Investigative properties of CeO$_2$ doped with niobium: A combined characterization and DFT studies

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Abstract: Catalytic capacity of ceria mainly stems from a facile switch in the Ce oxidation states from $+4$ to $+4 - x$. While various experimental and computational studies pinpoint the reduction chemistry of Ce atom through the creation of oxygen vacancies, the analogous process when ceria surface is decorated with cations remains poorly understood. Where such results are available, a synergy between experimental and first principle calculation is scarce. Niobium materials are evolving and their use in catalysis is being widely investigated due to their high surface acidity and thermal and chemical stability. This study aims to report structural and electronic properties of various configurations of mixed Ce–Nb oxides and elaborates on factors that underpin potential catalytic improvements. Evaluations of the samples through X-ray diffraction (XRD), Fourier transform infrared (FTIR), N$_2$-adsorption–desorption, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and thermogravimetric (TGA) analyses are examined and discussed. First principles density functional theory (DFT) calculations provide structural features of the Ce–Nb solutions at low concentration of Nb via computing atomic charge distribution. Contraction in the lattice parameter after Nb doping was confirmed with both XRD and DFT results. SEM analysis reveals particle growth at the loading of 50 wt%. FTIR results established the Ce–Nb–O bond at 1,100 cm$^{-1}$ and the TGA analysis confirms the thermal stability of Nb-doped ceria. Tetrahedral O atoms demonstrate an increase in electronegativity and this in turn facilitates catalytic propensity of the material because the O atoms will exhibit higher affinity for adsorbed reactants. Cerium oxide (CeO$_2$) after Nb doping displays a noticeable band gap narrowing, confirming the possible improvement in the catalytic behavior. The 4d states of the Niobium pentoxide (Nb$_2$O$_5$) is found to fill up the 4f states of CeO$_2$ around the Fermi energy level promoting electrons excitation in the CeO$_2$. Reported electronic, structural, and thermal characteristics herein indicate promising catalytic applications of niobium-promoted ceria.

Keywords: ceria, niobium pentoxide, particle growth, 4f states

1 Introduction

Doped or pure metal oxides have been widely deployed to improve the catalytic activity and selectivity of both oxidation and reduction reactions through substitution of the cation of the base metal oxide with the cation of a second metal oxide [1]. Niobium pentoxide (Nb$_2$O$_5$) exhibits amorphous or crystalline structures, and possesses wide band gap, good chemical stability, efficient electron injection efficiency, and efficiently serves as acid catalyst for the production of a wide array of chemicals and fuels [2,3]. Defected Nb$_2$O$_5$ synthesized either through incorporation of ad-atoms or oxygen exhibits promising catalytic capacity in nicher industrial operations [4,5]. The promotional effect of Nb$_2$O$_5$ as a second metal or metal oxide in operations such as catalysis is gaining attention due to the relative ease of their reaction with other metal oxides to form mixed metal oxide phases with a complex structure [6]. This complex structure could result from the distortion of niobium oxide deposited on the parent metal or originated from the actual disruption of the chemical bonds at the surface of the parent oxide [1,7]. In either case, electron transfer occurs, and the active centers are the dopants or the oxygen atoms close to the dopants, leading to a material behavior that departs from the pure metal oxides [1].
The synthesis of a truly homogenous-mixed oxide with a profound improvement in catalytic activity is a channeling endeavor. The presence of other materials such as impurities in the precursors might as well contribute to the observed changes in their performance [1].

On the other hand, cerium oxide (CeO$_2$) enjoys various applications due to the inherent electrical, chemical, and physical properties [8]. Stand-alone CeO$_2$ has been effective in numerous catalytic applications, most prominently in the semi-hydrogenation of alkenes to alkenes [9], and water and gas splitting reactions [10]. Due to their profound redox properties, efficient oxygen storage ability, and low cost, CeO$_2$ has been deployed as mixed oxide catalyst for enhanced performance [11]. Among the various metal oxides, CeO$_2$ offers high interaction with Nb$_2$O$_5$ [7]. As a reducible oxide, CeO$_2$ could switch oxidation from Ce$^{4+}$ to a reduced form as Ce$^{3+}$ by interaction with the Nb$^{5+}$ of the niobium oxide [12]. This phenomenon induces a notable effect on the chemistry of the mixed oxide formed. The selective catalytic reduction (SCR) performance of CeO$_2$ displays significant improvement when doped with niobium oxide owing to the strong acidity and redox ability of the latter [12]. A 100% selectivity to N$_2$ was achieved for NO reduction in NH$_3$–SCR reaction when cerium was doped with niobium [13–15].

