Understanding the Effect of Caesium Promotion on the Preparation and Activation of Copper-Based Low-Temperature Water-Gas Shift Catalysts

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DECLARATION

I, Daniela Maria Farmer, 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 thesis.
The water-gas shift (WGS) reaction has been extensively researched due to its widespread application. Its purpose is to yield the maximum amount of hydrogen, thermodynamically favoured at low temperatures, making the efficiency and stability of the Cu-based low-temperature shift (LTS) catalyst a necessity. Typically, commercial LTS catalysts are composed of CuO/ZnO/Al₂O₃ (molar ratio 0.6:0.3:0.1); however, this catalyst formulation is also used for methanol synthesis, making MeOH an undesirable by-product which can cause reactor degradation. Caesium promotion (ca. 1 wt.%) has been reported to inhibit this side reaction but is thought to lead to instability in the catalyst early on, making activation crucial.

Initially, alterations to the CuO/ZnO/Al₂O₃ (molar ratio 0.6:0.3:0.1) coprecipitation method were investigated to determine which conditions afforded catalysts with comparable properties to those employed in industry. This ensured all activation tests were commercially relevant.

Understanding how the microstructure of the active Cu⁰ component in the commercially applicable CuO/ZnO/Al₂O₃(-Cs₂O) catalyst evolves under various H₂ partial pressures in the presence/absence of Cs was determined at beamline ID15A, ESRF, where time-resolved 1D XRD and spatially-resolved XRD-CT (X-ray diffraction computed tomography) data were collected for [H₂] of 1, 2.5 and 5 %. These were compared to catalysts with higher copper loading (CuO/ZnO/Al₂O₃(-Cs₂O), molar ratio 0.8:0.1:0.1) to elucidate the importance of the zincite support and the effect of the promoter on sintering mechanisms, dislocation character and stacking fault probability.

Steam incorporation during activation was also investigated in a commissioned reactor set-up to elucidate possible early onset deactivation mechanisms resulting from the Cs-promoter. The coprecipitation method was scaled-up in order to produce industrially relevant pellets for activation testing, which were then characterised using XRD, Hg porosimetry and mechanical strength testing. This highlighted the effects of phase segregation caused by Cs-incorporation, and the susceptibility of the ZnO support sintering in wet environments.
Research in catalysis is driven by three important catalytic properties: (1) activity, (2) selectivity, and (3) lifetime. With regards to the Cu-based LT-WGS catalyst, the effect of caesium promotion has already been established in the literature to inhibit CH$_3$OH by-product formation whilst maintaining high conversion rates of CO and H$_2$O to CO$_2$ and H$_2$, but the resulting catalyst stability has not been explored/reported. The aim of this work is not to develop an optimal catalyst for LT-WGS operation but to interrogate the catalyst formulation currently employed in industry. Industrial start-up protocols were followed, providing a greater understanding of possible deactivation mechanisms occurring along the catalyst bed, which is invaluable for the application of these catalysts. Early onset deactivation mechanisms in the preparation and activation of these systems as a direct result of the Cs-promoter were identified and investigated.

The impact of this work on the catalyst industry is substantial. Typical lifetimes of LT-WGS catalysts are between 2-4 years, and their rate of deactivation is considered predictable; however, the presence of the Cs-promoter at low weight loading has proven to shorten this considerably. Understanding how caesium affects the catalyst lifetime allows for industry to identify and avoid the conditions in which early failure occurs, preventing detrimental economic fallout from unexpected plant shutdowns. The principal aim of plant operators is to achieve optimal catalyst performance throughout its lifetime. Mechanical failure of the pellets would cause a pressure drop in the catalyst bed of the LTS reactor, which, if operation were able to continue, would require the catalyst load to be reduced, producing less H$_2$, and consequentially less NH$_3$. Alternatively, if the catalyst undergoes severe morphological changes resulting in agglomeration of the active copper component, intrinsic activity would be minimised/non-existent and the whole catalyst bed would need to be replaced. The loss in earnings from the CO converted in the LTS reactor would be substantial. Additionally, if the catalyst failure was not anticipated, catalyst producers may not have sufficient reserves (many tons) to get the plant back online, resulting in an added delay (and expense) to prepare the catalyst to order.

In terms of catalyst preparation, for both catalyst manufacturers and academic ventures, the impact of hydrotalcite-like compounds expressed in the initial catalyst precipitate warrants further investigation. Ultimately, Al$_2$O$_3$ is incorporated as a structural promoter; however, if (amorphous/poorly crystalline/crystalline) HTLCs promote phase segregation of the active component, an alternative synthesis method needs to be developed to ensure spinels are formed in preference to these.

Lastly, the application of microstructural analyses to these systems has not previously been reported. The findings and the novel use of XRD-CT to map stacking fault probabilities across the plane of the catalyst bed furthers our understanding of CuO/ZnO/Al$_2$O$_3$(-Cs$_2$O) catalysts and opens up a new method to interrogate other catalytic systems.
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Chapter 1: INTRODUCTION

The production of pure hydrogen (H\textsubscript{2}) has been heavily investigated due to its many and diverse applications.\textsuperscript{1} The most well known use of H\textsubscript{2} is as an alternative low carbon fuel source, also known as the Hydrogen Economy.\textsuperscript{2,3} However, H\textsubscript{2} is used in a myriad of industrial processes for indirect energetic uses (e.g. Fischer-Tropsch synthesis, methanation, etc.) and non-energetic uses (e.g. the synthesis of ammonia (NH\textsubscript{3}), methanol (CH\textsubscript{3}OH), etc.).\textsuperscript{4} Today, the main source of hydrogen (ca. 95 \%) is generated from the reforming of hydrocarbons;\textsuperscript{4,5} however, this generates unwanted by-products such as carbon monoxide (CO). In order to maximise the amount of H\textsubscript{2} produced and reduce the pollutant concentration to ensure the process is economically and environmentally friendly, the water-gas shift (WGS) reaction can be used.\textsuperscript{6}

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]

Equation 1.1: Water-gas shift reaction\textsuperscript{7}

The WGS reaction aims to completely oxidise carbon monoxide and reduce water (H\textsubscript{2}O) into carbon dioxide (CO\textsubscript{2}) and high-purity hydrogen.\textsuperscript{8} Its use was first reported in 1888 when a combination of carbon monoxide and steam was passed over red-hot refractory material.\textsuperscript{9} This then evolved into a high temperature (HT) iron oxide/chromium oxide catalyst bed that was developed by BASF in the 1960s; however, there were still noticeable amounts of CO remaining in the reactor stream as CO removal is more effective at low temperatures (LT).\textsuperscript{10,11} It was also in this decade that the introduction of the heterogeneous copper-containing low-temperature shift (LTS) catalyst bed revolutionised the whole process.\textsuperscript{12} The combination of passing the hydrocarbon feedstock first over the HT catalyst bed and then the LT catalyst bed significantly reduced the overall amount of unconverted CO and is now common practice in industry.\textsuperscript{8,12}

The aim of this project is to investigate the preparation and activation of the low-temperature water-gas shift (LT-WGS) catalyst. Commercial catalysts are generally composed of 70:30 copper and zinc oxide (Cu:ZnO) and use alumina (Al\textsubscript{2}O\textsubscript{3}) as a support.\textsuperscript{13} Approximately 80 \% of industrial catalytic processes are dominated by the use of heterogeneous catalysts, also known as solid catalysts.\textsuperscript{14} Due to their complex compositions, it is sometimes a challenge to determine their optimum structures and activities.\textsuperscript{15} It is understood that the active component of the LTS catalyst is the metallic copper nanoparticles (Cu\textsuperscript{0}), but there is still some debate surrounding the roles of the supporting components.\textsuperscript{16,17} To fully comprehend the operation of the LT-WGS catalyst, we must first understand the relationship between the surface and bulk structure of the catalyst during activation.\textsuperscript{18}
1.1. What is Catalysis?

There is a growing demand worldwide for energy, (pharmaceutical-, petro-, fine-, commodity-) chemical products, and a reduction in greenhouse gas emissions; employing the use of catalysts offers new routes to reduce energy consumption, prepare new materials and limit waste production, overall reducing our environmental impact. Catalysts are primarily categorised into three types: (1) homogeneous catalysts, which are in the same phase (i.e. liquid or gaseous) as the reactants, (2) heterogeneous catalysts, where the catalyst and reactants are in different phases (i.e. solid/gas, solid/liquid, or liquid/gas), and (3) biocatalysts, which employ the use of enzymes. The majority of industrial processes utilise solid catalysts that are operated heterogeneously, therefore only heterogeneous catalysis will be considered.

Catalysis is commonly defined as the process of incorporating a compound, known as a catalyst, to accelerate a chemical rate of reaction, without impacting the position of equilibrium; overall, the catalyst reduces the activation energy necessary for the reaction to proceed (see Figure 1.1). It is taught that a catalyst’s morphology remains unaffected by the reaction, but in practice this is not the case. Heterogeneous catalysis can be described as a cyclic process in which reactants adsorb to the catalyst surface, form intermediate structures, and when the products are released (desorbed), the surface regenerates to its initial state. The active sites in heterogeneous catalysts are thus located on the surface and are comprised of metal nanoparticles, typically dispersed on an inert support with high surface area.

Figure 1.1: Schematic illustrating a heterogeneous catalyst’s effect on a reaction’s activation energies, where $E_A$ corresponds to the energy for adsorption, $E_S$ the energy for surface reaction, $E_D$ the energy for desorption, and $E_G$ the energy for gas phase reaction (without use of the catalyst); image taken from J. C. Védrine, Metal Oxides in Heterogeneous Catalysis, ed. J. C. Védrine, Elsevier Inc., Amsterdam, 2018, ch. 1, pp. 1-41.
1.2. Syngas Production

The water-gas shift reaction is well studied as it has been shown to yield the maximum amount of hydrogen gas from syngas. Syngas is composed of a mixture of H\textsubscript{2} and 12-40 vol.% CO\textsubscript{2}, and can be produced by a variety of processes: methane steam reforming, partial oxidation, and autothermal reforming (also known as oxidative steam reforming). In industry, the favoured method for syngas production is steam reforming (see Equation 1.2) of either methane, ethane, propane, butane or natural gas (dependent on cost and local abundance), which is then followed by the WGS reaction to yield hydrogen. The hydrogen can then be used to synthesise products of industrial importance e.g. NH\textsubscript{3} and CH\textsubscript{3}OH. An additional benefit of the WGS reaction is that it completely oxidises CO gas as it is a criterion pollutant.

To highlight the main use for the WGS reaction, Figure 1.2 details a schematic for the industrial production of ammonia. A hydrocarbon feed is passed through multiple reactors, each with a different purpose and containing separate catalysts at different temperatures and conditions. The WGS reaction is utilised as it produces the optimal amount of hydrogen from the feedstock that can be reacted with nitrogen in the Haber-Bosch process to form ammonia.

![Figure 1.2: Schematic for the industrial production of ammonia from a hydrocarbon (HC) feed; image adapted from J. R. Ladebeck and J. P. Wagner, Handbook of Fuel Cells – Fundamentals, Technology and Applications, eds. W. Vielstich, A. Lamm and H. A. Gasteiger, John Wiley & Sons, Ltd, Chichester, 2003, ch. 16, pp. 190-201.]

\[ \text{HC Feed} \rightarrow \text{Steam} \rightarrow \text{Air} \rightarrow \text{HTS} \]

\[ \text{Purification} \rightarrow \text{Pre-Reformer} \rightarrow \text{Primary Reformer} \rightarrow \text{Secondary Reformer} \]

\[ \text{Reforming} \rightarrow \text{CO\textsubscript{2}} \rightarrow \text{Methanation} \rightarrow \text{NH\textsubscript{3} Synthesis Loop} \]

\[ \text{Ammonia} \]
1.2.1. Methane Steam Reforming

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \]
\[ \Delta G_{298K}^\theta = -58.1 \text{ kJ mol}^{-1}, \ \Delta H_{298K}^\theta = +205.9 \text{ kJ mol}^{-1} \]

*Equation 1.2: Steam reforming of methane* \(^7,32\)

Steam reforming of methane (and other hydrocarbons) is endothermic (*Equation 1.2*); it needs to be carried out at high temperatures in order to shift the equilibrium reaction to favour the formation of the desired hydrogen/carbon monoxide co-products.\(^33,34\) Generally, the reformate gas contains approximately 20% CO\(_2\), as well as a mixed ratio of H\(_2\), CO and CH\(_4\).\(^35\) The concentration of carbon monoxide is dependent on the operating conditions and raw materials used, but can be approximated at 8-15 vol.%.\(^36\) The WGS reaction can then be implemented to further enrich the syngas with hydrogen and reduce the CO content.\(^33,36\)

1.2.2. Water-Gas Shift Reaction

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
\[ \Delta G_{298K}^\theta = -28.6 \text{ kJ mol}^{-1}, \ \Delta H_{298K}^\theta = -41.2 \text{ kJ mol}^{-1} \]

