



Beyond surface redox and oxygen mobility at pd-polar ceria (100) interface: Underlying principle for strong metal-support interactions in green catalysis

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ABSTRACT

When ceria is used as a support for many redox catalysis involved in green catalysis, it is well-known that the overlying noble metal can gain access to a significant quantity of oxygen atoms with high mobility and fast reduction and oxidation properties under mild conditions. However, it is as yet unclear what the underlying principle and the nature of the ceria surface involved are. By using two tailored morphologies of ceria nanocrystals, namely cubes and rods, it is demonstrated from Scanning Transmission Electron Microscopy with Electron Energy Loss Spectroscopy (STEM-EELS) mapping and Pulse Isotopic Exchange (PIE) that ceria nanocubes terminated with a polar surface (100) can give access to more than the top most layer of surface oxygen atoms. Also, they give higher oxygen mobility than ceria nanorods with a non-polar facet of (110). A new insight for the possible additional role of polar ceria surface plays in the oxygen mobility is obtained from Density Functional Theory (DFT) calculations which suggest that the (100) surface sites that has more than half-filled O on same plane can drive oxygen atoms to oxidise adsorbate(s) on Pd due to the strong electrostatic repulsion.

1. Introduction

Platinum group metals (PGMs) on a ceria support system have been shown to exhibit strong metal support interactions or so called SMSI

[1–3]. In contrast to traditional supports such as carbon and titania, PGM metals on ceria supports have been shown to exhibit enhanced catalytic activity. Both theoretical and experimental studies since the 1980s have explored the effects of using ceria support [4], the

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properties of which have been thought to be due to the reducible nature of the ceria. PGM/ceria has been applied in three-way catalysts to remove hydrocarbons/CO/NO_x from exhaust gas [5–7], CO oxidation to CO₂ [8–10], water gas shift reaction to produce H₂ [11,12], oxygen sensors [13–15] and solid oxide fuel cells for clean energy [16–18]. The excellent activity of ceria-based catalysts in these applications is attributed to the ceria oxygen storage capacity, facile oxygen vacancy formation and fast surface oxygen mobility properties. The ability of ceria to shift easily between the oxidised and reduced state ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$) under operating conditions is suspected to be of importance for all of these processes [6,7,19–21].

Ceria, CeO₂, has a cubic fluorite crystal structure, space group of *Fm* $\bar{3}$ m [6,22]. The Ce cations are arranged in a face-centred cubic structure with the O anions filling the tetrahedral holes. The lattice constant for the cubic unit cell is 5.41 Å. Each Ce cation is bonded to eight O anions while each O anion is bonded to four Ce cations. In contrast, in its fully reduced form, ceria Ce₂O₃ has a hexagonal structure, space group of *P* $\bar{3}$ m1. It has been suggested that ceria can be partially reduced which retains the fluorite structure of CeO₂ for the intermediate non-stoichiometric compositions of CeO_{2-x}, 0.5 < x [23,24]. Hence, a large quantity of oxygen vacancies can be formed in ceria without major structural changes.

The low-index surfaces of ceria are (111), (110) and (100); each of them varies in their surface structure and stability [25–28]. The (100) ceria surface is known to have a significant net dipole moment perpendicular to its surface, thus regarded as a polar surface. Any variation in the surface properties of the different surfaces would lead to a difference in their metal-support interaction(s) and the modification of the unique properties of ceria mentioned earlier. According to the Wulff construction, the crystal planes exposed on the surface of a crystalline material are determined by its morphology [29]. Thus, the surface exposed by a nanoparticle can be influenced by controlling its morphology and this has led to desire for the morphology-controlled synthesis of various materials. It has been reported that CeO₂, CuO, TiO₂ and Co₃O₄, show examples of different morphologies such as nano-sized cubes, rods, belts, plates and octahedrons [30–32]. Varying the exposed surface facets exposed of the nanoparticle will result in an alteration of its surface chemistry, which in turn will influence its catalytic properties. One of the earliest studies on the role of morphology on catalysis was performed by Zhou et al. who reported that single crystalline rod-shaped ceria showed higher catalytic activity in the CO oxidation reaction compared to traditional polycrystalline ceria nanoparticles, despite the surface area of the rods being lower [9]. The enhanced catalytic activity of morphology-controlled ceria was also evident for other catalysed reactions such as methanol and ethanol reforming [33,34] and the water-gas shift reaction [35,36]. Controlling and tailoring the morphologies of the support oxide can also alter the properties of the catalyst, especially when the support contributes to the catalytic properties through SMSI [37–40]. The effect of different surfaces of ceria, studied through varying nanoparticle shape, has been

discussed extensively in the literature and attributed to variations in the surface area, energy of oxygen vacancy formation, surface stability, surface reconstruction and the presence of defects [41,42]. However, less attention has been paid to the effect of surface polarity on catalysis.

The origin for the interesting surface redox and fast oxygen mobility properties of the ceria surfaces still remains obscure. Placing metal nanoparticles on ceria, not only increases metal dispersion but also promotes catalytic redox properties by synergistic effects on to the three-phase interface. More importantly, the nature of the ceria surface in relation with these phenomena and their underlying principles have not been much optimised and elucidated. There were sometimes conflicting information where metal-ceria rods with exposed (110)/(100) surfaces were claimed to give best catalytic activity [43] whereas superior performances of metal-ceria cubes were also reported [44]. Obviously, their surface area, nature of surface and the depth of accessible ceria oxygen which are highly dependent on reaction conditions are all important factors.

This present study is concerned with the investigation of the role of different ceria surfaces as a support for Pd nanoparticles in heterogeneous solid catalysis, by carefully controlling the morphologies of the ceria supports. We envisage that synthesising these ceria morphology supports could result in significant enhancement in the catalytic properties of the supported Pd in the catalyst test reactions leading to rational tuning towards superior catalytic performance. In addition, we aim to characterise these different ceria surfaces to gain a deeper understanding into the surface chemistry of this unique support that provides exciting properties such as oxygen vacancy formation and oxygen mobility. In order to achieve these objectives, we have synthesised single crystalline ceria morphologies that expose a specific surface followed by deposition of Pd nanoparticles onto the ceria morphologies. The properties of these Pd deposited ceria morphologies would then be investigated by Scanning Transmission Electron Microscopy with Electron Energy Loss Spectroscopy (STEM-EELS), Pulse Isotopic Exchange (PIE) and Density Functional Theory (DFT).

2. Results and discussion

As summarised in Fig. 1, noble metal particles can gain access to a significant quantity of oxygen atoms as a result of the facile oxygen vacancy formation and fast surface oxygen mobility associated with the ceria support. This is harnessed for a wide range of applications including CO oxidation [45]. But the nature of the ceria surface involved, and how critical a particular surface orientation may be, remains unclear.

