Thermodynamic Evolution of Cerium Oxide Nanoparticle Morphology using Carbon Dioxide.

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ABSTRACT: Surface morphology is known to affect catalytic activity, as some surfaces show greater activity than others. One of the key challenges is to identify strategies to enhance the expression of such surfaces and also to prevent their disappearance over time. Here, we apply density functional theory to the catalytic material CeO₂ to predict the effect of adsorbed CO₂ on the morphology of the material as a function of temperature and pressure. We predict that CO₂ adsorbs as surface carbonates and that the magnitude of the adsorption energy is surface dependent, following the order {100} > {110} > {111}. We show that this difference leads to selective thermodynamic enhancement of {100} surfaces as a function of CO₂ partial pressure and temperature. Finally, we show how the calculated surface free energies as a function of external conditions can be deployed to predict changes in the equilibrium particle morphology. These include the prediction that ceria nanoparticles prepared in the presence of supercritical CO₂ will favour enhanced cube-like morphologies.

Introduction

Controlling the size and morphology of nanoparticles is an important consideration when designing materials, particularly catalysts,¹⁻⁸ not least because nanoparticle morphology and surface composition have a significant effect on reaction selectivity and reactivity.⁹⁻¹³ A good example of this effect can be seen with cerium dioxide (ceria, CeO₂) nanoparticles, where the properties are influenced by their morphology and hence the particular surfaces expressed. Ceria finds applications in soot oxidation/three-way catalysts,¹⁴ water gas shift reactions,¹⁵⁻¹⁶ solid oxide fuel cells,¹⁷ and biomedicine.¹⁸

A variety of CeO₂ nanoparticle morphologies are observed: octahedral, cubes and rods.^{17, 19} The lowest energy {111} surfaces form an octahedron and thus the nano-octahedron is the thermodynamically most stable form.²⁰⁻²² In practice, different synthesis conditions access other morphologies.²³⁻²⁹ These include nano-cubes comprised of {100} surfaces³⁰⁻³¹ and nano-rods comprised of a mixture of surfaces (the actual surface structure of rods has been the subject of considerable debate³²). The {100} and {110} surfaces are higher in energy than the {111} and thus nano-cubes and nano-rods are nominally less stable than nano-octahedra. As a result, nano-cubes and nano-rods might degrade over time and form less reactive nano-octahedra (Figure 1);²¹ surface faceting of ceria nanopowder and nanocubes has been demonstrated at 730°C³³ and 600°C³⁴ respectively. Clearly, having synthesised particles expressing particularly facets it is also useful to examine how to protect these shapes from degradation.

Some molecules, such as water, and hydroxyl groups when adsorbed at the surface of CeO₂ nano-cubes can stabilise the reactive {100} surfaces and thus, in theory, prevent the degradation of nano-cubes to nano-octahedra.^{20-21, 30} However, despite the many studies on the adsorption of small molecules on ceria, key questions remain. For example, how do molecules present during synthesis, post-synthetic treatments or during catalytic processes, modify the expression and evolution of specific surfaces?³⁵ Recent work on water adsorption has shown that water molecules stabilise the {100} surface relative to the {111} surface in CeO₂.²¹ But one molecule that has not been studied in this context is CO₂. CeO₂ comes into contact with CO₂ in several applications and synthesis processes including three-way catalysts and soot oxidation catalysts,^{14, 36} where CO oxidizes to CO₂, in water gas shift reactions, where H₂O + CO → H₂ + CO₂,^{15, 37} and in dry reforming processes, where CH₄ + CO₂ → 2CO + 2H₂.³⁸⁻³⁹

Catalytic studies have shown that adsorption of CO₂ can result in the formation of strongly bound surface carbonate species; carbonates are responsible for a reduction in the catalytic activity of ceria and this is known as carbonate poisoning.^{16-17, 40-47} Computational work has shown that carbonate species can form at the surface,⁴⁸⁻⁴⁹ but findings are complicated by the large differences in the behaviour of different surfaces. Surface carbonates are formed on many metal oxides such as Yttria Stabilized Zirconia (YSZ),⁵⁰ ZrO₂,⁵⁰ MgO,⁵¹ BaTiO₃,⁵² TiO₂,⁵³⁻⁵⁶ Fe₂O₃,⁵⁷⁻⁵⁹ and Al₂O₃.⁶⁰

Figure 1- Schematic illustrating the relationship between nanoparticle shape and stability/reactivity. The {100} and {111} surfaces are represented by blue and red planes.