*Equation 1.3: Water-gas shift reaction* \(^7,8\)

The negative enthalpy of the water-gas shift reaction indicates the reaction is moderately exothermic and therefore needs to be carried out at low temperature to favour the thermodynamic products CO\(_2\) and H\(_2\).\(^37\) The reaction is exergonic and so does not need to be carried out at high pressure;\(^38\) the equilibrium reaction is largely temperature dependent, therefore, the lower the temperature, the more CO is converted.\(^39\) However, the reaction temperature must be high enough to activate the gases to reach chemical equilibrium.\(^39\) Initially, synthesis gas is passed over an iron-based catalyst in the HT shift reactor. The temperature of this reactor is generally 623-673 K and reduces the CO content to approximately 2-3 vol.%. This is further decreased to < 0.3 vol.% during the low-temperature WGS reaction at 453-473 K.\(^36\) Research has found that copper-based catalysts are generally better LTS catalysts despite their instability in the presence of oxidant gases. Supported catalysts such as ternary CuO/ZnO/Al\(_2\)O\(_3\) have generally been used to try and circumvent this problem (see *Section 1.3.2*).\(^39\)

1.3. The Active Catalyst Components

A successfully synthesised LT-WGS catalyst needs to have three key characteristics to maximise its catalytic activity: copper nanoparticles (NPs) containing surface defects, multiple
reactive Cu/ZnO interfaces, and a large Cu\(^0\) surface area.\(^{40-44}\) It is widely accepted that the active sites on the LTS catalyst are metallic copper nanoclusters.\(^ {16}\) Despite it being the active component, it is impractical to purely use elemental copper due to its very low stability towards sintering.\(^ {17}\) Therefore, supports were introduced to overcome this problem. When copper-based LTS catalysts are used for methanol synthesis, there is an obvious benefit to the Cu NPs being supported on irreducible oxides as they favour CO\(_2\) conversion to CH\(_3\)OH.\(^ {45}\) This effect is seen at a much lower rate for the water-gas shift reaction as water activation is the rate limiting step, but it results in extended catalyst lifetime.\(^ {45}\) Therefore, how the copper nanoparticles adhere to the metal oxide supports can influence the activity and thermal stability of the final LTS catalyst.\(^ {46}\)

1.3.1. The Binary Cu/ZnO Catalyst

Initially, zinc promoted binary copper-zinc oxide-catalysts were employed in industry.\(^ {47}\) Zinc is present in the oxide form (ZnO) which possesses a wurtzite structure in which half the tetrahedrally coordinated holes between the hexagonal close-packed (HCP) oxide ion layers are occupied by zinc ions. The homogeneous distribution and dispersion of ZnO throughout the catalyst are important properties of high active catalysts as demonstrated by work on the model binary Cu/ZnO system.\(^ {48}\) When zinc is deposited on the Cu(111) surface, the reaction rate can be increased by an order of magnitude. Neighbouring zinc and metallic copper atoms with a high contact area therefore appear to facilitate the WGS reaction.\(^ {49}\) A low Cu-Cu coordination number is required for maximal effect; however, this is dependent on the gas phase composition, e.g. with water present in the feed the coordination number increases.\(^ {50}\) Under WGS reaction conditions, water selectively adsorbs to the ZnO, mainly hydroxylating the (10\,\bar{1}0) surfaces.\(^ {51}\) The benefits of low coordination numbers are seen under strongly reducing conditions when the strong metal-support interactions (SMSI) cause the partially reduced zinc oxide species to partly migrate onto the copper particles.\(^ {43,49,52}\) Though the nature of the active sites is not yet fully known, it is understood that the reduced Cu\(^0\) and ZnO are involved in their formation.\(^ {53}\)

Not only do the ZnO particles act as geometrical spacers between the Cu NPs, stabilising them, but more catalytically active sites are believed to form \textit{in situ} due to the SMSI. The latter is believed to be a synergetic effect.\(^ {48,54}\) A prerequisite for the synergism between copper and zinc oxide is that they need to be in close contact, which is facilitated by the similar ionic radii of Zn\(^{2+}\) and Cu\(^{2+}\), allowing zinc to easily integrate into the CuO crystal lattice.\(^ {55-57}\)

1.3.1.1. The Role of Copper

Face-centred cubic (FCC) copper NPs are the active component in the Cu/ZnO/Al\(_2\)O\(_3\) catalyst that is associated with its catalytic activity.\(^ {16,58}\) Bart and Sneeden found, via X-ray photoelectron spectroscopy (XPS), that surface amorphous copper oxide (\textit{a-CuO}) phases present in the Cu/ZnO catalyst, at 30-80 wt.% loading, were a result of the crystalline copper oxide (\textit{c-CuO}) structure becoming distorted.\(^ {51}\) The electronic configuration of Cu\(^{2+}\) is \((t_2g)^2(e_g)^3\), which
gives an octahedral coordination (Figure 1.3). However, Jahn-Teller distortion is applied due to the need to break the degeneracy in the $e_g$ orbitals, forming a distorted octahedron $(t_{2g})^6(d_{z^2})^2(d_{x^2-y^2})$.\textsuperscript{59,60}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{octahedral_distortions.png}
\caption{The expected Jahn-Teller octahedral distortions for Cu(II) complexes. Both distortions cause a net reduction in electronic energy due to electrons in the $e_g$ subshell; the energy of two electrons is lowered whilst one electron energy is raised.\textsuperscript{60} The elongated configuration is a result of the lone electron occupying the $d_{x^2-y^2}$ orbital, causing more Coulombic repulsion between the ligands and the Cu electrons along the z-axis; this makes it more energetically favourable.\textsuperscript{61} The symmetry label E corresponds to a doubly degenerate asymmetrically occupied state and the symmetry labels A or B represent a nondegenerate state (each set of levels is symmetrically occupied).\textsuperscript{62}}
\end{figure}

It was proposed that incorporation of Zn\textsuperscript{2+} ions in the surface layer of the copper oxide crystallites forms the $\alpha$-CuO. As the surface becomes more enriched with Zn\textsuperscript{2+} ions, a highly deformed octahedral geometry is produced causing the copper ions in the CuO to form additional weak bonds between neighbouring and free O\textsuperscript{2-} ions.\textsuperscript{51} This explains the monoclinic symmetry shown in Figure 1.4 where five separate energy levels are achieved as the degeneracy has been completely removed, achieving $D_{2h}$ symmetry.\textsuperscript{59,60}
The distorted coordination shows the $e_g$ orbitals are divided by energy $\delta_2$ into two separate orbitals. Due to two of the three electrons occupying the $d_{z^2}$ orbital, there is a net reduction in energy of $\frac{1}{2} \delta_2$ making it a favourable environment.\textsuperscript{59,60}

When the loading of copper exceeds 80 wt.\%, the following trends are evident as the Cu concentration increases: (1) the amount of $c$-CuO, whose Cu$^{2+}$ ions have square-planar coordination, increases with decreasing ZnO concentration, and (2) the concentration of $a$-CuO found on the surface decreases. This further supports that $a$-CuO is facilitated by the presence of ZnO.\textsuperscript{51}

There is much debate about whether the copper-zinc oxide-based catalyst performance is related to the available Cu$^0$ surface area or if there are other parameters that the catalyst is more sensitive to.\textsuperscript{61} However, it was clear that an alternative catalyst to the binary system needed to be found for industrial purposes, as time proved they did not have sufficient thermal stability to operate in steam at the necessary temperatures (around 473-523 K). In order to extend the catalyst’s lifetime in the forcing conditions, an additional support was included.\textsuperscript{47}

### 1.3.2. The Ternary Cu/ZnO/Al$_2$O$_3$ Catalyst

Cu/ZnO catalysts supported on Al$_2$O$_3$ are ideal for industrial applications.\textsuperscript{17} Refractory oxides such as Al$_2$O$_3$ and TiO$_2$ are favourable support materials as they are relatively inert, but exhibit high porosities, specific surface areas, and thermal and mechanical stability properties.\textsuperscript{64} The industrially applied Cu/ZnO/Al$_2$O$_3$ catalyst utilises approximately 10-20 mol.\% gamma-Al$_2$O$_3$ as a structural promoter.\textsuperscript{54,65}

There is some debate regarding the promotional effects of an alumina support. Some papers propose that the purpose of the alumina is solely to prevent the catalyst from sintering.\textsuperscript{66} It is known that when this transition metal oxide is incorporated into the catalyst as Cu/Al$_2$O$_3$, a highly dispersed Cu$^0$ is formed. This leads to an increase in WGS activity, confirming Cu NPs are the active component; therefore, incorporation of alumina in the precipitate is an added
dispersion property which helps to prevent sintering of the catalyst, improving the overall activity.\textsuperscript{63,67} When combined with zinc, a ZnAl\textsubscript{2}O\textsubscript{4} spinel is formed which further contributes to the catalyst’s stability as it acts as an additional geometrical spacer between the copper crystals. When the ZnO/Al\textsubscript{2}O\textsubscript{3} supports are separated from the active copper component, no activity is seen, as expected.\textsuperscript{51}

Both ZnO and Al\textsubscript{2}O\textsubscript{3} are considered supports for the copper in the LT-WGS catalyst as the oxides and spinels hinder the crystallization of the copper phase by acting as stabilisers.\textsuperscript{51} Despite Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts currently being almost exclusively used as low-temperature shift catalysts, there is much debate surrounding the role of the support and promoter, the active site nature and the reaction mechanism(s).\textsuperscript{17}

The notion that Al\textsubscript{2}O\textsubscript{3} is purely a structural promoter and has no direct role in catalysis is, however, contradicted by other evidence. The inert support plays a key role in the catalytic reaction not only by stabilising the Cu\textsuperscript{0} crystallites and improving the catalyst’s morphology, but also by enabling the formation of hydrotalcite precursors (see Section 1.6.3); these have been correlated with high final catalytic activity.\textsuperscript{68} The enhanced stability and morphology of the hydrotalcite-like phases are thought to be a result of the Al\textsuperscript{3+} being incorporated in the tetrahedrally coordinated sites of the ZnO lattice.\textsuperscript{69} Reduction is believed to activate the enrichment of aluminium cations on the ZnO surface of the catalyst.\textsuperscript{70}

\textgamma-Al\textsubscript{2}O\textsubscript{3} appears to be the preferred transition alumina to use for the LTS support, though the reasoning behind this is not clear. Its textural properties – such as its acid/base characteristics and high surface area to volume ratio – are a result of the \textgamma-Al\textsubscript{2}O\textsubscript{3} phase composition, surface chemical composition and local microstructure.\textsuperscript{71} \textgamma-Al\textsubscript{2}O\textsubscript{3} is considered to be a defect spinel from space group \textit{Fd\textbar{3}m}. Depending on the compound it is derived from, \textgamma-Al\textsubscript{2}O\textsubscript{3} can have a cubic lattice (from amorphous precursors), a cubic lattice and a tetragonal distortion (from boehmite), or a tetragonal structure.\textsuperscript{72} In the case of the cubic spinel defect, the cubic close packing (CCP) of the oxygen atoms creates octahedral and tetrahedral sites which the aluminium atoms occupy.\textsuperscript{71}

1.3.3. The Role of the Support

The surface-specific activity, also known as the turnover frequency, and the catalyst selectivity are dependent on the nature of the active sites, for example the size, shape and composition of the Cu nanoparticles. The number of active surface sites can be increased per unit weight of metal by reducing the size of the NPs, thereby increasing the overall activity of the catalyst.\textsuperscript{64} Despite it being a common assumption that the presence of alumina increases the number of active sites, this is actually a result of electronic promoters.\textsuperscript{69,73} Electronic promoters like ZnO have the ability to modify the active sites which in turn affects the kinetics of the reaction.\textsuperscript{69}
1.3.3.1. Catalyst Bulk Structure

When porous supports are employed, accessibility of the active sites must be considered. Pellets are utilised in industry as opposed to fine powder grains in order to prevent pressure drops in the reactor; however, this limits the mass-transfer capabilities of the active sites and thus makes the macroscopic distribution of the active sites an important factor. During the catalytic process, the reaction fluid passes through the catalyst pores to reach the active sites. However, products may form in the interior of the grains faster than diffusion is able to take them away, causing the interior to be relatively inactive. For this reason, the rate of mass-transfer of reactants to and products from the active sites is dependent on the external surface area, \( S_p \). Thus, the Thiele modulus, \( \phi \), can be used to calculate the degree of mass-transfer limitations.