Ceria nanocrystals favouring particular crystal facets were synthesised by hydrothermal method⁴⁶. Typically, cerium salt precursor was dissolved in basic aqueous solution. The colloidal solution of cerium hydroxide nuclei was formed and further oxidised to ceria at elevated temperature. The particle size was controlled by the relative rates of nucleation and growth processes while the shape control results from

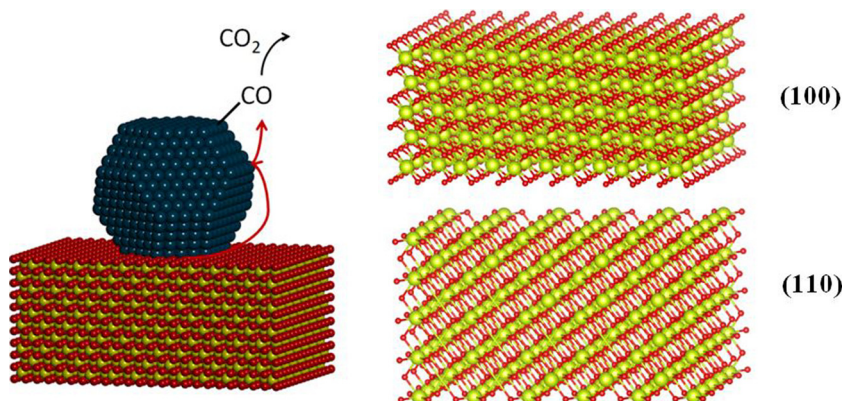


Fig. 1. Pd metal can gain access to stored surface and sub-surface oxygen atoms from ceria for oxidative removal of adsorbate such as CO to CO₂. Two surface termination of ceria nanocrystals are compared, namely (100) surface associated with the cube morphology and rods (110) associated with rods. The ceria (100) surface with O-termination is known to have a dipole net charge perpendicular to the surface, hence a polar surface. Oxygen ions are red, cerium ions yellow and Pd is blue.

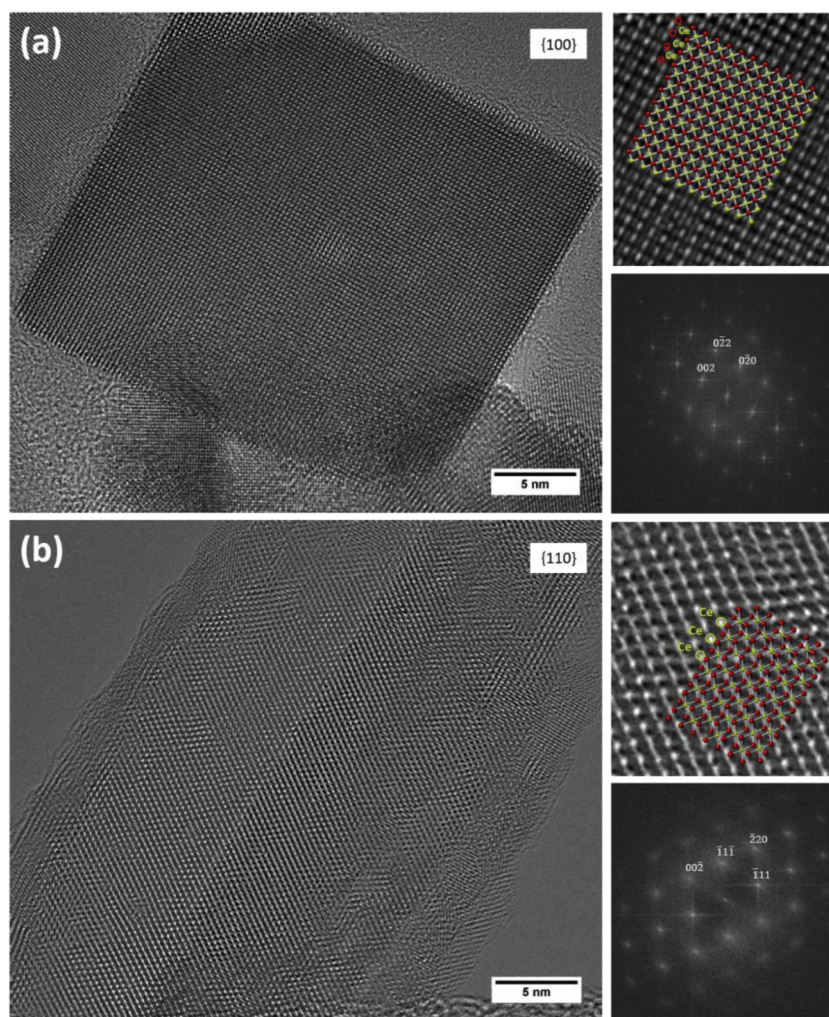


Fig. 2. (a) Exit wave restored from HR-TEM images showing ceria cubes with predominately polar (100) surfaces, overlaid with the expected model crystal structure; (100) FFT of the HR-TEM image. (b) HRTEM image showing ceria rods with predominately non-polar (110) surface overlaid with the expected model crystal structure; (110) FFT of the HRTEM image.

preferential growth of different crystal facets. The particle size and shape are influenced by many reaction conditions such as reaction temperature, reaction time, precursor concentration, pH value and pressure [9] [46],. In this work, two different shapes of ceria nanoparticles, namely cubes and rods, were carefully synthesised (SI section S1). Their particle size and size-distribution were determined by Transmission Electron Microscopy (TEM) images by measuring the diameters of more than 150 particles. Mean particle sizes of cubes of ceria with a predominantly polar (100) surface were 21.5 ± 6.0 nm (BET surface area of $22 \text{ m}^2 \text{ g}^{-1}$) while ceria rods had particle sizes of 6.5 ± 1.6 nm in width and 25–180 nm in length with a non-polar (110) surface (BET surface area of $75 \text{ m}^2 \text{ g}^{-1}$) (Fig. 2 and Figs. S1–S2). The application of exit wave restoration to high resolution (HR) TEM images (Fig. 2a) clearly shows the distinctive and alternating layers of Ce^{4+} and O^{2-} resulting in terminal (100) surface. The corresponding Fast Fourier Transform (FFT) of the HRTEM also matches with the expected model describing the ceria cubes. On the other hand, the principal surface for ceria rods (Fig. 2b) is (110). The FFT of the HRTEM matches the ceria rods' expected structural model.

Deposition-precipitation method was used to deposit Pd nanoparticles on the ceria morphologies. The surfaces and morphologies of the ceria cubes and rods were maintained upon Pd deposition (SI section S1). The particle size of the Pd nanoparticles on both rods and cubes were in range of 1–3 nm, with mean particle size of 2.0 nm.