Thus, in this work we present a computational investigation of the interaction of carbon dioxide with the most important low index surfaces of CeO_2 ({111}, {110} and {100}), with particular emphasis on carbonate formation. Since the surfaces of ceria are often found to be oxygen deficient, we also consider how the adsorption of CO_2 modifies the surface free energies of reduced ($\text{CeO}_{1.9}$, oxygen deficient) surfaces in addition to stoichiometric (CeO_2) surfaces. Once these energies are evaluated, we explore how the equilibrium morphology changes as a function of CO_2 chemical potential and thereby provide a prediction on what conditions are required to thermodynamically stabilize the high energy surfaces, for example the more reactive {100}.

Methodology

Bulk Models. The structure of stoichiometric bulk CeO_2 retains the fluorite crystal structure (space group Fm-3m) despite a small expansion of the unit cell, which is well-documented effect for the *ab initio* methodology employed in this study.⁶¹ The simulated lattice parameter ($a=0.545$ nm) compares well with the experimental lattice parameter of ($a=0.541$ nm).⁶²

Surface Models. Model surface structures were generated using the METADISE code.⁶³ 3D boundary conditions were used throughout, and the surfaces were modelled using the slab method⁶⁴ in which a finite number of crystal layers is used to generate two identical surfaces via the introduction of a vacuum gap perpendicular to the surface. A vacuum gap of 15 Å was used to minimize the interaction between images. The {100} and {110} slabs with a $p(2 \times 2)$ expansion of the surface unit cell included 13 and 7 atomic layers (24 and 28 CeO_2 units, respectively), while the {111} slab with a $p(2 \times 3)$ expansion included 12 atomic layers (24 CeO_2 units). The {100} surface is a polar surface and has been modelled using previously established methodologies.⁶¹

The number of potential configurations for adsorbed carbon dioxide on surfaces of ceria is extremely large and many have been proposed in the literature.⁶⁵ We have studied the associative adsorption of CO_2 on the surfaces of ceria i.e. CO_2 molecules adsorbed onto a surface oxygen to form a carbonate (CO_3) species. We have also studied sub-stoichiometric surfaces of ceria, where an oxygen vacancy is introduced, which leaves two electrons that localize and reduce two cerium atoms from Ce^{4+} to Ce^{3+} ; these surfaces are referred to as reduced surfaces in this article and correspond to stoichiometry of $\text{CeO}_{1.9}$. For reduced surfaces, configurations were constructed to ensure that a CO_2

oxygen fills the vacancy. In some configurations where a carbonate was set at the start of the calculation, the surface oxygen-carbon bond was found to break but the CO_2 molecule remained loosely bound to the surface; these configurations are referred to as “molecular CO_2 ”.

Finally, to investigate the effect of CO_2 chemical potential, four surface concentrations of CO_2 were investigated for each surface: 0.13, 0.25, 0.38 and 0.51 CO_2/nm^2 on the {111}; 0.12, 0.23, 0.35 and 0.47 CO_2/nm^2 on the {110}; and 0.17, 0.33, 0.50 and 0.67 CO_2/nm^2 on the {100}. These concentrations correspond to 1, 2, 3 and 4 CO_2 species on each surface. In each case, different adsorption geometries were investigated and corresponded to monodentate, bidentate and tridentate adsorption configurations.

Calculation details. Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code,⁶⁶⁻⁶⁷ within which projector augmented-wave pseudopotentials and a plane wave cutoff of 500 eV were used with the sampling of the Brillouin zone sampled using a $5 \times 5 \times 5$ Monkhorst-Pack grid for the bulk materials (CeO_2 and Ce_2O_3) and $2 \times 2 \times 1$ for the slabs. Calculations were carried out using the generalized gradient approximation (GGA) exchange-correlation functional of Perdew (PBE), with the +U correction of Dudarev⁶⁸ to account for on-site Coulombic interactions. A U value of 5 eV is applied to Ce f states as this value has been utilized successfully in other studies.^{21, 48, 69-71}

The structures were relaxed until the residual forces on each atom were less than 10 meV Å⁻¹. All calculations were spin polarized and an initial ferromagnetic ordering was used throughout, which has been shown to produce no difference in the energetic of CeO_2 systems.⁶¹

Surface Energies and Thermodynamic Framework. The surface energy (γ) can be calculated from the energy of the systems containing the slab with n Ce cations (E_{Slab}) the energy per formula unit of ceria stoichiometric bulk (E_{Bulk}) and the surface area (A), according to eq 1.