To provide an atomic base insight into the observed catalytic improvement of mixed Ce–Nb oxides, it is essential to comprehend governing structural and electronic attributes of these configurations. For instance, doping metal oxides that display dissimilar cation–oxygen bond lengths affects their catalytic behavior; however, a robust evaluation of such scenario necessitates materials modeling via density functional theory (DFT) calculations [1]. Experimentally, the various available spectroscopy techniques could be used to underpin structural changes from the pure metal oxides after doping. Literature provides a detailed account on pure oxide forms of CeO$_2$ and Nb$_2$O$_5$ [16]. However, to the best of our knowledge, studies that report properties of the mixed Ce–Nb oxides from both experimental and DFT studies are rather scarce.

Thus, this article aims to evaluate the energetic, atomic, and electronic features of clean, defect-free, and doped CeO$_2$(111) and Nb$_2$O$_5$(111) structures using DFT and to confirm the formation of the mixed oxides using material characterization techniques. The main motivation behind this work is to illustrate attributes that may improve the catalytic activity of Nb–Ce–O materials.

2 Materials and methods

2.1 Materials preparation

Cerium–niobium mixed oxide samples were prepared with the incipient wet-impregnation method. The cerium(IV) oxide (Sigma Aldrich; 99.99%) was first dried in an oven for 2 h at 200°C to drive out moisture. Nb$_2$O$_5$ (Sigma Aldrich; 99.99%) serves as the precursor with the loading of Nb$_2$O$_5$ varied from 1.5, 2.5, 3.0, and 50 wt%. Aqueous solution of the samples was added to an identified mass of CeO$_2$. The resulting mixtures were heated at 70°C for 30 min on a magnetic stirrer at a stirring rate of 150 rpm. The samples were then dried overnight at 100°C. Calcination was carried out under the flow of air for 4 h at 550°C with a heating rate of 10°C/min. Powder X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (PANalytical Instrument, X’Pert Powder, Philips, Holland) equipped with CuK radiation ($k = 1.540598$ nm) and operated at 45 mV and 40 mA. The scanning was performed within 2θ range of 10–80° with a step size of 0.02°/min. A Quantachrome Instrument (NOVAtouch NT 2LX, USA) performed the N$_2$ adsorption and desorption experiment. All the catalyst samples were outgassed at 300°C for 3 h utilizing liquid nitrogen (N$_2$) at the temperature of −196°C. The Brunauer–Emmett–Teller (BET) surface areas were computed by employing partial pressure ($P/P_0$) in the ranges of 0.02–0.35, which are reliable based on the obtained C constant values [17].

The Barrett–Joyner–Halenda (BJH) was used to determine the average pore size and the pore size distribution with $P/P_0$ range of the desorption branches of 0.80–0.35. The Fourier Transform Infrared (FTIR) analysis was performed with FTIR Spectrometer (Jasco Corporation, Japan). Before analysis, the catalyst samples were mixed with potassium bromide (KBr; Sigma Aldrich) initially dried in the oven at 105°C in order to eliminate possible water interference. The recorded spectra were varied in the range of 4,000–400 cm$^{-1}$. A multifunctional general-purpose scanning electron microscope (SEM) by (JEOL JSM. 6010 PLUS/LA) integrated with Energy Dispersive Spectroscope (EDS) was used to perform surface and elemental analyses. The instrument is equipped with an auto-coater which enables the sample to be coated with gold particles before analysis. In order to investigate the thermal stability and the composition of the pure and prepared samples, Thermogravimetric analysis (TGA) was carried out with (TGA Q50 V20.10 Build 36 analyzer). The temperature was changed from 0 to 650°C at a heating rate of 10°C/min under the flow of nitrogen.
2.2 Computational details