2.1. STEM-EELS mapping

Scanning Transmission Electron Microscope (STEM) coupled with Electron Energy Loss Spectroscopy (EELS) was used to investigate the reduction of the ceria morphologies, both pure and Pd-deposited [47–51]. By analysing the relative intensities of the Ce M5/M4 core-loss peaks, the Ce^{4+} and Ce^{3+} oxidation states can be distinguished and localised (Fig. S5). The reducibility of the ceria is its unique property that might contribute to the SMSI with Pd, as the oxygen from the ceria can be utilised for catalytic reaction through oxygen reverse-spillover. This reduction of Ce^{4+} to Ce^{3+} is usually accompanied with formation of oxygen vacancy. The positional $\text{Ce}^{4+}:\text{Ce}^{3+}$ composition would provide useful information on the depth of reduction in the ceria support. Furthermore, it also provides the location of the deposited Pd nanoparticles.

Fig. 3 shows the mapping of $\text{Ce}^{4+}:\text{Ce}^{3+}$ and Pd from analysing the STEM-EELS spectra, where each pixel is an individual EELS spectrum. An example of a single EELS spectra processed from the STEM-EELS data is shown in Fig. S5. The ceria $\text{Ce}^{4+}:\text{Ce}^{3+}$ composition mapping (Fig. 3 Ce^{4+} Map) are represented in greyscale, where white indicates presence of Ce^{4+} whilst black represents presence of Ce^{3+} and cyan show the areas of the image where Ce is not present. For the Pd mapping (Fig. 3 Pd map), white represents where Pd is present and black where Pd is absent.

Based on the temperature programmed reduction (TPR) studies, the

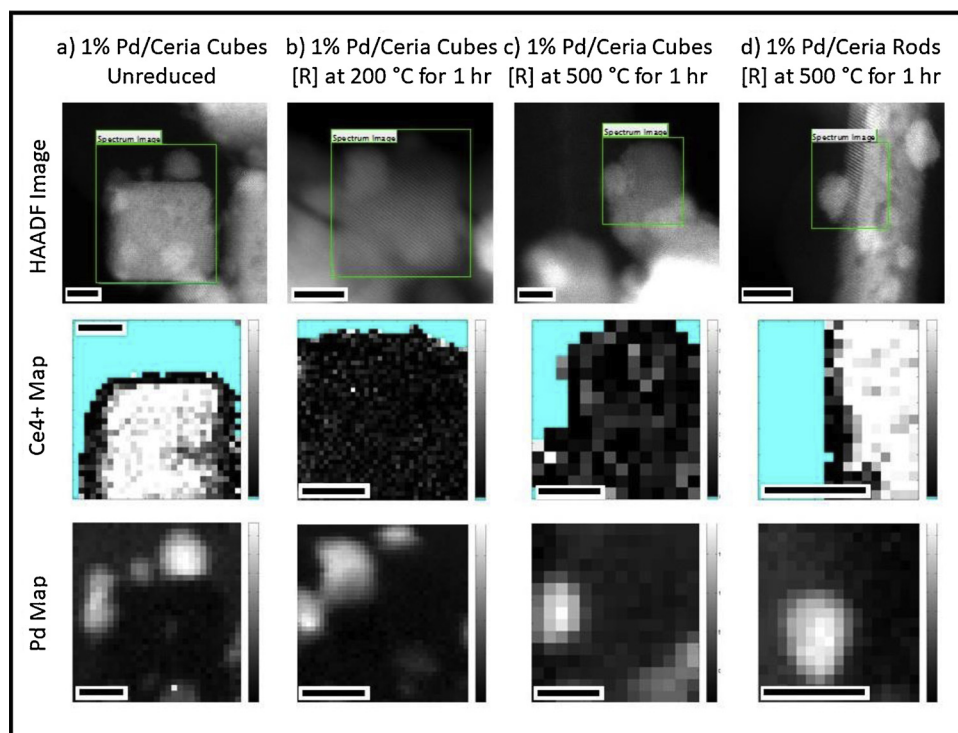


Fig. 3. STEM HAADF images and the STEM-EELS Ce^{4+} and Pd compositional mapping for a) 1% Pd/ceria cubes without pre-reduction, b) 1% Pd/ceria cubes reduced in H_2 at 200 °C for 1 h c) 1% Pd/ceria cubes reduced in H_2 at 500 °C for 1 h d) 1% Pd/ceria rods reduced in H_2 at 500 °C for 1 h (Ce^{4+} map is represented in greyscale, where white indicates presence of Ce^{4+} whilst black represents presence of Ce^{3+} and cyan show the areas of the image where Ce is not present and Pd Map is displayed by white where Pd is present and black where Pd is absent). Electron flux was fixed at $5.0 (\pm 0.5) \times 10^8 \text{ e/nm}^2$ and all the scale bars are 5 nm. Deep layer reduction of ceria can be observed on the Pd/ceria cubes samples pre-reduced at 500 °C and 200 °C, whereas for 1% Pd/ceria rods pre-reduced at 500 °C, the reduction appears to be limited to the surface only. Some surface reduction can also be observed on the unreduced 1% Pd/ceria cubes sample which could be attributed to the electron beam reduction.

reduction temperature for surface oxygen on pure and metal deposited ceria is below 500 °C, while the reduction of ceria bulk oxygen is initiated at 700 °C [9,52] (Fig. S14). When the 1% Pd/ceria cubes and rods were pre-reduced with H_2 gas at 500 °C for 1 h, their STEM-EELS indicated surface oxygen reduction on the ceria rods support as expected, however on the ceria cubes, more extensive reduction was observed where reduction occurred in deeper layer oxygens beyond the topmost surface of the ceria (Fig. 3 c and d). The 1% Pd/ceria cubes were also pre-reduced at 200 °C, where it is expected that there would not be any reduction taking place since pure and metal deposited ceria require temperature higher than 200 °C for surface oxygen reduction, however STEM-EELS suggested that the reduction occurred on the surface as well as to the deeper oxygens (Fig. 3b). Since the pre-reduction is carried out at low temperature, this gives an indication that more extensive reduction in the deeper layer of the ceria cubes is kinetically driven, implying fast oxygen mobility through the polar (100) surface of the cubes as a gateway. For comparison, the 1% Pd/ceria cubes without any pre-reduction showed no reduction to the deeper oxygens, although surface oxygen reduction was still observed despite no pre-reduction treatment carried out, possibly as a result from the action of the electron beam (Fig. 3a). This deep layer reduction was also observed on Pd/ceria cubes system in our previous study by Ambient Pressure X-ray Photoelectron Spectroscopy (Fig. S13) [53].