$$\gamma_{\text{Bare}} = \frac{E_{\text{Slab}} - E_{\text{Bulk}}}{2A} \quad (1)$$

The calculated surface energy for the {111}, {110} and {100} was 0.67, 1.05 and 1.41 Jm⁻² respectively. This is in agreement with previous computational work.^{21, 69, 72-73}

Equation 1 provides the surface energy at 0 K and is not representative of the operating conditions of the various catalytic processes, and the synthesis and sintering conditions. In order to analyse the thermodynamic stability of the surfaces, when exposed to a given environment, it is important to account for the effects of the temperature and pressure of the surrounding atmosphere. This can be employed by applying *ab initio* atomistic thermodynamics. In this approach, the system is considered to be in thermodynamic equilibrium with a gas phase environment, which is treated as a reservoir, therefore exchanging particles with the system without changing its chemical potential. This strategy has been used in previous studies.^{21, 71, 74} The surface energy of a surface in equilibrium with an oxygen and carbon dioxide gas phase reservoir is calculated as follows:

$$\gamma = \frac{E_{\text{Slab}} - nE_{\text{Bulk}} - aO_2 \mu_{O_2} - bCO_2 \mu_{CO_2}}{2A} \quad (2)$$

where aO_2 and bCO_2 are the excess number of surface oxygen and carbon dioxide species in the slab, while μ_{O_2} and μ_{CO_2} are their respective chemical potentials. Equation 2 gives the surface energy at 0 K (T^0), temperature dependence is introduced as follows:

$$\gamma = \frac{E_{slab} - E_{bulk} - aO_2 \mu_{O_2} - bCO_2 \mu_{CO_2} - aO_2 \mu_{O_2}(T) - bCO_2 \mu_{CO_2}(T)}{2A} \quad (3)$$

The chemical potential as a function of temperature is accounted for by the following formula (shown for CO_2 where we have used previously for $CaCO_3$ ⁷⁵ but also used for O_2):

$$\mu_{CO_2}(T) = \mu_{CO_2}^0(T^0) + \Delta h_{CO_2}(T^0, T) - T \cdot s_{CO_2}(T) \quad (4)$$

where s_{CO_2} and Δh_{CO_2} are taken from experimental tabulated data.⁷⁶ If it is assumed that carbon dioxide and oxygen behave as ideal gases, then the effect of the gas partial pressure on its chemical potential is given by (again, only shown for CO_2):

$$\mu_{CO_2}(T) = \mu_{CO_2}^0(T) + \frac{1}{2} k_B T \log\left(\frac{\rho_{CO_2}}{\rho^0}\right) \quad (5)$$

The difference in chemical potential due to temperature and partial pressure becomes:

$$\Delta\mu_{CO_2}(T) = \mu_{CO_2}(T) - \mu_{CO_2}^0(T^0) \quad (6)$$

This is a complex dataset to visualise and it is often necessary to reduce the number of dimensions by fixing the partial pressure (or chemical potential) of one gas. We have looked at two extreme scenarios for carbon dioxide adsorption, adsorption on reduced surfaces (Low O_2 pressure) and adsorption on stoichiometric surfaces (High O_2 pressure).

The equilibrium crystal morphologies were generated based on the surface free energies calculated with equation 3 and constructed with a Wulff construction.^{64, 77-78} The surface area of each surface as a function of temperature and pressure was calculated from the Wulff construction and these values were combined to give the surface area ratio between all surfaces under certain temperature and pressure.

Analysis was conducted using the surfinpy code.⁷⁰ Wulff constructions were generated using the pymatgen code⁷⁹ and all figures were drawn using VESTA.⁸⁰

Results and Discussion

Surface Energetics on CO_2 Sequestration. We considered mono, bi and tridentate adsorption of CO_2 as a surface carbonate (CO_3) on stoichiometric and oxygen deficient CeO_2 surfaces. At the lowest surface concentration of CO_2 considered, we find that tridentate adsorption is always favoured on the three CeO_2 surfaces (Figure 2). The geometry of the adsorbed CO_3 is similar on the $\{110\}$ and $\{111\}$ surfaces, where the CO_3 species is orientated at an angle to the surface (Figure 2b and c). In contrast, on the $\{100\}$ surface the carbonate ion adsorbs parallel to the surface (i.e. it lies flat) with each of the three CO_3 oxygen atoms bridging between two surface cerium atoms. The calcu-

lated CO_3 geometry on each surface is in agreement with previous theoretical studies.^{44, 48} Interestingly, a surface oxygen of the stoichiometric $\{100\}$ surface moves by 0.3 Å to accommodate the carbonate (Figure 2a). This rearrangement of the surface oxygen atoms has been previously reported on the addition of phosphate molecules⁶⁹ but this is the first time that it has been shown that adsorbed CO_2 modifies the surface structure of CeO_2 to this extent.