The CASTEP code performs all the structural optimizations and energy estimations [18] within the DFT framework to examine the properties of CeO$_2$ and Nb$_2$O$_5$. Generalized gradient approximation is employed to obtain precise structural parameters and the exchange–correlation function of Perdew–Burke–Ernzerhof is adopted in the local density approximation. On the fly pseudopotential describes the interaction between the valence electron and the ion core. The energy of the convergence tolerance is set at 0.001 eV/atom. The maximum force, maximum stress, and maximum displacement are set at 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. To describe the on-site Coulomb interactions for the Nb 4d and Ce 4f states, effective Hubbard $U$ parameters of 3.0 and 4.5 eV are employed, respectively. This choice of $U$ value follows from previous theoretical investigations [19,20]. The plane wave cutoff energy amounts to 320 eV and a $k$-point sampling of $2 \times 2 \times 1$ was generated by the Monkhorst–Pack scheme. The doping is performed by substituting the Ce atom of the CeO$_2$ with Nb, and the electronic changes are examined. Appropriate choice of dopant concentration is essential to preserve the catalytic activity of the materials. Low concentration of dopant is preferred over the high value because the recombination rate of electron/hole pair is decreased and the reaction rate such as photodegradation is improved [21]. Thus, computations are performed by replacing the Ce atom with one Nb atom.

3 Results and discussion

3.1 XRD patterns

The diffraction patterns observed for the referenced pure CeO$_2$ and all the prepared catalysts are shown in Figure 1. Conventionally, doped oxide displays a similar structure as that of the host oxide [1]. The patterns observed are typical of the pure fluorite cubic CeO$_2$ structure (JCPDS 43-1002) [22]. All except one (50 wt% loading) of the XRD results show an absence of the peaks associated with Nb-containing species. This might be due to either low loading or high dispersion. In our experiment, the Nb loading exceeded the optimum solubility weight of Nb (1.4 wt%) on CeO$_2$, appropriately, the absence of Nb peaks is ascribed to a high dispersion [23]. The dispersed state of Nb$_2$O$_5$ phase on the CeO$_2$ is in the NbO$_3$ form and the presence as metallic Nb cannot be excluded.

This signifies that the crystallinity of the CeO$_2$ is not distorted with Nb incorporation [1,22,24,25]. However, at a 50.0 wt% Nb loading, the effect of loading is observable with the formation of two new peaks from Nb$_2$O$_5$ around 22° and 50°.

The lattice parameters were computed from the XRD peaks in order to investigate the doping effect. The inter-planar spacing was evaluated with the Bragg’s law, equation (1), and the lattice parameter was calculated with equation (2). The crystallite sizes of the samples were computed with the Scherrer’s equation (equation (3)) by utilizing the full width at half maximum (FWHM).

\[
d = \frac{n\lambda}{2\sin \theta'}, \tag{1}
\]

\[
a = d \cdot \sqrt{h^2 + k^2 + l^2}, \tag{2}
\]

\[
D = \frac{k\lambda}{\beta \cos \theta'}, \tag{3}
\]

where $d$ signifies the inter-planar spacing, $\lambda$ is the wavelength, $a$ is the lattice parameter, $h$, $k$, and $l$ denote the miller indices, $\beta$ is the FWHM, $k$ is the Scherrer constant, $D$ represents the crystallite size, and $\theta$ stands for the Bragg or diffraction angle. The equations were applied to the peak highest intensity, CeO$_2$(111) plane. The results obtained are shown in Tables 1–3. The pure CeO$_2$ gave the highest value of the lattice parameter 5.410 Å which is in good agreement with previous experimental values of 5.410 Å [26,27] and computed values of 5.490 Å [28].

The doped samples assume lower lattice parameter. This decrease in value is associated with the contraction of the CeO$_2$ lattice, and the possible substitution of the Ce$^{4+}$ by the Nb$^{5+}$ [29,30]. This is due to the lower ionic
radius of niobium (0.64 Å) compared with cerium (0.97 Å) which induced the contraction of the crystal lattice [31]. The incorporation of neodymium (Nd) into CeO₂ expands the crystal lattice owing to the higher ionic radius of Ce⁴⁺ (0.970 Å) when compared to Nd³⁺ (1.109 Å) [10]. The shifts in lattice parameter are vital in confirming the formation of doped oxide [1]. This assertion is further corroborated with the result of the crystallite size enlisted in Table 3. Although significant variations in the crystallite size of all the samples were not prevalent, (maximum difference of ±1.8), this difference further supports the formation of doped oxides. This is in agreement with the findings of Amarsingh [31] that the substitution of pentavalent ions such as Nb in CeO₂ does not initiate significant reduction in the crystallite size. Thus, pure CeO₂ affords the highest size of 26.154 nm. Additionally, the minute reduction in the crystallite size suggests that the incorporation of Nb into CeO₂ crystal inhibits the grain growth of the CeO₂, as later shown with the SEM results [25]. However, this assertion remains valid at low loading. Increasing the Nb loading was found to affect the CeO₂ phase, with the formation of new peaks at the highest loading. The slight increase in the intensity at the (311) plane corresponding to the peaks at 2θ = 56.37° confirms that the amorphous Nb₂O₅ is incorporated into the CeO₂ crystals and that the CeO₂ content is decreased, compensating for the minute decrease in the crystallinity [13,32].

