Oxygen Storage Chemistry of Nanoceria

DOU DU
Abstract

The versatile redox chemistry of ceria (CeO$_2$) originates from its Ce$^{4f}$ electron, which plays the key role in changing the oxidation state of Ce between +IV and +III. Ceria is, among other things, a material that can act as a powerful oxygen buffer with a high oxygen storage capacity (OSC). This is used in many technical applications, such as the three-way catalyst, cleaning exhausts from gasoline vehicles. This thesis is concerned with the dramatic OSC effect observed experimentally in the literature for very small ceria nanoparticles (NPs) at lower temperatures, where the effect was found to be accompanied by the formation of superoxide ions (O$_2^-$).

The main aim of the thesis work was to develop strategies to allow us to discover the origin of the OSC phenomenon, and to simulate temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments and collect useful mechanistic insight about these processes. Quantum-mechanical (DFT) calculations, partly with modified DFT functionals, and later augmented by microkinetic (MK) modelling building on the DFT-results, made it possible to model the large and complex NP systems needed to make detailed comparisons between theory and experiment feasible.

At first, a suitable DFT functional for nanoceria was needed. We turned to hybrid functionals, and more specifically, the non-local Fock exchange contribution within the hybrid functional HSE06 was explored. The amount that gave the best overall description was determined (15%, labeled HSE06' below) and was used in subsequent studies. Moreover, an accompanying HSE06'//PBE+U computational protocol was constructed (HSE06' energies calculated for pre-optimized structures at the PBE+U level); this made it possible to use the hybrid functional for large ceria systems.

With the modified HSE functional, we scrutinized a previously proposed OSC model, namely the "supercharge" model for nanoparticles loaded on the outside with superoxide ions at low-coordinated ridge sites, enabled by the oxidation of Ce$^{3+}$ to Ce$^{4+}$. In the previous study, adsorption energies were calculated using the PBE+U density functional, which does not give adsorption energies in agreement with experiment. With the new HSE06' functional, together with the Redhead equation, we obtained an estimated oxygen desorption peak at ca. 415 K, in much better agreement with the experimental TPD peak at 440 K. However, this calculation could still not explain the large broadening of the experimental TPD spectrum. An oxygen adsorption energy model was then formulated which took Ce coordination and superoxide ion coverage into account. With microkinetic simulations based in this energy model, we achieved a broad simulated TPD signal, which was largely in agreement with the experimental spectrum.

Finally, an improved “supercharge” model was assessed concerning its ability to mimic the temperature-programmed reduction (TPR) experiments reported in the literature for H$_2$ interacting with ceria nanoparticles. We proposed that the reduction process follows a Langmuir-Hinshelwood reaction mechanism, which gave a simulated TPR spectrum in good agreement with the experimental results.

In summary, the goals listed above were achieved: we managed to simulate TPD and TPR spectra, using a DFT-based MK approach; the results were in good agreement with experiment and useful mechanistic insight about these processes and the OSC mechanism was derived from the MK simulations and the DFT analyses.

Keywords: Nanoceria, Density Functional Theory, Hybrid Functional, Oxygen Storage Capacity.

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To my dear parents!
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  Screened hybrid functionals applied to ceria: Effect of Fock exchange
   D. Du, M. J. Wolf, K. Hermansson and P. Broqvist

II  From ceria clusters to nanoparticles: Superoxides and supercharging
    D. Du, J. Kullgren, K. Hermansson and P. Broqvist

III Simulated temperature programmed desorption experiments for calcined nanoceria powders
   D. Du, J. Kullgren, K. Hermansson and P. Broqvist
   Manuscript.

IV  Simulated temperature programmed reduction by H₂ — a key to understanding OSC on nanoceria
    D. Du, K. Hermansson, P. Broqvist, and J. Kullgren
    Manuscript.

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1. Introduction

1.1 Background

Two Swedish chemists Jöns Jakob Berzelius and Wilhelm Hisinger discovered cerium in the year 1803 [1]. Martin Heinrich Klaproth discovered it independently in the same year. The name cerium is inspired by the dwarf planet Ceres. Cerium (Ce) is the 58th element in the periodic table, the second element in the lanthanide series. It is the most abundant rare earth element, thus relatively cheap, which makes it a good candidate for technical applications.

Cerium is also the lightest element having $f$ electrons, which are the reason for its interesting chemical properties. The electronic configuration of the Ce atom can be formulated as [Xe]4f$^1$5d$^1$6s$^2$. It has two common oxidation states, namely Ce$^{3+}$ and Ce$^{4+}$, leaving one Ce $4f$ electron in the Ce$^{3+}$ ion while all Ce $4f$ orbitals are empty in the Ce$^{4+}$ ion. Reduction and oxidation (the redox processes) of cerium is at the core of its chemistry.

Cerium oxide (CeO$_2$) is called ceria. Ceria is extensively used in catalytic processes [2]. One notable application is in the three-way catalyst (TWC) in automobiles, where it is used together with metals like Pt, Pd and Rh. The TWC converter is a single device that eliminates all three major pollutants (CO, hydrocarbon H$_x$C$_y$ and NO$_x$) generated by the combustion process. This elimination occurs through oxidation processes (formula 1.1 and 1.3) and reduction (formula 1.2) reactions. Ceria being well-known for its oxygen storage capacity (OSC) [3] it is used as an oxygen buffer to support the oxidation reactions in the TWC. As shown in formula 1.4, stoichiometric CeO$_2$ can release oxygen at high temperature.

\[
\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad (1.1)
\]

\[
2\text{CO(g)} + 2\text{NO(g)} \rightarrow 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g}) \quad (1.2)
\]

\[
2\text{C}_x\text{H}_y(\text{g}) + (2x + \frac{1}{2}y)\text{O}_2(\text{g}) \rightarrow 2x\text{CO}_2(\text{g}) + y\text{H}_2\text{O}(\text{g}) \quad (1.3)
\]

\[
\text{CeO}_2(\text{s}) \leftrightarrow \text{CeO}_{2-x}(\text{s}) + \frac{y}{2}\text{O}_2(\text{g}) \quad (1.4)
\]

In addition, ceria is commonly used as an electrolyte in solid oxide fuel cells (SOFC) as ceria-based materials can improve the fuel cell performance [4]. Ceria has also been used in combustion reactions and other catalytic reactions [2]. In recent decades, in view of the rapid development of nanoscience and nanotechnology, much ceria-related research has shifted towards the nanoscale [5, 6]. The surface to volume ratio increases significantly in nanoceria compared to larger particles, which makes a nanosystem more active in surface reactions. Nanoceria is used as a scavenger to remove free radicals from the human body [7]. For example, it can be used to protect the retina (the light-sensitive layer of the eye) from degeneration [8].
One interesting finding for nanoceria is their extra oxygen storage capacity reported by Xu et al. [9] in 2010. In their research, these authors found that, for nanoceria, there is a size dependence of the OSC and that a new OSC peak emerges in temperature-programmed reduction (TPR) experiments at low temperature when the particle becomes smaller than 5 nm. By fitting the OSC spectra (using Gaussian functions), they identified a new peak at about 675 K. Furthermore, they found the formation of superoxide-like species on the nanoceria using EPR and XPS, which was reported in literature for the first time.

The origin of this peak was unclear at the time. In 2015, Renuka et al. [10] re-investigated the OSC for nanoceria. Two different sizes of nanoceria, namely 3.7 and 11 nm, were compared in TPR experiments. A peak at 675K for 5.1 nm nanoceria was found by Xu et al. [9]. The two (Xu et al.’s and Renuka et al.’s) TPR experiments are fully consistent with each other.

Understanding the mechanism behind this phenomenon (the increase of the OSC for small ceria NPs) would be very helpful for the design of nanoceria catalysts with significantly improved catalytic performances. Theoretical work can be a powerful tool to study the principles of chemical reactions, in particular if high-performance computing (HPC) infrastructure is available, allowing to use the most advanced methods. Yet, since even the most powerful theoretical approach cannot model a full 'real' system, choices have to be made. In the present thesis, I will thus mainly focus on the following points:

Precedingly, both theoretical and experimental studies [11, 12, 13, 14, 15, 16, 17] have found that oxygen adsorption leads to the formation of peroxide or superoxide ions at the oxygen vacancy sites on a ceria surface. Which type of adsorbed oxygen species is formed depends on the locations of the excess Ce$^{3+}$ ions. In 2011, Preda et al. [18] showed by calculations that the superoxide anions can be formed at low coordinated Ce$^{3+}$ sites. In 2013, Kullgren et al. [19] proposed a so-called "supercharge" oxygen adsorption model to explain the nanoceria OSC. In this theoretical model, the oxygen molecules adsorb directly on corner and edge sites of Ce$^{3+}$ ions in octahedral particles. Each Ce$^{3+}$ at corner and edge site adsorbs one oxygen molecule and forms one superoxide anion. The model successfully explains the size dependence of the OSC for nanoceria and formation of the superoxide species.

However, there are still many unsolved problems; for instance, the calculated oxygen adsorption energy found was too low to fit with the experimental temperature-programmed desorption (TPD) data. A systematical study to examine and explore the details of the "supercharge" model was thus deemed necessary; it will be elaborated in this thesis. A more comprehensive discussion about oxygen adsorption on ceria and the term "supercharge" model will be given in particular in chapter 4.
1.2 Scope of this thesis

When I started the thesis project, the "supercharge" model had already been presented in Ref. [19] and [20]. Our hypothesis is that the "supercharge" oxygen adsorption model is the key to explain the extra OSC observed for nanoceria. I thus tried to further validate the "supercharge" model under different circumstances by comparing its results with reliable experimental data from the recent literature. In this I focused mainly on two experiments, namely the TPD data by Wang et al. [21] and TPR by Xu et al. [9] and Renuka et al. [10].

The first problem to solve was that the normal DFT calculations based on the DFT+U method yield too small binding energies for the oxygen adsorption. I made the hypothesis that the problem might be due to an inadequate description of the localized f-electrons when the PBE+U functional is used. It was clear that we need a better functional, namely hybrid functional. As shown in Fig. 1.1 (paper I), I studied the performances hybrid functional HSE06 for bulk ceria systems by tuning the fraction of the Fock exchange. Subsequently, I investigated the oxygen adsorption on small ceria clusters and nanoparticles (NPs) in paper II. I built the small ceria clusters and nanoparticles model that were employed in Ref. [19, 20] and optimized the structures through different types of DFT calculations.

As presented in Fig. 1.1 (paper II), I added the oxygen molecules to the ceria clusters and NPs according to the "supercharge" model. With the bespoke functional from paper I, I managed to obtain oxygen adsorption energies in good agreement with the peak position in the experimental TPD spectrum. However, this could not explain the observed broadening of the experiment. I therefore introduced the idea of taking into accounts both the coordination number of the adsorption Ce sites and the degrees of surface coverage by oxygen molecules when the adsorption energy is computed. This is published in paper III and led to a significant broadening of the simulated TPD spectrum.

The TPR experiments in Ref. [9] and [10] involved the reduction of H2 on 3-5 nm ceria nanoparticles. One of the main difficulties was to try to build a complete reaction model including all relevant reactions. Another one was to treat NPs which may be small for experimentalists but large for computations. In paper IV, we constructed a microkinetic simulation model, based on the "supercharge" model, to overcome both of these difficulties. Finally, we obtained a simulated TPR spectrum, which was in good agreement with experiments.

The entire thesis project is based on extensive calculations on the supercomputers at the Swedish National Infrastructure for Computing (SNIC). A supercomputer is a massively parallel computer for general-purpose computing with many nodes and Central Processing Units (CPUs). Supercomputers are crucial for modern scientific research and development, not only in materials chemistry but in a range of other compelling areas such as climate...
simulation, astrophysics and molecular sciences including life sciences. The supercomputers Triolith and Tetralith at SNIC in Lund, both with about 25 000 CPU cores, were heavily used for my thesis project.

**Overviews of my thesis work**

<table>
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![Simulated TPR spectrum](image1)

**Figure 1.1.** An overall sketch of this thesis project. In **paper I**, I studied the bulk ceria system. The figure shows the unit cell of CeO₂. The modified hybrid functional HSE06' gave a good description of the bulk ceria properties. In **paper II**, we studied both small ceria clusters and nanoparticles (NPs). We obtained the correct simulated TPD peak position. In **paper III**, we studied the coordination number and coverage dependent oxygen adsorption energy, which explains the broadening of the TPD. In **paper IV**, we used the microkinetic simulation to explain the TPR process. Gray atoms are cerium and red ones are oxygen. Gold atoms represent the oxygen in the superoxide ions. Blue-violet stands for the Ce³⁺ ions and blue atoms are hydrogen. The same color code will be used throughout this thesis.