Mullins et al. found that low exposures (5-20L) of CO_2 at 180K resulted in a tridentate carbonate species and a small amount of physisorbed CO_2 at surface concentrations of 5 nm² (CeO_2) and 7.8 nm² ($CeO_{1.7}$).⁴⁴ Our results indicate that CO_2 adsorption geometry is concentration dependent. At low concentrations the entire CO_2 population is predicted to adsorb in a tridentate geometry, but as the concentration increases, carbonate ions display a mixture of adsorption geometries, due to the competition between an increased number of Ce-O bonds and a steric repulsion between CO_3 ions. Thus, the surface concentration is a crucial consideration when attempting to rationalise the adsorption experiments probing the geometry.

In all calculations on $\{110\}$ and $\{100\}$ surfaces, we find that the carbonate species is the energetically preferred form of adsorbed CO_2 and it is only on the $\{111\}$ surface at the highest concentration (0.51 CO_2 /nm²) that we see a mixture of molecularly adsorbed CO_2 and CO_3 species, which is in agreement with experiment.⁴⁸

The reduced surfaces are oxygen deficient and the removal of oxygen leaves two undercoordinated cerium atoms. The most stable configurations of adsorbed CO_2 are those that maximize the surface coordination of the undercoordinated cerium ions (Figure 2d-f). Any attempt to stabilise CO_2 configurations with monodentate geometries relaxed into tridentate geometries or to less stable bidentate configurations. The average bond lengths between the carbonate oxygen and surface cerium atoms are smaller for monodentate adsorption configurations (2.17 Å) and longer for tridentate configurations (2.5 Å). Thus showing, perhaps unsurprisingly, that it is more energetically favourable for the surface to regain its coordination with multiple long bonds, as opposed to smaller numbers of stronger bonds.

The adsorption energy of CO_2 on stoichiometric and reduced CeO_2 surfaces as a function of CO_2 concentration is shown in Figure 3. The magnitude of the adsorption energy of CO_2 follows the order $\{100\} > \{110\} > \{111\}$ at all concentrations and all surfaces. This can be explained by the change in coordination of surface cerium atoms upon CO_2 adsorption. Cerium at the $\{111\}$ surface is 7-fold coordinated, whereas is 6-fold coordinated on the $\{100\}$ and $\{110\}$ surfaces. More favourable CO_2 adsorption energies at the $\{110\}$ and $\{100\}$ surfaces are due to surface cerium atoms increasing their coordination from 6 to 7/8 depending on CO_2 concentration. The Ce atoms at the $\{111\}$ surface are 7-fold coordinated with respect to oxygen, and thus there is a smaller energetic gain in recovering the 8-fold coordination.

Figure 2 - Adsorption geometry for a single carbonate species on the stoichiometric (CeO_2) {100}, {110} and {111} (a, b, c) and reduced ($\text{CeO}_{1.9}$) {100}, {110} and {111} (d, e, f) surfaces. The {100} surface is shown from above the surface plane and the {110} and {111} surfaces are shown from the side. For clarity, cerium, oxygen, and carbon atoms are displayed in dark green, red, and lime. Oxygen from the CO_2 molecule are shown in blue and the surface oxygen bonded to the CO_2 molecule is shown in purple. The view of the {100} surface is in plane view (looking down), whereas the views of {110} and {111} are side on with the oxide surface perpendicular to the page.

At the lowest coverage considered, the adsorption energy on the {111} and {100} surfaces are in good agreement with previous work.^{44, 48} However, Cheng et al. calculated the adsorption energy of CO_2 on the {110} surface and concluded that it is physisorbed as molecularly adsorbed CO_2 and did not form a carbonate.⁴⁹ In contrast, we find that the lowest adsorption energy corresponds to forming a carbonate ion. Indeed, we calculate that it is more stable by 1.06 eV relative to the molecularly adsorbed CO_2 . Even including the van der Waals corrections, which are normally required for molecular adsorption, the difference when we applied the approach due to Klimes et al, only changed to 0.99 eV.⁸¹ Hence, we can be confident that carbonate formation is the thermodynamically preferred form this surface, in keeping with findings for the other low index surfaces.