### 3.2 FTIR analysis

The FTIR results present the possible presence of the Nb phases on the CeO₂ as shown in Figure 2. All the Nd-doped CeO₂ samples show the absence of the carboxylic groups C=O stretching at 1,700 cm⁻¹ and C–O asymmetric stretching at 1,380 cm⁻¹ that are typical of Nb containing species. This is indicative that the sample contains only Nb₂O₅ [17]. The spectra of the Nb₂O₅ exhibits the surface Nb=O stretches at the region of 1,050–948 cm⁻¹ [33]. The Nb–O peak at 929.52 cm⁻¹ denotes the stretching vibrations of Nb–O of Nb₂O₅ units and the Nb–O peak at 880 cm⁻¹ is due to angular vibrations [33]. In addition to the OH groups on pure CeO₂, the characteristic stretching vibrational peaks associated with the Ce–O bond is observed around 590 cm⁻¹ [34].

The characteristic peaks associated with the lattice vibrations of metal–oxygen bonds are observed for the

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### Table 1: Miller indices of the XRD peaks

| N | 2θ  | θ   | sinθ | sin²θ | Ratio | Index | D   |
|---|-----|-----|------|-------|-------|-------|-----|
| 1 | 62.94 | 14.270 | 0.0465 | 0.0216 | 3      | 111   | 3.12384 |
| 2 | 62.11 | 14.555 | 0.0489 | 0.0238 | 4      | 200   | 2.70270 |
| 3 | 62.37 | 14.850 | 0.0513 | 0.0264 | 8      | 400   | 1.91020 |
| 4 | 62.73 | 14.150 | 0.0473 | 0.0224 | 11     | 311   | 1.63032 |
| 5 | 62.91 | 14.350 | 0.0493 | 0.0245 | 12     | 222   | 1.55997 |
| 6 | 62.35 | 14.450 | 0.0513 | 0.0264 | 16     | 400   | 1.35040 |
| 7 | 62.73 | 14.850 | 0.0473 | 0.0224 | 19     | 331   | 1.24053 |
| 8 | 62.91 | 14.350 | 0.0493 | 0.0245 | 20     | 420   | 1.20841 |

### Table 2: Inter-plane spacing and lattice parameters of the prepared samples

| Sample          | 2θ  | θ   | D   | A   |
|-----------------|-----|-----|-----|-----|
| Pure CeO₂       | 28.54 | 14.270 | 3.12384 | 5.41065 |
| 1.5 wt% Nb–CeO₂ | 28.59 | 14.295 | 3.11849 | 5.40138 |
| 2.5 wt% Nb–CeO₂ | 28.65 | 14.325 | 3.11209 | 5.39031 |
| 3.0 wt% Nb–CeO₂ | 28.66 | 14.330 | 3.11103 | 5.38846 |
| 50 wt% Nb–CeO₂  | 28.70 | 14.350 | 3.10679 | 5.38111 |

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### Table 3: Crystallite size of the prepared samples

| Sample          | Crystallite size (nm) |
|-----------------|-----------------------|
| CeO₂            | 26.154                |
| 1.5 wt% Nb–CeO₂ | 24.354                |
| 2.5 wt% Nb–CeO₂ | 25.328                |
| 3.0 wt% Nb–CeO₂ | 25.932                |
| 50 wt% Nb–CeO₂  | 28.707                |

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Figure 2: FTIR spectral of the pure and doped samples.
Nb-doped samples with the increase in the loading. The peak observed around 1,123 cm$^{-1}$ is typical of Ce–Nb–O spectral which affirms the formation of doped mixed oxide sample [35]. With the additional loading, the Nb=O disappeared (at 50 wt% Nb–CeO$_2$), and the observed broadened peak of Nb–O shows the incorporation of the niobium ions into the CeO$_2$ lattice, resulting in little distortion [23,31,36]. In comparison to the pure CeO$_2$ spectra, the stretching mode vibration of Ce–O at around 590 cm$^{-1}$ in the other samples shifted to a lower wavenumber. This indicates the weakening of this bond in favor of the formation of the Ce–Nb–O linkage [31,37].