In terms of software, all the density functional theory calculations were performed with the Vienna Ab *initio* Simulation Package (VASP) [22, 23, 24, 25].
Computational chemistry research involves considerable work with programming and scripting. I have thus written many Python scripts to automate the construction of input structures, for example, to analyze the results and to store and administer data. I built my own Python library, embedded inside the Atomic Simulation Environment (ASE) [26]. In addition, I used many other programs to analyze my results and plot figures. For instance, I used the Bader program [27, 28] to examine the oxidation states of the cerium atoms. Jmol [29] was used to plot high-quality 3D molecular structure. The microkinetic modeling code was written by Dr. Jolla Kullgren using Octave. This thesis was typeset using the \LaTeX typesetting package.

1.3 Summary of each paper

In paper I, I focused on studying the effect of the Fock exchange included in the HSE06 functionals on the bulk ceria properties. I found that 15% Fock exchange gave the best overall description for these systems. We named this optimal hybrid functional HSE06′. However, hybrid functionals are very expensive to use, and therefore I proposed an alternative approach for large and complex ceria systems, namely a composite protocol consisting of a HSE06′ single-point energy (SPE) calculation at the PBE+U fully optimized structure. We label it HSE06′//PBE+U. A single-point energy calculation means minimizing the molecular energy and specifying this particular point in the molecular configuration space.

In paper II, we then used HSE06′ to reinvestigate the "supercharge" model. As shown in Fig. 1.1, we studied both fully reduced small clusters and partially reduced nanoparticles and their interactions with oxygen molecules. We found that each Ce$^{3+}$ ion on the ridges and corners of an octahedrally NP can adsorb one oxygen molecule and form superoxide and Ce$^{4+}$ ions. Full optimization at the HSE06′ level was used for the small ceria clusters and the single-point composite HSE06′//PBE+U(5eV) method for nanoparticles up to 1.6 nm in diameter. The latter method gave much stronger adsorption than the PBE+U functional. Using the energies from the composite method for these quite small systems, a formula for the average oxygen adsorption energy per NP was derived in terms of the site-resolved oxygen adsorption energies at corner and ridge sites. This formula was then used together with the Redhead equation to estimate the temperature for the oxygen desorption peak for much larger NPs. For NPs with sizes in 8-13 nm, i.e. in the experimental range, the estimated desorption peak temperature converged to 415 K, which is in good agreement with the 439 K value given by the TPD experiment [21]. The experimental TPD results in Ref. [21] give a very broad spectrum. No broadening effects were included in our TPD simulation model as we calculated only the average oxygen adsorption energy for a nanoparticle.
The work in **paper III** aimed at giving an explanation for broadening effects in the experimental TPD spectrum. Instead of using the average adsorption energy, we calculated here the energy for each specific oxygen adsorption at different oxygen coverages. Our DFT calculations have shown that the Ce coordination number has a very large effect on the oxygen adsorption energy. In the paper, we suggest that the introduction of subsurface oxygen vacancies create 5-coordinated Ce sites, which also would explain the high reduction grade of the ceria NPs observed in the experimental work in Ref. [9]. In addition, we noticed a quite small coverage dependence in the oxygen adsorption energy when adsorption on sites with the same coordination numbers (e.g. just ridge sites) were compared. By using linear regression, we formulated a coordination number and coverage dependent oxygen adsorption energy for different size ceria nanoparticles. This expression was then used in a microkinetic model to simulate TPD spectra. The obtained spectra were in good agreement with experiment, this time both concerning the peak positions and the spectral widths.

In **paper IV**, another set of key experiments for nanoceria were in focus, namely the TPR experiments by Xu et al. [9] and by Renuka et al. [10]. In the TPR experiment, $\text{H}_2$ was used as the reducing agent. The TPR peak was observed at about 660 K in the two experiments for NPs of the order of 4-5 nm. In particular, we studied how $\text{H}_2$ molecules interact with the surfaces and dissociate, and how the resulting protons react with the superoxide ions. Here I employed force-field based Metropolis Monte Carlo simulations to find the locations of the $\text{Ce}^{3+}$ ions on ceria NPs, then I computed a large number of reaction barriers for the dissociation $\text{H}_2$, its mobility, etc. Finally I constructed a microkinetic simulation model to describe the TPR process involving the interaction of hydrogen molecules with nanoceria. We found that a Langmuir-Hinshelwood reaction mechanism is in keeping with the TPR experiments. The peak of the simulated TPR spectrum, resulting from the microkinetic simulations for a 5 nm large particle (as in the experiment), is in good agreement with the experimental TPR results. It should be noted that the many reactions studied in this were computationally costly since we found it necessary to resort to the PBE+$U$ approach.

In summary, **paper I** presented HSE06′ as a promising approach to enable the calculation of oxygen chemistry on large nanoceria systems. **Paper II-IV** scrutinized the "supercharge" oxygen adsorption model presented earlier in the literature. The model was validated by simulating TPD and TPR spectra which were found to compare well with experimental spectra in the literature. In particular, the "supercharge" model for oxygen adsorption on nanoceria is seen to capture the essential features explaining the increase of OSC for nanoceria observed experimentally.
2. Methods

We are in the era of modeling and simulating in silico, owing to the rapid development in computer hardware and software. Computer simulations are widely used in chemistry research and development. A computer simulation can lead to chemical insights difficult (or even impossible) to obtain from experiments alone. Nanosystems are a case in point, their small size and complex and rapid reactions make it difficult to capture the necessary information by experiments alone. On the other hand, a model, here the so-called "supercharge" model, must be confronted with experiment, which can be difficult. This is the starting point of this investigation.

For a real material, even with the largest conceivable supercomputer, the computing power still severely limits the choice of properties (observables) that can be computed. Hence, drastic simplifications and approximations must often be used in computational studies. For given computational resources, the tradeoff is often between the accuracy of the results for specific systems and the analytic capabilities as well as the ability to yield general insights. Depending on the simulated systems and research purposes, computational chemists also need to balance accuracy and speed. Quantum mechanical (QM) methods are usually accurate (and the accuracy can be controlled), but computationally expensive. They offer detailed information such as molecular "orbitals", electron densities and densities of state. In contrast, molecular mechanics (MM) methods using pre-established force fields (FF) are much faster, but with less detailed information. In these FF methods, the potential interaction energies are parameterized into mathematical expressions. The optimal parameters are certainly different for different systems, but trying to determine them in some way contradicts the purpose of the method. FF methods are, however, commonly used to study large and complex systems such as the extended ceria surfaces and nanoparticles of interest here. There are also semi-empirical computational chemistry methods, which aim at making a bridge between quantum mechanics and molecular mechanics methods.

In this thesis project, electronic properties are essential since I want to use the "supercharge" model, which involves charge transfer and Ce 4f electron localisation. Thus, I mainly employed a quantum mechanics method, density functional theory (DFT). The localisation of the Ce 4f states is, however, problematic if studied with standard DFT methods. Two DFT methods, namely the PBE+U and the hybrid functional HSE06, are typically used to overcome this problem. After tests, however, I preferred to use a bespoke hybrid functional, HSE06', to apply to the "supercharge" model. Due to the high computational cost of such hybrid functionals, the size of the systems is severely restricted. Thus, I propose and study the HSE06'/PBE+U protocol, which aims at reducing the computing costs connected with hybrid functional calculations.
The TPR and TPD experiments involve high temperature, we thus employed kinetic methods to simulate them. *Molecular dynamics* (MD) simulations are an excellent tool to analyze chemical reactions. In an MD simulation, the motions of the nuclei are computed by solving the classical equations of motion numerically. The molecular interactions can be evaluated by QM, MM or mixed (QM/MM) methods. However, a quantum mechanics molecular dynamics simulation would be too expensive for our systems. Instead, we used the Redhead equation to obtain estimated temperature for the oxygen desorption peak. Furthermore, we employed microkinetic simulations to study the TPD and TPR experiments.

### 2.1 Quantum chemistry and density functional theory

The so-called "modern" quantum mechanics provides an easier way to explore chemistry. With the help of the rapid development of high-performance computing, we are able to study many chemical reactions on computers. It remains, however, that the Hartree-Fock (HF) approach is the basis of quantum chemistry. In this approach, a single Slater determinant is used to describe the wavefunction $\Psi(r)$. Each electron "feels" the average potential of all other electrons. The Schrödinger equation ($E\Psi(r) = \hat{H}\Psi(r)$) is solved iteratively and self-consistently. The Schrödinger equation in the Hartree-Fock approximation is non-linear, which is why it can only be solved iteratively. This is done through the *self-consistent-field* (SCF) method.

The Hartree-Fock ansatz does not consider electron correlations. Its main strength is that it is based on the variational principle, which guarantees an upper bound to the true HF ground state energy. In order to go beyond this HF energy, one can mix several Slater determinants for the representation of the wavefunction, keywords for this are: configuration interaction, coupled cluster, multireference configuration interaction methods and several more. However, the biggest problem for such calculations is still the limitation by the computing power. Normally, the Hartree-Fock computing time scales as $N^4$, where $N$ is the number of basis functions.

Many efforts have been made to improve the computing speed, for instance by smartly truncating the configuration interaction to include only certain excited states. Other efforts have also been devoted to improving the algorithms, e.g. through an efficient parallelisation.

The Density Functional Theory methods provide an alternative to the rigorous variational approach just described. They have been developed in the last third of the 20th century and quickly became the most popular tools to study many chemistry related problems. DFT methods often offer reasonable accuracy without compromising speed.

The core of DFT calculations is solving the Kohn-Sham equation [30], which reads:
\[ E[\rho] = T_s[\rho] + \int v_{\text{ext}}(r) \rho(r) dr + V_H[\rho] + E_{\text{xc}}[\rho] \]  

(2.1)

where the total energy \( E \) is a function of the electron density \( \rho(r) \). \( T_s \) is the kinetic energy. \( v_{\text{ext}} \) is the external potential and \( V_H \) is the Hartree (Coulomb) energy. \( E_{\text{xc}} \) is the exchange-correlation energy, which is the only unknown term. Very many exchange-correlation functionals, suitable for different systems, have been (and still are) developed for DFT.

### 2.2 The DFT+\( U \) functional

In all my papers (I-IV), DFT+\( U \) is the main calculation method. Different \( U \) values were employed for different purposes.

Because of the 4\( f \) electrons, Ceria belongs to the strongly correlated materials. For such systems standard DFT calculations typically yield a wrong band structure with a small band gap between the highest occupied valence band (HOVB) and the lowest unoccupied conduction band (LUCB). Ceria has narrow and partially filled Ce 4\( f \) states, which are particularly difficult to describe correctly with standard methods. However, obtaining an electronic structure as exact as possible is very important for studies of redox reactions. Particularly, for our "supercharge" model, we need a good electronic structure to accurately calculate the oxygen adsorption energies. More discussion on this point can be found in Chapter 4.3.

The Hubbard model [31, 32] is used here for the strongly correlated (\( d/f \)) electrons in order to overcome this problem, while the remaining valence electrons are treated with a standard DFT functional. This method is called DFT+\( U \). The Hubbard-like term is simply added to the localised (\( d/f \)) electrons in the DFT+\( U \) functional. The total energy of the DFT+\( U \) functional is:

\[ E_{\text{DFT+U}} = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}} \]  

(2.2)

where \( E_{\text{DFT}} \) is the DFT total energy to be corrected. \( E_{\text{Hub}} \) includes the electron-electron interactions between the strongly correlated electrons represented by the Hubbard Hamiltonian. The double count (dc) term \( E_{\text{dc}} \) must be removed from the total energy. DFT+\( U \) can be introduced in two different ways. One has been developed by Liechtenstein et al. [33], explicitly setting the on-site Coulomb parameter \( U \) and the on-site exchange parameter \( J \). On the other hand, Dudarev et al. [34] proposed a single effective parameter \( U_{\text{eff}} = U - J \). We used the effective \( U_{\text{eff}} \) value for Ce 4\( f \) electrons of all DFT+\( U \) calculations. Therefore the total energy is computed as in the Eq. 2.3:

\[ E_{\text{DFT+U}} = E_{\text{DFT}} + \sum_m \frac{U_{\text{eff}}}{2} \text{Tr}(\rho^m - \rho^m \rho^m) \]  

(2.3)
where $\rho^m$ is the atomic orbital occupation matrix. The energy correction term introduces the penalty $U_{\text{eff}}$ value. This $U$ value can be evaluated by different methods such as linear response approach [35] or simply fitting to experimental data. A considerable amount of literature has been published concerning suitable $U$ values for ceria systems. For instance, Castleton et al. [36] systematically studied $U$ values and the oxygen vacancies in ceria. Based on the localisation of the Ce 4$f$ electrons in the bulk with oxygen vacancies, they concluded that values of about 6 eV for LDA+$U$ and about 5.5 eV for GGA+$U$ are suitable. In paper I, we suggested a $U$ value of 3 eV for an overall good description of bulk ceria properties.