As a control experiment, ceria cubes without Pd were also tested, with samples pre-reduced at 500 °C and without reduction pre-treatment (Fig. S6). Both samples showed similar Ce^{4+} EELS mapping where there was no deep layer reduction of oxygens in the ceria cubes. This suggests that Pd is required to gain access to these deeper layers of oxygen, hence Pd acts as a surface catalyst for these deeper oxygens to be reduced. In general, the extensive reduction of oxygen beyond the top layer in the ceria cube support was only observed on the ceria cubes with the (100) polar surface with Pd nanoparticles deposited on them. However, deep layer oxygen reduction layer did not occur for the ceria rods with predominantly (110) surfaces.

STEM-EELS was also used to study the kinetics of the reduction of the ceria cubes support, as the electron beam could be used to reduce the sample whilst mapping the EELS spectra through the consecutive

scans [47,50,51]. This reduction was observed on the unreduced samples ceria cubes with and without deposited Pd (Fig. 3a and S6b respectively). Although mechanistically, the reduction with electron beam might be different from chemical reduction with a reducing species such as H_2 , this study would give in-situ comparison of the reduction kinetics between the samples by controlling and fixing the electron flux of the beam.

Fig. 4a show three consecutive EELS Ce^{4+} mappings of unreduced 1% Pd/ceria cubes. The 1st measurement shows that only the surface of the ceria cubes was reduced, as observed previously, but as more EELS measurements are taken, the deep reduction of the oxygens beyond the surface layer becomes increasingly apparent. With this information, the rates of reduction were calculated and mapped to their corresponding areas (Fig. 4d). The rates of reduction are represented by the visible light colours spectrum where red signified the fastest rate of reduction, green as no reduction and blue as oxidation was taking place.

The oxygen in the deeper and extensive regions of ceria cubes experienced the fastest rate of reduction between the 1st and 2nd scan; the rate decreased between the 2nd and the 3rd scan as most of these oxygen atoms had already been reduced. This mapping of the reduction kinetics has also suggested that the fastest reduction rates occurred at the ceria-Pd interface, where nearly all of the Ce^{4+} had been reduced to Ce^{3+} at the region around the Pd even before the 1st scan was taken (Fig. 4a Scan 1). Thus, the rate of reduction at the ceria-Pd interface appeared minimal, as most of the Ce^{4+} has been reduced prior to the 1st scan (Fig. 4d Rate 1). High reduction rates were also observed in ceria regions close proximity to the Pd nanoparticles, especially in the mapping between 1st and 2nd scan. In general, the reduction rates appeared higher between the 1st scan and the 2nd scan (Fig. 4d Rate 1) compared to that between the 2nd scan and 3rd scan (Fig. 4d Rate 2), which could be due to high proportion of Ce^{4+} when the 1st scan was taken, compared to 2nd scan where most of the Ce^{4+} had been reduced, thus slowing down the reduction rate.

The rate of reduction of 1% Pd/ceria cubes by the electron beam was also compared with that of ceria cubes without deposited Pd (Fig. 4 and S7). Without Pd, the reduction of the deep layer oxygens appeared minimal even after 5 scans. These reduction rate studies agree with the

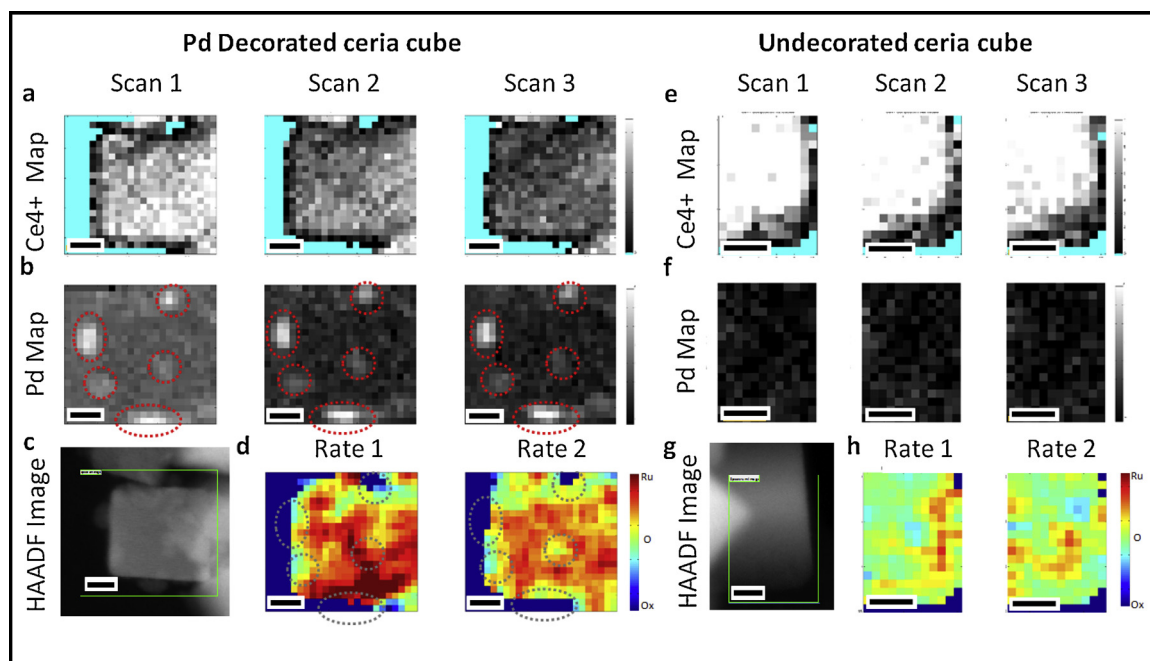


Fig. 4. Compositional EELS mapping of unreduced 1% Pd/ceria cubes and pure ceria cubes. a) The Ce^{4+} maps after 1st, 2nd and 3rd STEM-EELS scans with an electron flux of $5.0 (\pm 0.5) \times 10^8 \text{ e/nm}^2$ [2] for a) 1% Pd ceria cubes and e) pure ceria cubes. The corresponding Pd mapping with the position of Pd particles marked with red dotted circles for b) 1% Pd/ceria cubes and f) pure ceria cubes. STEM HAADF image of c) 1% Pd/ceria cubes and g) pure ceria cubes. The rate of reduction between subsequent scans (represented by the visible light colours spectrum where red signifies the fastest rate of reduction, green as no reduction and blue as oxidation was taking place and Pd regions are highlighted as white dotted circles) for d) 1% Pd/ceria cubes and h) pure ceria cubes. All the scale bars are 5 nm. Fast reduction rates appear to be concentrated on areas with Pd nanoparticles, indicating Pd is promoting the reduction of ceria at the three-phase interface. The Pd-ceria interface is also needed to reduce the deeper layer oxygen which suggests that Pd acts as a gateway to access the oxygen in the deeper layer, through the (100) surface of the cube. This deep layer reduction could not occur in the absence of Pd as observed in the STEM-EELS of pure ceria cubes.

previous observation that surface Pd catalyses the reduction of these deeper oxygens.