The adsorption energy is more favourable on the reduced surfaces compared to the stoichiometric surfaces; this is again rationalised in terms of coordination. Reduction of CeO_2 involves the removal of surface oxygen, which lowers the surface Ce coordination; CO_2 adsorption heals this undercoordination by adsorbing an oxygen directly into the oxygen surface vacancy.

Figure 3 - Adsorption energies for CO_2 adsorbing as a carbonate species on the stoichiometric (dashed lines) and reduced (solid lines) low index CeO_2 surfaces. The {111}, {110} and {100} surfaces are shown in orange, green and blue.

Temperature and Pressure Dependent Stability of Adsorbed CO₂. In order to investigate the surface stability as a function of temperature, oxygen and carbon dioxide partial pressures, we present phase diagrams for each surface. These phase diagrams account for a wide range of surface compositions, including stoichiometric and reduced, and also whether CO₂ is present or not. Their surface free energies, as detailed in the methodology, can be expressed as a function of the chemical potential of adsorbed CO₂ and surface O₂.

Figure 4 shows the most stable surface compositions as a function of CO₂ and O₂ chemical potential differences ($\Delta\mu_{\text{O}_2}$ and $\Delta\mu_{\text{CO}_2}$) for the three CeO₂ surfaces. By relating chemical potential difference to partial pressure, $\Delta\mu = RT\ln(p_{\text{O}_2}/p^0)$, we see that low $\Delta\mu_{\text{O}_2}$ conditions (negative values on the phase diagram) corresponds to oxygen reducing conditions i.e. the surfaces are oxygen deficient. In contrast, at high $\Delta\mu_{\text{O}_2}$ (positive values on the phase diagram), which corresponds to oxidising conditions, the surface is fully oxidised, i.e. stoichiometric. At low $\Delta\mu_{\text{CO}_2}$ conditions, CO₂ is not present at the surface. In both reducing and oxidising regimes, increasing $\Delta\mu_{\text{CO}_2}$ stabilizes the adsorption of CO₂ on the surface. We can illustrate the change in composition of the surface phase by considering the temperature range: 298 K and 600 K, which is typically of interest in catalytic processes and unit activities for the gases, i.e. partial pressures 1 bar. The resulting phase behaviour of the different surfaces between 298 – 600 K are marked with a black line on the phase diagrams in Figure 4. The {100} surface, shows no change in surface stoichiometry (Figure 4c) over this temperature range, i.e. the most stable composition is 3.32 CO₂/nm² adsorbed at the reduced surface. The most stable surface composition of the {110} surface is 2.35 CO₂/nm² adsorbed at the stoichiometric surface at 298 K, and on heating to 600 K is partially reduced and has 1.17 CO₂/nm² adsorbed. For the {111} surface the most stable composition has 1.30 CO₂/nm² adsorbed on the stoichiometric surface at 298 K and on heating to 600K results in a bare stoichiometric surface with CO₂ desorbed. Notably, on all three surfaces, at low T (298 K) when both gases are fixed to a pressure of 1 bar, adsorbed CO₂ is stable on the surfaces. However, all surfaces behave in a very different way, indicating that this difference can be used to tune and control adsorption depending on what surfaces are expressed in the nanoparticles.

In general, the phase diagrams in Figure 4 illustrate that at sufficiently low $\Delta\mu_{\text{O}_2}$ values (reducing conditions < -2.5 eV), i.e. low oxygen partial pressures, it is possible to transition between different CO₂ coverages exclusively on the reduced surface by varying μ_{CO_2} . Likewise, at sufficiently high $\Delta\mu_{\text{O}_2}$ values (oxidising conditions > 0.5 eV), it is possible to transition between different CO₂ coverages by varying $\Delta\mu_{\text{CO}_2}$. Two component phase diagrams can also be visualized considering the chemical potential of one component as a function of temperature while maintaining constant the chemical potential of the other component. To isolate the effect of surface reduction on the adsorption of CO₂, we fixed the chemical potential of oxygen and explored the adsorption of CO₂ on the reduced surfaces (low $\Delta\mu_{\text{O}_2}$) and the stoichiometric surfaces (high $\Delta\mu_{\text{O}_2}$) as a function of temperature. This data can be tested using Temperature Programmed Desorption (TPD) experiments, and allows predictions to be made about the state of the surface under catalytically relevant temperatures.³⁵ Figure 5a-f shows phase diagrams

of CO₂ partial pressure as a function of temperature for each surface, where the different regions of the diagrams represent the most stable surface composition (i.e. those with the lowest

Figure 4 - Thermodynamic surface phase diagram of the CeO₂ {111} (a), {110} (b) and {100} (c) in a constrained equilibrium with O₂ and CO₂ gas phase. The differently shaded areas mark the stability regions of various surface structures for a given chemical potential of O₂ and CO₂. The black circles correspond to a CO₂ and O₂ pressure of 1 bar between 298 and 600 K and thus the transition between phases when the partial pressures of both gases are fixed, and the temperature is allowed to vary.