The effective diffusion coefficient, \( D_e \), of the reactant is dependent on the other species present and the pressure of the reactor, it is independent of the catalyst pore radius.

\[
\phi = \frac{V_p}{S_p} \sqrt{\frac{k_r}{D_e}}
\]

*Equation 1.4: Thiele modulus*

Where

- \( V_p = \) pellet volume / cm\(^3\)
- \( k_r = \) first order rate constant / s\(^{-1}\)
- \( D_e = \) effective diffusion coefficient / cm\(^2\) s\(^{-1}\)

In general, the Thiele modulus is calculated for spherical catalyst pellets; however, the pellets discussed in this report are cylindrical. This configuration exhibits a different volume-to-surface ratio (a spherical pellet with the same radius affords a \( V_p/S_p \) value three times greater than a cylindrical pellet), and so the characteristic length is given by *Equation 1.5.*

\[
\begin{aligned}
V_p &= \pi (R_p)^2 \cdot 2x_p \\
S_p &= 2\pi (R_p)^2 + (2\pi R_p \cdot 2x_p)
\end{aligned}
\]

*Equation 1.5: Characteristic length, as defined by the volume-to-surface ratio*

Where

- \( R_p = \) pellet radius / 0.25 cm
- \( 2x_p = \) cylindrical pellet length / 0.39 cm (\( x_p = 0.20 \text{ cm} \))

When the Thiele modulus is large (\( \phi > 0.3 \) as stated by P. Munnik *et al.*), then internal reactant diffusion through the catalyst pores is rate limiting. Therefore, if the reaction is slow,
homogeneous macroscopic metal distributions of the active phase are favoured as reactants then have time to diffuse to the active sites. For fast catalytic reactions or if there is a problem with secondary reactions, egg-yolk or eggshell distributions may be preferred. Egg-white distributions are only achieved if the reactants contain poisons, such as chlorine or sulfur, which then react with the active sites on the outskirts of the catalyst body (where there is low metal loading).\(^{64}\)

![Figure 1.5: Examples of macroscopic metal distributions of the active phase across a support body: (a) homogeneous distribution, (b) egg-yolk distribution, (c) eggshell distribution, (d) egg-white distribution.\(^{64}\)](image)

1.4. Preparation of Low-Temperature Shift Catalysts

There are two main methods which are used when preparing copper-based LTS catalysts: impregnation and coprecipitation.\(^{77}\) Though impregnation is deemed an easier, inexpensive method, it does not achieve as high a metal loading as coprecipitation; typically the metal loading for impregnation is \(< 30 \text{ wt.\%}\). In contrast to this, the metal loading for coprecipitation is approximately \(60 \text{ wt.\%}\) and can be as high as \(80 \text{ wt.\%}\). The high metal loading ability of catalysts prepared by coprecipitation makes them ‘self-supporting’ or ‘bulk’ catalysts. In conjunction with this, these catalysts also have relatively high metal dispersion, which increases the WGS activity.\(^{77}\)

For catalysts containing expensive active components such as precious metals, impregnation of a support is used. The pore-volume of the support determines the maximum volume of the active component solution that can be incorporated; therefore, it is essential the required metal loading is present in said solution.\(^{78}\) Once impregnation has been carried out and a homogeneous dispersion of the active phase has been achieved, the precursor phase can be thermally activated after the drying step.\(^{79}\) A clear advantage of this method is that no waste water is formed as an unwanted by-product and the active components are completely dispersed amongst the support. However, when the active catalytic components are relatively cheap, the loading is dependent on the desired activity per unit volume/weight of the catalyst making impregnation and drying inefficient.\(^{78}\) For the purpose of this review only coprecipitation will be considered as it is the most frequently applied.\(^{80}\)

The term “coprecipitation” is generally used as an all-encompassing method for mixed salt solution precipitations. The precipitation process involves different metal species
simultaneously precipitating out of solution either alongside the support or through binary precipitate formation. Coprecipitation is ideal for catalysts composed of multiple components as it yields the most homogeneous macroscopic metal distribution of heterogeneous catalysts. It is a highly versatile single process as various combinations of metallic and/or non-metallic supporting agents can be incorporated into the final catalyst. When the method is used for the generation of stoichiometrically defined precursors, the precipitate phases require a calcination and/or reduction stage in order to produce the desired catalyst (see Section 1.5).

Figure 1.6: Schematic for the preparation, activation and operation of the ternary Cu/ZnO/Al₂O₃ catalyst

1.4.1. Precipitation

To elaborate on the preparation process, the precursor (e.g. malachite (Cu₂CO₃(OH)₂), hydrotalcite ((Cu,Zn)₆Al₂CO₃(OH)₁₆), etc.) is precipitated from an aqueous solution of the Cu, Zn and Al metal nitrates (Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O). Metal nitrates are used as the active metal and support salts as they are highly soluble when mixed with alkaline reagents in aqueous media. Some groups have favoured utilising metal chlorides or sulphates; however, especially for industrial applications, limiting the amount of poison the catalyst is exposed to is essential (see Section 1.8.5).

The precipitation is initiated by the addition of a precipitating agent. This induces a chemical reaction or a reduction in solubility, creating a phase-separation of the solid precipitate
and the super-saturated homogeneous solution. Due to the high supersaturation, amorphous precursors are repeatedly formed as the precursor phases.\textsuperscript{82}

Hydrolysis of the copper(II) ions is evident by the neutralisation of the starting acidic solution with the basic sodium carbonate precipitating agent. At pH 3 a plateau is evident in which the Cu\textsuperscript{2+} begins precipitating out of solution. Similarly, this can be seen with the Zn\textsuperscript{2+} solution; however, here the precipitation occurs at pH 5. This difference in hydrolysis behaviour means that if the reaction mixture pH is not carefully controlled, the Cu\textsuperscript{2+} precipitates out of solution first, followed by Zn\textsuperscript{2+}, which would not be considered a true-coprecipitation as a mixed binary precipitate is not formed. In order to overcome this problem, the pH must be kept constant throughout; this is achieved by simultaneously dosing the metal nitrate solution with the precipitating agent.\textsuperscript{41} This form of coprecipitation is also known as a low supersaturation method;\textsuperscript{42} the resulting precipitate has a homogeneous distribution of Cu\textsuperscript{2+} and Zn\textsuperscript{2+} (and Al\textsuperscript{3+}) cations. It is unclear whether this method also qualifies as a true coprecipitation or a sequential precipitation, where single droplets precipitate temporally and spatially rather than concurrent coprecipitation of the entire batch solution (see Appendix 7.1.1 for titration curves).\textsuperscript{41}

With this insight we can deduce that, to guarantee that the Zn\textsuperscript{2+} (and Al\textsuperscript{3+}) precipitates are formed, the pH of the reaction mixture should not be lower than pH 5. It has also been found that if the pH exceeds pH 9, oxolation of the basic Cu(OH)\textsubscript{2} to stable tenorite, CuO, occurs, unfavourably disaggregating the Cu/Zn precipitate.\textsuperscript{41}

\[
\text{Cu}_2(OH)_3(NO_3) + \text{OH}^- \rightarrow 2\text{CuO} + 2\text{H}_2\text{O} + \text{NO}_3^- \tag{1.6}
\]

\textit{Equation 1.6: Formation of tenorite}\textsuperscript{83}

The most commonly used precipitating agent is Na\textsubscript{2}CO\textsubscript{3}; however, NaOH, NaAlO\textsubscript{2} and/or NaHCO\textsubscript{3} can also be incorporated depending on the desired precursor phase.\textsuperscript{11} The pH is kept constant by adding either the acidic metal nitrate solution or the alkaline sodium carbonate solution dropwise to the reaction mixture.\textsuperscript{67} However, G. Simson \textit{et al.} found that the use of sodium hydroxide as a precipitating agent produces a catalyst with a markedly lower surface area (conventional batch precipitation with Na\textsubscript{2}CO\textsubscript{3}: \textit{ca.} 80 m\textsuperscript{2} g\textsuperscript{-1}, whereas batch precipitation with NaOH: \textit{ca.} 18 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{84}

\textbf{1.4.1.1. Support Properties}

Although the solubility properties of oxidic supports have not been explicitly considered, it is known that partial dissolution can occur in acidic or alkaline solutions which may have an impact on the synthesis of the catalyst.\textsuperscript{64} A high concentration of hydroxyl groups can be found on the surface of oxidic supports. These are essential for the metal precursor to interact with the support as they act as adsorption sites, being either protonated or deprotonated depending on the
pH of the reaction mixture and the support. Each support has an individual pH in water where the net charge of the hydroxyl surface groups is zero, also known as the point of zero charge (PZC). Above the PZC, the surface is negative as the hydroxyl groups are deprotonated, and below the PZC the surface is positive. Both ZnO and Al$_2$O$_3$ are amphoteric oxides, therefore in aqueous solutions they adopt this dissolution behaviour. An extensive list of all the PZCs associated with each metal oxide is supplied by M. Kosmulski et al.

1.4.2. Ageing

Following precipitation, the desired crystalline precursor is transformed from the initial amorphous precipitate during ageing. Depending on the ageing method (e.g. controlled or uncontrolled pH), the phase composition of the end precursor can vary greatly (see Section 1.6).

1.4.2.1. The Effects of pH

When the reaction mixture is left to “free age” in the mother liquor, this means that the pH is not being controlled. We can see that the pH gradually increases throughout the ageing process which is due to the evolution of CO$_2$ from the precursor slurry.

$$\text{CO}_2^- + \text{H}^+ \rightarrow \text{HCO}_3^-$$
$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

*Equation 1.7: Evolution of CO$_2$*

At low pH, pure copper phases are obtained, e.g. CuO, which give larger particles than those formed from slurries aged at higher pH values. The optimal pH values of the precipitation are dependent on the thermodynamic speciation of each of the reaction components. Therefore the temperature must also be carefully considered when designing the experiment.

The composition of nitrate derived ternary catalysts precipitated at pH 7 and calcined at 623 K consist not only of CuO, ZnO and spinel (CuAl$_2$O$_4$, ZnAl$_2$O$_4$) phases, but also a small wt.% of OH$^-$ and CO$_3^{2-}$ groups (from remaining water and carbon dioxide). Formation of the precursor phase is dependent on the anion skeleton holding onto hydroxyl and carbonate groups throughout the low temperature thermal treatments.

1.4.2.2. The Effects of Ageing Time

Care must also be taken to ensure the precursor slurry is not aged for too long as it can cause disadvantageous deterioration of the catalytic activity and porosity of the final catalyst. The literature states that when the precipitated catalyst precursors are aged for more than 30 min, they show a considerable increase in activity as this determines the microstructural characteristics of the catalyst.
It is suspected that the relationship between copper activity on ZnO and microstrain is an important factor when considering catalyst preparation, as the lattice strain is believed to modify the active copper surface area.\cite{18, 90} In order to capitalise on this correlation, the synthesis should be tailored to favour microstrain in the copper particles. However, in theory, all variables involved in the coprecipitation affect the catalyst’s microstructural features.\cite{18} B. L. Kniep \textit{et al.} reported the presence of a small degree of strain in the malachite precursor phase (unsupported copper precursor), which is enhanced when ZnO is incorporated in the precursor phase.\cite{18} Therefore, the lattice strain is enhanced by the presence of defects allowing us to conclude that the function of the incorporated zinc oxide is not solely to stabilise the copper NPs against sintering and disperse the copper particles homogeneously.\cite{91} It has been suggested that there are three possible reasons for the strain: (1) imperfections in the copper lattice due to zinc incorporation, (2) Cu and ZnO being epitaxially orientated, or (3) Zn NPs preventing the copper from fully reducing.\cite{18, 90}

The longer the LT-WGS catalyst precursor phase is aged, the greater the microstrain present in the copper particles; this is shown \textit{via} X-ray diffraction (XRD) patterns which display different crystallographic properties for the particle size and microstrain depending on ageing time. This lends itself to catalyst ageing being important in determining the microstrain and morphology of the precipitate particles, thus also synthesising a catalyst with high specific and catalytically active surface area.\cite{18, 53}

### 1.4.3. Washing

It is important to filter and wash the catalyst precursors thoroughly with distilled water to remove any remaining sodium and nitrates as these impurities can lead to particle agglomeration and sintering during any thermal treatment (see \textit{Section 1.8}).\cite{54, 64} This is also a major drawback of coprecipitation as large amounts of salt solution (NaNO$_3$) are generated which need to be disposed of.\cite{77}

### 1.4.4. Chemical Memory

Coprecipitation is considered a relatively difficult method as the reaction conditions need to be carefully controlled. In a single process, the chemical phase(s), dispersion and surface area of the active phase are created simultaneously. The porous structure and the particle size and shape are also determined by agglomeration of metal nitrate particles and precursor phase aggregates.\cite{77, 92} However, thus far there is not a single process method that can be employed that satisfies all the ideal conditions required as these individual properties are dependent on separate process conditions such as the nature of the stirring. Therefore, to limit human error and ensure its reproducibility, specialist equipment\cite{77} such as semi-automatic synthesis equipment can be employed.\cite{93} This is because the catalytic performance of the product is dependent on the “chemical memory” of the system. During each preparation step, care must be taken to carry out
the method with precision since any changes could lead to the formation of a different precursor phase and thus a completely new catalyst product.\textsuperscript{53}

As there are many parameters that must be considered when optimizing ternary Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts, binary Cu/ZnO samples are used as model systems.\textsuperscript{54} It is known that there is a linear relationship between the available metallic copper surface area and the performance of the catalyst.\textsuperscript{63} However, it is unclear how adapting various parameters affects this. It has been reported that the copper metal area available to undergo the WGS reaction can be increased, for example, by increasing the concentration of the Na\textsubscript{2}CO\textsubscript{3} precipitating agent (nitric acid can also be used\textsuperscript{67}) or by optimizing the method to favour small particle sizes.\textsuperscript{94} M. J. Climent \textit{et al}. suggested that sonification of samples during crystallization produces crystals with smaller grain size and finer structure.\textsuperscript{95} Alternatively, at precipitating temperatures > 333 K and at a pH of 6-7, P. Munnik \textit{et al}. determined that high metallic copper surface areas could be achieved.\textsuperscript{64}

As previously stated, minute variations in the chemical parameters of the precursor preparation, such as the pH or temperature, can significantly alter the end precursor composition. In addition to these, the “non-chemical” parameters must also be taken into account, for example the stirring speed and batch size of the reaction. All these factors must be carefully controlled in order to ensure the reproducibility of the experiment, which is one of the largest problems industry is currently faced with.\textsuperscript{41} In summary, the chemical memory refers to the catalyst’s properties being highly dependent on each individual parameter associated with the precipitation and ageing process.\textsuperscript{86}

1.5. Activation

Activation of the copper-based low-temperature shift catalysts occurs in two stages: calcination and reduction.

