Porous thin films toward bridging the material gap in heterogeneous catalysis

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Abstract An attempt has been made to bridge the material gap, existing between ideal single crystals and real-world powder nanocatalyst employed in surface science and heterogeneous catalysis, respectively. Simple wet chemical method (sol-gel and spin-coating deposition) has been applied to make continuous Ce₁₋ₓZrₓO₂ (x = 0–1) (CZ) thin films with uniform thickness (~40 nm) and smooth surface characteristics. Uniform thickness and surface smoothness of the films over a large area was supported by a variety of measurements. Molecular beam (MB) studies of O₂ adsorption on CZ surfaces reveals the oxygen storage capacity (OSC), and sticking coefficient increases from 400 to 800 K. Porous nature of Ce-rich CZ compositions enhances O₂ adsorption and OSC, predominantly due to O-diffusion and redox nature, even at 400 K. A good correlation exists between MB measurements made on CZ films for oxygen adsorption, and OSC, and ambient pressure CO oxidation on powder form of CZ; this demonstrates the large potential to bridge the material gap. CZ was particularly chosen as a model system for the present studies, since it has been well-studied and a correlation between surface science properties made on thin films and catalysis on powder CZ materials could be a litmus test.

Graphical abstract Ambient catalysis on ceria-zirconia nanocatalyst correlates well with surface properties measured through molecular beam on thin film and close the material gap.

Keywords Heterogeneous catalysis, Material gap, Ceria–zirconia, Thin film, Oxygen storage

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Introduction Traditionally, surface science methods employed ideal single-crystal materials to explore the fundamental aspects of heterogeneous catalysis under ideal/controlled conditions, like ultra high vacuum (UHV) and atomically clean surfaces.¹⁻⁹ Indeed, single-crystal surfaces that have been investigated by surface science method consist only catalytically active materials. However, real-world catalyst, in general, operates under high temperature and at ambient or high-pressure conditions.¹⁰⁻¹¹ Extremely different conditions most often lead to a "disconnect" between the findings from ideal and real-world conditions.²,³ This is further compounded by the complexity of real-world catalysts, by the addition of several components, such as co-catalyst, spacers, stabilizer, and promoters (electronic and structural).¹⁰⁻¹¹ How different components of a catalyst interact with each other remains to be explored by surface analysis methods in a reliable manner. Complexity of the real-world catalyst material and simplicity of the ideal single crystal leads to a huge material gap that exists between the two conditions. A possible way to address the above problem is to make the real-world catalyst in the form of thin films with surface qualities closer to that of single crystal, so as to represent and retain the complexities of the industrial catalysts and the simplicity of the single crystal simultaneously. This is expected to decrease the material gap to a significant level. Although, there could be complications such as diffusion of surface-adsorbed species into bulk, the above approach is, in our opinion, definitely worth in terms of reproducing the overall properties of real-world catalysts. In view of the net advantages, we ventured into making high-quality thin films by simple chemical method and characterized the same by physico-chemical, particularly surface science, means.

Over the years, surface science studies on single crystals and metal nanoparticle/metal oxide model surfaces lead to molecular level understanding of catalysis.¹⁻¹⁵ In this regard, one of the major challenges is to develop catalytically relevant thin films to bridge the material gap between surface science and heterogeneous catalysis. Such thin-film models are closer to the “real world” catalyst and more importantly when coupled with in situ surface sensitive techniques, such as molecular beam (MB) studies, ambient pressure photoelectron spectroscopy¹⁶⁻²⁰ could give more reliable and complex
kinetic data with further insights into the understanding of working of a catalyst. To make the attempt more meaningful, we chose a material that is catalytically active on its own without any other components. In fact, ceria–zirconia (CeO$_2$–ZrO$_2$) (CZ) is a material, widely employed for different applications, of our choice for this study. We report here on the simple chemical mean to prepare homogeneous thin films, with an exclusive aim to bridge the material gap to a significant extent. Further, present method can also be very well extended to make high-quality thin films for various applications, from window coating to solar cells for photovoltaics.

Although thin-film preparation reports are available in the literature, our method is significantly different, especially in achieving desirable surface qualities along with smooth surfaces as well as textural characteristics. In fact, thin films reported in this manuscript represent a typical industrial catalyst to a good extent. We also underscore the efforts made in the past along the idea of bridging the material gap. Niemantsverdriet et al., successfully employed spin-coating technique for creating metal-supported thin films for exploring molecular level details of reactions ranging from ethylene polymerization to Fischer–Tropsch synthesis. Similarly, sol–gel dip coating method employed by Brinker et al. is another convenient way for making high-quality thin films for mimicking catalytically relevant surfaces. However, many problems are yet to be answered, importantly the correlation between surface properties measured on thin films under ideal conditions and catalysis on corresponding powder materials and measured at ambient pressure and high temperatures.

CZ mixed oxide is a versatile material for various applications, such as solid oxide fuel cell (SOFC), three-way catalytic converter (TWC), and oxygen storage capacity (OSC). This is due to thermal stability or sinter resistivity, and the ability to retain surface area and OSC after high-temperature treatment, compared to pure ceria. Since catalysis aspects of CZ are well-known, this study employs the same to validate the methodology and the hypothesis involved. There are various thin-film preparation methods available such as sol–gel, dip coating, and physical vapor deposition. Among various methods, sol–gel synthesis with spin-coating method is a very simple and cost-effective method for the preparation of thin films. Indeed, the above combination is good for the deposition of thin homogeneous film over a large surface area. The advantage of the sol–gel method is that the particle of the film does not aggregate due to electrostatic repulsion irrespective of amorphous or crystalline nature of the film. Above all, this method could be practised in any wet chemical laboratory, since the requirements is very minimal.