Figure 5 - Pressure vs Temperature phase diagrams for the stoichiometric (CeO₂) {111} (a), {110} (b), {100} (c) and the reduced (CeO_{1.9}) {111} (d), {110} (e) and {100} (f) surfaces. The CO₂ coverage (CO₂/nm²) of each phase is added to the phase diagram. Temperature of desorption for the stoichiometric (CeO₂) (g) and reduced (CeO_{1.9}) (h) surfaces. The ambient CO₂ conditions at Venus, Earth and Mars surfaces have been added as reference points. The {111}, {110} and the {100} surfaces are shown in green, orange and blue. The temperature of desorption at pressures ranging from -12 $\log_{10}(P_{CO_2})$ (bar) to 4 $\log_{10}(P_{CO_2})$ (bar) in increments of 2 are marked at the corresponding locations on the plots.

surface energy at those specific values of temperature and pressure). At low T (blue region), the surfaces are partially covered with carbonate species, whereas at high T (red region) carbonate species are not stable at the surface and thus are not present. The transition between the two region represents the temperature range of desorption of CO₂ from the surface. At high $\Delta\mu_{O_2}$ (stoichiometric surfaces), CO₂ desorbs from the {111} first, followed by the {110} and then the {100} at any given pressure (Figure 5 a,b,c,g). At low $\Delta\mu_{O_2}$ (reduced surfaces), the

introduction of oxygen vacancies greatly increases the temperature range that adsorbed carbonate is stable on the surfaces. This is due to the surface healing effect where CO₃ species formed at the surface allow the surface cerium to regain their partial coordination (Figure 5 d, e, f). Based upon the pressure vs temperature phase diagrams, we have calculated the temperature of desorption for CO₂ (removal of carbonate from the surface) species at the {111}, {110} and {100} surfaces as a function of CO₂ pressure (Figure 5g/h). The desorption temperatures

represent the transition between a bare surface and a surface with CO_2 adsorbed as a carbonate.

Senanayake and Mullins reported weakly bound CO_2 on the {111}, which started desorbing at 150 K and was left with only a small amount of carbonate at 200 K.^{43, 65} Temperature Programmed Desorption experiments are typically run under UHV (10^{-12} bar) and within our model we predict the removal of CO_2 at 127 K on the {111} at these conditions. Removal of CO_2 at low temperatures on the {111} is reported by Staudt et al. who could not detect any CO_2 on the {111} surface at 300 K.⁸² Senanayake et al. determined that carbonates were removed from the {111} surface of CeO_x/Au on heating to 300 K.⁴³ These observations are consistent with our findings as we predict that the partial pressures of CO_2 would need to be above 100 bar to be confident of detecting carbonates at 300 K.

We note that carbonate is bound much more strongly on the {100} and thus the desorption temperatures are much higher at this surface compared to the {110} and {111}. Albrecht et al. found that carbonate species on the {100} are stable up to 600 K for stoichiometric ceria and 700 K for partially reduced ceria ($\text{CeO}_{1.9}$) under ultra-high vacuum conditions.⁴⁴ We predict under these conditions that CO_2 desorbs by 450 K on stoichiometric ceria and 550 K on reduced ceria. It is worth noting that our reduced ceria model is $\text{CeO}_{1.916}$ which is not as oxygen deficient as the experimental samples, and of course we have assumed that there are no impurities present either at the surface or in the gas. Clean {100} surfaces are also difficult to synthesise, which arises from the flexibility of the surface oxygen network that can easily access many different surface oxygen arrangements with very small energy differences.^{20, 35}

Our calculations suggest that oxidation of the surface removes / hinders the adsorption of carbonates from / to the surface, as the reduced surfaces have considerably higher desorption temperatures compared to stoichiometric surfaces (up to 200 K). Oxygen vacancies are reactive sites and are often desirable in catalytic reactions, however carbon dioxide interacts so strongly with the vacancies that the catalyst may lose its efficiency. It is clear that efficiency may be restored as the temperature increases (and CO_2 desorbs). However, this comes at a higher cost as more energy is required to remove CO_2 from reduced compared to stoichiometric surfaces. In the Water Gas Shift Reaction, Feng et al. have shown that ceria redox reactions proceed via a stable carbonate intermediate; the coverage of this intermediate is dependent on the surface Ce^{3+} concentration.⁴⁵ We show that reduced surfaces have a considerably stronger interaction with carbonates compared to the stoichiometric surfaces and given that Ce^{3+} concentration is dependent on the concentration of oxygen vacancies, we can infer that the experimental observations of Feng et al., is likely to be attributed to the strong interaction between CO_2 and the oxygen vacancies.