2.3 Hybrid functional

In paper I, we studied the performance of the hybrid functional HSE06 with different fractions of Fock exchange on bulk ceria systems. In paper II, we used the hybrid functionals to compute the oxygen adsorption energies.

The choice of a suitable exchange-correlation functional is generally problematic in DFT calculations. In the DFT community, Jacob’s ladder [37] is used to describe the different levels of exchange-correlation approximations to the exact ground state solution. The local density approximation (LDA) [38] is the lowest step in the ladder. By introducing the gradient of the density, the generalized gradient approximations (GGA) [39], one can climb a step higher. By adding the exact exchange, one reaches a much higher level of theory. The exact exchange is computed with the Hartree-Fock method, namely Fock exchange. In this method, the self-interaction error (see Eq. 2.4) is cancelled by the mathematical rule of the linear algebra (Slater determinant is zero if any two spin orbitals are the same). While there is finite self-interaction error in LDA and GGA functionals. The Hartree term for a one-electron system is not zero as shown in Eq. 2.4, which is caused by the self-interaction error.

$$\frac{1}{2} \int \int d^3 r d^3 r' \frac{n_1(r)n_1(r')}{|r-r'|} \neq 0 \quad (2.4)$$

By mixing the Fock exchange with other exchange-correlation functionals, we obtain the hybrid functionals. In the HSE06 hybrid density functional, the Fock exchange is mixed with the Perdew-Burke-Ernzerhof (PBE) [40] functional.

$$E_{XC}^{\omega \text{HSE}} (\alpha, \omega) = \alpha E_{\text{HF,SR}}^{X} (\omega) + (1-\alpha) E_{\text{PBE,SR}}^{X} (\omega) + E_{\text{PBE,LR}}^{X} (\omega) + E_{C}^{\text{PBE}}$$

There are two parameters in the HSE functional shown in Eq. 2.5 as $\alpha$ and $\omega$. $\alpha$ is the fraction of the Fock exchange. $\omega$ is the screening parameter, which separates the interactions into long and short range parts as shown in Eq. 2.6.
\[
\frac{1}{r} = \frac{\text{erfc}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r}
\]  

(2.6)

where \( \text{erf}(x) \) is the Gaussian function of error and \( \text{erfc}(x) = 1 - \text{erf}(x) \). The introduction of the screening parameter \( \omega \) aims at avoiding heavy computing effects and problems in the evaluation of the long-range Fock exchange with little loss of accuracy. As displayed in Fig. 2.1, tuning \( \omega \) will modify the relative contributions of the short and long range interactions. When \( \omega \) is zero, there is only a short range term in the exchange-correlation functional, which becomes identical to the PBE0 functional. On the other hand, when \( \omega \) tends to infinity, there is only a long range term in Eq. 2.5, which becomes identical to the PBE functional.

\[\text{Figure 2.1.} \text{ Demonstration of how the screening parameter } \omega \text{ works with two different values (0.2 and 0.6). For the smaller } \omega \text{ value (0.2), the short range term carries more contribution to the } \frac{1}{r} \text{ function than for the larger value (0.6).}\]

### 2.4 Our HSE06′//PBE+U computational protocol

The biggest obstacle to use hybrid calculations are the computing costs, which prohibits using these functionals for full geometry optimizations of ceria systems. For instance, our hybrid calculations for ceria NPs cost approximately 15 times more than PBE+U calculations.

Among computational chemists it is common to use single-point energy (SPE) calculations of a accurate method. SPE calculations reduce computing cost without losing much accuracy, compared to full geometry optimizations with a same method. Here we investigated the hybrid functional HSE06′ single-point energy calculations on the fully optimized structures from PBE+U calculations. We found that this protocol can get results for CeO\(_2\) reduction energy close to the ones from fully relaxed HSE06′ calculations. However, we clearly see a lattice parameter dependence. Such supercells are employed to calculate the oxygen vacancy formation energy, which may entail large
deviations in the energies. Note that PBE+U functionals always give larger lattice parameters than HSE06'. In such cases, we can shrink the cell using fractional atomic coordinates according to the lattice parameter obtained from hybrid calculations on smaller unit cells.

In paper II, we employed the same protocol to study ceria clusters and nanoparticles. For the ceria clusters, we compared the results with fully relaxed hybrid functional calculations. The HSE06′/PBE+U protocol still gave good results for the cluster formation and average oxygen adsorption energies. Therefore, we employed the HSE06′/PBE+U protocol to study large ceria NPs in paper II and III.

2.5 Redhead equation

The temperature programmed desorption is a chemical method, which is commonly used to study adsorption of molecules on surfaces. TPD was originally proposed by Cvetanović and Amenomiya [41] in 1967. In the TPD experiment, the temperature $T(t)$ normally increases with time at a constant rate $\beta$.

$$T(t) = T_0 + \beta t \quad (2.7)$$

where $T_0$ is the initial temperature and $t$ is the time. The rate of desorption can be written as:

$$-\frac{d\Theta}{dt} = k_d \Theta^n \quad (2.8)$$

$\Theta$ is the surface coverage. $k_d$ is the desorption rate constant and $n$ is the desorption order. According to the Arrhenius equation, the desorption rate constant can be written as:

$$k_d = A \exp\left(-\frac{E_d}{RT}\right) \quad (2.9)$$

Substituting the desorption rate constant into Eq. 2.8, one obtains the Polanyi-Wigner equation [42], which is:

$$-\frac{d\Theta}{dT} = -\frac{d\Theta}{dt} \frac{dt}{dT} = A \frac{\Theta^n}{\beta} \exp\left(-\frac{E_d}{RT}\right) \quad (2.10)$$

For the first-order desorption ($n=1$), the desorption energy $E_d$ is given by the Redhead equation [43].

$$E_d = RT_p \left[ \ln\left(\frac{AT_p}{\beta}\right) - 3.46 \right] \quad (2.11)$$

where $T_p$ is the temperature for the maximum of the desorption, which corresponds to the peak in the TPD spectrum. In paper II, we used the average
oxygen adsorption energy as \( E_d \) with the Redhead equation to obtain the simulated desorption peak temperature \( T_p \).

### 2.6 Microkinetic simulations

In paper III and IV, we used a microkinetic simulation to obtain TPD and TPR spectra. In 2013, Wang et al. [44] proposed a microkinetic simulation method to study the temperature programmed desorption for the metal oxide systems. A simple desorption adsorption model can be written as (Eq. 2.12).

\[
A^* \leftrightarrow A + \ast
\]  

(2.12)

\( A \) is the adsorbed molecule and \( \ast \) is the adsorption site on the surface. The desorption rate \( r_{\text{des}} \) is given by the equation:

\[
r_{\text{des}}(t) = \frac{-d\Theta_{A^*}}{dt} = \frac{P_T}{C_T \sqrt{2\pi m_A k_B (T_0 + \beta t)}} \frac{q_A q_*}{q_{A^*}} e^{-E_{\text{des}}/R(T_0 + \beta t)} \Theta_{A^*} \]  

(2.13)

The prefactor of this equation is derived from the collision theory [45]. \( P_T \) is the total pressure. \( C_T \) is the concentration of reaction sites on the surface. \( m_A \) is the molecular mass of the adsorbate \( A \). \( k_B \) is Boltzmann’s constant (1.38064852 \( \cdot \) 10\(^{-23} \) J/K). \( T_0 \) is the initial temperature and \( \beta \) is the ramping parameter. \( q_A \), \( q_* \) and \( q_{A^*} \) are partition functions. \( E_{\text{des}} \) is the desorption energy. \( R \) is the gas constant (8.314 J/mol). \( \Theta_{A^*} \) is the coverage of the adsorbate \( A \). In a TPD experiment, the spectrum is related to the desorption rate \( r_{\text{des}} \). The relationship between the surface coverage of \( A \), \( \Theta_{A} \), and time \( t \) can be obtained by solving the ordinary differential equation 2.13 numerically.
3. Hybrid vs. PBE+\(U\) functionals for ceria (Paper I)

**Question:** Is there a functional which yields a better description of ceria properties than the PBE+\(U\) approach?

**Objective:** Try to find an optimal HSE06 functional by tuning the fraction of the Fock exchange. Furthermore, try to reduce the high computing cost of the hybrid functional.

**Methods:** PBE, PBE+\(U\)(\(U=2,3,4,5\text{eV}\)), HSE06(\(\alpha=10,15,20,25\%\))

**Calculated properties:** Bulk ceria geometric structure, electronic band structure, stability and full/partial reduction energy.

There are three kinds of pure bulk ceria, which are stoichiometric and fully or partially reduced, namely \(\text{CeO}_2\), \(\text{Ce}_2\text{O}_3\) and \(\text{CeO}_2-x\) (see Fig. 3.1). One can obtain the \(\text{CeO}_2-x\) system by removing the oxygen atoms from the stoichiometric ceria. The \(\text{Ce}^{4+}/\text{Ce}^{3+}\) redox states are at the heart of the ceria chemistry.

Fortunately, we have many experimental data for bulk ceria, which makes it possible to evaluate our calculated results. Usually, the \(U\) value in the GGA+\(U\) functional needs to be changed to describe experimental results. It is a common consensus that there exists no single \(U\) value which can achieve an excellent overall description of the bulk ceria properties [19]. In the last decade, many studies have shifted towards using the hybrid functional HSE06 to study the bulk ceria systems [46, 47, 48, 49, 50]. The results from HSE06 showed significant improvements over PBE+\(U\) functionals. However, the density of states are overestimated by HSE06. In paper I, we focused on the effects of the Fock exchange, aiming at improving the performance of the HSE06 functional on ceria properties. Furthermore, we also demonstrated the results of PBE+\(U\) functional with different \(U\) values for comparison.

![Figure 3.1](image-url). (a) \(\text{CeO}_2\) unit cell as a fluorite structure, (b) \(A\)-type \(\text{Ce}_2\text{O}_3\) unit cell and (c) \(\text{CeO}_2-x\) bulk structure. Red atoms are oxygen and gray atoms are cerium. Black is the oxygen vacancy. The blue isosurfaces show the Ce 4\(f\) electron spin densities.
3.1 Geometric structure

Stoichiometric ceria (CeO$_2$) has a fluorite structure, which belongs to the space group Fm3m. Fig. 3.1 (a) shows the geometric structure of the CeO$_2$ unit cell. It has only one lattice parameter $\alpha$. Previously, most DFT calculated $\alpha$ value were compared to the room temperature experimental data [46, 47, 51, 49] with moderate success. Therefore we extrapolated the experimental values to 0 K, which made it really comparable to our calculated data. The extrapolated $\alpha$ value is 5.39 Å. All the U values still tend to overestimate the lattice parameter $\alpha$; HSE06(25%) gave the best lattice parameter, which is 5.394 Å.

The bulk modulus is another important experimental property. Due to different experimental conditions, the experimental bulk modulus for CeO$_2$ varies from 204 to 230 GPa [52, 53]. All PBE+U functional results are far from the experimental range. On the other hand, the bulk modulus by HSE06(15%) is found to be 208 GPa. One can see that the default HSE06(25%) gives the best result, which is consistent with the fact that it provides the best lattice parameter. Besides, all hybrid functionals gave values closer to the experimental data than PBE+U.

![Figure 3.2. Spin densities of Ce 4f electrons in A-type Ce$_2$O$_3$. (a) antiferromagnetic (AF) and (b) ferromagnetic (FM). Color violet is the spin up and green is the spin down.](image)

In Ce$_2$O$_3$, all cerium ions are in Ce$^{3+}$ states. There are three phases for Ce$_2$O$_3$, namely the A-type (see Fig. 3.1 (b)), B-type and C-type. However, there is no experimental evidence for the existence of a B-type Ce$_2$O$_3$. The A-type is most commonly phase found in experiments. However, it has been suggested that the C-type structure is the most thermodynamically stable phase. This is consistent with the calculations presented in paper I. We focused in paper I on the A-type Ce$_2$O$_3$. It has a hexagonal structure, which belongs to the space group $P\overline{3}2/m1$. The hexagonal structures are compared based on their volume. The results are presented in Table 3.1. Most PBE+U lattice parameter are overestimated, which is consistent with the bulk CeO$_2$ results. Interestingly, all functionals give the volume of antiferromagnetic (AF) Ce$_2$O$_3$
larger than that of the corresponding ferromagnetic (FM) one. All hybrid functionals underestimate the lattice parameters. The PBE functional gives values very close to the experimental data. We find that the AF electronic structure has the lowest energy with all functionals, which is consistent with previous computational and experimental results. Fig. 3.2 shows the Ce $4f$ spin densities of the FM and AF Ce$_2$O$_3$.

**Table 3.1.** Optimised lattice constants for the antiferromagnetic and ferromagnetic A-Ce$_2$O$_3$. In paper I, only data for the antiferromagnetic state was presented.