Herein, we report the synthesis and thorough textural characterization of CZ thin films which could be utilized for several surface science studies for understanding the redox properties of this material under *operando* conditions. Further the present method of thin-film preparation also can be extended to variety of oxide surfaces. CO oxidation was evaluated in powder form to explore the redox nature of CZ catalysts. MB method was employed to measure the fundamental adsorption characteristics, such as sticking coefficient (s), bulk OSC, and how porosity influences the OSC.

### Experimental section

#### Preparation of Ce$_{1-x}$Zr$_x$O$_2$ thin films

Precursors for the sol–gel synthesis of CZ are cerium (III) nitrate (Ce(NO$_3$)$_3$·6H$_2$O, Loba Chemie) and zirconium oxychloride (ZrOCl$_2$·8H$_2$O, Thomas Backer), and ethanol (C$_2$H$_5$OH 99.9%, Thomas backer). 0.1 M solution of CZ is made by adding cerium (III) nitrate with zirconium oxychloride in required stoichiometric proportion in ethanol to form Ce$_{1-x}$Zr$_x$O$_2$. 0.434 g of cerium nitrate and 0.322 g of the zirconium oxychloride were added to 20 ml of ethanol to prepare Ce$_{1-x}$Zr$_x$O$_2$. The solution was stirred for 3 h. The clear transparent sol has been utilized for spin coating on Si wafer (99.9999% pure and 0.625-mm thick – MaTeck, Germany), before it is converted into gel. 5 µl of the above solution was taken in a micropipette and spun coated on 2.5 cm$^2$ area of Si wafer at a spinning speed of 8500 rpm for 120 s. The above procedure was followed for the preparation of thick film of about 500–600 nm, by repeating the spin-coating procedure for six–eight times. Thin/thick film was kept at 313 K in an oven for 48 h; subsequently, the temperature was raised to 373 K and heated for 12 h. Finally, the above films were heated to 773 K in a muffle furnace at a heating rate of 2 deg/min in static air and calcined for 1 h. Nanocrystalline thin film was also prepared directly on the Au–Pt grid by the same procedure adopted for Si wafer, especially for HRTEM measurements. High-quality pure CeO$_2$ thin films could not be prepared by the above procedure, and poor-quality CeO$_2$ films formed also peels off from the Si-surface relatively easily. Zr-addition to ceria dramatically improved the adhesion characteristics, and hence most of the results are given for CZ thin films.

The thickness of the film depends on many factors, such as spinning speed, viscosity of the solvent, and spin duration. Each factor has its influence on the thickness of the film. The optimum condition for the formation of the required thickness of the film was fixed by several attempts. Although several different conditions have been attempted, the best-quality thin films obtained are reported in this communication. In fact, there is scope to improve the surface quality of the films, by varying the viscosity of the solvent, spinning speed, etc.

#### Instrumental methods

Structure and crystallinity of the CZ thin and thick films were determined by PANalytical X’pert Pro dual goniometer diffractometer. Sample was rotated throughout the scan to minimize the preferential orientation. CuKα$_{	ext{I}}$ (1.5418 Å) radiation source with Ni filter was used for X-ray diffraction (XRD). Data collection was carried out using the flat sample holder in Bragg–Brentano geometry. Sample was scanned at a step size of 0.00835 deg/s. Thickness of the film was determined by the profilometer (Dektak profilometer). Thickness of CZ thin film was measured with the step distance of 200 nm per scan over a distance of about 2 mm. HRTEM (FEI – 300 kV instrument) analysis was carried out in a bright field mode with selected area electron diffraction pattern (SAED). Nanocrystalline thin film was drop casted after sonication on the carbon-coated copper grid. Further, as-prepared thin films on Au–Pt grid (Ted Pella, USA) were also employed for HRTEM measurements. Morphology of the thin film was...
determined by AFM at ambient conditions using a multi-mode scanning probe microscope installed with the nanoscope IV controller (Veeco Instrument Inc., Santa Barbara, CA.) and SEM (FEI, Quanta 200 3D). Energy dispersive X-ray (EDX) analysis was performed in the SEM system in the spot profile mode on the specific zone of thin film.\textsuperscript{49} N\textsubscript{2} adsorption–desorption isotherms for powder materials were recorded with Quantachrome Autosorb automated gas sorption system (NOVA 1200). Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area from the adsorption branch of the isotherm. Pore size distribution was calculated from nitrogen sorption isotherm using Barrett–Joyner–Halenda (BJH) method. XPS measurements have been made using a custom built ambient pressure XPS system from Prevac and equipped with VG Scienta SAX 100 emission controller monochromator using AlK\textalpha\ anode (1486.6 eV) in transmission lens mode.\textsuperscript{48,49} Photoelectrons are energy analyzed using VG Scienta’s R3000 differentially pumped analyzer. The spectra were recorded at pass energy of 50 eV. Deviations of the error in BE reported is within ±0.1 eV.