These STEM-EELS studies have clearly demonstrated that Pd is needed to activate the oxygen in the ceria. In addition, in the case of the ceria cubes, the Pd also permits the reduction of the deeper oxygens through the (100) surface despite their having lower BET surface area than the rods. Hence, this could potentially be used as a model system where Pd with a ceria-cube support gains access to a higher degree of inner reducible oxygen reservoir compared to the Pd with a ceria-rod support, where only surface oxygen is available.

2.2. Pulse isotopic exchange (PIE)

Pulse isotopic exchange (PIE) experiments were used to determine the rate of oxygen exchange of the Pd deposited ceria morphologies [54–57]. The rate of oxygen exchange provides important information about the kinetics of the oxygen mobility and reactivity within these structures. The samples were originally maintained in equilibrium with 21 % $^{16}\text{O}_2/\text{Ar}$ carrier gas mixture and pulses with a known volume of 22 % $^{18}\text{O}_2/\text{Ne}/\text{Ar}$ mixture were injected to the ceria samples, resulting in an exchange between the ^{16}O in the ceria and the ^{18}O . The relative intensities of the outlet gas of the pulse isotopic exchange experiment for Pd deposited ceria cubes and rods samples, for temperatures between 425–550 °C are shown in section S2 of the SI. The general trend observed was that as the temperature was increased, the $^{18}\text{O}_2$ peak decreased and $^{16}\text{O}^{18}\text{O}$ peak increased indicating faster ^{18}O incorporation into the material and a faster oxygen dissociation rate. The $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ peaks were integrated to obtain the areas so that the mole fractions of $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ in the gas outlet could be calculated. These were used to derive the surface incorporation or exchange rate, R_o (Eq. 1). The details of the calculations are shown in section S2 of the SI.

$$R_o = -\frac{2p\text{O}_2}{R_s} \cdot \frac{F}{T} \ln \left(\frac{f_{g,o}^{18}}{f_{g,i}^{18}} \right) \quad (1)$$

where R_o is the surface exchange rate ($\text{mol O m}^{-1} \text{ s}$), $p\text{O}_2$ is the partial pressure of oxygen, R is the gas constant, S_r is the surface area of the oxide sample, F is the gas flow rate and T is the temperature.

The Arrhenius plot of surface exchange rates at temperatures 425–550 °C is shown in Fig. 5. In general, the Pd/ceria cube with (100) surface appear to have faster surface exchange rate compared to the Pd/ceria rods with (110) surface despite the fact that ceria cube gives lower surface area than ceria rods. The faster rate is indicated by higher R_o in the corresponding temperatures reflecting higher quantity of surface active sites presumably the surface oxygen vacancies (SI section S3) on polar ceria for the exchange. It is known that formation of oxygen vacancy is a thermodynamic favoured process, the use of higher temperature will give higher degree of oxygen vacancy especially in Ce oxide which is facilitated by lower redox energy change from cerium (IV) to cerium (III). Although the surface is at equilibrium in 21 % O_2 , it is thought that there is still a significant degree of surface oxygen vacancies far from surface saturation at the reaction temperatures especially on ceria cubes than rods, as shown by the EPR (Fig. S3). Thus, the faster oxygen exchange rate indicated by PIE experiment could be correlated with the higher amount of surface oxygen vacancies in the case of cube sample due to the more facile redox nature of its surface oxygen.

Furthermore, the two samples however, show a similar same gradient and hence activation energy (Table 1), suggesting a very similar oxygen exchange mechanism presumably taken place on the ceria surface.

On the other hand, the STEM-EELS experiments have clearly demonstrated that Pd deposition enhances the rate of oxygen mobility of the ceria surface with lower kinetic barrier for reduction, which appears to be in disagreement with the observations in the PIE experiments.

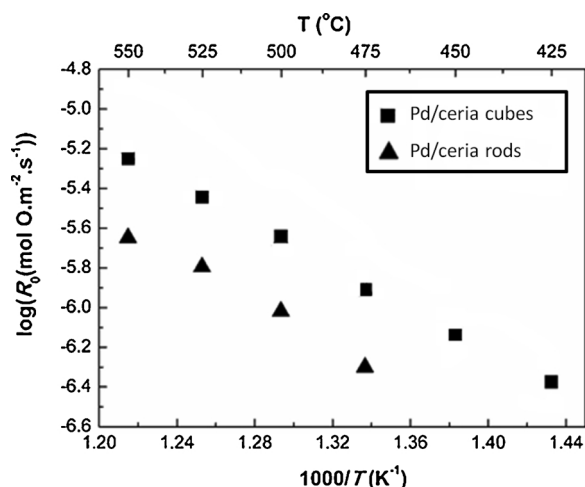


Fig. 5. Arrhenius plots of the rate of oxygen exchange from PIE measurements of 1% Pd/ceria cubes and rods. The 1% Pd/ceria cubes and rods appeared to have faster oxygen exchange rates compared to 1% Pd/ceria rods in all the tested temperatures, presumably due to higher quantity of active sites presumably the oxygen vacancies for exchange on ceria in the former case. The Arrhenius plots for the two samples have the similar gradient indicating similar oxygen exchange mechanism.

Table 1

Activation energies for the rate of oxygen exchange calculated from the Arrhenius plot in Fig. 5.

Sample	Activation Energy (kJ/mol)
1% Pd/ceria cubes	100
1% Pd/ceria rods	100

Such disagreement is thought to be due to the experimental conditions of the samples, as STEM-EELS was performed under reducing conditions but the PIE was carried out under oxidising conditions. Inactive PdO was formed under oxidising conditions instead of Pd⁰, which might not promote the oxygen mobility of the ceria but block some of the active surface sites of the ceria. To address this issue, a second set of experiments were performed similar to the original experiments but with the samples pre-reduced in 5% H₂/Ar at 350 °C for 30 min before the PIE measurements were taken. The downside of this pre-reduction method was that the samples were not in equilibrium with the 21 % ¹⁶O₂/Ar carrier gas mixture, hence Equation 1 could not be used to calculate the rate of oxygen exchange. However the oxygen exchange rates could still be analysed by observing the isotopic oxygen fractions of ¹⁸O₂ and ¹⁶O¹⁸O in the gas outlet. Generally, increasing the temperature results in the decreasing fraction of ¹⁸O₂ which indicated the loss of ¹⁸O due to oxidation of the sample structure. An increasing fraction of ¹⁶O¹⁸O can be due to an increase in the oxygen dissociation and spillover rates (backward and forward) possibly combined with an increase in the oxygen exchange rate with the deeper oxygens through the surface (which results in a loss of ¹⁸O from gas phase and solid surface).