<table>
<thead>
<tr>
<th>Functional</th>
<th>a, c (Å)</th>
<th>Volume (Å$^3$)</th>
<th>B (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE+U(5 eV) AF</td>
<td>3.917, 6.184</td>
<td>82.169</td>
<td>121</td>
</tr>
<tr>
<td>PBE+U(5 eV) FM</td>
<td>3.916, 6.166</td>
<td>81.888</td>
<td>120</td>
</tr>
<tr>
<td>PBE+U(4 eV) AF</td>
<td>3.908, 6.172</td>
<td>81.633</td>
<td>121</td>
</tr>
<tr>
<td>PBE+U(4 eV) FM</td>
<td>3.909, 6.158</td>
<td>81.490</td>
<td>120</td>
</tr>
<tr>
<td>PBE+U(3 eV) AF</td>
<td>3.900, 6.169</td>
<td>81.260</td>
<td>121</td>
</tr>
<tr>
<td>PBE+U(3 eV) FM</td>
<td>3.900, 6.139</td>
<td>80.864</td>
<td>120</td>
</tr>
<tr>
<td>PBE+U(2 eV) AF</td>
<td>3.891, 6.148</td>
<td>80.610</td>
<td>121</td>
</tr>
<tr>
<td>PBE+U(2 eV) FM</td>
<td>3.888, 6.068</td>
<td>79.438</td>
<td>120</td>
</tr>
<tr>
<td>HSE06(25%) AF</td>
<td>3.854, 6.089</td>
<td>78.325</td>
<td>133</td>
</tr>
<tr>
<td>HSE06(25%) FM</td>
<td>3.853, 6.055</td>
<td>77.847</td>
<td>132</td>
</tr>
<tr>
<td>HSE06(20%) AF</td>
<td>3.858, 6.099</td>
<td>78.617</td>
<td>131</td>
</tr>
<tr>
<td>HSE06(20%) FM</td>
<td>3.856, 6.062</td>
<td>78.059</td>
<td>129</td>
</tr>
<tr>
<td>HSE06(15%) AF</td>
<td>3.859, 6.103</td>
<td>78.709</td>
<td>128</td>
</tr>
<tr>
<td>HSE06(15%) FM</td>
<td>3.858, 6.061</td>
<td>78.127</td>
<td>126</td>
</tr>
<tr>
<td>HSE06(10%) AF</td>
<td>3.863, 6.109</td>
<td>78.950</td>
<td>125</td>
</tr>
<tr>
<td>HSE06(10%) FM</td>
<td>3.860, 6.067</td>
<td>78.285</td>
<td>124</td>
</tr>
<tr>
<td>PBE AF</td>
<td>3.840, 6.097</td>
<td>79.941</td>
<td>98</td>
</tr>
<tr>
<td>PBE FM</td>
<td>3.831, 6.068</td>
<td>77.126</td>
<td>122</td>
</tr>
<tr>
<td>Expt.</td>
<td>3.891(1), 6.059(1) [54]</td>
<td>79.443</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 Electronic structure

Castleton et al. [36] gave a very detailed summary of the band structure for bulk CeO$_2$ as obtained from experiments. We determined two important band gaps from the calculation: $E_{gap}^a$ and $E_{gap}^b$. $E_{gap}^a$ is the band gap between the maximum of the O $2p$ band to the minimum of the Ce $4f$ band. $E_{gap}^b$ is the band gap from the maximum of O $2p$ band to the minimum of the Ce $5d$ band. The experimental band gap $E_{gap}^a$ is found in a narrow range between 2.8 and 3.0 eV. However, due to different experimental methods and equipment resolution, there is a large scatter in $E_{gap}^b$, ranging from 6.0 to 8.0 eV. Fig. 3.3 shows a comparison of the calculated and experimental band gaps. It can
be seen that only HSE06(15%) gives results in the experimental ranges. All PBE+U functionals severely underestimate $E_{gap}^a$. The band gaps are strongly correlated with the reduction energies.

![Figure 3.3](image)

*Figure 3.3. Calculated band gaps $E_{gap}^a$ and $E_{gap}^b$ of bulk CeO$_2$ for varying $U$ and $\alpha$ values, figure (a) and (b), respectively. Green areas are the corresponding experimental ranges.*

### 3.3 Partially reduced ceria

The partial reduction (oxygen vacancy formation) reaction is shown in Eq. 3.1.

$$\text{CeO}_2(s) \rightarrow \text{CeO}_{2-x}(s) + \frac{x}{2}\text{O}_2(g) \quad (3.1)$$

The formation of this oxygen vacancy in bulk ceria is at the origin of the oxygen storage capacity [55]. Furthermore, oxygen vacancies on the ceria surface may lead to many important applications; for example, the vacancy sites strongly bind with adsorbates [56].

**Oxygen vacancy in ceria.** We created CeO$_{2-x}$ systems by removing oxygen atoms from the supercell of the stoichiometric ceria. We calculated vacancy formation energies for various oxygen vacancy concentrations by using supercells of different sizes as shown in Fig. 3.4. We constructed the supercells by repeating the primitive unit cell of CeO$_2$ in all three dimensions.

One oxygen vacancy creates two Ce$^{3+}$ ions. It is commonly acknowledged that the two Ce $4f$ electrons will localise near the oxygen vacancy site. However, there are two kinds of positions for Ce$^{3+}$ ions, namely the nearest neighbour (NN) and the next-nearest neighbour (NNN) of the O vacancy site. Fig. 3.5 presents all the NN and NNN cerium atoms connected to one oxygen vacancy site. The four NN cerium atoms form a tetrahedral structure with the oxygen vacancy site at its centre. There are twelve NNN cerium atoms. The two Ce$^{3+}$ ions can be localised on these 16 cerium atoms in many different ways. Scanning-Tunneling Microscopy (STM) figure revealed that at least
one Ce$^{3+}$ ion is not in the NN site [57]. Many DFT studies gave the most stable configuration as both Ce$^{3+}$ ions in NNN sites (NNN+NNN configuration) [58, 59, 60].

![Figure 3.4](image_url)

*Figure 3.4. Repeated unit cell of CeO$_2$ to form supercells of different sizes.*

Besides, it is also important to note that different Ce 4$f$ orbitals lead to significant differences in the vacancy formation energies, up to 0.4 eV [58]. Allen and Watson [58] proposed the occupation matrix control method to find the most stable configuration for a given CeO$_{2-x}$ system. However, we used another approach to obtain correct ceria oxygen vacancy structures. We preoptimized the structures using a Ce pseudopotential with each $f$ electron treated as a core electron. We compared the energy difference between occupation matrix control and our method. The total energies and the structures were almost identical.

![Figure 3.5](image_url)

*Figure 3.5. One oxygen vacancy (the black atom) in bulk CeO$_2$ with its nearest neighbour and next nearest neighbours in two different orientations.*

**Band structure.** The creation of two Ce 4$f$ electron will lead to localised states in the band structure of CeO$_2$. We studied how the parameters $\alpha$ and $\omega$ in hybrid functional and the $U$ value in PBE+$U$ influence the electronic band structure.

The experimental band gap O 2$p$ $\rightarrow$ Ce 4$f^{\text{occ}}$ ranges from 1.5-2.5eV. The band gap O 2$p$ $\rightarrow$ Ce 4$f^{\text{unocc}}$ for the CeO$_{2-x}$ system should be similar to the bulk CeO$_2$, where the experimental value is 2.8-3.0 eV. We found that there is no single $U$ value giving a good descriptions for both band gaps. The default
HSE06(25%) overestimated them and HSE06(15%) still gave the best results. However, they are still out of the range. We note that when the $\alpha$ value increases ($\alpha > 30\%$), the band gap $O\ 2p \rightarrow Ce\ 4f^{occ}$ value becomes smaller. On the other hand, increasing the $\omega$ value will decrease the band gap $O\ 2p \rightarrow Ce\ 4f^{unocc}$. To obtain both $E_{gap}^{O2p\rightarrow Ce4f^{occ}}$ and $E_{gap}^{O2p\rightarrow Ce4f^{unocc}}$ values within the experimental ranges requires high values for both $\alpha$ and $\omega$. I found that with $\alpha = 50\%$ and $\omega = 0.55\ \text{Å}^{-1}$, one obtains $E_{gap}^{O2p\rightarrow Ce4f^{occ}} = 2.46\ eV$ and $E_{gap}^{O2p\rightarrow Ce4f^{unocc}} = 4.07\ eV$, both within the experimental ranges.

**Ce 4f electronic localisation.** One cannot measure the exact degree of localisation of the Ce 4f electrons. Castleton et al. [36] studied how the $U$ values in the PBE+$U$ functional affects the Ce 4f electronic localisation. $U = 6\ eV$ gave the highest localisation. In paper I, we also studied how the $\alpha$ value in the hybrid functional changes the Ce 4f electronic localisation. Interestingly, HSE06(25%) gave a similar degree of localisation as – PBE+$U(4eV)$. The degree of the localisation for HSE06(15%) is between PBE+$U(3eV)$ and PBE+$U(2eV)$. Generally, decreasing the $U$ and $\alpha$ values lead to the delocalisation of the Ce 4f electrons.

### 3.4 Oxygen molecule

A good description of the oxygen molecule is essential to obtain correct energetic results for the ceria chemistry. For instance, to calculate the oxygen vacancy formation energy and the ceria reduction energy, we need the total energy of the oxygen molecule. We also need it for the oxygen adsorption energy in papers II-IV.

![Molecular Orbital Diagram](image)

**Figure 3.6.** The molecular orbital diagram of the ground state oxygen molecule.

The ground state of the $O_2$ molecule is in a triplet state, which contains two unpaired electrons (c.f. Fig. 3.6). The superoxide anion has only one unpaired electron, which is in a doublet state. Moreover, the peroxide anion is in a singlet state, which has no unpaired electron.
Among the several important chemical properties of an oxygen molecule, we have, for example, the dissociation and ionisation energies and the electron affinity. Since it is difficult to treat charged systems with VASP, we compute all the energies with local basis-set program Gaussian 09. However, we can still get the oxygen dissociation energy $D_e$ with the VASP program. The results for $D_e$ and the oxygen-oxygen bond distance $d$ are reported in Table 3.2 for both VASP and Gaussian calculations. There is a constant energy difference between VASP and Gaussian calculations, which is about 0.15 eV. Interestingly, the HSE06(25%) gives the best result for the oxygen dissociation energy in any VASP calculation.

Table 3.2. A comparison of VASP and Gaussian calculations for the oxygen molecule dissociation energy and oxygen-oxygen bond distance. Gaussian calculations are done with local basis-set aug-cc-pVQZ.

<table>
<thead>
<tr>
<th>Functional</th>
<th>VASP $D_e$ (eV)</th>
<th>Gaussian $D_e$ (eV)</th>
<th>VASP $d$ (Å)</th>
<th>Gaussian $d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSE06 (25%)</td>
<td>5.21</td>
<td>5.36</td>
<td>1.210</td>
<td>1.192</td>
</tr>
<tr>
<td>HSE06 (20%)</td>
<td>5.38</td>
<td>5.52</td>
<td>1.214</td>
<td>1.197</td>
</tr>
<tr>
<td>HSE06 (15%)</td>
<td>5.55</td>
<td>5.68</td>
<td>1.218</td>
<td>1.202</td>
</tr>
<tr>
<td>HSE06 (10%)</td>
<td>5.73</td>
<td>5.84</td>
<td>1.223</td>
<td>1.207</td>
</tr>
<tr>
<td>PBE</td>
<td>6.09</td>
<td>6.24</td>
<td>1.232</td>
<td>1.218</td>
</tr>
<tr>
<td>Expt.</td>
<td>5.212 $\sim$ 0.002$^1$</td>
<td>1.2075 [61]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.5 Summary

**Paper I** focuses on the density functional methods. We managed to develop a better functional to study the bulk ceria systems, which is the HSE06 hybrid functional with a 15% Fock exchange, namely HSE06’. However, we suggest that $U = 3$ eV is the best value to describe bulk ceria properties with the PBE+$U$ functional. Furthermore, the HSE06’//PBE+$U$ protocol made it possible to study large ceria systems like ceria NPs.

1. Hybrid functionals give a better descriptions of the bulk ceria systems than the PBE+$U$ functionals in general.

2. By decreasing the fraction of the Fock exchange to 15%, we can have a very good overall description for the bulk ceria systems.

3. We proposed a computational protocol, HSE06’//PBE+$U$, which can be used to study large ceria systems.

$^1$The experimental value from Ref. [62] "corrected" with zero-point energy.
4. Temperature programmed desorption of \( \text{O}_2 \) (Papers II and III)

**Questions:** What is the accurate average oxygen adsorption energy for the "supercharged" ceria nanoparticles? What factors influence the oxygen adsorption energy?