1.5.1. Calcination

During calcination (573-773 K), the hydroxycarbonate precursors degas as CO\textsubscript{2} and/or H\textsubscript{2}O to form the oxide intermediate CuO/ZnO/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{16,53,67} Within the calcined sample, the Cu:Zn ratio on the surface of the catalyst remains the same; therefore, the composition and structure of the intermediate is dependent on the hydroxycarbonate precursor formed in the coprecipitation process.\textsuperscript{51} This is very important as the homogeneously dispersed arrangement of copper and zinc species needs to be maintained to obtain the desired high activity of the catalyst.\textsuperscript{41}

Despite the carbonates decomposing to give CO\textsubscript{2}, a large concentration of high-temperature carbonates remains in the calcined catalyst which have been correlated to an optimised copper dispersion and Cu/ZnO interfacial region.\textsuperscript{53} Residual carbonate is thought to stabilise the catalyst structure by forming a copper suboxide species that enhances the chemical activity of the overall catalyst.\textsuperscript{16} Consequently, the formation of smaller active particles is
achieved after reduction. From binary studies of the Cu/ZnO hydroxycarbonate intermediates, it has been demonstrated that during reduction, these remaining phases enable highly active sites to form on the surface.\textsuperscript{16}

To use zincian malachite (see Section 1.6.1) as an example of a precursor phase used in the LT-WGS catalyst, thermogravimetric analysis shows that the precursor decomposes in two stages. The following parameters are based on the binary system, as for the ternary system the stages occur at lower temperatures. Following the initial desorption of physisorbed H$_2$O and CO$_2$, the primary step occurs at approximately 553 K. Here, water and carbon dioxide concurrently desorb and form the following intermediate phase:\textsuperscript{93}

$$2(Cu,Zn)_2(OH)_2(CO_3) \rightarrow (Cu,Zn)_4O_3CO_3 + 2H_2O + CO_2$$

\textit{Equation 1.8: Formation of a high-temperature carbonate intermediate from zincian malachite}\textsuperscript{93}

This phase is referred to as a high-temperature carbonate (HT-CO$_3$\textsuperscript{2-}) in which dispersion of the nanoparticles is preserved. Changes to the crystallinity of the catalyst occur in the second stage. Here, the metal oxides are formed after 753 K which is highlighted by the release of CO$_2$:\textsuperscript{93}

$$(Cu,Zn)_4O_3CO_3 \rightarrow 4(Cu,Zn)O + CO_2$$

\textit{Equation 1.9: Complete decomposition of the zincian malachite precursor}\textsuperscript{93}

\subsection*{1.5.2. Reduction}

Once the catalyst has been activated via calcination, the reduction can take place to form the porous microstructure of aggregates which make up the active catalyst.\textsuperscript{16,51} In the second catalyst activation step, copper is reduced to a metallic copper state. It is thought that at this stage the copper and zinc oxide compounds form an intimate mixture on the alumina support as the Zn$^{2+}$ and Al$^{3+}$ cations present in the calcined catalyst stabilise the CuO and facilitate its reduction to metallic Cu.\textsuperscript{51,96} A fourth component, e.g. an alkali metal promoter, can also be incorporated for stability purposes; however, it may affect the reduction conditions (see Section 1.7.1).\textsuperscript{96}

Industrially, the catalyst is reduced in a dilute hydrogen flow. According to Bart and Sneedon, from the temperature-programmed reduction (TPR) profile of the Cu/ZnO/Al$_2$O$_3$ catalyst we can identify four kinds of copper species based on their reduction temperatures: (1) $a$-CuO phases at 463 K, (2) Cu$^{2+}$ found in the ZnO lattice at 483 K, (3) $c$-CuO at 493 K, and (4) Cu$^{3+}$ found in the alumina phase at 503 K. During the reduction process, the copper undergoes two stages of reduction at varying temperatures:\textsuperscript{51}
\[
\text{Cu}^{2+} \rightarrow \text{Cu}^{1+} \rightarrow \text{Cu}^{0}
\]

*Equation 1.10: Reduction of copper(II) ion*\(^{51}\)

However, not all of the Cu\(^{2+}\) is reduced to the active metallic copper as the copper ions embedded in the zinc oxide lattice are thought to remain stabilised as Cu\(^{1+}\).\(^{51}\) The degree of reduction is therefore important; if needed, the catalyst can be further reduced in either pure H\(_2\) or CO gas, although there is some debate regarding whether a fully reduced catalyst would display any catalytic activity. It is noteworthy that the composition of the reduced catalyst is independent of the carrier gas used.\(^{51}\)

1.6. **Phase Evolution of the Precursors**

Current Cu/ZnO/Al\(_2\)O\(_3\) catalysts that are used in industry generally contain a high content of copper (50–70 wt.\%) and are synthesised from hydroxycarbonate precursors. Determining which precursor phase is the most efficient for the low-temperature water-gas shift reaction is incredibly important as they have varying catalytic properties.\(^{53}\)

1.6.1. **Malachite/Zincian Malachite/Rosasite**

Structurally, rosasite and zincian malachite, \((\text{Cu},\text{Zn})_2\text{CO}_3(\text{OH})_2\), are very similar making it difficult to differentiate between the two solid solutions. They differ only by their total zinc metal content, where (zincian) malachite can contain as low as 0 wt.% Zn and rosasite is generally between 33–50 wt.%. It has been reported that as a result of this difference in composition, they possess two crystallographically distinct structures (as shown in *Figure 1.7*) due to separate orientations of their space group symmetry operators \((P2_1/a)\).\(^{86,97}\) However, confirming this via XRD has proven challenging as the precipitated samples are poorly crystalline making it difficult to distinguish variations in their crystalline structures. This has led to the terms being used synonymously.\(^{86}\)
Figure 1.7: Comparison of the crystal structures of (a) malachite and (b) rosasite$^{97}$

When identifying malachite-type precursor phases, XRD peaks in the 2θ-range below 30° are considered fingerprint reflections in catalysis research. However, this region offers no insight into the Cu:Zn ratio of the LT-WGS catalyst as their positions remain more or less the same for varying compositions of the malachite precursors. Though this could be rationalised by the similar ionic radii of Cu$^{2+}$ and Zn$^{2+}$, it is clear the cell parameters are modified by changes to the (20-1) and (21-1) peak positions found between 31-33 °2θ.$^{97}$ Therefore, using the $d$-spacing of the (20-1)- and (21-1)-reflections, we can determine distinct structural differences between malachite (Cu$_2$CO$_3$(OH)$_2$) and zincian malachite. The malachite crystal structure is arranged as a CuO$_6$ octahedra, $d^9$, therefore the elongated Jahn-Teller distorted coordination is preferred. As Zn$^{2+}$ ions, $d^{10}$, are atomically substituted into the structure forming zincian malachite, the substitution of the Jahn-Teller Cu$^{2+}$ ions shifts the reflections to lower $d$-spacings (higher angles) in the XRD patterns.$^{16,97,98}$ It has been experimentally shown that the copper surface area and $d$(20-1)-spacing of the precursor phase are related, suggesting the maximum content of zinc that should be incorporated into the Cu/ZnO catalyst model is 28 wt.%. When the zinc content is shifted above the critical composition up to 50 wt.%, the rosasite precursor is formed.$^{98}$ To summarise, the $d$-spacing of the precursor reflections is a useful indicator of the amount of zinc contained within the malachite structure.$^{97}$

Zincian malachite is generally the preferred precursor phase to focus on when designing a low temperature water-gas shift catalyst.$^{98,99}$ Industrially, the optimal Cu:Zn ratio used is between 2-3:1. Zincian malachite has a mixed cationic sub-lattice due to copper oxide’s and zinc oxide’s dissimilar crystal structures. This is shown by the trend of its $d$(20-1) spacing, highlighting
the perfect distribution of the copper and zinc elements on an atomic level. Once the precursor has undergone thermal decomposition, individual CuO and ZnO nanoparticles are formed. As CuO and ZnO are already homogeneously intermixed throughout the lattice, and they maintain their nanostructured arrangement upon reduction, zinic malachite is a favoured phase to form as opposed to the intermixing of a Cu-rich and a Zn-rich precursor phase.98

When preparing the precursor phase, the initial precipitate formed is generally that of zincian georgeite, \((\text{Cu},\text{Zn})\text{CO}_3(\text{OH})_2\), which is a poorly crystalline precursor to zincian malachite consisting of large and bulky particles. This type of delayed crystallization appears to be exclusive to the malachite system. Once the precipitate has aged, thin needles can be seen in the electron microscopy (EM) image, which are indicative of the formation of zincian malachite. The size of the particles during this step is not dissimilar to the final size of the copper particles (typically 5-15 nm), meaning a high Cu surface area should be achieved. Critically, the porosity and the unique meso-structure of the Cu/ZnO/Al\(_2\)O\(_3\) catalyst are predetermined during the ageing process.98 Subsequently, the zincian malachite needles are thermally decomposed into mostly copper- and zinc oxide NPs during the calcination step. In order to preserve the porosity and needle-like meso-structure of the monoxide intermediate, the calcination temperature cannot be too high. Both of the above steps are required to form the desired alternating structure of Cu and ZnO NPs found in commercial Cu/ZnO/Al\(_2\)O\(_3\) catalysts, once the catalyst has been further activated via reduction.98

When the copper content of the Cu/ZnO model is approximately between 60-72 wt.%, an aurichalcite precursor phase is formed alongside the zincian malachite phase. However, increased amounts of aurichalcite in the precipitate cause a decrease in copper surface area as the total copper content in the sample is lowered.98 D. Waller et al. showed that, by ensuring the slurry is aged sufficiently in the mother liquor, the presence of aurichalcite in the precursor phase can be prevented.100 The literature data shows that it is possible to differentiate between the rosasite and aurichalcite phases using infrared (IR) spectroscopy according to their fingerprint bands. IR spectra of each of the precursors give absorption bands in separate regions corresponding to O-H stretches (4500-2500 cm\(^{-1}\)), asymmetric C-O stretching of carbonate anions in the \(v_3\) mode (1700-1100 cm\(^{-1}\)) and further carbonate bands in the \(v_2\) and \(v_4\) modes as well as O-H deformation vibrations (1200-600 cm\(^{-1}\)). There are also distinct skeletal M-O vibrations associated with each phase < 600 cm\(^{-1}\), especially unique for rosasite, highlighting the sensitivity to the Cu/ZnO ratio; the identifiable band for rosasite is observed at 666 cm\(^{-1}\).86

By increasing the amount of Al\(^{3+}\) incorporated into the catalytic system, it is harder to obtain a phase pure zinic malachite precursor as the excess aluminium crystallises to give a hydrotalcite-like compound as a by-phase (see Section 1.6.3).73 As aluminium is incorporated into the malachite structure, a clear unit cell contraction of the \(d(20-1)\)-reflection can be seen in the corresponding XRD patterns, which is not visible in the absence of zinc. This change can therefore only be attributed to the Al\(^{3+}\) showing there are non-Jahn-Teller ions present in the lattice. It was
determined by M. Behrens et al. that the maximal incorporation of aluminium into the malachite structure was up to 3 wt.%, which is significantly lower than the aforementioned maximum amount for Zn$^{2+}$ at 28 wt.%. This difference in amounts is a result of the capabilities of the Cu$^{2+}$ sites to carry excess positive charge on them.\textsuperscript{73}