MB experiments reported here was performed in a homemade 12 L capacity molecular beam instrument (MBI)\textsuperscript{50} evacuated with a turbo-molecular drag pump to a base pressure of 2 × 10\textsuperscript{−10} Torr. MBI is equipped with a quadruple mass spectrometer (Pfeiffer, HiQuad\textsuperscript{51}, QMG 700 with QMA 410, 1—128 amu) for the detection of all the relevant species of the reaction, a sputter ion gun for cleaning the sample surface, a molecular beam douser for the beam generation and a shutter to allow or block the beam at will. More details are available in Refs\textsuperscript{50}. CZ film deposited on a square Si disk (12 × 12 mm\textsuperscript{2}) was mounted on niobium sample holder, which is spot-welded with tantalum wires for heating and the temperature is measured by a Cr–Al (K-type) thermocouple, spot-welded to the backside of the sample holder. The whole sample assembly can be resistively heated up to 1200 K, and cooled to 120 K with liquid nitrogen, controlled through a homemade temperature controller. A systematic set of kinetic studies of O\textsubscript{2} adsorption on CZ films was carried out as a function of temperature and CZ composition. Changes observed in the partial pressures of O\textsubscript{2} was then carried out as a function of temperature and CZ composition. Changes observed in the partial pressures of O\textsubscript{2} was then converted into parameters, such as sticking coefficient (s), rate of adsorption, OSC by following a calibration procedure described in our earlier publications.\textsuperscript{51,52} Results reported in the present manuscript is reproducible within an error margin of 10%. Results obtained in MBI on thin films are correlated to that of the results obtained on powder CZ materials at ambient pressure, and probably this is the first such report.

\textbf{CO oxidation}

CO oxidation was carried out in a fixed bed glass reactor under atmospheric pressure. Details of the reactor was described elsewhere,\textsuperscript{53} and given in supporting information (see SI-1 in supporting information). Reaction gas mixture (O\textsubscript{2}: CO: N\textsubscript{2} = 5:1:19) was allowed to flow at a rate of 25 ml/min in the fixed bed reactor containing 250 mg catalyst, and calculated GHSV was 6000 cm\textsuperscript{3}/g h. Catalytic activity was recorded in terms of percent conversion of CO to CO\textsubscript{2} molecule using the following equation (Equation 1).

\begin{equation}
X_{\text{CO}} = \left( \frac{P_{\text{CO,in}} - P_{\text{CO,out}}}{P_{\text{CO,in}}} \right) \times 100
\end{equation}

\textbf{Results and discussion}

\textbf{X-ray diffraction analysis}

Different composition of CZ solid-solution films formed by sol–gel method was characterized by XRD to determine the structure, and the results are shown in Figure 1a and b for thin and thick films, respectively. Thin films of Ce-rich compositions exhibit diffraction features from selective crystallographic planes and they are indexed to cubic (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes indicating the presence of cubic fluorite structure.\textsuperscript{54,55} Appearance of a broad peak around 2\(\theta\) = 28.36°, corresponds to (1 1 1) plane in CeO\textsubscript{2}. However, on Zr\textsuperscript{4+} doping in CeO\textsubscript{2}, there is a gradual shift in (1 1 1) peak toward higher angle, due to the smaller ionic radius of Zr\textsuperscript{4+} (0.84 Å) than Ce\textsuperscript{4+} (0.97 Å), and a consequent decrease in the cell parameter of the lattice. Smaller size Zr\textsuperscript{4+} compensates the structural stress generated by bigger Ce\textsuperscript{4+} and maintains structure. There is a shift in peak parameter which indicates the formation of solid solution that is clearly shown and indicated in Figure 1.

Lattice defects in the fluorite structure of CeO\textsubscript{2}, lattice occurs due to doping of Zr\textsuperscript{4+} in CeO\textsubscript{2}. Diffraction feature at 2\(\theta\) = 30.55° corresponds to the tetragonal (1 1 1) peak of pure ZrO\textsubscript{2}, thin film. Sharp and narrow features at 2\(\theta\) = 33.2, 47.65, and 56.52° corresponds to Si (2 0 0), Si (2 2 0), and Si (3 1 1) planes, respectively.\textsuperscript{56} Above Si features appears on all thin and thick films, arises from the substrate Si wafer and it has been employed as internal reference too. It is also to be mentioned that Si remains largely in elemental form, rather than SiO\textsubscript{2}, in spite of calcination at 773 K in air. Thick film (500–600 nm thick) diffraction data are shown in Figure 1b for comparison as well as confirmation. Indeed, a systematic shift in all cubic features.

Dotted line is shown to indicate the shift in diffraction features of cubic structure and they are guide to eye. Inset in b is shown to indicate the disordered mesoporosity with Ce-rich compositions of CZ powder material. Si features also reiterates that the substrate does not undergo oxidation, even after calcination at 773 K in air atmosphere.

