binding energy difference between these two components is about 1.4 eV which is in line with earlier reported values. It is noticed from the Hf 4f\textsubscript{5/2} XP spectra that the Hf is present mainly in 4+ oxidation state. The slightly resolved peaks at about 184.6 and 182.2 eV for Zr 3d of CZ sample assigned to the Zr 3d\textsubscript{5/2} and Zr 3d\textsubscript{3/2}, respectively, are well matched with the values reported in the literature for ZrO\textsubscript{2}\textsuperscript{23}. The splitting energy between the Zr 3d\textsubscript{3/2} and Zr 3d\textsubscript{5/2} photoemission feature is ~2.4 eV, which agrees with the earlier reports\textsuperscript{34}.

For ceria-based metal oxides, the OSC property has a significant influence on several catalytic applications. Both the surface and bulk oxygen contribute to the measured OSC. In the case of pure ceria, the influence from these two factors is moderate due to small surface area and low bulk oxygen mobility. The OSC increases when ceria is doped with other metal ions. This is mainly due to the increased surface area and participation of bulk oxygen. The OSC of all the catalytic materials followed the order: CH > CL > CP > CZ. The respective OSC values are listed in Table 1. Interestingly, the CH sample shows the highest OSC among the investigated samples despite its low surface area. Here, Hf\textsuperscript{4+} is enriched in

Fig. 7—La 3d, Pr 3d, Hf 4f and Zr 3d XP spectra of Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} (CZ), Ce\textsubscript{x}Hf\textsubscript{1-x}O\textsubscript{2} (CH), Ce\textsubscript{x}Pr\textsubscript{1-x}O\textsubscript{2-δ} (CP) and Ce\textsubscript{x}La\textsubscript{1-x}O\textsubscript{2-δ} (CL) solid solutions calcined at 773 K.

Fig. 8—Conversion of CO (%) versus temperature (K) for Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} (CZ), Ce\textsubscript{x}Hf\textsubscript{1-x}O\textsubscript{2} (CH), Ce\textsubscript{x}Pr\textsubscript{1-x}O\textsubscript{2-δ} (CP) and Ce\textsubscript{x}La\textsubscript{1-x}O\textsubscript{2-δ} (CL) solid solutions calcined at 773 K.
the bulk, which facilitates the oxygen mobility. In the case of CL and CP, the presence of different valence metal ions enhances the OSC by creating oxygen vacancies via charge compensation mechanism. The existence of oxygen vacancies is confirmed from Raman analysis.

The catalytic study chosen for the present ceria-based solid solutions was CO oxidation due to their OSC property. The CO conversion over all the catalytic materials calcined at 773 K against the temperature is shown in the Fig. 8. The activity studies were also in line with the OSC values. The efficiency of the catalysts was measured in terms of the light-off-temperature \( T_{50} \). As expected, the CH solid solution showed better performance than other solid solutions. The 50 % conversion of CO for the CH, CL, CP and CZ samples was observed at 573, 635, 655 and 693 K, respectively. These results indicate that the CH solid solution is the most active for the title reaction among various samples.

Conclusions

Various doped ceria samples have been designed and prepared by a modified coprecipitation method and characterized by various state-of-the-art characterization techniques and examined for CO oxidation activity. Formation of solid solutions is confirmed from the structural and redox characterization techniques. With increasing calcination temperature, there is a gradual increase in the crystalline size and a decrease in the BET surface area as expected for all the catalysts due to the sintering phenomenon. The existence of oxygen vacancies is well understood from the Raman and UV–vis DRS studies. The designed nanosized solid solutions are highly promising for CO oxidation and related reactions. The CH sample exhibits the highest OSC among all the catalytic materials investigated. The CO activity over various catalysts follows the order: \( \text{CH} > \text{CL} > \text{CP} > \text{CZ} \). There is a lot of scope for designing a choice of morphological nanosized ceria-based mixed oxide catalysts with innovative properties useful for CO oxidation and related reactions.

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