Chapter 1

Introduction

The aim of this chapter is to discuss the industrial uses of CeO_2, both as a fast ion conductor and as a promoter in exhaust catalysts. Additionally, we relate these uses to the overall structure of the thesis. From an atomistic point of view these applications are dependent upon ion migration and surface phenomena. As such, both the theoretical and experimental literature concerning cerium dioxide will be discussed. We begin by a description of fluorite lattice.

1.1 Cerium Dioxide

Cerium dioxide (also known as ceria) has the fluorite structure (Figure 1.1), which consists of a simple cubic oxygen sub-lattice with the cerium ions occupying alternate cube centres. In perfect ceria the oxygen ions have a formal charge of -2; the anions are tetrahedrally coordinated to the cerium ions and octahedrally coordinated to the surrounding oxygen atoms. The oxygen - oxygen distance is 2.705Å, this is half the lattice parameter. The cerium ions have a formal charge of +4 (the electronic

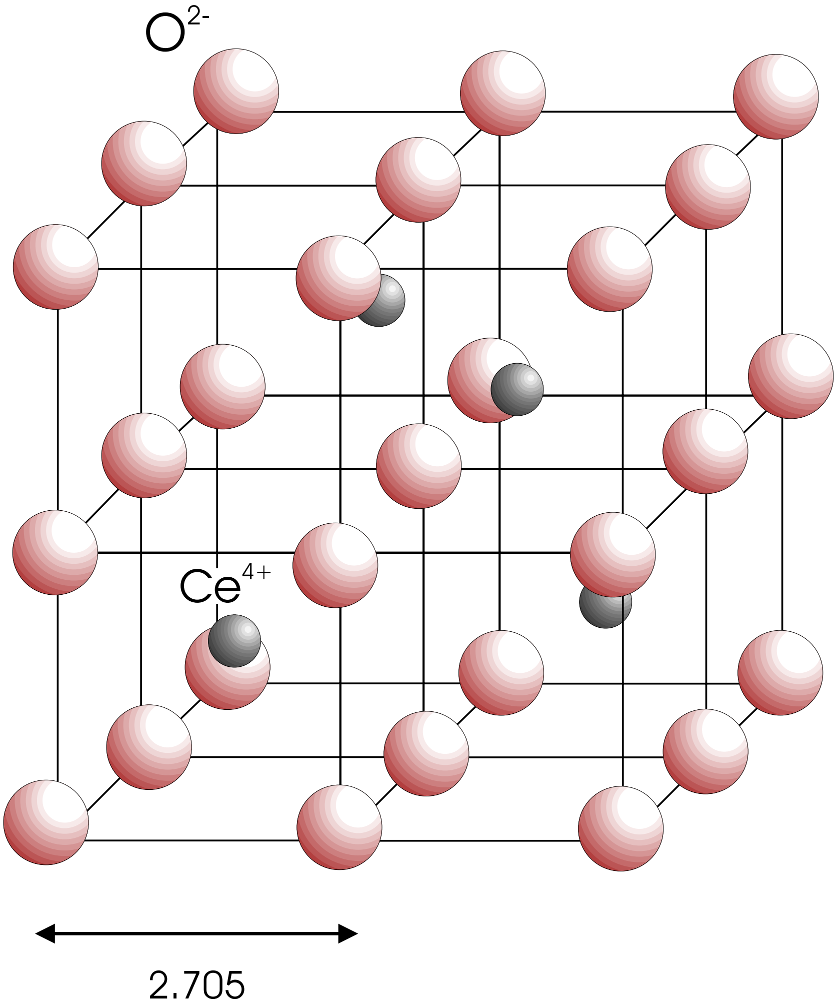

Figure 1.1: A unit cell of CeO_2

structure is [Ne]5d^{10}) and are coordinated to eight oxygen ions.

1.2 Commercial applications of cerium oxide

CeO_2 has a range of commercial uses; as a catalyst in its own right for the syngas process (the conversion of CO and H_2 to methanol and hydrocarbon) [1, 2], as an active support for various precious metal catalysts, in oxygen sensors [3], and as an electrolyte in Solid Oxide Fuel Cells (SOFC). The two biggest uses of CeO_2 are as a fast ion conductor in SOFC's and as a promoter in car exhaust catalysts. These rely on properties of bulk ion migration and surface structure, respectively.