((1 1 1), (2 2 0), and (3 1 1)) toward higher angle with increase in Zr-content is observed. However, predominant tetragonal phase for ZrO\textsubscript{2} was observed. Further, a decrease in full-width at half maximum (FWHM) of all characteristic features is observed with increasing Zr-content indicating an increase in the crystallite size from 5 to 27 nm. A careful comparison of Figure 1a and b suggests the presence of above features (2 0 0) and (3 1 1) and shift to higher angle is also discernible on thin films. Above all, XRD data confirms the solid-solution nature of CZ in thin and thick film forms. Inset in Figure 1b shows the low-angle XRD recorded with thick films. Ce-rich compositions show a single diffraction feature between 2\(\theta\) = 0.5° and 1.5° highlighting the disordered mesoporosity.\textsuperscript{55,59} Zr-rich CZ compositions does not show similar feature, since the surface area is low (see Table 1). Further, similar disordered mesoporous feature was not observed with thin films, due to small amount of material, and broad diffraction features of nanocrystalline material would subsides features due to mesoporosity.
Table 1 | Surface area, surface and bulk composition, and core level binding energy of CZ

| Material          | Surface area (m²/g) | Atom (%) | Binding energy (eV) |
|-------------------|---------------------|----------|--------------------|
|                   |                     | O  | Ce | Zr | O 1 s | Ce 3dₓᵧ | Zr 3dₓᵧ | Ce/Zr ratio |
| CeO₂              | 112                 | 62.3 | 37.6 | 0.0 | 530.2 | 883.3 | – | – |
| CeₓZr₁₋ₓO₂        | 102                 | 61.6 | 33.5 | 4.9 | 530.2 | 883.3 | 182.4 | 7.60 |
| CeₓZr₁₋ₓO₂        | 98                  | 61.8 | 25.7 | 12.5 | 530.3 | 883.3 | 182.4 | 2.20 |
| CeₓZr₁₋ₓO₂        | 92                  | 60.1 | 16.7 | 23.2 | 530.4 | 883.8 | 182.6 | 0.94 |
| CeₓZr₁₋ₓO₂        | 13                  | 58.1 | 10.9 | 31.0 | 530.5 | 883.2 | 182.6 | 0.43 |
| CeₓZr₁₋ₓO₂        | –                   | 56.1 | 4.3 | 39.6 | 530.5 | 883.2 | 182.6 | 0.02 |
| ZrO₂              | –                   | 58.9 | 0.0 | 41.1 | 530.6 | – | 182.7 | 0.00 |
XRD, TEM, profilometer, AFM, sorption isotherm results (Figures 1–3, SI 2–3) demonstrate the presence of disordered mesoporosity and the same aspect lead to rough surface characteristics in Ce-rich CZ films. It is expected that a porous material lead to rough surface. Nonetheless, the present preparation procedure leads to thin film with very low (2 nm) to rough (20–30 nm) surface characteristics; it is also to be underscored that the surface roughness is dependent on material’s composition.35 It is expected, in general, that such studies would lead to better quality thin films. Atom percent of Ce, Zr, and O was measured by EDX and the results are shown in Table 1. EDX analysis demonstrates a linear increase

AFM measurements have been repeated for films prepared in different batches and at different spots. Similar results are reproduced highlighting the reproducibility of the surface texture by sol–gel with spin-coating method. Surface profile of Si wafer and a reference single crystal (Ag (111)) are shown in SI-4. Surface roughness, especially spikes, observed on CZ thin films is partly attributed to that of Si wafer employed in the reported results. Further surface profiles of Ag (111) single crystal underscores a comparable surface quality of thin films reported in this communication.

Increase in surface roughness is attributed, in part, to the increasing porosity of thin films with increasing Ce-content. Figure 2 TEM images of the Ce$_{1-x}$Zr$_x$O$_2$ thin films. Images in a, c, and e panels were due to sample scraped from Si wafer and drop casted on TEM grid. Images in b, d, and f panels were recorded on thin films prepared on Pt–Au grid directly. a Disordered mesoporous structure of CeO$_2$. Homogeneous but porous surface was observed for $b$ Ce$_{0.9}$Zr$_{0.1}$O$_2$, and $d$ Ce$_{0.7}$Zr$_{0.3}$O$_2$. Nanorod structure was observed for $c$ Ce$_{0.9}$Zr$_{0.1}$O$_2$ and $e$ Ce$_{0.7}$Zr$_{0.3}$O$_2$. A single nanorod is shown in the inset of $e$. $f$ Lattice fringes observed on Ce$_{0.7}$Zr$_{0.3}$O$_2$. 

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no significant difference was observed. Binding energy (BE) of O 1s and 3d\textsubscript{5/2} core levels of Ce and Zr are given in Table 1. BE of O 1s core level varies within a small range of 530.2 to 530.6 eV, and corresponds to lattice oxygen in ceria.\textsuperscript{61–63} However, a gradual increase in the BE of O 1s from CeO\textsubscript{2} to ZrO\textsubscript{2} through CZ solid solution (Table 1) indicates a change in electronic interaction within CZ lattice. BE for the Zr 3d\textsubscript{5/2} core level in ZrO\textsubscript{2} (Table 1 and Figure SI-5) is observed at 182.7 eV, which is in agreement with the BE of Zr\textsuperscript{4+} reported in literature.\textsuperscript{64,65} As the Ce-content increases, a shift toward lower BE by 0.3 eV of Zr 3d\textsubscript{5/2} core level is observed with a marginal increase in the FWHM. This indicates a significantly altered electronic environment of Zr upon doping in CeO\textsubscript{2} lattice.