1.6.2. Aurichalcite/Hydrozincite

Aurichalcite, (Cu,Zn)$_5$(CO$_3$)$_2$(OH)$_6$, has a complex sheet structure, also known as a platelet morphology.\textsuperscript{51} It is composed of close-packed oxygen double layers which are parallel to Cu(100). As Figure 1.8 suggests, the insides of these double layers are made up of 60\% octahedral (M1) and 40\% tetragonally elongated (M2) sites.\textsuperscript{51,101} Zinc ions preferentially occupy the tetrahedral sites whereas copper migrates towards the octahedral sites, although substitution of Cu by Zn can occur in the octahedral holes.\textsuperscript{51} On the outside of the double layers, tetrahedral (M3) and trigonal bipyramidal (M4) sites are found. These layers have hydrogen bonding on one side, between the carbonate oxygen and the hydroxyl groups, and metal-oxygen bonding on the other.\textsuperscript{101}

![Crystal structure of aurichalcite](image)

Figure 1.8: The crystal structure of aurichalcite \textsuperscript{101} (see Appendix 7.1.2 for coordination environment)

As aurichalcite has the highest zinc metal content of the mixed hydroxycarbonate precursors, it is unsurprising that of the Cu/Zn containing phases it is most structurally related to hydrozincite, Zn$_5$(CO$_3$)$_2$(OH)$_6$.\textsuperscript{86} Both these precursors are monoclinic and twinned.\textsuperscript{102} The only differing structural features of hydrozincite include both the absence of M4 sites and the lack of hydrogen bonding between any of the layers as shown in Figure 1.9.\textsuperscript{101}
If there is either aurichalcite or hydrozincite present in the precursor phase, the XRD pattern yields a strong characteristic (200)-reflection at 13°2θ. Deciphering between the phases can be accomplished by identifying the presence of a strong (121)-reflection at 34°2θ corresponding to aurichalcite. With increased copper content, the (002)-reflections of the hydrozincite diffraction patterns shift to lower d-spacing. This may be due to the copper substituting the zinc in the octahedral sites, causing the axial bonds to shorten marginally. When aurichalcite is substituted with zinc, the (121)-reflections are shifted slightly to higher d-spacing values where they overlap with the (002)-reflections of hydrozincite. These shifts are indicative of both series being equally substituted. B. Bems et al. have shown that aurichalcite can also be identified using infrared spectroscopy, giving weak adsorptions around 970 and 1200 cm⁻¹.

1.6.3. Hydrotalcites

There is a group of minerals found in nature based on the brucite structure (Mg(OH)₂). These anionic clays are known as hydrotalcite-like compounds (HTLCs) or lamellar double hydroxides/layered double hydroxides (LDHs). For the purpose of this review they shall be referred to as HTLCs. HTLCs are composed of brucite-like positively charged octahedral sheets. The overall positive charge is a result of the divalent Mg²⁺ cation being substituted for a trivalent cation (Al³⁺ or Fe³⁺). The cationic hydroxyl surface charge is counterbalanced by the presence of exchangeable anions (CO₃²⁻) in the brucite interlayer. Interlayer water molecules can also be found as they help stabilise the structure through hydrogen-bonding between the
water, anions, and hydroxyls. Another stabilising factor is the electrostatic interactions between the anions and the LDH.

By incorporating an Al\(^{3+}\) support to form the ternary WGS system, the most favoured Cu-poor phase formed becomes a hydrotalcite-like compound rather than the aurichalcite precursor phase. The type of hydrotalcite precursor synthesised is dependent on the moles of Zn in the reaction mixture. For example, if there are 6 moles of Zn present, the zincian hydrotalcite phase, \(\text{Zn}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O}\), is solely formed whereas if there are 0 moles of Zn present, the cuprian hydrotalcite phase, \(\text{Cu}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O}\), is gained.

A broad range of possible compositions for HTLCs can be prepared with the general formula \([\text{M}^{2+}]_{1-x}\text{M}^{3+}\text{x}(\text{OH})_{2y}\text{H}_2\text{O}\) where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) are found in the hydroxide layers at the octahedral positions, \(x = 0.2-0.4\), and \(\text{A}^{-}\) is the interlayer anion, \(\text{CO}_3^{2-}\), therefore \(n = 2\). Multiple divalent and trivalent metals can be incorporated into the brucite layer affording many different structural arrangements, including the LT-WGS relevant ternary hydrotalcite of type \((\text{Cu,Zn})_{1-x}\text{Al}_x(\text{CO}_3)^x/2(\text{OH})_2\) (see Figure 1.10). These HTLCs are of great interest as catalysts.

Problems in synthesising phase pure Cu/Zn/Al hydrotalcites occur when the Al content is below \(x = 0.25\). Low quantities of the trivalent Al\(^{3+}\) ions affect the coordination requirements of Cu\(^{2+}\), destabilising the HTLC structure by creating Jahn-Teller distortions between the brucite layers. Therefore, synthesising an industrially relevant phase pure Cu/Zn/Al HTLC precursor has proven challenging as the composition necessary is unattainable using the coprecipitation method. As previously stated, ideally an industrial catalyst would contain a Cu:Zn ratio of 70:30 with 10-20 mol.% Al, but when this is attempted, other copper-containing by-phases are generated as a result of the low aluminium content.

![Figure 1.10: Structural arrangement of the hydrotalcite-like compound](image)

Similar to the binary precursor phases, hydrotalcite-like compounds can also be distinguished using IR and Raman spectroscopy. However, as the samples are coloured green/blue, when the Raman spectra are recorded, they absorb the incident excitation of the laser.
beam, decomposing the samples. This makes it difficult to measure them using this method, although at low intensities a spectrum can still be obtained. Therefore, if possible, hydrotalcite-like compounds should show characteristic Raman bands at 1053, 1065 and 1085 cm\(^{-1}\).106

Much research has been conducted regarding the suitability of Cu/Zn/Al hydrotalcite-like compounds as LT-WGS catalyst precursors. Within this homogeneous structure, there is high dispersion throughout the brucite layers due to the octahedral sites coordinating the Cu, Zn and Al metal species. Following reduction, the even distribution of the metal species can still be seen as well as enhanced metal-oxide interactions.65

Though it has been reported that aurichalcite and hydrotalcite-like precursors form catalysts with smaller copper particles, M. Behrens et al. have considered them undesirable phases as the Cu particles become encapsulated in their meso-structures due to large oxidic aggregates. This makes them inaccessible to undergo any catalytic reaction.73

1.6.4. Georgeite

The structural composition of georgeite found in nature is Cu\(_5\)(CO\(_3\))\(_3\)(OH)\(_4\)\(\cdot\)6H\(_2\)O.109 However, when the mineral is synthesised, compositional variations can be expected due to it being an amorphous compound.99 Previously, georgeite and malachite were considered iso-compositional as when the georgeite precursor comes in contact with water, the ageing process is initialised and the precursor undergoes a quick transformation into malachite.110 However, S. A. Kondrat et al. found that the [CO\(_3^{2-}\)]/[Cu\(^{2+}\)] molar ratios are higher for georgeite, suggesting that georgeite is a separate phase.99

During the synthesis of the georgeite precursor phase, M. A. J. Hartig et al. reported a distinct pH drop associated with its formation. This is a result of the hydrolysis reaction that occurs on product precipitation; there is an increase in proton concentration and a decrease in copper and carbonate concentration.67

An experimentally obtained IR spectrum for georgeite exhibits three carbonate related peaks;99 an intense, broad doublet around 1400 cm\(^{-1}\) arising from the asymmetric C-O stretching vibration, a weaker doublet at 1100 cm\(^{-1}\) corresponding to the symmetric C-O stretching vibration, and a final representative peak around 837 cm\(^{-1}\) due to the wagging vibration of carbonate.54 There is also a characteristically broad OH peak present at 3408 cm\(^{-1}\).99

1.6.5. Gerhardtite

As the LT-WGS catalyst is prepared from metal nitrates, gerhardtite, Cu\(_2\)(OH)\(_3\)(NO\(_3\)), is a relevant phase to consider when characterising precursor phases. B. Bems et al. showed that the best way to do this was to study the infrared spectrum; gerhardtite shows sharp peaks at 1385 cm\(^{-1}\) and 1050 cm\(^{-1}\). The former peak is clearly due to the asymmetric N-O vibration of nitrate and will also be evident in the sample spectra if the precursors have not been thoroughly washed.54
1.7. Inhibiting Methanol Production

Supports and promoters are added in small amounts to the desired catalyst in order to improve its physical structure, e.g. pore or surface size, the electronic structure or the crystallinity. The best promoters to utilise in the LT-WGS catalyst are platinum or gold; however, these are expensive and rare. There is a demand to find alternative promoters which also effectively enhance the catalytic activity of the catalyst at low temperatures.

A major factor that can impact a company’s productivity is the selectivity of their WGS catalyst. If there is an increase in by-product formation, the amount of hydrogen generated is reduced and the CO$_2$ stream becomes contaminated (i.e. with methanol, amines or acetaldehyde) causing a variety of technological issues. A particular drawback when using the low-temperature Cu/ZnO/Al$_2$O$_3$ catalysts is their tendency towards methanol synthesis.

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} \\
\Delta G_{298K}^0 &= -25.3 \text{ kJ mol}^{-1}, \Delta H_{298K}^0 = -90.64 \text{ kJ mol}^{-1} \\
\text{CO}_2 + 3\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\Delta G_{298K}^0 &= +3.3 \text{ kJ mol}^{-1}, \Delta H_{298K}^0 = -49.5 \text{ kJ mol}^{-1}
\end{align*}
\]

*Equation 1.11: Synthesis of methanol*

Once methanol has accumulated in the reacting gas atmosphere, not only can it condense in the pores of the catalyst pellets, but its presence in the CO$_2$ removal system causes emissions from the plant to become environmentally hazardous. Subsequently a new type of catalyst is needed to avoid this problem. Though the literature is sparse, some have reported that the formation of methanol can be reduced by 90% by utilizing alkali metals as promoters in the synthesis of copper-based LTS catalyst.

1.7.1. Alkali Promotion

We are interested in promoting our Cu/ZnO/Al$_2$O$_3$ LT-WGS catalysts with alkali metal ions as they have been seen to alter the catalyst’s metal surface adsorption properties. Alkali metals have proven effective in promoting water dissociation when used in conjunction with various transition metal surfaces which sparked interest to design an alkali metal-promoted LTS catalyst. These changes to the electronic effects make the adsorption of CO more favourable and since then a variety of alkali metals have been investigated to enhance the system’s catalytic activity.

Alkali metals create new basic sites on the catalyst surface which have been shown to form stronger bonds with the adsorbed gas due to an electron transfer reaction between the promoter and the copper surface. The electronic promoting capabilities of alkali metals is
attributed to their nucleophilic nature, meaning they are electron donors.\textsuperscript{114} When they are introduced onto oxide surfaces, they react with available surface electron acceptors via a one-electron donation.\textsuperscript{58} The unpaired electron in the ground state is readily donated due to the low ionization energy of the alkalis. This increases the surface’s overall electron density and may promote the chemisorption of CO and oxygen.\textsuperscript{114,118}

Whether alkali or alkaline earth metals are more suited to being electronic or textural promoters is a common theme amongst these papers. Many groups have found that the abilities of the metals as promoters are influenced by their electron donation properties. Therefore as alkaline earth metals are more electronegative than alkali metals, they have a weaker promotion effect in comparison.\textsuperscript{116}

As mentioned previously, when alkali metals are incorporated into the LT-WGS catalyst they are considered to be electronic and structural promoters. This is because they have the ability to influence the catalyst’s selectivity, activity, and lifetime.\textsuperscript{11} It is the general consensus in the literature that the incorporation of alkali metals reduces the active surface area of copper, resulting in a textural change that delivers a slower rate of reaction.\textsuperscript{7,11} The challenge is to find a promoting method that inhibits methanol production without compromising the catalytic surface area.\textsuperscript{7}

Of the alkali metals studied, caesium was found to have the least effect on the Cu\textsuperscript{6} surface area (Cs << K < Na < Li).\textsuperscript{7} However, the detrimental effects are already evident at low Cs\textsubscript{2}O concentrations and are thought to be due to either the promotion of alkali metals localised on the alumina support or the catalyst micropores being mechanically clogged by superficial carbonates.\textsuperscript{7} P. Kowalik \textit{et al.} showed that there is a linear relationship between the amount of caesium added and the activity of the Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst. The optimum Cs\textsubscript{2}O content was determined to be 1-1.2 wt.% as it had the least effect on the overall copper surface area, but strongly inhibited the methanol side reaction.\textsuperscript{11}

A detrimental effect on the LTS catalyst caused by the addition of caesium is that it increases the maximum reduction temperature of the catalyst.\textsuperscript{7} The higher activation energy required is a result of the alkali metal inhibiting copper oxide from being reduced.\textsuperscript{11,119}