Fig. 6 shows the isotopic oxygen fractions of the ¹⁸O₂ and ¹⁶O¹⁸O upon PIE with the reduced (black) undeposited and Pd deposited ceria morphologies at different temperatures, compared with their respective unreduced samples (red). In light of the STEM-EELS mapping results, the same profiles of ¹⁸O₂ attenuation and ¹⁶O¹⁸O enhancement on both the undeposited ceria morphologies with and without pre-reduction treatment clearly indicate that the isotopic oxygen exchange is confined to the near surface of ceria crystal. (Fig. 6 a and b). On the other hand, with the Pd deposited samples, it is interesting to note that the lower fraction of ¹⁸O₂ over pre-reduced Pd deposited samples compared to those without pre-reduction could be attributed to both the oxidation of

Pd to Pd¹⁸O and the oxidation of ceria.

By comparing the oxygen fraction of ¹⁶O¹⁸O of the Pd deposited ceria cubes and rods, there is a significant increase in the ¹⁶O¹⁸O fraction for the Pd/ceria cubes upon pre-reduction (Fig. 6c), whereas it remained almost unchanged for Pd/ceria rods (Fig. 6d).

The ideal situation is to analyse the whole balances (uptakes and evolution of isotopic species) to separate the re-oxidation process from the PIE process. Unfortunately, for the present set-up, during our PIE study, 21 % ¹⁶O₂ was kept flowing together with the added pulse of ¹⁸O₂ on top (some degree of lateral mixing), and we monitored the decrease in the content of ¹⁸O₂ and formation of ¹⁶O¹⁸O of the pulse in the background of ¹⁶O₂ by mass spectrometry (see S3). Thus, we cannot tell whether there is any formation of ¹⁶O₂.

There is a simultaneous re-oxidation and evolution of isotopic fractions which are complex to disentangle and resolve at this stage. However, the increase in ¹⁶O¹⁸O fraction for the Pd/ceria cubes might be attributed to an additional pathway for the combination of ¹⁸O and ¹⁶O. The re-association of ¹⁶O and ¹⁸O presumably occurs on the Pd surface, where ¹⁶O can be accessed by reverse spillover of oxygen from deeper oxygens through the (100) surface (as indicated by STEM-EELS). This reverse spillover effect on the Pd/ceria cubes could also explain why with pre-reduction, the ¹⁸O₂ fraction for the Pd/ceria cubes is generally higher (lower uptake of ¹⁸O₂) than the Pd/ceria rods across the different temperatures, where with the cubes, the Pd is re-oxidised by both ¹⁸O₂ and reverse spillover from the ceria (Scheme 1).

2.3. Density functional theory (DFT)

DFT was used to investigate the stability and energy of oxygen vacancy formation of the different ceria surfaces. Although the main focus of this paper is to compare the polar CeO₂ (100) surface of the cubes with non-polar (110) surface of the rods. (111), (110) and (100) surface models were all modelled by 2 × 2 periodic slab models with 7 Ce atomic layers. The bottom two Ce atomic layers and the coordinated O layers were fixed and a vacuum layer of 12 Å along the z direction perpendicular to the surface was employed to prevent spurious interactions between the repeated slabs in all these models. The calculations of CeO₂(111) and (110) surface, which are type II surfaces according to the Tasker classification with no dipole moment [13], used a 4 × 4 × 1 k-point sampling grid. The CeO₂ (100) is type III surface, which introduced a dipole perpendicular to the surface upon cleaving. Previous studies have found that the high surface energies of ceria resulted in their high reactivity. Most DFT calculations and other computational modelling studies on ceria surfaces are in agreement that amongst the low index ceria surfaces, (111) is the most stable surface with the lowest surface energy [22,28]. However, the order of surface energies between (100) and (110) has been disputed [22,25–27], [58–60]. This disagreement between the stability of (100) and (110) surfaces might be due to the previous omission of surface polarity and the limitation of computational studies.

Fig. 7 shows the structural models of (111), (110) and (100) ceria surfaces in plane and side views. The calculated surface energies of these ceria surfaces from the literature are also summarised in Table 2. The (100) surface has been reported by Kim et al to be terminated by O via their direct recoil spectroscopy / low energy ion scattering of Kr experiments [61]. It has been argued that it is possible to produce a net dipole moment perpendicular to the surface with alternately charged planes with a repeat unit consisting of only two planes. As a result, the polar (100) surface is highly unstable due to the strong electrostatic repulsion of similar charged ions within the same plane. There are a number of ways for a polar surface to reduce its high surface energy, namely bringing in opposite charged species on its polar surface from the environment through an adsorption process [55]. Alternatively, surface reconstruction by removing oxygen to generate oxygen vacancies and simultaneously altering the oxidation state of metal cations, favourable for transition metal oxides, will reduce or eliminate surface