**Objective:** Make an accurate evaluation of the oxygen desorption energy.

**Methods used:** PBE+\( U(5\text{eV}) \), HSE06, HSE06′, HSE06′/PBE+\( U \)

**Calculated properties:** Cluster formation energy, oxygen adsorption energy, Bader charges

Several experiments have shown a dramatically increased oxygen storage capacity for ceria nanoparticles smaller than \( \sim 5 \text{ nm} \) [9, 10]. Previously, the "supercharge" model [19, 20] successfully demonstrated the size-dependence of the OSC. However, the computed oxygen binding energy was too small to explain the experimental observation. We hypothesize that the problem comes from an incorrect description of the localised \( \text{Ce} \ 4f \) states with respect to the \( \text{O} \ 2p \) states by the PBE+\( U \) functional. In paper I, we obtained the HSE06′ functional, which excellently reproduced the bulk ceria density of states. Here we use it to reinvestigate the oxygen adsorption on nanoceria with the "supercharge" model.

4.1 Ceria clusters and nanoparticles

The octahedral shape habit, where a large amount of \( \{111\} \) facets are exposed (see Fig. 4.1), is the most stable structure of ceria nanoparticles. Ceria systems are generally expensive to calculate: we had to limit the DFT calculations to ceria clusters and small nanoparticles. Previously, Kullgren et al. [20] used an evolutionary algorithm to find the most stable structure for small size ceria clusters. The number of cerium atoms in these clusters varied from 2 to 10. Here, I investigated the same clusters with the HSE06 and HSE06′ functionals. Primarily, I considered the stoichiometric clusters (STO), where all the cerium ions are in \( \text{Ce}^{4+} \) states. We also studied the fully reduced clusters (RED), where all cerium ions are in \( \text{Ce}^{3+} \) states. Figs. 4.2 and 4.3 present the geometric structures of these STO and RED clusters, optimised with the HSE06′ functional. Only the reduced cluster \( \text{Ce}_6\text{O}_9 \) has an octahedral shape. In addition, I also studied two stoichiometric and two reduced ceria nanoparticles in paper II, which have an octahedral shape (see Fig. 4.4). The reduced ceria nanoparticles have "perfect" octahedral structures, while the stoichiometric ceria NPs are partially truncated.
Figure 4.1. The transmission electron microscopy (TEM) image of octahedral nanoce-ria. Reprint with permission from "Probing Defect Sites on CeO₂ Nanocrystals with Well-Defined Surface Planes by Raman Spectroscopy and O₂ Adsorption" [13]. Copyright ©2010 American Chemical Society.

Figure 4.2. The stoichiometric ceria clusters, (a) Ce₄O₈, (b) Ce₆O₁₂, (c) Ce₈O₁₆ and (d) Ce₁₀O₂₀.

4.2 Context: Oxygen adsorption and the "supercharge" model

Oxygen temperature programmed desorption (O₂-TPD), and temperature programed reduction by H₂ (H₂-TPR) experiments are typically used to study the oxygen storage capacity of ceria materials. The O₂-TPD experiment gives the amount of desorbed O₂ at each temperature. The desorption peak temperature can be used to estimate the average oxygen adsorption energy. On the other hand, TPR experiments measure the amount of consumed reducing gas.

Figure 4.3. The fully reduced ceria clusters, (a) Ce₄O₆, (b) Ce₆O₉, (c) Ce₈O₁₂ and (d) Ce₁₀O₁₅.
Xu et al. [9] reported the size-dependent OSC for ceria nanocrystals through H$_2$-TPR experiments. The authors found that there is a correlation between the surface to bulk oxygen ratio and the OSC. Electron paramagnetic resonance (EPR) experiment showed the existence of O$_2^-$ species on 5.3 nm and smaller ceria NPs. A hidden TPR peak was revealed at 675 K by fitting the data by Gaussian functions. The authors claimed that the O$_2$ molecules were chemisorbed at Ce$^{3+}$ sites, which contributed to the extra OSC for the nanoceria (< 5 nm). The origin of this phenomenon was unclear for them. However, they suggested it may be due to dioxygen interaction with a vacancy.

DFT studies [12, 14, 15, 16, 17], vibrational spectroscopy [63] and EPR experiments [11] showed that both superoxide and peroxide species can be formed at the oxygen vacancy sites on ceria surfaces. Each oxygen vacancy creates two Ce$^{3+}$ ions, which makes it possible to transfer two Ce 4$f$ electrons to O$_2$ and form peroxide at the vacancy site. The adsorption energy of the peroxide ion can be as high as 1.72 eV (PBE+U(4.5eV)) [12]. However, a subsurface O vacancy can transfer one excess electron to an adsorbed O$_2$, forming a superoxide ion near the vacancy site [64]. Besides, an O vacancy site with a trivalent dopant (such as La) can have only one connected Ce$^{3+}$ ion available, which also leads to superoxide ion formation [65].

Besides being adsorbed at vacancy sites, Preda et al. [18] showed by DFT calculations that oxygen can also be adsorbed on a low coordinated Ce$^{5+}$ site,
forming thus a superoxide ion. Later, Kullgren et al. [19] established a "supercharge" oxygen adsorption model to study and explain the extra OSC of the small nanoceria. In this model, oxygen molecules are chemisorbed on top of Ce$^{3+}$ ions at corner and ridge sites. The Ce 4$f$ electrons in these ions transfer to the oxygen molecules and form the superoxide species (O$_2^-$). Each Ce$^{3+}$ ion at a ridge or corner site adsorbs one oxygen molecule. For an octahedral ceria NP, Ce$^{3+}$ ions are located at all six corners and part of the ridge sites. After being "supercharged" with O$_2$, all the cerium atoms are in +4 oxidation states. Fig. 4.5 shows this reaction mechanism by plotting the change in spin density of the Ce 4$f$ electrons.

The "Supercharge" model succeeded in explaining the TPR experiments from two perspectives. Primarily, it confirmed the formation of the superoxide species. Furthermore, it demonstrated the size-dependence for the OSC of nanoceria. However, the model has a severe problem: the oxygen binding energy is too weak, which is inconsistent with the TPD and TPR experiments. In 2016, Wang et al. [21] performed an O$_2$-TPD experiment with 12.8 nm ceria nanoparticles. The TPD revealed two O$_2$ desorption peaks at 439 K and 731 K. The high temperature peak is attributed to the desorption of atomic oxygen. The low temperature peak is related to the desorption of the molecular oxygen, which is what the "supercharge" model describes. Furthermore, two TPR experiments by Xu et al. [9] and Renuka et al. [10] indicated that the superoxide species must survive above room temperature. Therefore, we reinvestigated our "supercharge" model in the light of this TPD [21] and TPR [9, 10] work.
4.3 Investigation of the O$_2$ adsorption on nanoceria

*Functional dependence.* In paper I, we found that HSE06' yields a good description of the density of states for the bulk ceria systems. Correct values for the band gaps are essential if one wants to study the oxygen adsorption energy in the "supercharge" model, as shown in Fig. 4.6. When one Ce$^{3+}$ ion adsorbs one O$_2$, the Ce $4f$ electron transfers from the Ce $4f$ occupied state to the O $2p$ states of the adsorbed O$_2$. The difference in energy eigenvalues between these two states contributes a significant part of the oxygen adsorption energy.

![Figure 4.6. Sketch of the density of state relationship to the "supercharge" model.](image)

Lowering the $U$ value in PBE+$U$ and the $\alpha$ value in the HSE06 functionals leads to increased band gaps between the occupied Ce $4f$ states and the O $2p$ states. It enhances the oxygen adsorption energies to the ceria clusters and NPs. However, decreasing $U$ and $\alpha$ values causes the delocalisation of the Ce $4f$ states. Paper I gave the smallest acceptable $U$ and $\alpha$ values, 3.0 eV and 15%, respectively.

I tested the HSE06'//PBE+$U$ protocol in comparison with the HSE06' full optimisation on all ceria clusters. All average adsorption energy differences were less than 0.1 eV per O$_2$ molecule, which is less than 10% of the average adsorption energy. We are now confident to use HSE06'//PBE+$U$ to study the oxygen adsorption energies for large ceria nanoparticles. The so-obtained average oxygen adsorption energies for all the three octahedral shaped cluster and NPs (see Fig. 4.7) are presented in Table 4.1.

*Site specific oxygen adsorption energies.* For the large ceria NPs, the oxygen molecules can be adsorbed at ridge and corner sites. Corner sites have four oxygen neighbours, and ridge sites have six oxygen neighbours. There is a strong correlation between the cerium coordination number and the oxygen
Table 4.1. Average oxygen adsorption energies for octahedrally shaped nanoceria: 1 cluster and 2 nanoparticles. The geometric structures are presented in Fig. 4.7.

<table>
<thead>
<tr>
<th>Number of Ce</th>
<th>6</th>
<th>19</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the clusters (nm)</td>
<td>0.5</td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td>PBE+U $E^\text{avg}_{\text{ads}}$ (eV)</td>
<td>0.72</td>
<td>0.68</td>
<td>0.60</td>
</tr>
<tr>
<td>HSE06'//PBE+U $E^\text{avg}_{\text{ads}}$ (eV)</td>
<td>1.41</td>
<td>1.36</td>
<td>1.27</td>
</tr>
</tbody>
</table>

adsorption energy. The reduced Ce$_8$O$_{12}$ cluster has 3, 4 and 5-coordinated cerium atoms. I computed the oxygen adsorption energy on different coordinated cerium atoms, the results are shown in Table 4.2. Low-coordinated Ce$^{3+}$ (3) has a much higher oxygen adsorption energy than the high-coordinated Ce$^{3+}$ (5). Therefore, we need to consider the difference between oxygen desorption at corner and ridge sites.

Table 4.2. Oxygen adsorption energies for differently coordinated Ce$^{3+}$ sites in the cluster Ce$_8$O$_{12}$.

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE+U</td>
<td>1.57</td>
<td>1.40</td>
<td>1.21</td>
</tr>
<tr>
<td>HSE06</td>
<td>2.17</td>
<td>2.04</td>
<td>1.76</td>
</tr>
<tr>
<td>HSE06’</td>
<td>2.27</td>
<td>2.18</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Perfect octahedral ceria NPs. In paper II, we have three octahedrally shaped nanoceria, which are Ce$_6$O$_9$ (cluster), Ce$_{19}$O$_{32}$ (NP) and Ce$_{44}$O$_{80}$ (NP). These have 6, 12 and 16 Ce$^{3+}$ ions, respectively. In Ce$_6$O$_9$, all 6 Ce$^{3+}$ are on the corner sites. Ce$_{19}$O$_{32}$ and Ce$_{44}$O$_{80}$ also have 6 Ce$^{3+}$ corner sites and furthermore 6 and 10 Ce$^{3+}$ ridge sites, respectively. When each Ce$^{3+}$ ion adsorbs one oxygen molecule, they form the "supercharged" cluster and NPs which are shown in Fig. 4.7.

For the ceria nanoparticles, we cut ideal octahedral structures from bulk structure. Table 4.3 lists the data for these nanoparticles. The $L$ value is the number of cerium atoms along each ridge. One can use this value to compute other data, like the number of cerium atoms on the surface ($C_{\text{surf}}$), which is equal to $4(L^2 - 2L + \frac{3}{2})$. More importantly, we can estimate the size (diameter) of the ceria NPs, which can be expressed as $a(L - 1)$. Where $a$ is the CeO$_2$ lattice parameter. The number of Ce$^{3+}$ ions in each NP is $4L$, which determines the maximum number of adsorbed oxygen molecules for the "supercharge" model.
Table 4.3. Data for the perfect octahedral nanoparticles. L is the number of cerium atoms along each ridge. Ce and O are the numbers of the cerium and oxygen atoms in the NPs. \( \text{Ce}_{\text{surf}} \) is the total number of cerium atoms at the top surface, including corner and ridge sites. \( \text{Ce}_{\text{edge}} \) is the total number cerium atoms at ridges including the corner sites. \( d \) is the diameter (size) of the nanoparticles.