## 1.8. Deactivation

Catalyst deactivation can be defined as the loss of catalytic selectivity and/or activity over time. It is a major concern for industrial catalyst manufacturers as it can cost billions of dollars a year to shut down a plant and replace a deactivated catalyst. Though it is inevitable that a catalyst will eventually decay, these timescales vary greatly depending on the catalyst’s composition and preparation method, e.g. 6 months – 15 years.\textsuperscript{120} Deactivation processes are not always irreversible; for some catalysts a regeneration method can be employed to reactivate the catalyst, which is a cost efficient way to replace a spent catalyst.\textsuperscript{121} Cu-based LT-WGS catalysts, as reported by M. D. Argyle and C. H. Bartholomew, have a typical lifetime of 2-4 years.\textsuperscript{122}
1.8.1. Water Condensation

The instability of copper towards oxidant gases is known and, though promoters such as ZnO and Al$_2$O$_3$ may lessen these effects, water vapour present in the reaction system can have detrimental effects. Condensation present in the reactor reduces the catalytic activity of the water-gas shift catalyst due to oxidation of the active species and/or causing them to aggregate. Subsequently, the reactor atmospheres must be carefully controlled to prevent fluctuations between oxidative and reductive operating conditions.$^{123}$

Water vapour can also accelerate the rate of sintering by structurally modifying and crystallizing the oxide supports to a higher degree.$^{124}$ This is particularly the case at high temperatures when a support with high surface area is incorporated in the catalyst.$^{120}$ However, water vapour is also added to the atmosphere of the reaction vessel in order to facilitate the chemical interaction between the water and the surface oxides. Overall the surface diffusion is increased, which accelerates the rate of pore widening.$^{125}$ When trying to minimise these effects, it is important to maintain a careful ratio of steam/dry gas (CO/CO$_2$). Too little steam causes coke laydown which deactivates the catalyst, whereas too much reduces the efficiency of the reaction and increases costs.$^{10}$

1.8.2. Particle Growth

Catalyst stability is a major concern, therefore preventing poisoning of active sites and irreversible particle growth is important.$^{64}$

In order to prevent the growth of metal particles, strategies such as utilizing oxygen carriers (e.g. CeO$_2$) to enhance the metal-support bonding interaction energy$^{126}$ or introducing a metal with a higher-melting point through alloying$^{127}$ have been employed in the past. However, limiting the chemical composition of the catalyst also limits the catalyst’s function.$^{55}$

Studies have shown that it is not only individual properties associated with the catalytic NPs, such as particle size, that solely affect the particle growth mechanism. Nanoparticle spatial distributions have also proven to be a contributing factor.$^{55}$ Size restrictions associated with industrial catalysts mean high metal loading prepared catalysts (high density of active sites) are utilised to optimise the activity per unit volume. The local particle density as well as the distance between particles should also be taken into consideration as the literature states that the stability and functionality of the catalyst is correlated to the maximal spacing between copper particles.$^{64}$

1.8.3. Alkali Metals

Alkali metals can also act as poisons, deactivating the catalyst if present in too high a concentration ($> 2$ wt.%). Rather than enhancing the activity, they decrease it and can heighten the catalyst’s water sensitivity.$^{96,128}$ This is particularly relevant to residual sodium left in the sample after catalyst preparation. If the catalyst is not thoroughly washed, sodium in the form of NaNO$_3$ increases the crystallinity of the catalyst by inhibiting CuO from interacting with ZnO
and Al₂O₃. This has various detrimental effects on the catalyst activity. It has been found that the amount of sodium impurities left in the sample can be reduced when the pH is kept constant during the coprecipitation method in comparison to the decreasing pH series.

1.8.4. Sintering

Sintering is a thermal process and kinetically slow, therefore it occurs at elevated temperatures. It deactivates the catalyst by collapsing the support leading to decreases in support area and/or the catalytic surface area. This can result from the collapse of pores in the active phase crystallites or the growth of metal crystallites in the catalytic phase. There are other effects of sintering that occur that are compatible with the reduction in surface area, for example grain growth and a change in catalyst density. The bulk of the catalyst generally remains unchanged throughout a reaction whereas metal surface atoms can be mobile depending on the conditions. This is because atoms at the surface have lower coordination numbers, can be energetically changed by species adsorbing to them, and can be rearranged when thermally activated well below the melting point of the material, \( T_M \). The two latter points are the main contributions to metal surfaces gaining enough mobility to reach a quasi-equilibrium state, i.e. to achieve an equilibrated metal surface (EMS).

There is a relationship between the cohesive energy and thermal sintering for metals. This is suggested by the vacancy diffusion in the bulk, which is the principal sintering mechanism. Transition metals can be arranged according to their increasing stability towards sintering: Ag < Cu < Au < Pd < Fe < Ni < Co < Pt < Rh < Ru < Ir < Os < Re. From this we can understand that, in comparison to other common metallic catalysts, it is unsurprising that copper-based LTS catalysts are more vulnerable to thermal sintering. This can also be illustrated by calculating the Hüttig temperature.

The Hüttig temperature, \( T_H \), helps predict the onset of surface mobility, and hence EMS, at ca. \( 1/3 T_M \). An example of this is copper, which has a melting point of 1356 K. When the equation is applied, this gives a Hüttig temperature of ca. 452 K. When compared to iron which has a \( T_M \) of 1808 K and a \( T_H \) of ca. 603 K, it is clear why catalysts that are copper-based must be operated at lower temperatures than those that are iron-based. By employing a temperature below the Hüttig temperature, the chances of the catalyst sintering or undergoing agglomeration are significantly reduced.

In addition to surface diffusion, we can look at the bulk diffusion of atoms and ions by considering the Tammann temperature, \( T_{TAM} \), which is defined as \( 0.5 T_M \). This qualitative temperature is the point at which bulk-to-surface migrations can occur amongst the ions in the solid catalyst.

To circumvent/minimise thermal sintering, oxides have been incorporated into the catalysts as they have higher thermal stability. Typically unreduced LT-WGS commercial catalyst compositions include Al₂O₃ as well as the standard CuO and ZnO. Thermal stabilisers can also
be incorporated into the catalysts to reduce the chances of the catalyst sintering. In the case of using alumina as a support, potential promoters that can be used to improve the thermal stability are La, Si, Zn and Ba.\textsuperscript{120} The manufacturing method also has a large impact on the thermal stability of the catalyst, which is looked at in Section 1.4.\textsuperscript{130}

1.8.5. Poisoning

Poisoning is where impurities, reactants or products are strongly chemisorbed on catalytic sites. Whether a species is considered a poison depends on its adsorption strength relative to the catalytic species competing for the active sites.\textsuperscript{120} For low temperature water-gas shift Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts, deactivation by sulfur and/or chlorine poisoning is a major concern as the resulting catalysts have a comparatively shorter lifetime.\textsuperscript{47,96}

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The hydrocarbon feedstock can be the source of the sulfur- and chlorine-containing compounds. The feedstock is generally reduced by desulphurisation before processing so that there is less than 1 ppm sulfur present. It is also possible for the location of the plant to influence poisoning as these species can be found in the process air or plant steam. Process air can be filtered and washed while plant steam can be eliminated as a source of poisons by designing the boiler to prevent any carry-over of contaminants.\textsuperscript{130}

1.8.5.1. Sulfur

As copper-based WGS catalysts operate at low temperatures, adsorption of poisons is thermodynamically favourable. The $\Delta H_1$ enthalpy change in Equation 1.12 shows that copper is particularly receptive to sulfur as a poison. If sulfur is present in the gas stream, it accumulates on copper due to its heightened sensitivity to site-blocking poisons.\textsuperscript{130}

\[
2\text{Cu}(s) + \text{H}_2\text{S}(g) \rightarrow \text{Cu}_2\text{S}(s) + \text{H}_2(g)
\]

\[
\Delta H_f^\circ = -59.4 \text{ kJ mol}^{-1}
\]

\textit{Equation 1.12: Sulfurisation of copper oxide by hydrosulfuric acid}\textsuperscript{130}

Sulfur-poisoning is a fast and irreversible process making the concentrations of adsorbed molecules throughout the catalyst particles non-uniform. An atom of sulfur strongly adsorbed to the metal surface not only blocks multiple reaction/adsorption sites, but also inhibits adsorbed reactants from interacting with each other, preventing the surface diffusion of these reactants. Neighbouring metal atoms are also electronically modified as a result of the strong chemical bond formed, affecting their ability to dissociate and/or adsorb reactant molecules. However, this effect is limited to 5 a.u..\textsuperscript{120}
The ZnO present in the catalysts not only acts as a promoter, but also effectively removes hydrosulfuric acid, \( \text{H}_2\text{S} \), from the reactant feed by forming zinc sulfide. This protects the copper crystallites from sulfur-poisoning.\textsuperscript{130}

\[
\text{ZnO} \,(s) + \text{H}_2\text{S} \,(g) \rightarrow \text{ZnS} \,(s) + \text{H}_2\text{O} \,(g)
\]
\[
\Delta H^\circ_2 = -76.7 \text{ kJ mol}^{-1}, \quad \Delta S^\circ_2 = -3.0 \text{ J mol}^{-1} \text{K}^{-1}
\]

*Equation 1.13: Sulfurisation of zinc oxide by hydrosulfuric acid*\textsuperscript{130}

Two types of zinc sulfide have been found in plant samples: wurtzite (\( \alpha \)-ZnS) and sphalerite (\( \beta \)-ZnS).\textsuperscript{130} Of the two, sphalerite is the most stable form < 1293 K.\textsuperscript{121} It has been found that ZnO-containing LT-WGS catalysts’ capability to convert CO to CO\(_2\) drops to just over 30% in a 200 ppm H\(_2\)S stream for 80 h.\textsuperscript{121} The Al\(_2\)O\(_3\) support plays no role in protecting the catalysts from poisons.\textsuperscript{130}

Surface reconstruction forms stable –O-Cu-O-Cu-O strings when Cu(110) reacts with oxygen at ≥ 298 K. Various other transient, reactive oxygen species are found on the Cu(110) face which contribute towards catalyst poisoning by both sulfur- and chlorine-containing compounds.\textsuperscript{130}

**1.8.5.2. Chlorine**

Halides are exceptionally poisonous for Cu catalysts; however, chlorine is generally only encountered in hydrogen and ammonia plants.\textsuperscript{47} As can be seen from *Equation 1.14*, the reaction of copper with hydrochloric acid is not as thermodynamically favourable as with H\(_2\)S. However, it has been shown experimentally that when it is not possible for bulk formation of crystalline CuCl to occur, Cu(I) chloride species are generated on the surface. A. M. Beale *et al.* also detected crystalline Cu\(_2\)Cl and CuSO\(_4\) phases located on the edge of the sample.\textsuperscript{121} As a result of this, small amounts of chloride in the system allow a surface migration sintering mechanism of Cu crystallites to take place.\textsuperscript{130}

\[
\text{Cu} \,(s) + \text{HCl} \,(g) \rightarrow \text{CuCl} \,(s) + \frac{1}{2} \text{H}_2 \,(g)
\]
\[
\Delta H^\circ_3 = -43.5 \text{ kJ mol}^{-1}
\]

*Equation 1.14: Chlorination of copper oxide by hydrochloric acid*\textsuperscript{130}

In the case of chloride poisoning, ZnO offers no protection against catalyst deactivation of this variation.\textsuperscript{47} The formation of zinc chloride is not preferable as its high surface mobility
adds to structural changes which destructively destabilise the activity of the catalyst, reducing its thermal stability.\textsuperscript{130}

\[
\text{ZnO}(s) + 2\text{HCl}(g) \rightarrow \text{ZnCl}_2(s) + \text{H}_2\text{O}(g)
\]

\[
\Delta H^\circ_4 = -121.8 \text{ kJ mol}^{-1}, \quad \Delta S^\circ_4 = -117.2 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\textit{Equation 1.15: Chlorination of zinc oxide by hydrochloric acid}\textsuperscript{130}

However, as can be seen from the thermodynamics of the equations, any chloride present in the Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst is preferentially associated with zinc over copper. Again, the aluminium support has limited to no effect.\textsuperscript{130}

\textbf{1.8.5.3. Guard Beds}

As previously stated, employing the use of ZnO to remove chloride from the gas-phase levels is not possible. ZnO is only useful to retain sulfur poisons. However, eliminating chloride poisoning is essential, therefore industry employs the use of guard beds to reduce the poisoning effects.\textsuperscript{47,130}

Before the syngas reaches the main catalyst bed containing the copper-based low-temperature water-gas shift catalyst, it is passed through a sacrificial guard bed which is approximately 25\% of the main bed size.\textsuperscript{132} This generally contains alkalised alumina to absorb the chlorine poisons, although a guard bed of the same catalyst (Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}) has proven for some to be just as effective.\textsuperscript{130}

A guard bed is useful as it can extend the lifetime of the catalyst and results in continuous peak performance. As the poison mechanism is diffusion-limited, in some cases it is beneficial for the absorbent to be small pellets as they have a higher poison capacity. However, poisoning occurring for other reasons such as maloperation can present additional problems.\textsuperscript{47}

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Chapter 2: **Fundamentals and Theoretical Details**