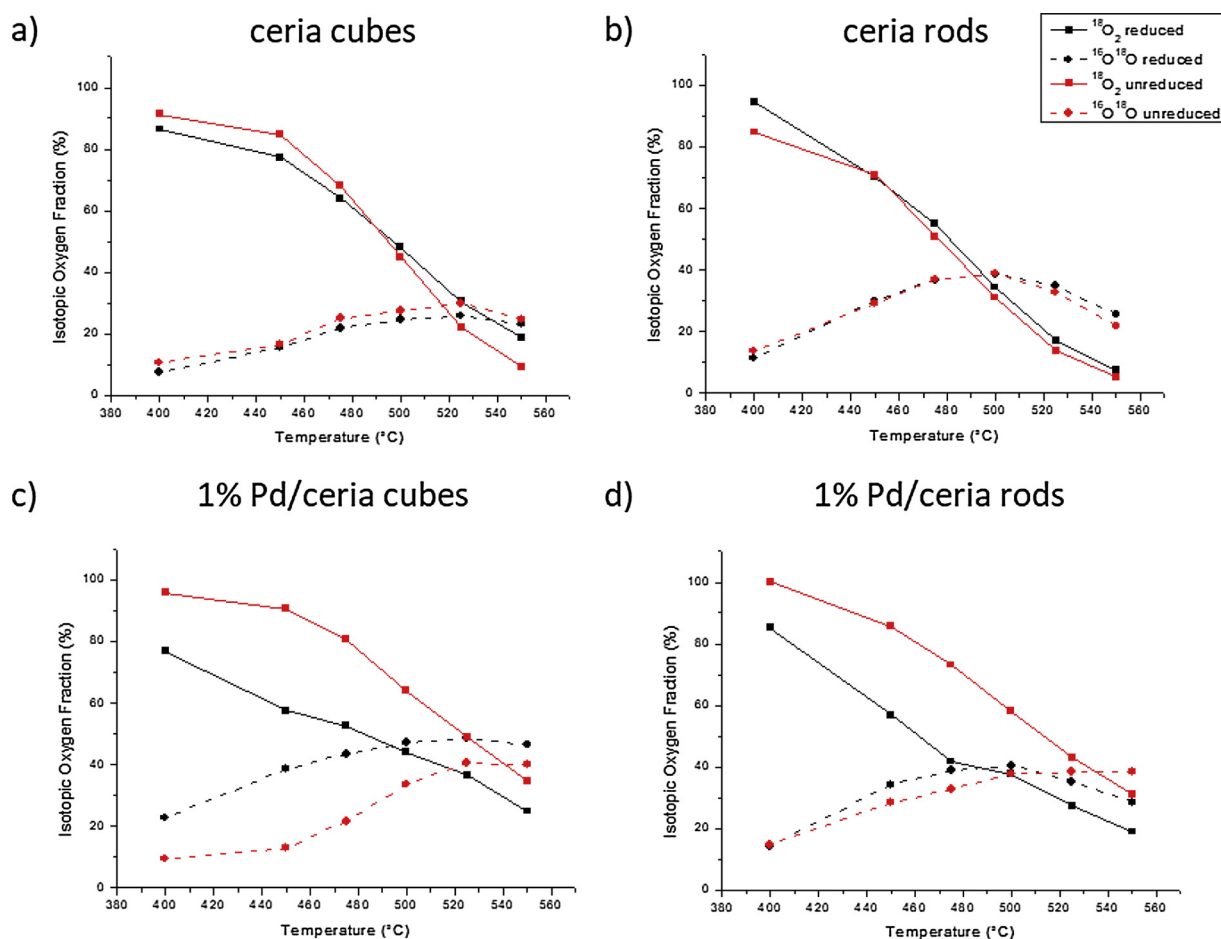
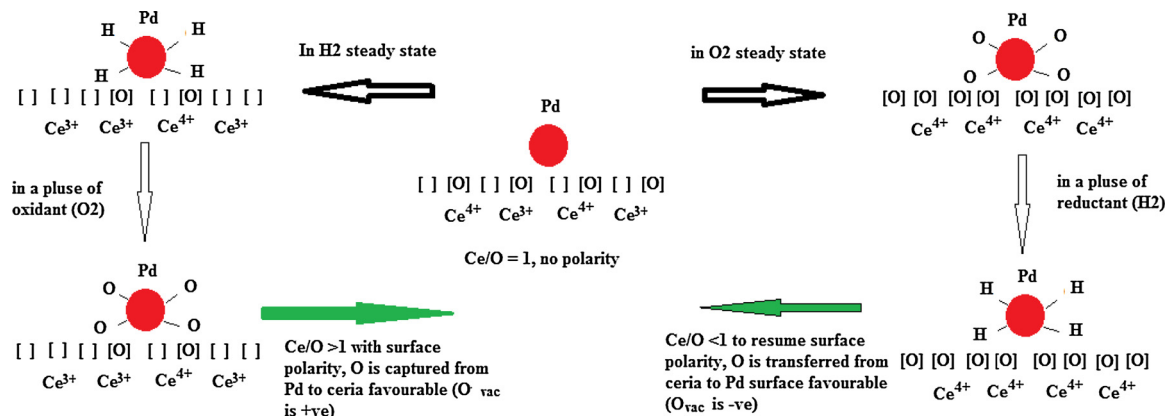


Fig. 6. Isotopic oxygen fractions of $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ from PIE measurements of a) ceria cubes b) ceria rods c) 1% Pd/ceria cubes d) 1% Pd/ceria rods at different temperatures. The pre-reduction treatment appears to have no significant effect on the $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ fractions for undeposited ceria cubes and rods compared to the reduced sample. However, with the Pd deposited samples, pre-reduction resulted in lower $^{18}\text{O}_2$ fraction for both Pd/ceria cubes and rods samples, which might be due to the $^{18}\text{O}_2$ uptake to re-oxidize the reduced Pd^0 to PdO . The increase in $^{16}\text{O}^{18}\text{O}$ fraction upon pre-reduction can only be observed for the Pd/ceria cubes samples which can be attributed to the reverse oxygen spillover effect from the ceria cubes to the Pd metal, hence providing an additional pathway for the combination of $^{16}\text{O}^{18}\text{O}$. The reverse oxygen spillover effect appears to be minimal for the Pd/ceria rods, where the $^{16}\text{O}^{18}\text{O}$ fraction remained unchanged upon pre-reduction treatment.

polarity. The latter is expected to take place in the case of CeO_2 where redox process involving the cerium ions can occur with low activation energy [56]. This accounts for the higher quantity of oxygen defects we observed over our Pd/Ce (100) samples by Electron Paramagnetic Resonance (EPR) (SI section S3).

Traditionally, it is uncommon to model metal oxide slab with surface polarity. As a result, the typical DFT model as in the case of M. Nolan [26], was to cancel the surface polarity of (100) by removing half of the surface oxygen from the fully oxygen coverage- making it cation to anion in stoichiometry. Hence, with this stoichiometric surface, the



Scheme 1. Due to greater sensitivity to changing gas environment over Pd surface than ceria, the Pd metal surface on CeO_2 can gain access to large quantity of mobile oxygen atoms reversibly via (100) polar surface layers with the alternative cations and anions layers arrangement due to change in polarity within the same planes.