<table>
<thead>
<tr>
<th>L</th>
<th>Ce</th>
<th>O</th>
<th>Ce_{surf}</th>
<th>Ce_{edge}</th>
<th>O_{surf}</th>
<th>O_{edge}</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>19</td>
<td>32</td>
<td>18</td>
<td>18</td>
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<td>54</td>
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<td>90</td>
<td>348</td>
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<td>12</td>
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<td>2288</td>
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<td>240</td>
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<tr>
<td>13</td>
<td>1469</td>
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<td>678</td>
<td>138</td>
<td>804</td>
<td>264</td>
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<tr>
<td>14</td>
<td>1834</td>
<td>3640</td>
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<td>150</td>
<td>948</td>
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</tr>
<tr>
<td>15</td>
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<td>954</td>
<td>162</td>
<td>1104</td>
<td>312</td>
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</tr>
<tr>
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<td>2736</td>
<td>5450</td>
<td>1110</td>
<td>174</td>
<td>1272</td>
<td>336</td>
<td>8.10</td>
</tr>
<tr>
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<td>3281</td>
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<td>1278</td>
<td>186</td>
<td>1452</td>
<td>360</td>
<td>8.64</td>
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<td>7752</td>
<td>1458</td>
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<td>384</td>
<td>9.18</td>
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<tr>
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<td>4579</td>
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<td>1650</td>
<td>210</td>
<td>1848</td>
<td>408</td>
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<tr>
<td>20</td>
<td>5340</td>
<td>10640</td>
<td>1854</td>
<td>222</td>
<td>2064</td>
<td>432</td>
<td>10.26</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c|c|c|c|c|c}
(2L^3 + L)/3 & 4(L^2 - 2L + \frac{1}{2}) & 4(L^2 + L - 6) & 2(Ce - L) & 12(L - \frac{3}{2}) & 24(L - 2) \\
2 & 4(L^2 + L - 6) & 0.54(L - 1) & 24(L - 2) & 24(L - 2) & 0.54(L - 1) \\
\end{array}
\]

Figure 4.7. In paper II, we studied three octahedral shape supercharged ceria cluster and NPs, which are presented from left to right, \( \text{Ce}_6\text{O}_9 \cdot 6\text{O}_2 \), \( \text{Ce}_{19}\text{O}_{32} \cdot 12\text{O}_2 \) and \( \text{Ce}_{44}\text{O}_{80} \cdot 16\text{O}_2 \).
**Average oxygen adsorption energy.** The average oxygen adsorption energies can be decomposed into average oxygen adsorption energies at corner \( E_{\text{corner}}^{\text{ads}} \) and ridge \( E_{\text{ridge}}^{\text{ads}} \) as presented in Eq. 4.1. The number of corner sites \( n_{\text{corner}} \) in octahedral NPs is always six. The number of ridge sites \( n_{\text{ridge}} \) increases as the size of the NPs increases. Therefore, for large NPs, the average oxygen adsorption energy at the ridges will dominate the \( E_{\text{avg}}^{\text{ads}} \). In Fig. 4.8, one can see that the adsorption energy tends to converge to the \( E_{\text{ridge}}^{\text{ads}} \) (1.20 eV). The energy difference between the PBE+U and HSE06′ functional is about 0.7 eV. However, the values in Table 4.4 are fitted according to Eq. 4.1. The values calculated by DFT have some discrepancies compared to these fitted data.

\[
E_{\text{ads}}^{\text{avg}} = \frac{n_{\text{corner}} \times E_{\text{ads}}^{\text{corner}} + n_{\text{ridge}} \times E_{\text{ads}}^{\text{ridge}}}{n_{\text{corner}} + n_{\text{ridge}}}
\]  

(4.1)

Table 4.4. **Fitted average oxygen adsorption energies for ridge and corner.**

<table>
<thead>
<tr>
<th>Functional</th>
<th>( E_{\text{ads}}^{\text{ridge}} ) (eV)</th>
<th>( E_{\text{ads}}^{\text{corner}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE+U</td>
<td>0.51</td>
<td>0.76</td>
</tr>
<tr>
<td>HSE06′</td>
<td>1.20</td>
<td>1.44</td>
</tr>
</tbody>
</table>

![Figure 4.8](image.png)

**Figure 4.8.** (a) Average oxygen adsorption energies for three octahedral nanoparticles. (b) The predicted average oxygen adsorption energies as a function of the diameter of the NPs.

**Redhead equation results.** I used the data from Table 4.4 to estimate the oxygen desorption peak temperature using the Redhead equation. The result for the desorption peak of ceria NPs (3-10 nm) was at 415K with the HSE06′ data, whereas PBE+U gave only 199 K. The TPD experimental oxygen desorption peak for ceria NPs (8-13 nm) is found at 439 K [21]. The estimated desorption temperature by HSE06′ is thus in good agreement with the exper-
imental data. Fig. 4.9 shows the estimated desorption peak temperature as a function of the nanoparticle size.

Figure 4.9. Estimated oxygen desorption temperature for different ceria nanoparticle size by Redhead equation.

4.4 TPD: The bridge between $E_{\text{ads}}$ and experiment

In 2016, Wang et al. [21] conducted oxygen temperature programmed desorption (O$_2$-TPD) experiment on ceria nanoparticles (12.8 nm). The experiment raised the temperature from room temperature to 800 °C in a ramp of 10 °C per minute. The spectrum revealed a broad low-temperature desorption peak ranging from 50 °C to 300 °C. The centre of the peak is at 166 °C (439 K).

The position of the TPD spectrum peak. In paper II, we used the average oxygen adsorption with the Redhead equation to estimate the desorption peak temperature. The HSE06' functional alleviated the weak binding energy problem caused previously by the PBE+$U$ functional, giving a much higher average oxygen adsorption energy and a higher desorption peak temperature, in agreement with experiment.

The width of the TPD spectrum. A single average oxygen adsorption energy can, however, not explain the broadening of the desorption spectrum. In the beginning, we thought the size distribution of the nanoceria could influence the measured width of the peak. In the experiments, it is impossible to have nanoparticles of only one size in the sample. For instance, Xu et al. [9] gave the size distribution of nanoceria for their experiment. I tried to introduce the size dependence by using a Gaussian function to mimic the distribution of the NPs. However, the microkinetic simulation gave a sharp peak, which is inconsistent with the TPD spectrum. Fig. 4.8 (b) shows that there are very small variations in the average oxygen adsorption for large ceria NPs ($>4$ nm). $E_{\text{avg}}^{\text{ads}}$ quickly converges to the value of $E_{\text{ridge}}^{\text{ads}}$, which is 1.2 eV. Therefore, size
dependence cannot explain the broadening of the TPD spectrum. We made further investigation into this problem.

4.5 Simulation of the shape of the TPD spectrum

The research in paper III was conducted in five steps, listed below:

1. **Exploration of the coverage dependence.** I found that the oxygen adsorption energies are coverage dependent.

2. **Decomposition of the $E$ according to the ABC model.** In order to understand the coverage dependence, we tried to analyse the oxygen adsorption energy by decomposing it into three major parts. We found a correlation between the electrostatic potential and $E_{\text{ads}}$.

3. **Five-coordinated cerium matters.** In perfect ceria nanoparticles, there are no 5-coordinated cerium atoms. However, experiments show a large amount of Ce$^{3+}$ ions on ceria NPs. This may due to many subsurface oxygen vacancies, which lead to 5-coordinated Ce at the ridges, yielding $E_{\text{ads}}$ values between the ridge (CN=6) and corner (CN=4) values.

4. **A simple fitting model.** Since $E_{\text{ads}}$ is strongly correlated with coverage and coordination numbers, we developed a formula, using regression, to reproduce, and later predict, the oxygen adsorption energies.

5. **Microkinetic simulation of the TPD.** By using the coverage dependent oxygen adsorption energies conjunction with a microkinetic simulation, Eq. 2.13, we obtained a simulated TPD spectrum. Finally, we compared our simulated TPD spectrum with the experimental results by Wang et al. [21].

In more detail:

![Diagram](image)

*Figure 4.10. Oxygen adsorption energy calculated by desorbing the oxygen molecules one by one. Start from the ridge sites.*
Here, we computed the oxygen adsorption energy by removing the adsorbed oxygen molecules one by one. As we have shown, the binding energies are much lower for the ridge Ce\(^{3+}\) sites. We started by removing the ridge site oxygen atoms and then the ones at corner sites. We obtained each oxygen adsorption energy as shown in Fig. 4.10. There is a linear dependence in the O\(_2\) adsorption energy with the number of desorbed O\(_2\) molecules. The slope is larger for corner Ce atoms than for the ridge ones. The superoxide ions will push the electrons back to the cerium atoms during desorption, which form Ce\(^{3+}\) ions again.

In order to rationalize this dependence, we found it useful to decompose the O\(_2\) adsorption process into the following steps:

(A) An electron is taken from a Ce\(^{3+}\) ion and brought to the vacuum level:
\[\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + e^- \text{(vac.)}\]

(B) The electron is transferred to an O\(_2\) molecule also located in vacuum:
\[e^- \text{(vac.)} + O_2(g) \rightarrow O_2^-\]

This corresponds to the electron affinity (EA) of the O\(_2\) molecule.

(C) The superoxide species formed in the previous step interacts, electrostatically, with the Ce\(^{4+}\):
\[O_2^- + \text{Ce}^{4+} \rightarrow [\text{Ce} - O_2]^{3+}\]

The model is illustrated in Fig. 4.11. We have fitted the energy to this model using many of the O\(_2\) adsorption events that were calculated with DFT. Thus, we have calculated both the location of the Ce 4f-level (A) and the electrostatic potential above the Ce\(^{3+}\) ions where the O\(_2\) becomes adsorbed (C), both with respect to the vacuum level. The electrostatic potential was measured on a constant electron density isosurface of 0.01 eV/Å\(^3\), see Fig. 4.11. The electron affinity of the O\(_2\) molecule (B) was taken from Ref. [66] where it was calculated to be 0.40 eV at the same level of theory as used here.

By combining the three measures, A+B+C, we get an estimate of the O\(_2\) binding energy. Fig. 4.11 shows a comparison between A+B+C and the corresponding \(E_{\text{ads}}\) for a number of structures. It is apparent that the agreement in terms of absolute values is poor. However, the relative variations are well captured by this simple model and there is a strong correlation between A+B+C and \(E_{\text{ads}}\). We note that neither A nor C are sufficient to explain the observed trends in coverage and site dependence. However both are sufficient if one is only interested in the variations within each of the populations (ridges and corners). For larger particles, the corner positions (six of them) are largely outnumbered by the ridge positions. Therefore, the ridge sites contribute to the majority of the TPD spectrum.

There is a big energy gap between the ridge and corner sites, as presented in Fig. 4.10. As mentioned in paper I, the coordination number have a large effect. In our ceria NPs, the coordination number is 6 and 4 for ridge and corner site cerium atoms, respectively. 5 coordinated cerium atoms are missing in our model. TPR experiments [9, 10] have shown that approximately...
Figure 4.11. The top panel shows our current understanding for the oxygen adsorption over a reduced ceria NP. The labels A, B and C are explained in full detail in the text. In short, an electron located at a reduced cerium cation is brought to the vacuum level (A). The electron is subsequently transferred to an oxygen molecule to form a superoxide ion (B). The superoxide ion is bound to the NP by a favourable electrostatic interaction with the NP (C). The bottom left panel show the projection of the electrostatic potential on an isosurface of constant electron density of 0.01 e/Å³. This map is used to evaluate the electrostatic potential (C). The bottom right panel shows the correlation between the O₂ adsorption energy calculated with DFT, E_{ads}, and A+B+C.

30% of the total cerium atoms were Ce³⁺. This fact indicates the existence of a large number of oxygen vacancies. DFT results showed that O vacancies can be stabilised at the subsurface of ceria {111} [15, 17]. By creating subsurface oxygen vacancies near the ridge cerium sites, we obtained 5-coordinated cerium sites there.

For example, removing two subsurface oxygen atoms from a Ce₄₄O₈₀ NP creates four 5-coordinated Ce at ridges. Moreover, it introduces 4 extra Ce³⁺ ions on these ridges, which means the NP can absorb more oxygen molecules. The adsorption energies are shown in Fig. 4.12 ; the calculated E_{ads} (CN=5) is — between the one for 4- and 6-coordinated sites.

I explicitly calculated the oxygen adsorption energies for each individual superoxide ion on ceria NPs. We classified the computed values according to the coordination number (4, 5 and 6) into three groups. We found a linear relationship between the oxygen adsorption energies and coverage (Θ) in each group. Therefore, we fitted the data with linear regression; the oxygen adsorption energies (E_{ads}^{CN}(Θ)) can thus be formulated as:
Figure 4.12. Ce$_{44}$O$_{78}$-20O$_2$ nanoparticles. The black circles indicate the location of the subsurface oxygen vacancies. 100% coverage corresponds to having O$_2$ molecules adsorbed at all ridge and corner Ce$^{3+}$ sites.

\[ E_{\text{ads}}^{\text{CN}}(\Theta) = -k_{\text{CN}}\Theta + E_{\text{ads}}^{\text{CN}}(0) \]  

where \(-k_{\text{CN}}\) is the fitted slope. \(E_{\text{ads}}^{\text{CN}}(0)\) is the oxygen adsorption energy at zero coverage. We obtained three linear functions for the three CNs. We find for the fitted \(k_{\text{CN}}\) values: \(k_4 > k_5 > k_6\). In paper II, each octahedral ceria NP has 4\(L\) Ce$^{3+}$ ions. The total number of ridge and corner Ce sites are 12\((L - \frac{3}{2})\). By introducing subsurface oxygen vacancies, all ridge and corner Ce sites can be saturated with Ce$^{3+}$ ions. All can adsorb oxygen molecules and form superoxide ions. We defined this as 100% coverage. Furthermore, we formulated the number of 4-, 5- and 6-coordinated Ce sites as 6, 8\(L - 18\) and 4\(L - 6\) , respectively. For a ceria NP with a given \(L\) value, we can estimate all the coverage dependent oxygen adsorption energies \(E_{\text{ads}}(\Theta)\) by using Eq. 4.2.