The electromagnetic spectrum (*Figure 2.1*) encompasses a range of techniques, depending on the type of wavelength employed, to interrogate catalytic samples. The majority of characterisation techniques that have been used for the work in this thesis fall within the range $10^{-11}$-$10^{-3}$ m (X-rays to infrared), however, other complementary techniques have also been utilised.\(^1\)


2.1. **X-ray Techniques**

2.1.1. **Generation of X-rays**

The first Nobel Prize for Physics (1901) was awarded to the German physicist Wilhelm Röntgen for his discovery of X-rays in 1895. Initially, he was unsure of their nature and so, for brevity, coined the term “X-ray”.\(^3\) It is now understood that X-rays are electromagnetic radiation whose wavelengths are in the Ångström range ($1\ \text Å = 10^{-10}\ \text m$).\(^4\) When X-ray techniques are used to interrogate a material, three possible mechanisms can occur: absorption, scattering and emission, which will be discussed in this section.\(^5\)

2.1.1.1. **Conventional X-ray Sources**

Conventional/laboratory X-ray sources utilise either a sealed or rotating anode X-ray tube to generate X-ray photons. For the purpose of this report, only sealed X-ray tubes will be
considered, in which a stationary anode paired with a cathode are contained within an evacuated chamber. It is imperative that the anode, also known as the metal target, is cooled to prevent damage as most of the energy supplied to the tube (ca. 0.5-3 kW) is converted into thermal energy.\(^2\)

X-ray photons are generated when an accelerated, high-energy electron beam interacts with the cooled metal target (diagram in Appendix 7.2.1.1).\(^4\) The cathode, generally an electrically heated tungsten filament, emits the electron beam and the electrons are accelerated by applying a high electrostatic potential (30-60 kV).\(^2\) Radiation is emitted when the electrons decelerate following their collision with the target; this radiation is termed Bremsstrahlung (literally translated from German as deceleration radiation) and is composed of a continuous range of wavelengths (white radiation) that give a broad, featureless pattern. Superimposed on this are sharp, high-intensity discrete peaks that are characteristic of the target metal emission lines.\(^2,4\)

When the electrons are bombarded at the metal target (usually Cu), they cause an inner orbital electron (1s, 2s or 2p) to be ejected, creating a core hole. A higher energy electron then transitions to a lower energy to fill the hole, in turn emitting the remaining energy in the form of an X-ray photon. As shown in Figure 2.2, if the core hole is created in the K shell \((n = 1)\), two possible types of radiation are emitted: \(K_{\alpha}\), where the high energy electron transitions from the L shell \((n = 2)\), and \(K_{\beta}\), where the electron transitions from the M shell \((n = 3)\). It is important to note that the \(K_{\alpha}\) peak is composed of both \(K_{\alpha 1}\) and \(K_{\alpha 2}\) characteristic wavelengths which are produced by \(2p_{1/2} \rightarrow 1s_{1/2}\) and \(2p_{3/2} \rightarrow 1s_{1/2}\) transitions, respectively. It is also possible for other transitions to occur into other shells, but these are not shown.\(^4,6\)

![Bohr diagram](http://pd.chem.ucl.ac.uk/pdnn/inst1/xrays.htm)

**Figure 2.2:** Graphical representations of K-radiation generation: (a) Bohr diagram in which the black dotted boxes represent the core hole left by the ejected electron and the red arrows highlight the type of K-radiation produced depending on the transitioning high energy electrons origin,\(^6\) and (b) a typical X-ray spectrum illustrating the characteristic spectral lines for a Cu anode; image adapted from http://pd.chem.ucl.ac.uk/pdnn/inst1/xrays.htm.\(^7\)
2.1.1.2. Synchrotron X-ray Sources

In comparison to conventional X-ray sources, synchrotrons produce a beam that is highly collimated, energy tuneable and horizontally polarised, which has a brilliance that is twelve orders of magnitude (third generation synchrotrons) greater making them a much more advanced source of electromagnetic radiation.\textsuperscript{2,8} Brilliance is a measure of the source of synchrotron radiation (SR) and takes into account the brightness (photon flux), the angular divergence of said photons, the spatial cross-section of the beam and, finally, the amount of photons which fall within a bandwidth (BW) of 0.1 \% of a given energy range (ph s\(^{-1}\) mrad\(^2\) mm\(^2\) 0.1\% BW). In general, the smaller the angular divergence, the brighter the photon beam at a given wavelength.\textsuperscript{9} Using X-rays, both hard (> 4 keV) and soft (< 4 keV), the structure of materials and living matter can be interrogated with atomic resolution.\textsuperscript{2,6,9}

Free electrons are generated through thermionic emission in the electron gun by heating the (tungsten) cathode under vacuum. An electric field is then applied towards an anode to create an electron beam, which is pre-accelerated in the linear accelerator (LINAC) to a suitable energy. The microwaves and radio waves not only accelerate the electrons to velocities comparable to the speed of light (\(c = 2.998 \times 10^8\) m s\(^{-1}\)), but also divide the stream into bunches before they enter the booster ring. In the booster ring, the electron bunches are accelerated to the energy of the storage ring (see Table 2.1) using radiofrequency (RF) energy sources.\textsuperscript{2,6,9}

\textit{Table 2.1: Synchrotron sources used in this report; more information can be found at www.diamond.ac.uk and www.esrf.eu}

<table>
<thead>
<tr>
<th>Location</th>
<th>Facility Name</th>
<th>Energy / GeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harwell, UK</td>
<td>Diamond Light Source (DLS)</td>
<td>3</td>
</tr>
<tr>
<td>Grenoble, FR</td>
<td>European Synchrotron Radiation Facility (ESRF)</td>
<td>6</td>
</tr>
</tbody>
</table>

Once the electron bunches are at the desired energy and velocity, they are injected into the storage ring which is polygon shaped. Here, magnets are used to control their trajectory and ensure a small beam size is maintained; bending magnets (dipoles) direct the path of the electrons, quadrupoles are employed to focus the beam and sextupoles reduce the electrons’ energy dispersion (chromaticity).\textsuperscript{2,6,9}

There are three possible types of beamlines for third generation storage rings, as shown in Figure 2.3; both DLS and the ESRF use an alphanumeric string to identify the beamline’s source of radiation (e.g. “B” or “BM” for bending magnet, and “I” or “ID” for insertion device, accompanied by a number). At each corner of the storage ring, the electron beam interacts with a bending magnet and emits SR tangentially to the beam which is polychromatic and of relatively low intensity. Wiggler and undulator insertion devices are placed in the straight regions of the storage ring and offer intense, collimated, beams of varying (tuneable) sizes. Wigglers, as the
name suggests, “wiggle” the beam along a sinusoidal path using magnets with alternating polarity to produce SR with a wide, horizontal fan of X-rays that are harder and have greater flux. Undulators operate in the same fashion; however, the distance between the magnetic poles is shorter, creating a more brilliant, narrow beam. RF cavities are spaced around the storage ring as well to replenish the energy lost when synchrotron radiation is emitted.2,6,9

![Diagram of a synchrotron](image)

**Figure 2.3: Schematic of a third generation synchrotron**

After the electron beam is accelerated through either a bending magnet or an insertion device, the emitted SR is directed towards the beamline. The beamline consists of three key sections: the front-end, the beamline optics and the experimental hutch, which are encased in lead-lined, thick concrete walls to shield against any leaked radiation (depicted in *Figure 2.4*). The front-end is where a direct connection of the beamline to the storage ring is made; a metal safety shutter is located in this section that, when closed, inhibits X-ray photons from traveling the length of the beamline and also allows the optics hutch to be accessed. Here, the desired wavelength is selected using a monochromator and the photons are transported and focused onto the sample by adjusting the X-ray mirrors (done solely by beamline personnel, depending on the scope of the proposed experiment). Finally, the experimental hutch houses the experimental set-up and a state-of-the-art detector. In general, most of the set-up (beam/sample/detector alignments, measurements, shutter) can be controlled from the control hutch, outside of the lead-lined experimental hutch.9
Figure 2.4: Schematic of a beamline; image taken from http://www.esrf.eu/about/synchrotron-science/beamline.

2.1.2. X-ray Diffraction

In 1914, Max von Laue was awarded the Nobel Prize for Physics when he demonstrated the electromagnetic nature of X-rays through their diffraction in crystals. He chose to study X-rays for diffraction as they have short wavelengths with high frequency (ca. $10^{10}$ m and ca. $10^{18}$ Hz), which is of the same order of magnitude as the interatomic distances (ca. 1 Å) between the atoms within a given crystal structure. When a crystal is placed in the path of the waves, the interference caused generates a diffraction pattern with reflections of varying intensity depicting the lattice points present in the plane ($hkl$). This is plotted as a function of X-ray counts (intensity) vs. the diffraction angle, $\theta$. Two types of interference occur when two elastically scattered X-ray waves are in the same region of space: constructive and destructive interference (Figure 2.5). This either results in an enhanced amplitude when their peaks/troughs are in-phase with each other (constructive interference), and thus a clear diffraction pattern, or a diminished amplitude when they are out-of-phase (destructive interference).
In general, as heavier atoms contain more electrons than lighter atoms, they act as stronger scattering centres making it easier to determine their atom locations within the unit cell. However, a limitation of this is that, as heavier atoms have the same order as the wavelength of the X-rays, scattered X-rays from the same atom interact and reduce the observed intensity of the measured reflections. Therefore, as depicted in Appendix 7.2.1.2, the scattering factor is proportional to the atomic number.\textsuperscript{2,4,10}

Crystalline (ordered) materials exhibit diffraction patterns due to periodicity within the three-dimensional lattice structure, restricting the scattered X-rays to certain directions by acting as a diffraction grating. This causes a series of high intensity reflections to be recorded across a $2\theta$-range that are unique to the phase(s) present in the crystal. Contrastingly, the disordered structure of amorphous materials scatter X-rays in all directions making it impossible to determine their crystal structure by diffraction.\textsuperscript{10}

X-ray diffraction is a powerful, non-destructive tool that is utilised to determine the geometries of atoms within crystalline materials as opposed to inferring their likely orientations from their morphology and symmetry.\textsuperscript{10} Analysis, however, proved challenging, and two methods for treating crystal diffraction were born: the first was established by Max von Laue in 1912,\textsuperscript{12} and the second by father and son William Henry Bragg and William Lawrence Bragg in 1913.\textsuperscript{13}

\subsection*{2.1.2.1. Laue Equations}

Max von Laue was the first to relate the geometries of the incident and diffracted beams of X-rays in the form of the Laue equations (\textit{Equation 2.1}).\textsuperscript{12} He found that in order for strong diffraction reflections to be measured, these equations must be simultaneously satisfied. As shown in \textit{Figure 2.6}, a diffraction pattern arises when an incident X-ray beam interacts with a periodic lattice (with spacing $a$), scattering the diffracted beam at an angle of $\varphi$; each reflection is a unique result of in-phase scattering from each of the $(hkl)$ planes present, defining the atoms location in reciprocal space. However, this method of analysis is most suited to single crystals due to their periodicity; a single crystal consists of a unit cell that is repeated in three-dimensional space.\textsuperscript{2,10}
\begin{align*}
a (\cos \psi_1 - \cos \phi_1) &= h \lambda \\
b (\cos \psi_2 - \cos \phi_2) &= k \lambda \\
c (\cos \psi_3 - \cos \phi_3) &= l \lambda
\end{align*}

Equation 2.1: Laue equations

Where \( a, b, c \) = crystallographic axes of the unit cell
\( \psi_{1,3} \) = angle the incident X-ray beam intersects the lattice row
\( \phi_{1,3} \) = angle the diffracted X-ray beam scatters from the x-axis
\( h, k, l \) = Miller indices
\( \lambda \) = wavelength of radiation used

Figure 2.6: Depiction of Laue’s theory of diffraction from lattice points with spacing a. Constructive interference occurs when a path difference (\( p_2 - p_1 \)) is equal to an integral number of wavelengths (\( \lambda, 2\lambda, 3\lambda, \text{etc.} \)).

2.1.2.2. Bragg’s Law

W. H. Bragg and W. L. Bragg were the first to employ the use of X-ray diffraction in solving crystal structures and were awarded the Nobel Prize for Physics in 1915. Bragg’s law is primarily used to calculate the angle, \( \theta \), at which the incident X-ray beam must intersect the crystal structure in order to guarantee that constructive interference will occur. It is suited to studying powder samples as not all crystallites are orientated constructively and so an average is taken of the phase(s) present.