Ce 3d core level spectra are shown in Figure SI-5 for different CZ compositions. Nature of Ce 3d spectrum is very complex. However, \(v\) and \(u\) features are characteristic of Ce\textsuperscript{3+} oxidation state at 885.5 and 904.2 eV, and corresponds to the Ce (III) 3d\textsubscript{3/2}–O 2p\textsuperscript{−} configuration.\textsuperscript{66,67} Interestingly, thin film with 50% Ce-content shows considerable broadening of the peak at 883.4 eV (feature \(v\) for Ce(IV) 3d\textsubscript{3/2}–O 2p\textsuperscript{−} configuration) in the XPS than other Ce compositions. This broadening is attributed to the presence of Ce\textsuperscript{3+} at BE 885.5 eV (\(v\)) and its corresponding 3d\textsubscript{5/2} component at 904.0 eV (\(u\)). The formation of Ce\textsuperscript{3+} at high Zr loadings in the thin films is not surprising due to the defects structures (such as oxygen vacancies, Zr\textsuperscript{4+} on surface) present at nanosize regimes. Ce 3d peak intensity decreases nonlinearly with increasing Zr-content underscoring a change in surface composition (Table 1), while bulk composition, measured by EDX, shows a linear decrease in Ce-content with increasing Zr concentration. Indeed, high signal-to-noise ratio observed for Zr-containing films underscores an increase in Zr-content on the surface.

**Catalytic CO oxidation on ceria-zirconia**

Powder Ce\(_{1-x}\)Zr\(_x\)O\(_2\) materials prepared by sol–gel method were evaluated for catalytic activity for CO oxidation. CO oxidation activity of four different catalyst compositions are plotted as a function of temperature and shown in Figure 4. Indeed, we made an attempt to measure CO oxidation activity with CZ thin films; due to very small amount of material (<<1 mg) present in thin film, no significant activity was observed at ambient pressure.

No CO oxidation activity was observed up to 573 K for Ce\(_{0.3}\)Zr\(_{0.7}\)O\(_2\); gradually the CO oxidation to CO\(_2\) increases and about 21% CO conversion was observed at 673 K. An onset of catalytic activity was observed at 573 K for Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) with CO conversion of about 6.5%. An onset of catalytic activity was observed at lower temperature for other catalysts which depends on the Ce-content present in the catalyst. With increasing Ce (or decreasing Zr) content, CO oxidation activity also increases. 50% CO conversion to CO\(_2\) was observed at 600 and 555 K with Ce\(_{0.7}\)Zr\(_{0.3}\)O\(_2\) and Ce\(_{0.9}\)Zr\(_{0.1}\)O\(_2\) compositions, respectively. 100% CO conversion and CO\(_2\) production was observed at 635 K (620 K) for Ce\(_{0.9}\)Zr\(_{0.1}\)O\(_2\) (CeO\(_2\)) composition. Catalytic activity reported in Figure 4 is in good agreement with activity data reported earlier.\textsuperscript{68–71} High Zr-content in CZ materials requires high temperature to reach the same extent of CO\(_2\) production (say 10 or 50%) demonstrating the OSC and oxygen availability for CO oxidation is gradually
decreasing. However, it is to be reminded that Zr-containing CZ solid solution largely retains the surface area and OSC even after high-temperature treatment (>1000 K); while CeO₂ and less than 20% Zr-containing CZ shows a drastic reduction in surface area and OSC after high-temperature treatments. These aspects are thoroughly discussed in literature reports and hence not discussed further.

Oxidation catalytic activity of CZ mainly depends upon the redox oscillation between Ce⁴⁺ and Ce³⁺. Due to doping of smaller ionic radii Zr⁴⁺ (0.84 Å) in ceria lattice (Ce³⁺/Ce⁴⁺ – 1.14 Å/0.97 Å), there is a contraction in the lattice, and hence there is a decrease in bond length Ce–O of Ce–O–Zr. However, significant change observed in XRD (Figure 1) and XPS features (Figure SI-5) suggests valence fluctuations toward more Ce³⁺ with increasing Zr⁴⁺ content to compensate the ionic size changes. OSC represents the ability of the CZ solid solution to shift from Ce³⁺ to Ce⁴⁺ under oxidizing conditions with charge compensation facilitated via oxygen occupancy. Although all CZ films were subjected to similar calcination treatments, more Ce⁴⁺ found in Ce-rich films indicates the larger abundance of oxygen for reaction, than Zr-rich compositions, due to higher OSC in the former. Indeed, this is an apt system and worth exploring by surface sensitive methods, such as molecular beam methods. To investigate on bridging, the material gap aspects and an enhanced catalytic activity of ceria-rich composition, O₂ adsorption measurements have been made on CZ thin films by MBI as a function of temperature. Interestingly, a one-to-one correlation was found between ambient pressure CO oxidation activity and O₂ adsorption characteristics and OSC measured through MBI.
temperature and the kinetic results are shown in Figure 5a–c. Figure 5 shows the O₂ uptake from the O₂ molecular beam with respect to time as a function of temperature on three different CZ compositions. At \( t = 26 \) s, the O₂ molecular beam was turned on into the MBI chamber; however, the shutter is in place prevent any direct interaction between catalyst (thin film) surface with the O₂ molecular beam. At \( t = 38 \) s, the shutter was removed to allow the beam to interact directly with catalyst surface. A small amount of adsorption from the background cannot be ruled out between \( t = 26 \) and 38 s; however, this is within the error limit of 10% reported in this manuscript and not taken into account for any calculation. A finite drop in O₂ pressure at \( t = 38 \) s demonstrate the adsorption of oxygen on the catalyst surface (Figure 5a). Initial drop in pressure observed increases with increasing temperature for any given CZ composition. Initial decrease in pressure provides the initial sticking coefficient \( (s_0) \) of O₂ on the virgin surface, which will be discussed later. High rate of O₂ adsorption observed at the point of shutter opening decreases with increasing time of exposure at 400 K (Figure 5a). Indeed, this observation indicates the saturation of the surface layers with oxygen coverage \( (\theta) \). Shutter oscillation, by closing and opening the shutter for about 30 s, does not change the O₂ partial pressure supporting the saturation of catalyst surface (not shown). Nonetheless, the amount of O₂ adsorption required to saturate the surface layers increases with increasing temperature. Indeed, O₂ adsorption was observed up to \( t = 340 \) s for 600 K. A black trace shown with 600 K data is the reference experiment carried out after the saturation of surface (dark yellow trace); reference experiments are identical to that of the original experiments, except the shutter was not closed throughout the experiment. At 700 K, O₂ adsorption continues to be observed up to \( t = 400 \) s, albeit at a lower rate of adsorption, compared to the rate observed at \( t = 38 \) s. Surprisingly, initial rate of adsorption at 800 K was observed till the end of the experiment at \( t = 400 \) s; a simple comparison between the reference and the original experiments testifies this conclusion. Above observation demonstrates an increasing O₂ uptake at high temperatures, and this is attributed to O-diffusion into the subsurface layers and bulk.