The intensity of the peak of Nb–O identified at wavenumber of 929.52 cm$^{-1}$ on the pure Nb$_2$O$_5$ sample becomes lessened as the Nb$_2$O$_5$ loading was increased from 1.5 wt% to 3.0 wt%. This shows that the further addition of Nb might facilitate the reduction in NbO to metallic Nb [13]. Thus, the interaction of Nb with CeO$_2$ is strengthened, while the interaction between Nb–O and CeO$_2$ is weakened. Also, higher Nb loading enhances both the Brønsted acidity and strong Lewis acidity. These acidic sites serve as the active centers for surface-assisted reaction and are associated with the Nb–O and Nb–O–Nb bonds present in NbOx species. Increasing Nb loading beyond the dispersion capacity will limit the formation of the Brønsted and Lewis acid sites [13]. However, as observed at 50 wt% loading, the broad and intense peak of NbO reappeared. This suggests that a very high loading diminishes the catalytic activity of cerium-niobium mixed oxide. Exceeding the monolayer coverage will lead to the formation of multilayer inactive NbOx.

3.3 $N_2$ adsorption–desorption

The isotherms plot and the structural properties of the prepared samples obtained with the $N_2$ adsorption–desorption analysis are depicted in Figure 3 and Table 4, respectively. All the prepared sample shows a typical type IV isotherms associated with the capillary condensation in mesopores. The pure samples show the H1 type hysteresis loop and the addition of Nb to CeO$_2$ preserves the H1 type. This observation is consistent with the earlier

Figure 3: $N_2$ adsorption–desorption isotherms for the prepared samples. (a) CeO$_2$; (b) Nb$_2$O$_5$; (c) 3 wt% doped, and (d) 50 wt% doped Nb–CeO$_2$. 
report involving Nb–CeO₂-doped catalysts [38]. The values of the pore diameter obtained for all the samples show a mesoporous structure. The pore cerium oxide gives a particle size of 3.4 nm in agreement with the values between 3.24–3.89 nm earlier reported for ceria prepared via precipitation method [39]. Likewise, the pore volume obtained for all the samples is approximately constant despite increasing the Nb loading, suggesting the samples entail a narrow particle size distribution [40]. However, the observable differences result from the evaluated BET surface area. The Nb₂O₅ gives the lowest surface area of 38.451 m²/g, while a value of 50.437 m²/g is obtained for CeO₂. Loading the CeO₂ with Nb decreases the surface area from 43.815 m²/g at 1.5 wt% Nb–CeO₂ to 40.833 m²/g at 50 wt% Nb–CeO₂. The minimal reduction observed among the doped materials in the BET surface area might have evolved from the blocking effect on the sample pores due to the incorporation of the Nb on the samples’ inter-particle volume. This is supported by the slight decrease shown in the pore volume [13]. Similar results have been reported for the nanostructured CeO₂ doped with platinum [40].

### 3.4 SEM and EDS analyses

The elemental composition, morphology, and shape of the prepared samples are analyzed with the SEM. The SEM images and EDS mapping of the cerium oxide and the niobium-doped cerium oxide are displayed in Figures 4 and 5. The pure cerium particles show cerium as fine and well dispersed, with uniform morphology and with the absence of any specific shape [24,41]. This fine structure suggests that CeO₂ is able to withstand the operational temperature.

![Figure 4: SEM images and EDS mapping obtained for the materials (a) CeO₂; (b) Nb₂O₅; (c) 2.5 wt% doped, (d) 3 wt% doped, and (e) 50 wt% doped Nb–CeO₂.](image-url)
employed during the calcination process [39]. The morphology of the pure Nb₂O₅ discloses fine particles together with agglomerated and sponge shaped particles. The doped samples present similar structure as that of the pure CeO₂ sample at low to moderate loading of 1.5–3.0 wt% of Nb.