In order to compare with the TPD experiment by Wang et al. [21], we simulated the TPD spectrum for 100% O$_2$ covered ceria nanoparticles with an average size of 10 nm. We assumed that the particle size follows a normal distribution with a \(\sigma\) of 1.0 nm. We computed TPD spectra for each particle size, individually, and summed them up according to size distribution thereby obtaining the simulated TPD spectrum shown in Fig. 4.13.

There are three peaks in Fig. 4.13. A sharp peak between 300 K and 400K corresponds to O$_2$ desorption from the 6-coordinated Ce sites. A wide peak appears between 400K and 500K, which is the O$_2$ desorption from the 5-coordinated Ce sites. A small peak at 600 K is the oxygen desorption from
the six corner sites. The position and width of the simulated TPD signal is in good agreement with the experiment. Our result indicates that the 5-coordinated Ce must play an important role in the OSC of the nanoceria. Furthermore, the creation of the 5-coordinated Ce by subsurface vacancies also explain the mystery of the 30% Ce\(^{3+}\) ions in the ceria nanoparticles.

![Graph of O\(_2\) signal vs. T (K)](image)

*Figure 4.13.* The simulated O\(_2\) temperature programmed desorption spectrum for perfectly shaped ceria nanoparticles of average size 10 nm.

### 4.6 Summary

In paper II, we focus on examining the "supercharged" model with the modified hybrid functional HSE06'. In paper III, we found the coordination number and coverage dependence of the oxygen adsorption energies. In final, we were able to reproduce the TPD spectrum by microkinetic simulation, which was in good agreement with the O\(_2\)-TPD experiment by Wang et al. [21].

1. By using the HSE06' functional, the "supercharged" model keeps unchanged. The oxygen molecules are still chemisorbed as superoxide ions and the trend in the size-dependence is the same as PBE+\(U\) results.

2. The computed oxygen adsorption energies are strongly dependent on the functional used and its parameters. The oxygen adsorption energy correlates with the characteristics of the Ce 4\(f\) states with respect to the O 2\(p\) states. Decreasing the \(U\) and \(\alpha\) values in the PBE+\(U\) and HSE06 functionals leads to an increase in oxygen adsorption energies.

3. The effect of the coverage dependence is small but still not negligible. 5-coordinated Ce sites play an important role in the adsorption of the oxygen on ceria nanoparticles and is needed to reproduce the TPD experiment.
5. Temperature programmed reduction of nanoceria by H$_2$ (Paper IV)

**Questions:** Can we mimic the experimental H$_2$-TPR spectrum with calculations? How does the H$_2$ molecule interact with the "super-charged" ceria nanoparticles?

**Objective:** Explore the reaction mechanism of the temperature programmed reduction of nanoceria by H$_2$.

**Methods used:** PBE+$U$(3eV), Force-field-based Monte Carlo optimization, Microkinetic simulation

**Calculated properties:** Reaction barriers, reaction energies, TPD spectrum profiles

**Paper IV** focused on the reduction of nanoceria by hydrogen since the experiments showing nanoceria OSC used H$_2$ as the reducing agent [9, 10]. In those experiments, the consumption of the reactive gas was measured for ceria nanoparticles. In order to explain the observed enhancement of the OSC for small nanoceria, we examined how nanoceria interacts with H$_2$.

### 5.1 H$_2$ dissociation on ceria

In a first step, we studied how hydrogen molecules dissociate on ceria nanoparticles. Previously, several studies of the H$_2$ dissociation on the \{111\} surface of bulk CeO$_2$ [67, 68, 69, 70, 71]. García-Melchor and López [69] and Fernández-Torre et al. [70] revealed a heterolytic path for the dissociation (see Eq. 5.1). They showed that the heterolytic path has a smaller energy barrier (0.85 eV) than the homolytic path (1.21 eV). However, the heterolytic path will lead to homolytic products at the end. This reaction path was supported by recent research [72], where the intermediate species Ce-H was found experimentally. Both theory [67, 68, 69, 70, 71] and experiments [73, 72] agree that the final products after H$_2$ dissociation on the \{111\} surfaces are hydroxyl (OH$^-$) groups and Ce$^{3+}$ ions.

$$
2\text{Ce}^{4+} + \text{H}_2(\text{g}) + 2\text{O}^2^-_{\text{latt}} \rightarrow \text{Ce}^{4+} + \text{Ce}^{4+}\text{H}^- + \text{O}^2^-_{\text{latt}} + \text{O}^2^-_{\text{latt}} \\
\rightarrow 2\text{Ce}^{3+} + 2[\text{O}_{\text{latt}}\text{H}]^- 
$$

(5.1)

$$
\text{Ce}^{4+} + \text{Ce}_{\text{ads}}^{4+} + \text{H}_2(\text{g}) + \text{O}^2^-_{\text{latt}} + \text{O}^2^-_{\text{ads}} \rightarrow \text{Ce}^{4+} + \text{Ce}^{4+}\text{H}^- + \text{O}^2^-_{\text{ads}} + \text{O}^2^-_{\text{latt}}\text{H}^+ \\
\rightarrow \text{Ce}^{3+} + \text{Ce}_{\text{ads}}^{4+} + [\text{HO}_2]^-_{\text{ads}} + [\text{O}_{\text{latt}}\text{H}]^- 
$$

(5.2)

Most computational studies have given a dissociation barrier for H$_2$ in the range from 0.85 to 1.0 eV depending on the functionals and the computational settings (for
example the $U$ value). Negreiros et al. [71] reported a predicted activation energy and temperature from reaction free-energy hypersurface mapping, they were 1.10 eV and 430-470K, respectively. Our PBE+$U$(3eV) calculations also gave the dissociation barrier as about 1.0 eV on the stoichiometric ceria {111} surface. However, in our "supercharged" clusters, the presence of the adsorbed superoxide ions offer an alternative path for the hydrogen dissociation. We found that the reaction follows a similar heterolytic path as the surface dissociation shown in Eq. 5.2 and Fig. 5.1. Both for the small cluster (Ce$_4$O$_6$·4O$_2$) and for a large NP (Ce$_{44}$O$_{80}$·16O$_2$), the reaction barriers are 1.2 eV.

![Figure 5.1](image.png)

**Figure 5.1.** H$_2$ dissociates near one of the superoxide ions on the Ce$_4$O$_6$·4O$_2$ cluster. (a) Initial state for the dissociation, where H$_2$ approaches a superoxide ion. (b) Transition state with a heterolytic dissociation. (c) In the final state one HOO$^-$ ion, one OH$^-$ ion, and one Ce$^{3+}$ ion have been formed. The reaction formula is also shown in Eq. 5.2.

### 5.2 The important role of Ce$^{3+}$ for the H$_2$-TPR

Kullgren et al. [19] employed perfect octahedral nanoparticles as a model to study the oxygen adsorption and the OSC effect using DFT calculations. In an ideal octahedron the percentage of Ce$^{3+}$ decreases rapidly with increasing particle size. Only the six corners and some of the ridge Ce sites are in the Ce$^{3+}$ state as shown in Fig. 5.2 (a). As mentioned in the previous chapter, there may also be extra Ce$^{3+}$ ions present coming from subsurface O vacancies. Indeed, in the Xu et al. [9] TPR experiment, about 30% of the cerium ions were Ce$^{3+}$ ions for all their size-selected ceria nanoparticles in the range from 4.4 to 10 nm. We therefore extended our model to also take such a high concentration of Ce$^{3+}$ ions into account, and specifically so in the microkinetic simulations to mimic their TPR spectra.

Before the microkinetic (MK) simulations, we used force-field Monte Carlo simulated annealing optimizations to suggest the locations of the Ce$^{3+}$ ions for a 30% Ce$^{3+}$ concentration in a 5 nm NP and found that all the Ce$^{3+}$ ions were located at the surface near the corners and ridges and formed rows, as shown in Fig. 5.2 (b). The simulated Ce$^{3+}$ distribution is in good agreement with the mapping obtained from electron energy loss spectroscopy [74]. In the microkinetic simulations we started from such a
model, after having decorated all the ridges with superoxide ions, i.e. we formed a supercharged NP.

A large number of DFT calculations of the H$_2$ reaction with small supercharged ceria clusters, nanoparticles and the extended surface were performed to explore reaction paths and to provide reaction energies and energy barriers as input for the MK simulations. Among other things, the DFT calculations showed that the dissociation barrier of H$_2$ increases with the concentration of Ce$^{3+}$ ions near the reaction site.

From these results we predict that in the case of a large accumulation of Ce$^{3+}$ ions at or next to the ridges, where the superoxide ions will like to reside, incoming H$_2$ molecules in the vicinity of the ridges would be prevented from dissociating. Therefore we have excluded hydrogen dissociation near a superoxide ion (as in Fig. 5.2) from the set of reactions explored in the MK simulation. Interestingly, only a small number of Ce$^{4+}$ ions are located at the centre of the surface as presented in Fig. 5.2 (b). Consequently, the H$_2$ dissociation is restricted to the centre of the {111} facet, where there are Ce$^{4+}$ ions. H$_2$ acts as an electron donor. One hydrogen dissociation leads to the formation of two Ce$^{3+}$ ions. The entire top surface will quickly be saturated with Ce$^{3+}$ ions after a few H$_2$ dissociations. Then the Ce$^{3+}$ shell will hinder the H$_2$ dissociation processes, as shown in Fig. 5.3.

Furthermore, we scrutinized the O$_2$ desorption reaction. As discussed in chapter 4, O$_2$ molecules will bind much stronger with the ceria nanoparticles at such high Ce$^{3+}$ concentration. This will prevent the O$_2$ desorption from happening at low temperature; on these grounds this reaction was excluded from the MK simulation.

![Figure 5.2](image-url)

*Figure 5.2. The locations of the Ce$^{3+}$ ions on the prefect octahedral ceria nanoparticle (5 nm), geometry optimized in Monte Carlo simulated annealing optimization. (a) the number of Ce$^{3+}$ ions in the ideal model. (b) 30% of Ce$^{3+}$ ions.*

Primarily, we considered a simple reaction mechanism, namely Eley-Rideal, in which a H$_2$ molecule directly reacts with a superoxide ion. Two possible scenarios are presented in Fig. 5.3. In scenario I, one H$_2$ molecule dissociates on the top of the superoxide ion and forms two OH$^-$ groups. However, the dissociation barrier is high (2.1 eV). In scenario II, H$_2$ molecules dissociates following the reaction path as shown in Fig. 5.1. The reaction barrier as mentioned is about 1.0 eV. However, due to the Ce$^{3+}$ "rows" near the corners and ridges, scenario II is unlikely.
5.3 Our reaction mechanism for the H$_2$-TPR

We constructed a microkinetic simulation based on the DFT-calculated reaction barriers and energy profiles. We discovered that it is useful to describe the reaction progress in terms of two stages when the temperature is increased. This is shown in Fig. 5.4.

1\textsuperscript{st} stage. The H$_2$ molecules start to dissociate at about 450 K. The dissociation creates protons at the centre of the surface and Ce$^{3+}$ ions near the corners and ridges. The protons stay at the dissociated top-layer oxygen sites. The surface is quickly saturated with Ce$^{3+}$ ions. Then, the H$_2$ dissociation will stop.

2\textsuperscript{nd} stage. At about 550 K, the temperature is high enough to overcome the proton mobility barrier, about 1.7 eV. The proton mobility follows a two-step process. First it moves from a top-layer oxygen site to a sub-layer oxygen site close by. Then, it may move back to a nearby top-layer oxygen site. The protons start to "random walk" on the surface and can thus approach the superoxide ions. Once a proton approaches a superoxide ion, it can climb onto its top and form a HOO$^-$ ion. Another proton can then climb on top of an HOO$^-$ ion and form two OH$^-$ ions. More protons will move to the OH$^-$ site and form water molecules. A maximum of two water molecules can form on a superoxide site. This water is physically adsorbed on the NP. It costs about 0.5 eV to desorb it. The formation of intermediate species and water molecules "consumes" Ce 4$f$ electrons, which leads to a significant decrease of the Ce$^{3+}$ concentration. As a consequence, many more H$_2$ molecules can dissociate; this is shown by the simulated TPR spectrum at about 620 K. This TPR signal is in agreement with the TPR experiments [9, 10].