It is also to be mentioned that between any two O₂ adsorption experiments, thin-film surface was reduced in hydrogen \((1 \times 10^{-7} \) Torr at 700 K) for 30 min. This is to regain the original surface characteristics and to avoid any cumulative oxygen coverage due to earlier experiment. It is well known that at high temperatures, Mars–van Krevelen (MvK) mechanism prevails in ceria and other oxide-based catalysts, which helps for oxygen diffusion into the bulk under oxidizing conditions.\(^75–77\) Indeed, MvK mechanism\(^75\) is responsible for increasing O₂ uptake at high temperatures. Oxidation of Ce³⁺ to Ce⁴⁺ requires atomic oxygen on the surface. Increasing amount of O₂ uptake observed at high temperatures is due to the diffusion of oxygen into subsurface layers and bulk, which helps to oxidize Ce³⁺ in those layers to Ce⁴⁺. Highly porous nature associated with Ce-rich compositions of CZ thin film helps for oxygen diffusion into the bulk CZ.

A comparison of O₂ uptake observed on Ce₀.7Zr₀.3O₂ (Figure 5b) and Ce₀.5Zr₀.5O₂ (Figure 5c) thin films to that of Ce₀.9Zr₀.1O₂ composition (Figure 5d) demonstrate few important points:
With increasing Zr-content, the O₂ uptake decreases at any given temperature. Indeed, marginal amount of O₂ adsorption was observed for Ce₀.₉Zr₀.₁O₂ up to 600 K suggesting the nature of catalyst, and catalyst surface is very different, compared to Ce₀.₅Zr₀.₅O₂. In addition, the initial rate of O₂ adsorption on virgin surfaces also decreases with increasing Zr-content for any given temperature. Both the above observations is indicating the nature of surface changes from highly oxidizable at high Ce-content to increasingly non-oxidizable (or reducible) with increasing Zr-content. Indeed, the textural characteristics of CZ thin films also changes from highly porous for Ce-rich compositions to less-porous material with Zr-rich compositions. A combination of increasingly non-oxidizable and non-porous nature with increasing Zr-content restricts the O₂ adsorption as well as O-diffusion into the sub-surface layers and bulk. Microscopy, profilometer, and sorption isotherm results fully support the above points (Figures 2–3; ESI-2–3) and indicates the porosity contributes dominantly in the Ce-rich compositions.

From Figure 5, we can calculate the extent of O₂ adsorption at various temperatures. Along with O₂ adsorption experiments, very similar reference measurements were also made (see 800 and 600 K data sets in Figure 5) in which shutter was in closed position throughout the experiment and hence direct interaction between O₂ MB and sample surface is fully avoided. Reference experiments were carried out for all temperatures after surface saturation. Figure 6 demonstrates the procedure adopted to calculate different quantities, such as total oxygen uptake s and initial s (s₀). Procedure reported by Liu et al.³⁸ also leads to very similar results; however, we adopted the subtraction method with reference experiment, due to simple procedure. It is to be noted that this method may not be applicable to molecules which adsorbs strongly on the chamber walls, such as NH₃ and H₂O. A simple subtraction between reference and direct adsorption experiments (Figure 6a) provides the extent of adsorption and rate of oxygen adsorption as a function of time (Figure 6b). Integration of the above area provides the total oxygen uptake or OSC (θ osc; Figure 6c). A plot of cumulative sum of θ osc and time indicates the first-order diffusion of O atoms into the subsurfaces/bulk.