The effect of adsorbed carbon dioxide on the temperature to reduce the surfaces of ceria is shown in Figure 6. The plot gives the reduction temperature for the surfaces in the absence and presence of CO_2 . In all cases adsorbed CO_2 lowers the reduction temperature effectively making the surface more susceptible to reduction. For example, at atmospheric partial pressures of oxygen, the introduction of CO_2 lowers the reduction temperature by 53, 98 and 191 K for the {111}, {110} and {100} respectively. In general, sequestration of CO_2 has greatest impact on the reduction temperatures of the {100}, whereas there is only a small change seen for the {111} surface. This effect can be ascribed to surface coordination. CO_2 molecules adsorbing as

carbonates effectively introduce two oxygen atoms, which increase the coordination of surface Ce ions, and as noted earlier, the {100} has the lowest Ce coordination and hence is most affected.

Figure 6 - The reduction temperatures at pressures ranging from $-12 \log_{10}(P_{\text{O}_2})$ (bar) to $8 \log_{10}(P_{\text{O}_2})$ (bar) in increments of 1 are marked at the corresponding locations on the plots. The reduction temperature is defined as the temperature required to reduce the stoichiometric surface through the removal of one surface oxygen atom.

A Thermodynamic Strategy to Predict Nanoparticle Morphology Evolution. The performance of CeO_2 catalysts is influenced by particle morphology, as well as composition and stoichiometry of the exposed surfaces.^{17, 20} Research has demonstrated that adjusting synthesis conditions gives rise to different CeO_2 particle shapes, such as cubes ({100}), octahedra ({111}) and rods (mixture of {110} and {100}),⁸³ and that different surfaces have different catalytic efficiencies.⁸⁴⁻⁸⁷ We have combined a simple yet effective thermodynamic computational strategy for calculating surface free energies and applying them to the standard Wulff construction to suggest a synthetic pathway to generate nanoparticle morphologies as a function of experimentally tuneable conditions such as those of pressure and temperature. Clearly, the Wulff construction has a number of assumptions, not least it is based on equilibrium morphologies, but these are more likely to hold when considering nanoparticles and hence this process should help to guide the synthesis.

Based on the surface free energies calculated in the previous section, we have performed a Wulff construction as a function of temperature and partial pressure of CO_2 at high fixed $\Delta\mu_{\text{O}_2}$ (oxidising conditions – stoichiometric surface) and low fixed $\Delta\mu_{\text{O}_2}$ (reducing conditions – reduced surface). Figure 7 shows the effect of CO_2 partial pressure on the equilibrium particle morphology; i.e. Figure 7 shows the thermodynamic driving force varies with conditions leading to different morphologies. The desorption temperature curves for each surface has been overlaid on each plot to illustrate the regions of the morphology phase diagram where each surface is being stabilized by carbonate species. For example, the stoichiometric {111} surface has a very low CO_2 desorption temperature whereas the {100}

surface has comparatively high desorption temperatures. The region of the phase

Figure 7 - Particle morphology phase diagram for the stoichiometric and reduced surfaces. Wulff constructions are shown for the stoichiometric (high $\Delta\mu_{CO_2}$) and reduced (low $\Delta\mu_{CO_2}$) surfaces. These correspond to a {111}:{110}:{100} ratio of 63:12:35 (a), 85:0:15 (b) and 100:0:0 (c) for the stoichiometric surface and 0:0:100 (d), 43:12:45 (e) and 100:0:0 (f) for the reduced surface. For clarity the {111}, {110} and {100} facets are shown in red, orange and blue respectively. The desorption temperatures for the {111} (orange), {110} (green) and {100} (blue) are shown on each phase diagram to illustrate the regions

where carbonates are stable and thus influencing the morphology.

diagrams between these lines is the region where the surface energy of the {100} is being lowered by adsorbed carbonate species while the {111} is not. This lowering of one surface energy relative to another is why adsorbed species affect the equilibrium morphology significantly.