1.2.1 Exhaust Catalysts

Many cars now contain catalytic converters to remove the noxious pollutants that result from burning hydrocarbons in car engines (Figure 1.2). The primary products of combustion are carbon dioxide and water. However, incomplete combustion, impurities in the fuel, and the high pressures in engines can result in a cocktail of pollutants in the exhaust gas, particularly NO_X, CO, and hydrocarbons. The 'three way' automotive catalyst can reduce such pollutants by providing lower energy reaction pathways for the three main oxidation and reduction reactions that remove such compounds (Table 1.1).

Typically, an automotive catalyst consists of a honeycomb monolith (Figure 1.3) made of corderite, onto which a 'washcoat' is deposited. A washcoat is an aqueous suspension of alumina, together with important base metal promoters and stabilisers. This coat increases the effective surface area over which the exhaust gases can pass, and is fixed to the monolith by calcining at high temperatures. Precious metals such as Rh, Pt, and Pd are deposited onto the surface, either by impregnation or ion exchange of a precious metal salt (such as $PtCl_6^{2-}$) onto the support. Finally the catalyst is fired reducing the precious metal ions to their elemental state.

The most widely used catalyst promoter and stabiliser is CeO_2. It plays several important roles in the conversion of pollutants, including alumina stabilisation, improving the precious metal dispersion, and most importantly, enhancing the catalytic

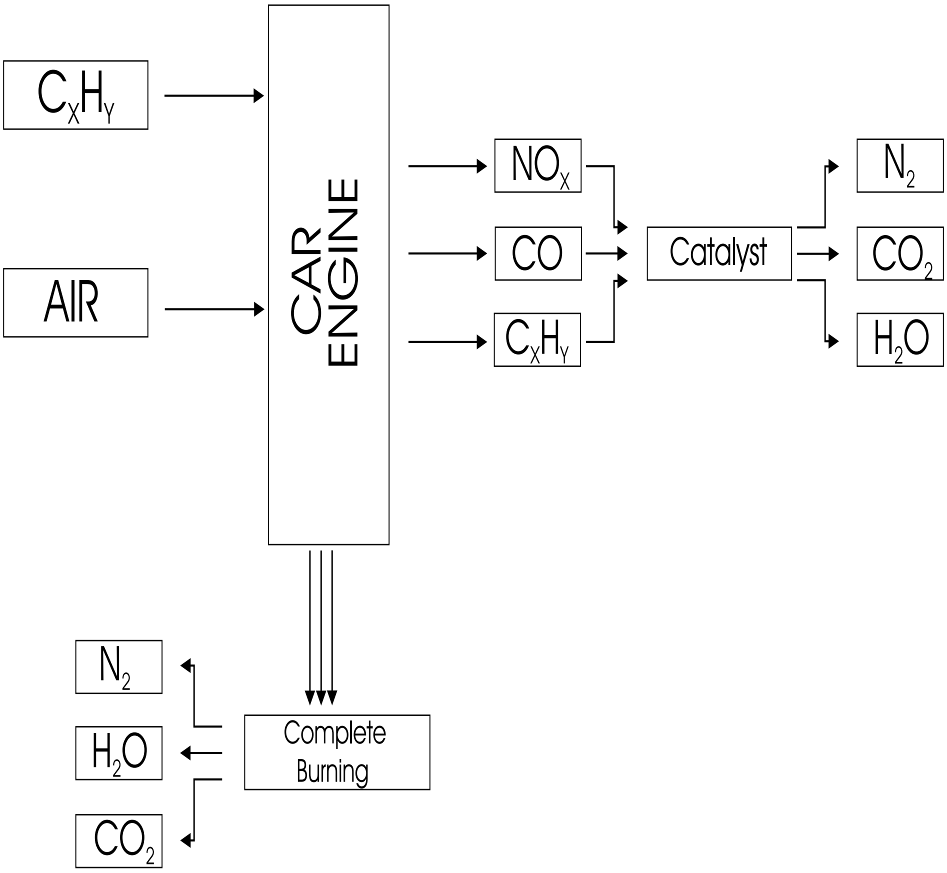

Figure 1.2: Schematic representation of the process in a car engine

Reaction		
$C_XH_Y + (x + \frac{y}{4})O_2$	$\rightarrow$	$xCO_2 + \frac{y}{2}H_2O$
$2CO + 2NO$	$\rightarrow$	$N_2 + 2CO_2$
$2CO + O_2$	$\rightarrow$	$2CO_2$

Table 1.1: Conversion reactions in auto-exhaust catalysts

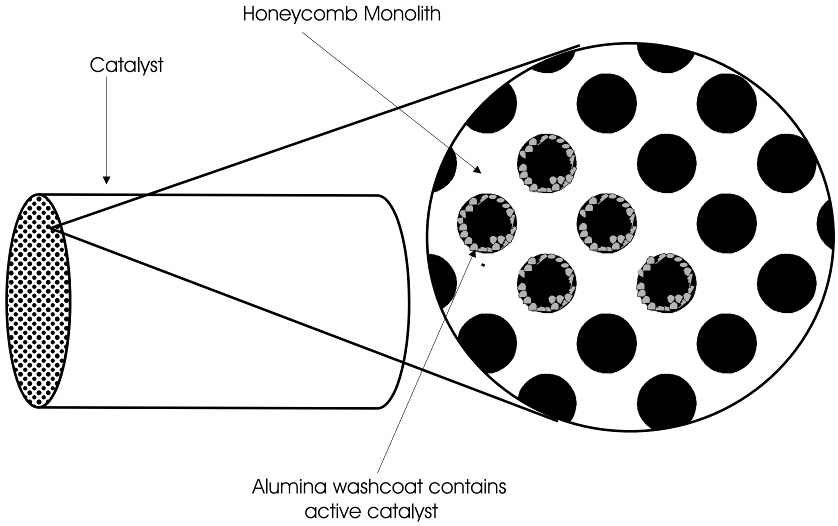

Figure 1.3: An exhaust monolith

activity of the precious metal.

The catalyst normally operates at temperatures between 300°C and 900°C. When a car engine is started the catalyst is cold and is not immediately active. Initially, the system is heated by the exhaust gases, taking 50 - 200 seconds before the first signs any activity. The catalyst is working at its optimum when it becomes self-heating as a result of the exothermic reactions taking place within it. The time taken for the catalyst to go from being merely 'warmed up' to it being self-heated is known as the 'light off time'. In the period before the 'light off time' the car engine is also producing the most emissions, mainly in the form of hydrocarbons and CO due to incomplete combustion. Thus, a primary concern of much catalysis research has been to produce more active catalysts, promoting conversion of pollutants at much lower temperatures and therefore, lowering the 'light off time'.

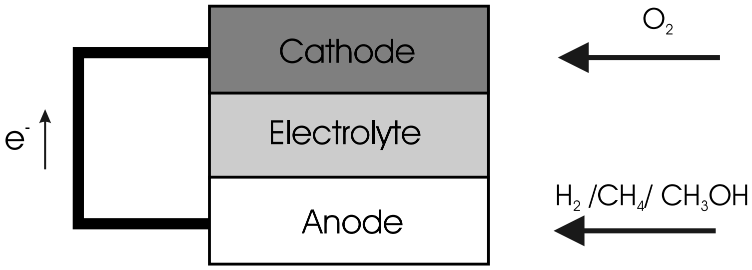

Figure 1.4: A schematic representation of a Solid Oxide Fuel Cell

1.2.2 Solid Oxide fuel Cells

A fuel cell is a device for the production of electrical energy from the direct conversion of chemical energy. The reactions occur across an electrochemical cell which consists of an electrolyte, a cathode, and an anode (Figure 1.4). The operation of the device is based on the presence of a chemical potential gradient across the electrolyte, which provides a driving force for ionic conduction from the cathode to the anode.

In SOFC's the electrolyte is a slab of an oxygen ion conductor, typically Gd doped ceria. The chemical potential gradient between the electrodes is a result of the difference in oxygen partial pressure between the two sides. At the anode/electrolyte interface, the fuel gas (normally H_2) reacts with the electrolyte's lattice oxygen ions,

$$H_2(g) + O_O^x \rightarrow H_2O + 2e^- + V_O^{\bullet\bullet} \tag{1.1}$$

The resulting electrons travel around the external circuit to the cathode, where they reduce gaseous oxygen to form lattice oxygen ions,

$$2e^- + V_O^{\bullet\bullet} + \frac{1}{2}O_2(g) \rightarrow O_O^x \tag{1.2}$$

The circuit is completed by the migration of oxygen vacancies through the electrolyte.

1.3 Cerium Dioxide; An overview of experimental and theoretical studies

1.3.1 Bulk

Ceria's wide use as an electrolyte in SOFC's and in oxygen sensors is related to two very important properties. Firstly, its open fluorite structure allows the anions to migrate through the lattice relatively unhindered [4]. Secondly, it can undergo a large departure from stoichiometry under reducing conditions, with little change in phase [5]. Under such conditions the Ce^{4+} ions are reduced to Ce^{3+}. Although in many materials the resulting electron is not truly localised on a single cation site, in CeO_2, the electron does exist as a small polaron [6], i.e a Ce^{3+} ion. The presence of the polaron is charge compensated by the formation of an oxygen vacancy [**?**, 7], i.e.

$$2e^{-} + 2Ce_{Ce}^{X} + O_{O}^{X} \rightarrow 2Ce_{Ce}^{\prime} + V_{O}^{\bullet\bullet} + \frac{1}{2}O_2(g) \tag{1.3}$$

A similar compensation mechanism exists when CeO_2 is doped with subvalent ions, e.g. +2 or +3 ions;

$$2Ce_{Ce}^{X} + 4O_{O}^{X} + M_2O_3 \rightarrow 2M_{Ce}^{\prime} + 3O_{O}^{X} + V_{O}^{\bullet\bullet} + 2CeO_2 \tag{1.4}$$

Studies have shown that doping with trivalent cations improves the oxygen ion conductivity significantly [8, 9]. Recent studies have also shown that in highly non-stoichiometric ceria cation diffusion is possible and is the rate determining step for grain boundary migration [10].

In addition to numerous experimental studies, there have been a number of theoretical studies. Two important examples include the classical study by Butler *et al.*

[11] and the Quantum Mechanical study of Hill and Catlow [12]. The former study showed that trivalent cation defects in CeO_2 can associate with the charge compensating $V_O^{\bullet\bullet}$ defects; and that the binding energies are dependent on the size of the cation defects.

In the latter study, restricted Hartree-Fock calculations indicate the CeO_2 is considerably ionic, transferring 2.35e from the cerium atom to the oxygen. Additionally, the study showed that the omission of relativistic effects did not greatly affect the results; the lattice parameter was calculated to be 5.385Å only 0.5% lower than the experimental value of 5.411Å. Recently, other quantum mechanical studies have confirmed these findings [13].

1.3.2 Surface

There have been numerous studies on the catalytic properties and surface structure of CeO_2. Hence the review presented here is not meant to be exhaustive, but is aimed to be representative.

It was mentioned previously that CeO_2 is primarily used as a promoter and stabiliser in autoexhaust catalysts. Its interaction with the Al_2O_3 support and precious metals is complex and as yet not clearly understood. It was initially thought that ceria's main function was that of 'oxygen storage' [14, 15]. However, it has been shown to play other important roles [16]. Oxygen storage is the process whereby CeO_2 promotes the oxidation of hydrocarbons and CO in fuel rich conditions (i.e. when there is insufficient air to completely oxidise the fuel) by providing oxygen. In fuel lean conditions it removes oxygen thus promoting the conversion of NO_X to N_2. Summers and Ausen [17] attribute the increased catalytic activity of Pt/CeO_2 systems to the oxygen ‘donation’ properties of ceria.