Processed data shown in Figure 6 for Ce₀.₉Zr₀.₁O₂ at 600 K demonstrates the rate of adsorption; large extent of adsorption at the time of shutter opening indicating a high s. Similar rate of adsorption was maintained for about 35 s, after shutter opening and this is indicated by similar s observed up to t = 75 s. Indeed, this trend fully supports the precursor mediated adsorption,⁷⁹ ⁸⁰ and the same trend was observed at other temperatures too. However, adsorption rate begins to decline at t > 80 s and a gradual decrease was observed till t = 260 s, and no further net adsorption was observed at higher time. Total oxygen adsorption calculated was equal to 12 ± 1 ML, which is much higher than 1 ML, if adsorption was restricted only to top surface layer, indicating three different possibilities: (a) diffusion of oxygen into the subsurface layers, as well as (b) large number of surface atoms exposed to molecular beam from external and internal (pores) surfaces, due to highly porous nature of Ce₀.₉Zr₀.₁O₂; (c) Bulk diffusion of oxygen atoms occurs after a and/or b. In contrast to bulk CeO₂ single crystals, which corresponds to θ osc = 0.25 ML, about 1.5 order of magnitude higher θ osc observed experimentally at 600 K on Ce₀.₉Zr₀.₁O₂ fully supports the porous nature as well as oxygen diffusion into subsurface layers. Precursor mechanism suggested indicates the surface adsorption at the beginning of the experiment (t = 38–70 s) and simultaneous diffusion of oxygen into subsurface layers. A careful look at the decrease in the rate of oxygen adsorption at later time (t > 80 s) hints the saturation of surface layers, which makes the diffusion difficult. It is also to be remembered the pre-reduction treatment in H₂ for 30 min at 700 K, before any O₂ adsorption experiment. Pre-reduction treatment creates oxygen-vacancy sites and this could be another factor for oxygen adsorption; however, this factor remains the same for all experiments. Oxygen adsorption measured at 600 K on Ce₀.₅Zr₀.₅O₂ and Ce₀.₇Zr₀.₃O₂ compositions is also processed in the same manner, and the results are given in Figure SI-6. A notable decrease in cumulative oxygen coverage by one (two) order of magnitude from Ce₀.₉Zr₀.₁O₂ to Ce₀.₇Zr₀.₃O₂ (Ce₀.₅Zr₀.₅O₂) demonstrates the role of porosity in fast diffusion of oxygen atoms into the bulk, which facilitates MVK mechanism. Indeed, oxygen adsorption capacity decreases with increasing Zr-content is evident from this data analysis, and oxygen adsorption is increasingly restricted to the surface layers.

A detailed analysis of data at all temperatures demonstrates the contribution of both factors (oxygen diffusion and porosity) at all temperatures, but to a different extent as it depends on the CZ composition. Cumulative θ osc and s are shown in Figure 7 for Ce₀.₇Zr₀.₃O₂ thin film to complement the
data shown in Figure 6. Similar $s$ value observed for the first three monolayers of $\theta_O$ highlights the precursor mediated adsorption followed by the diffusion of oxygen atoms into the subsurface layers through porous network. Due to the large depth of irregular and vertical porous layers of about 30 nm (Figure 3), it would be difficult to quantify the depth of oxygen diffusion. Nonetheless, oxygen diffusion is likely to occur till the regular layers, which begins below the above porous layers. Peculiar and random oscillations in $s$ were observed from virgin surfaces to oxygen-saturated CZ layers. Extent of oscillation decreases with increasing smoothness or surface quality (Si-6) hinting the oscillation is due to porous nature of the thin films, and this requires further investigation.

Figure 8 shows the extent of $O_2$ adsorption on Ce$_{0.9}$Zr$_{0.1}$O$_2$ film at various temperatures, by following the procedure explained in Figure 6. We consider the results shown for 400 K as a reference experiment for adsorption exclusively on surfaces and with no oxygen diffusion, especially in view of zero oxidation activity at 400 K. The results shown in Figure 8 explain few important points and they are listed below: (a) A gradual increase in the oxygen adsorption or oxygen coverage (by integrating the dotted line area) at higher temperatures suggesting the onset of oxygen diffusion above 400 K. (b) Rate of oxygen adsorption on virgin surfaces, at the time of shutter removal at $t = 35$ s, gradually increases with temperature suggesting an increase in $s$ as well as $s$ at higher time. (c) Initial rate of adsorption was gradually extended for higher time as well, and the same increases with increasing temperature. Indeed, 800 K results shows the similar rate of adsorption from $t = 35$–240 s; even at $t > 240$ s, only a marginal decline in oxygen adsorption was recorded. This fully supports the precursor mediated adsorption followed by oxygen diffusion into subsurface/bulk layers. (d) High value of $s$ and rate of adsorption at high temperatures is due to oxygen diffusion, which is fully supported by point c. Some peculiar and random signal fluctuation was observed in the processed data, especially at high temperatures, is attributed to an increasing diffusion into subsurface layers, which is indicated for Figure 7. Further, a significant-to-large difference in substrate temperature and $O_2$ molecular beam at ambient temperature also could be partially responsible for fluctuations. $s_0$ and $\theta_{OSC}$ were calculated from the experimental data shown in Figure 9 for three CZ compositions. $s_0$ increases linearly between 400 and 800 K for all three CZ compositions. Although high $s_0$ was observed with Ce-rich composition, all three CZ compositions shows a similar increase in $s_0$ over the temperature range. This indicates a possibility of large number of oxygen vacancies on Ce-rich surfaces than Zr-rich compositions; porous nature of Ce-rich surfaces also helps for higher $s_0$.