Using ultra high vacuum (UHV) conditions as a reference point (i.e. below 10^{-10} $\log_{10}(P_{CO_2})$ (bar)), for stoichiometric CeO_2 , there is a clear preference for octahedral nanoparticles at temperatures above 210 K. However, with increasing pressure, the surface of the nanoparticle is increasingly comprised of {100} and {110} surfaces. In the case of reduced CeO_2 , octahedral nanoparticles are stabilized above 400 K under UHV conditions. Thus to generate thermodynamically stable nano-octahedra displaying the most stable {111} surface, it is necessary to limit the adsorption of CO_2 molecules on the high energy {100} / {110} surfaces. Indeed, CO_2 molecules on ceria cause an increase in the expression of the {100} surface at the expense of the {111} because of a disparity between the CO_2 adsorption energy on each surface. Hence, high pressures of CO_2 , low temperatures and reduced ceria are a conceivable combination to generate highly reactive nanocubes.

Supercritical carbon dioxide. There is much interest from an environmental and sustainable point of view in using supercritical fluids (SCFs) in synthesis and processing.⁸⁸ Part of the motivation for using SCFs, particularly in synthesis is that current methods for preparing metal salts often require very high temperatures and there can be additional challenges in separation and purification, especially for nanoparticles which are known to easily agglomerate. Supercritical CO_2 (sc CO_2) has received less attention because generally metal salts are less soluble than in sc H_2O for example. However, we see (Figure 7) that nanocubes are the thermodynamically favoured particle shape at temperatures above 305 K and 75 bar ($\log_{10}(p_{CO_2})$ bar = 1.8), which is where in its' phase diagram, CO_2 becomes supercritical. Thus we predict that if ceria nanoparticles are processed in sc CO_2 then nanocubes will result. Clearly, there are a number of caveats, not least we have not as yet considered the effect of the presence of water or other hydrogen containing species, which may be a strong constraint on the purity of sc CO_2 . We have also neglected other species such as CO, although given that ceria is a well-known catalyst for converting CO to CO_2 , this should be less of an issue. Finally, we have assumed that with pure sc CO_2 the partial oxygen pressure is low and hence the reduced surface is favoured. However, even if we assume that reducing agents are not present, we note that CO_2 confers a significant enhanced stability to the reduced {100} surface, see Figure 5. Hence, if O_2 partial pressures of less than 0.1 bar are present, it would result in the stabilization of the reduced {100} at 450 K and at CO_2 partial pressure of 10 kbar perfect cubes are the thermodynamically favoured shape (figure 8). Thus, even if not used for synthesis but as a post synthetic treatment to clean the nanocubes, use of sc CO_2 should ensure that there is no degradation and will act to conserve the reactive {100} surfaces.

Figure 8 - Particle morphology phase diagram CeO_2 as a function of oxygen and carbon dioxide partial pressure at 450 K. Wulff constructions are shown for CeO_2 nanocubes and octahedra

Conclusions

We have demonstrated using an important catalyst, CeO_2 , that atomistic modelling can capture the energetics of CO_2 adsorption on ceria surfaces, and how that ultimately the change in surface stability drives a thermodynamic change in the shape of ceria nanoparticles. The results reveal that

1. Whether in oxidising or reducing conditions, CO_2 is adsorbed as carbonate species on low index surfaces of ceria. There is an energetic cost to desorb CO_2 from the surfaces following the order $\{100\} > \{110\} > \{111\}$ and is correlated to cerium coordination number at the respective surfaces.
2. The presence of CO_2 increases the reducibility of ceria surfaces; indeed, the scavenging of oxygen from carbonated surfaces of ceria occurs at lower temperatures.
3. Thermodynamic driven evolution of nanoparticles in catalytic processes will see $\{100\}$ surfaces promoted over $\{111\}$ at lower temperatures and higher CO_2 partial pressures, while $\{111\}$ surfaces are promoted over $\{100\}$ surfaces at higher temperatures and lower CO_2 pressures.
4. Processing ceria nanocubes in scCO_2 is predicted to conserve the particle shape.

As the starting material (a nanoparticle) for a catalytic process must sustain a large number of catalytic cycles it is important to not only choose a shape that is reactive but also a shape that can be conserved during the process. Manipulation of catalyst nanoparticle of ceria will need to be optimized by bearing in mind these simple rules so that they can last longer in the catalytic process needed.

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ARS carried out the simulations, designed and carried out the data analysis, ARS, MM and SCP devised the study and ARS wrote the manuscript with contributions from all authors.

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