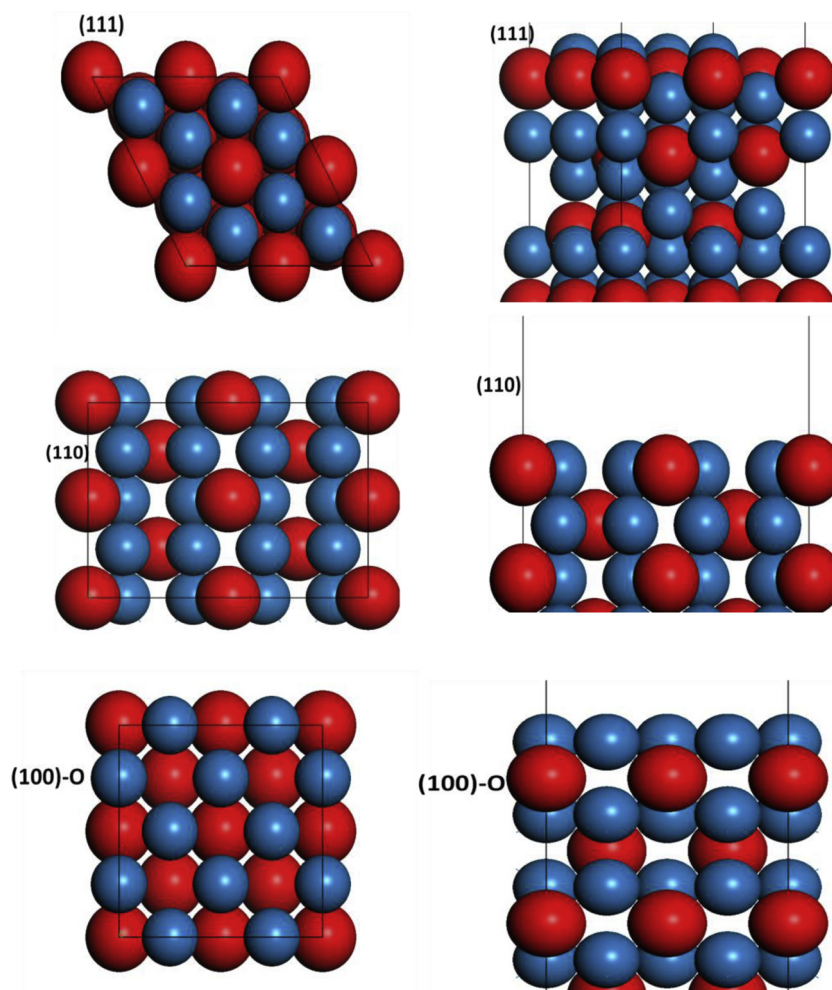


Fig. 7. Planar and side views of ceria (111); (110); O-terminated (100) surfaces.

Table 2

DFT calculated energy of oxygen vacancy formation of different ceria surfaces.

Surface	Surface energy* / Jm^{-2}	Calculated energy of oxygen vacancy formation (eV)
111	0.69(0.68)	3.08
110	1.26(1.01)	1.99
100	2.05(1.41)	-1.98
100 _{O-half}	-	2.40
100 _{O-half + 1}	-	-1.56

Remark: 111: refers to (111) non-polar surface, 110: (110) non-polar surface, 100: (100) polar surface with full oxygen cover, (100)_{O-half}: (100) reconstructed neutral stoichiometry surface with half surface oxygen removed, (100)_{O-half + 1}: (100) neutral surface with one more oxygen on this surface. *Unrelaxed and (relaxed) values of ceria surface energies are reported from ab initio DFT calculations [26].

energy for the removal of another oxygen is positive. In essence, we have also modelled the reconstruction of (100)-O (oxygen terminated surface) by removing half of oxygen atoms which can eliminate the dipole moment as 100_{O-half} surface.

However, as seen from Table 2, when one oxygen atom is added into the reconstructed (100) surface (100_{O-half + 1}), the oxygen vacancy formation (-1.56 eV) becomes more favourable than the (110) surface (1.99 eV), implying (100) is then becoming the less stable surface in the CeO_x , $1 < x \leq 2$ range. This could possibly result in many oxygen sites available to accommodate further oxygen atoms to regenerate the full polar surface in order to re-establish electrostatic repulsion whereas no

low energy site is envisaged from the stoichiometric inter-dispersed Ce^{4+} and O^{2-} in non-polar surfaces.

The electrostatic repulsion within the oxygen rich (100) layers gives the strong thermodynamic tendency to push the oxygen atoms from this surface to further layers beyond and to oxidise the adsorbate(s) on the overlying Pd, providing the greater accessibility of oxygen from this surface [53]. Similarly, the higher energy for oxygen vacancy formation for the CeO_x , $1 \leq x$ range within oxygen depleted (100) could result in favourability for oxygen to can be taken up from Pd (Scheme 1). Thus, the observations we have made in the STEM-EELS and PIE experiments demonstrate that the ceria cubes via the polar (100) surface as a gateway are far more superior to rods with non-polar (110) surface in terms of oxygen mobility and oxygen reservoir content (oxygen storage capacity). We attribute the dynamic reduction and oxidation properties of Pd/CeO₂ catalysts to the existence of a polar (100) surface layer as the active surface gateway to gain access to the inner lattice oxygens, switching from oxygen overdosed or underdosed to the state of half-filled oxygen, due to their instability. As a result, for conditions involving deep reduction and oxidation during the catalytic cycle, metal-ceria cubes interface can benefit more superior performance than other morphologies despite the cubes usually having lower surface area.

3. Conclusions

The redox properties of the Pd deposited on ceria cubes with polar (100) surface and rods with non-polar (110) surface were investigated with Scanning Transmission Electron Microscopy with Electron Energy Loss Spectroscopy (STEM-EELS), Pulse Isotopic Exchange (PIE) and

Density Functional Theory. STEM-EELS indicated deep oxygen reduction can be achieved through the polar (100) surface with Pd as a gateway, where deep reduction was observed for pre-reduced Pd/ceria cubes and not on the rods. The in-situ reduction rate study also suggested that fast reduction is observed around the Pd-ceria interface. PIE experiments showed higher $^{16}\text{O}/^{18}\text{O}$ fractions for the pre-reduced Pd/ceria cubes compared to the rods, indicating an increase in reverse oxygen spillover from the more accessible deeper layers of ceria (100) surface. These observations are in agreement with DFT calculation where on the ceria (100) surface, removal of oxygen to form oxygen vacancy is thermodynamically favourable when Ce/O ratio < 1 and replenishing of this oxygen vacancy is more favoured when Ce/O ratio > 1.

For the application of green catalysis, there may likely be a coexistence of different index facets in nano-ceria particle, which is commonly used as a support material for a wide range of catalysis. The accessibility of this deep oxygen and fast oxygen mobility through the partial coverage of the polar (100) facet is clearly significant. Dependence on reaction conditions such as temperature, nature of metal and atmosphere used, the thermodynamic and kinetic possibility of reconstruction of this facet cannot be discounted. It is therefore not yet able to estimate the impact of this finding to ceria catalysis in real practice under reaction conditions. On the other hand, these studies may provide an insight in the unique properties of ceria supported catalysts that a large quantity of (100) at high oxygen content has been commonly observed, which may lead to future appropriate catalyst design.

Author contributions

AHM and YL prepared and tested the catalysts. SMF, NPY and AHM performed the TEM and STEM-EELS mapping, SMF, SW, SJH, TJP and AHM analysed and processed the data; WC, EIP, BR and AHM carried out PIE experiments under the supervision of ISM. JQ performed the DFT calculations. AHM, KT, IM and SCET wrote the manuscript. SCET supervised the overall project.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2020.118843>.

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