In summary, our simulations revealed that the TPR experiment follows a Langmuir-Hinshelwood mechanism. H$_2$ cannot directly react with the adsorbed oxygen molecules due to the Ce$^{3+}$ ion protection. First H$_2$ dissociates at the centre of the $\{111\}$ surface. Then, it can move to the superoxide ions and form water molecules. The reaction barrier for the proton mobility is the threshold for the entire reaction processes.
Figure 5.4. Sketch of TPR reaction mechanism. In the 1\textsuperscript{st} stage, the H\textsubscript{2} dissociation starts from the centre of the surface, which produces H\textsuperscript{+} and Ce\textsuperscript{3+} on the ceria nanoparticle’s surface. In the 2\textsuperscript{nd} stage, the surface is saturated by Ce\textsuperscript{3+} ions. The H protons start to mobile and form water at the superoxide sites.

5.4 Summary

In paper IV, we found a Langmuir-Hinshelwood reaction mechanism through the microkinetic simulation for the temperature programmed reduction by hydrogen. The results are in agreement with the TPR spectrum by Xu et al. [9]. Understanding this reaction mechanism is useful for ceria catalyst research and design.

1. Hydrogen dissociation can occur near a superoxide ion, which leads to one H\textsuperscript{+} on a lattice oxygen and a HOO\textsuperscript{−} group. However, due to the large amount of Ce\textsuperscript{3+} ions near the superoxide ions, most H\textsubscript{2} molecules dissociate at the centre of the \{111\} surface, where the reaction barrier is about 1.0 eV.

2. A 30\% Ce\textsuperscript{3+} concentration yields Ce\textsuperscript{3+} rows near the corners and ridges of the octahedral nanoparticles. The Ce\textsuperscript{3+} rows protect the oxygen molecules from desorption and keep the H\textsubscript{2} dissociation away from the superoxide ions. It prevents the formation of water at low temperature.

3. The proton mobility is the threshold for the water formation. The water will form and leave from the superoxide sites once the temperature is high enough (> 550 K) to overcome the H proton mobility barrier.
6. Concluding remarks

In this thesis, I explore the nature and some ways to enhance the potential of nanoceria for the storage of oxygen. I used theoretical methods and calculations based on the "supercharge" model previously proposed by members of our group. I conducted these studies from three perspectives, First a fundamental one, namely how to develop a better, i.e. more efficient, functional for accurate DFT-calculation of the oxygen adsorption energy. Second we found and studied the coordination number and coverage dependence of the oxygen adsorption energy. Third we used a microkinetic simulation to explore the reaction mechanism of the TPR process.

Concerning the first point: for the properties of bulk ceria, I managed to obtain a functional better than the GGA+$U$ one, namely the HSE06', which is essentially a 15% Fock exchange HSE hybrid functional (instead of 25%, the default value). In addition, we are presently also investigating a computational cheaper HSE06'//PBE+$U$ consisting of a PBE+$U$ structure optimisation and a single-point energy calculation.

I later used the HSE06' and HSE06'//PBE+$U$ functionals to reinvestigate the the increase in oxygen storage capacity observed for small ceria nanoparticles (characteristic dimension $\approx 5$ nm). The hybrid functional improved on the PBE+$U$ estimate for the adsorption energy. Using the Redhead equation, I obtained a simulated first-order desorption peak temperature of, at least, 415 K, which is in agreement with the TPD experimental. However, the broadening of the desorption spectrum could not be explained. Therefore, I investigated the coverage dependence of the oxygen adsorption energy. I found a discrepancy in these energies; this is correlated with the size of the NPs and their degree of reduction. I obtained a simulated TPD spectrum through a microkinetic simulation, it shows the correct peak position and broadening.

Below I summarize the most important findings and conclusions from all four studies:

1. The newly developed hybrid functional gives a reasonably good overall description of the geometries, density of states and energies of bulk ceria systems. Reducing the Fock exchange fraction($\alpha$ value) to 15% leads to a very good description of the electronic DOS and full reduction energy. We named the modified hybrid functional HSE06'. Not unexpectedly, HSE06' does not reproduce all properties perfectly. We also devopped the HSE06'//PBE+$U$ computational protocol, which is, in many cases, able to reduce the cost of computing without losing much accuracy.

2. The hybrid functional HSE06' yields oxygen dsorption energy that are much higher than with the PBE+$U$(5eV) functional. It fixed the problem in our "supercharge" model: the adsorbed $O_2$ molecules are binding too weak by PBE+$U$(5eV) calculations. The hybrid functional does not alter the "supercharge" model’s reaction mechanism, which is Ce $4f$ electron transfer and superoxide ion formation. However, compared to PBE+$U$(5eV), HSE06' increases the average oxygen binding energy by about 0.7 eV, which is significant. From the average oxygen adsorption energy we estimate the desorption peak temperature to be around 415 K, close to the experimental value of 439K.
3. **The coordination number and coverage dependence is the key to explain the broadening of the TPD spectrum.** I found that the coordination number at the adsorption Ce sites is the most important parameter influencing the values of $E_{ads}$. The coverage dependence also contributes to small variation. We suggested that the 5-coordinated Ce atoms at the ridge make a large contribution to the TPD spectrum. The 5-coordinated Ce atoms were created by introducing subsurface O vacancies.

4. **A Langmuir-Hinshelwood mechanism explains the TPR experiments for nanoceria.** The microkinetic simulation revealed that the TPR follows a Langmuir-Hinshelwood mechanism. A large amount of Ce$^{3+}$ ions on the surface prevents H$_2$ from reacting directly with the superoxide ions. It rather starts to dissociate from the centre of the surface. The proton mobility is thus the threshold for water formation. The water molecules will be formed and desorbed from the superoxide ion sites once the temperature is high enough to overcome the mobility barrier.

In conclusion, we are very confident in the efficiency of the "supercharge" model. It has been tested in careful studies. However, some challenges remain, based on the current work. For instance, it is not entirely clear how large amounts of Ce$^{3+}$ ions (30%) present on the surface and influence the structure of the nanoparticles. A more elaborate model for the reactions may be needed to continue the examination and development of the "supercharge" model.
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8. Svensk sammanfattning

Reducerbara metalloxider med hög redox(reduktion-oxidation)aktivitet vid låga temperaturer är viktiga komponenter inom många teknologiska användningsområden. Ett sådant område är heterogenkatalys, där de används både för industriell framställning av kemikalier och för miljöförbättring, t.ex. genom avgasrening. Ceriumoxid (CeO₂), även kallad ceria, är ett typexempel på ett sådan kommersiellt viktig redoxaktiv metalloid. Metallatomerna i ceria, dvs ceriumatomerna, kan ganska lätt reduceras från Ce⁴⁺ till Ce³⁺ och bilda Ce₂O₃ i en reducerande omgivning, för att sedan relativt enkelt kunna återoxideras igen till CeO₂ i en oxiderande miljö. Cerias redoxkemi gör den idealisk som syrebuffert vid oxidationskatalys, dvs ceria har hög syrelagringskapacitet (oxygen storage capacity, OSC) och är idag en av huvudkomponenterna i så kallade trevägskatalysatorer (TWCs) som används i avgasefterbehandlingssystem för bensinbilar.

Cerium är grundämne nummer 58 i periodiska systemet och är det första elementet som har en f-elektron i sitt grundtillstånd, och tillhör lantanidgruppen. I ceria är f-tillstånden inte besatta, utan utgör istället de lägst liggande besatta tillstånden. Om Ce-joner i CeO₂ reduceras från Ce⁴⁺ till Ce³⁺ så innebär det att dessa 4f-tillstånd kommer att besättas, vilket leder till lokalisera tillstånd i bandstrukturen. Det är för övrigt dessa ”lokala” elektroniska tillstånd och deras egenskaper som står för i stort sett all redoxkemi hos ceria och i mångt och mycket styr över hur ceria växelverkar med sin omgivning. Just hur molekyler växelverkar med perfekta och defekta ceriaytor (med eller utan reaktiva f-elektroner) är ett område där intensiv forskning pågår internationellt, och här förekommer ceria i flera olika roller,t.ex. som katalysator, eller som aktivt supportmaterial för andra katalysatormaterial. Exempel på de senare är de ädla (eller halvädla) metallerna Au, Cu, Pt, Pd och Rh, oftast i form av atomer eller kluster. Syreadsorption, vätedissociation, och den s.k. vattengasskiftreaktionen är viktiga exempel där experiment har visat att metallatomer eller metallkluster på ceria kan fungera som kemiskt aktiva säten som katalyserar reaktionerna. Från många av de tidigare studierna står det klart att olika yters orientering (morphologi), samt olika defekter såsom steg, dislokationer, vakanser eller dopanter, alla kan påverka redoxaktiviteten hos ceria. Lediga syreplatser (oxygen vacancies), hur de bildas och läks, är speciellt intressanta för ceriakemin, eftersom dessa naivt kopplas direkt till syrebuffringsförmågan som är så viktig för många tillämpningsområden. Varje förlorad syreatom leder till bildandet av två Ce³⁺ joner nära vakansplatsen. Syremolekyler som adsorberas vid en syrevakans på ytan binds ofta hårt ("kemisorption") och bildar laddade syremolekyler, nämligen superoxidjoner (O₂⁻) eller peroxidjoner (O₅²⁻).

Under de senaste årtiondenet har forskningen alltmer skiftat fokus från ytor till nanopartiklar av ceria, så kallat nanoceria. Nanoceria har genom experiment visat sig ha en extra hög redoxaktivitet, samt är aktiv redan vid låga temperaturer. Orsaken till detta är att nanopartiklar har ett stort ytvolymförhållande och former med många olika säten som hörn, kanter och facetter. För ceria har man funnit att just sådana ”nanospecifika” säten är extra redoxaktiva jämfört med säten på de vanliga ytorna. Man har till och med sett att nanoceria kan fungera som antioxidant i biomedicinska tillämpningar, där de kan användas för att eliminera fria radikaler i levande celler. En annan intressant katalysrelaterad observation är att mycket små ceria-nanopartiklar, med en diameter mindre än 5 nm, har uppvisat en oväntat stor syrebuffringskapacitet (OSC), större än
vad som är möjligt givet reaktionsformeln för ren CeO$_2$. Dessa experiment ligger till grund för en stor del av forskningen som presenteras i den här avhandlingen som handlar om nanocerias redoxaktivitet, och hur den kan stylas genom att modifiera storlek, stökiometri och morfologi (och form).


Den räda tråden i mitt forskningsarbete har varit att utveckla metoder för att undersöka redoxaktiviteten hos nanoceria genom att simulera två olika typer av experiment, nämligen temperaturprogrammerad desorption (TPD) och temperaturprogrammerad reduktion (TPR). Dessa metoder används för att experimentellt få ett mått på olika materials redoxegenskaper. Det första steget i forskningsprojektet var att undersöka vilken tätthetsfunktional som bäst beskriver ceria (både som bulkmaterial och i form av nanoceria) och dess f-elektroner (artikel I och II), vilket visade sig vara att använda s.k. hybridfunktionaler. Mer specifikt, så gjordes detta genom att anpassa andelen av s.k. icke-lokal Fock exchange i HSE06 funktionalen tills vissa experimentella egenskaper, t.ex. struktur, bandgap och reduktionsenergi, kunde reproduceras. Då dessa funktionaler är beräkningsmässigt väldigt dyra att använda, så utvecklades och testades också olika metoder för att snabba upp beräkningarna. Framförallt så utvecklades och testades ett beräkningsschema där vi förroptimerar alla strukturer med standard DFT, använder en skalfaktor baserat på bulkoptimeringar för att korrigera de ofta överestimerade bindingslängderna med standard DFT, följt av en ”single point” beräkning med hybrid-DFT. Detta schema användes framförallt i artikel II för att modellera större ceriapartiklar.

I artikel III och IV utvecklades mikrokinetiska modeller för att simulera TPD och TPR experiment. Grunden i dessa modeller är adsorptions- och reaktionsenergier beräknade med DFT. Den största delen av beräkningstiden har här gått åt till att undersöka olika reaktionsmekanismer för hur superoxidjoner adsorberade på nanokluster av ceria reagerar med väte i bildandet av vatten, alltså det som sker i TPR experimenten. I artikel III, så används DFT för att skapa en modell för hur adsorp-


För att sammanfatta, genom mina noggranna beräkningsstudier och jämförelse med experimentella data, anser jag att modellen för superladdad syrebuffningsförmåga ger en trolig förklaring till den extra OSC-effekten som har observerats experimentellt för riktigt små ceria nanopartiklar. Vidare har mina mikrokinetiska simuleringar av TPD och TPR spektra visat att modellen klarar av att ge både kvalitativ och kvantitativ överensstämmelse med experimentella spektra och därmed bidragit med ny kemisk insikt hur redoxaktiviteten hos nanoceria kan kontrolleras på atomär nivå, och slutligen optimeras för olika applikationer.
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title "Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology").