Combined Scattering and Spectroscopic Structure Determination of Nano-catalysts

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I, Adam Hugh Clark, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.
Abstract

Several types of nano-catalysts, which includes oxides, supported mono and bimetallic catalysts have been used extensively for a range of catalytic reactions. Understanding the structure and reactivity has been a main theme to elucidate structure-function relationships. Herein, the behaviour of nano-catalysts has been studied using a range of experimental tools, with Synchrotron Radiation techniques as the major component. In addition, a range of analysis methods have been explored to determine structure using in situ and ex situ methods.

Investigations into the structure of bimetallic silica supported PtZn nano-particles were conducted in situ during exposure to formic acid using X-ray absorption spectroscopy (XAS). Here it has been demonstrated that Zn is highly dispersed and bonded to the channel walls within the SBA-15 porous silica, whilst Pt forms oxide particles within the channels, in the as-synthesised form. On exposure to formic acid conversion of ZnO like species to Zn formate is observed to occur concurrent to the reduction of Pt oxide to Pt metal nano-particles.

The redox characteristics of ceria supported platinum group metal (PGM) samples and ceria coated PGM metals supported on alumina have been studied in detail. XAS has been employed following the oxidation state of both the cerium and supported PGM, in addition to X-ray total scattering following the lattice structural changes, under in situ reduction-oxidation conditions. Detailed analysis has elucidated a promoted reduction of ceria upon reduction of the initial PGM oxide is
observed. In the case of the inverse ceria alumina catalysts partial re-oxidation is observed upon cooling under a reducing atmosphere. Upon exposure to air, a full re-oxidation of the ceria support takes place, however only a partial oxidation (passivation), of the PGM to occur. Further reduction cycles result in ca room temperature reduction of the PGM and ceria.
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Nomenclature

Concise list of all abbreviations used herein.

Facilities

- APS - Advanced Photon Source
- ESRF - European Synchrotron Radiation Facility
- DLS - Diamond Light Source

Experimental Methods

- ATR - Attenuated Total Reflectance
- DxPDF - Differential X-ray Pair Distribution Function
- EXAFS - Extended X-ray Absorption Fine Structure
- FDMNES - Finite Difference Method Near Edge Structure
- HERFD - High Energy Resolution Fluorescence Detection
- HRXANES - High Resolution X-ray Absorption Near Edge Structure
- IGA - Intelligent Gravimetric Analysis
- IR - Infra-red
• MS - Mass Spectrometry

• SAXS - Small Angle X-ray Scattering

• TEM - Transmission Electron Microscopy

• TPR - Temperature Programmed Reduction

• WAXS - Wide Angle X-ray Scattering

• XANES - X-ray Absorption Near Edge Structure

• XAS - X-ray Absorption Spectroscopy

• xPDF - X-ray Pair Distribution Function

• XRD - X-ray Diffraction

Other

• DW - Debye-Waller

• FT - Fourier transform

• HDP - Homogeneous Deposition Precipitation

• HSA - High Surface Area

• IES - Impregnation in Excess Solution

• MEE - Multiple Electron Excitation

• MSR - Mean Square Relative Deviation

• OSC - Oxygen Storage Capacity

• PDF - Pair Distribution Function

• PGM - Platinum Group Metals
• RDF - Radial Distribution Function

• RF - Radio Frequency

• UV - Ultra Violet

• WGS - Water Gas Shift
Chapter 1

Introductory Material

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1.1 Heterogeneous Catalysis

Catalysis is defined by the increase in rate of a reaction due to the presence of a catalyst. A catalyst is a substance which is not consumed during a catalysed reaction but acts to reduce the free energy required to transform a reactant to a transition state. As such a catalysed reaction has a lower activation energy and results in an increased rate of reaction compared to an uncatalysed reaction if all other conditions remain unchanged. There are three main categories of catalysis, heterogeneous, defined by the catalyst and reactants being in different phases, and homogeneous catalysis, whereby the catalyst and reactants are in the same phase. The third category pertains to enzymes and biocatalysts. The work presented herein will focus on the use of supported metal heterogeneous catalysis.

The main benefit provided by the use of heterogeneous catalysts is that the products and the catalyst can often easily be separated out. Typically in heterogeneous catalysis, the catalysts are solid phase with catalytic reactions taking place through the surface adsorption of reactants. Adsorption of reactants can take place via two routes, physisorption and chemisorption. In physisorption only a small change in the electronic structure of the adsorbate is induced through van der Waals forces. Whereas chemisorption involves the direct sharing of electrons between the adsorbate and the adsorbent.

Catalysis on surfaces can be described by three main mechanisms in the bimolecular model: Langmuir-Hinshelwood, Rideal-Eley and the Precursor mechanisms. The Langmuir-Hinshelwood mechanism involves the adsorption of two molecules onto a surface. Through surface diffusion the two molecules interact, react and then subsequently desorb from the surface. The Rideal-Eley mechanism is described by one molecule adsorbing to a surface and the second, having never adsorbed, reacting with the new molecule then desorbing. The Precursor mechanism involves the adsorption of one molecule onto a surface with a second colliding with the surface.
to form a mobile precursor derivative. Subsequent interaction with the adsorbed molecule leads to the formation and desorption of a new molecule. When considering supported metal catalysis, reactants can adsorb onto either the support matrix or the catalyst surface.

The decomposition of a substance (R) on a surface site (S) can be described by the equation:

$$R + S \rightleftharpoons RS \rightarrow Product$$

(1.1)

R is the reactant and S is the adsorption site on the surface of a material which are in equilibrium with the adsorbed species RS. The reaction rate is then defined as;

$$r = \frac{dC_R}{dt} = k\theta C_s$$

(1.2)

where $k$ is the kinetic rate constant for the surface reaction, $\theta$ is the surface coverage and $C_s$ is given as the total number of adsorption sites. In the steady state approximation this can be expressed as:

$$r = \frac{k_1k_2C_RC_S}{k_{-1}C_R + k_2}$$

(1.3)

where $k_1$ and $k_{-1}$ refer to the rate constants for adsorption and desorption respectively and $k_2$ is the rate constant for reaction of adsorbed species. In the case where the rate limiting step is determined by the adsorption or desorption, $r$ is approximately equal to $k_1C_RC_S$, a first order rate equation in respect to the reactant. In the case of the reaction of adsorbed species being the rate limiting step one can consider the low and high concentration of reactants limits. In the low limit the reaction rate
can be shown to be a first order rate equation in respect to the reactant;

\[ r = K_1 k_2 C_R C_S \]  \hspace{1cm} (1.4)

where \( K_1 \), the adsorption equilibrium constant, is given as the ratio of the adsorption and desorption rate constants. Whilst in the high concentration limit the rate of the reaction is shown to be zeroth order with respect to the reactant;

\[ r = k_2 C_S \]  \hspace{1cm} (1.5)

Evident in the above example of the simple decomposition reaction, the number of surface sites plays an integral role in the rate of a reaction. As such the surface area of a catalyst is critical. To enhance the surface area of catalysts, nano-structuring is used. The structure of porous materials such as zeolites, aluminium phosphates and mesoporous silicates naturally leads to exceptionally high surface areas on the order of hundreds of \( m^2/g \). In the case of nano-particulate metals, dispersion over a high surface area support matrix is often used. In this thesis mesoporous silica in the form of SBA-15 and a high surface area ceria are used as supports for nano-particulate metal catalysts.

### 1.2 Porous Silicates

#### 1.2.1 Production of Mesoporous Silicates

Porous silicate structures come in many forms with a range of pore size and distributions. When concerning pore sizes between 2 and 50 nm the prefix \( \text{Meso} \) is applied whose Greek definition means ‘in between’. Microporous materials are those with pores smaller than 2 nm including caged zeolite, porous silicates and aluminium phosphate materials. Macroporous materials refer to those with pore sizes larger
than 50 nm\textsuperscript{[14,15]}

Mesoporous silicates are synthesized in the presence of surfactants to template the condensation of silica. Commonly several sources of silica are used: tetraethylorthosilicate and methylorthosilicate for example. The temperature, pH and composition of the reaction mixture play a key role in the degree and type of condensation. As such, the described conditions determine the form of the mesostructure and the pore structure.

A wide range of porous silicate materials exist with different mesoporous structuring. MCM-41 exhibits a hexagonal packing of channels, whereas MCM-48 has a cubic mesostructure and MCM-50 a lamellar structuring consisting of layered stacking of silica interspersed by pores. The type of condensation is somewhat dependent on the concentration of surfactant in the solution. Above the critical micelle concentration (CMC) the self assembly formation of mesoporous silicates occurs, shown in Figure 1.1. The CMC is affected by synthesis parameters such as the temperature and pH, however it is also affected by the chain length of the surfactant used\textsuperscript{[16]}

**Figure 1.1:** Effect of the concentration of surfactant on the structure of the mesoporous silica produced, Figure reproduced from\textsuperscript{[16]}

### 1.2.2 Structural Properties of SBA-15

Similarly to the aforementioned MCM-41, SBA-15 is a type of porous silicate that forms regular hexagonally stacked channels, the hexagonal stacking is shown using end on transmission electron microscopy (TEM) in Figure 1.2. The synthesis of
SBA-15 results in long channels to form with a tuneable pore diameter, between 50 and 300 Å, with a narrow distribution.\textsuperscript{17}

\textbf{Figure 1.2:} The structure of SBA-15 viewed end on using TEM, illustrating the hexagonal packing of the amorphous silica walled channelled pores, is shown in a. Average pore dimensions are 60 Å, 89 Å, 200 Å and 260 Å respectively for A, B, C and D. Image is reproduced from Zhao et al.\textsuperscript{17}

\textbf{Figure 1.3:} An example indexed X-ray diffraction pattern of an SBA-15 sample arising from the hexagonal stacking of channelled pores collected at an incident X-ray photon wavelength of 1 Å.
The hexagonal stacking of the SBA-15 channels can be considered, in the case of a 2D stacking extending with channels of infinite length, as diffraction points. The subsequent diffraction pattern shows reflections at low $Q$ related to the $p6mm$ spacegroup. The relatively low $Q$ of the reflections is due to the large distance between the diffraction centres, the pores rather than atoms within a crystalline structure. An indexed diffraction pattern acquired from a powder SBA-15 sample is shown in Figure 1.3 for an incident photon wavelength of 1 Å. There are 5 clear reflections, when using a logarithmic scale for the intensity, illustrating the high degree of ordering of the channels stacking in a hexagonal pattern.

The supporting of nano-particles within SBA-15 is often accomplished through precipitation methods whereby metal nano-particles can be grown within the channels of the SBA-15 through the reduction of the relevant metal precursor\textsuperscript{18–23}. Measurements of the surface area using BET often lead to a rise, compared to blank SBA-15, interpreted as caused by the presence of nano-particles within the SBA-15 channels. Adsorption-desorption hysteresis loops are a result of capillary condensation within mesopores restricting uptake or through the ink bottle effect which can be increased by the presence of nano-particles within the pores\textsuperscript{24}. In conjunction with TEM performed on samples with the presence of metallic nano-particles in the silica channels can be confirmed, an example of Pt nano-particles supported in SBA-15 is shown in Figure 1.4.

![Figure 1.4](image-url)

**Figure 1.4:** Example TEM image illustrating the presence of Pt nano-particles in the channelled pores of SBA-15.
While the channels of the SBA-15 are formed of well ordered, hexagonally stacked, pores, the walls are formed of amorphous silica. The disorder of the silica can be seen in the presence of $Q_2$, $Q_3$, $Q_4$ peak splitting in $^{29}$Si NMR[15][25]. This has been interpreted as relating to the different surface bonding sites of silicon suggestive of a degree of disordering in the pore walls. $Q_4$, the dominant peak, relates to tetrahedral bonding of $Si(OSi)_4$, with $Q_3$ to $Si(OSi)_3OH$ silanol species the second most prominent and a small quantity $Q_2$ being $Si(OSi)_2(OH)_2$ species. It has previously been reported that the acidity due to the silanol groups of the $Q_2$ sites is less than that of the $Q_3$ sites. The bonding of metallic nano-particles to the silica surface can be considered as taking place through various surface sites, defective or otherwise. The preference of metals to grow either spherically within the pore of the SBA-15 or through attachment to the pore-walls may depend on the relative acidity of the nucleation sites available.

1.3 Ceria

1.3.1 Industrial Use of Cerium

Cerium is located within the lanthanide series and has the electronic configuration $[Xe]4f^15d^16s^2$. Though being part of the ‘rare-earth metals’ cerium itself is not rare, forming a similar proportion of the Earth’s crust to copper at an estimated 66 ppm. Cerium metal is unstable in the presence of oxygen, readily oxidising to form oxides in the range between $Ce_2O_3 - CeO_2$. The nature of cerium to be stable in two oxidation states Ce(III) and Ce(IV) is exploited in the production processes used in the recovery of cerium from mineral ores, commercially this is achieved mainly through solvent extraction method[27][29].

Cerium containing compounds are widely used industrially. Cerium(IV) sulfate and ceric ammonium nitrate are used as strong oxidising agents due to the ability of the Ce(IV) to readily accept an electron and transform to Ce(III). Cerium carboxylates are used to improve the properties of silicone polymers and in drying agents in
Cerium is used within metallurgy in several areas; as part of mischmetal, along with La, Pr and Nd, is used to improve the properties of high-strength low-alloy steels. Cerium containing compounds are widely used in the catalytic cracking of crude oil, elsewhere in the oil related industries cerium dioxide, ceria, has found major use within the automotive industries as a catalyst support for the conversion of pollutants such as $NO_x$ and $CO$ in exhaust emissions;

$$2CO + O_2 \rightarrow 2CO_2$$  \hspace{1cm} (1.6)

$$2NO_x \rightarrow N_2 + xO_2$$  \hspace{1cm} (1.7)

where $CO$ is oxidised to form $CO_2$ and $NO_x$ undergoes decomposition to $N_2$ and $xO_2$. As part of a three-way catalyst ceria also promotes the conversion of unburnt hydrocarbons into $CO_2$ and $H_2O$. With regulatory guidelines and requirements on the pollutants from auto-exhaust emissions becoming more stringent ceria is also being used as a fuel additive to suppress the production of particulate emissions from diesel.

### 1.3.2 Structural Properties of Ceria

Ceria forms a cubic fluorite unit cell formed by an fcc lattice of 12 cerium atoms with 8 oxygen atoms forming an inner cube tetrahedrally coordinated to the cerium cations, shown in Figure 1.5A. The octahedral holes found within the centre of the fluorite structure are clearly observed in Figure 1.5B, here the unit cell is shown centred on the oxygen atoms with the cubic bonding environment of the cerium with respect to the oxygen shown. The octahedral holes are considered to be a feature which gives rise to the ionic conduction through the lattice.

Ceria is considered to be naturally defective with a true composition in the region between $Ce_2O_3 - CeO_2$. The fluorite related phases have been shown to be stable in a range of compositions, $CeO_x$ for $1.714 < x < 2$, representing a continuum.
Figure 1.5: Figures illustrating the fluorite lattice structure of ceria. A shows the unit cell centred on the cerium cations with the tetrahedral coordination of the oxygen bonding to cerium highlighted with red shaded polyhedra. B gives the fluorite unit cell centred on the oxygen atoms with the cubic coordination of the cerium to the oxygen shown in green shaded polyhedra. The green atoms represent cerium cations and red is used to represent oxygen anions.

of disordered non-stoichiometric phases with diffraction studies showing only an increase in lattice parameter as the value of $x$ decreases, shown in Figure 1.6. The lattice expansion is commonly modelled by the relative increase in ionic radius of Ce(III) in comparison to Ce(IV), 1.14Å and 0.97Å respectively.

Figure 1.6: Effect of reduction on the lattice expansion of ceria. Figure reproduced from Catalysis by Ceria and related materials.

An empirical formulation of the lattice expansion of ceria due to dopants has been
derived taking into account the dopant ionic radius and the change in valance state:

\[ a_{Ce}(nm) = 0.5413 + \sum_k (0.0220\Delta r_k + 0.00015\Delta z_k)m_k \]  

(1.8)

where \( \Delta r_k \) is the difference in ionic radius, \( \Delta z_k \) is the difference in valance state and \( m_k \) is the mole fraction of the dopant in the ceria structure. The dotted line in Figure 1.6 is calculated by considering Ce(III) ions as dopants into the 8 fold coordinated cerium site of ceria lattice in this formalism with \( \Delta z_k \) equal to \(-1\) and \( \Delta r_k \) of 0.017 nm.

The reversible reduction of Ce(IV) to Ce(III) within the ceria lattice results in the formation of oxygen vacancies.

\[ CeO_2 \rightleftharpoons CeO_{2-x} + \frac{x}{2}O_2 \]  

(1.9)

\[ O_o \rightleftharpoons \frac{1}{2}O_2 + V_{o}^{**} + 2e' \]  

(1.10)

\[ 2Ce_{Ce} + 2e' \rightleftharpoons 2Ce_{Ce}^{'} \]  

(1.11)

Where the overall equation 1.9 shows the change in stoichiometry due to the removal of oxygen from the ceria lattice and equations 1.10 and 1.11 describe the

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\(^1\)Whilst ceria is often described as being purely formed of cerium in the tetravalent state, there is continued discussion as to whether this is the case. Cerium atoms have been noted as not losing all of the four valence electrons, instead a partially occupied 4f electron is proposed to exist. Measurements of the oxidation state of cerium ions in what are classically thought of as tetravalent such as cerocene have pointed towards an intermediate-valent state. X-ray photoemission spectroscopy (XPS) is often used to determine the ratio of Ce(III) to Ce(IV). In the case X-ray absorption studies, the small pre-edge feature at the bottom of absorption edge is often related to a partially occupied 4f electron present within ceria. The presence of a partially occupied 4f electron has in particular made the study of ceria using computational methods particularly challenging.
formation of an oxygen vacancy, $V_o^{••}$ at a lattice site oxygen, $O_o$, which results in the reduction of two cerium lattice sites from Ce(IV), $Ce_{Ce}$, to the reduced Ce(III) state, $Ce_{Ce}'$. The symbols $'$ and $•$ are used here to represent negative and positive charges respectively to indicate the movement of charge.

The presence of defects within ceria increases its conductivity, as such ceria has found uses as a solid oxide electrolyte and in catalysis\cite{47,49}. The conductivity of ceria is due to both electronic conduction, by polaron hopping, and through the ionic conduction of oxygen. In catalysis the transport of oxygen plays a key role in oxidation reactions. The diffusion of oxygen in ceria is of particular interest in the automotive industry when considering three-way catalysts where the formation of oxygen vacancies and transport of oxygen to a catalytically active site, often referred to as reverse oxygen spill-over, is vital to the catalytic activity of ceria based materials. The ability of ceria to transport oxygen is also important in the longevity of a catalyst where cycling of reduction and subsequent regeneration by oxidation, involves the transport of oxygen from the surface into the bulk to combine with lattice oxygen vacancies.

The ability of ceria to store and release oxygen is often measured through determination of the quantity, per gram of catalyst, of a reducing gas that is oxidised through transient anaerobic conditions, the OSC\cite{51,53}. The naturally high value of the OSC for ceria makes it an ideal candidate for a three-way catalyst due to the supply and demand for oxygen varying through lean and rich conditions in auto-exhaust emissions. However, ceria has a relatively low thermal stability, characterised as a decreased surface area after ageing by catalytic cycling. To increase the thermal stability studies undertaken on doping with zirconium have shown that after ageing a greater surface area can be maintained\cite{54}.

Along with the greater thermal stability associated with the doping of zirconium it
has also been demonstrated that the doping leads to a marked improvement in the OSC of ceria based materials. The largest OSC obtained for ceria zirconia materials has been reported as 219 $\mu$molO/g for the composition $Ce_{0.63}Zr_{0.37}O_2$. Figure 1.7 gives the experimental OSC for a range of compositions from $ZrO_2$ to $CeO_2$ as a function of the cerium content.

**Figure 1.7**: Effect of Zr doping on the OSC of ceria conducted at 400°C.

The effect of temperature on the OSC of ceria and ceria-alumina materials with supported Pt and Rh loading has also been studied. Greater OSC is observed at elevated temperatures, suggesting oxygen further from the surface are transported. The effect of supported PGMs has been investigated on both ceria and ceria-zirconia materials showing a direct promotion of increased OSC as a result of supported PGMs.

Measurement of the oxidation state of cerium within these materials can be directly related to the OSC. XAS methods on the Ce $L_3$ edge probe the oxidation state of the cerium atoms whereby the concentration of Ce(III) can be extracted throughout *in situ* experimentation. Pulsed experiments under isothermal conditions yield results mimicking those obtained from OSC due to the fraction of Ce(III) observed being directly related to the number of oxygen atoms released from the ceria lattice. As such, experiments following the dynamic change in oxidation state of cerium with temperature can be used to provide an upper limit for the OSC available at any
particular temperature.

1.4 Supported Metal Catalysts

The efficiency of a heterogeneous catalyst used industrially largely depends on the surface area of the active phase participating in a particular reaction. Supported catalysts have, in many areas, found to be particularly useful in the anchoring of catalytic materials to both maintain the lifespan and to increase the active surface area. Naturally high surface area materials such as zeolites, aluminium phosphates and porous silicates are often used, due to their channelled or caged structuring, as supports for catalysis. Copper exchanged zeolites, for example, have found wide use in the selective catalytic reduction of $\text{NO}_x$ in the presence of $\text{NH}_3$ and in the desulfurization of fuels, whereas mesoporous silicates, in particular SBA-15, have been studied for Fischer-Tropsch synthesis, oxidation and dehydrogenation catalysis among others.

Metal oxide materials have long been used as supports in catalysis. Extensively metal oxide supports have been used for the Haber-Bosch process on iron oxide on alumina supports as an example. Most heterogeneous photocatalytic processes are performed using metal oxide materials, such as $\text{TiO}_2$, due to their nature as semiconductor materials. Semiconductor materials are able to extend the lifetime of electron-hole pairs due to the presence of a band-gap. $\text{ZnO}$ with supported Au or Cu has been employed for use within the water gas shift reaction for the production of hydrogen. The use of $\text{CeO}_2$ as a support relates to its unique material properties for the storage and release of oxygen.

The strong metal-support interaction has long been studied for its ability to change the chemisorption properties of platinum group metals (PGM) supported on metal oxide supports, commonly $\text{ZnO}$, $\text{CeO}_2$ or $\text{TiO}_2$. In many systems the interaction between metallic particles and the support directly influences their catalytic
behaviour. The bonding interactions of the support and metal can lead to the spreading of the metal over the support resulting in a high dispersion. In other cases the aversion to bonding can lead to the formation of large metallic particles. In many cases the inter-facial region between the metal and the support create regions of particularly enhanced catalytic activity\textsuperscript{82–86}. The term strong metal-support interaction has also been related to the electronic metal-support interaction\textsuperscript{87} whereby there can be a small transfer of electrons from the support to metal or vice versa. This $\delta^{\pm}$ charge can play an important role in the catalytic reactivity through van der Waals interactions.

1.4.1 Catalyst Preparation

Supported metal catalysts are used to allow for the high dispersion of nanostructured particles onto a support matrix that typically has a high surface area. Thus, a very high active surface area can be produced for the purpose of heterogeneous catalysis. The specific surface area, a measure of the surface area per mass unit of a material, of a metal particle can be approximated using the hard sphere model\textsuperscript{88}:

$$S_A = \frac{6}{\rho d}$$  \hspace{1cm} (1.12)

This gives the specific surface area, $S_A$ for a given density $\rho$ and crystallite size, $d$. Figure 1.8 gives the specific surface area for both Pt and Pd particles as a function of particle diameter. Another measure often used is the dispersion, $D$, of the metal across a surface which can be given by the ratio of the number of surface atoms, $n_s$, over the total number of atoms, $n_p$;

$$D = \frac{n_s}{n_p} = \frac{A_p A_p}{n_p}$$  \hspace{1cm} (1.13)

This can be approximated by considering the surface area of the particle, $A_p$, and of an individual atom within the surface, $A_d$, which for Pt is approximately 6.55
Å². By the nature of the atomic radii of Pt and Pd being very similar the dispersion curve, shown in Figure 1.8 as a dashed line, is relevant for both Pt and Pd.

**Figure 1.8:** Calculated specific surface area and dispersion for Pt and Pd particles assuming a close-packed (111) plane surface across the particle. The specific surface area, solid lines, for Pt is given by • whilst Pd is given by ○. The dispersion curve is shown as a dashed line and marked by †. Figure reproduced from 88

Due to small nano-particles having vastly increased specific surface areas there is a desire to prepare catalysts that are able to limit the sintering of such particles under catalytic operation. In particular catalysis performed at elevated temperatures can lead to the sintering and agglomeration of particles to form larger particles, which leads to a decrease in the active surface area of a catalytic material and as such reduced effectiveness. Preparation of supported metal catalysts to produce the small nano-particles required to maximise the surface area and stability of the active catalytic phase is often carried out by one of two main methods: impregnation   

89, 91
Catalyst preparation is highly dependent on the conditions used during impregnation. The interaction and fixation with the support surface of metal precursors is via exchange of surface OH groups or by adsorption onto the surface. As such the concentration density of OH groups on a surface of a support can directly affect the ability of a metal precursor to affix to the surface. The deposition of anions onto a surface are favoured when a support is protonated causing a positive surface charge. Cations are favoured when there is a negative charge on the surface. The pH required for the preparation of a Pt catalyst varies depending on the support material. A silica support will start to adsorb $[\text{Pt}((\text{NH}_3)_4]^2^+]$ at around pH 6, whereas $\gamma$-alumina requires a pH of 8 and above. The difference between these are related directly to pH at which the point of zero surface charge lies.

Impregnation involves the addition of a metal precursor solution to a support material. This can be performed in one of two methods: impregnation in excess solution (IES) or pore volume impregnation. The latter relates to using only enough liquid to fill the pore volume of the support material whilst IES refers to the dipping of a support into a solution of the metal precursor. High metal loadings can be achieved using either method through successive treatments.

Precipitation is usually performed by homogeneous deposition precipitation (HDP) with increasing or at constant pH. The advantage of HDP methods revolve around the ability to produce a high metal loading with high dispersion onto a support, this can be particularly challenging with impregnation techniques. In HDP the support is mixed with a basic solution in a controlled manner by injection of usually either NaOH or NH$_3$ solutions. To produce a homogeneous distribution of the desired metal catalysts the metal hydroxide is introduced into the stirred solution and the pH is altered slowly to favour the nucleation onto the support surface rather
than within the solution bulk. As such it is possible to produce highly dispersed, very small, nano-particles homogeneously over a surface.

### 1.4.2 Supported Platinum Group Metal Catalysis

The catalysis by supported PGMs is discussed below on either of the studied support materials within this thesis: mesoporous silica in the form of SBA-15 and ceria based systems.

Catalysis involving PGM supported on ceria based catalysts covers a broad spectrum of areas. Pt and Pd catalysts have long been used for catalytic combustion. Whilst Rh has been studied for its strong metal-support interaction with ceria and the decomposition of nitrous oxides. Ag ceria catalysts have been noted for the ability of ceria to maintain Ag in an oxidised state at elevated temperatures and has found use as a catalyst for the oxidation of ethylene and CO oxidation. Ceria supported Cu, Au and Pt catalysts have shown promise in the water gas shift reaction (WGS).

Ceria supported Pt has been studied extensively in numerous areas of catalysis. Pt has been shown to be active towards both oxidation and reduction reactions and as such has been employed extensively in three-way catalysts in the automotive industry. Pt ceria catalysts have also been used for the WGS reaction. The example of the WGS reaction is outlined below due to its applicability to the research on the reducibility and recycleability of ceria based systems that has been extensively carried out herein. The reactivity of ceria based catalysts towards the WGS reaction depend upon the oxygen storage capacity (OSC) of ceria. The ability of ceria to both release oxygen for the oxidation of CO and to scavenge oxygen to split $H_2O$ play an important role.

\[ CO + H_2O \rightleftharpoons H_2 + CO_2 \]  

\[ (1.14) \]
The WGS reaction involves the conversion of CO and H\textsubscript{2}O to H\textsubscript{2} and CO\textsubscript{2} or the reverse. Pt ceria catalysts have been used most extensively in low temperature shift catalysis. The reverse spill-over of oxygen from ceria to Pt gives rise to the oxidation of adsorbed CO to CO\textsubscript{2}, whereas surface defects in the form of oxygen vacancies on ceria have been demonstrated to split water into H\textsubscript{2} and a mobile O, shown in Figure 1.9\textsuperscript{[116]}

The following equations describing the WGS reaction use the notation such that the symbols $'$ and • are used here to represent negative and positive charge respectively to indicate the movement of charge. Whilst $V_{o}^{••}$ and $O_{o}$ describe a lattice oxygen vacancy and lattice site oxygen respectively and $Ce_{Ce}^{'\prime}$ and $Ce_{Ce}$ are used to describe lattice site cerium atoms in the Ce(IV) state and reduced state Ce(III) respectively.

\begin{equation}
CO + Pt \rightarrow CO_{absorbed} \tag{1.15}
\end{equation}

\begin{equation}
V_{o}^{••} + 2Ce_{Ce}^{\prime} + H\textsubscript{2}O \rightarrow O_{o} + 2Ce_{Ce} + H\textsubscript{2} \tag{1.16}
\end{equation}

\begin{equation}
CeO\textsubscript{2} + CO_{absorbed} \rightarrow V_{o}^{••} + 2Ce_{Ce}^{\prime} + CO\textsubscript{2} \tag{1.17}
\end{equation}

Due to the ability of surface oxygen vacancies to split water, ceria catalysts have also found particular use in electrolysis as a semiconductor electrode and in fuel cell applications.
The decomposition of $N_2O$ over a Rh/ceria catalyst is another example of significance in the use of ceria as a support material where not only does ceria provide a source of oxygen but also can actively participate in the decomposition through the healing of surface vacancies. The main decomposition route follows the interaction between oxidised Rh and $N_2O$ to reduce the Rh and form $N_2$ and $O_2$, shown in equations 1.18 and 1.19.

The following equations use notation of a similar form as the above. $Rh'_Rh$ and $V_{o_{Rh}}$ refer to the reduced lattice site Rh atoms and vacancy oxygen atoms in the rhodium oxide and similarly $Ce'_Ce$ and $V_{o_{Ce}}$ refer to reduced lattice site cerium atoms and vacancy oxygen atoms in the ceria support.

$$N_2O + Rh_2O_3 \rightarrow N_2O_{adsorbed} \quad (1.18)$$

$$N_2O_{adsorbed} \rightarrow V_{o_{Rh}} + 2Rh'_Rh + N_2 + O_2 \quad (1.19)$$
The transport of oxygen from ceria to the reduced Rh restores the catalytically active site, shown in equation 1.20. However, as shown in equation 1.21, the rhodium oxide can also be restored through the adsorption and decomposition of a second $N_2O$ molecule.

$$CeO_2 + V_{oRh}^{**} + 2Rh_{Rh}^I \rightarrow V_{oCe}^{**} + 2Ce_{Ce}^I + Rh_2O_3$$  \hspace{1cm} (1.20)

$$2Rh_{Rh}^I + V_{oRh}^{**} + N_2O \rightarrow Rh_2O_3 + N_2$$  \hspace{1cm} (1.21)

Finally the re-oxidation of ceria can be completed through the decomposition of a third $N_2O$ molecule, shown by equation 1.22.

$$2Ce_{Ce}^I + V_{oCe}^{**} + N_2O \rightarrow CeO_2 + N_2$$  \hspace{1cm} (1.22)

As such the properties of ceria aid the decomposition of $N_2O$ due to the high surface area, high oxygen storage capacity and ease of reduction allowing for the transfer of oxygen to the supported Rh.

The properties of porous silicates, extremely high surface area and channel structuring, allow for the confinement of nano-particles within the channels to reduce problems of sintering. Channelled silicates have been used to support Pt for a range of applications.

Pt supported in the channels of MCM-41 has shown remarkable ability towards the total preferential oxidation of CO over a wide range of operating temperatures\[^{[21]}\]. A similar catalyst prepared on amorphous silica showed no such reactivity. Experiments performed on a similar channelled silica, FSM-16, with supported Pt demonstrated that the pore size had a significant effect on the reactivity of Pt supported
mesoporous silicates. Larger pore diameters result in increased reactivity\textsuperscript{122,123}. The mechanistic processes involved in the preferential oxidation of CO in mesoporous silicates have been studied\textsuperscript{118}. Silanol groups in close proximity to Pt were shown to be catalytically active towards the oxidation of CO\textsuperscript{124,123}. Regeneration of these active sites occur through the dissociation of \( O_2 \) and \( H_2 \) which are part of the preferential oxidation reaction mixture. The role of silanol groups in contact with Pt was confirmed with the use of isotopic labelling experiments showing the uptake of support oxygen atoms in the oxidation of CO.

The modification of the surface of SBA-15 with Cu or Fe in the presence of Ti or Al have been shown to be highly active and with increased selectivity towards the \textit{DeNO}_x\textsuperscript{x} reactions\textsuperscript{125–127} as well as for methanol oxidative decomposition\textsuperscript{128}. The introduction of Al and Ti into SBA-15 results in the formation of strong Lewis acid sites, with the subsequent deposition of Cu or Fe resulting in highly dispersed isolated cations on the SBA-15 surface. Other methods of increasing the dispersion of active sites over an SBA-15 catalyst surface have been proposed. Novel use of vacuum calcination and \( H_2 \) reduction have shown to significantly increase the dispersion of Pt resulting in the formation of 2D clusters or single atom sites, vastly improving the activity towards CO oxidation\textsuperscript{129}.

Bimetallic systems formed of Pd and Ag supported on SBA-15 have shown high catalytic activity towards the production of \( H_2 \) from \( NH_3BH_3 \). In particular the catalytic activity of these materials has been demonstrated to be enhanced through the localised surface plasmon resonances of Ag under visible light radiation\textsuperscript{130,131}.  

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1.5 Aims and Objectives

The main aim of this thesis is to determine the structural changes that occur in catalytic materials during \textit{in situ} experimentation. To achieve a detailed understanding of the studied catalytic materials extensively XAS and X-ray scattering methods have been employed. Being able to effectively exploit the advantages of different experimental methods to study the dynamic structural changes of materials requires the development of advanced characterisation and analysis methods. This aims to explore the detailed analysis through the application of new methodologies to following, with high temporal resolution, the dynamical structure of catalytic materials under \textit{in situ} reaction conditions.

Chapter Three will focus on the structural changes observed on bimetallic and monometallic SBA-15 supported catalysts during exposure to formic acid probed using X-ray techniques. The decomposition of formic acid is seen as a route for on-demand hydrogen production. To investigate the use of supported PtZn nanoparticle catalysts towards the decomposition of formic acid, XAS methods have been extensively employed. XAS provides unique insight into the nature of bimetallic materials due to the element specific nature probing only the local environment around an absorbing atom. To enhance the analysis and interpretation novel analysis methodologies have been developed using of dose-response curves with the aim of providing a unique insight into the structural characteristics of SBA-15 supported catalysts.

In Chapter Four the redox characteristics of ceria supported catalysts is undertaken using a combination of XAS and X-ray scattering methods. The temporal resolution achievable in X-ray total scattering methods allows for the development of new analysis methodologies through consideration of how materials expand with temperature and changing structure. Here combined interpretation is employed to develop a detailed understanding of the promoted reduction of ceria and the strong
metal-support interaction with supported PGMs.

In Chapter 5, the metal-support interaction in model ceria coated alumina supported PGM inverse catalysts is explored. The analysis methods developed from the analysis of ceria supported PGM catalysts is applied to the more complex systems with the aim of following the dynamic structure changes of each individual component. Detailed analysis is carried out using XAS and X-ray scattering methods to develop a fundamental understanding of the redox properties of ceria based catalysts and the role of the metal support interaction in promoting the reduction of ceria.

Overall this thesis aims to provide a comprehensive understanding of the promoted ceria reduction and to the dynamic structure of monometallic and bimetallic SBA-15 supported PtZn catalysts. Novel analysis methods and routines are developed and employed to provide an enhanced analysis of data with high temporal resolution to give a unique insight into the structure of the studied materials during *in situ* experimentation.
Bibliography


# Chapter 2

## Experimental Techniques

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The work presented within this thesis focuses on the structural characterisation of materials under *in situ* experimentation. As such it is necessary to both introduce the main experimental techniques employed and to mention the facilities that have been used to conduct much of the presented work. The local coordination environment surrounding a particular element type has been extensively probed using X-ray absorption spectroscopy (XAS) methods. These have been conducted at DUBBLE (BM26A) ESRF, ID26 ESRF, B18 DLS and I20-scanning DLS. Whereas X-ray total scattering experiments used to extract the variations in the extended lattice structure have been accomplished using 11-ID-B APS and I15 DLS. Characterisation of *ex situ* samples has also been completed using small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) methods from data collected at I22 DLS.

The following chapter is intended as an introduction to the theory behind the two main branches of experimental techniques that have been undertaken during the course of this thesis: X-ray Absorption Spectroscopy and X-ray scattering. The limitations on both techniques is discussed to highlight their complimentary nature for the determination of material structure during *in situ* experimentation.

### 2.1 Synchrotron Radiation

#### 2.1.1 Development of the Modern Synchrotron

Synchrotron radiation is the emitted electromagnetic radiation caused by the acceleration of a charged particle in a curved path. Classically, any acceleration of a charged particle, linearly or otherwise, will yield electromagnetic radiation. However, in the case of a synchrotron, the circular nature of an electron’s path within a storage ring is the origin of the emitted electromagnetic radiation, ”synchrotron radiation”.

Whilst knowledge of the emittance of electromagnetic radiation by the acceleration of charged particles had been known since the invention of the X-ray tube
in 1895, synchrotron radiation was first observed in 1947 at the General Electric Synchrotron. The first use of synchrotron radiation for the studies of materials was conducted in 1956 at a parasitic source at the Cornell Synchrotron in the UV-region of the electromagnetic spectrum reporting the transmission of beryllium and aluminum foils. The first generation of synchrotrons formed with the development of electron storage rings. The advancement of storage rings proved to be a vastly superior source of synchrotron radiation due to the circulation at a fixed energy for a number of hours resulting in the ability to produce synchrotron radiation with a spectrum that does not change with time and so achieves greater beam stability. The first second generation synchrotron was the Synchrotron Radiation Source at Daresbury Laboratory, 1977, specifically designed and dedicated for the production of synchrotron light for experimentation with a 2-GeV electron storage ring.

The development of insertion devices, undulators and wigglers, produce synchrotron light by oscillating the electron beam by using a series of magnets within the straight sections of a synchrotron, accelerating the electrons in the horizontal plane of the beam. An undulator is typically formed of a series of permanent magnets designed to give a constructive interference effect producing a highly collimated beam with high spectral brightness. The tuning of the wavelengths of the harmonics produced is done through mechanical adjustment of the gap between the magnet poles. Wigglers, whilst fundamentally rather similar to undulators, typically use fewer permanent magnets to produce a higher flux continuous spectrum of radiation.

With the advancements in insertion devices, the first hard x-ray third generation source was opened in 1994, the European Synchrotron Radiation Facility (ESRF). The ESRF is comprised of a 6 GeV storage ring and optimised for high brightness allowing for high spatial and temporal resolution. Synchrotron light is now used for a vast array of techniques for the study of matter. Ranging from X-ray spectroscopy
probing the absorption, emission and reflectance of materials to crystallographic
techniques studying the lattice structuring and ordering of materials. The high
temporal resolution in particular allows in situ or operando studies to be conducted
elucidating the state of matter under the conditions in which they are used industri-
ally.

2.1.2 Generation of Synchrotron Light

A modern synchrotron is a combination of the advancements in accelerator tech-
nologies. The initial acceleration of an electron beam is performed by a linear ac-
ccelerator which produces an electron beam with relativistic energies. For example
the linear accelerator at the APS accelerates electrons from an electron gun to 450
MeV, this equates to a speed of greater than 99.999% the speed of light. Further
acceleration is achieved using a booster ring prior to injection into the storage ring.

Figure 2.1: Diagram showing the general layout of a modern synchrotron facility. The
Figure is reproduced from Diamond Light Source.

A storage ring is formed of a circular path where the electron beam travels within
high vacuum and is directed by bending magnets. Synchrotron light is produced at
bending magnets tangential to the circular path of the electrons. Insertion devices
are placed within the short straight sections between the bending magnets and, as
previously described, produce further collimated beams of synchrotron light. As
the electron beam travels, producing synchrotron light, energy is lost per revolution, given by \( \Delta E_e \):

\[
\Delta E_e = \frac{4\pi}{3} \frac{e^2}{m_e c^2} \left[ \frac{E}{m_e c^2} \right]^4
\]  

(2.1)

To maintain the energy of the electron beam a radio frequency (RF) cavity is used. RF cavities use a longitudinal electric field to accelerate electrons maintaining both the energy and bunching of the electrons. The nature of the RF cavity to oscillate through both accelerating and decelerating phases allows for, when synchronous to the bunch timing, "slow" electrons to receive a greater acceleration than "fast" electrons within the electron beam, illustrated in figure 2.2.

Figure 2.2: Illustration of the effect of an RF cavity to both accelerate and maintain the electron bunching within the electron beam of a storage ring. The Figure is reproduced from Synchrotron Radiation: Basics, Methods and Applications.

The bunching of the electrons is maintained via a stability condition that allows only those electrons with a phase within \( \pm 10\% \) of the RF cavity to remain stable. Those electrons which do not stay within a stability condition do not travel in a circular path and as such are lost from the storage ring. This results in the steady decay of the storage ring current. Usually synchrotrons operate in one of two modes: decay, where the beam is topped up after typically 12 hours to restore the beam current, or
continual top-up, which aims to maintain the storage ring current through the nearly continual addition of electrons into the storage ring.

**Figure 2.3:** Depiction of the dependence of the spectral distribution on the storage ring energy and critical energy of a bending magnet. The Figure is reproduced from Synchrotron Radiation: Basics, Methods and Applications.[16]

The properties of a synchrotron depend directly on the energy of the storage ring electron beam. In particular, the spectral distribution of the light produced by a synchrotron. Figure 2.3 illustrates the storage ring energy dependence on the spectral distribution produced from a bending magnet. Here the critical energy is marked for several storage ring energies. The critical energy is defined as the energy whereby the sum of radiative power is equal above and below this energy. The critical energy can be shifted to higher values for insertion devices. As such the facilities are built specialising in different regions of the UV to X-ray part of the electromagnetic spectrum.

The unique properties of a synchrotron: highly collimated, high intensity, pulsed time structure and the broad range of light produced, from UV to X-ray, allow for a unique set of experiments to be conducted exploring the structure of matter under reaction conditions. Experimental techniques span spectroscopies such as X-ray absorption and emission as well as UV and IR, along with scattering methods utilising diffraction and inelastic, small angle and total scattering techniques. Figure
2.4 illustrates the current techniques available at beam lines at DLS.

Figure 2.4: Diagram illustrating the range of experimental techniques performed at a modern synchrotron. Figure reproduced from Diamond Light Source.

2.2 X-ray Absorption Spectroscopy

The fundamental concept of X-ray absorption spectroscopy relates directly to the electronic and geometric structure of materials. The first observation of an absorption edge was reported by de Broglie, shortly followed by the first measurement of an X-ray absorption fine structure by Fricke. By considering the electronic structure of an atom one can consider the origin of an absorption edge.

An XAS spectrum represents the value of the absorption coefficient of a material dependent on the incident photon energy. In general the absorption coefficient of an element depends strongly on both its atomic number and the energy of the incident photon. The absorption coefficient, $\mu$, is shown in equation 2.2 as a function of density, $\rho$, atomic number, $Z$, atomic mass, $m_Z$ and $E$, the energy of the X-ray photon.

$$\mu \approx \frac{\rho Z^4}{m_Z E^3} \quad (2.2)$$
If a neutral atom contains Z protons, it has Z electrons. Z is defined as the atomic number of an atom. According to the current knowledge of the electronic structure of atoms described by the Schrödinger equation, electrons occupy distinct orbitals. The orbitals closest to the atomic centre, the nucleus, require a higher amount of energy to liberate an electron from, defined as the binding energy. Table 2.1 gives the atomic levels present within the standard definition of orbitals and is related directly the subshell notation. This is the origin of the naming convention for the various XAS edges: K, L₁, L₂, L₃ and onwards. Where the K edge relates to the absorption edge arising from the increased probability of the absorption of an X-ray occurring with energy relating to the binding energy of a 1s electron.

**Table 2.1:** Table of the atomic levels present within the standard subshell notation of electronic orbitals.

<table>
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<th>Subshell</th>
<th>Orbitals (n l m)</th>
<th>Atomic Level</th>
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<tr>
<td>K</td>
<td>1 0 0</td>
<td>1s₁/₂</td>
</tr>
<tr>
<td>L₁</td>
<td>(2 0 0)</td>
<td>2s₁/₂</td>
</tr>
<tr>
<td>L₂</td>
<td>(2 1 0)</td>
<td>2p₁/₂</td>
</tr>
<tr>
<td>L₃</td>
<td>(2 1 1), (2 1 -1)</td>
<td>2p₃/₂</td>
</tr>
<tr>
<td>M₁</td>
<td>(3 0 0)</td>
<td>3s₁/₂</td>
</tr>
<tr>
<td>M₂</td>
<td>(3 1 0)</td>
<td>3p₁/₂</td>
</tr>
<tr>
<td>M₃</td>
<td>(3 1 1), (3 1 -1)</td>
<td>3p₃/₂</td>
</tr>
<tr>
<td>M₄</td>
<td>(3 2 1), (3 2 -1)</td>
<td>3d₃/₂</td>
</tr>
<tr>
<td>M₅</td>
<td>(3 2 2), (3 2 -2), (3 2 0)</td>
<td>3d₅/₂</td>
</tr>
<tr>
<td>N₁</td>
<td>(4 0 0)</td>
<td>4s₁/₂</td>
</tr>
<tr>
<td>N₂</td>
<td>(4 1 0)</td>
<td>4p₁/₂</td>
</tr>
<tr>
<td>N₃</td>
<td>(4 1 1), (4 1 -1)</td>
<td>4p₃/₂</td>
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<td>N₄</td>
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<tr>
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<td>(4 3 3), (4 3 1), (4 3 -1), (4 3 -3)</td>
<td>4f₇/₂</td>
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When the energy of the incident photon beam is equal to or greater than the binding energy of a core-level electron the absorption results in the excitation of an electron
into an unoccupied or continuum state. This resonance greatly increases the absorption coefficient of the material being probed and results in an absorption ‘edge’ in an XAS spectrum. The transition of an excited electron to higher states is largely governed by the dipole selection rule, $\Delta l = \pm 1$, however quadrupole transitions can also occur and are particularly noticeable in systems with tetrahedral symmetry or those exhibiting Jahn-Teller effects distorting octahedral symmetry. Typically quadrupole features are most prominent in the pre-edge region of an XAS spectrum.

The structure of an XAS spectrum is dependent on the local coordination geometry surrounding the specific element type being probed. An XAS spectrum can be divided into two distinct regions, X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). Typically the XANES region encompasses pre-edge features as well as the few tens of eV above the absorption edge. The EXAFS region extends from tens of eV above the absorption edge onwards. The features present in the XANES relate to the availability of unoccupied states, valance states\[21\]. Whilst the oscillations in the EXAFS relate to scattering of a photo-electron and interference with itself resulting in a modulation of the absorption coefficient, either constructive or destructive interference.

Figure 2.5 depicts the absorption of a photon by an absorbing atom, shown in blue. The resulting photo-electron has the possibility of scattering off the electrons of a nearby atom, red, and return to the absorber atom. Since the absorption depends on the availability of an electronic state with appropriate energy and momentum, the absorption coefficient is altered by the presence of the photo-electron which was scattered back from a neighbouring atom. The difference between the resulting absorption spectrum from an isolated atom, blue, and that arising when another atom is present for scattering to occur, red, is given as a trace of the absorption probability beside. Here it is clear that there is a modulation of the absorption spectrum due to the presence of locally coordinated atoms arising from the interference of a
photo-electron with itself.

**Figure 2.5:** Illustrating of the origin of EXAFS from the interference of a scattered photo-electron with itself. Figure reproduced from Introduction to EXAFS

In the EXAFS region of an XAS spectrum the feature of interest is the energy dependant oscillations in the absorption coefficient, \( \mu(E) \). This can be extracted by:

\[
\mu(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)} \tag{2.3}
\]

where \( \mu_0(E) \) is defined as the absorption due to an isolated atom and \( \Delta \mu_0(E_0) \) is the edge step required to normalise the spectrum to 1 absorption event.

Typically when representing EXAFS, k space is used instead of energy dependence. This is due to the nature of EXAFS to be one of an interference effect and as such is treated in terms of the photo-electron wavenumber, \( k \). By considering the quantum mechanical representation of energy being related to the mass and momentum of the ejected electron it is possible to arrive at a representation of \( k \) in terms of the energy above the absorption edge, \( E - E_0 \) and the mass of the photo-electron, \( m_e \):

\[
k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}} \tag{2.4}
\]
Figure 2.6: Figures illustrating the form of an XAS spectrum collected in transmission geometry of a Pt foil standard sample. Figure A gives the raw data whilst B shows the normalised and flattened spectrum along with the fitted background relating to the absorption from an isolated Zn atom. Figures C and D give the extracted K and R space EXAFS plots respectively.

Example Figures showing the raw data, normalised and flattened, K space and R space data are shown in Figure 2.6. The theory of EXAFS was developed by Stern and considers EXAFS to be fundamentally a local structure phenomenon, with the scattering of an ejected photo-electron within the local structure surrounding and absorbing atom to being the cause of the oscillations in the EXAFS region of an XAS spectrum. The EXAFS equation derived by Lytle, Stern and Sayers describes the contribution of each feasible scattering path to the total signal:\[\chi(k) = S_o^2 \sum_i N_i \frac{f_i(k)}{kR_i^2} e^{-\frac{2R_i}{\lambda(k)}} e^{-2k^2\sigma_i^2} \sin(2kR_i + \delta_i(k))\] (2.5)
Consideration of different parts of the EXAFS equation gives an understanding of
the reason why EXAFS is fundamentally a local structure probe. In particular the
terms:

\[ \frac{f_i(k)}{k R_i^2} \quad \text{and} \quad e^{-2R_i/\lambda(k)} \quad (2.6) \]

Here the inverse dependence explicitly on the length of the scattering path squared,
\( R_i^{-2} \), affects directly the amplitude of the contribution from a particular scattering
to the total EXAFS signal, is shown in the first term of 2.6. Whilst the exponential
decay of the signal depending on the length of the scattering path and the mean
free path of the photo-electron, \( \lambda(k) \), also directly affects the amplitude of the con-
tribution from a particular scattering path, shown by the second term highlighted
in 2.6. To contribute to the EXAFS, a photo-electron must scatter elastically, the
\( \lambda(k) \) term accounts for all forms of interactions whereby there is a loss of energy
from the photo-electron, be it by inelastic scattering or through the excitation of
a valence electron in a scattering atom. This term also accounts for the core-hole
lifetime resulting in a change in the state of the absorbing atom, either through,
for example, the ejection of an Auger electron or through fluorescence with both
processes resulting in a higher orbital electron filling the core hole created by the
absorption of an X-ray photon. A change in state of the absorbing atom results in a
different overlap between the initial state, when the photo-electron was ejected and
final state when the photo-electron returns to the absorbing atom after the scattering
from neighbouring atoms.

Other terms that effect the amplitude of the EXAFS equation relate directly to the
number of neighbouring scattering atoms following a particular scattering path.
This is expressed by a multiplicative term, \( N_i \), describing the degeneracy of a scat-
tering path, equivalent to the coordination number for a single scattering path.

The $S^2$ term at the front of the EXAFS equation is described as the amplitude reduction factor and takes into account the incomplete overlap of the initial and final states of the absorbing atom. This is due to the adjustment of the orbitals caused by the presence of a core-hole resulting in a reduced screening of the positive charge from the nucleus of an atom. Fermi’s Golden Rule states that the probability of an event occurring depends on the similarity of the initial and final states, therefore a difference between the initial and final states will reduce the probability of an event occurring. The modelling of the amplitude reduction factor to account for this effect is typically performed using a suitable known standard material and usually has a value between 0.7 and 1.0\cite{24,25}. However the amplitude reduction factor can also vary depending upon the experimental set up used such as harmonics and detector non-linearity as well as sample issues such as self-absorption and sample inhomogeneity.

When the thermal and static disordering in a material are small, the cumulant expansion of the EXAFS equation can be used to model the broadening of the distribution of the inter-atomic distances. In the limiting case where all disorder is normal (i.e. higher order terms are zero), this is done through consideration of the mean square radial displacement signified by $\sigma^2$, the first order approximation of the cumulant expansion is given by;

$$e^{-2k^2\sigma_i^2} \quad (2.7)$$

Phase shifts, $\delta(k)$, and the proportionality constant, $f(k)$, result from the scattering of a photo-electron with a neighbouring atom and, as such, are element dependant. The proportionality constant in simplistic terms relates to the probability of scattering elastically off a neighbouring atom as well as other geometric effects. The phase
shift can be due to several effects. In particular, the interaction between the photo-electron and the potential of an atom, slowing down when exiting the potential of an atom and speeding up when entering the potential of an atom. Often, such as in the FEFF programs \cite{26}, which are used to calculate the phase shifts, the potential of an atom is treated in the muffin tin approximation, whereby each potential field is treated as a screened potential experienced by the photo-electron and is spherically symmetric centred on a given atom nucleus.

XAS spectra can be measured in various methods: transmission geometry \cite{21}, fluorescence detection (including high energy resolution) \cite{21,27-29}, electron yield (partial and total) \cite{30,31} or using the less well known new technique of high energy resolution off-resonant spectroscopy \cite{32,33}. The work presented herein has been collected in either transmission geometry or using high energy resolution fluorescence detection method.

### 2.2.1 Transmission XAS

Transmission geometry is the simplest measurement method for acquiring an XAS spectrum. Transmission geometry allows for a direct measurement of the absorption coefficient, whereby the absorption coefficient can be shown to be calculated directly from the intensity of the X-ray beam prior, \( I_0 \), and after the sample, \( I_t \):

\[
\mu = ln \left( \frac{I_0}{I_t} \right)
\]  

(2.8)

Ion chambers are commonly used for this purpose. A typical ion chamber is formed from a gas filled parallel plate capacitor with a high voltage applied across it. The ionisation of the gas induced by the X-ray beam result in a cascade of charged particles which can then be collected and the signal suitably amplified to allow for a measurable current to be formed. When used for both upstream and downstream measurements of the X-ray beam intensity, this geometry forms the most common
measurement approach, the transmission geometry. An illustration of a transmission geometry beam line set up (with the option of fluorescence detection) is shown in Figure 2.7.

A typical XAS measurement performed in transmission geometry requires the use of a monochromator to provide a variable energy photon beam and is collected in either step scan mode, where each energy of the XAS spectrum is measured sequentially in steps, or using an oscillating monochromator which is motor driven through a single movement allowing for rapid data collection. A typical beamline uses a double bounce monochromator formed from usually Si(111), Si(220) or Si(311) crystals, depending on the energy range being probed. The double bounce monochromators are often formed on a single channel cut crystal thus keeping both diffraction faces in perfect rotational uniformity whilst also deflecting the X-ray onto the same plane, though vertically displaced, as to when entering. Focusing mirrors are used to create a beam with tuneable size on the sample.Whilst harmonic rejection mirrors are used to filter out higher order diffraction harmonics to achieve a beam of desired energy. After the sample it is common for there to be reference channel whereby the absorption spectra of a suitable reference foil can be collected simultaneously to allow for the alignment of spectra in-case there is variation in the energy calibration.

Figure 2.7: Illustrating of the key components forming a XAS beam line with measurement performed in transmission geometry or through standard resolution fluorescence detection mode.
2.2.2 High Energy Resolution Fluorescence Detection X-ray Absorption Near Edge Structure

Fluorescence detection methods for the collection of XAS spectra rely upon the relaxation of an excited atom. Singly ionised or excited states with a core hole may decay via one of two processes, the Auger process or through X-ray fluorescence. The Auger process involves the filling of a core-hole with an accompanied emission of an electron as the release of energy. Auger electrons may be detected above the sample surface as a method of acquiring a surface sensitive XAS spectrum at variable probe depths into a sample.

Figure 2.8: Diagram depicting the possible X-ray fluorescence emission lines, image is reproduced from X-ray data booklet.[25]

X-ray fluorescence related to the filling of a core-hole with a higher orbital electron and subsequent release of the energy difference as an X-ray photon is a much more commonly used method for measuring an XAS spectrum. Figure 2.8 depicts the E1 fluorescence lines for the decay of an atom with a core level hole. Here it is clearly shown that there are several decay channels through which any core hole may be filled. Measurements using X-ray fluorescence is commonly used for measurements
on thin films or highly diluted elements, such as when measuring small amounts of a dispersed element on a support matrix or in solution.

The emitted fluorescence can then be measured as a function of the incident X-ray beam energy. Energy discriminating fluorescence detectors then allow for the emission, within a chosen energy range, from the element being probed to be counted. Typically these are germanium solid state detectors. Due to the fact that these type of detectors must count and analyze each photon individually they have a limitation on the counting rate. Care must be taken not to saturate a detector. The intensity of the fluorescence yield, $I_f$, can then be related to the absorption coefficient:

$$\mu \propto \frac{I_f}{I_0}$$

High energy resolution fluorescence detection XAS is acquired using a beamline such as I20-scanning at DLS. A schematic for this beamline is given in Figure 2.9. Here the high energy resolution is achieved by the use of a 4 bounce monochromator to provide a highly defined incident beam energy along with an X-ray emission spectrometer. The spectrometer is formed of analyzing crystals which spread spatially the fluorescence photons through Bragg diffraction and a moveable fluorescence detector. This allows for the intensity of a particular spectral line to be measured as a function of the incident photon energy on the sample, as such a high energy resolution XAS spectrum can be acquired. The geometry of this type of spectrometer, Johann, uses bent analyzer crystals to diffract and focus the photons of a particular energy onto the counting fluorescence detector. Typically several analyzer crystals are used to increase the solid angle and as such the efficiency of the spectrometer.
2.2.3 Limitations of XAS

XAS methods provide a detailed insight into the local structural coordination chemistry surrounding a particular element in a material. XAS gives information on both the electronic state of an absorbing atom and its geometric coordination environment. Therefore XAS can be seen as a powerful technique for resolving the local structure of an absorbing element. There are several limitations of XAS methods:

- XAS techniques probe the entire sample volume in the X-ray beam. This leads to XAS being a spatially averaged representation of all components within a sample.

- EXAFS equation results in determination of coordination numbers with high accuracy to be difficult. This is due to the correlation with several parameters in a linear fashion. The amplitude of the EXAFS is directly related to the sigma squared, amplitude reduction and on higher order cumulant expansions when the Debye-Waller approximation does not hold.

- EXAFS can be seen to be fundamentally limited to being a local structure probe. This is due the amplitude of the EXAFS equation being dependant on inverse square of the radius.

- resolution on the refined bond distances is limited. The maximum resolution of
scattering distances is highly dependant on the maximum useable k range of the EXAFS. $\Delta R \geq \frac{\pi}{2\Delta k}$

- Scattering atoms with close atomic number (C,N,O) cannot be distinguished accurately due to the similarity in phase functions. However atoms with differing phase functions at the same distance can be accurately separated

Whilst XAS methods are fundamentally limited to being local structure probes, they have often been combined with other techniques. In particular X-ray scattering methods, XRD, SAXS and WAXS have often been combined to provide the long range structural information which is not possible to be obtained from XAS.

2.3 X-ray Scattering Techniques

The study of the structure of crystals was largely begun in the early 17th Century with the study of snowflakes. Kepler hypothesised that the hexagonal symmetry of snowflakes was a result of the regular packing of spherical water particles. Whilst Hauy discovered that the face of a crystal can be described by the stacking of regular blocks of the same size and shape. This leads to the notation that is still used in describing crystal planes. In mid 19th Century Miller described each face with a set of 3 integers, Miller Indices, which built upon the work of Hauy by describing crystals as a regular three-dimensional packing of atoms, or molecules, into a unit cell which is repeated along three principle directions. With the discovery of X-rays by Röntgen in 1895 the study of crystal symmetry using diffraction techniques did not take long to take hold.

2.3.1 X-ray Diffraction

Crystallographic studies of materials have long been used to understand the long range structure of materials. In particular, the crystal structure of solids. The crystalline nature of materials, when interacting with an incident X-ray or neutron beam, results in the diffraction into specific well defined angular positions. The measure-
ment of the diffraction angles using highly intense well defined energy radiation allows for the crystalline structure of a material to be established.

The scattering of X-rays by atoms is largely due to their interaction with the electrons. Whilst X-ray diffraction fundamentally arises from the interaction of X-ray photons with the electrons of an atom, the electron density within bonds is not enough to be observed. X-ray diffraction is an elastic scattering process, meaning that photons are scattered without the loss of energy. In Thomson scattering, a single electron is excited by an incident X-ray photon. The release of energy through the emittance of a photon with the same energy results in a spherical wave, the location of the photon is not known until it is measured and can be treated as a wave. As such the scattering of photons by electrons leads to the production of secondary spherical waves emanating from the electron. In a regular array of atoms, the interaction between the produced secondary spherical waves leads to an interference pattern. Whilst most directions interfere destructively, in some specific directions there is constructive interference. This can be described using Bragg’s law. This stipulates that if the scatterers are arranged symmetrically with a separation of \( d \), constructive interference will occur when the path difference between two scattered photons is equal to an integer number of wavelengths of the incident photons, resulting in the photons being deflected by an angle of \( 2\theta \).

\[
n \lambda = 2dsin(\theta)
\]  

(2.10)

In single crystal diffraction this leads to sharp diffraction spots being observed. However, in the case of powder diffraction, rings are observed due to the random orientation of powder particles within the X-ray beam, shown in Figure 2.10A. Spherical integration of the diffraction rings allows for a 1D diffraction pattern to be acquired, shown in Figure 2.10B. The common assumption made with powder diffraction is that the particles are arranged with random orientation. However, in
some systems preferential orientation can exist, such as in magnetic materials. Modern analysis programs can be used to extract the degree of preferential orientation should it exist.

Figure 2.10: Figures illustrating powder diffraction rings obtained on a CeO$_2$ sample and the spherically integrated 1D diffraction pattern in A and B respectively.

The difference in the intensity of the diffraction peaks observed is due to the relative concentration of atoms in a diffraction plane and the type of atoms present. Those with larger atomic number, and as such greater electron density due to the number of electrons, scatter X-rays more than lighter atoms. The structure factor, $F_{hkl}$ gives the intensity of the diffraction peaks, for a centrosymmetric perfect crystal this is given as:

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{-2\pi i (hx_j + ky_j + lz_j)}$$ \hspace{1cm} (2.11)

where the sum over all atoms in the Miller plane denoted by (hkl), $j$, in the unit cell with positional coordinates, $x_j$, $y_j$ and $z_j$ and with scattering factor given by $f_j$ for the jth atom. $F_{hkl}$ is the vector sum of the waves for all atoms in the miller plane defined by (hkl). Considering a simple 3-dimensional system of an FCC monoelemental crystal with atoms at positions $x_j$, $y_j$, $z_j = (0,0,0)$, (0.5, 0.5, 0), (0.5, 0,
(0.5) and (0, 0.5, 0.5) it is possible to reduce the structure factor, $F_{hkl}$, to;

$$F_{hkl} = f \left[ e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)} \right] = f \left[ 1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l} \right]$$  \hspace{1cm} (2.12)

This directly necessitates that $h, k$ and $l$ are all even or all odd for the reflection to be visible for a given Miller plane as all other combinations will result in a structure factor equal to 0. The intensity of a diffraction peak is proportional to the square of the structure factor. Correction for the observed intensities can be made such as for the polarisation of the incident X-ray beam, $p(\theta)$, and the correction for the angular dependent absorption, $A(\theta)$. The angular dependence on the structure factor results in the higher values of $2\theta$ reflections having weaker diffraction.

$$I_{hkl} = KL(\theta)p(\theta)A(\theta)m|F_{hkl}|^2$$  \hspace{1cm} (2.13)

where $K$ is a material constant and $m$ is the multiplicity correction. This form of the structure factor is only applicable for systems with long range order and relates only to the intensity and phase of a beam diffracted by a Miller plane within a crystal. Another form of structure function $S(Q)$ is used for disorder systems such as for the study of glasses, liquids and nanocrystalline materials which can exhibit large defects. These studies are often carried out using the Fourier transform of the $S(Q)$ to a real space pair distribution function.

### 2.3.2 X-ray Total Scattering and Pair Distribution Function

Pair distribution function analysis allows for a study of the local distortions and defect structures within complex materials. Its inherent ability to provide real space structural information on the distribution of atom pair distances gives a unique view into the challenging structural distortions of materials. In particular, pair distribution function (PDF) analysis has been used here to probe the local distortions...
present within otherwise highly crystalline materials\textsuperscript{46–48}.

In the study of complex materials it is often found to be that the local deviations and defects from the long range structure can account for the behaviour and functionality which was otherwise unexplained. Whilst Bragg’s law succinctly explains the diffraction arising from the interaction of photons, or neutrons, with the repeating lattice structure of crystalline materials. PDF methods yield information on the distribution of atom pair distances within a material.

\[
\rho(r) = \rho_0 g(r) = \frac{1}{4\pi N r^2} \sum_\nu \sum_\upsilon \delta(r - r_{\nu\upsilon})
\]

Equation 2.14 gives the atomic density function, \( \rho(r) \), in terms of the number density, \( \rho_0 \), and the atomic pair distribution function (PDF), \( g(r) \). Here the PDF is a continuous distribution of the sum of the distances separating any two atoms, denoted as \( \nu \) and \( \upsilon \). Often PDFs, an example of which is shown in 2.11, are given in the form of the reduced radial distribution function, \( G(r) \);

\[
G(r) = 4\pi r (\rho(r) - \rho_0)
\]

However, it is important to note that there are several other formalisms for the pair distribution function available within the literature\textsuperscript{49}. The form described here is commonly used for the study of disordered crystalline solids and is the form that will be used herein when describing the work undertaken on ceria and ceria coated systems.
Figure 2.11: Example \( G(r) \) obtained on a ceria sample. The range between \( R \) of 1.5 and 11 Å is chosen here to illustrate the usefulness of the PDF method to the local structural characterisation of materials.

Before analysis of data is possible, it is necessary to consider where the intensity signal originates from in any measurement. The total scattered intensity, \( I_T \) of an X-ray beam is formed of several contributions;

\[
I_T = I_C + I_{IC} + I_{MC} + I_{BG}
\]  

(2.16)

where \( I_C \) and \( I_{IC} \) relate to the coherent and incoherent scattering intensities respectively. \( I_{MC} \) is due to multiple scattering and \( I_{BG} \) is the total background intensity. The incoherent scattering is a result of Compton scattering. Compton scattering is as a result of a photon interacting with a charged particle, in this case an electron. The effect is an energy transfer from the photon to the electron causing an increase in the wavelength of the photon. Inverse Compton scattering can occur when an electron transfers energy to a photon, so decreasing the photon wavelength. The coherent scattering term is due to the interaction of an X-ray photon with an atom that results in no change in the energy of the photon, elastic scattering.

Measurement of the total intensity is straightforward, only requiring an incident
beam on the sample and, in the case of X-rays, a downstream 2D image plate. Correction for the background signal can be completed through adequate masking such as for any object between the sample and detector, for instance the beam stop and sample environment shadowing, and hot pixels on the detector. Measurement of an empty beam line and empty sample environment are also used to correct for the contributions that do not arise from the sample to the intensity signal. Explicit measurement of suitable backgrounds is required in total scattering experiments as unlike in diffraction when the background is removed by fitting a curve to the baseline of the diffraction peaks, the intensity between the Bragg reflection, the diffuse scattering, contain information on the local structure.

Whilst the multiple scattering term is largely due to scattering within the sample, it can also arise from double scattering involving both the sample and container. As such the $I_{MS}$ term must be minimised when undertaking any measurement.

The scattering amplitude originating from a sample can be described by considering the scattering of a beam with a set of $N$ atoms with spatial coordinates given by $R_j$ for the jth atom. The diffraction vector can be given from considering the wavevector of the incoming and scattered wave;

$$Q = k_{init} - k_{final}$$

(2.17)

The amplitude and phase of the scattered wave is given by the vector sum of all the atoms such that;

$$\Psi(Q) = \sum_{j=1}^{N} f_j e^{-iQ.R_j}$$

(2.18)

where the scattering amplitude of atom j is given by $f_j$. Multiplication of $\Psi(Q)$ with its complex conjugate, and in the simple case where all atoms are of the same
form, gives the scattered intensity of the coherent signal;

\[ I(Q) = \Psi(Q) \cdot \Psi^*(Q) = f^2 \sum_{j,k=1}^{N} e^{-iQ(R_j - R_k)} \]  

(2.19)

The structure function is then defined as the normalised intensity given by;

\[ S(Q) = \frac{1}{N} \sum_{j,k=1}^{N} e^{-iQ(R_j - R_k)} \]  

(2.20)

For an isotropic material, such as in the study of liquids or powders, the scattering factor can be further simplified such that in the limitation of elastic scattering, \( \lambda_{\text{initial}} = \lambda_{\text{final}} \), the magnitude of the diffraction vector becomes;

\[ Q = |Q| = \frac{4\pi \sin(\theta)}{\lambda} \]  

(2.21)

This yields the Debye scattering equation\(^{50}\),

\[ S(Q) = \frac{1}{N} \sum_{j,k=1}^{N} \frac{\sin(qr_{jk})}{qr_{jk}} \]  

(2.22)

where \( r_{jk} \) is the magnitude of the difference in positional coordinates of the jth and kth atoms. Figure 2.12A and 2.12B give examples of experimentally acquired I(Q) and S(Q) respectively for a high surface area ceria sample.

Up to this point the scattering from the elastic, coherent contribution, has been described. However, in the total scattering method the total scattered intensity of the beam includes, as previously stated, contributions from the inelastic and sample multiple scattering. Another factor to be considered is that atoms are not stationary during a measurement period. Approximation of the motion of atoms due to vibrations is achieved through Debye-Waller factors (DW)\(^{50,52}\). Vibrations arise from thermal motion as well as from zero-point quantum vibrations. The Debye-Waller
approximation is an expression of the lattice vibrations as a Gaussian function by which the distribution in atom positions around a crystallographic site over a period of time is modelled by;

$$\langle e^{iQR} \rangle \approx e^{iQ(\langle R \rangle)} e^{-\frac{1}{2}Q^2\langle u^2 \rangle}$$  \hspace{1cm} (2.23)

Here $\langle \ldots \rangle$ refers to the averaging over time, with $W$ given as the DW factor. The effect on the structure function is a decrease in the intensity of the Bragg peaks whilst the sharpness is maintained. The 'lost' intensity is instead spread over the entirety of $Q$ and is termed diffuse scattering. The other effect of the DW factor, due to its dependence on $Q$, is to decrease the intensity of Bragg peaks at high $Q$ significantly more than at low $Q$. Thus the signal at high $Q$ is almost entirely formed from the diffuse scattering. In powder measurements this forms a continuous background to the Bragg peaks and is usually discarded in diffraction methods using a fitted function.

The Fourier transform of the total scattering function yields the atomic pair distribution function, and the reduced form from equation 2.15. The PDF allows for a
direct measurement of the relative positions of atoms within a material. In the case of powders it is thus possible to determine the crystalline structure of a complex material.

\[
G(r) = 4\pi r \rho_0 (g(r) - 1) = \frac{2}{\pi} \int_0^\infty Q(S(Q) - 1) \sin(Qr) dQ
\]  

(2.24)

In practical terms, the measurement in \(Q\) is finite. The effect of this is to cause ripples and broadening of the pair distribution peaks. Therefore it is required to collect an adequate \(Q\) range to accurately represent the sample that is being studied to minimise the effect of termination ripples on the PDF. The effect of a maximum \(Q\), \(Q_{\text{max}}\), on the the Fourier transform to \(G(r)\) is shown in Figure 2.13 for calculated \(G(r)\)s relating to Au metal. For the purpose of clear comparison the value of \(\langle \langle u^2 \rangle \rangle\) has been set to 0.004 Å\(^2\) for all atoms. To perform the calculations PDFGui\(^{55}\) has been used. In modelling of PDF termination ripples are explicitly accounted for by the convolution of the \(G(r)\) with a window function.

**Figure 2.13:** Demonstration of the affect of \(Q_{\text{max}}\) on the Fourier transform to \(G(r)\) produced from the total scattering function. The FCC structure of Au has been used with a set value of \(\langle \langle u^2 \rangle \rangle\) of 0.004Å\(^2\) to show the broadening an artefacts introduced into the PDF by a finite \(Q\) measurement.
2.3.3 Limitations of X-ray Scattering

X-ray scattering methods allow for the detailed determination of the long range structure through conventional analysis of the Bragg diffraction. Furthermore, when X-ray scattering is collected in a total scattering approach, it is possible to extract detailed information on the local structural information through pair distribution function analysis. However there are several limitations on X-ray scattering approaches:

- atomic pair distribution function contains the interatomic distances between all atoms in the sample. As such the separation of phases information in a multicomponent system can be challenging to accomplish. One approach is through differential pair distribution function analysis, this is discussed in chapter 5 when considering ceria alumina supported catalysts.

- increasing radius, the inter-atomic distances between different coordination shells becomes convoluted. As such in the pair distribution function analysis a high $Q_{\text{max}}$ for the FT to real space is required to be able to accurately resolve the different coordination spheres.

- XRD methods are limited to being long range structure probes. XRD arises from the Bragg scattering within a crystalline material. As such local deviations are not resolved in XRD. Furthermore, where ordered defects occur these can result in averaging that does not accurately resemble the sample.

- X-ray scattering provides no direct measurement of the oxidation state of elements present in the sample, this can only be inferred from the structural stoichiometry.

The limitations of X-ray scattering methods can largely be overcome by considering other experimental techniques, such as XAS methods previously described. The work described in this thesis will be predominantly revolve around the combined interpretation in situ of XAS and X-ray scattering experiments. However, further
lab based and *ex situ* characterisation has also been undertaken to provide greater understanding of the materials and reactions that are studied here.
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Chapter 3

Structural Characterisation of PtZn Based Materials Under Reaction with Formic Acid

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3.6 Chapter Conclusion and Discussion . . . . . . . . . . . . . 153
The aim of this chapter is to investigate SBA-15 supported PtZn catalysts to determine the structural changes which occur on exposure to formic acid. Whilst no direct data has been collected following emitted gases, in situ XAS studies have been used to determine the structure of the SBA-15 supported mono-metallic and bimetallic PtZn systems. Novel analysis methods of the results obtained from the in situ XAS experiments using dose respose curves is developed to provide a unique insight into these materials. Furthermore, ex situ characterisation has been used to probe the structure of the initial samples using X-ray scattering methods. The structure of colloidal bimetallic PtZn particle is compared to the SBA-15 supported catalysts to understand the effect of surfactants in stabilising the metallic state and to promote a core shell structuring. Finally Quasi in situ XAS studies have been performed following the synthesis of silica supported Pt nano-particles using formic acid as a vapour phase reducing agent.

### 3.1 Introduction

Due to the concerns regarding global warming through the use of fossil fuels, there is significant drive towards using hydrogen as a sustainable energy source. The storage of hydrogen in chemical bonds is seen as a potential solution towards the storage problems of hydrogen. Formic acid is often discussed for the role a hydrogen storage material for a future hydrogen based energy production due to its relatively high volumetric density of hydrogen and the ability to modern catalytic materials towards dehydrogenation reactions for the on demand production of hydrogen\(^1\).\(^2\)

The decomposition of formic acid is of interest for the production of hydrogen. However, there are two competing processes:

\[
\text{HCOOH} \rightarrow H_2 + CO_2 \tag{3.1}
\]
Nano-particles have long been studied for their catalytic properties. The increased surface area available on nano-particles and single site catalysts has been demonstrated to improve the efficiency and in some cases selectivity of catalytic materials. Single site Zn(II) species have been previously synthesised using ion exchange with Al in zeolites to yield Zn bound to the surface of the zeolite wall. The result of this is to replace the Al Brønsted acid sites and form Lewis acid sites within the materials.

The local structure of the Zn site and method of binding to the surface of zeolites and silicates has been shown to form a tetrahedral coordination environment with oxygen, akin the the first coordination sphere of ZnO. In particular the work by Mei et al has shown that the Zn can bind to the channel walls of SBA-15 silica and be subsequently capped with Ti to produce a bimetallic single site catalyst structure. In addition to Zn, Pt is often used in catalysis to enhance the selectivity or activity of a reaction. Bimetallic PtZn catalysts have shown activity towards dehydrogenation and hydrogenation reactions and therefore are suggested to be a suitable material for the dehydrogenation of formic acid. Furthermore, it has been shown that the interface between Pt and Zn is catalytically active in the absence of a true bimetallic alloy.

Previous work on AgNi bimetallic nano-particles synthesised and supported in SBA-15 have shown to produce core-shell structures in the absence of any surfactants. The 2D nature of the SBA-15 channels acts to both limit the particle size, the maximum pore diameter is approximate 6nm, and to encourage the formation of phase segregated AgNi particles. This has also been shown in other transition
metal bimetallic systems\textsuperscript{23,25}. Therefore a similar synthesis procedure has been applied here with Pt and Zn to form either core-shell nano-particles or PtZn in close proximity to achieve a catalytically active material for the decomposition of formic acid.

To conduct studies on the structure of the as-synthesis SBA-15 supported PtZn materials various synchrotron based techniques have been applied. \textit{Ex situ} SAXS was used to determine the pore structure of the SBA-15, whilst \textit{ex situ} WAXS has been employed to determine the crystalline phases present relating to the Pt and Zn within the samples. XAS methods have been used here to both characterise the initial as-synthesised materials and to follow the structural changes upon exposure to formic acid. Here the results are presented for the \textit{ex situ} materials characterisation followed by the \textit{in situ} XAS studies on both the Pt $L_3$ edge and Zn $K$ edge.
3.2 *Ex situ* Materials Characterisation

3.2.1 Sample Synthesis

The SBA-15 supported 5wt% PtZn materials were synthesised by Elizabeth Raine, University of Oxford, using the following method. The nano-particles were synthesized without the use of surfactants using an incipient wetness precipitation technique. 2 ml pre-prepared platinum nitrate, zinc nitrate and ethanol solution was ground into 500 mg of SBA-15 using a pestle and mortar. After 10 minutes of grinding the powder was left to fully dry in air for at least 3 hours. The fully dried powder was calcined at 400°C with a ramp rate of 2°C min⁻¹ under nitrogen and then reduced at the same temperature under 5%H₂/Ar for 4 hours. The samples were then cooled to room temperature and ground for testing.

3.2.2 Transmission Electron Microscopy

The presence of Pt and Zn within the SBA-15 channels and the relative dispersion of metal was investigated with transmission electron microscopy (TEM). TEM was performed using a JEOL 3000F transmission electron microscope operated at 300 kV. TEM specimens were prepared by dispersing the dry catalyst powder in ethanol using sonication then pipetting 5µl of the sample dispersion onto holey-carbon coated copper grids.

The TEM images are shown in Figure [3.1](#). The empty SBA-15 is shown in Figure A and clearly shows the channelled nature of the SBA-15. B illustrates the Zn/SBA – 15 sample, no particles are observed to have formed within the SBA-15 channels. Figures C-F represent the Pt containing samples in increasing Pt content, each of which show evidence for the formation of nano-particles within the channels of the SBA-15.
3.2.3 Small Angle X-ray Scattering

3.2.3.1 Experimental Data Collection

Small angle x-ray scattering (SAXS) was collected at beamline I22 of the Diamond Light Source. Data collection was performed at 18 keV with a refined sample to detector distance of 9.8 m calibrated using a silicon standard material. Scans were performed *ex situ* with samples loaded into 2 mm polycarbonate capillaries. Total data acquisition time per sample of 1 s. An empty capillary was used to subtract the background from the data. A bare SBA-15 sample was also collected for comparative purposes.

A comparison of the SAXS data collected between 0.04 and 0.23 Å⁻¹ is shown Figure [3.2]. Bragg reflections emanating from the stacking of the SBA-15 channels in an hexagonal pattern can be seen. All samples show the hexagonal SBA-15 structure when compared to the as received SBA-15 sample, however, there can be seen to be peak splitting most prominently in the (110) and (200) reflections.

![SAXS data comparison](image.png)

**Figure 3.2:** SAXS shown in Q space collected on *ex situ* capillaries at beamline I22 of the diamond light source. Shown in a stacked plot are the as received SBA-15, Pt/SBA-15, Pt₈Zn₂/SBA-15, Pt₅Zn₅/SBA-15, Pt₈Zn₂/SBA-15 and Zn/SBA-15 samples from bottom to top. Here the Bragg reflections are indexed relating to the stacking of the SBA-15 structure.
3.2.3.2 SAXS Peak Fitting

Peak fitting has been conducted on the (200) reflection to extract the related lattice parameter of the SBA-15 stacking. Due to the peak being a relatively strong reflection and exhibiting the largest splitting a multiple peak fitting method could be undertaken accurately. Determination of lattice parameter, $a$, is achieved through consideration of the interplanar spacing, $d$, of an hexagonal lattice structure as shown in equation (3.3).

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (3.3)

Assuming infinite pores along the $c$ direction the final term can be dropped from equation (3.3). With rearrangement and consideration of the conversion between $d$ and $Q$ spaces it is possible to arrive at the form shown in equation (3.4).

$$a = \frac{4\pi\sqrt{h^2 + hk + k^2}}{\sqrt{3}Q}$$  \hspace{1cm} (3.4)

Thus for extraction of the lattice parameter, $a$, for a 2D hexagonal stacking of pores within the SBA-15 structure derived from the (200) Bragg reflection equation (3.5) is then employed, where $Q_{200}$ is the position of the (200) Bragg reflection in $Q$ space.

$$a = \frac{8\pi}{\sqrt{3}Q_{200}}$$  \hspace{1cm} (3.5)

With knowledge of the pore radius, $R_p$, it is also possible to extract the wall thickness, $\omega$, of the SBA 15 using (3.6).

$$\omega = a - 2R_p$$  \hspace{1cm} (3.6)

The peak splitting is interpreted as a change in lattice parameter for a proportion of the SBA-15 due to the distortion by the impregnation of Pt or Zn into the SBA-15.
Taking a ratio of the areas thus allows for determination of the fraction of SBA-15 with each associated lattice parameter. To fit the (200) Bragg peak a quadratic baseline function was used along with a Psuedo Voigt peak and a Gaussian peak. A Psuedo Voigt profile was chosen due to the as-received SBA-15 peak fitting to a Voigt profile with a Gaussian contribution allowing for a disordered spread of the lattice parameter on addition of the Pt and Zn into the synthesis. A Gaussian profile for the secondary peak was chosen to minimise the number of fitting parameters whilst showing to be a good fit to the data. For consistency the SBA-15 sample was also fitted with two peaks.

Figure 3.3 shows the peak fitting undertaken on the as received SBA-15, Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15 samples. Table 3.1 gives the fraction of the sample associated to each refined lattice parameters through the peak fitting of the (200) Bragg reflection.

Table 3.1: Table of results for the peak fitting of the (200) Bragg reflection originating from the hexagonal stacking within the SBA-15 structure in the SAXS data showing the position and area fraction for the two component model.

```
<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_1$ (Å)</th>
<th>Fraction</th>
<th>$a_2$ (Å)</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>112.81 ± 0.01</td>
<td>0.98 ± 0.04</td>
<td>109.60 ± 0.06</td>
<td>0.02 ± 0.04</td>
</tr>
<tr>
<td>Pt/SBA-15</td>
<td>113.12 ± 0.01</td>
<td>0.80 ± 0.07</td>
<td>110.08 ± 0.03</td>
<td>0.20 ± 0.07</td>
</tr>
<tr>
<td>Pt$_8$Zn$_2$/SBA-15</td>
<td>112.88 ± 0.01</td>
<td>0.75 ± 0.06</td>
<td>110.55 ± 0.02</td>
<td>0.25 ± 0.06</td>
</tr>
<tr>
<td>Pt$_5$Zn$_5$/SBA-15</td>
<td>113.06 ± 0.01</td>
<td>0.68 ± 0.08</td>
<td>110.05 ± 0.02</td>
<td>0.32 ± 0.08</td>
</tr>
<tr>
<td>Pt$_2$Zn$_8$/SBA-15</td>
<td>112.73 ± 0.01</td>
<td>0.89 ± 0.08</td>
<td>109.96 ± 0.09</td>
<td>0.11 ± 0.08</td>
</tr>
<tr>
<td>Zn/SBA-15</td>
<td>112.86 ± 0.01</td>
<td>0.85 ± 0.08</td>
<td>109.88 ± 0.06</td>
<td>0.15 ± 0.08</td>
</tr>
</tbody>
</table>
```
Figure 3.3: Peak fitting to the (200) Bragg reflection of the SBA-15 structure stacking. The samples here shown are: as received SBA-15, Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15. Black circles are used to show the data, with the red line depicting the fitted model. Dashed lines are used to show the Pseudo-Voigt and Gaussian profiles respectively on top of a quadratic baseline function.
Further analysis of the SAXS data was performed by Glen Smales employing McSAS to analyse the particle size distribution within the SBA-15 samples. Here the SBA-15 Bragg reflections have been removed from fitting. Figure 8 gives the size distribution present exhibiting two clear features. The first relating to the Pt particles within the SBA-15 pores and the second to the SBA-15 pores. There is no result given for the Zn/SBA-15 sample as this failed to converge and no clear particles due to Zn are expected to be observed. Table 3.2 gives the average Pt particle diameter and average SBA-15 pore diameter results. Here there is an observed trend in the Pt particle size dependant on the atom fraction of Pt within the each sample, with larger particles observed with increased Pt content.

![Graph](image)

**Figure 3.4:** Pt particle size and SBA-15 pore size distribution derived from SAXS using MCSAS for the Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15, Pt$_8$Zn$_{2}$/SBA-15 shown in black, red, blue and pink respectively.

**Table 3.2:** Table of results for the average Pt particle size and SBA-15 pore size derived from MCSAS fitting of the *ex situ* SAXS data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt Diameter (nm)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SBA-15</td>
<td>3.7 ± 1.7</td>
<td>6.0 ± 2.5</td>
</tr>
<tr>
<td>Pt$_8$Zn$_2$/SBA-15</td>
<td>3.4 ± 1.7</td>
<td>6.1 ± 2.5</td>
</tr>
<tr>
<td>Pt$_5$Zn$_5$/SBA-15</td>
<td>3.3 ± 1.6</td>
<td>5.5 ± 2.8</td>
</tr>
<tr>
<td>Pt$_2$Zn$_8$/SBA-15</td>
<td>3.3 ± 1.6</td>
<td>5.4 ± 2.8</td>
</tr>
</tbody>
</table>
3.2.4 Wide Angle X-ray Scattering

3.2.4.1 Experimental Data Collection

Wide angle x-ray scattering (WAXS) was collected at beamline I22 of the Diamond Light Source. Data collection was performed at 18 KeV with a refined sample to detector distance of 177 mm calibrated using a silicon standard material. Scans were performed *ex situ* within 2mm polycarbonate capillaries with total data acquisition time per sample of 1 s. An empty capillary was used to subtract the background from the data. A bare SBA-15 sample was also measured for comparative purposes.

Processing of the WAXS data has been performed using a generalised baseline subtraction program implementing an asymmetric least squares approach described by Eilers et al. This method allows for the direct comparison and peak fitting of the WAXS data to be performed. Comparison of the samples: Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15, Pt$_2$Zn$_2$/SBA-15 and Zn/SBA-15 samples is shown in Figure 3.5.

![Figure 3.5: WAXS shown in Q space collected on ex situ capillaries at beamline I22 of the diamond light source. The solid black lines give the Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15, Pt$_2$Zn$_2$/SBA-15 and Zn/SBA-15 samples from top to bottom. With the dashed line representing a bare SBA-15 sample, whilst the red peaks show a reference Pt metal phase.](image)
3.2.4.2 WAXS Peak Analysis

It is evident from visual inspection of Figure 3.5 that there is a general trend relating to higher crystallinity with increasing Pt content. This can be seen due to the appearance and sharpness of peaks in the WAXS spectra. This indicates that the Pt is forming crystallites within the SBA-15 support structure. Phase ID from the WAXS is consistent with that of metallic Pt with Table 3.3 giving the first 9 diffraction reflections relating to metallic platinum structure.

Table 3.3: Table giving the reflections of metallic Pt given in Q from Swanson et al.

<table>
<thead>
<tr>
<th>Reflection Index</th>
<th>Q (Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>2.776</td>
</tr>
<tr>
<td>200</td>
<td>3.199</td>
</tr>
<tr>
<td>220</td>
<td>4.537</td>
</tr>
<tr>
<td>311</td>
<td>5.319</td>
</tr>
<tr>
<td>222</td>
<td>5.547</td>
</tr>
<tr>
<td>400</td>
<td>6.404</td>
</tr>
<tr>
<td>331</td>
<td>6.982</td>
</tr>
<tr>
<td>420</td>
<td>7.158</td>
</tr>
<tr>
<td>422</td>
<td>7.840</td>
</tr>
</tbody>
</table>

It is also clear that there are no crystalline peaks in the Zn/SBA-15 sample indicating that there is a high dispersion of Zn throughout the SBA-15, potentially indicative of a binding of Zn to the walls of the silica. A general trend towards reduced peak intensity can observed upon increasing Zn content in the samples. This follows that as the Pt content reduces, the contribution from metallic Pt reduces.

3.2.5 Summary of Ex Situ Characterisation

The ex situ materials characterisation involving TEM, SAXS and WAXS analysis have provided convincing evidence for the formation of Pt nano-particles within the channels of the SBA-15 mesoporous silica support. Whilst the WAXS has given clear diffraction peaks relating to the Pt phase in all the Pt containing samples, no evidence for a crystalline Zn phase has been observed. Analysis of the Bragg
reflections visible in the SAXS data has shown there to be a distortion resulting in a splitting of the SBA-15 pore lattice upon formation of Pt nano-particles and interaction with Zn, thought to be highly dispersed over the silica walls. These findings are in agreement with the TEM images which show particles within the SBA-15 channels for the Pt containing samples and no particles are visible on the Zn/SBA-15 sample.
3.3 In situ XAS following the Decomposition of Formic Acid

When discussing the results observed on the Zn K and Pt L3 edges, the sample composition is given in respect of the edge which is being discussed. For example for a sample measured on the Zn K edge $Zn_xPt_{10-x}$ whilst on the Pt L3 edge this becomes $Pt_xZn_{10-x}$.

3.3.1 Experimental

The in situ X-ray Absorption Spectroscopy experiments following the structural changes to platinum and zinc based bimetallic and monometallic impregnated mesoporous silica, SBA-15, due to exposure to formic acid were undertaken at beamline B18 of the Diamond Light Source synchrotron. The samples investigated were 5 wt% : Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15, Pt$_8$Zn$_2$/SBA-15 and Zn/SBA-15. Both the Pt L3 and Zn K edges were measured where appropriate. The XAS measurements were conducted in transmission geometry using a Si(311) double crystal monochromator and in a step scan mode. Typically 150 mg of sample was ground and made into a 13mm diameter pellet. The Pt L3 edge was measured between 11336 and 12364 eV whilst the Zn K edge measured between 9462 and 10512 eV.

The samples were loaded into the reaction cell, Figure 3.6, and purged with nitrogen prior to initial ex situ measurement. Formic acid was then supplied in vapour phase by bubbling nitrogen at 30 ml min$^{-1}$ through liquid formic acid. The flow rate of formic acid vapour has been determined to be approximately 0.003 ml min$^{-1}$ at 30°C. The total exposure time to formic acid vapour was 1 hour 30 minutes.
3.3.2 XANES Observations

Typical XANES analysis undertaken through linear combination fitting cannot be applied here. When considering the Pt $L_3$ edge metallic nano-particles have demonstrated to have size dependent effects. In particular, the edge position of Pt nano-particles has been demonstrated to shift to higher energies depending on the particle size of Pt supported in SBA-15, whilst Dai et al. have interpreted differences in the white line intensity observed on Pt nano-particles to relate to the localisation of unoccupied states. Whilst on the Zn $K$ edge, no standard material can be used to accurately describe the XANES arising from isolated bonding of Zn to the SBA-15 silica wall.

3.3.2.1 Zn K Edge

To illustrate the quality of the data collected on the Zn $K$ edge surface mapping for all samples throughout the in situ experiments is shown in Figure 3.7 for the 4 Zn containing samples. Figure 3.7 shows the Zn/SBA-15 sample where the increase in the white line intensity during exposure to formic acid is here associated to the formation of a Zn formate phase by comparison to a Zn $K$ edge XANES spectra of a Zn Formate Dihydrate standard compound. Also evident is the decrease in intensity around 9680 eV as time progresses, giving a fingerprint region to the conversion process from the initial Zn silicate like starting material, as discussed by Mei et al., to the Zn formate phase.

**Figure 3.6**: Reaction Cell used for in situ decomposition of formic acid experiments at beamline B18 of the Diamond Light Source Synchrotron.
Figure 3.7: The surface maps show the intensity in the XANES region of the Zn K edge collected throughout the \textit{in situ} reaction with formic acid vapour. Each of the 4 Zn containing samples, Zn/SBA-15, Zn$_5$Pt$_2$/SBA-15, Zn$_5$Pt$_3$/SBA-15 and Zn$_2$Pt$_8$/SBA-15 in A,B,C and D respectively are plotted on the same colour scale for direct comparison.

XANES simulations using FDMNES\textsuperscript{35,36} have also been undertaken to establish the structure of the starting material on the Zn K edge experiments. Here FDMNES was employed in the finite difference method using self consistent calculations. The similarity between various standard materials and the resulting calculations are shown in Figure 3.8 as a gauge of the reliability of FDMNES in calculating the XANES spectra on the Zn K edge. The calculation of a bulk zinc silicate phase has been included for comparison to the experimental data collected during \textit{in situ} experiments and bears a resemblance to the spectra obtained for isolated Zn atoms bonded to the silica walls of SBA-15 reported by Yoshida et al\textsuperscript{37} and Mei et al\textsuperscript{15}. Yoshida et al showed that with the addition of ZnO to SiO$_2$ the XANES region exhibits a strong change towards a doublet and loses the intensity of the white line; whilst the EXAFS region exhibits the structure relating to an oxidic phase ZnO tetrahedron with the loss of the long range order seen through the disappearance of
the second coordination sphere predominately relating to the Zn-Zn interaction.

Mei et al have shown a system of zinc and titanium loaded SBA-15 mesoporous silica, more similar to that investigated here, where the XANES of a 1wt% loaded sample can be seen to closely resemble the related spectra described herein, see Figure 3.9B. The Zn here has been described as being bonded to the silica walls forming isolated ZnO like tetrahedral species with no obvious long range structure observed in the EXAFS region.

![Figure 3.8: Comparison of FDMNES simulated XANES spectra, A, with experimental spectra, B, obtained from B18 Diamond Light Source on the Zn K edge.](image)

Comparison between standard materials and the experimental spectra on the Zn K edge are shown in Figure 3.9 Along with the measured standards, A, a calculated spectra using FDMNES is shown for an isolated Zn tetrahedron, [ZnO₄]²⁻. The experimental spectra are shown overlayed, B, with an enhanced view of the top of the white line illustrating the differences between the 4 Zn containing samples. Here it can be seen that with the addition of platinum there is an increase in the white line intensity whilst also showing a change in the doublet feature to become less pronounced. This changes as a function of the Zn:Pt ratio. The comparison between the isolated ZnO tetrahedron and the experimental spectra relating to the Zn/SBA-15 sample is explicitly shown, C. Here it can be seen that there is a high agreement between the calculated XANES spectra using FDMNES and the experimental spec-
The interpretation of this result is that Zn is bonding to the surface of the silica channels forming isolated tetrahedra and not forming Zn or ZnO particles inside the silica channels.

**Figure 3.9:** Comparison of Zn standard materials are shown in Figure A. Here it is important to note that the isolated tetrahedron is a result of FDMNES calculation rather than experimental measurement. Figure B illustrates the starting material of the Zn and bimetallic ZnPt SBA-15 samples collected at Beamline B18 of the Diamond Light Source. Figure C shows a direct comparison between the experimental spectra relating to the Zn/SBA-15 sample and the FDMNES calculated spectra for an isolated ZnO tetrahedron.

A comparison between the experimental initial, prior to the exposure to formic acid vapour, and final, after 1hr30 exposure to formic acid vapour, XANES structures for the Zn/SBA-15 sample with an FDMNES calculated isolated tetrahedron, [ZnO$_4$]$^6$–, and a Zn formate dihydrate standard material is shown in Figure 3.10 parts A and B respectively. Here it can be seen that the final structure broadly resembles the Zn formate dihydrate standard in shape. However, there are noticeable differences that occur. The white line intensity of the final structure is increased in comparison to the Zn formate dihydrate standard. This could be explained by the increase in available states caused by defects in the material structure due to the formation occurring within the silica channels. There is also a broadening and dampening of the shoulder at 9685 eV in comparison to the standard. This can be explained by a the small crystallite size affecting the XANES region of the XAS.

Using this decrease in intensity at approximately 9680 eV as a fingerprint along with the increase in white line intensity to qualitatively analyse the XANES spectra for
the bimetallic ZnPt materials. The rate of conversion towards a Zn formate phase, but not solely to, is observed to follow a direct correlation to the ratio of Zn:Pt, increased Zn content leads to increased rate of Zn formate formation. Interestingly the Zn$_8$Pt$_2$/SBA-15 and Zn$_5$Pt$_5$/SBA-15 show completion of conversion quicker than the pure Zn sample taking approximately 15 and 18 minutes respectively and the Zn$_2$Pt$_8$/SBA-15 sample around 24 minutes. There is also a significant drop in the white line intensity of the materials as a function of Zn:Pt ratio. This is suggestive of a multiphase component in the XANES potentially relating to a bimetallic structure.

Figure 3.11 shows the final spectra in the XANES region for the 4 Zn containing samples. Here the edge position and the intensity of the white line is shown to be dependant on the ratio of Zn:Pt.

Figure 3.11: Illustration of the final Zn $K$ edge XANES spectra for the Zn samples, Zn/SBA-15, Zn$_8$Pt$_2$/SBA-15, Zn$_5$Pt$_5$/SBA-15 and Zn$_2$Pt$_8$/SBA-15.
3.3.2.2 Pt L$_3$ Edge

Surface mapping of the \textit{in situ} Pt L$_3$ edge experiments can be used to qualitatively analyse the XANES in a manner similar to that achieved on the Zn K edge data. Here the decrease in the white line and formation of a subtle peak at approximately 11605 eV can be used to fingerprint the reaction. Both of these relate directly to the reduction towards a metallic Pt state as seen in the comparison of the standard materials shown in Figure 3.13.

![Surface mapping of the in situ Pt L$_3$ edge experiments can be used to qualitatively analyse the XANES in a manner similar to that achieved on the Zn K edge data. Here the decrease in the white line and formation of a subtle peak at approximately 11605 eV can be used to fingerprint the reaction. Both of these relate directly to the reduction towards a metallic Pt state as seen in the comparison of the standard materials shown in Figure 3.13.](image)

\textbf{Figure 3.12:} The surface map shows the intensity in the XANES region of the Pt L$_3$ edge collected throughout the \textit{in situ} reaction with formic acid vapour. Each of the 4 Pt containing samples, Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15 in A,B,C and D respectively are plotted on the same colour scale for direct comparison.

The starting structure of the 4 Pt containing samples has been investigated using the Pt L$_3$ edge. Figure 3.13 gives a comparison of the standard materials, shown on the left, with the starting materials of the Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15 samples shown on the right. Here it can be seen that the white line intensity increases as the fraction of Pt decreases within the sample. An
increased white line is indicative of an oxidic state. Whilst none of the samples show a white line intensity close to that of the platinic acid they can be said to be partially oxidised. The XANES region suggest the samples are present in a majority metallic state in particular on the pure Pt/SBA-15 sample. However the gradient on the region between 11560 and 11600 eV and the increased white line for all samples also suggests a partially oxidised state when compared to the standard materials. The three bimetallic samples show similar levels of oxidation and is increased in respect to that of the Pt/SBA-15 sample. Due to the nature of particle size effects on the XANES of metallic clusters it is not possible to perform linear combination fitting to deduce the fraction of metallic to oxide phases present or any bimetallic contributions.

Through this qualitative approach the Pt/SBA-15 sample is observed to have completed the reduction to metallic Pt within approximately 30 minutes. Whilst the Pt$_8$Zn$_2$/SBA-15 and Pt$_5$Zn$_5$/SBA-15 are shown to be faster to convert taking approximately 15 and 24 minutes respectively. Interestingly the Pt$_2$Zn$_8$/SBA-15 appears to take longer at approximately 33 minutes, however, there is a clear trend in the relation between the conversion time and the fraction of Pt present in the
bimetallic samples towards taking longer for conversion as the Zn fraction increases.

From the Pt $L_3$ XANES all samples show a similar final structure suggesting complete conversion to metallic Pt. Figure 3.14 compares the final XANES spectra for each of the four Pt containing samples. Whilst there are subtle differences in the XANES the predominant phase, when compared to the standard materials, is evidently metallic Pt. Therefore it can be observed that exposure to formic acid aids the reduction of Pt from oxidic to metallic under an otherwise inert atmosphere.

![Figure 3.14](image)

**Figure 3.14:** Illustration of the final XANES spectra comparing the 4 Pt containing samples, Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15 measured on the Pt $L_3$ edge demonstrating all samples show a similar structure after exposure to formic acid.

In comparison to the results obtained from the Zn $K$ edge where there was a direct trend in the final XANES spectra relating to the fraction of Zn:Pt, the Pt $L_3$ edge shows no such trend and instead suggesting total conversion to metallic Pt is achieved for all samples. This suggests that the vast majority of the Pt is not interacting directly with the Zn and instead only a small proportion coordinates with the Zn. This may be occurring in a similar nature to how titanium has been described.
as interacting in Zn and Ti loaded SBA-15 in work published by Mei et al.15

When comparing the relative reaction times for the Zn conversion to Zn formate and the Pt reduction to metallic state there is a clear correlation. The Zn K edge shows a faster reaction time when the composition fraction is weighted towards the Zn fraction and similarly the Pt $L_3$ edge shows faster reaction times for the reduction to metallic state when the composition fraction is weighted towards Pt. Table 3.4 gives the qualitative time in minutes for the related reactions occurring as seen from the Zn $K$ edge and the Pt $L_3$ edge respectively. This inverse relationship is not unexpected in the case where the majority of the Pt is not interacting with the Zn. Where some Pt interacts with the Zn the increased relative ratio of PtZn forming a bimetallic nature may inhibit the conversion of the Zn to the Zn formate phase. Whilst the greater presence of Pt increases the relative surface area of oxidic phase platinum that can be reduced by the formic acid.

Table 3.4: Comparison of the qualitative results from the Zn $K$ edge and Pt $L_3$ edge XANES analysis for reaction completion time, in minutes, relating to the formation of Zn formate phase and reduction of partial oxidic Pt phase respectively on the bimetallic samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn $K$ Edge Conversion Time (min)</th>
<th>Pt $L_3$ Edge Conversion Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pt_5Zn_2$/SBA-15</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>$Pt_5Zn_5$/SBA-15</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>$Pt_2Zn_8$/SBA-15</td>
<td>15</td>
<td>33</td>
</tr>
</tbody>
</table>
3.3.3 EXAFS Data Analysis

The complete analysis of both the in situ Zn K edge and Pt L3 edge XAS experiments has been undertaken using Artemis. Preprocessing and normalisation of the data was undertaken using Athena\textsuperscript{38}. In the case of the Pt L3 edge analysis using a tri-phase model incorporating metallic Pt, oxidic Pt and a metallic like Pt-Zn interaction for the bimetallic systems. Coordination numbers and bond distances were varied whilst the sigma squared parameters were refined from standard materials and then held constant allowing for phase separation and number of parameters refined to be under the Nyquist criterion and to reduce high correlation between fitting parameters.

On the Zn K edge a linear combination of the refined Zn silicate, Zn formate phases and a metallic Zn-Pt interaction was performed. Similarly, the bond distances and sigma squared parameters were refined from standard materials and then held constant to remain under the Nyquist criterion on the number of fitting parameters. In the case of the metallic Pt-Zn interaction the bond distance and sigma squared was refined from the mid point of conversion on the Pt5Zn5/SBA-15 sample and then applied over all other samples. Linear combination fitting is possible here due to the experiment being performed isothermally and the local nature of the EXAFS fitting.

First the fitting results from the Pt L3 edge are discussed followed by the Zn K edge analysis results. Dose response curves have been applied to the fitting results to extract relative rate and time of conversion in a reliable and comparable manner. Where appropriate biphasic dose response curves have been used to extract information on the two-step conversion processes observed in particular on the Zn K edge.
3.3.3.1 Pt $L_3$ Edge

EXAFS analysis of the Pt $L_3$ edge was completed using a tri-phase model incorporating metal Pt, oxidic Pt and a metallic like Pt-Zn interaction. A surface map showing the structural changes on the Pt/SBA-15 sample in real space is shown in Figure 3.15. Here it can be seen that there is a transition towards a fully metallic like structure. Note the plot is not phase corrected and thus peaks are shifted to lower R than in a true RDF. Plotted alongside the surface map the intensity at 2.42 Å is shown relating to a metallic Pt-Pt interaction. Above the line profiles relating to the initial and final material are shown demonstrating the change in the EXAFS over the experiment. Typical fitting using the described tri-phase model are shown for the K-space and R-space in Figures 3.16 and 3.17 respectively to illustrate the quality of fits and agreement to the model.

**Figure 3.15:** The surface map shows the intensity of the non-phase corrected real space data collected for a Pt/SBA-15 sample. Line profiles to the top directly compare the structural changes between the initial and final material. Whilst the line profile to the side displays the intensity change at 2.42 Å related to the growth of a Pt-Pt correlation.
Figure 3.16: Fitting examples for each Pt containing sample, sample indicated on plot, for the initial, mid conversion and final EXAFS shown in K space with plotting weight of $K^2$. Shown left to right: Pt/SBA-15, Pt$_8$Zn$_2$/SBA-15, Pt$_5$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15.
Figure 3.17: Fitting examples for each Pt containing sample, sample indicated on plot, for the initial, mid conversion and final EXAFS shown in R space with plotting weight of $R^3$. Shown left to right: Pt/SBA-15, Pt$_2$Zn$_2$/SBA-15, Pt$_3$Zn$_5$/SBA-15 and Pt$_2$Zn$_8$/SBA-15A.
The analysis of the EXAFS on the Pt/SBA-15 sample gives a wealth of information regarding the structure of the catalyst during exposure to formic acid. Figure 3.18 gives the refined values for the bond distance, metallic nano-particle diameter and the relative fraction of metallic Pt throughout the in situ reaction extracted from the EXAFS analysis. Here it can be seen that there is a total conversion to metallic Pt by 30 minutes exposure to formic acid vapour, seen in the inlaid Figure. This correlates to the majority of the increase in Pt-Pt bond length and rise in the Pt-Pt coordination number.

From Figure 3.18 there can be seen to be a continual increase in the Pt nano-particle diameter after the complete conversion to metallic Pt. This suggests there is an agglomeration of Pt particles within the silica channels indicating no, or limited, interaction between the Pt and silica. The lack of any oxidic Pt in the final structure would concur with this interpretation as any interaction with the silica is expected to be via a surface oxygen.

Figure 3.18: Figure showing the values extracted from EXAFS fitting relating to the bond distance, and Pt nano-particle diameter and the relative fraction of metallic Pt is shown in the inset plot. Solid lines represent the fitted functions whilst the dashed red lines are an estimate of 1 standard deviation to the fitted models.
The conversion from Pt-Pt coordination number to nano-particle diameter was undertaken through assuming a spherical particle. A python script was used to generate spherical Pt particles in steps of 0.1 Å up to 74 Å in radius (14.8 nm diameter maximum). The coordination numbers were explicitly calculated for the first three coordination shells by considering the inter-atomic distances between all atoms in the generated cluster. The integral over a finite window of the inter-atomic distances pertaining to the distance of each coordination sphere respectively gives explicitly the value of the coordination number as a function of particle size radius. Extraction of Pt-Pt coordination numbers allows for fitting a linear relationship of the jth Pt-Pt coordination number, $CN_j$, multiplied by the total number of atoms in the cluster, $N_{tot}$, over radius squared, $R^2$, as a function of radius, shown in equation \[3.7\].

$$CN_j \times \frac{N_{tot}}{R^2} \propto R \quad (3.7)$$

The linear fit to equation \[3.7\] for the 1st Pt-Pt coordination shell is shown in Figure 3.19A. Figure 3.19B shows the fitting of the coordination number as a function of cluster radius for the first three coordination shells. Here it is evident that this modelling has a very strong agreement between the calculated coordination numbers and the fitted functions. This can then be used to determine the radius of any Pt particle from the refined coordination number from EXAFS in the spherical nano-particle approximation.
Figure 3.19: A an example linear fit to equation 3.7 for the first coordination shell of metallic Pt. B show the value of the coordination numbers for the first three coordination shells explicitly calculated through generation of spherical Pt particles and the fitted functions using the described procedure.

Complete analysis of all Pt containing samples is shown in Figure 3.20 giving the coordination numbers relating to the refined Pt oxide and metallic phases and where appropriate the Pt-Zn interaction. The EXAFS analysis was performed by considering a linear combination of metal and oxide phases present within the Fourier transformed data. Where appropriate an addition Pt-Zn interaction was also included through fitting but with a fixed distance of 2.70 Å and sigma squared parameter of 0.01 for all samples. This approach was used to allow reliable determination of the time dependant change in relative component speciation upon exposure to formic acid. The resultant data points have also been fitted with dose response curves with 1 standard deviation error margin plotted. Dose response curves model sigmoidal curves used to mode the response of a system to an external influence, in this is case to the exposure to formic acid. Dose response curves fitting allows for direct extraction of curve half time and relative width, relating to the conversion time and rate respectively.

\[ y = y_0 + \frac{\text{span}}{1 + 10^{P_{\text{in}}(-x)}} \]  

(3.8)
Here the half time is denoted by \( x \) whilst the hill slope, related to the rate of conversion, is given by \( P \). \( y_0 \) gives the value of \( y \) at time 0 and the span term is defined by the total change between the start and end in \( y \). Using this method of analysis it can be seen that with the addition of Zn there is a broadening and shift of the conversion to metallic Pt. This is in direct agreement with the qualitative XANES analysis. The Pt-Zn interaction in the Zn containing samples can be seen to be constant throughout the in situ experiments. Figures 3.16 and 3.17 show the fits to the initial, half conversion and final structures in K and R spaces respectively illustrating strong agreement in both K and R spaces towards the fitting model throughout the in situ XAS experiment on the Pt \( L_3 \) edge and are shown at the end of the chapter section.

The results of the Pt \( L_3 \) edge EXAFS analysis using dose response curves are shown in tables 3.5 and 3.6. The top half of the table gives the results of the dose response curve fitting to Pt-O coordination numbers refined from EXAFS analysis whilst the bottom half gives the results of the similar analysis of Pt-Pt coordination numbers during the in situ XAS experiments. The interaction between Pt and Zn is also visible on the plots, marked by the Pt-Zn coordination number. The Pt-Zn interaction is shown to be constant throughout the experiments.

**Table 3.5:** Results of the biphasic dose response curves analysis to the coordination number of Pt-O scattering path. Here the span refers to the total change in the Pt-O coordination number.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Span</th>
<th>Pt-O Half Time (min)</th>
<th>Span</th>
<th>Half Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>2.1 ± 0.1</td>
<td>3.5 ± 0.2</td>
<td>0.6 ± 0.1</td>
<td>18.3 ± 1.4</td>
</tr>
<tr>
<td>Pt(_8)Zn(_2)</td>
<td>3.4 ± 0.1</td>
<td>7.1 ± 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt(_5)Zn(_5)</td>
<td>3.2 ± 0.1</td>
<td>13.4 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt(_2)Zn(_8)</td>
<td>4.3 ± 0.1</td>
<td>18.7 ± 0.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.6: Results of the biphasic dose response curves analysis to the coordination number of the Pt-Pt scattering path. Here the span refers to the total change in the Pt-Pt coordination number.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Span</th>
<th>Half Time (min)</th>
<th>Span</th>
<th>Half Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pt$</td>
<td>3.2 ± 0.3</td>
<td>5.4 ± 0.3</td>
<td>1.5 ± 0.2</td>
<td>31 ± 8</td>
</tr>
<tr>
<td>$Pt_{8}Zn_{2}$</td>
<td>7.4 ± 0.2</td>
<td>7.9 ± 0.3</td>
<td>0.43 ± 0.1</td>
<td>50 ± 16</td>
</tr>
<tr>
<td>$Pt_{5}Zn_{5}$</td>
<td>7.5 ± 0.1</td>
<td>15.7 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$Pt_{2}Zn_{8}$</td>
<td>9.5 ± 0.1</td>
<td>20.9 ± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.20: Figure shows the refined coordination numbers relating to $Pt – O$, $Pt – Zn$ (shown on the left axis) and $Pt – Pt$ (shown on the right axis) for all the Pt containing samples: Pt/SBA, Pt/SBA-15, Pt$_{8}$Zn$_{2}$/SBA-15, Pt$_{5}$Zn$_{5}$/SBA-15 and Pt$_{2}$Zn$_{8}$/SBA-15 in A, B, C and D respectively. Solid lines represent the fitted dose response curves whilst dashed red lines give an estimate of 1 standard deviation from the fitted model.

Analysis using dose response curves for extracting the half time relating to the reduction of oxidic phase Pt through conversion to metallic Pt and the growth in the Pt-Pt CN provides further insight into these materials. In Tables 3.5 and 3.6 a clear delay between the half time of the reduction of Pt-O and the half time for the in-
crease in Pt-Pt coordination number can be seen for all samples. This may relate to particle sintering effects with not all oxidic Pt species being coordinated to the Pt nano-particles in the as-synthesised materials.

The order of reduction time can also be established through this methodology. Here it is shown that the half time of oxidic Pt reduction is inversely linearly dependent on the proportion of Pt within the sample. The half time is also determined to be independent of the initial Pt-O coordination number. Therefore the reduction of the oxidic Pt solely depends upon the presence of Zn; Zn acts to inhibit the reduction reaction. Figure 3.21 plots a linear fit to the half time for the reduction of the oxidic Pt and the proportion of Pt present in the sample.

![Figure 3.21](image)

**Figure 3.21:** Figure showing a linear fit to the half time of the initial oxidic Pt to the metallic phase as a function of Pt content in the samples.

### 3.3.3.2 Zn K Edge

The structural changes observed in the real space EXAFS on the Zn/SBA-15 sample are shown in Figure 3.22. Here the surface map shows the changes throughout the *in situ* experiment, note the radial distances are not phase corrected. By the side the intensity at 1.56 Å is shown indicating the transition from a tetrahedrally coordinated Zn—O environment to an octahedrally coordinated Zn—O environment. These relate to Zn bonded to the silica surface and to the Zn formate phase respectively. The line profiles relating to the initial and final structures are shown in the
top section of the Figure illustrating a shift towards a higher radial distance and increased intensity associated to the higher coordination number.

**Figure 3.22:** The surface map shows the intensity of the non-phase corrected real space data collected for a Zn/SBA-15 sample. Line profiles to the top directly compare the structural changes between the initial and final material. Whilst the line profile to the side displays the intensity change at 1.53 Å related to the change in coordination geometry of the ZnO.

To model the EXAFS a linear combination of Zn silicate and Zn formate refined phases has been used. The agreement between the data and fitting is shown for both the K and R spaces of the EXAFS are shown in Figures 3.23 and 3.24 respectively, illustrating the quality of the fitting and agreement to the model over the *in situ* XAS experiments on the Zn K edge for all samples investigated.
Figure 3.23: Example fits to initial, intermediate and final Zn K edge EXAFS in K space, plotted in $K^2$ weighting. Samples show from left to right, Zn/SBA-15, Zn$_8$Pt$_2$/SBA-15, Zn$_5$Pt$_5$/SBA-15 and Zn$_2$Pt$_8$/SBA-15 respectively.
Figure 3.24: Example fits to initial, intermediate and final Zn K edge EXAFS in R space, plotted in R^3 weighting. Samples show from left to right, Zn/SBA-15, Zn_{5}Pt_{2}/SBA-15, Zn_{5}Pt_{5}/SBA-15 and Zn_{2}Pt_{8}/SBA-15 respectively.
The conversion of the normalised Zn silicate to Zn formate is shown in Figure 3.25A. Here biphasic dose response curves have been fitted to all the curves with a 1 standard deviation error margin plotted as an indicator of agreement with the model. This method allows for direct extraction of the relative proportion of Zn silicate sites that are converted throughout the in situ experiments.

Of particular interest all samples exhibit a two-step conversion process and with increase in the Pt weighting of the sample, the fraction of Zn silicate remaining after exposure to formic acid increases. It is thought that the two-step conversion of Zn silicate like species to Zn formate is due to some of the Zn sites having nearby silanol groups which promote the formation of Zn formate phase upon exposure to formic acid. There is also shown to be a third category of Zn sites, those which are directly interacting with Pt and are not converted to Zn formate.

Figure 3.25A gives the conversion profiles for the Zn silicate phase. The pure Zn/SBA-15 can be seen to undergo the two-step total conversion process, whilst those samples containing Pt have the two-step conversion process and show a portion which does not undergo conversion to Zn formate. This gives credence to the suggestion that capping with Pt stabilises the Zn silicate site. The proportion of Zn silicate that remains after exposure to formic acid appears to depend linearly to the ratio of Pt:Zn, shown in Figure 3.25B.
Figure 3.25: A demonstration of the two-step conversion of Zn silicate to Zn formate B gives the linear fit to the remained of Zn silicate as a function of Pt:Zn ration.

The results of the biphasic dose response curve fitting are shown in table 3.7. Here the amplitude of each fitted dose response curve, their respective half times and the remaining fraction of the normalised Zn silicate phase are shown. The addition of Pt can also be said to increase the rate of Zn being leached from the samples as seen on the Zn$_8$Pt$_2$/SBA-15 and Zn$_5$Pt$_5$/SBA-15 curves.
Table 3.7: Table showing the values of the refined conversion events using biphasic dose response curves giving the proportion and half time for each along with the remaining Zn silicate like phase fraction. Here the span refers to the total change in the Zn silicate proportion of the sample for each conversion event.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Span</th>
<th>Half Time (min)</th>
<th>Span</th>
<th>Half Time (min)</th>
<th>Remainder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.87 ± 0.02</td>
<td>16.3 ± 0.2</td>
<td>0.13 ± 0.2</td>
<td>39.7 ± 0.4</td>
<td>0 ± 0.01</td>
</tr>
<tr>
<td>Zn&lt;sub&gt;8&lt;/sub&gt;Pt&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.86 ± 0.08</td>
<td>7.5 ± 0.8</td>
<td>0.10 ± 0.04</td>
<td>23 ± 2</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Zn&lt;sub&gt;5&lt;/sub&gt;Pt&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.82 ± 0.05</td>
<td>5.4 ± 1.3</td>
<td>0.07 ± 0.02</td>
<td>72 ± 5</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>Zn&lt;sub&gt;2&lt;/sub&gt;Pt&lt;sub&gt;8&lt;/sub&gt;</td>
<td>0.38 ± 0.06</td>
<td>14.0 ± 1.0</td>
<td>0.26 ± 0.06</td>
<td>72 ± 3</td>
<td>0.36 ± 0.02</td>
</tr>
</tbody>
</table>

The linear nature of the proportion of Zn silicate remaining after exposure to formic acid against the ratio of Pt:Zn suggests that the proportion of Zn silicate remaining depends directly on the surface area of the Pt nano-particles within the SBA-15 channels.

\[
R_{ZnSilicate} \propto A_{PtSurface} \tag{3.9}
\]

In the spherical approximation the surface area of a Pt nano-particle is linearly proportional to the number of atoms in the particle due to the fact that the number of atoms in the particle depends on its radius cubed;

\[
A_{surf} = 4\pi r^2 = \frac{4\pi KN_{Pt}}{r} \tag{3.10}
\]

By applying the assumption that each Pt nano-particle is uniform in size, each contains the same number of atoms. As such the total surface area of Pt in the sample is linearly dependent on the number of Pt atoms. This leads to the ratio of Pt:Zn being proportional to the ratio of surface areas if one also assumes the Zn bonds in isolated sites to the silica walls. By this approximation it is proposed that where Pt nano-particles cover the Zn bound the SBA-15 channel wall there is proposed to be no interaction between the formic acid and Zn.
Figure 3.26: Illustration of the importance of a long bonding oxygen at 2.45 Å to the fitting of the Zn\(_2\)Pt\(_8\)/SBA-15 sample. Left showing with whilst right shows without the long bonded oxygen.

Further to this finding, where the Zn loading is small it is evident that there is an unaccounted for contribution to the EXAFS spectra. Figure 3.26 demonstrates fitting undertaken with (left) and without (right) a long bonded oxygen contribution after 40 minutes exposure to formic acid for the Zn\(_2\)Pt\(_8\)/SBA-15 sample. Figure 3.27 overlays the conversion of the normalised Zn silicate phase with the coordination number of the long oxygen bonding environment. Here, it is clear that the first phase of conversion is completed without the long bonded oxygen, however, the second phase of conversion appears to be delayed by the formation of a long bonded oxygen environment. Either this acts as an intermediary state to promote the second conversion step or is removed by the second conversion as indicated by the decrease in the Zn–O long bond coordination number. The errors on fitting of this path can be seen to be greatly increased as shown by the 1 standard deviation.
The in situ XAS experiments on the Pt $L_3$ and Zn $K$ edges have shown how the PtZn/SBA-15 samples structurally change on exposure to formic acid. Analysis of the XANES has elucidated how the Zn undergoes conversion from a oxidic Zn state to a Zn formate phase. The initial structure is identified as Zn bound, as isolated ions, to the amorphous silica walls of the SBA-15. Concurrent to this, the Pt $L_3$ edge XANES results has shown the conversion of a partially oxidised Pt particle to a fully metallic state. The rate of the reduction of the initial oxidic Pt is shown to be dependent on the proportion of Zn in the sample, suggesting Zn inhibits this reduction reaction.

The XANES analysis is further corroborated by detailed analysis of the EXAFS on both the Pt $L_3$ and Zn $K$ edges. The rate of reduction of the initial Pt oxide was shown to be linearly dependent on the proportion of Zn in the sample. This was achieved through fitting of the reduction profiles with dose response curves to extract the half time of conversion. This linear relationship between the reduction

Figure 3.27: Comparison of the conversion of Zn silicate throughout the in situ experiment with the coordination number of Zn to a long bonded oxygen environment.

3.3.4 Summary of the In Situ XAS Studies
of oxidic Pt and the proportion of Zn is evidence that the reduction of oxidic Pt is solely dependent on the proportion of Zn in the sample. When considering the mono-metallic Pt/SBA-15 sample, there is evidence that there is a small amount of sintering in the Pt nano-particles. This is seen by the continual growth of the Pt nano-particles after the complete conversion of the partial presence of oxidic Pt in the as-synthesised sample. Estimation of the particle size was achieved through a spherical nano-particle approximation and was determined to be approximately 3.1 ± 0.1 nm after exposure to formic acid for 102 minutes and had reached a stable value. Further to this, there is shown to be a limited interaction between Pt and Zn as observed on the Pt $L_3$ edge which is constant throughout exposure to formic acid.

Analysis of the Zn $K$ edge EXAFS results has yielded a wealth of information pertaining to the Zn atoms within the SBA-15 samples. Here it has been demonstrated that the initial starting materials all exhibit a Zn silicate like phase where isolated Zn atoms bind to the amorphous silica walls. This is in agreement with the ex situ characterisation whereby no crystalline phase was observed in the XRD and WAXS analysis. Furthermore, the initial Zn silicate like phase where the Zn is tetrahedrally bonded to oxygen, has been shown to convert to an octahedral bonding environment akin to that of Zn formate. This is born out by the increase in Zn-O first shell co-ordination number and bond distance. The formation of Zn formate results in the leaching of Zn from the walls of the SBA-15 channels. As such the linear dependence of the conversion rate of the oxidic Pt is interpreted as a measure of the degree of blocking of the SBA-15 channels by Zn formate.

To model the EXAFS it was found that a linear combination of the initial Zn silicate and the final Zn formate phase was sufficient and accurately modelled all samples. When the Zn loading was low, there was evidence for an intermediate phase present through the coordination with a long bonded oxygen environment. The resultant conversion profiles yielded a two-step conversion process. This is thought to relate
to only some Zn silicate sites being present with nearby silanol groups. The half time and magnitude of each of the two conversion events has been modelled using biphasic dose response curves. The use of biphasic dose response curves has demonstrated that the rate of conversion of the Zn silicate is independent of the content of Pt in sample. However, the presence of Pt has been clearly shown to result in a proportion of the Zn silicate not undergoing conversion to Zn formate.

Further analysis has shown a linear dependence on the remaining Zn silicate phase after exposure to formic acid and the ratio of Pt:Zn. This has been interpreted by considering the covering of a portion of the Zn sites by the Pt nano-particles and would explain the minor Pt-Zn interaction observed on the Pt $L_3$ edge. With increasing ratio of Pt:Zn the ratio of surface areas increases linearly, in the approximation of a uniform Pt metal particle size. The greater the quantity of Pt present the greater the relative surface area of the Pt nano-particles which directly covers the SBA-15 walls. The lower the quantity of Zn the lower the proportion of the SBA-15 surface which is covered by bound Zn adatoms. The linearity of the ratio of Pt:Zn and the remaining proportion of Zn silicate directly implies that both the Pt nano-particles are formed with a uniform size and that the Zn is dispersed homogeneously over the SBA-15 surface. This is supported by the SAXS analysis demonstrating a narrow Pt particle size distribution within all samples.

The fact that Zn formate is formed through exposure to formic acid results in these materials not being suitable for the decomposition of formic acid to produce $H_2$. This is because these materials have been demonstrated to have a limited lifespan due to the leaching of Zn from the SBA-15 walls through to formation of Zn formate. However, the limited sintering of the Pt nano-particles suggests that they are stable within the SBA-15 and thus may be suitable catalytic materials in the absence of Zn. The catalytic activity of these samples has not directly been studied here.
3.4 Bimetallic PtZn PVP Encapsulated Particles

3.4.1 Introduction

The characteristics of many catalytic materials are noted to be highly dependent on the surface area and particle size of the active component. There are many potential routes to synthesising small nano-particles. The synthesis with polyvinylpyrrolidone (PVP) is one option to control the particle size and distribution of particle sizes obtained. PVP is a high molecular weight polymer consisting of $C = O$, $C - N$ and $CH_2$ functional groups and is not toxic.

PVP has been used in the synthesis of a variety of metallic and bimetallic systems to produce tuneable mono-dispersed nano-particles. The hydrophobic carbon chains of the PVP leads to repulsive forces that prevent the agglomeration of the metallic nano-particles to maintain the small mono-dispersed particle size. It is noted as stabilizing the metallic phase of the metal nano-particle contained within where other methods often lead to metal oxide particles forming. PVP can also be used to control the shape of nano-particles by promoting the growth of only specific crystal faces.

Here PVP is used in the synthesis of bimetallic core-shell PtZn nano-particles. The structure has been determined from ex situ XAS studies on the Pt $L_3$ and Zn $K$ edges. The synthesis with PVP is used to contrast with the SBA-15 supported PtZn materials previously described. The samples were synthesised by Elizabeth Raine, University of Oxford.

3.4.2 Sample Synthesis and Characterisation

Polyvinylpyrrolidone stabilized platinum nano-particles, Pt(PVP), were synthesized using a modified polyol method similar to that used by Bonet et al. 18 $\mu l$ of $aq.$ platinum(IV) nitrate solution (0.02 mmol) was added to a solution of 11 mg
(0.1 mmol) PVP (molecular weight 40,000) in 30 ml anhydrous ethylene glycol at 120°C. The solution was stirred under nitrogen for 2 hours at 120°C. After the reaction mixture was cooled to room temperature, the flow of nitrogen was stopped and hydrogen was bubbled through the solution. After 30 minutes of hydrogen flow the nitrogen was replaced. The addition of Zn was performed in a method similar to Gauthard et al. A given amount of zinc nitrate was added to the mixture, followed by stoichiometric amounts of sodium borohydride to fully reduce the zinc. The reaction was stirred for 30 minutes to allow zinc reduction onto the platinum surface. After this further reduction step the nano-particles were precipitated in acetone and washed with acetone 3 times before dispersing in ethanol.

Characterisation of the PVP samples was performed using XRD and TEM for the $Pt_8Zn_2$ PVP sample. The XRD phase analysis yields only a contribution from metallic Pt, there is no evidence for any crystalline Zn phase. The TEM shows the formation of small spherical nano-particles, measurement of the size distribution from 100 nano-particles yielded an average size of 3.61 nm, a typical TEM image is shown in Figure 3.28. The sample synthesis and basic characterisation reported here was performed by Elizabeth Raine, University of Oxford.

Figure 3.28: Typical TEM image obtained on the $Pt_8Zn_2$ PVP sample.
3.4.3 Experimental

The ex situ XAS experiments to determine the structure of platinum zinc based bimetallic PVP stabilised nano-particles were undertaken at Beamline B18 of the Diamond Light Source synchrotron. The samples investigated were ground into a powder and dispersed onto thin kapton tape. The XAS measurements were conducted in transmission geometry using a Si(311) double crystal monochromator and in a step scan mode for both the Zn K and Pt L\textsubscript{3} edges. The Pt L\textsubscript{3} edge was measured between 11336 and 12364 eV whilst the Zn K edge was measured between 9462 and 10512 eV.

3.4.4 XAS Analysis

The XANES region of the XAS spectra acquired on the Pt\textsubscript{5}Zn\textsubscript{5} and Pt\textsubscript{8}Zn\textsubscript{2} PVP samples are shown in Figure 3.29A and 3.29B for the Zn K edge and Pt L\textsubscript{3} edge respectively. Whilst the Pt L\textsubscript{3} appears to show a metallic phase, albeit dampened for the Pt\textsubscript{5}Zn\textsubscript{5} PVP sample, for both samples when compared to the reference foil. The Zn K edge XANES show the samples to have a significantly increased white line intensity when compared to the reference foil. The increase in white line intensity is associated to a charge transfer from Zn to Pt resulting in an increase in the density of unoccupied states in the Zn and is evidence for direct interaction between Pt and Zn. The EXAFS analysis presented below shows no evidence for the presence of a Zn oxide which would otherwise result in an increase in the white line intensity observed on the Zn K edge.

Modelling of the Zn K edge EXAFS has been performed using contributions pertaining to Zn-Zn interaction and Zn-Pt interaction. The fitting is shown in Figures 3.30 and 3.31 for the Zn K and Pt L\textsubscript{3} edges respectively. These Figures show the fitting to the R-space, K-space and Q-space data for both samples and the reference foils. Q-space is shown due to it being derived from the inverse FT of the real space data in the region of the fitting model. Therefore, Q-space can be used to illustrate that the deviation between the fit and data observed in K-space arises from contri-
Figure 3.29: A gives the XANES spectra obtained on the Zn K edge showing a reference Zn foil, the Pt$_5$Zn$_5$ PVP sample and the Pt$_8$Zn$_2$ PVP sample in black, red and blue respectively. B gives the XANES spectra obtained on the Pt L$_3$ edge showing a reference Pt foil, the Pt$_5$Zn$_5$ PVP sample and the Pt$_8$Zn$_2$ PVP sample in black, red and blue respectively.

butions outside of the fitting window in R-space. The results from the fitting to both the Zn K and Pt L$_3$ edges are shown in table 3.8. Here the results from the fitting are given in the top half of the table for the Pt L$_3$ edge and in the bottom half of the table for the Zn K edge. The table gives the refined distances, $\sigma^2$ parameter and coordination numbers for the metallic paths observed within the first coordination shell.
Figure 3.30: Figures showing from left to right the Pt$_5$Zn$_5$PVP sample, Pt$_8$Zn$_2$PVP sample and a Zn reference foil in R-space, K-space and Q-space from top to bottom respectively for Zn K-edge XAS experiments.
Figure 3.31: Figures showing from left to right the Pt$_5$Zn$_5$ PVP sample, Pt$_8$Zn$_2$ PVP sample and a Zn reference foil in R-space, K-space and Q-space from top to bottom respectively for Pt $L_3$ edge XAS experiments.
Table 3.8: Table showing the refined bond distances, disorder parameter $\sigma^2$ and coordination numbers relating to ex situ characterisation of PVP encapsulated Bimetallic PtZn systems. Top and bottom give the results for the Pt $L_3$ and Zn $K$ edges respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering Path</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$^5$Zn$^5$</td>
<td>Pt-Zn</td>
<td>2.70 ± 0.01</td>
<td>0.0107 ± 0.0020</td>
<td>3.55 ± 0.77</td>
</tr>
<tr>
<td>Pt$^5$Zn$^5$</td>
<td>Pt-Pt</td>
<td>2.77 ± 0.01</td>
<td>0.0059 ± 0.0014</td>
<td>7.92 ± 0.53</td>
</tr>
<tr>
<td>Pt$^8$Zn$^2$</td>
<td>Pt-Zn</td>
<td>2.67 ± 0.07</td>
<td>0.0132 ± 0.0023</td>
<td>1.33 ± 0.74</td>
</tr>
<tr>
<td>Pt$^8$Zn$^2$</td>
<td>Pt-Pt</td>
<td>2.76 ± 0.01</td>
<td>0.0051 ± 0.0015</td>
<td>9.25 ± 1.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering Path</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$^5$Zn$^5$</td>
<td>Zn-Pt</td>
<td>2.74 ± 0.04</td>
<td>0.0091 ± 0.0019</td>
<td>8.53 ± 1.28</td>
</tr>
<tr>
<td>Pt$^5$Zn$^5$</td>
<td>Zn-Zn</td>
<td>2.64 ± 0.07</td>
<td>0.0091 ± 0.0019</td>
<td>1.73 ± 0.41</td>
</tr>
<tr>
<td>Pt$^8$Zn$^2$</td>
<td>Zn-Pt</td>
<td>2.72 ± 0.04</td>
<td>0.0086 ± 0.0016</td>
<td>6.44 ± 0.87</td>
</tr>
<tr>
<td>Pt$^8$Zn$^2$</td>
<td>Zn-Zn</td>
<td>2.64 ± 0.07</td>
<td>0.0086 ± 0.0016</td>
<td>1.67 ± 0.65</td>
</tr>
</tbody>
</table>

As shown by the EXAFS modelling the bimetallic nano-particles can be said to be present in the form of a core-shell structure with Zn coating the surface of a Pt core. This is born out by the coordination number of the Pt-Pt being increased as compared to the Zn-Zn. When considering the $Pt^5Zn^5$ sample it is especially evident due to the fact that the Pt and Zn are present in equal number fraction within the sample. The Zn-Zn interaction is possible only in a phase segregated core-shell nano-particle system. However, the relatively high value of the Zn-Pt scattering path coordination number (on the Zn $K$) suggests there is a degree of alloy formation in both samples with a Zn inclusion into the Pt core.

Further to this, the scattering path lengths show that where there is interaction between Pt and Zn atoms, there is distortion in the inter-atomic distances. Metallic Pt, $\approx 2.77$ Å first shell half scattering path length, has a value greater than that of the metallic Zn, $\approx 2.64$ Å first shell half scattering path length, whilst the interacting bimetallic atom pairs have an intermediate bonding distance, an average of $\approx 2.71$ Å.
Å first shell half scattering path length is observed.

### 3.4.5 Summary

*Ex situ* XAS experiments have elucidated the structure of PVP stabilised PtZn nanoparticles. This study has shown, that in contrast to the SBA-15 supported samples, the PVP is able to stabilise the metallic state of the nano-particles. No evidence for inclusion of oxygen into the nano-particles is observed. Here it has been shown that the nano-particles exist in metallic state with a Pt core and surface Zn shell. Due to the increased coordination number of the Zn-Pt scattering path (observed on the Zn K edge) it is proposed that there is also a degree of alloy formation by the inclusion of Zn into the Pt core. The refined bond distances show that the interfacial region between the Zn and Pt exhibits a distorted structure; the Pt-Zn bond distance is shown to be $\approx 2.71 \text{ Å}$, this is midway between the Pt-Pt and Zn-Zn bond distances of $\approx 2.77 \text{ Å}$ and $2.64 \text{ Å}$ respectively. Furthermore the increase in the white line intensity observed on the Zn K edge is proposed to be due to charge transfer from the Zn to the Pt.
3.5 Quasi *In Situ* X-ray Absorption Spectroscopy Following the Formation of Pt Nano-particles

3.5.1 Introduction

Previous work following the preparation of supported platinum nano-particles typically has been conducted using platinum nitrate or hexachloroplatinic acid hexahydrate precursor. When using platinic acid, usually one of several reducing agents can be used, sodium borohydride and formic acid are common, to aid in the reduction step. Supported Pt/C has been reported to be produced in an aqueous slurry through reaction directly with formic acid. Elsewhere the use of formic acid as a direct reducing agent in comparison to sodium borohydride has been reported. Alegre et al reported that the use of formic acid as a reducing agent resulted a high metallic distribution with smaller crystallite size when compared to the route using the more traditional sodium borohydride synthesis. Here the formation of Pt nano-particles is studied using a vapour phase formic acid to reduce platinic acid mixed with fumed silica.

3.5.2 Experimental

The *in situ* X-ray Absorption Spectroscopy following exposure to formic acid were undertaken at Beamline B18 of the Diamond Light Source synchrotron on physically mixed samples containing platinic acid with fumed silica. The XAS measurements were conducted in transmission geometry using a Si(311) double crystal monochromator and conducted in a step scan mode. The sample was formed of 8 mg of platinic acid ground with 50 mg of fumed silica and made into a 13mm diameter pellet. The Pt $L_3$ edge was measured between 11336 and 12364 eV.

The sample was loaded into a reaction cell, shown in Figure 3.6 and purged with nitrogen prior to initial *ex situ* measurement. Formic acid was then supplied in vapour phase by bubbling nitrogen at 30 $ml\ min^{-1}$ through liquid formic acid. The flow rate of formic acid vapour has been determined to be approximately 0.003
at $30^\circ$C. The total period for exposure to formic acid was 1 hour and 30 minutes after which the samples were exposed to air and left for 10 minutes. Measurements were then performed under a nitrogen atmosphere post exposure to air.

### 3.5.3 XAS Analysis

Data reduction and normalisation was performed using the Athena software package. Figure 3.32 gives the spectra relating to the metallic and oxide standard materials along with the associated spectra for initial starting physical mixture of platinic acid with silica, after 1 hr 30 exposure to formic acid and after a 10 minute exposure to air. In addition to the normalised XANES spectra, the EXAFS in both K and R spaces are also shown. Fitting of the EXAFS data was completed using the Artemis software package.

Fitting to the EXAFS structure was completed using two paths for the Pt-O distances and a metallic Pt-Pt contribution. The structural parameters associated to the bulk platinic acid and metallic platinum standard materials are given in table 3.9. The crystallographic information files associated to the platinic acid and platinum metal were obtained from Scott et al.\textsuperscript{63} and Barth et al.\textsuperscript{64} respectively. Due to the resolution on the real space EXAFS as a result of finite $K$ range the two Pt-O paths were refined using join parameters for the bond distance, sigma squared and proportion of coordination numbers.

**Table 3.9:** Table showing the bond distance and coordination numbers for bulk platinic acid and platinum metal structures for comparison with refined parameters in the EXAFS fitting

<table>
<thead>
<tr>
<th>Material</th>
<th>Scattering Path</th>
<th>R (Å)</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinic Acid</td>
<td>Pt-O</td>
<td>2.06</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Pt-O</td>
<td>2.10</td>
<td>2</td>
</tr>
<tr>
<td>Platinum Metal</td>
<td>Pt-Pt</td>
<td>2.76</td>
<td>12</td>
</tr>
</tbody>
</table>

The data for both the XANES and EXAFS regions are shown in Figure 3.32.
the data and fit quality are illustrated for the physically mixed sample and the standard reference materials.
Figure 3.32: Figures showing the fitting to R and K spaces of the EXAFS, top and middle, of the standard materials and the physical mixture of platinic acid with fumed silica initial, after exposure to formic acid and after exposure to air, left to right. The bottom row shows the XANES spectra for the same samples.
The results of the EXAFS analysis to the initial sample are shown in table 3.10. With the results of the EXAFS analysis to the post treatment with formic acid shown in table 3.11 while under N₂ flow. Here it is evident that the EXAFS analysis shows the initial starting physical mixture sample bares a close resemblance to the oxide standard. After treatment with vapour phase formic acid the sample remains in the oxide form showing no changes occurring in either the EXAFS or XANES regions. This confirms that the Pt-O coordination environment conforms to that of the platinic acid standard.

**Table 3.10:** Table showing the refined bond distances, disorder parameter σ² and coordination numbers for the initial physical mixture sample.

<table>
<thead>
<tr>
<th>Scattering Path</th>
<th>R (Å)</th>
<th>σ²</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-O</td>
<td>1.99 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>3.89 ± 0.12</td>
</tr>
<tr>
<td>Pt-O</td>
<td>2.03 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>1.95 ± 0.06</td>
</tr>
</tbody>
</table>

**Table 3.11:** Table showing the refined bond distances, disorder parameter σ² and coordination numbers relating to post treatment with formic acid vapour.

<table>
<thead>
<tr>
<th>Scattering Path</th>
<th>R (Å)</th>
<th>σ²</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-O</td>
<td>2.00 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>3.57 ± 0.41</td>
</tr>
<tr>
<td>Pt-O</td>
<td>2.04 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>1.79 ± 0.21</td>
</tr>
</tbody>
</table>

Whilst the EXAFS results for the pre and post treatment with formic acid vapour show some subtle difference in both the coordination number and Pt-O bond distances these are both within error tolerance of a bulk platinic acid structure.

The XANES spectra acquired after exposure to air, shown in Figure 3.32, give a distinct metallic fingerprint in the suggestion of a total conversion to metallic Pt when compared to the Pt foil data. Similarly the EXAFS in both K and R spaces appear to be metallic in nature, although visibly dampened. Fitting of the EXAFS allowing for both metallic and oxide phases to be present has been completed using the Artemis software package. Due to the low contribution from the oxide phase to the EXAFS the σ² parameter and bond distances were set from the refinements.
achieved previously when considering the sample after treatment with formic acid to reduce the effect of highly correlating parameters.

The results of the EXAFS fitting are shown in table 3.12. Here it is evident that the major phase component is metallic with oxide phase being within error tolerance of no presence. The refinement of the Pt-Pt coordination number reveals there is a formation of Pt nano-particles due to the under-coordination in respect to bulk Pt, 10.22 instead of 12. By assumption of a spherical particle model this equated to a particle diameter of approximately 42 Å, see Figure 3.19B.

![Table 3.12: Table showing the refined bond distances, disorder parameter \(\sigma^2\) and coordination numbers relating to post exposure to air.](image)

<table>
<thead>
<tr>
<th>Scattering Path</th>
<th>R (Å)</th>
<th>(\sigma^2)</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-O</td>
<td>2.00 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>0.13 ± 0.16</td>
</tr>
<tr>
<td>Pt-O</td>
<td>2.04 ± 0.08</td>
<td>0.00377 ± 0.00195</td>
<td>0.07 ± 0.08</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>2.75 ± 0.04</td>
<td>0.00636 ± 0.00072</td>
<td>10.22 ± 1.20</td>
</tr>
</tbody>
</table>

3.5.4 Summary of the Quasi In Situ XAS Study

The exposure of platinic acid mixed with fumed silica to formic acid vapour under flow of \(N_2\) has been shown to result in no observed change in the structure of the platinic acid. Upon the exposure to an oxygen atmosphere the reduction of the platinic acid to platinum metal has been demonstrated to occur. The reduction to platinum metal has been shown to result in the formation of metallic nano-particles with a diameter of approximately 4 nm.

Given the current available data, no conclusions are made as to the reason exposure to air is required, however it may relate to formation of intermediate states between the formic acid and fumed silica through interaction with silanol groups. Further experiments using IR methods may be able to provide useful insight into the process, and why there is a need for an oxygen source, for the formation of supported Pt nano-particles from platinic acid using formic acid as the reducing agent.
3.6 Chapter Conclusion and Discussion

In this chapter the work has been carried out in collaboration with Elizabeth Raine, University of Oxford who performed the sample synthesis and TEM imaging of the PtZn PVP stabilised and SBA-15 supported samples. The XAS, SAXS and WAXS analysis has been solely performed by myself.

The bulk of this chapter has focused on the characterisation, \textit{ex situ} and \textit{in situ}, of the structure of PtZn bimetallic nano-particles supported in the channels of SBA-15. \textit{In situ} characterisation has been performed using XAS methods on the Pt \(L_3\) and Zn \(K\) edges. \textit{Ex situ} characterisation has focussed upon the use of SAXS and WAXS experiments to determine the pore structure and crystalline phases present within the SBA-15 supported PtZn samples. Here it has been demonstrated that Zn is highly dispersed and bonds in isolation to the amorphous silica walls of the SBA-15 whilst Pt forms nano-particles confined within the channels. On exposure to formic acid, the Zn is demonstrated to leach from the surface of the SBA-15 and form a Zn formate phase, whilst the initial partial presence of oxidic Pt is shown to reduce to form Pt metal nano-particles. The proportion of Zn which is not leached from the SBA-15 surface is shown to depend linearly on the ratio of Pt:Zn, and as such thought to relate to the coverage of Zn adatoms by Pt nano-particles with the pores of the SBA-15.

The synthesis of fumed silica supported Pt nano-particles through the reduction of platinic acid by vapour phase formic acid has been followed using XAS on the Pt \(L_3\) edge. It has been shown that the reduction of the formic acid depends upon there being an available source of oxygen. This has been demonstrated by quasi \textit{in situ} studies to determine the Pt structure prior to formic acid exposure, after exposure to formic acid vapour in \(N_2\) gas flow and after the exposure of the sample mixture to air. The reason for the requirement of a source of oxygen has not been determined but may relate to the reaction of formic acid to surface silanol groups to form an
Finally, the structure of PVP stabilised PtZn nano-particles has also been determined using XAS techniques. Here it has been demonstrated that PVP is able to stabilise the metallic nature of both Pt and Zn. Further to this it has been determined that the PtZn nano-particles are formed of a Pt core and Zn shell and there is limited evidence for a partial alloying to occur.
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Chapter 4

Reducibility and Recycleability of Ceria Supported Catalysts

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<td>4.6.2.3</td>
<td>Pt L3 Edge XANES</td>
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<td>4.6.2.4</td>
<td>Tabulation of XANES Analysis Results and Conclusion</td>
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</tbody>
</table>
The purpose of this chapter is to determine the redox properties of ceria based materials. Here in situ XAS studies have been conducted in addition to is situ X-ray total scattering experiments to follow both the oxidation state of cerium and the structural changes that occur in the fluorite ceria lattice upon reduction with hydrogen. The effect of PGMs to promote ceria has all been studied through consideration of the strong metal-support interaction. The ability of PGMs to promote the reduction of ceria towards low temperatures has been ascribed to the hydrogen spill-over from PGMs to the ceria support.

The recyclability of ceria supported catalysts has also been studied using the same techniques after a room temperature oxidation. This has shown to result in a markedly different behaviour of the ceria based materials. The reduction of ceria has been shown to be promoted at room temperature and is irrespective of the PGM supported or the wt% loading. It has been proposed that room temperature oxidation only results in a mild surface oxidation, passivation, of the PGMs to occur, whilst full re-oxidation of the support ceria is observed.

The complex redox characteristics of a high surface area ceria support in the absence of PGMs has also been established. Whilst the formation of reduced Ce(III) ions is shown to occur upon heating, the return to near full Ce(IV) is observed upon cooling in a reducing atmosphere. Whilst previously this behaviour has been associated to the sintering of nano-particulate ceria, here an alternative is proposed. Evidence for a bulk cerium hydride phase is presented through joint consideration of XAS and X-ray total scattering experiments.

4.1 Introduction

Though ceria can be utilised within many areas of catalysis, it is extensively used as a support for catalysts such as transition metals or platinum group metals (PGMs). These can be used as a single metallic or in combination with other PGMs
as a bimetallic system. Although costly, their long life makes them cost effective,[4] their ability to be dispersed onto a support reduces the cost whilst increase efficiency due to an increased surface area to volume ratio[5]. Noble metals have also been noted to enhance the redox performance and the OSC of the support on which the PGM has been dispersed.[6–9]

This is further complicated by strong metal support interaction (SMSI) which describes the interaction between the metal and the metal support. This effect was first reported by Tauster et al.[10,11] investigating the reduction of metals supported on titania. This showed that CO and H₂ chemisorption was inhibited though not explainable by either poisoning, sintering of metal particles or the encapsulation of metals.[10] This effect is important in three-way catalysis in improving dispersion of the metals on a support as well as reducing sintering, for example the Pt-O-Ce interaction acts as an anchor point from which there is a limitation in the sintering of Pt particles on the surface support.[12] Furthermore the loading of PGMs on a ceria support promotes the surface reduction and removal of oxygen.[13]

In the case of Pd supported on ceria, there is an increase in the OSC, catalytic ability and a promoted reduction from Pd(II) to Pd metal because of a synergistic relationship between the Pd ions and the ceria support.[14,15] The surface interaction between Pd-Ce has been reported showing the formation of metal clusters and of a mixed metal phase $Pd_xCe_{1−x}O_2$.[16] NOₓ and CO conversion[17,20] is promoted by Pd on ceria by a Pd-Ce interaction. There are a few mechanisms in which the SMSI can be formed through such as alloy formation,[21] diffusion of metal into the support/encapsulated by the support,[22] and formation of bonds between the metal and support (via an intermediary oxygen).[23] The electronic interactions forming PGM-M or PGM-O-M structures have been observed by several methodologies.[24,25]

Pt and Pd surface-support interactions have been reported to exist using Raman
spectroscopy whilst resulting in a highly dispersed metal. EXAFS of supported Pt catalysts on the Pt L\textsubscript{3} edge show that where alumina is used as the support Pt-Pt bond formation occurs, indicating metal particle formation. If the Pt is supported onto a ceria based support there is the formation of a Pt-O-Ce bond suppressing any sintering of Pt particles whilst aging. When treated under reducing conditions, the Pt-O-Ce interaction breaks down and Pt metal particles are dispersed across the ceria based support. Due to the support dependent nature of this effect, it would imply the electron density of the oxygen in the support could be the root of this effect. Lin et al reported using a combined methodology that Pt can be found in an oxidic state showing the complete dispersion of the Pt nanoparticles across the ceria support and partial reduction of the ceria by hydrogen spill-over. Furthermore, experiments using energy dispersive EXAFS to follow the oxidation of CO have shown that upon introduction of NO there is a non-oxidative rapid re-dispersion of Pd over the ceria-zirconia surface with the release of CO\textsubscript{2} with subsequent partial re-oxidation of the supported Pd in the absence of CO.

The SMSI can be formed by alloy formation or the encapsulation of the metal within the support. The main driving force for the encapsulation is to minimise the surface energy. SMSI is prone to occur in catalytic support materials with low surface energy e.g. ceria, titania in comparison to silica or alumina. The drive to minimise the surface energy is evidenced using HRTEM as this shows Pd particles covered by a layer of the ceria based support. The incorporation can expand the lattice parameter of the ceria based support and induce strain into the material which can be a driving force for anion migration in the support. The encapsulation, generally, only occurs under reducing conditions above 500°C whilst alloy formation is encountered above 900°C e.g. CePt\textsubscript{5} phases are reported when reducing Pt/Ceria at 900°C.

The SMSI effect has been widely used in discussions of ceria supported metal nano-
particle systems. However, Campbell has coined the term electronic metal support interaction (EMSI), a more specific description of the underlying cause for the often outstanding catalytic activity, which results from a high degree of contact between highly dispersed PGM nanoparticles and ceria with a high surface area. In particular the EMSI between Pt clusters on a ceria support has been shown to exhibit a maximum for Pt clusters of approximately 1.5 nm with small amounts of Ce(III) present within the support structure. The level and nature in which the PGM and support interaction can occur is dependent on synthesis procedure, the support and precious metal loaded.

In light of the significant literature on PGM ceria systems work here has been undertaken here to understand the metal support interactions between Pd, Pt and Rh nano-particles and a high surface area ceria support. The first section of the chapter will describe the characterisation of ceria materials using ex situ and in situ lab based methods. The remainder of the chapter will focus on the in situ study, using primarily XAS and X-ray total scattering synchrotron radiation methods, of the redox characteristics of ceria and on the effect of PGM on the promoted reduction of ceria.
4.2 Characterisation of As-Received Ceria Supported PGM Catalysts

The ceria supported PGM samples investigated were provided by Johnson Matthey and were synthesised by pore volume impregnation. The metal additions were achieved using Pd nitrate, Pt nitrate and Rh nitrate solutions (commercially available from Johnson Matthey). The required volume of diluted metal salt solution was added to approximately to fill the pore volume of the high surface area (HSA) ceria support. Materials were dried at 105°C and fired at 500°C in air. Each PGM was supplied in 1wt%, 2.5wt% and 5wt% concentrations supported over a HSA ceria.

Here temperature programmed reduction (TPR), X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) has been performed by scientists at Johnson Matthey, Sonning Common. Infra-red spectroscopy and intelligent gravimetric analysis (IGA) were performed in addition to the aforementioned characterisation.

4.2.1 Temperature Programed Reduction and Oxidation

Temperature Programmed Reduction (TPR) follows the uptake (or release) of hydrogen through a temperature ramp of a sample. Here the uptake of hydrogen is measured on ceria samples and is indicative of the reduction profile of the samples. TPR analysis has been undertaken on PGM loaded ceria samples and the HSA CeO$_2$ support. TPR was performed using a Micromeritics AutoChem II 2920 instrument. The samples were, under 5%H$_2$/N$_2$ flowing at 30 ml min$^{-1}$, heated from 25°C to 1100°C at 10°C min$^{-1}$. The results for the Pt containing samples, Pd containing samples, Rh containing samples and the bare HSA ceria support are shown in Figures 4.1a-d respectively.
The TPR shows clear uptake of hydrogen dependent on the temperature and PGM. Analysis of the TPR has been performed to report the temperature at which the maximum uptake of hydrogen is observed on all samples is given in table 4.1.

**Table 4.1:** Table of temperatures of maximal TPR $H_2$ uptake for Pd, Pt and Rh loaded ceria samples measured using TPR.

<table>
<thead>
<tr>
<th>PGM</th>
<th>Temperature of Reduction ($^\circ$C)</th>
<th>wt% loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>Pd</td>
<td>72</td>
<td>78 &amp; 112</td>
</tr>
<tr>
<td>Pt</td>
<td>116</td>
<td>165</td>
</tr>
<tr>
<td>Rh</td>
<td>73</td>
<td>78</td>
</tr>
</tbody>
</table>

The Pd and Pt samples can clearly be seen to have a dependence on the wt% loading of PGM of the temperature at which maximal hydrogen uptake is observed. The increase in wt% loading results in a decrease in the temperature at which hydrogen uptake is observed. The uptake of hydrogen relates to the reduction of the initial oxidic PGMs and to the reduction of the ceria support. Whilst the Pd and Pt samples show a clear correlation between the decrease in wt% loading of PGM and the increase in the temperature of the maximal hydrogen uptake, the hydrogen uptake on the Rh samples can be observed to be independent of wt% loading, within reasonable tolerance. The maximal uptake of hydrogen observed on the HSA ceria support was measured at 400$^\circ$C.

Experiments following the uptake of oxygen after a reduction cycle in a reducing $H_2$ atmosphere has been completed has been used to demonstrate the promoted partial reduction of the ceria support in the presence of PGMs. The uptake of oxygen as function of time for all samples is shown in Figure 4.2. Here all supported PGM samples are shown to exhibit similar behaviour with the major uptake of oxygen occurring after approximately 5 minutes, the delay here is proposed to be caused by the large sample environment volume.
Figure 4.1: TPR graphs showing the uptake of hydrogen as a function of temperature. A, B, C and D give the TPR results for the Pt, Rh, Pd and high surface area ceria support respectively.
Figure 4.2: Graphs showing the uptake of oxygen as a function of time. A, B, C and D give the results for the Pt, Rh, Pd and high surface area ceria support respectively. Here the high surface area ceria support is shown on the same scale as the Pt sample to give a sense of the limited uptake of oxygen.
4.2.2 Intelligent Gravimetric Analysis

Intelligent Gravimetric Analysis (IGA) involves measuring in situ the mass of a sample. The loss or gain in sample mass can then be attributed to the expected steps throughout a reaction such as the loss of oxygen through a reduction reaction or adsorbates attaching to the surface of a sample. The experimental equipment utilised allows for microgram differences in mass to be measured. To measure these differences a sample is suspended on a cord, counter balanced by a 100 mg mass. IGA has been used to determine the mass loss from \( \text{CeO}_2 \) during heating in an oxidising atmosphere. This is to determine if adsorbants or contaminants are removed from the sample. In conjunction to IGA mass spectrometry was also performed.

IGA has revealed that under a constant flow in an oxidising atmosphere, \( 5\%O_2/He \), there is significant mass loss upon heating. The results of the sample mass are shown in Figure 4.3A and establish that a 2.5 mg mass drop occurs during heating. The mass of the HSA \( \text{CeO}_2 \) sample undergoes this loss between room temperature and 200°C before stabilising. Also in Figure 4.3A the signal pertaining to \( \text{CO}_2 \) measured using mass spectrometry, blue, downstream from the IGA is shown. Here there is clear production of \( \text{CO}_2 \) suggesting there is adsorbed carbonate species on the as-received HSA \( \text{CeO}_2 \) sample.

A second heating cycle was then undertaken to ascertain whether the process is repeatable or if it is a one time effect. This is shown in Figure 4.3B. Here the mass of the HSA \( \text{CeO}_2 \) sample is shown and remains approximately constant throughout the experiment. This confirms that the mass loss is only observed during the first heating cycle and can be attributed to the desorption of adsorbed carbonate species as \( \text{CO}_2 \).
Figure 4.3: A illustrates the mass of the HSA CeO$_2$ support as a function of temperature during the first heating cycle with an overlay of the CO$_2$ signal acquired using downstream mass spectrometry, shown as black and blue respectively. B shows the mass of the HSA CeO$_2$ support as a function of temperature during the second heating cycle demonstrating no further mass loss is observed.

4.2.3 Infra-red Spectroscopy

IR has been used to demonstrate the presence of cerium carbonate like species within the HSA ceria samples. This is thought to decompose upon heating and is given off as the CO$_2$ mass loss which is observed in the IGA-MS measurements. Figure 4.4 gives the IR spectra obtained on the HSA ceria sample with the carbonate associated bands marked.

Figure 4.4: Comparison of the IR transmission fraction for the HSA ceria sample and a Cerium Carbonate Hexahydrate standard material. The C=O absorption bands are marked by dashed lines with the wavenumbers are given above.
4.2.4 X-ray Diffraction

XRD patterns were collected on a Bruker AXS D8 instrument using the Cu $K_{\alpha}$ emission, $\lambda = 1.54184$ Å. The data was collected between a $2\theta$ range of 10 to 130 $^\circ$. No reflections relating to the PGM phases, metallic or oxidic, were observed. All reflections were identified as relating to the fluorite ceria phase. Crystallite size analysis was performed using the LVol-IB method and the results are shown in table 4.2. The individual patterns are shown in the supplementary information. The results show that all samples are of approximately 5.3 ± 0.1 nm crystallite size.

Table 4.2: Table of results for crystallite size analysis using the LVol-IB method of the PGM/CeO$_2$ samples as received.

<table>
<thead>
<tr>
<th>PGM</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt% loading</td>
</tr>
<tr>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>Pd</td>
<td>5.38 ± 0.09</td>
</tr>
<tr>
<td>Pt</td>
<td>-</td>
</tr>
<tr>
<td>Rh</td>
<td>-</td>
</tr>
</tbody>
</table>

4.2.5 ICP Analysis

ICP analysis has been conducted on the supported PGM samples to determine the wt% loading of each respective PGM on the samples provided, the results are shown in table 4.3. The target loadings were 5%, 2.5% and 1%. Detailed ICP analysis performed on the HSA ceria support is given in table 4.4 showing that the ceria sample is of high purity and thus the catalytic behaviour of these samples can only be attributed to the ceria support, and where appropriate the supported PGMs.

Table 4.3: Table of results for ICP analysis performed on the PGM containing samples.

<table>
<thead>
<tr>
<th></th>
<th>wt% loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>Pd</td>
<td>4.76</td>
</tr>
<tr>
<td>Pt</td>
<td>4.78</td>
</tr>
<tr>
<td>Rh</td>
<td>4.75</td>
</tr>
</tbody>
</table>
Table 4.4: Table of results for ICP analysis performed on the HSA ceria support sample.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>≤20</td>
</tr>
<tr>
<td>Ba</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>≤10</td>
</tr>
<tr>
<td>Ca</td>
<td>≤10</td>
</tr>
<tr>
<td>Cu</td>
<td>≤1</td>
</tr>
<tr>
<td>Fe</td>
<td>15</td>
</tr>
<tr>
<td>Ga</td>
<td>≤5</td>
</tr>
<tr>
<td>Ge</td>
<td>≤5</td>
</tr>
<tr>
<td>K</td>
<td>≤10</td>
</tr>
<tr>
<td>La</td>
<td>≤30</td>
</tr>
<tr>
<td>Mn</td>
<td>≤1</td>
</tr>
<tr>
<td>Na</td>
<td>≤10</td>
</tr>
<tr>
<td>Nd</td>
<td>≤20</td>
</tr>
<tr>
<td>Ni</td>
<td>≤1</td>
</tr>
<tr>
<td>P</td>
<td>180</td>
</tr>
<tr>
<td>Pr</td>
<td>≤30</td>
</tr>
<tr>
<td>S</td>
<td>≤50</td>
</tr>
<tr>
<td>Si</td>
<td>55</td>
</tr>
<tr>
<td>Ti</td>
<td>1</td>
</tr>
<tr>
<td>V</td>
<td>10</td>
</tr>
<tr>
<td>W</td>
<td>≤10</td>
</tr>
<tr>
<td>Zr</td>
<td>≤10</td>
</tr>
</tbody>
</table>

4.2.6 Summary of Lab Based Characterisation

The characterisation of the reactivity of the samples has been undertaken using TPR and subsequently TPO. The uptake of hydrogen is shown to be greatly increased in the presence of PGM supported on the HSA ceria. This is also shown to be a direct inverse correlation between the wt% of supported Pd and Pt and the temperature at which maximal hydrogen uptake lies. The Rh containing samples can be clearly seen to all have a maximum hydrogen uptake at a similar temperature and thus show no dependence on the loading. TPO has shown that after exposure to \( H_2 \) all samples take up oxygen in a broadly similar profile; this is interpreted as the ceria being partially reduced with lattice oxygen vacancies which are filled upon exposure to \( O_2 \). The bare HSA ceria support shows minimal uptake of oxygen suggesting no
such reduction has occurred.

Analysis of the samples using IGA-MS and IR techniques have shown there to be a surface adsorbed carbonate species in the as-synthesised samples. Upon heating this surface carbonate is decomposed and $CO_2$ desorbs from the sample, as seen from the sample mass loss and MS signal. Further analysis has been conducted using XRD which has shown all samples exhibit a very similar particle size. In the XRD patterns no phase is shown relating to PGM, metallic or oxidic, and there is no clear effect on the ceria lattice parameter by the addition of PGMs.

ICP analysis has shown the samples to be very consistent in the wt% loading of PGM and close to the intended 5wt%, 2.5wt% and 1wt% values. In addition, ICP was also employed to determine the concentration of impurities in the HSA ceria support. No large impurity was found and thus the redox chemistry investigated herein is proscribed to the affect of the PGMs and the ceria itself.
4.3 Redox Chemistry of Ceria using High Resolution XANES on the Ce $L_3$ Edge

Understanding the mechanism of reduction of Ce(IV) ions in ceria, in particular in the presence of PGMs is vital for the development of ceria based catalysts. Metal-support interaction operates in these systems to provide unusual catalytic behaviour. Reported here are results from X-ray absorption spectroscopy recorded using high-resolution fluorescence mode, which reveals that the reduction differs considerably depending on the type of PGM metal present in the system. These results suggest that metal support interaction (MSI) is responsible for the reduction of Ce(IV) to Ce(III) at lower temperatures compared to the systems where the metal-support interaction is absent or negligible. Conversion of Ce(IV) to Ce(III) is probed through exposure to a reducing atmosphere up to a maximum temperature of 200°C. Further to this the unusual redox behaviour of the HSA ceria support is investigated in the absence of PGM. Here it has been demonstrated that upon heating in $H_2$ there is a significant contribution to the XANES spectra arising from the formation of Ce(III) ions. However, when cooling in the same $H_2$ atmosphere there is a near total re-oxidation to the Ce(IV) state.

4.3.1 Experimental Data Collection

High-resolution fluorescence detection XAS measurements at the Ce $L_3$ edge were conducted by monitoring the intensity of the Ce $L\alpha_1$ photo emission line at 4840 eV using the high-resolution emission spectrometer at I20-1 beamline at the Diamond Light Source on the PGM/Ceria systems. Typically 3.5 mg of the sample was mixed with 60 mg of fumed silica and pressed into a pellet and subsequently mounted into an in situ cell. In this study the samples were provided by Johnson Matthey and were PGM/ceria materials with either 5wt% Pd, Pt or Rh. Previous TPR for Rh, Pt and Pd samples show a significant absorption of hydrogen below 100°C, see Figure 4.1. The redox chemistry of these samples were probed by heating in a 4%$H_2/He$ atmosphere where measurements were performed isothermally at various temperatures. Due to the limitations on the in situ cell it was not possible
to heat safely above 200°C as a result of using kapton windows and a PTFE liner. A modified cell was used to collect the data on the HSA ceria sample allowing data collection up to a maximum of 400°C at a subsequent beamtime. The analysis of the high resolution XANES (HRXANES) was performed using Athena in a peak fitting methodology.

4.3.2 XANES Fitting

The resolution of the XANES features achieved using HERFD measurements allow for the determination of more features within the XANES spectrum due to the reduced convolution with the instrumental broadening in energy. A peak fitting methodology has been employed for the extraction of the Ce(IV) and Ce(III) content within the samples during in situ reduction experiments on the Ce L₃ edge and has been conducted using the Athena software package. The complex structure of the Ce L₃ edge is due to the 2p³/2 to the 5d⁵/₂ orbital transition. When considering the Ce(IV) peaks B and C arise from the crystal field splitting present within the ceria structure for the screened 2p³/2 to the 5d⁵/₂ transitions. Elsewhere it has been reported that the peaks D₁ and D₂ relate to the unscreened excited states relating to multi-electron processes. Additionally a pre-edge feature has been associated to 2p to 4f transition and is labelled A. The Ce(III) associated peaks are labelled as E and F. An example of HRXANES measured on the Ce L₃ edge is shown in Figure 4.5 for the HSA ceria sample at 400°C, clearly illustrating the enhanced resolution of the features arising from the ceria structure.
Figure 4.5: Example fitted HRXANES structure for the HSA ceria sample at 400°C with labelled peaks A-F. The Ce(IV) and Ce(III) contributions are shown by the shaded red and blue areas respectively.

The position, width and amplitude were refined from a Ce $L_3$ HRXANES spectra of the HSA ceria sample at 400°C and are given in table 4.5. During refinements of all other spectra the peak widths and positions are held constant, only the amplitudes are refined. The methodology allows for the proportion of Ce(III) in the sample during the in situ reduction experiments to be extracted.

Table 4.5: Table of results for XANES fitting giving the peak positions, widths and amplitudes for the HSA ceria sample at 400°C. The position and width values are then kept constant for all other refinements.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>Width (eV)</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge</td>
<td>5725.69 ± 0.05</td>
<td>0.477 ± 0.028</td>
<td>1.000</td>
</tr>
<tr>
<td>A</td>
<td>5720.18 ± 1.31</td>
<td>0.679 ± 0.200</td>
<td>0.109 ± 0.022</td>
</tr>
<tr>
<td>B</td>
<td>5726.72 ± 0.12</td>
<td>1.106 ± 0.047</td>
<td>2.283 ± 0.036</td>
</tr>
<tr>
<td>C</td>
<td>5730.61 ± 0.09</td>
<td>1.609 ± 0.030</td>
<td>4.512 ± 0.041</td>
</tr>
<tr>
<td>D1</td>
<td>5738.10 ± 0.14</td>
<td>3.781 ± 0.162</td>
<td>4.361 ± 0.076</td>
</tr>
<tr>
<td>D2</td>
<td>5740.66 ± 0.31</td>
<td>1.033 ± 0.073</td>
<td>1.014 ± 0.042</td>
</tr>
<tr>
<td>E</td>
<td>5724.69 ± 0.16</td>
<td>1.395 ± 0.052</td>
<td>2.065 ± 0.037</td>
</tr>
<tr>
<td>F</td>
<td>5728.67 ± 0.57</td>
<td>0.954 ± 0.149</td>
<td>0.481 ± 0.034</td>
</tr>
</tbody>
</table>
Figure 4.6: Illustration of the HRXANES fitting undertaken on the HSA ceria, 5%Pd, 5%Pt and 5%Rh samples shown left to right. Here the fits achieved on the datasets relating to the initial, maximum temperature and final points during the reduction cycle are shown from top to bottom respectively. The peak areas relating to Ce(IV), shaded red, and Ce(III) shaded blue are shown.
Example fits are shown for all samples for spectra relating to the initial starting material, at maximum temperature (for the PGM sample 200°C and for the HSA ceria sample 400°C) and the final spectra collected at approximately 30°C are shown in Figure 4.6. The areas relating to the Ce(III) and Ce(IV) peaks have been used to extract the value of the Ce(III) proportion within the ceria samples by equation 4.1.

$$[Ce(III)] = \frac{A[Ce(III)]}{A[Ce(III)] + A[Ce(IV)]}$$ (4.1)

The results of the peak fitting are shown in Figure 4.7 giving the proportion of Ce(III) as a function of temperature. Here it is evident that the presence of PGM loaded onto the HSA ceria promotes the reduction of ceria towards low temperatures. In the absence of PGM, the ceria support has been heated to a higher temperature to show the unusual redox behaviour, there is clear formation of Ce(III) upon heating in the $H_2$ atmosphere. However, upon cooling within the same $H_2$ atmosphere there is a clear oxidation back to almost fully Ce(IV) oxidation state.

**Figure 4.7:** Graph showing the result of the Ce $L_3$ HRXANES plotting the proportion of Ce(III) throughout the *in situ* reduction experiments. The 5%Rh, 5%Pt, 5%Pd and HSA ceria sample results are shown in green, red, blue and black respectively.
4.3.3 Summary of Ce $L_3$ HRXANES

The use of HRXANES and in-particular the peak fitting methodology for the extraction of the Ce(III) contribution to the XANES structure has shown to be a powerful method in following the in situ reduction of ceria. The peak fitting methodology described here is shown to be a robust tool for the interpretation of the evolution of the Ce $L_3$ edge XANES throughout in situ reduction experiments.

Analysis of the HRXANES on the 5%Pd, 5%Pt and 5%Rh samples has demonstrated that the supported PGMs promote the reduction of ceria. The Rh sample is shown to promote the ceria reduction at the lowest temperature, followed by Pd and subsequently Pt, as seen from the relative position of the reduction profiles observed in Figure [4.7]. The promotion of the reduction of ceria is thought to be due to the hydrogen spill-over mechanism coupled with the reverse oxygen spill-over mechanism. The dissociation of hydrogen on the surface of PGMs and subsequent spill-over to the ceria-PGM interface allows for the removal of oxygen from the ceria support. The reverse oxygen spill-over mechanism relates to the migration of bulk lattice oxygen to the ceria-PGM interface. As such both are proposed to participate in the PGM promoted reduction of ceria. The promoted reduction of ceria is temperature irreversible in an $H_2$ atmosphere and relates directly to the removal of lattice oxygen from the ceria.

The HSA ceria support itself shows formation of Ce(III) in $H_2$ whilst heating, however when the sample is cooled in $H_2$ almost full re-oxidation to Ce(IV) is observed. This directly implies that in the HSA ceria sample there is no removal of oxygen from the ceria lattice. Lattice oxygen removal would result in a temperature irreversible, whilst in a $H_2$ atmosphere, reduction of the ceria. Further discussion on this phenomenon is presented when considering the X-ray total scattering experiments.
4.4 Linear Thermal Expansion of Ceria

Measurement and discussion of the thermal expansion properties of ceria and nano-particulate ceria is vital towards understanding the redox properties of the ceria materials when considering results derived from XRD refinements. Here the thermal expansion properties of bulk ceria and nano-particulate ceria have been investigated using X-ray total scattering. To determine the linear thermal expansion coefficient and its dependence on temperature a comparison of a linear and quadratic model has been used. The samples investigated here are a NIST ceria diffraction standard material, quoted as having a crystallite size of approximately 380 nm, and a HSA ceria sample which has been shown to have a particle size of approximately 5 nm.

Previous studies in the literature suggest that there is both a temperature dependence and a particle size dependence on the linear thermal expansion coefficient of ceria. The effect of dopants into the ceria lattice on the linear thermal expansion properties have also been studied elsewhere. The values obtained here on the HSA ceria sample are used to aid the interpretation of the lattice parameter obtained from Rietveld refinements from in situ X-ray total scattering experiments probing redox properties of ceria and ceria supported systems.

4.4.1 Experimental Data Collection

Total Scattering allows for the measurement of the thermal expansion of ceria. This has been accomplished through heating NIST ceria and HSA ceria samples in a 20%O₂/N₂ environment. Due to the observation of the release of carbon dioxide from the high surface area ceria sample upon heating these results are derived from the controlled cooling from 450°C to room temperature with a ramp rate of 10°C/min. Data was collected using the I15-1 beamline at Diamond Synchrotron. The sample was loaded into a 0.9mm internal diameter fused quartz capillary. The data was processed using DAWN science and xPDFsuite to obtain the total scattering pair distribution function G(r)s.
4.4.2 XPDF Refinement Results

Analysis has been undertaken using PDFGui to extract the lattice parameter of the fluorite ceria phase, fitting to a maximum radius of 20 Å and refining the lattice parameter and thermal disorder parameters relating to the cerium and oxygen atoms. Comparison of an assumed linear thermal expansion and a temperature dependent instantaneous linear thermal expansion model are shown for both samples investigated. Typically the weighted residual from the fitting was 0.11 for all datasets. Refinements undertaken on the high surface area ceria sample assumed a spherical particle for modelling the dampening of the PDF whereas this was not used when considering the NIST sample due to the large crystallite size, 390 nm.

Figures 4.8A and 4.8B show the fitting undertaken to the $\Delta l/L$ as a function of temperature for a linear and quadratic model of expansion respectively. Effects observed on cooling have been solely attributed to the thermal contraction of the ceria fluorite lattice. Whilst the linear model is seen to represent the data well, the residual sum of squares (RSoS) can be used as a measure for comparison of the fitting. In the case of the fitting to the NIST ceria sample the RSoS is calculated as $7.29 \times 10^{-7}$ and $2.09 \times 10^{-7}$ respectively for the linear and quadratic fitting. Similar results were achieved on the HSA ceria sample.

Comparison of the results for the HSA ceria and NIST ceria sample is shown in Figure 4.9. Here there is a marked decrease, in both the linear and quadratic models, in the thermal expansion coefficient for the HSA ceria sample in comparison to the NIST ceria sample. This may be due to the nano-particulate nature of the HSA ceria sample. A study to correlate the particle size on the expansion of the ceria lattice with temperature could potentially be a method by which the particle size of ceria nano-particles can be extracted. Studies have shown nano-particle thermal expansion is dependent upon the particle size, in particular ceria shows a decrease in thermal expansion with decreasing particle size. However, here PDF studies using
Figure 4.8: Graphs depicting the fitting to extract the thermal lattice expansion coefficient of the NIST ceria sample using a linear model, A, and quadratic model, B, for the dependence of $\Delta l/L$ with temperature to extract the temperature independent and dependant thermal lattice expansion coefficients.

Continuous data collection during heat ramping allow for the difference between a linear and quadratic models to be determined. Fundamental mechanical properties of materials such as the bulk modulus and heat capacity depend on its response to temperature, as such total scattering experiments may provide a method by which such material properties can be extracted.

Figure 4.9: Graph showing the linear thermal expansion coefficient and temperature dependant thermal expansion coefficients, dashed and solid lines, for the NIST ceria and HSA ceria samples, shown in black and red respectively.
4.4.3 Summary of Linear Expansion Analysis

Here it has been demonstrated that the thermal expansion properties of ceria depend both on the crystallite size and the temperature. The HSA ceria sample is shown to have a reduced linear thermal expansion coefficient when compared to the larger NIST ceria sample. Meanwhile the effect of temperature on the thermal expansion has been approximated to be a 2nd order correction on the linear thermal expansion coefficient. However, this is only found to be a small effect noted by the limited deviation from the linear thermal expansion coefficient.

In the linear expansion approximation the HSA ceria sample is noted as having a thermal expansion coefficient of \((10.03 \pm 0.01) \times 10^{-6} \, K^{-1}\). This value will be used to aid the interpretation of the instantaneous expansion coefficient of the ceria materials. Expansion not arising from thermal expansion of the ceria lattice, that which has an instantaneous lattice expansion coefficient greater than \(10 \times 10^{-6} \, K^{-1}\), is interpreted as being due to the experimental conditions.
4.5 Rapid X-ray Total Scattering Studies Probing the Promoted Reduction of Ceria

4.5.1 Experimental Data Collection

The reduction of various ceria based materials was followed using x-ray total scattering at beamline 11-ID-B at the APS. This study completed 3 redox cycles using 5% $O_2/He$ as the oxidising atmosphere and 3.5% $H_2/He$ as the reducing atmosphere. Approximately 20mg of sample were loaded into quartz capillaries. The temperature was ramped from 30°C to 450°C with the temperature recorded on the sample using a thermocouple within the quartz capillary. This beamline allows for the rapid collection of total scattering data with a time resolution achieved of 2 seconds. This corresponds to a temperature resolution of 0.33 °C during a ramp of 10°C min$^{-1}$ between data points and a total of approximately 10,000 datasets were collected per sample over a period of 6 hours.

Conversion of the image data was undertaken using Fit2D and an empty capillary was measured for purposes of background subtraction. The resultant I(Q) data was then Fourier transformed using xPDFsuite in a batch process to give the data in terms of real space, G(r). Redox cycling experiments were carried out on various PGM/ceria samples: 1%, 2.5% and 5% of Pd, Pt and Rh loaded ceria, as well as the HSA ceria sample.

4.5.2 XRD and XPDF Analysis

The total scattering data can also be analysed, prior to the FT to real space, by refining the Bragg diffraction component using Rietveld analysis methods. For this purpose GSAS was employed to extract the lattice parameter of the ceria phase of the sample. Rietveld analysis of the total scattering data was performed for all samples. Analysis was also performed using PDFGui to refine the ceria fluorite lattice structure observed in the PDF. However, due to the results being fundamentally
the same as those observed with the Rietveld analysis they are not presented here.

Surface maps showing the diffraction between $2.4^\circ$ and $4.4^\circ 2\theta$ for the HSA ceria, 5%Pd, 5%Pt and 5%Rh are shown in Figure 4.10 parts A, B, C and D respectively. The formation of PGM metal nano-particles is suggested due to the subtle increase in intensity observed, when compared to the HSA ceria sample, at $3.65^\circ 2\theta$, for the Pd(111) and Pt(111) reflections, and at $3.75^\circ 2\theta$ for the Rh(111) reflection. Further to this partial oxidation is, although these features are subtle, suggested upon exposure to oxygen due to the sudden decrease in intensity, marked by a change to a dark blue colour. This coincides with the introduction of oxygen at approximately 105 minutes. A partial oxidation of the PGM metal nano-particle would result in a decrease in the intensity of the PGM(111) reflections. Whilst clear peaks are observed for the Pd(111) and Pt(111) reflections, the presence of Rh(111) is less clear.

Peak fitting of the PGM reflections, on the 5%PGM samples, has been undertaken to extract the lattice parameter of the supported PGM nano-particles throughout the redox experiments. Peak fitting methods yield large amounts of data pertaining to the PGM phase. Here, results are shown for the lattice parameter, relative crystallinity analyses and where possible, analysis has been performed to extract the Debye temperature of the PGM metal phase.
Figure 4.10: Figures depicting the XRD between 2.4° and 4.4° 2θ. The intensity is given depending on colour of the surface map. The temperature is given as a function of time as the black trace overlay. Subtle differences in the region around 3.70° 2θ between the PGM samples and the HSA ceria are suggestive of PGM metal formation. Figures A, B, C and D represent the HSA ceria, 5% Pd, 5% Pt and 5% Rh samples respectively. The PGM(111) reflection are labelled and identified by the dashed black line.
4.5.2.1 Ceria XRD and XPDF Analysis

Rietveld analysis\textsuperscript{51} of all samples has been performed using GSAS\textsuperscript{59,60} to extract the lattice parameter of the crystalline ceria phase present in the sample; an example Rietveld refinement fit is shown in Figure 4.11. GSAS was operated in batch refinement mode using a model refinement relating to the HSA ceria support at room temperature as the starting point for all samples. The sequential fitting in batch operation takes the refined parameters from the previous fit as the starting point, as such it is possible to reduce the error on the refinements. During the XRD Rietveld refinements only the lattice parameter, thermal disorder parameters, scale factor and the background were refined. Oxygen occupancy was not explored due to the strong correlation with both the scale factor and the thermal disorder parameters. The XRD contains only limited information regarding the oxygen atoms due to the difference in scattering factors of cerium and oxygen respectively.

![Figure 4.11: Example Rietveld refinement between 1.2° and 22° 2θ completed on the HSA ceria support sample. Here the data is given in black points, the Rietveld fit is shown in red whilst the Chebyshev polynomial background and fit residual are shown in dashed blue and black line respectively.](image)

The HSA ceria support has also been investigated through peak fitting to the PDF $G(r)$. For this purpose a generalised peak fitting program was developed for rapid analysis of in situ X-ray total scattering experiments during the data collection. Detection of peaks is carried out using a peak finding algorithm with a baseline
fitted using an asymmetric least squares approach. Demonstration of the peak fitting is shown in Figure 4.12A. Here peak fitting has been applied to a high surface area ceria sample with a maximum radius of 10.7 Å with automatic peak searching employed for the initial estimates of the peak positions shown as red crosses. The residual of the fitting is shown as the black line below the fit, whilst the data is given in blue circles and a green line gives the fit to the data. Here also shown is the baseline extracted using an asymmetric least squares algorithm. Figure 4.12B gives the reduced G(r), baseline subtracted, for the ceria sample demonstrating the data upon which the fitting using Gaussian profiles.

![Figure 4.12A](image1.png)

**Figure 4.12:** A Example pair distribution function G(r) peak fitting to a high surface area ceria sample between 0 and 10.6 Å. The baseline is shown as a red dotted line with the data shown in blue and the fit shown in green. Red crosses are used to illustrate the position of the fitted peaks. B is an example of the reduced G(r) used for peak finding and surface mapping.

The results obtained on the HSA ceria support XRD are shown in Figure 4.13A throughout two redox cycles, black. Also shown on this Figure is the Ce-Ce inter-atomic distance obtained from peak fitting of the PDF data. The temperature on the Figure is displayed by the blue line, whilst the grey and white areas are used to display the atmosphere experienced by the sample, 5%O₂/He and 3.5%H₂/He respectively. There are several features shown that are of particular interest when
exploring the unusual redox behaviour of the ceria support.

Firstly the initial lattice parameter is shown to be expanded as compared to the oxidised sample after the first reduction cycle. The starting lattice parameter is refined to be $5.4164 \pm 0.0003 \, \text{Å}$, whilst the re-oxidised sample exhibits a lattice parameter of $5.4090 \pm 0.0003 \, \text{Å}$. The difference here can be explained by considering the lattice contraction that occurs between 20 and 25 minutes, a temperature range between $100^\circ C$ and $170^\circ C$. This temperature range correlates with the release of $CO_2$ and drop in sample mass observed in the IGA-MS experiment previously discussed. The initial presence of carbonate species is also shown in the IR. Therefore the contraction in the ceria lattice is ascribed to the removal of carbonate species that are adsorbed onto the surface. The second reduction cycle shows a minor contraction upon heating, demonstrating that the majority of surface carbonates are removed during the first reduction cycle.

![Figure 4.13](image)

**Figure 4.13:** A shows the lattice parameter refinement obtained from Rietveld analysis for the HSA ceria support sample, black. Here the Ce-Ce distance obtained from peak fitting of the PDF is also shown for comparison, red. Whilst the blue overlay represents the temperature during the redox cycling experiment. The grey and white areas show the atmosphere the sample is exposed to, 5% $O_2/He$ and 3.5% $H_2/He$ respectively. The typical error on the Ce-Ce distance and lattice parameter are shown by error bars in red and black on the Figure. B shows an enhanced view of the difference observed upon cooling using XRD and peak fitting refinements.

The second point of note regarding the lattice parameter and Ce-Ce distance refinements occurs upon cooling under a reducing dilute $H_2$ atmosphere. Below $100^\circ C,$
at a time between 100 and 105 minutes and again at a time between 200 to 205 minutes for the second redox cycle, a sharp contraction in both the lattice parameter and the Ce-Ce distance is observed. Crucially here is the fact that at these points no oxygen has been introduced into the system. Figure 4.13B gives an enhanced view of the cooling portion for the first redox cycle. Here the distinct difference between the Ce-Ce distance extracted from peak fitting of the G(r) and the lattice parameter refinement from XRD is visible. This directly suggests that there is a very local distortion in the environment surrounding the cerium cations.

The local distortion in the ceria lattice is further evidenced by the similar behaviour, albeit with much greater error, observed on the Ce-O distance at approximately 2.34 Å, Figure 4.14A. When plotting the 3rd Ce-Ce distance, approximately 6.6 Å, overlayed with the Rietveld lattice parameter this distortion upon cooling is not shown, Figure 4.14B, instead following the Rietveld refined lattice parameter very closely.

**Figure 4.14:** A shows the lattice parameter refinement obtained from Rietveld analysis for the HSA ceria support sample, black. Here the Ce-O distance obtained from peak fitting of the PDF is also shown for comparison, red. The temperature is not shown for the purpose of plot clarity. The grey and white areas show the atmosphere the sample is exposed to, 5%O₂/He and 3.5%H₂/He respectively. The typical error on the Ce-O distance and lattice parameter are shown by error bars in red and black on the Figure. B gives the similar plot for the 3rd Ce-Ce distance.

The expansion of the ceria lattice, above that due to thermal expansion, is inter-
interred as due to the formation of Ce(III) ions within the fluorite lattice. The nature of the ceria lattice parameter to collapse upon cooling in H₂ suggests that oxygen is not removed from the lattice, present Ce(III) is converted to Ce(IV). Therefore the expansion in the HSA ceria support lattice and the observed Ce(III) fraction from Ce L₃ XANES analysis must be due to an alternative process. This is suggested as the formation of a cerium hydride phase within the fluorite ceria lattice, whereby hydrogen is absorbed into the ceria lattice. Hydrogen is proposed to exist within the octahedral holes at the centre of the fluorite lattice in a positive oxidation state surrounded by a cube of O²⁻ anions. Upon cooling the presence of hydrogen is proposed to be unstable in the contracted ceria lattice and is released. As this is not proposed to occur on the PGM containing samples, further discussion of a potential cerium hydride is left until Chapter 5 where further evidence is put forward for ceria coated alumina supported PGM samples.

4.5.2.2 Pd(111) Peak Fitting and Pd/Ceria Rietveld Analysis

Peak fitting to the 5%Pd/CeO₂ sample was undertaken using a custom written code for generalised peak fitting. The baseline was subtracted using an asymmetric least square approach and a single Gaussian was used to extract the Pd(111) reflection, position and area, for analysis of the relative ‘crystallinity’ and lattice parameter of the supported Pd nano-particles. The crystallinity, χ, is calculated by considering the ratio of the peak area Aₖ and the maximum area observed of the Pd(111) reflection Aₘₐₓ:

\[
\chi = \frac{A_k}{A_{max}} \quad (4.2)
\]

whilst the lattice parameter, a, is derived from the Bragg equation such that, for the (111) reflection:

\[
a = \frac{\lambda \sqrt{3}}{2 \sin \frac{\theta}{2}} \quad (4.3)
\]
where $\lambda$ is the wavelength of the incident X-ray beam, 0.1432 Å, and $2\theta$ is given by fitting the Pd(111) reflection position using a Gaussian profile. Fitting was only possible where a peak was present, as such fitting is not given below 15 minutes, equivalent to 80°C. Therefore, the formation of Pd nano-particles by reduction of initial PdO can be said to occur at above 80°C. Fitting results are shown in Figure 4.15A giving the extracted lattice parameter, black data points, from the Pd(111) reflection and the relative crystallinity, blue data points, of the Pd nano-particles to illustrate the particle growth. Figure 4.15B gives an example fit to a dataset at a time of 80 minutes into the redox experiment, equivalent to a temperature of approximately 250°C during the cooling phase of the first redox cycle.

![Figure 4.15: A shows the lattice parameter extracted from the Pd(111) XRD reflection, black, along with the relative crystallinity, blue. The temperature as a function of time is given by the red trace overlay, whilst the white and grey areas give the gas which is being flowed, 3.5%H$_2$/He and 5%O$_2$/He respectively. B gives an example Gaussian peak fit, green, used to obtain the lattice parameter and peak area. The base line is shown as a red dashed line and the data is given in blue.](image)

Extraction of the Pd lattice parameter provides a wealth of information on the Pd phase present within the 5%Pd/CeO$_2$ sample. Here, the growth of the Pd phase can be seen to occur above 80°C through the increase in the crystallinity, whilst the sharp rise in the lattice parameter upon cooling back to 30°C is interpreted as the formation of a Pd hydride phase with a maximum lattice parameter observed of 3.945 ± 0.001 Å. Upon introduction of oxygen this Pd hydride is shown to be
removed through the collapse of the lattice parameter down to $3.895 \pm 0.001 \, \text{Å}$, which is only slightly enlarged compared to that reported for bulk Pd metal of $3.867 \, \text{Å}$ by Davey. The decrease in crystallinity associated with the formation of Pd hydride suggests a degree of disorder being introduced into the system. The further drop in crystallinity is associated with the introduction of oxygen into the capillary. This is suggested to be due to a partial oxidation, thus decreasing the quantity of metallic Pd in the sample. No clear PdO phase is observed in the XRD suggesting any PdO does not form a clear crystalline phase.

Further to this, the introduction of oxygen is associated with a rise in temperature recorded on the thermocouple mounted within the capillary. Figure 4.16 shows the temperature as a function of time, specifically this is shown for around the oxidation step of the redox cycling experiments. Endotherms and exotherms are visible, and marked. On switching of gas there is initially a drop in temperature which can be regarded as due to the a possible temperature difference in the gases. The second feature displays a sharp increase in temperature to a maximum of nearly $40^\circ \text{C}$, which can be related to the exothermic oxidation reaction. Once the oxidation is complete, the temperature of the sample can clearly be shown to drop and settle at $30^\circ \text{C}$, the set point of the furnace. These temperature variations are considered to be a measure of the exhaust gas temperature immediately after the sample. The sharp drop in temperature implies there is no significant increase in the bulk temperature.

\footnote{Error estimation is performed through consideration of a covariance matrix during the refinement procedure and does not serve to represent systematic errors introduced through data correction and integration procedures.}
Figure 4.16: Graph showing the temperature changes observed during the oxidation step after a reduction cycle has been completed for the 5% Pd/CeO$_2$ sample.

Figure 4.17A gives the XRD surface map relating to the Pd(111) reflection with the baseline removed to clearly show the growth of the Pd metallic phase in the first reduction cycle, signified by the increase in intensity. This is followed by the hydride formation, visible by sharp shift to lower 2$\theta$, and partial oxidation, noted by the reduced intensity of the Pd(111) reflection after the introduction of oxygen at room temperature. This Figure also depicts the second cycle of reduction to demonstrate the rapid rise in the Pd(111) intensity once exposed to H$_2$ whilst also showing that no growth in the Pd nano-particles is observed. Using the refined lattice parameter during the heating phase of the second cycle it has been possible to determine the Debye temperature of the supported Pd nano-particles.

The Debye temperature can be extracted by consideration of the thermal lattice volume expansion and the internal energy. Grünesian theory shall be introduced in further detail in Chapter 5 when considering the properties of supported Au. Figure 4.17B illustrates the fitting of the lattice volume expansion using Grünesian theory, the red line plots the theoretical value of the lattice volume showing strong agreement with the experimental data during heating on the second cycle of reduction in a dilute 3.5%H$_2$/He atmosphere. The extracted value of the Debye temperature is 276 ± 6 K which is in close agreement to literature values of 274 K for bulk Pd.$^{68,69}$
Figure 4.17: A gives the reduced diffractogram for the region covering the Pd(111) reflection on the 5\%Pd/CeO$_2$ sample. The temperature as a function of time is shown by the black trace overlay. B shows the fitting to lattice volume during the heating phase of the second reduction cycle with Gr"unessian theory to extract the Debye temperature of Pd, theoretical value of the Pd lattice volume is shown in red.

The discussion of the Rietveld analysis of the Pd containing samples shall proceed through consideration of the refined ceria lattice parameter and related instantaneous expansion coefficient. Figure 4.18A illustrates the lattice parameter of the fluorite ceria phase throughout the first and the start of second reduction cycle for experiments on the 5\%Pd, 2.5\%Pd and 1\%Pd samples shown in black, red and blue respectively. The temperature is shown as a green overlay. Here it is evident that the effect of Pd is to promote the reduction of the ceria, a non linear expansion of the lattice parameter with temperature is observed. Linear expansion with temperature would be signified by the gradient of the lattice parameter being constant as a function of temperature. Upon cooling in $H_2$ only thermal contraction is observed which suggests there is no further reduction and moreover no oxidation of the ceria support. The introduction of oxygen is noted to cause a sharp decrease in the ceria lattice parameter, this is associated with the oxidation of the ceria.

Further analysis of the heating phase of the first reduction cycle is shown by considering the instantaneous expansion coefficient. shown in Figure 4.18B. Here it is possible to determine more clearly the effect of the wt\% loading of Pd. The peak
maxima here observed in the instantaneous expansion coefficient as a function of
temperature show remarkable resemblance to those observed in the TPR previously
discussed, see Figure 4.1. Therefore the expansion of the ceria lattice and as such
the reduction of the ceria lattice, can be directly related to the uptake of hydrogen
observed in TPR measurements. There can be seen to be a direct correlation be-
tween the temperature of the ceria reduction and the $wt\%$ loading of Pd, the greater
the $wt\%$ loading the lower the reduction temperature of ceria.

Figure 4.18: A shows the lattice parameter refinement obtained from Rietveld analysis for
the Pd containing samples, black, 5\%Pd, red, 2.5\%Pd and blue, 1\%Pd. The
grey and white areas show the atmosphere the sample is exposed to, 5\%O$_2$/He
and 3.5\%H$_2$/He respectively. Temperature is given by the green overlay. B
gives instantaneous expansion coefficient derived for each of the Pd contain-
ing samples as a function of temperature for the heating cycle of the first
reduction cycle.

Analysis of the second reduction cycle demonstrates a different redox behaviour as
compared to the first. Upon introduction of $H_2$ into the capillary an almost instan-
taneous lattice expansion is observed. Here the reduction temperature can be said
to be independent of the $wt\%$ loading of the Pd. The introduction of oxygen, whilst
fully oxidising the ceria support, results in an easily reducible oxide surface on the
supported Pd particles. Further analysis of this is carried out when considering the
XAS experiments on the Pd $K$ edge.

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4.5.2.3 Pt(111) Peak Fitting and Pt/Ceria Rietveld Analysis

Similar analysis on the Pt(111) reflection observed in the XRD for the 5%Pt/CeO$_2$ sample has been performed using peak fitting. The surface map shown in Figure 4.19A gives the baseline corrected peak intensity throughout two reduction-oxidation cycles. Here it is noticeable that the signal to noise ratio of the data is somewhat reduced as compared to the 5%Pd sample, shown in Figure 4.17A. The lattice parameter error given from the covariance matrix of the Gaussian peak fitting gives a value of ±0.004 Å, 4 times greater than that of the Pd sample. Therefore only analysis of the Pt lattice parameter and relative crystallinity have been performed. Analysis using Grünesian theory requires a lower error on lattice parameter data points to provide a meaningful result. Further to this, as can be seen in Figure 4.19A there is a suggestion of particle sintering during the second redox cycle which may affect the validity of the application of Grünesian theory which requires lattice volume expansion to be derived only from thermal effects.

Figure 4.19B displays both the lattice parameter, black, and crystallinity, blue, as a function of time through the first reduction-oxidation cycle. The red overlay displays the temperature. A note regarding the crystallinity, for the purpose of plot clarity this has been smoothed using a Savitzky-Golay filter of the first order and window size 80 data points. A plot showing the raw crystallinity data and the smoothing have been shown in the supplementary Figures. The lattice parameter of the metallic Pt nano-particles, at room temperature prior to oxidation is refined to be 3.922 ± 0.004 Å, this compared favourably to 3.920 Å reported by Davey.$^{67}$

It can be remarked that there is a steady rise in crystallinity of the 5%Pt sample throughout the shown redox cycle. This is attributed to the reduction of Pt$O_2$ like species to Pt metal and then the growth of the Pt metal nano-particle through sintering. Upon introduction of oxygen there is an increase in Pt lattice parameter observed. Concurrent to this there is a significant drop in the relative crystallinity
suggesting only 37% of the previous Pt metal phase is present upon oxidation. Reduction in the relative crystallinity is attributed to the partial oxidation of Pt.

**Figure 4.19:** A shows the reduced diffractogram for the region covering the Pt(111) reflection on the 5%Pt/CeO$_2$ sample. The temperature as a function of time is shown by the black trace overlay. B gives results of the lattice parameter and relative crystallinity refinements. The temperature as a function of time is shown by the red trace overlay. The grey represents the introduction of oxygen atmosphere whilst the white area relates to measurements under dilute 3.5%H$_2$/He.

Similar analysis has been performed on the Pt containing samples. Here, as with the Pd containing samples, the Rietveld refined lattice parameter is shown throughout the first reduction cycle and the heating phase of the second, Figure 4.20A. During the first reduction cycle, the expansion of the ceria lattice is observed to be highly dependent on the wt% loading of Pt. The higher the wt% loading of Pt, the lower the reduction temperature of ceria.

Further analysis of the lattice expansion of ceria observed upon heating during the first reduction cycle is shown in Figure 4.20B through consideration of the instantaneous expansion coefficient as a function of temperature. Here, similar to the Pd samples, resemblance to the TPR on these samples is observed. Upon cooling, during the first reduction cycle, a linear thermal contraction is observed, which suggests there is no further reduction or any oxidation of the ceria support. With the introduction of oxygen at room temperature a sharp drop in the ceria lattice parameter
observed for all samples. This is associated to the oxidation of the support ceria.

![Graph](image1.png)

**Figure 4.20:** A shows the lattice parameter refinement obtained from Rietveld analysis for the Pt containing samples, black, 5%Pt, red, 2.5%Pt and blue, 1%Pt. The grey and white areas show the atmosphere the sample is exposed to, 5%O₂/He and 3.5%H₂/He respectively. Temperature is given by the green overlay. B gives instantaneous expansion coefficient derived for each of the Pt containing samples as a function of temperature for the heating cycle of the first reduction cycle.

The second reduction cycle is notable for the lack of dependence on the wt% loading of the Pt to the reduction temperature of the ceria. Here all Pt containing samples are shown to reduce rapidly after the introduction of H₂ into the reaction capillary. This is indicated by the alignment, in time and temperature, of the expansion inflection of the second reduction cycle.

### 4.5.2.4 Rh(111) Peak Fitting and Rh/Ceria Rietveld Analysis

The baseline subtracted Rh(111) reflection is shown in the surface map of Figure 4.21A. Here again the signal to noise ratio is reduced and as such only analysis of the lattice parameter and crystallinity have been performed. The error on the lattice parameter is given as ±0.005 Å. From the surface map there is also evidence of particle sintering during the second redox cycle, as such analysis using Grünesian theory, like in the 5%Pt case, has not been attempted here.

The results of the peak fitting analysis are shown in Figure 4.21B. The lattice pa-
parameter of the metallic Rh nano-particles, at room temperature prior to oxidation is refined to be $3.824 \pm 0.005 \, \text{Å}$, this result is similar to the lattice parameter reported by Hall et al.\textsuperscript{70} of $3.920 \, \text{Å}$. Similar to the Pd and Pt analysis, the relative crystallinity is shown as the blue trace and illustrates the formation of metallic Rh nano-particles through the reduction of oxidic Rh and particle sintering. Upon introduction of oxygen, the majority of the Rh(111) intensity is lost, the relative crystallinity suggests only 22% of the metallic Rh remains. The remainder of Rh is either oxidised or re-dispersed over the ceria support.

![Figure 4.21](image-url)

**Figure 4.21**: A gives the reduced diffractogram for the region covering the Rh(111) reflection on the 5%Rh/CeO$_2$ sample. The temperature as a function of time is shown by the black trace overlay. B gives results of the lattice parameter and relative crystallinity refinements. The temperature as a function of time is shown by the red trace overlay. The grey represents the introduction of oxygen atmosphere whilst the white area relates to measurements under dilute 3.5%H$_2$/He.

The analysis of the Rh containing samples yielded results that are similar in nature to those obtained on the Pd and Pt containing samples. However, whilst the Pd and Pt samples showed a clear dependence on the wt% loading of the supported PGM metal, the Rh sample shows no such dependence. The lattice expansion observed in the ceria support is independent of the loading of Rh. This is seen in the alignment of the inflection in the lattice expansion upon heating in $H_2$. Again the instantaneous expansion coefficient was employed to determine the temperature at which the maximum rate of lattice expansion is observed, this supports the previous state-
ment and shows all samples observe a maximum expansion rate at approximately 130°C.

The independence of the temperature of reduction and the wt% loading of Rh may be due to the dispersion of Rh being high. Comparison of the intensity of the diffraction peaks relating to the Pd(111) and Rh(111) for the same 5wt% loading demonstrates that there is significantly less crystalline metallic Rh present. The diffraction by metallic Rh nano-particles is only observed above approximately 200°C suggesting the Rh nano-particles are particularly small. As such Rh is more highly dispersed over the ceria support. It can also be noted that the TPR profiles for all the Rh containing samples show a similar temperature for the uptake of hydrogen, albeit at a lower temperature than that at which the ceria lattice expansion is observed. This suggests the spill-over of hydrogen from Rh may be limiting the rate of reduction of the ceria support. When compared to the much longer isothermal measurements undertaken on the Ce L₃ edge, the expansion of the ceria lattice is somewhat delayed in comparison to the formation of Ce(III). This gives credence to the suggestion the promoted reduction of ceria may be a hydrogen dissociation limited process below approximately 130°C. The dissociation of hydrogen depends upon the availability of metallic Rh surfaces. As such the rate of reduction of the initial oxidic Rh metallic state and subsequent sintering of the metallic Rh to form nano-particles is thought to be the cause of the difference between the isothermal and dynamic measurement modes for the Ce L₃ XAS and X-ray total scattering experiments. The properties of the supported Rh are discussed in further detail when considering the Rh K edge XAS experiments.

The second reduction cycle, after oxidation of the Rh containing samples, shows reduction occurring with minimal delay from the introduction of H₂. As with the Pd and Pt samples the reduction of the ceria, observed through the lattice expansion, is noted to occur at near room temperature and coincide for all samples.
Figure 4.22: A shows the lattice parameter refinement obtained from Rietveld analysis for the Pd containing samples, black, 5%Rh, red, 2.5%Rh and blue, 1%Rh. The grey and white areas show the atmosphere the sample is exposed to, 5%O$_2$/He and 3.5%H$_2$/He respectively. Temperature is given by the green overlay. B gives instantaneous expansion coefficient derived for each of the Rh containing samples as a function of temperature for the heating cycle of the first reduction cycle.
4.5.3 Tabulation of X-ray Scattering Results and Summary

Broadly speaking, the results of the XRD analysis relating to the promoted reduction of ceria by PGMs has been shown to be in agreement with the HRXANES analysis. The lattice expansion of ceria has been attributed to the formation of Ce(III) ions within the fluorite ceria lattice. All samples show a lattice expansion above that of linear thermal expansion during heating under a $H_2$ atmosphere. To extract the temperature at which the maximum rate of expansion is observed analysis of the instantaneous expansion coefficient has been performed, the results of which are shown in table 4.6. Here the reported temperatures are given for the peak maxima observed in the instantaneous expansion profiles shown previously.

**Table 4.6**: Table of results for maxima of the instantaneous expansion coefficients during the heating portion of the first reduction cycle in $H_2$.

<table>
<thead>
<tr>
<th>wt% loading</th>
<th>$\alpha_{\text{inst}}$ maximum ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>111</td>
</tr>
<tr>
<td>Pt</td>
<td>137</td>
</tr>
<tr>
<td>Rh</td>
<td>141</td>
</tr>
<tr>
<td>2.5%</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>106, 145</td>
</tr>
<tr>
<td>Pt</td>
<td>169, 221</td>
</tr>
<tr>
<td>Rh</td>
<td>132</td>
</tr>
<tr>
<td>1%</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>168</td>
</tr>
<tr>
<td>Pt</td>
<td>205</td>
</tr>
<tr>
<td>Rh</td>
<td>141</td>
</tr>
</tbody>
</table>

Here all temperatures reported for the maxima of the instantaneous ceria lattice expansion coefficient appear to be systematically offset from those reported in the TPR analysis, table 4.1. The cause of this could be due to several differences between the TPR and XRD analyses. TPR profiles are representative of the whole sample and as such give the convoluted contributions from both the reduction of the initial PGM oxide and the reduction of the ceria. In the case where the PGM oxide reduction is a precursor step prior to the reduction of ceria, as is proposed by considering the hydrogen spill-over mechanism from the PGMs in metallic state, the maxima of the TPR profiles may be lower than the maxima of the instantaneous ceria expansion profiles.
Further to this, the reduction of the ceria by hydrogen spill-over may depend on the size of PGM nano-particles and the relative surface area of the PGM in metallic phase. As seen in the analysis of the PGM(111) reflection in the XRD for the 5wt% samples, there is a significant growth in the PGM particle sizes during heating. This is seen in the increase in the relative crystallinity derived from the PGM(111) peak area. Whilst the Pd nano-particles are quick to form, the Pt and Rh nanoparticles can be seen to grow slowly and do not reach a maximum size during the heating cycle. As such, the relative crystallinity provides evidence of nano-particle sintering. To investigate the effect of the PGM oxidation state on the reduction of ceria, XAS has been performed on the Pd K, Rh K and Pt L3 edges. Further discussion on the PGM promoted ceria reduction shall be given after the analysis of the PGM XAS experiments.

Evidence for the passivation of the samples through partial oxidation at room temperature is observed. Here a sharp ceria lattice contraction for the PGM containing samples is shown to occur upon the introduction of oxygen. The subsequent second reduction cycle has shown dramatically different redox behaviour. The reduction of the ceria is observed at near room temperature upon introduction of H2 and is independent of the PGM or its respective wt% loading. All PGM containing samples give the same result.

The analysis of the PDF and XRD of the HSA ceria support gives an interesting insight into the redox chemistry. Here it has been established that the lattice expansion of the HSA ceria sample is reversible with temperature. However, the expansion of the ceria lattice cannot be attributed to thermal expansion. When considered in combination to the HRXANES analysis, it is clear that the expansion of the ceria lattice is primarily due to the formation of Ce(III) ions in the fluorite lattice. The reduction of Ce(IV) is reversible and as such does not relate to the removal of lattice oxygen. It is proposed that the absorption of hydrogen into the ceria lattice octa-
hedral hole is stabilised in an expanded ceria lattice, and as such is removed upon cooling. The structure of a bulk cerium hydride like phase is discussed in further detail when considering the similar unusual redox behaviour on ceria coated alumina supported PGM catalysts. Furthermore, the analysis of XPDF using a peak fitting methodology has shown there is a local deviation in the ceria fluorite lattice on the HSA ceria sample. Whilst a deviation in the Ce-Ce distance at 3.8 Å from the lattice parameter refined using Rietveld analysis is seen, no such behaviour is observed at higher distances. This provides clear evidence for a local disordering and may be due to a distortion caused by the presence of hydrogen in the proposed octahedral hole site at the centre of the ceria lattice unit cell.
4.6 XAS Experiments on PGM Metal Edges

4.6.1 Experimental Data Collection

*In situ* XAS data was collected in transmission mode at BM26A (DUBBLE) at the ESRF. The XAS data, measured in step scans, on the Rh K edge, energy range of 23000 - 24200 eV, and Pd K edge, energy range 24150 - 25600 eV, using 150 mg of pelletised sample. The beamline was equipped with a Si(311) double crystal monochromator and harmonic rejection mirrors. Data were obtained at RT under \(N_2\), then isothermally at intermediate points up to 450 \(^\circ\)C in a reducing dilute \(3.5\%H_2/N_2\) atmosphere before cooling back to RT, purging in \(N_2\) and oxidising in synthetic air, \(20\%O_2/N_2\). A partial second reduction cycle was performed to capture the different reduction behaviour in the reducing dilute \(3.5\%H_2/N_2\) atmosphere. The samples investigated were ceria supported 1\%, 2.5\% and 5\% Pd and Rh. Due to exhaustion of hydrogen gas supplies the second cycle of reduction was not performed on the 1\%Pd/CeO\(_2\) sample.

Similarly BM26A was used for *in situ* experiments performed on the Pt L\(_3\) edge, energy range 11400 and 12425 eV, in transmission geometry. For the Pt L\(_3\) experiments a Si(111) double bounce monochromator was used. Here 100 mg sample was pelletised, the mass of sample useable was limited due to the absorption, at these energies, of the ceria support. Without the use of a fluorescence detector, it was not possible to collect *in situ* data on the 1\%Pt/CeO\(_2\) sample, whilst the lack of available time resulted in the second cycle of reduction not being performed on the 2.5\%/CeO\(_2\) sample.

4.6.2 XANES Analysis

XANES analysis has been performed by using LCF fitting\(^{[22]}\) of the relevant oxide and metallic PGM phases. For Pd containing samples this involves \(PdO\) and \(Pd\) metal. For Rh containing samples, \(Rh_2O_3\) and \(Rh\) metal. Whilst for Pt containing samples, \(PtO_2\) and \(Pt\) metal. The standard datasets were collected, in the case of
the oxide materials, from pelletised powders of fumed silica mixed with idealised sample mass to obtain an edge jump of approximately 1. In the case of metals, these were collected on standard reference foils.

Linear combination fitting has been demonstrated to be a powerful method for extracting the relevant phase contributions in a sample from known standard reference data. The standard datasets used for the LCF analysis following the in situ experiments on the PGM XAS edges are shown in Figure 4.23 in the left hand column. Key spectra relating to the initial sample, after reduction and after passivation by room temperature oxidation, are shown in the middle column of Figure 4.23 for the 5% PGM/CeO₂ samples. Here it is evident, particularly in the case of the 5% Rh/CeO₂ sample, that the passivation step results in only the partial oxidation of the samples and that LCF using the relevant standard materials should provide a reliable result for the extraction of present phase fractions. Example fitting for the passivated samples are shown in the right hand column illustrating the agreement between the experimentally acquired data and the LCF fitting. It is worth noting that the extended region, post edge, shows some deviation from the fitting. This is attributed to the effect on the XANES of nano-particulate metals. Nano-particles have dampened extended features due to the reduced average number of near neighbours.
Figure 4.23: Figures depicting the XANES analysis undertaken on the PGM edge XAS; Pd $K$, Pt $L_3$ and Rh $K$ are shown top to bottom respectively. Here the difference between the oxide and metallic PGM XANES structures are shown by the relevant standard materials. Selected spectra for the 5wt% Pd, Pt and Rh ceria samples are shown for the initial, after reduction and after passivation by room temperature oxidation to illustrate the points during the redox experiments. Example LCF fitting is shown for the partially oxidised passivated 5wt% Pd, Pt and Rh to demonstrate the LCF method.
Figure 4.24: Figures depicting the XANES analysis undertaken on the PGM edge XAS; Rh $K$, Pd $K$ and Pt $L_3$ are shown top to bottom respectively. Here the 5wt%, 2.5wt% and 1wt% samples are shown left to right. On each Figure the gas environment during measurement is indicated, shaded grey areas relate to a reducing dilute $H_2$ atmosphere whilst white areas pertain to dilute $O_2$ or $N_2$. On all Figures, the left Y-axis gives the temperature (black line), whilst the right Y-axis gives the LCF fraction relating to PGM oxide (red line) and metallic (blue line) phases.
The results of the LCF analysis is shown in Figure 4.24. Here, from top to bottom, the results are shown for the Rh K edge, Pd K edge and Pt L3 edge respectively, whilst left to right relate to the \( wt \% \) loading of the PGM phase, 5\%, 2.5\% and 1\% respectively. The shaded area in the Figures relate to being under the dilute 3.5\% \( H_2/N_2 \) atmosphere whilst the white areas relate to \( N_2 \) and \( O_2 \). The left Y-axis of these Figures give the temperature, black line, whilst the right Y-axis gives the LCF obtained phase fraction for oxide, red line, and metallic, blue line as a function of time through the \textit{in situ} experiment. The results are discussed below in order of the PGM content.

4.6.2.1 Rh K Edge XANES

The Rh containing samples are shown to undergo reduction from \( Rh_2O_3 \) to near total Rh metal by 100\(^{\circ}\)C. The earliest reduction is observed on the 5\% sample showing approximately 50\% Rh metal at 50\(^{\circ}\)C. In contrast 2.5\% and 1\% Rh samples show only approximately 30\% and no reduction respectively at 50\(^{\circ}\)C. Therefore a clear trend in the \( wt \% \) loading of the Rh and the onset of reduction can be observed, the higher the loading the lower the reduction temperature, although all are within a narrow temperature range. This is consistent with the TPR profiles for these samples as discussed earlier and shown in Figure 4.1b. Further to this, the alignment of the reduction temperature of Rh oxide and the expansion of the ceria lattice observed in xPDF, gives evidence of a direct interaction between the supported Rh in the promoted reduction of ceria. This is suggestive of a hydrogen spill-over from the Rh surface to the interface with ceria as driving the ceria reduction.

The passivation of the samples by RT oxidation reveals another clear trend, the lower \( wt \% \) loading of Rh the greater the oxidation that occurs. The 5\%, 2.5\% and 1\% samples show approximately 50\%, 60\% and 75\% oxidic phase after oxidation, Figure 4.25 illustrates the XANES spectra obtained after passivation. This oxidation is interpreted as surface layer oxidation of the present Rh metal nano-particles supported on the ceria. As such the fraction of Rh oxide observed after oxidation is
expected to be dependent on the particle size of Rh nano-particles prior to oxidation.

![Figure 4.25](image)

**Figure 4.25:** Demonstration of the spectra obtained on the Rh $K$ edge post RT oxidation for the Rh containing samples, 1%, red, 2.5%, blue, and 5%, black. Dotted lines correspond to energy points that can be used for fingerprinting the XANES spectra.

Where data was available, on the 5% and 2.5% Rh samples, the analysis of the partial second reduction cycle shows a rapid total reduction of the proposed surface Rh oxide layer. Reduction to Rh metal is observed to occur by 50°C. When considering the xPDF analysis, previously presented, this is also expected to occur on the outstanding 1%Rh/CeO$_2$ sample.

### 4.6.2.2 Pd K Edge XANES

The Pd containing samples have been analysed considering the reduction of a PdO phase to Pd metal. The phase composition profiles during the *in situ* experiments undertaken on the Pd containing samples are shown as the middle row in Figure 4.24. When considering the TPR profiles relating to the Pd containing samples, Figure 4.1c, one can observe that the 5% and 2.5% both show uptake of hydrogen between 50°C and 100°C, as such the separation of these two samples in terms of reduction onset is not observed in the Pd $K$ edge XAS experiments. Isothermal measurements were performed at 50°C and 100°C with no intermediate measurements. The reduction of the PdO to Pd can be said to occur by 100°C observed by the XANES analysis, this is in agreement with the TPR. One can only postulate
that the reduction of the 5%Pd/CeO₂ sample precedes the 2.5%Pd sample by comparison of the xPDF results and the TPR. The 1%Pd/CeO₂ sample is observed to undergo reduction by 150°C, this also is in agreement with the TPR results.

The passivation by RT oxidation of the Pd containing samples yields a similar trend to that observed in the Rh containing samples, a greater fraction of oxidation is observed with decreasing Pd loading. The 5%, 2.5% and 1% samples show approximately 20%, 35% and 45% oxidic phase after oxidation, related spectra are shown in Figure 4.26. Again the degree of oxidation is thought to be dependent on the Pd nano-particle size, smaller particle size resulting in a greater surface area and, as such, greater fraction of oxidation.

![Figure 4.26](image_url)

**Figure 4.26:** Demonstration of the spectra obtained on the Pd K edge post RT oxidation for the Pd containing samples, 1%, red, 2.5%, black, and 5%, blue. Dotted lines correspond to energy points that can be used for fingerprinting the XANES spectra.

The partial second cycle of reduction was performed on all Pd containing samples. All samples show a complete reduction of PdO, from passivation, to Pd metal before 100°C. This is a clear decrease in the temperature required to reduce the PdO present on the 1%Pd/CeO₂ sample. In combination with the xPDF analysis this shows that the passivation process is only a mild oxidation with all samples now exhibiting the same reduction behaviour on the second cycle.
4.6.2.3 Pt $L_3$ Edge XANES

Similar analysis has been performed on the Pt containing samples, shown as the bottom row in Figure 4.24. Here the 5% and 2.5% Pt samples are shown. The reduction of the 5%Pt/CeO$_2$ sample is observed to occur at low temperatures, approximately 40% reduction is observed to occur by 50°C. Whilst the 2.5%Pt/CeO$_2$ appears to show some Pt metal present in the initial sample, the reduction of the PtO$_2$ phase present is shown to occur by 200°C, somewhat delayed in respect of the 5% sample. The initial starting spectra obtained on the Pt samples are shown in Figure 4.27A demonstrating that the 2.5% sample shows a partial metal fraction, finger printed by the decreased white line intensity compared to the other samples. The TPR profile, Figure 4.1a, is in agreement with these findings with the maxima of the hydrogen uptake on the 2.5% sample occurring above 150°C. Due to a combination of lack of experiment time and the low metal loading of the 1% sample no in situ experiments were performed on the Pt $L_3$ edge. Ex situ characterisation shows a total PtO$_2$ phase present.

![Figure 4.27: A XANES spectra obtained on the Pt $L_3$ relating to the initial Pt containing samples, 1%, blue, 2.5%, red and 5%, black. Here it is clearly demonstrated that the 2.5% is partially reduced prior to exposure to the dilute 3.5%H$_2$/N$_2$ atmosphere. B Demonstration of the spectra obtained on the Pt $L_3$ edge post RT oxidation for the Pt containing samples, 2.5%, red and 5%, black clearly demonstrating an equal proportion of oxidation.](image-url)
Passivation of the 5% and 2.5% Pt samples by RT oxidation indicates that both of these materials exhibit approximately 35% oxidation, this is in remarkable agreement to the results obtained considering the Pt(111) reflection crystallinity analysis. The interesting result here is that this oxidation appears to be independent of the Pt loading and therefore suggests a similar particle size of Pt present, assuming that the oxidation is limited to the surface. The spectra relating to the passivated 5% and 2.5% Pt samples are shown in Figure 4.27B demonstrating the equal proportion of oxidation observed.

The partial second reduction cycle was performed on the 5%Pt/CeO$_2$ sample. A total reduction to metallic Pt of the passivated sample is observed to occur by 100°C. This is in agreement with the xPDF analysis. The behaviour of the outstanding 2.5% and 1% Pt samples can only be inferred from the available analysis of the xPDF. XAS experiments would be expected, as with the other PGM supported catalysts, to show a reduction to metallic Pt to occur below 100°C allowing for the spill-over of hydrogen to the ceria interface to promote the reduction of ceria.

Supplementary Figures are given in Appendix B for all the LCF fits on the PGM edges.
4.6.2.4 Tabulation of XANES Analysis Results and Conclusion

The tabulated results of the XANES analysis undertaken on the ceria supported PGM samples is shown in table 4.7 which gives the temperature at which at least 50% of the initial oxidic PGM has converted to metallic state and table 4.8 which gives the proportion of the oxidised PGM after exposure to $O_2$.

**Table 4.7:** Results showing the temperature at which 50% of the PGM can be found in metallic state during reduction in $H_2$.

<table>
<thead>
<tr>
<th>wt% loading</th>
<th>Pd</th>
<th>Pt</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2.5%</td>
<td>50</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>1%</td>
<td>150</td>
<td>-</td>
<td>150</td>
</tr>
</tbody>
</table>

**Table 4.8:** Results showing the proportion of the PGM which is found in an oxidic state after exposure to $O_2$ at room temperature.

<table>
<thead>
<tr>
<th>wt% loading</th>
<th>PGM oxide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>Pd</td>
</tr>
<tr>
<td>2.5%</td>
<td>Pt</td>
</tr>
<tr>
<td>1%</td>
<td>Rh</td>
</tr>
</tbody>
</table>

Due to the lack of temperature resolution on the PGM XANES data the results have a large degree of uncertainty in the temperature of onset of reduction, ±50°C and give no informative insight into the rate of either the reduction of the re-oxidation processes. However, by considering the temperature at which at least 50% of the initial PGM oxide has reduced, a clear trend can be established in terms of the Pt and Pd samples. The greater the wt% loading of PGM the lower the reduction temperature. This is in agreement with the TPR and XRD results previously discussed and suggests that the reduction of PGM oxide to metallic state is a precursor step to the reduction of the ceria support by the hydrogen spill-over mechanism. Moreover,
the temperature at which reduction is observed can be noted to be concurrent with the hydrogen uptake observed in TPR. When considering the Rh samples there is no obvious trend in the reduction temperature as a function of loading, this agrees with the XRD and TPR analysis.

The oxidation of the PGMs upon introduction of $O_2$ shows a clear trend for the Pd and Rh samples. A larger proportion of PGM oxide is found with decreasing loading of PGM. This result suggests that the particle size of the Pd and Rh is proportional to the wt% loading if one considers the oxidation to relate to a surface oxidation with a metallic core remainder. Conversely, the Pt samples show no such correlation and as such it is suggested that the Pt nano-particles form a uniform particle size independent of the wt% loading of Pt.

Where a partial second cycle of reduction has been performed, the conversion of the present oxidic PGM to metallic state is shown to rapidly occur and appears to be independent of the wt% loading or the PGM present. The result further suggests that the reduction of the ceria depends upon there being an available metallic PGM surface for the dissociation and subsequent spill-over of hydrogen.

### 4.7 Conclusion and Combined Interpretation

When considering the results that have been presented here, it is clear that the effect of PGMs is to promote the reduction of ceria through the dissociation of hydrogen and subsequent spill-over to the ceria-PGM interface. The promoted reduction of ceria by PGM loading is shown to be irreversible in respect to temperature, demonstrating that oxygen is removed from the ceria lattice. This is confirmed by significant uptake of oxygen after a reduction cycle has been completed on the PGM
loaded samples and only minor uptake of oxygen observed for the ceria support.

Whilst XAS experiments on the PGM and Ce $L_3$ edge has explored the oxidation state of the PGMs and the cerium, X-ray total scattering experiments have been shown to be particularly powerful in understanding the promoted reduction of ceria. The expansion of the ceria lattice observed in X-ray total scattering has been directly correlated to the partial reduction of ceria observed on the Ce $L_3$ edge by HRXANES. Quantification of the instantaneous expansion coefficient has proven to be a particularly insightful analysis tool in understanding the effect of both the supported PGM and its respective wt\% loading on ceria.

In the case of the supported Pd samples there is a clear inverse correlation between the temperature of the promoted ceria reduction and the wt\% loading of Pd. This has been shown through extensive analysis of the X-ray total scattering and through XAS experiments on the Pd $K$ edge. X-ray total scattering experiments analysed to yield the instantaneous expansion coefficient upon heating have directly shown there to be an inverse dependence on the wt\% loading and the temperature of the promoted ceria reduction. Furthermore analysis of the Pd(111) peak contribution to the X-ray total scattering has shown the formation of Pd nano-particles is rapid upon reduction of the initial oxidic Pd, when compared to the Pd $K$ XAS experiments following the oxidation state of Pd. Sintering of the Pd nano-particles is shown to occur through consideration of the Pd(111) peak area to extract the relative crystallinity. This particle sintering is shown to only occur during the heating cycle and suggests that the Pd is reasonably mobile over the ceria surface. Upon cooling in $H_2$ the formation of a Pd hydride is shown to occur below 100$^\circ$C due to the large increase in the Pd lattice parameter. The cooling cycle data has also been used to extract the Debye temperature of Pd in the 5wt\% sample and is found to be $276 \pm 6 \, K^{-1}$. 

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In the case of the supported Pt samples, a similar inverse correlation between the temperature of the promoted ceria reduction and the wt% loading is observed. However in the case of Pt this is seen not to be a linear dependence of loading. Peak fitting undertaken on the Pt(111) reflection has demonstrated that there is a slow sintering process that occurs with elevated temperatures, evidenced by the gradual increase in the relative crystallinity curve. The Pt particles are suggested to be small due to the relative weakness in the Pt(111) reflection intensity throughout. This suggests that the Pt is strongly interacting with the ceria support and is not mobile across it. When considering the redox profile of the 2.5%Pt sample the ceria can be seen to undergo a two-step reduction. This can be rationalised by the results of the Pt L3 edge which shows that a portion of the Pt is present in metallic form at room temperature. The spill-over of hydrogen is mediated by the metallic surface. The second reduction step occurs once the remaining oxidic Pt is reduced to metallic form. From this it is clear that the rate limiting step to the reduction of ceria is the available surface area of the Pt in metallic state.

The Rh containing samples have shown no such dependence on the rate or temperature of the promoted reduction. The overlap of the TPR and instantaneous expansion coefficients in temperature has shown that the reduction of the ceria happens at the same temperature and at approximately the same rate irrespective of the wt% loading of Rh. This result directly suggests that the promoted reduction of ceria is not rate limited by the available surface area of Rh in metallic state. Furthermore the reduction temperature of the initial oxidic Rh is independent of the wt% loading. This suggests that the Rh is present in a similar state across all samples from consideration of the Rh K edge analysis. Analysis of the Rh(111) reflection in the total scattering suggests that the Rh is present in a highly dispersed form and only forms very small nano-particles due to the relative weakness of this reflection when compared to the Pd(111). Furthermore the sintering of the Rh is shown to be minimal throughout the reduction from consideration of the relative intensity of the Rh(111) reflection. This suggests that Rh has a strong interaction with the ceria
surface and is reasonably immobile.

After the introduction of oxygen, all PGM containing samples undergo a rapid re-oxidation of the support ceria and a partial oxidation of the PGM is shown to occur. This partial PGM oxidation is suggested to only be a surface oxidation of the supported PGM particles. As such the degree of oxidation can be used as an indirect method of analysing the particle size of the supported PGM nano-particles. Larger particles have a reduced surface to bulk ratio and as such will a smaller proportion of the PGM will oxidise. Using this interpretation, the particle size of supported Pd and Rh samples is shown to correlate with the wt% loading. However this trend is not observed for the Pt samples suggesting the Pt is present in uniform particles. Although no experiments were performed on the Pt L₃ edge in situ on the 1%Pt sample.

The second reduction cycle of the PGM containing samples has shown that the oxidation of the samples at room temperature only acts to passivate. Upon introduction of hydrogen a rapid reduction in both the ceria and supported PGM is observed at near room temperature. This suggests that the PGM oxide is only loosely bound and is given as evidence towards only a mild surface oxidation of the PGM nanoparticles occurring. Furthermore, this behaviour has shown that once the PGMs are in metallic form they are able to dissociate hydrogen and promote the extraction of oxygen from the ceria lattice. Thus the differences observed in the first reduction cycle can be solely attributed to the reducibility of the initial oxidic PGMs rather than to their relative ability to dissociate and spill-over hydrogen once in the metallic state.

When considering the unusual redox behaviour observed in both XAS experiments on the Ce L₃ edge and using X-ray total scattering, with analysis of both the Bragg diffraction and pair distribution function, there is a very unexpected result. Here
it has been shown that the ceria undergoes reduction in $H_2$ at elevated temperatures. However, upon cooling still within $H_2$ both sets of experiments have shown a re-oxidation process occurring. The Ce L$_3$ edge XAS has shown a near total re-oxidation to Ce(IV) oxidation state from a partial Ce(III) presence at 400°C. The X-ray total scattering has shown a collapse in the expanded ceria lattice upon cooling back to near its original value. The discrepancy has been associated to the removal of surface carbonate species in the first heating cycle below 200°C evidenced by IGA-MS and IR. Therefore, the reduction of the HSA ceria sample is proposed to be not from the removal of lattice oxygen but to the absorption of hydrogen into the octahedral hole in the centre of the ceria lattice unit cell. This cerium hydride like phase within the fluorite ceria lattice is discussed further in the following chapter.
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Chapter 5

Unusual Redox Chemistry of Inverse Ceria Alumina Supported Catalysts

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This chapter focuses on the unusual behaviour of ceria in inverse catalysts formed from ceria coated alumina supported PGM nano-particles, an example of which is shown in Figure 5.1 for a ceria/Au/alumina inverse catalyst. The redox properties of these materials, Au, Ag, Pd, Pt and Rh containing samples, have been investigated using high resolution XANES (HRXANES) on the Ce $L_3$ edge, corresponding transmission XAS measurements performed on the PGM edges and using differential X-ray pair distribution function analysis (DxPDF). Prior to discussion of the experimental results, the structural and electronic interactions between PGM and support ceria and inverse catalysts are discussed, followed by a description of the analysis methods that have been employed for these studies.

Whilst the previous chapter has identified the redox characteristics of ceria supported PGM materials, here novel inverse ceria alumina catalysts are studied to probe in more detail the strong metal-support interaction by increasing the relative surface area of ceria in contact with the PGMs. Whilst unusual behaviour is observed with partial reoxidation occurring on the Pd, Pt and Rh sample, the nature of ceria, bare and with supported Ag and Au has shown to be fascinating. These materials have shown, after reduction in hydrogen, a complete re-oxidation upon cooling occurs. Through the application of Gr"unesian theory this behaviour has been proposed to be due the formation of a cerium hydride phase within the fluorite ceria latter.

Figure 5.1: Illustration of an inverse ceria alumina supported Au catalyst showing a cross section through an Au nanoparticle on an alumina surface with a coating of ceria. Aluminium, cerium, oxygen and gold are shown as purple, green, red and gold respectively.
5.1 Introduction

As previously described, ceria supported PGM catalysts have a wide range of industrial uses in heterogeneous catalysis\textsuperscript{[1][3]}. The principle understanding of the reactivity of ceria supported PGM catalysts to hydrogen revolves around the strong metal support interaction (SMSI) and the dissociation of hydrogen with subsequent spill-over to the ceria surface. The SMSI effect has been reported in partially reducible oxides as migration of the support to cover the nano-particulate metal particles leading to a decrease in the chemisorption of $H_2$ and CO onto the supported metal nano-particles\textsuperscript{[4][5]}. The SMSI effect has been discussed widely when considering the interaction of nano-particles with ceria\textsuperscript{[6][9]}. As shown in the previous chapter, the hydrogen spill-over mechanism is active in the ceria supported PGM systems and results in a reduction of the ceria by removal of lattice oxygen. The SMSI properties may be due to either electronic or structural interactions between the supported PGM and ceria.

Electronic interactions are related to the charge transfer between the support and PGM, so called electron metal-support interaction (EMSI)\textsuperscript{[11]}. The EMSI has been shown to occur in various PGM/ceria systems. The EMSI interaction is a more specific description of the underlying cause for the often outstanding catalytic activity in PGM/ceria systems and has been shown to results in a high degree of contact between the highly dispersed PGM nano-particle and a ceria support with high surface area\textsuperscript{[12][16]}. In particular the EMSI between Pt clusters on a ceria support has been shown to exhibit a maximum for Pt clusters of approximately 1.5 nm with small amounts of Ce(III) present within the support structure\textsuperscript{[13]}. The growth of Pt clusters results in an increasing amount of Ce(III) present within the ceria structure without the formation of O vacancies.

Although the SMSI effect, in particular in systems supported on titania\textsuperscript{[7]}, is widely seen to suppress the chemisorption capacity of $H_2$ or CO, on ceria systems it is
noted to enhance the catalytic activity. In addition, more recently, Collier and co-workers found that the presence of PGMs enhances the redox (reducibility) behaviour of ceria\textsuperscript{17–19}. The precise nature of the reduction of ceria in presence of PGM is still debated, however, two possible mechanisms has been proposed: (a) electronic/geometric interaction between metal and ceria support and (b) hydrogen spill-over from the reduced noble metal to the surface of the oxide. The work by Collier and co-workers used work function of the metal to explain the electronic interaction at the interface leading to the promotional effects of PGM on the reduction of ceria. Elsewhere it has been reported that the inclusion of small Pt nano-particles supported on ceria result in the favourable oxygen transfer to Pt with vacancy formation within the ceria nano-structure\textsuperscript{20}.

Studies investigating the SMSI through the structural interaction and effects of dopants within the ceria lattice, both experimental\textsuperscript{21,23} and computational\textsuperscript{20,22,24,26} to the role of metal dopant on the OSC of ceria. It is proposed, for example, both Pd and Pt (in divalent state) doped systems undergo modifications to accommodate the divalent ions in the square planar configuration, which appear to result in the under-coordinated state around some of the oxygens; this is believed to be the cause for the ease of oxygen removal that is related to OSC\textsuperscript{24,27}. The nature of atomically dispersed PGM species on ceria catalysts has been explored using photoemission spectroscopy where Pt and Pd in square-planar surface sites have shown remarkable stability towards heating. With Pt having an increased stability compared to Pd\textsuperscript{22}. The increase in stability of these dispersed PGM species enables the prolonged life of these catalytic materials. The stability of atomically dispersed $Pt/CeO_2$ structures in $H_2$ atmosphere has been shown to be decreased through the absorption of $H_2$ onto the ceria surface resulting in hydroxyl formation and reduction of Pt(II) to neutral Pt(0) and then subsequent formation of Pt agglomerates and the localisation of an electron by the formation of a hydroxyl group reducing the Ce(IV) to a Ce(III) centre\textsuperscript{8,28}. 

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Unusual reduction and oxidation behaviour of Ce(IV) ions in a pyrochlore oxide system has shown to occur; whereby reduction is observed upon heating in a $H_2$ atmosphere and re-oxidation occurs upon cooling again with $H_2$. The unusual behaviour was explained due to sintering effect after high-temperature treatment, whilst other recent developments surround the formation of so called inverse catalysts, where typically metal nano-particles are encased within the supporting oxide structure. Inverse catalysts have demonstrated increased catalytic activity compared to their conventional counterparts. Inverse catalysts have also been shown to increase the lifetime of the catalysts and provide a novel approach towards limiting the sintering of metal nano-particles.

The following chapter aims to highlight the unusual redox properties of various ceria coated alumina supported PGM inverse catalysts supplied by Johnson Matthey. A systematic study of the effect of PGMs in promoting the reduction of ceria in these materials is presented. While characterisation studies on these materials has been reported by Collier and co-workers, here X-ray absorption spectroscopy is employed to monitor the changes in the oxidation state of Ce(IV) ions and PGM oxides in reducing conditions. The measurement at the Ce $L_3$ edge has the advantage of probing directly the density of unoccupied states by measuring the $2p_{3/2}$ core level to $5d_{5/2}$ transition which can be directly interpreted for the change in oxidation state. Further to this, X-ray total scattering experiments have been conducted for the purpose of extraction the local and medium range structure through differential pair distribution function analysis of the contribution pertaining to the fluorite ceria phase present within the samples.
5.1.1 Experimental Data Collection and Analysis Methods

5.1.1.1 High Energy Resolution Fluorescence Detection XANES on the Ce L₃ Edge

Whilst conventional XAS techniques may provide detailed information, we exploited the most advanced XAS technique, high energy resolution fluorescence detection (HERFD) method at the Ce L₃ edge. Conventional transmission X-ray absorption spectroscopy was also preformed at the Rh and Pd K edges as well as the Pt L₃ edge to follow the reduction of the PGM oxide to metallic states.

High-resolution fluorescence detection XAS measurements at the Ce L₃ edge were conducted at ID20-1 beamline at the Diamond Light Source on the ceria/PGM/alumina systems through monitoring the intensity of the Ce Lα₁ photo emission line at 4840 eV. In a typical experiment, about 12 mg of the sample was mixed with 50 mg of fumed silica and pressed into a pellet and loaded into an in situ cell. The cell was purged with N₂ prior to heating to 250°C in a 3.5%H₂/He atmosphere followed by cooling to room temperature under the same atmosphere. Data normalisation and peak fitting was performed using the Athena software package.

In these experiments on the inverse ceria/PGM/alumina catalysts, the oxidation state of ceria has been probed using the Ce L₃ edge HERFD-XANES. Analysis of the XANES structure is performed using a peak fitting methodology previously reported in the literature. Example fitting to a spectrum collected on the ceria/Pd/alumina sample at 250°C is shown in Figure 5.2. This spectrum clearly exhibits both Ce(III) and Ce(IV) ions, indicated by the blue and red shaded areas respectively. The pre-edge feature, A, associated to the partially occupied 4f electron within the fluorite ceria structure. B and C are associated to the crystal-field splitting within the cubic fluorite structure of the 2p → 4f⁰, 5d transition. While D₁ and D₂ relate to the unscreened excited states exhibiting crystal field splitting. The
singlet, $E$, for the $2p \rightarrow 4f^1, 5d$ transition for a Ce atom with 3+ oxidation state.

$$[\text{Ce(III)}] = \frac{A[\text{Ce(III)}]}{A[\text{Ce(III)}] + A[\text{Ce(IV)}]}$$ (5.1)

To extract the relevant fraction of the cerium ions in Ce(III) and Ce(IV) oxidation states the ratio of the peak areas associated to the relevant states, as described above, is determined through equation 5.1.

![Figure 5.2](image)

**Figure 5.2:** Demonstration of peak fitting methodology applied to extract the fraction of Ce(III) and Ce(IV), denoted by the shaded blue and red areas respectively.

### 5.1.1.2 Fluorescence XAS on the PGM Edges

Fluorescence detection XAS measurements at the Pt $L_3$, Rh $K$ and Pd $K$ edges were conducted at BM26A beam-line at the ESRF at 11500 eV, 23200 eV and 24300 eV respectively. In a typical experiment, approximately 50 mg of the sample was pressed into a pellet and loaded into an *in situ* cell. The cell was purged with $N_2$ prior to heating to 250°C in a 5%H$_2$/He atmosphere followed by cooling to room temperature under the same atmosphere. Here conventional linear combination fitting to known standard materials was performed using the Athena software on the relevant combination of: PdO, PtO$_2$ and Rh$_2$O$_3$ oxide standards with Pd, Pt and Rh metal foil standards.
5.1.1.3 X-ray Total Scattering

X-ray total scattering experiments were conducted at ID15-1 beam-line at the Diamond Light Source. Measurements were performed at a refined sample to detector distance of 198.3 mm with a photon energy of 76690 eV. A 2D PerkinElmer image plate detector was used, with an integration time for each frame of 1 s with 5 frames then averaged. Samples were loaded into fused quartz capillaries with an internal diameter of 0.9 mm. A hot air blower directly below the sample was used to heat to 250°C at a ramp rate of 10°C min⁻¹. Samples were then cooled at 10°C min⁻¹ to room temperature. Through the capillary a flow rate of 5%\( \text{H}_2/\text{N}_2 \) of 30 ml min⁻¹ was passed throughout the experiments. Conversion to integrated line spectra being performed with DAWN Science⁴²,⁴³ and Fourier transformation performed using xPDFsuite⁴⁴.

Expansion of the fluorite ceria lattice has been extracted as previously described on the PGM/ceria systems. Here, however, the contribution from the alumina support is required to be removed. To achieve this differential xPDF has been used. The alumina support is removed from the total scattering data prior to Fourier transformation. For this purpose an alumina sample was heated under the same reducing conditions as the ceria/PGM/alumina samples. The subsequent datasets were then temperature matched to allow for any expansion of the alumina to be accounted for. The integrated total scattering patterns relating to the \( \text{CeO}_2/\text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) samples acquired at room temperature are shown in Figure 5.3A along with the background collection of an empty fused quartz capillary.

Correction for the background capillary from both the \( \text{CeO}_2/\text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) samples allows for the direct weighted subtraction of the alumina total scattering pattern from the ceria alumina total scattering pattern yielding only the contribution from the \( \text{CeO}_2 \) phase present. Figure 5.3B displays the final corrected I(Q) for the background and alumina subtracted data. The capillary background subtraction was
accomplished using xPDFsuite whereas the alumina subtraction was completed using a bespoke python program to subtract the temperature matched alumina dataset from the respective ceria alumina dataset.

![Figure 5.3: Figures A Graph showing the removal process of the alumina contribution (black) and the capillary (blue) from the total scattering intensity (red) for the ceria alumina sample. The contribution fraction of the alumina is determined from inspection of the relative peak intensities and the G(r). B Graph showing the reduced total scattering intensity pertaining to only the contribution from the ceria phase.](image)

Fourier transformation was then completed using xPDFsuite using a Q range of 16.5 Å\(^{-1}\). The resulting pair distribution function G(r) shows clear resemblance to the fluorite ceria phase as previously observed from the PGM/Ceria reducibility and recycleability studies. Figure 5.4A gives the radial pair distribution function G(r) for the individual processing steps undertaken during the differential xPDF method. Here the raw data is shown before background subtraction. The G(r) for the background capillary data also shown indicating there is a low R feature associated with the quartz silica structure. The background subtracted data clearly shows the removal of the capillary as seen in the sharpening of the first peak at approximately 1.8 Å. Here the ceria alumina data shown clearly exhibits a sum of fluorite ceria and alumina components.
Figure 5.4: Figures A Graph showing the various contributions to the total scattering G(r), the data is scaled and so the intensity does not represent the contribution intensity in the total G(r) but serves the purpose of illustrating the removal of various contributions to arrive at only the ceria phase information to give a differential pair distribution function. B Graph illustrating the quality of fit to, and as such agreement with, a fluorite ceria phase. The fit is shown in black, the data as red and the residual of the fit is shown offset below in blue.

The G(r) acquired from a pure alumina sample is shown with the resultant ceria phase extraction above, which is then used for fitting using PDFGui. This shows that the alumina has been successfully removed evidenced by the removal of the peaks at 1.8 Å and 3.4 Å. An example fit is shown in Figure 5.4B using a fluorite ceria phase fitted to the differential pair distribution function extracted from a $0.15(CeO_2)0.85(Al_2O_3)$ sample. Typical weighted residual of 0.15 is achieved for fitting to a maximum radius of 20 Å. Throughout the in situ experiments the spherical particle approximation was used to model the dampening of the G(r) due to finite particle size and was refined from the first dataset in each experiment and then assumed to be constant throughout the reduction reaction.
5.2 XRD Refinements

Prior to discussion of the DxPDF and HRXANES results, the analysis of the XRD portion of the X-ray total scattering data shall be considered. Here the contributions from both the ceria and alumina phases are analysed to extract their lattice parameters and to determine the structural changes that are observed upon heating and cooling in a $H_2$ atmosphere. Where possible, and clear, the XRD refinements have also modelled the present PGM nano-particle contribution, in metallic state, to the X-ray total scattering.

The structure of the alumina has been determined from consideration of a bare alumina support material and can be seen to represent a $\gamma-Al_2O_3$ phase, Figure 5.5A illustrates a Rietveld refinements to the $\gamma-Al_2O_3$ support. Using the model fit, GSAS\textsuperscript{46} was employed in sequential fitting mode using EXPGui\textsuperscript{47} to extract the $\gamma-Al_2O_3$ lattice parameter during heating to 240°C and subsequent cooling to RT under a $H_2$ atmosphere, Figure 5.5B. The contraction that is observed upon heating is interpreted as an effect of the heat treatment to anneal the alumina or remove adsorbed surface species, such as hydroxyl or carbonate groups rather than a change in the composition or phase of the $\gamma$-alumina. The lattice parameter of $\gamma$-alumina at room temperature prior to heating and after heating has been refined as $7.8542 \pm 0.0014 \, \text{Å}$ and $7.8517 \pm 0.0014 \, \text{Å}$. The crystallographic information file used for the XRD refinements quotes the lattice parameter of $\gamma$-alumina to be 7.887 Å and is derived from a theoretical study of the structure of $\gamma$-alumina by Gutierrez et al\textsuperscript{48}. Further to this, significant anisotropic strain broadening is required to accurately represent the structure. Paglia et al\textsuperscript{49} have previously reported that the local structure of $\gamma$-alumina retains an oxygen sublattice structure akin to a stacking fault, this effect may be the cause of the anisotropic strain broadening observed.
Figure 5.5: Figures A Demonstration of the quality of fit achieved for a RT XRD refinement on the $\gamma$-alumina structure. B plot of the alumina lattice parameter during heating and cooling under a $H_2$ atmosphere

Further analysis has been undertaken on the cooling phase to extract the linear thermal expansion coefficient of $\gamma$-alumina. As with the previously discussed analysis undertaken on the NIST ceria and HSA ceria samples, both a temperature independent model and a temperature dependent model of the expansion coefficient have been used through fitting of a linear and quadratic functions to the extracted $\gamma$-alumina lattice parameter. Figure 5.6 gives the results of this analysis, the quadratic model is shown in red whilst the linear model is shown in black. Also given is the residual sum of squares as a measure of the agreement between the data and the fitting models, from which the temperature dependent quadratic model can be shown to represent the data with higher accuracy than the linear model.

A two-phase model has been used in XRD refinements consisting of ceria and $\gamma$-alumina. By assuming the ceria and alumina phases in all samples have the same relative disordering, values of $U_{iso}$ parameters, it is possible to extract their phase phase fraction to characterise the composition of the samples, shown in table 5.1. The contribution from the Au Phase is also extracted due to its metallic state in the initial material. None of the other materials had clear evidence for PGM in their starting form. The fitting to the initial starting material for all samples is shown at the end of the section in Figure 5.8. The estimation of the phase fraction due to the
Figure 5.6: Results of the linear and quadratic modelling to the thermal expansion of γ-alumina.

The presence of Pd has been completed through consideration of the final material after heating in \( H_2 \).

Table 5.1: Results showing the proportion of the PGM which is found in an oxidic state after exposure to \( O_2 \) at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ceria (%)</th>
<th>Alumina (%)</th>
<th>PGM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria/Alumina</td>
<td>14.65</td>
<td>85.35</td>
<td>-</td>
</tr>
<tr>
<td>Ceria/Pd/Alumina</td>
<td>17.67</td>
<td>81.42</td>
<td>0.91</td>
</tr>
<tr>
<td>Ceria/Pt/Alumina</td>
<td>18.30</td>
<td>81.70</td>
<td>-</td>
</tr>
<tr>
<td>Ceria/Rh/Alumina</td>
<td>16.58</td>
<td>83.42</td>
<td>-</td>
</tr>
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<td>Ceria/Ag/Alumina</td>
<td>17.15</td>
<td>82.85</td>
<td>-</td>
</tr>
<tr>
<td>Ceria/Au/Alumina</td>
<td>16.13</td>
<td>82.98</td>
<td>0.89</td>
</tr>
</tbody>
</table>

The XRD refinements are shown in Figure 5.7 showing both the refined lattice parameter for the ceria and alumina phases, blue and black respectively. The refinements for all samples are shown here to demonstrate that the alumina does not contribute to reaction further than being a support material. Alumina is noted for being an irreducible material. Furthermore, as can be seen here the structure of the alumina behaves as previously discussed in regards to a bare γ-alumina material. All samples show a decrease in lattice parameter of the γ-alumina when comparing the final and initial materials. This is attributed to the removal of surface contaminants.
such as hydroxyl groups.

From Figure 5.7 it is also evident that the behaviour of the Pd, Pt and Rh containing samples is somewhat different to that observed on the Ag, Au and bare ceria alumina samples. Here the Pd, Pt and Rh containing samples are shown to undergo a reduction process culminating in an expanded ceria lattice in respect to the starting material. The Ag, Au and bare samples however show significant lattice expansion followed by lattice contraction on cooling. The redox properties of these samples are discussed further after the alumina portion is removed using DxPDF methods. In light of the different redox behaviour observed in the XRD refinements, the Pd, Pt and Rh samples are discussed followed by the Ag, Au and bare ceria alumina samples.
Figure 5.7: Graphs illustrating the structural changes that are observed upon heating and cooling the ceria alumina samples in a $H_2$ atmosphere. Ag, bare, and Au samples are shown on the top row, from left to right. Pt, Rh and Pd samples are shown on the bottom row, left to right.
Figure 5.8: Fitting examples for the Au, Ag and Pd, shown as left, middle and right, on the top row, with Pt, Rh and bare ceria alumina samples shown similarly on the bottom row. Illustrating the quality of the two-phase XRD refinements for the initial starting materials.
Understanding the mechanism of reduction of Ce(IV) ions in inverse ceria-alumina catalytic systems, in particular in the presence of PGMs is vital for the development of ceria based catalysts. Metal-support interaction (MSI) operates in these systems to provide unusual catalytic behaviour. Here X-ray absorption spectroscopy results recorded using high-resolution fluorescence mode, are presented which reveal that, depending on the type of PGM metal present in the system, the reduction and re-oxidation in reducing atmosphere differ considerably. Here the findings suggest that SMSI is responsible for the promoted reduction of Ce(IV) to Ce(III), whilst the re-oxidation is suggested to occur at the ceria alumina inter-facial regions.

While characterisation studies on this system have been reported by Collier and co-workers here the power of XAS methods are exploited to monitor the changes in the oxidation state of Ce(IV) ions and PGM oxides in reducing conditions, due to its element specific nature and furthermore, the measurements can be conducted at operating conditions. In addition measurement at the Ce $L_3$ edge has the advantage of probing directly the density of unoccupied states by measuring the $2p_{3/2}$ core level to $5d_{5/2}$ transition which can be directly interpreted for the change in oxidation state. Further to this, X-ray total scattering experiments have been conducted for the purpose of extraction of the local and medium range structure through differential pair distribution function analysis of the contribution pertaining to the fluorite ceria phase present within the samples.

### 5.3.1 Peak Fitting of the Ce $L_3$ edge HRXANES

Here the high resolution XANES spectra were modelled, as previously described, by employing a peak fitting methodology. Direct extraction of the Ce(III) fraction from the ratio of fitted peak areas, using equation 5.1, has allowed for the unusual
redox chemistry outlined herein to be identified.

The results of the peak fitting are shown in Figure 5.9. Here the onset temperature for the reduction of ceria is shown to clearly depend upon the supported PGM. Whilst the Pt containing sample exhibits an onset of reduction at room temperature, Pd and Rh containing samples exhibit reduction of ceria at temperatures above 100°C and 150°C respectively.

![Graph displaying the results of the peak fitting analysis on the ceria/PGM/alumina (PGM = Pd, Pt and Rh) for the extraction of the Ce(III) percentage during in situ reduction experiments. The Pd, Pt and Rh samples are shown in black, red and blue respectively.](image)

**Figure 5.9:** Graph displaying the results of the peak fitting analysis on the ceria/PGM/alumina (PGM = Pd, Pt and Rh) for the extraction of the Ce(III) percentage during in situ reduction experiments. The Pd, Pt and Rh samples are shown in black, red and blue respectively.

Comparison of the HRXANES spectra at room temperature, 250°C and at final temperature, 30°C are shown for each sample in Figure 5.10 from left to right Pd, Pt and Rh containing samples are given. Here the partial re-oxidation, seen from the shift in the edge position and reduction in the peak intensity relating to the Ce(III) oxidation state, is visible. The individual peak fits relating to these three key temperatures are shown in Figure 5.11 with red shaded areas relating to the Ce(IV) contribution and blue to the Ce(III) contribution to the total spectra.
Figure 5.10: Graph displaying the spectra obtained at room temperature (initial), 250°C and back at room temperature after cooling in $H_2$ (final) as black, red and blue traces respectively. The Figures, left to right, as associated to the Pd, Pt and Rh containing ceria alumina samples concurrently.
Figure 5.11: Fitting examples for the Pd, Pt and Rh, shown as left, middle and right, containing ceria alumina samples at initial room temperature, 250°C and final room temperature, top to bottom respectively. Here the shaded red area relates to the Ce(IV) contribution and the Ce(III) contribution is given in shaded blue.
5.3.2 XANES Analysis of the PGM edges

XANES analysis has been performed through linear combination fitting of the Pt L3, Rh K and Pd K edges using suitable reference materials\[50\]. In this case \(PtO_2\), \(PdO\) and \(Rh_2O_3\) oxide phases were used as well as the relevant metallic phases for each PGM. The results for each PGM are shown in Figure 5.12 following the conversion of PGM oxide to metal with Pd, Pt and Rh shown from left to right respectively.

![Graphs showing the PtL3, PdK and RhK edge results, left to right, illustrating the formation of metallic phase PGM particles from the initial PGM oxides present.]

When considering the results in combination with the Ce \(L_3\) edge results shown previously it is clear there is a direct correlation between the reduction onset of the PGM oxide starting material and the reduction of the ceria component of the support. This directly suggests the ceria reduction is preceded by the dissociation of hydrogen on the metallic PGM particles. The removal of oxygen from the ceria is thought to occur at the interface between the metallic PGM particle and the ceria, thus the mobility of oxygen towards the interface is crucial to the reduction of the bulk ceria, the reverse spill-over mechanism. Further Figures showing the linear combination fitting are given in the supplementary information.

5.3.3 Differential X-ray Pair Distribution Function Analysis

Finally, the promoted reduction of the ceria component of the ceria coated alumina supported PGM catalysts was studied using differential x-ray total scattering. Re-
moval of the alumina phase contribution to the total scattering was performed as previously described to leave only the scattered intensity relating to the PGM and ceria phases. No clear contribution relating to the PGM was observed in the Fourier transformed data, \( G(r) \), and thus only the ceria phase contribution was included into the fitting methodology.

The results of the fitting undertaken in PDFGui are shown in Figure 5.13. Here a clear difference is observed depending on the PGM contained within the sample, however this is less pronounced than observed in XAS methods. The difference between the DxPDF and XAS methods is thought to relate to the difference in measurement modes. XAS measurements were performed in step scan modes where each individual measurement is performed in isothermal conditions. However, DxPDF measurements were performed during ramping at 10\(^{\circ}\)C/\( \text{min} \). Thus the total exposure time to the reducing hydrogen atmosphere is at any one data point is vastly reduced. The kinetics governing the reduction of the PGM and ceria have not been studied here, but either of these processes may require a non negligible time to occur at lower temperatures. This would result in a different reduction profile observed when continuously ramping due to system having not have time to reached thermodynamic stability.

The greatest difference between XAS and XPDF is observed is between the results obtained on the Pt containing sample. This may relate to the kinetics of the hydrogen spill-over from Pt or the reverse oxygen spill-over from the ceria lattice to the Pt ceria interface with either process being slower to occur than with Pd and Rh. Further analysis of the DxPDF results has been conducted through extracting the instantaneous expansion coefficient. Demonstration of the expansion of the ceria lattice, compared to room temperature lattice parameter, \( \Delta l \), as a fraction of the lattice parameter of ceria, \( L \), as a function of temperature is shown in Figure 5.14 with black relating to the heating phase and red the cooling phase of the reduction.
**Figure 5.13:** Graph showing the refined ceria lattice parameter derived from fitting of the DxpDx PDF G(r) during heating and cooling cycles. Here black, red and blue showing the Pd, Pt and Rh ceria alumina samples respectively.

\[ \alpha = \frac{\Delta l}{L} \cdot \frac{1}{\Delta T} \]  

(5.2)

**Figure 5.14:** Demonstration of the method for calculation of the instantaneous lattice expansion coefficient for the ceria/Pd/alumina sample. Here the change in length over original length is plotted against temperature during the heating and cooling phases in black and red respectively. The instantaneous expansion coefficient is derived through the derivative of these curves.

From here the instantaneous derivative of both the cooling and heating phases can
be extracted which relates directly to the instantaneous expansion coefficient. Figure 5.15 gives the instantaneous expansion coefficient as a function of temperature during the reduction experiments for the Pd, Pt and Rh containing samples respectively. The y-axis scale is kept constant for all samples to give a visual comparison of the magnitude of the instantaneous expansion coefficient. As such, it is evident that the expansion of the ceria lattice is observed to occur in the order Pd>Pt>Rh due to the magnitude of the instantaneous expansion coefficient being largest.

\[ \alpha_{\text{inst}} = \frac{dA}{dT} \]  

(5.3)

The vertical dashed black line is added to Figure 5.15 to show the inflection point, approximately at 110°C, for the expansion coefficient. This is interpreted as the point at which the expansion of ceria, above that of linear thermal expansion, occurs. Of particular interest here is that this appears to occur at the same temperature for all samples, as illustrated by the dashed black line. Expansion not related to the linear thermal expansion of ceria has been attributed to the reduction of ceria with the formation of Ce(III) ions within the fluorite lattice. DxDPDF analysis here is probing the bulk lattice parameter of the ceria phase, thus reduction of ceria that occurs at the surface or interface with the PGM may not be observed. As such the results are interpreted as the point at which the reduction of the bulk ceria lattice occurs induced by the extraction of oxygen from the ceria lattice. This can proceed by two methods: reverse oxygen spill-over to the PGM or the hydrogen spill-over onto the the ceria surface and subsequent migration of oxygen to the ceria surface from a lattice site. The ability of oxygen to migrate to the PGM interface or to the ceria surface may be a temperature dependent process.
Figure 5.15: Figures giving the instantaneous thermal expansion during heating and cooling cycles shown for Pd, Pt and Rh ceria alumina samples. For reference the dashed vertical line indicates the onset of thermal expansion relating to the formation of Ce(III) ions. With the dashed horizontal lines shown for $\alpha = 0$. 

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As such the light off of the instantaneous expansion coefficient, and the difference to the point of reduction of ceria observed in Ce $L_3$ XAS measurements can be considered as the point at which oxygen is able to be extracted from the bulk lattice sites. Of the three types of thermally induced defects, the formation of oxygen vacancy-interstitial pairs are the most energetically favourable, $\Delta E = 3.2eV$.

$$O_o \rightarrow V_o^{**} + O''_i$$ (5.4)

Here $O_o$ represents a lattice site oxygen, $V_o^{**}$ a vacant lattice oxygen site and $O''_i$ an interstitial oxygen. Thus the transport of oxygen from the bulk to the surface is likely to be mediated by the formation of bulk oxygen vacancy-interstitial pairs. Therefore the DxFPDF measurements suggest that the reduction of ceria, observed in continual ramping may be a diffusion limited process below approximately 100°C, evidenced by the offset between the reduction of the ceria observed by Ce $L_3$ HRXANES in isothermal measurements and the dynamic DxFPDF measurements for the Pt containing sample.

Further to this, the difference in the magnitude of the instantaneous expansion coefficient above the point of inflection between the different PGM samples is here suggested to relate to the rate of desorption of $H_2O$ or the ability of the PGM to dissociate and spill-over hydrogen. These two processes can both affect the rate of the reduction of ceria and are also dependent on the surface area of PGM metal present within the sample. When compared to the fraction of metallic phase PGM observed in the XAS analysis, the rate of lattice expansion can be seen to directly correlate with the proportion of metallic phase PGM present; with near total conversion of oxidic Pd to metallic phase, the rate of ceria lattice expansion is greatest, whilst for only partial conversion of oxidic Pt and Rh observed, the maximum rate of lattice expansion is reduced for Pt and further for the Rh containing sample. This suggests that the surface area of available PGM in metallic phase is critical to the rate of re-
duction of the ceria phase, be it through either the dissociation of $H_2$ or desorption of $H_2O$ processes.

Upon cooling, unlike in the HRXANES on the Ce $L_3$ edge, there is no evidence for any re-oxidation in the bulk of the ceria. This is due to the contraction in the lattice parameter being consistent with that of thermal contraction behaviour. All samples are observed to have an average instantaneous expansion coefficient of approximately $-8.6 \times 10^{-6} K^{-1}$ during the cooling cycle with no significant deviation observed. This suggests that there is no re-oxidation of the bulk ceria lattice during cooling and that any reoxidation observed in the HRXANES occurs at the sample surface.

This particular kind of analysis, through consideration of the instantaneous derivative of a measured parameter, is only possible where there is a large number of data points and cannot be carried out with any particular significance for the reduction profiles of either the PGM or ceria phases observed from XAS methods. However, has proved to give insightful results based upon the expansion coefficient derived for DxFPDF studies.

### 5.3.4 Conclusions

The unusual redox behaviour of ceria coated alumina supported PGM catalysts has been studied using XAS and PDF methods. The derived Ce(III) content from Ce $L_3$ HRXANES experiments with the corresponding fluorescence detection XAS for the Pd $K$, Pt $L_3$ and Rh $K$ edges for inverse ceria/alumina catalysts give an insight into the redox properties of the ceria phase within these materials. We observe a varying temperature of onset and maximum rate of reduction depends directly on the particular PGM within the inverse ceria/alumina catalysts. Whilst the Pt containing sample exhibits an onset of reduction at room temperature, Pd and Rh containing samples exhibit reduction of ceria at temperatures above 100°C and 150°C.
respectively. The direct correlation between the promoted reduction of ceria and the oxidation state of PGM suggests the dissociation of hydrogen only occurs on the PGM in metallic form and that the resultant spill-over of atomic hydrogen or reverse oxygen spill-over towards the PGM-ceria interface drives the reduction of ceria arising from the SMSI or EMSI effect.

Consideration of the DxPDF refined lattice parameters yields an expanded lattice which can be rationalized as due to Ce(III) being present in the bulk structure of the ceria phase, Ce(IV) ions being smaller than Ce(III). The discrepancy between the onset of reduction observed in the HRXANES and the lattice expansion of the Pt containing ceria/alumina inverse catalyst is thought to be due to the difference between the step-scan isothermal mode of data collection, in the case of the XAS, whilst the DxPDF measurements were performed under a continual ramping of temperature. By plotting the DxPDF results in the form of the instantaneous expansion coefficient, the continual ramping is proposed to be oxygen diffusion limited on the migration of oxygen from the lattice bulk to the surface. Analysis of the gradient associated to the linear contraction observed upon cooling yields an average linear thermal expansion coefficient of $-8.6 \times 10^{-6} \text{K}^{-1}$, which is in line with the reported linear thermal expansion coefficient of ceria elsewhere and suggests there is no re-oxidation of the bulk ceria lattice. Although the expansion coefficient is on the lower end of the values obtained through PDF methods on the pure high surface area support, previously described in Chapter 4, using a quadratic function fitted to the lattice parameter.

Further to this the rate of the reduction is proposed to be directly dependent on the fraction of oxide phase PGM that has been converted to metallic phase. This can be explained through consideration of the surface area of metallic phase PGM. The greater the reduction to metallic phase, the greater the surface area available for the dissociation of $H_2$. However, to complicate matters, the process may also be limited
by the dissociation of $H_2O$ from the catalytically active interface between metallic PGM and $CeO_2$. Although both of these effects point towards the limitation on rate of lattice expansion, reduction of bulk ceria, to be due to the availability of active sites for the extraction of oxygen.

Finally, it is also observed that upon cooling there is evidence from the HRXANES, whilst still in a reducing hydrogen atmosphere, for a partial re-oxidation of the ceria on Pt and Pd containing samples of approximately 7% and in the case of the Rh containing catalyst of approximately 2%. When considering the linear thermal expansion coefficient derived from the DxFPDF the corresponding contraction associated with the formation of Ce(IV) ions is not observed. This is proposed as being due to the nature of the DxFPDF analysis performed to be sensitive only towards the bulk crystalline characterisation through fitting of the fluorite ceria phase. Due to lack of associated re-oxidation of the Pd, Pt or Rh it is proposed that the observed partial re-oxidation of the ceria occurs in the inter-facial regions between the ceria and alumina resulting in a restructuring that is not observed clearly in the DxFPDF.
5.4 XAS and DxPDF Studies of Ceria Coated Alumina Supported Au and Ag Inverse Catalysts

Due to the nature of the redox chemistry of the Au, Ag and bare samples materials being fundamentally different from those mentioned above, Pd, Pt and Rh containing samples, they been considered separately. The Au sample provides a unique insight into the properties of these materials due to the fact that the Au component does not undergo any phase transformation and can be found as metallic nanoparticles from the onset. In contrast the Ag containing sample, whilst exhibiting similar behaviour to the Au catalyst is proposed to be very highly dispersed as no evidence for Ag is observed in the DxPDF. Here, in particular, the thermal properties of the supported Au are discussed.

In situ studies on the thermal properties of Au in inverse ceria alumina supported catalysts have been conducted between 295 and 623 K. Precise structural information is extracted on the metallic Au phase present in a 0.85 wt% Au containing inverse ceria alumina catalyst. The thermal properties are modelled using Grüneisen theory of volumetric thermal expansion towards the extraction of the Debye temperature, $170 \pm 7 \text{K}$, and the static disorder contribution to the temperature dependent atomic displacement parameter, $0.00050 \pm 0.00001 \text{Å}^2$, refined from differential X-ray Pair Distribution Function analysis.

5.4.1 Differential X-ray Pair Distribution Function Analysis

Differential X-ray pair distribution function was analysed as previously described for the Pd, Pt and Rh containing samples. Extraction of the lattice parameter of the ceria phase shows some unexpected behaviour for the Ag, Au and bare sample. Figure 5.16A gives the ceria lattice parameter for the Ag, Au and bare sample extracted from DxPDF fitting undertaken in PDFGui. Alongside Figure 5.16B highlights the before and after of the sudden contraction of the ceria lattice parameter observed on the Au containing sample upon cooling at ca. $100^\circ \text{C}$. The surface map shows...
the same region of $G(r)$ as expressed by the above line profiles but for the entire experiment. Time is given from start to the end of the experiment from bottom to top. This illustrates the shift in lattice parameter that is observed along with the reduction in peak intensity due to the increase of thermal disorder in the sample.

![Figure 5.16](image)

**Figure 5.16:** Figures a gives the lattice parameter extracted from fitting of the DxF Data for the ceria/PGM/alumina (PGM = Ag, Au, none) samples. Alongside, b, a surface map of 3Å to 6Å region of the $G(r)$ is shown for the Au containing sample with time from start to end of the experiment from bottom to top. Line profiles pertaining to the before and after of the collapse of the ceria lattice parameter are shown to highlight the degree of collapse and are illustrated on the surface map.

Extraction of the instantaneous expansion coefficient has also been performed, shown in Figure 5.17. Here the clear difference to the similar Figure for the Pd, Pt and Rh samples is the cooling phase of the experiments. Under cooling all samples examined here can be seen to undergo a collapse in lattice parameter, signified by the negative value of the expansion coefficient. Moreover, due to the shape of the curve for the instantaneous expansion coefficient being approximately Gaussian, this contraction event can be said to be due to a single process.

Further to this the onset and maximum rate of the expansion of the ceria lattice can be extracted from the instantaneous expansion coefficient during the heating phase of the experiment by inspection of Figure 5.17. Here the onset of the ceria
lattice expansion can be said to occur at approximately 150°C, 175°C and 200°C respectively for bare, Ag and Au containing samples. The maximum expansion rate is observed at approximately 250°C, 200°C and 225°C for bare, Ag and Au samples respectively. The rate of the ceria lattice expansion can also be noted to be much greater in the presence of Ag and Au suggesting there is a direct interaction between both of these metals and the gaseous $H_2$ towards the dissociation and subsequent spill-over to the ceria surface.
Figure 5.17: Graph showing the instantaneous expansion coefficient extracted for the Ag, Au and bare ceria alumina inverse catalysts. A point of note is that unlike in the similar Figure for the Pd, Pt and Rh samples the Y axis scaling is unique for each sample.
Further insight into these materials is achieved through the application of Grünesian theory to the lattice volume expansion and modelling of structural disorder using the Debye model for the ceria/Au/alumina sample.

5.4.2 Application of the Debye model and Grünesian Theory of Thermal Expansion

The extraction of the information pertaining to the 0.85wt% Au present within the ceria alumina inverse catalyst is possible largely due to the high scattering factor of Au and the fact that it is present only in metallic state and as such does not undergo any phase transformation. The fitting to the DxDPDF G(r) obtained relating to the Au and ceria phases after the removal of the alumina from the total scattering allows for the separation of the phase information of the Au from the ceria, an example fit is shown in Figure 5.18 where the Au component is shown explicitly as a blue trace below the fitted data.

![Graph showing the room temperature G(r) between 2 and 20 Å for the ceria/Au/alumina sample. Here the data is shown in black, the fit in red and the extracted Au component of the fit is shown as a blue trace offset below.](image)

**Figure 5.18:** Graph showing the room temperature G(r) between 2 and 20 Å for the ceria/Au/alumina sample. Here the data is shown in black, the fit in red and the extracted Au component of the fit is shown as a blue trace offset below.

Here the heating phase of the experiment is explored in detail through application of Grüneisen theory to the expansion of solids. Grüneisen theory allows for the expression of the thermal unit cell volume expansion through consideration of the
Debye temperature\textsuperscript{51,53}.

\[
V(T) = \frac{V_t}{2k_0a_V} \left( 1 + 2k_0 - \sqrt{1 - \frac{4k_0U}{Q_0}} \right) \tag{5.5}
\]

Where \(V_t\) is the unit cell volume at a reference temperature, \(t\), here chosen to be the value obtained at 294 K (room temperature), \(a_V\) is determined from the ratio of \(V_t/V_0\). \(k_0\) is a function of the derivative of the bulk modulus, \(K_0\), with pressure, whilst \(Q_0\) relates to the Grüneisen parameter, \(\gamma_G\), and \(U\) is given by the internal energy.

\[
k_0 = \frac{\frac{dK_0}{dP} - 1}{2} \tag{5.6}
\]

\[
Q_0 = \frac{K_0V_0}{\gamma_G} \tag{5.7}
\]

Here the value of \(\frac{dK_0}{dP}\) has been set from Dewaele \textit{et al.}\textsuperscript{54} at 6 giving \(k_0\) to be 2.5. The internal energy is determined for consideration of the Debye model and is described by the equation \textsuperscript{5.8} Where \(\theta_D\) is the Debye temperature, \(R\) the gas constant, \(n\) is given by the number of atoms in the formula unit and \(T\) describes the temperature on absolute scale.

\[
U = 9nRT \left( \frac{T}{\theta_D} \right) \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} \, dx \tag{5.8}
\]

Extension of this allows for the Debye temperature to be used directly to determine the dynamic contribution to the atomic displacement parameter of Au, given in
\[ \langle u_{\text{dynamic}}^2 \rangle = \frac{3\hbar^2}{m_{\text{Au}}k_B\theta_D} \left( \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D} \frac{x}{e^x - 1} \, dx \right) \] (5.9)

Here the \( m_{\text{Au}} \) is defined as the atomic mass of Au and \( k_B \) the Boltzmann constant. Therefore the static disorder contribution to atomic displacement parameter can be extracted, equation 5.10, where \( U_{\text{iso}} \) is the refined atomic displacement parameter for isotropic thermal displacement.

\[ \langle u_{\text{static}}^2 \rangle = U_{\text{iso}} - \langle u_{\text{dynamic}}^2 \rangle \] (5.10)

Exploring the lattice volume expansion of Au as a function of temperature using Grünneisen theory, equation 5.5, shows a strong agreement between the expansion of the experimental and theoretically determined lattice volume from a refined Debye temperature, \( \theta_D \), of 170 ± 4K, as shown in Figure 5.19A. Application towards investigating the static disordering, equation 5.10, of the Au through the Debye model for the internal energy, equation 5.8, has been achieved using the refined value of \( \theta_D \) from the expansion of the Au lattice. Figure 5.19B shows the correlation between the refined \( U_{\text{iso}} \) and the Debye model where the static disordering has been established as 0.00085 ± 0.00004 Å².

There is a strong agreement between the Debye model for internal energy and the atomic displacement parameter between 293 and 500 K. Above this there can be seen to be a deviation from theory resulting in a lower than predicted \( U_{\text{iso}} \) value; this implies a higher Debye temperature in this region potentially due to the formation of surface hydride species. Typically hydride species have elevated Debye temperatures when considered against their metallic counterparts. Evidence for surface gold hydride species has previously been reported.
The interplay between the ceria and Au phases shows remarkable correlation; the inflection in the lattice volume of ceria occurs at the same temperature as the deviation of the Au $U_{iso}$ from the Debye model. Figure 5.16A gives the lattice parameter of the ceria phase. The expansion of the ceria lattice is due to three competing effects; the reversible reduction of the Ce(IV) to Ce(III) oxidation state which has a larger ionic radius, linear thermal expansion, and the insertion of hydrogen into the ceria lattice forming a cerium hydride phase. The presence of cerium hydride after treatment with hydrogen at elevated temperatures has previously been reported through an inelastic neutron spectroscopy study after the formation of surface oxygen vacancies. With the formation of the cerium hydride showing greatly increased lattice expansion above thermal expansion of ceria. The middle Figure of 5.17 gives the instantaneous linear thermal expansion coefficient for the Au containing sample illustrating the expansion above 400K.

5.4.3 Peak Fitting of the Ce $L_3$ edge HRXANES

As with the Pd, Pt and Rh containing samples, the oxidation state of cerium is investigated with HRXANES and discussed in combination to the DxPDF to provide an insight into the particularly unusual and unexpected properties of these, Ag and Au.
containing materials. However, due to lack of material, there is no data concerning the oxidation state of cerium in the bare ceria alumina sample.

Experiments following the oxidation state of cerium within ceria were performed using the HRXANES. Figure 5.20 gives an example peak fitting to the structure of the HRXANES spectra acquired at 623 K which exhibits substantial Ce(III) shown by the presence of a peak growing centred around 5725 eV, illustrated as peak E shaded blue. However, upon cooling the majority of formed Ce(III) is re-oxidised to Ce(IV) without the presence of an oxidising atmosphere. Figure 5.21 shows the fraction of Ce(III) extracted from HRXANES analysis during the heating and cooling cycles under a reducing 3.5%H₂/He atmosphere for both the Au and Ag containing samples. Whilst the majority of the Ce(III) is converted upon cooling there is a small proportion that remains, this is attributed to remaining surface oxygen vacancies and defects that mediate the formation of a cerium hydride species.

**Figure 5.20:** Graph showing Ce(III) content in Ag, red, and Au, blue, containing ceria alumina inverse catalysts over *in situ* reduction experiments performed during heating and cooling.
Figure 5.21: Fitting examples for the Ag and Au, shown top and bottom, containing ceria alumina samples at initial room temperature, 250°C and final room temperature, left to right respectively. Here the shaded red area relates to the Ce(IV) contribution and the Ce(III) contribution is given in shaded blue.
5.4.4 Conclusions

In summary, here it is shown how differential X-ray total scattering methods can be used to probe the thermal properties of individual phases present within a complex multiphase material. Here, the Debye temperature of Au has been determined to be 170 ± 4 K whilst modelling of the refined atomic displacement parameter through consideration of the internal energy using the Debye model shows a clear deviation from the theoretical values at temperatures exceeding 500 K. This has been interpreted as the possible formation of surface Au hydride species that have been reported elsewhere in Au/ceria catalysts\textsuperscript{57,58}. This possible formation of surface Au hydrides does not affect the refined lattice parameter and as such is not observed when modelling the Au lattice volume using Grüneisen theory applying the Debye model.

The interplay between the structural changes in the Au and the formation of cerium hydride and Ce(III) is explored through consideration of the ceria lattice expansion upon heating in the reducing 5%\(H_2/He\) atmosphere between 293 and 623 K; above 400 K the lattice parameter of the ceria is observed to expand and is associated to initially the formation of Ce(III) ions and to the presence cerium hydride due to the reversible nature observed upon cooling. The oxidation state of cerium was explored using HRXANES showing a substantial presence of Ce(III) at elevated temperatures, approximately 25% and 20% for the Au and Ag samples respectively, with the re-oxidation to majoritively Ce(IV) when cooled, approximately 7% Ce(III) presence. These results demonstrate that there is substantial reduction that occurs without the removal of oxygen from the ceria lattice further pointing towards the formation of a high temperature stable bulk cerium hydride like structure within the ceria lattice for both the Au and Ag containing samples.

Whilst detailed analysis of the Au phase present was possible, such analysis was not possible on the Ag containing sample; no clear metallic Ag phase was observed. As
such the application of the Grüneisen analysis would not be applicable in this system. However, the interpretation of the formation of a bulk hydride phase within the ceria lattice of the Au sample is also applied to the bare and Ag containing samples. The collapse of the expanded lattice parameter of the ceria phase observed on the three samples is attributed to the release of hydrogen from the lattice, the bulk hydride phase within the ceria lattice is proposed to only be stable in an expanded ceria lattice. The lattice parameter of stoichiometric ceria, $\text{CeO}_2$ at room temperature is 5.411 Å whereas $\text{CeH}_3$ is noted to have a lattice parameter of 5.539 Å.

5.4.4.1 Cerium Hydride Structure

The structure of cerium hydride, $\text{CeH}_2$ has been observed to form a fluorite phase, similar to that of ceria. A dense cerium hydride phase, $\text{CeH}_3$, has also been observed which contains hydrogen atoms placed within the octahedral and tetrahedral sites, with cerium anions occupying the cubic sites, shown in Figure 5.22A. As such one can propose a structure such that hydrogen gas, $\text{H}_2$ is dissociated and sits in the octahedral holes of the ceria lattice with a positive charge induced by the surrounding cubic oxygen sub-lattice, shown in Figure 5.22B which highlights the octahedral geometry of the described hydrogen site. Charge balance is achieved through conversion of Ce(IV) to Ce(III) by localisation of an electron from the hydrogen atoms. Furthermore, this structure is proposed to not be stable in the presence of oxygen vacancies within the bulk ceria lattice and as such cannot be used to describe the unusual redox behaviour observed in the Pd, Pt and Rh containing ceria alumina inverse catalysts.
Figure 5.22: Figures illustrating the suggested structure of the cerium hydride phase, CeH₃. 
(a) gives the unit cell of a stoichiometric CeO₂H phase, b highlights the position of the hydrogen to be within the octahedral hole at the centre of the ceria lattice unit cell. Green, red and silver spheres represent cerium, oxygen and hydrogen respectively.

5.5 Summary

In summary, an unusual redox behaviour of CeO₂ in reducing atmosphere is observed using X-ray absorption near edge structure at Ce L₃ edge, in particular in presence of certain platinum group metals. The redox behaviour of Pd, Pt and Rh containing samples is shown to be vastly different from that of Au, Ag and bare ceria alumina samples.

In the case of the Pd, Pt and Rh samples, the onset of reduction of Ce(IV) coincides directly with the reduction of PGM and occurs at a much lower temperature compared to bare ceria alumina. This is suggested to be due to the interaction of metal oxide with CeO₂ by sharing oxygen at the interface. This reduction occurs due to loss of oxygen from the lattice and thus becoming irreversible in the case of Pt, Pd and Rh containing inverse ceria alumina catalysts. Further to this reduction, the expansion of CeO₂ lattice structure provides evidence for bulk Ce(III) ions being stabilised within the fluorite ceria lattice arising from the migration of oxygen
in a reverse oxygen spill-over mechanism towards the PGM-ceria interface (PGM = Pd, Pt or Rh). The partial re-oxidation upon cooling of the ceria observed in the HRXANES on the Ce $L_3$ edge is proposed to be due to a restructuring of the ceria/alumina inter-facial region. This is due to the absence of any contraction in the bulk lattice structure observed in DxPDF above that expected through thermal contraction or reduction in refined metallic fraction of the respective PGMs demonstrating there is not oxidation of the PGMs upon cooling. Whilst the difference between the redox behaviour of Pt containing sample observed by isothermal Ce $L_3$ edge XAS and dynamic DxPDF measurements is proposed to be caused by the diffusion of oxygen being a limited process below approximately 100°C.

The Au, Ag and bare ceria alumina samples are shown to exhibit behaviour much unlike the aforementioned samples. This behaviour has not been found previously reported in literature. The expansion of the ceria lattice, and subsequent collapse upon cooling is proposed to be due to the formation of a bulk hydride phase within the ceria lattice. The absorption of hydrogen into the available octahedral hole is suggested to cause a reduction in a nearby Ce(IV) cation to Ce(III) and result in the expansion of the ceria lattice. The associated reduction of Ce(IV) is observed in HRXANES on the Ce $L_3$ edge. Upon cooling the contraction of the ceria lattice is proposed to cause the release of the hydrogen in the octahedral holes and results in the collapse of the ceria lattice along with re-oxidation of cerium to Ce(IV).


Chapter 6

General Conclusions and Future Work

The primary aim of this thesis has been to determine the structure-function relationships of catalysts under in situ reactions and to develop new analysis methodologies towards extracting unique insight into the materials studied. The dynamic structural changes of SBA-15 supported mono-metallic and bimetallic PtZn based catalysts have been studied during exposure to formic acid primarily using in situ XAS methods. Ceria supported catalysts have been studied to elucidate the metal support interaction and PGM promoted ceria reduction using several XAS and X-ray total scattering methods, whilst ceria coated alumina supported PGM catalysts have been studied to follow the unusual redox chemistry of inverse catalysts and the PGM promoted ceria reduction.

6.1 Chapter 3 - Structural Characterisation of PtZn Based Materials Under Reaction with Formic Acid

The initial characterisation of the as-received samples using SAXS and WAXS in combination to TEM provided clear evidence for the formation of Pt nano-particles in the channels of the mesoporous SBA-15 channels. No crystalline Zn phase was observed in the WAXS analysis. Analysis of the SAXS data using peak fitting has demonstrated a distortion in the SBA-15 pores due to the presence of Pt and Zn. Furthermore, in situ XAS experiments on the Pt $L_3$ and Zn $K$ edges have been utilised to explore the local coordination environment around the Pt and Zn atoms.
Ex situ XAS characterisation has demonstrated that Zn binds to the amorphous silica walls of the SBA-15 in isolated sites. Pt has been shown to present as metallic nano-particles with a partially oxidised surface.

Analysis of the in situ XAS using dose response curves have provided a unique insight into the conversion of Zn silicate like phase to a Zn formate structure concurrent to the reduction of the surface Pt oxide to metallic state. The conversion of Zn from siliate to formate is interpreted as leaching of Zn from the surface of the SBA-15. The remaining portion of Zn silicate after exposure to formic acid has been shown to directly depend on the surface coverage with Pt nano-particles. Due to the formation of Zn formate, these materials are proposed to have a limited lifetime.

The structure of Pt core Zn shell nano-particles has been determined from combined Pt $L_3$ and Zn $K$ edge ex situ XAS. Synthesis using PVP as a capping agent has been demonstrated to stabilise the metallic nature of these particles, no oxidic coordination was found for either Pt and Zn. Finally, quasi in situ studies following the formation of Pt nano-particles using formic acid in vapour phase has shown to produce small nano-particles and may provide a new method for the formation of supported Pt catalysts.

Further work regarding the SBA-15 supported PtZn catalytic materials can be envisioned for investigated alternative metals towards the decomposition of formic acid. Furthermore, the formation of single site Zn bound to the walls of channelled SBA-15 provides a unique material. Single site heterogeneous catalysts are currently attracting significant attention due to their unique catalytic properties$^{[1,3]}$. Mesoporous zinc silicates have been shown to be catalytically active towards alkane oxidation and alkene epoxidation$^{[4]}$. Single site Zn(II) ions have also shown to be catalytically active for propylene hydrogenation and propane dehydrogenation$^{[5]}$. Therefore
further work using the analysis methods developed here can be envisioned to explore the catalytic activity of single site catalysts and more specifically Zn/SBA-15. Whilst the methods employed here can be extended towards the search for similar single site catalysts.

6.2 Chapter 4 - Reducibility and Recycleability of Ceria Supported Catalysts

The redox characteristics of ceria supported PGM catalysts has been extensively studied to elucidate the promoted reduction of ceria. X-ray scattering and XAS methods have observed the structural changes to the fluorite ceria lattice that occur throughout reduction in hydrogen. The expansion of ceria lattice observed in X-ray scattering has been correlated to the formation of Ce(III) ions observed from HRXANES on the Ce\text{L}_3\text{edge}. In the case of Pt, Pd and Rh ceria supported materials, the formation of Ce(III) ions has been rationalised by the removal of oxygen from the ceria lattice. The hydrogen spill-over from Pt, Pd and Rh in metallic state has been proposed to drive the reduction of ceria.

The redox properties of the ceria support in the absence of supported PGMs has been shown to be remarkably different to the supported catalysts. Here the formation of Ce(III) ions has been demonstrated during heating in a $H_2$ atmosphere. Upon cooling the Ce(III) ions are demonstrated to re-oxidise to Ce(IV) observed using HRXANES on the Ce\text{L}_3\text{edge}. This unusual behaviour has also been corroborated using X-ray scattering studies. Hydrogen has been proposed to be absorbed into the fluorite ceria lattice within the octahedral holes to form a cerium hydride like phase. Similar results have also been shown using inelastic neutron scattering experiments\textsuperscript{6}. IR and X-ray scattering has also provided evidence for the presence of carbonaceous species in the as-received samples. The correlation between the mass loss observed in IGA, the production of $CO_2$ and the lattice parameter decrease at around 170°$C$ points directly towards the removal of surface carbonate.
Further work to understand the redox characteristics of the ceria support to confirm the presence of the proposed cerium hydride phase should be undertaken. Studies using IR methods for hydrogen coordination may provide significant insight into the potential presence of a cerium hydride phase. One can also propose neutron total scattering to follow to absorption of deuterium as a potential method of validating the proposed hydrogen site in the octahedral holes of the fluorite lattice. Furthermore, \textit{in situ} IR studies may be able to shed further light on the initial structure of the carbonate species present and to the decomposition process that occur upon heating. To further understand the passivation processes through room temperature oxidation, time resolved XAS methods can be used. This would give further insight into an redispersion mechanisms that have previously been proposed on ceria supported Pd catalysts\textsuperscript{21}. Further X-ray scattering experiments can also be considered to investigate the isothermal reaction kinetics to distinguish between the rate of reduction and the ability of each PGM to dissociate and spill-over hydrogen.

6.3 Chapter 5 - Unusual Redox Chemistry of Inverse Ceria Alumina Supported Catalysts

The study of novel ceria coated alumina supported PGM inverse catalysts has been conducted through the application of analysis methods developed in the study of ceria supported PGM catalysts. Here the behaviour of each of the three phases components has been extensively studied to elucidate the unusual redox properties of these materials.

X-ray scattering methods analysed in two phase Rietveld refinements and the advanced differential X-ray pair distribution function methods in combination to HRXANES on the Ce \textit{L}_3 edge have given a unique insight into the unusual reduction and subsequent re-oxidation processes that occur on these materials. The
majority of the reduction observed on the Pt, Pd and Rh containing samples can be adequately described by the removal of oxygen from the ceria lattice in a traditional reduction mechanism. Significantly different behaviour has been established to occur on the Ag, Au and bare ceria alumina samples. The Ag, Au and bare ceria alumina samples have been shown to undergo a partial reduction of Ce(IV) to Ce(III) concurrent to the expansion of the ceria lattice upon heating in \( \text{H}_2 \). However, upon cooling a full re-oxidation is observed. As such this redox behaviour cannot be explained by the removal of oxygen from the ceria lattice. An alternative in the form of hydrogen absorption has been proposed to occur in a similar nature to that previously described on the HSA ceria support in Chapter 4.

Further analysis undertaken through application of Grüesian theory describing the volumetric expansion of materials to elucidate the characteristics of the Au phase present within the the ceria/Au/alumina sample. This has provided evidence for a Au hydride phase present due to the deviation from the Debye model for the thermal disorder in mono-elemental systems. The use of enhanced analysis methods through consideration of theoretical models has proven to be highly valuable in understanding the complex redox chemistry exhibited here.

Further work using IR experiments would greatly develop the proposed formation of Au and cerium hydride phases under exposure to hydrogen at elevated temperatures. Computational studies using DFT methods would be highly complementary to determine the potential structure of any cerium hydride like phases within the fluorite ceria lattice. Furthermore, experiments using high time resolution on the Ce \( L_3 \), Ag and Au edges would build upon the results presented here. High time resolution would allow for a dynamic ramping similar to the X-ray total scattering experiments. X-ray scattering experiments to probe the isothermal reaction kinetics would be able to provide further insight into the strong metal-support interaction observed here.
Bibliography


Appendix A

Appendix - Chapter 3

Figure A.1: WAXS fitting shown in Q space for the as-received Pt/SBA-15, Pt₈Zn₂/SBA-15, Pt₅Zn₅/SBA-15, Pt₆Zn₂/SBA-15. Here the Bragg reflection is given as the Pt(111).
Appendix B

Appendix - Chapter 4

- Pd $K$ edge LCF fitting for the 5wt% Pd/ceria smaples are shown in figure B.1
- Pd $K$ edge LCF fitting for the 2.5wt% Pd/ceria smaples are shown in figure B.1
- Pd $K$ edge LCF fitting for the 1wt% Pd/ceria smaples are shown in figure B.1
- Pt $L_3$ edge LCF fitting for the 5wt% Pt/ceria smaples are shown in figure B.1
- Pt $L_3$ edge LCF fitting for the 2.5wt% Pt/ceria smaples are shown in figure B.1
- Rh $K$ edge LCF fitting for the 5wt% Pd/ceria smaples are shown in figure B.1
- Rh $K$ edge LCF fitting for the 2.5wt% Pd/ceria smaples are shown in figure B.1
- Rh $K$ edge LCF fitting for the 1wt% Pd/ceria smaples are shown in figure B.1
- Ce $L_3$ edge HRXANES peak fitting graphs for the HSA ceria sample are shown in figure B.9
- Ce $L_3$ edge HRXANES peak fitting graphs for the 5wt% Pd/ceria sample are shown in figure B.10
- Ce $L_3$ edge HRXANES peak fitting graphs for the 5wt% Pt/ceria sample are shown in figure B.11
- Ce $L_3$ edge HRXANES peak fitting graphs for the 5wt% Rh/ceria sample are shown in figure B.12
Figure B.1: Graphs showing the LCF fitting of the Pd K edge HRXANES for the 5wt% Pd/ceria samples.
Figure B.2: Graphs showing the LCF fitting of the Pd K edge HRXANES for the 2.5wt% Pd/ceria samples.
Figure B.3: Graphs showing the LCF fitting of the Pd K edge HRXANES for the 1wt% Pd/ceria samples.
Figure B.4: Graphs showing the LCF fitting of the Pt $L_3$ edge HRXANES for the 5 wt% Pt/ceria samples.
Figure B.5: Graphs showing the LCF fitting of the Pt $L_3$ edge HRXANES for the 2.5wt% Pt/ceria samples.
Figure B.6: Graphs showing the LCF fitting of the Rh K edge HRXANES for the 5wt% Rh/ceria samples.
Figure B.7: Graphs showing the LCF fitting of the Rh K edge HRXANES for the 2.5wt% Rh/ceria samples.
Figure B.8: Graphs showing the LCF fitting of the Rh K edge HRXANES for the 1wt% Rh/ceria samples.
Figure B.9: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the HSA ceria sample.
Figure B.10: Graphs showing the peak fitting of the Ce L₃ edge HRXANES for the 5wt% Pd/ceria sample.
Figure B.11: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the 5 wt% Pt/ceria sample.
Figure B.12: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the 5wt% Rh/ceria sample.
Appendix C

Appendix - Chapter 5

• Pd $K$ edge LCF fitting for the ceria/Pd/alumina samples are shown in figure C.1
• Pt $L_3$ edge LCF fitting for the ceria/Pt/alumina samples are shown in figure C.2
• Rh $K$ edge LCF fitting for the ceria/Rh/alumina samples are shown in figure C.3
• HRXANES peak fitting for the ceria/Pd/alumina samples are shown in figure C.4
• HRXANES peak fitting for the ceria/Pt/alumina samples are shown in figure C.5
• HRXANES peak fitting for the ceria/Rh/alumina samples are shown in figure C.6
• HRXANES peak fitting for the ceria/Ag/alumina samples are shown in figure C.7
• HRXANES peak fitting for the ceria/Au/alumina samples are shown in figure C.8
Figure C.1: Graphs showing the LCF fitting of the Pd K edge HRXANES for the ceria/Pd/alumina samples.
Figure C.2: Graphs showing the LCF fitting of the Pt $L_3$ edge HRXANES for the ceria/Pt/alumina samples.
Figure C.3: Graphs showing the LCF fitting of the Rh K edge HRXANES for the ceria/Rh/alumina samples.
Figure C.4: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the ceria/Pd/alumina samples.
Figure C.5: Graphs showing the peak fitting of the Ce L$_3$ edge HRXANES for the ceria/Pt/alumina samples.
Figure C.6: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the ceria/Rh/alumina samples.
Figure C.7: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the ceria/Ag/alumina samples.
Figure C.8: Graphs showing the peak fitting of the Ce $L_3$ edge HRXANES for the ceria/Au/alumina samples.