Figure 4 demonstrates the EDS mapping of the prepared samples. CeO₂ and Nb₂O₅ reveals a homogenous well dispersed atoms of the constituent elements. The addition of 1.5 and 2.5 wt% of Nb do not show any presence of Nb atoms in the mapping analysis (Figure 4c, only 2.5 wt% loading is present). However, as confirmed by the EDS profiles later, there is the presence of Nb atoms at this loading values. This can be attributed to the very high dispersion and incorporation of the Nb atoms into the CeO₂ [42]. Increasing the loading to 3 wt%, Nb atoms are detected by the EDS mapping (not too conspicuous), and the atoms are well dispersed over the CeO₂ surface. This further confirms that the non-detection of the Nb atoms at lower loading cannot solely be attributed to complete absence of Nb atoms. The Nb atoms becomes more feasible at 50 wt%, with the high concentration at the corner of the sample. This might have resulted from the possible Nb agglomeration due to high loading. Additionally, the high dispersion observed at low loading of Nb loading together with the reduction in the calculated values of crystallite size indicates the strong interaction between the CeO₂ and Nb₂O₅ oxides of the doped samples [43]. The EDS profiles confirm the presence of only cerium, niobium, and oxygen on all samples. For the pure samples, the identified oxides are CeO₂ and Nb₂O₅, confirming the purity of the starting materials. Weak peaks associated with Nb atoms are observed on the doped CeO₂ samples.

Additionally, the quantitative EDS analysis reveals that increase in the loading weight gives a corresponding increase in the amount of Nb deposited on the CeO₂. The % atomic composition predicts the formula for the 1.5 wt%, 2.5 wt%, 3.0 wt%, and 50.0 wt% samples as Ce₀.985Nb₀.015O₂, Ce₀.975Nb₀.025O₂, Ce₀.97Nb₀.03O₂, and Ce₀.5Nb₀.5O₂, respectively. This further affirms the incorporation of the Nb into the CeO₂ lattice and the reduction in the Ce atom.

### 3.5 TGA analysis

Figure 6 shows the TGA measurements obtained for pure CeO₂ and Nb₂O₅ samples. In order to determine the thermal effects on the doped oxides, only samples with 3.0 and 50 wt% are considered. Pure CeO₂ shows a mass loss of about 1.4%, and equilibrium is reached at about 350°C. This loss is ascribed to the H₂O present in the sample surface [10]. This result is in good agreement with mass loss of about 1.3% and 350°C that was reported earlier [10]. Similarly, the doped samples show a mass
loss at about 1.1%, suggesting that the crystallinity of CeO$_2$ is preserved after the doping [44]. The impregnation of Nb in CeO$_2$ is found to affect the thermal stability of the doped samples, reducing the mass loss as the temperature is raised [45,46]. This is corroborated with the result of enhanced thermal stability obtained for the pure Nb$_2$O$_5$ samples. Two stages of mass loss are observed for the Nb$_2$O$_5$. Stage 1 (about 1.5% loss), the interval 50–450°C encompasses the elimination of the adsorbed H$_2$O, and stage 2 (6.2% loss) between 450 and 600°C signifies the loss of structural H$_2$O [44,47,48]. As observed, after about 450°C, all the samples assumed a steady value, thus the calcination temperature was kept below 600°C.

### 3.6 CeO$_2$ structure and charge distribution analysis

The effect of Nb content on CeO$_2$ has been evaluated with the DFT calculations. The electronic interaction and distribution are examined on the CeO$_2$(111) structure. CeO$_2$ exhibits a fluorite crystallographic structure with the Ce atoms located at the face center cubic (fcc) positions, while the O atoms prefer the tetrahedral sites. Addition of the Nb atoms preserves the fluorite structure, a result previously confirmed with our XRD analysis.

Figure 7 shows the optimized geometries of the bulk and surface structures of both the perfect CeO$_2$(111) and niobium-doped structures. The optimized bulk and surface geometries of Nb$_2$O$_5$(111) are likewise shown. The lattice parameter of the perfect CeO$_2$ stands at 5.464 Å and slightly shrinks to 5.284 Å after Nb doping. This reduction trend agrees with the XRD prediction where the lattice parameters reduce with increase in the loading weight of Nb. Although, our calculation result gives a sizeable reduction in the lattice parameter as compared with XRD values, both results confirm that Nb doping reduces the lattice parameter [1].