$\theta_{OSC}$ calculated by integrating area under $O_2$ adsorption curve (Figure 9b) shows some interesting insights of oxygen interaction with CZ surfaces. $\theta_{OSC}$ increases linearly up to 600 K, and then it increases exponentially; indeed, 700 and 800 K data points measured from Figure 9a shows that the surfaces are not completely saturated for Ce$_{0.9}$Zr$_{0.1}$O$_2$, while other compositions shows saturation within the time frame of the experiment. Highly porous textural characteristics associated with Ce$_{0.9}$Zr$_{0.1}$O$_2$ indeed, accelerates oxygen diffusion to a predominant level. Increasing Zr-content changes toward less-porous nature and making it more dense material with lower rate of oxygen diffusion. In fact, high porous character with Ce-rich composition is the main reason for its sintering behavior at high temperatures. Insignificant OSC observed with high Zr-content (0.3 and 0.5) surfaces up to 600 K reiterates that these surfaces are less amenable for oxidation. Comparable OSC observed between Ce$_{0.9}$Zr$_{0.1}$O$_2$ and Ce$_{0.1}$Zr$_{0.9}$O$_2$ at 500 and 800 K, respectively, implies the nature of surface changes from oxidizable to non-oxidizable.

It is also to be mentioned that Si wafer is vulnerable for oxidation at high temperatures. Our efforts to explore silicon oxidation state by XPS were not successful, mainly due to limited probing depth (< 10 nm). Nonetheless, porous layers and underlying 30–40 nm thick layers of CZ would predominantly adsorb oxygen, and hence the probability of silicon oxidation is small under the present measurement conditions. Further, XRD results shows high-intensity Si features (Figure 1), suggesting the possibility of Si oxidation is limited. However, we do not want to rule out the oxidation of Si layers by consuming few percent of oxygen measured in MBI experiments (Figure 9b), especially at 700–800 K, due to continuous oxygen adsorption (Figure 8). Saturation of oxygen adsorption ≤ 600 K rules out the possibility of oxygen diffusion up to the Si substrate.

A comparison between CO oxidation activity, measured on powder catalyst at ambient pressure (Figure 4), and $\theta_{OSC}$ measured on thin film at high vacuum (Figure 9) demonstrates a good correlation between them. As $\theta_{OSC}$ increases, oxidation activity also increases. Early onset of CO oxidation (10% conversion) observed at 490 K, 50 and 100% CO conversion correlates well with $\theta_{OSC}$ observed at 500, 555, and 600 K, respectively, for Ce$_{0.9}$Zr$_{0.1}$O$_2$. Although OSC was found to increase at higher temperature, it is to be noted that the CO oxidation was carried out at ambient pressure, which is 8–9 orders of magnitude higher than the pressure in MB experimental conditions. 100% CO oxidation observed at 600 K suggests an enhancement in OSC at higher pressure and hence an increase in oxidation activity. Indeed, same reason holds good for other compositions too. For e.g., Ce$_{0.1}$Zr$_{0.9}$O$_2$ shows insignificant OSC at 600 K, whereas in powder form it shows 50% CO oxidation activity around the same temperature. Onset of catalytic activity for Ce$_{0.9}$Zr$_{0.1}$O$_2$ was observed at 573 K with little conversion of 6.5% is well correlated with O$_2$ uptake results as there is marginal O$_2$ adsorption takes place at 600 K and below this temperature generally no O$_2$ adsorption takes place as was observed from Figures 5c and 9b.

Conclusion

Uniform nanocrystalline ceria-zirconia (CZ) thin film was prepared by sol–gel synthesis and spin-coating combination. Above combination is a potential method to prepare the film in a nanothick regime with high surface quality and uniform morphology over a large area. The profilometer result confirms the thickness of the film in nanoregime. Uniform and high-quality surface characteristics were measured and corroborated by several methods.

Molecular beam studies have been carried out on CZ thin films under ideal surface science conditions and it provides the fundamental and necessary catalytic properties, such
as OSC, oxygen sticking coefficient on thin film surfaces. An increase in OSC along with oxygen sticking coefficient with increase in Ce-content in the CZ film was observed. Highly porous nature of Ce-rich CZ film is partly responsible for the above observations. CO oxidation catalytic activity measured at ambient pressure on powder CZ materials and found that the most active catalyst for CO oxidation is Ce$_3$Zr$_2$O$_7$. Indeed, a good correlation exists between the oxygen sticking coefficient, OSC measured on CZ thin films in molecular beam instrument at high vacuum, and CO oxidation activity measured on CZ powder materials at ambient pressure. This aspect needs to be evaluated with different or modified approach to ascertain the prevalence of MvK mechanism in CZ materials. In fact this helps to investigate and confirm the oxygen diffusion into the subsurfaces and bulk of CZ. In fact this helps to ascertain the prevalence of MvK mechanism in CZ materials. It is worth exploring the synthesis method reported herewith to prepare different catalyst materials and evaluate the same under operando conditions to bridge both material gap and pressure gap. This likely leads a better understanding of heterogeneous catalysis.

Supporting Information (SI) available
CO oxidation setup (SI-1), Textural properties (SI-2), AFM of CZ films (SI-3), Surface profiles of reference materials (SI-4), XPS measurement of Ce and Zr 3d core levels (SI-5), and oxygen uptake quantification (SI-6) is given in the SI.

Supplementary material
The supplementary material for this paper is available online at http://dx.doi.org/10.1080/2055074X.2015.1133269.

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