An atomistic explanation of this behaviour was provided by Jin *et al.* [18, 19] who carried out IR, XPS, and TPD studies of the oxidation of CO to CO_2 on Pt/CeO_2 catalysts. They proposed that CO adsorbs onto a Pt particle and then migrates to a corner site where it removes an oxygen from the CeO_2 to from CO_2. This results in the formation of an oxygen vacancy on the CeO_2 surface, and is associated with the reduction of a Ce^{4+} ion to Ce^{3+}. The resulting vacancy can then act as an active site for NO_X reduction [20].

Recently, the studies of Hardacre *et al.* [21] have shown that refinements must be made to this model for CO oxidation. In their studies they find that a Pt particle completely encapsulated by a thin film of CeO_2 is a more effective catalyst than one with exposed Pt sites. They postulate that Pt *promotes* the CeO_2 to act as a catalyst by reducing the Ce^{4+} to Ce^{3+}, thus lowering the oxygen vacancy formation energy. This metal encapsulation - support promotion hypothesis may additionally explain the low temperature catalytic behaviour of ceria [22] and has been seen in HRTEM studies at 873K for Pd [23]. To add to the controversy, the work of Ying *et al.* [24] on nano-crystalline CeO_{2-x} indicates that oxygen vacancies play a minor role in CO oxidation and that O_2^- and other electronic defects are the active sites, whose presence has been observed by ESR [25].

In comparison to the extensive experimental work carried out on CeO_2, surface simulations of the material are still in their infancy. Much of the previous work has been carried out by Sayle *et al.* [26, 27, 28] who showed that the formation of oxygen vacancies in ceria is surface specific. Of the three surfaces they studied, the high index (310) surface was the most favourable for vacancy formation. These results have been corroborated to some extent by the experimental work of Padeste *et al.* [29] and Hardacre [21]. Hardacre showed that the more disordered the CeO_2 film around the Pt particle the better its catalytic activity. They rationalise this in terms of there being more high index faces which are more likely sites for catalytic activity. Padeste *et al.* found similar results for the reduction of CeO_2 by H_2.

In addition to playing an important role in the catalytic cycle, CeO_2 also interacts with the γ - alumina washcoat and plays an important role in stabilising it [20]. Its behaviour has been studied by XPS, XRD, and TPR [30]; these have shown that on heating in air at 800°C, Pt on both CeO_2 and CeO_2/Al_2O_3 substrates resulted in the formation of a Pt-CeO_2 interacting species with an oxidation state Pt^{2+} (attributed to PtO). This is completely reduced by H_2 at 500 °C to Pt metal. Similar behaviour is seen with Pd [31] which is converted to PdO; however it is reduced to Pd metal more readily than Pt due to its weaker interaction with CeO_2.

Finally, ceria has also been shown to play a role in the promotion of the water gas shift reaction;

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1.5}$$

This has been shown to occur both with bare ceria [32] and precious metal / CeO_2 systems [33] , [34] via a formate intermediate.

1.4 Aim of study

The present work has several aims; firstly, to model the surfaces and bulk of CeO_2 in a systematic way. Secondly, to examine several aspects of the methods used with a view to justify or rationalise the approximations and assumptions that underlie them.

1.4.1 Bulk

We will study several dopants in CeO_2, both as point defects and defect clusters. We try to provide physical interpretations for the trends seen in the defect configurations and relate these results to those obtained by a number of different experimental techniques. In addition, we examine the assumption that infinite dilution calculations can be extrapolated to real systems which have high defect concentrations and whether good physical models of defect - defect interactions in such systems can be obtained.

1.4.2 Surfaces

In this part of the thesis, we study the structure of a number of CeO_2 surfaces and attempt to derive a crystal morphology of ceria. We examine the dependence of these results on the short range parameters used, and whether the parameters derived from bulk experimental data can be applied to surface studies. Additionally we compare and contrast static infinite surface calculations with molecular dynamics studies of finite surfaces in nano-crystals and, in particular, how the results affect type III surfaces.

Overall this work may elucidate the processes involved in the removal of pollutants from car exhausts and solid oxide fuel cells, in the hope that it will add to the basic scientific understanding of CeO_2 surfaces and bulk ceria. In addition, it attempts to validate the models and methodologies used in these studies by comparing and contrasting them with experimental data and other modelling techniques.