Table 5 enlists the bond length of the considered structures. Generally, Ce–O bond distance is used to validate the possible expansion or contraction of the crystal lattice of doped materials. Ionic radius of dopants is essential in determining the behavior of the bond length. Earlier reports have provided contrasting observation. For instance, CeO$_2$ doped with Yb, Er, and Y presents a similar Ce–O and dopant-oxygen distances, while for Gd, Sm, La dopants, observed distances were higher for the dopant-oxygen than the Ce–O distance. It is expected that dopants with higher ionic radius than Ce should induce higher dopant-oxygen distance, and dopants having lesser ionic radius should give lesser bond distance. This is not always true, because similar distance was observed for Ce–O and Yb–O, Er–O and Y–O, despite Yb, Er, and Y possessing higher ionic radius [49].

Perfect CeO$_2$ shows a Ce–O bond length of 2.370 Å, which is in a perfect agreement with 2.352 Å and 2.340 Å reported previously [10,27]. The Ce–O distance in the perfect CeO$_2$ demonstrates an overshoot of 0.073 Å in the bulk as compared to the surface. In comparison with the doped structures, the Ce–O distance shortens by 0.011 Å for the bulk, while an increase of 0.066 Å is observed for the surface (in reference to experimentally measured value for the bulk CeO$_2$). The Nb–O bond...
distance amounts to 2.287 Å for the bulk and 2.127 Å for the surface, which reasonably agrees with the experimentally reported values of 1.73–2.26 Å [50]. The Nb–O distance in the pure Nb2O5 structure is shorter in the surface than the corresponding value in the bulk by 0.16 Å. After doping, the Nb–O is found to reduce by 0.096 Å for the bulk and by 0.187 Å for the surface.

Thus, our result demonstrates that doping Ce with Nb ensures the reduction in the Ce–O and Nb–O distances, which corroborates the result of the lattice parameter. The contraction in the bond length of both Ce–O and Nb–O bonds obtained with DFT is indicative of the contraction of the oxygen atoms and not the Nb environment itself.

Figure 8 shows a disparate charge distribution for the bulk and surface structures of the perfect and Nb-doped CeO2. The perfect bulk structure shows that the atomic charge on O atom are constant at −0.330 e, while the Ce atom maintains a positive charge of 0.660 e throughout the structure. Introducing the Nb atom to the bulk structure reveals that the electronegativity values of the tetrahedral O atoms are improved with a charge increase of 0.01 e. This is expected to improve the catalytic tendency of the material since the O atoms will assume more affinity for adsorbed reactant [51]. Simultaneously, after doping, the Ce atoms are less positively charged (i.e., there is presence of more electrons), suggesting that the Nb atoms derives more reduction on the two Ce atoms bounding the tetrahedral O atoms, engendering the Ce atoms more reactive. The edge and corner Ce atoms surrounding the bulk CeO2 are likewise reduced to that obtained for the perfect bulk structure. This is a desirable result for improved catalyst performance, ratifying the possible interswitch of Ce atom oxidation state between Ce4+ to Ce4-x [10].

Table 5: Bond distance (Å) of the optimized structures

| Bond type | Perfect CeO2 (bulk) | Perfect CeO2 (surface) | Doped CeO2 bulk | Doped CeO2 surface | Perfect Nb2O5 bulk | Perfect Nb2O5 surface |
|-----------|---------------------|------------------------|-----------------|---------------------|-------------------|----------------------|
| Ce–O      | 2.443               | 2.370                  | 2.432           | 2.436               | —                 | —                    |
| Nb–O      | —                   | —                      | 2.191           | 1.940               | 2.287             | 2.127                |
3.7 Analysis of total and partial density of states (TDOS and PDOS) of CeO$_2$ and Nb$_2$O$_5$

The TDOS and the PDOS are calculated to explicate the electronic states of the prepared samples and to provide information germane to contribution of the orbitals around the Fermi energy level ($E_f = 0$ eV, represented by the dotted lines) [52]. Figure 9 shows the DOS of both the bulk and surface un-doped CeO$_2$. The band width is examined between $-5$ and $-20$ eV for all structures. The pure bulk CeO$_2$ reveals the concentration of electrons with a narrow band within the $0$–$5$ eV region, and a relative electron distribution at a higher energy. Our calculated band gap of Nb$_2$O$_5$ amounts to 3.037 eV, a value that is in a very good accord with the corresponding experimental measurement of 3.09 eV [21]. The electron concentration in the doped sample, Nb–CeO$_2$, shifts to a higher energy level and demonstrates a band gap of 1.086 eV (that is, a reduction of 0.614 eV), in a close agreement with the analogous experimental value which shows a reduction of 0.59 eV in the band gap for Pb–CeO$_2$ system [53]. This reveals that lower unoccupied molecular orbital and higher unoccupied molecular orbital are shortened, accounting for improved electron excitation into the conduction band. The band gap reduction observed shows that Nb will significantly promote the optical and catalytic properties of the mixed oxide [21].

Figure 10 portrays the PDOS of the prepared samples. The O 2s and Ce 3p states lie at the lowest energy band (not shown) and the O 2p and Ce 4f states interact around the Fermi energy level with a hybridization of the Ce 5d and Ce 4f states [54]. The bandwidth of the O 2p band is 4.2 eV and the Ce 4f states exhibit a spacing of 1.5 eV which agrees with the computational values of 4.5 and 1.4 eV for O and Ce, respectively [28]. Our computed values for O 2p–Ce 5d orbitals band gap shows a band separation of 5.7 eV, which is in a good agreement with
literature values reported between 5.3–5.7 eV [28]. Nb$_2$O$_5$ reveals an O 2p bandwidth of 6 eV mainly concentrated at the top of the valence band. The Nb 4d states span between −5 eV and 8 eV. The p and d electrons are found to be active at the Fermi level, with some contribution of Nb 2p states around the conduction band leading to high interaction between the O-2p, Nb-4p, and 4d states. There is an overlap between the Nb 4p states and 2p states at the regions of 2–6 eV. The Nb-doped CeO$_2$ shows that, in addition to the occupied Ce 4f states around 2 eV, more 4f electrons that are absent in the pure CeO$_2$ now concentrates around 4–6 eV (segment marked with arrow). The presence of excess electrons can either be initiated through the creation of oxygen vacancies or the addition of dopant. These excess electrons would occupy the Ce 4f states, localizing on individual Ce atoms [28]. This infers that the f states occupation observed herein originates from the addition of Nb atoms. In addition, the Nb 4d electrons which are conspicuous in the pure Nb$_2$O$_5$ sample is redundant after doping, indicating the possible electron transfer to the Ce 4f states, thus, reducing the Ce$^{4+}$ to Ce$^{3+}$. The availability of Ce$^{3+}$ is known to promote catalytic reactions, and the excess electron gain by the 4f would give rise to n-type conductivity and the charge carrier in the band [55]. Similar analogy involving peaks shortening and disappearance was used to confirm electron transfer between atoms of similar doped systems [56].

4 Conclusion

Nb$_2$O$_5$ is found to improve the properties of CeO$_2$ in terms of the narrowed band gap and the electronic states of the Ce and O atoms. Experimental results of XRD confirm the formation of new peaks associated with Nb at high loading, and the EDS analysis detects the presence of Nb. There is a narrow distribution of the crystallite size of the prepared samples with the reduction in BET surface area as the Nb loading increases. TGA analysis predicts that the calcination temperature should be limited to below 600°C. DFT calculations support the experimental observation pertinent to the decrease in the lattice parameter of the CeO$_2$ when Nb atom is incorporated. The Hirshfeld charges reveal the reduction in Ce atom after Nb doping with maximum reduction in the Ce atoms nearer to the Nb atom. The electronegativity values of the tetrahedral O atoms are increased by 0.01 e after Nb doping. This will promote the catalytic tendency of the material since more O atoms will exhibit higher affinity for adsorbed reactants. Analysis of the TDOS successfully
re-produces the experimentally measured analogous values for pure CeO$_2$ and Nb$_2$O$_5$. Nb doping is found to improve the semi conductivity nature of CeO$_2$ through the reduction in the band gap of CeO$_2$ by $\sim 0.60$ eV. PDOS identifies the filling of the Ce-4f states from the Nb-4d states electron which is expected to improve the catalytic capacity of CeO$_2$.

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