As Figure 2.7 illustrates, the incident beam is diffracted by two consecutive lattice planes with interplanar distance \( d_{hkl} \). For the scattered waves to be in-phase, the second wave must travel an additional distance equivalent to a multiple of the wavelength, \( n\lambda \) (where \( n \) is an integer). We then define the path distance as \( AB + BC = 2d_{hkl} \sin \theta \), allowing maxima intensities (reflections) to be calculated as.
\[ n\lambda = 2 \ d_{hkl} \sin \theta \]

However, it is generally accepted to treat reflections from \((nh, nk, nl)\) planes as 1st order, giving the Bragg equation:

\[ \lambda = 2 \ d_{hkl} \sin \theta \]

*Equation 2.2: Bragg’s law*

*Figure 2.7: Geometrical illustration of Bragg’s law*

2.1.2.3. Wave-Particle Duality

Louis de Broglie was awarded the Nobel Prize for Physics in 1929 for experimentally demonstrating the wave-like behaviour of particles (electrons). He concluded that any particles that travel with a linear momentum \((p = mv\), where \(m\) is mass and \(v\) is velocity\) have a wavelength that can be calculated using the de Broglie relation (*Equation 2.3*) which shows that particles with a high linear momentum, have a short wavelength.\(^{14}\)

\[ \lambda = \frac{h}{p} \]

*Equation 2.3: de Broglie equation*

Where \(h = \) Planck’s constant / \(6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}\)

To conclude, not only do electrons (and all other particles) behave as waves, but electromagnetic radiation behaves as particles, also known as the wave-particle duality.\(^{14}\)
2.1.3. X-ray Diffraction Computed Tomography

X-ray diffraction computed tomography (XRD-CT) is a very powerful technique that combines both powder XRD and conventional computed tomography (CT). Tomography is an excellent imaging technique that utilises X-rays to create two-dimensional images of the cross-section of bulk materials. As opposed to conventional CT, which measures the absorption of X-rays (see Appendix 7.2.1.3), when used in conjunction with XRD, it is the diffracted/scattered X-rays that are monitored using a large-area 2D detector.\(^{15,16}\) It was first demonstrated for material applications by Harding et al. using a conventional X-ray source and is now mainly employed using synchrotron radiation.\(^{15,17}\) Heterogeneous catalysts are able to be probed with SR in a non-destructive, non-invasive fashion, allowing all physicochemical changes to be monitored \textit{in situ}.\(^{15,18-20}\)

\textit{Figure 2.8} illustrates that the raw tomographic scan can be considered a four-dimensional matrix \((X \times Y \times T \times R)\), where \(X \times Y\) represents the size of the 2D powder \textit{diffraction image} (shown as Debye-Scherrer rings), \(T\) is the number of translation steps and \(R\) is the number of rotation steps. While the sample is interrogated with a highly collimated, monochromatic X-ray beam, it is translated along an axis perpendicular to the beam \((T)\) and rotated \((R)\) to typically cover an angular range of 0-180°. The acquired 2D pattern is then azimuthally integrated, allowing it to be reconstructed as a 1D diffraction pattern \((T \times R)\), considered an observational point, \(d\), known as the third spectral dimension in the sinogram volume \((T \times R \times d)\).\(^{15}\) A reconstructed real-space image of the catalyst bed plane \((T \times T \times d)\) can then be acquired by applying a mathematical algorithm to perform filtered back-projection of the sinogram to create an image.\(^{15,21}\) Within this reconstructed image, each tomographic voxel corresponds to a diffraction pattern unique to that part of the sample, meaning exceptionally detailed analysis can be carried out regarding the materials’ chemical structure (e.g. evolving phase distribution).\(^{15}\) When these scans are also taken along the length of the catalyst bed, acquiring 3D spatial resolution, this can be considered a 5D-imaging technique (1D spectral and 3D spatial as a function of time).\(^{22}\) The spatial resolution of the reconstructed images can be fine-tuned by reducing the size of the X-ray photon beam (< 100 × 100 μm\(^2\)).\(^{15}\)
There are many advantages to using XRD-CT to understand the local chemistry in catalytic materials. As mentioned above, each pixel corresponds to a single diffraction pattern allowing thorough chemical maps of the catalyst’s crystalline components to be constructed. Additionally, it also allows unknown phases present to be identified as they are not lost in the bulk as they would be with conventional XRD measurements. Rietveld data analysis of the changing physical (e.g. crystallite sizes, micro-/macrostrain and lattice parameters) and thermal (e.g. atomic displacement) properties can also be evaluated, allowing an extensive understanding of the interrogated material’s properties to be surmised.

2.1.4. X-ray Fluorescence

When characterising heterogeneous catalysts, X-ray fluorescence (XRF) spectrometry is often utilised for elemental analysis. XRF is a non-destructive technique that not only identifies potential impurities present, but also quantitatively describes the concentration of each element present (from a concentration range of ppm to 100 %).  

There are two kinds of X-ray spectrometer for XRF analysis: energy-dispersive instruments and wavelength-dispersive instruments. For this report, despite the lack of resolution, only energy-dispersive spectrometers will be considered as they are capable of detecting any
element, data acquisition time is fast, they are user friendly and the instruments are relatively affordable.\(^5\)

As previously mentioned in Section 2.1.1.1, when an X-ray beam interacts with an (Ag) anode, inner shell electrons are released causing outer shell electrons to occupy the vacancies. The mechanism of XRF is shown in Figure 2.9 (a) where the energy released is in the form of secondary X-rays (fluorescence). Multicomponent systems can be interrogated with this technique as each element emits an X-ray photon with a characteristic energy depending on its unique electron distribution. The intensity of this secondary X-ray spectrum allows the concentration of each element present to be determined.\(^23\) Also depicted in Figure 2.9 (b) is the alternative Auger effect in which the remaining energy of the outer shell electron is transferred to a secondary electron that is then ejected.\(^23,24\)

![Figure 2.9: Schematic representation of (a) XRF and (b) the Auger effect\(^24\)](image)

### 2.2. Optical Spectroscopy Techniques

When characterising heterogeneous catalysts, it is common practice to employ optical radiation techniques as they are fast, efficient, and non-destructive. When a sample is interrogated with electromagnetic radiation in the ultraviolet, visible and infrared range (10\(^{-8}\) -10\(^{-3}\) m), some of the energy is absorbed; this can be categorised by three different kinds of energy: rotational, vibrational, and electronic. Rotational energy is characteristic of the absorption of longer wavelengths with lower frequency of infrared (IR) radiation: 25-500 \(\mu\)m. Vibrational energy arises when mid-infrared radiation is absorbed, causing the bonds of the functional groups to, as the name suggests, vibrate: 2-25 \(\mu\)m. Electronic energy occurs when ultraviolet (UV) and visible (Vis) radiation is absorbed, promoting an electron to a higher energy level: 0.2-0.8 \(\mu\)m.\(^23\)
2.2.1. **Infrared Spectroscopy**

Infrared radiation was first discovered by William Herschel in 1800; however, it was only in the 1960s that IR spectroscopy started to be routinely used in the analysis of heterogeneous catalysts. IR spectroscopy is a very useful technique to employ as inorganic and organic functional moieties can be determined from characteristic absorption bands in the IR spectrum. A molecule is considered infrared active if a net change in dipole moment is present as it vibrates; when this occurs, covalently bonded atoms/functional groups absorb the infrared energy, \( E \), at a vibration frequency, \( \nu \), that corresponds to the natural vibration frequency of the bond.\(^1,28\)

There are two main types of vibrations: molecular deformation (bond bending) and bond stretching (see Appendix 7.2.2.1).\(^1\) The motion of a molecule, \( N \), in space is described by the three Cartesian coordinates: \( x, y \) and \( z \), giving it three degrees of freedom (3\( N \)). Every molecule has three degrees of translational freedom about the axes; however, only a non-linear molecular has three degrees of rotational freedom as it has a principal symmetry axis. By comparison, a linear molecule has two degrees of freedom for rotational motion. With this knowledge, the number of degrees of vibrational freedom (IR active and inactive) can be calculated as such:\(^1,29\)

![Equation 2.4: Calculation for the number of degrees of vibrational freedom\(^29\)](image)

The spectrum obtained (absorbance/transmittance \( \text{vs. wavenumber} \)) details the energy difference between the ground and excited vibrational energy states. The spatial wavenumber, \( \tilde{\nu} \), denotes the number of waves observed per centimetre (cm\(^{-1}\)) and is inversely proportional to the length of one wave, \( \lambda \) (Equation 2.5).\(^26,28\) In the lower wavenumber region, peaks associated with the rotational energy are observed, whereas vibration energy peaks for molecules with greater bond strengths (force constants) and lighter atoms are recorded at higher \( \tilde{\nu} \).\(^26\)

![Equation 2.5: Spatial wavenumber calculation](image)

2.3. **Thermoanalytical Techniques**

Thermoanalytical techniques are an important set of characterisation methods that should be employed when studying the bulk properties of low-temperature water-gas shift catalysts. Many of the techniques, e.g. thermogravimetric analysis (TGA) and differential thermogravimetry (DTG), utilise a linear temperature program to monitor the mass consumed by
the CuO/ZnO/Al$_2$O$_3$ catalyst. However, though this is useful, the focus of catalytic research lies in elucidating the gas-solid interactions, predominantly during activation of the catalyst. To do this, techniques such as temperature-programmed reduction (TPR), desorption (TPD) and oxidation (TPO) are used to investigate how the gaseous environment evolves as the temperature is increased.$^{30}$

Table 2.2: Summary of thermoanalytical techniques and their applications$^{31}$

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Technique</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
<td>Mass variation</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential thermogravimetry</td>
<td>Mass variation</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-programmed reduction</td>
<td>Reductant consumption while a temperature program is run</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature-programmed desorption</td>
<td>Any variation while a temperature program is run</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature-programmed oxidation</td>
<td>Oxidant consumption while a temperature program is run</td>
</tr>
</tbody>
</table>

2.3.1. Thermogravimetric Analysis Coupled with Differential Thermogravimetry

Thermogravimetric analysis coupled with differential thermogravimetry (TGA-DTG) is commonly used to evaluate changes to the weight of a catalyst upon heating.$^{31}$

TGA allows changes in mass to be monitored where, for example, decreases in mass could be associated with desorption, reduction, or dehydration of the sample and increases could be evidence of adsorption or oxidation. The sample is contained in a (platinum) crucible and placed in a closed furnace in an atmosphere of either air or an inert gas (likely N$_2$). Changes in mass are recorded as a function of time as the desired temperature program is carried out. A symmetric balance is used to ensure errors are minimised.$^{31,32}$

DTG is the derivative of the thermogravimetric signal. As with TGA, mass deviations are plotted as a function of time and identify physicochemical changes occurring, such as morphological changes and possible interactions with the surrounding atmosphere. Differential thermogravimetry is very useful to determine the stability of the catalyst across a range of catalysts and, in terms of calcination, the stability of the hydroxycarbonate precursor phases.$^{31,32}$

2.3.2. Temperature-Programmed Reduction

Temperature-programmed reduction with hydrogen is a popular characterization technique when studying supported and unsupported solid oxide catalysts.$^{33,34}$ When considering the LTS catalyst, CuO is the main reducible species present, totalling a minimum of 60 % of the overall composition. Equation 2.6 shows that the reduction of CuO is exothermic and so it is
advantageous to utilise low concentrations of hydrogen in order to prevent sintering of the active species.\textsuperscript{35} As water is a by-product of the reduction process, the stoichiometric equation for CuO reduction in the presence of CO has also been included due to its presence in the hydrocarbon feedstock.

\[
\text{CuO} + \text{H}_2 \rightleftharpoons \text{Cu} + \text{H}_2\text{O} \quad \Delta H_{298\text{K}} = -88.2 \text{ kJ mol}^{-1}
\]

\[
\text{CuO} + \text{CO} \rightleftharpoons \text{Cu} + \text{CO}_2 \quad \Delta H_{298\text{K}} = -153.7 \text{ kJ mol}^{-1}
\]

\textit{Equation 2.6: Reduction of CuO}\textsuperscript{35}

A thermal conductivity detector (TCD) measures the reducing gas consumption (H\textsubscript{2} or CO content) and generates a spectrum from which the maximum reduction temperature, \(T_m\), can be extrapolated; the shape of the profile indicates any changes in oxidation state.\textsuperscript{30} Unfortunately, it is hard to draw comparisons from reported TPR studies as the resultant reduction profiles are very sensitive to changes in experimental parameters. For example, varying the total hydrogen concentration in the reducing gas feed as well as the heating ramp rate has been found to alter the maximum reduction rate of the catalyst; when the heating rate is increased, the \(T_m\) increases, and by increasing the reductant concentration, the \(T_m\) decreases.\textsuperscript{36}

This phenomenon was initially investigated by D. A. M. Monti and A. Baiker who defined a characteristic number, \(K\), to determine appropriate parameters to achieve reliable TPR profiles with improved sensitivity.\textsuperscript{36} Though not defined in \textit{Equation 2.7 (a)}, the heating rate must be between 6 and 18 K min\(^{-1}\) for \(0.9 < K < 2.3 \text{ min}\) to be satisfied; for \(K < 0.9 \text{ min}\), the sensitivity proves too low to gain a reliable profile and for values \(K > 2.3 \text{ min}\), too much H\textsubscript{2} is consumed. An important note is that ideally < 66 \% of the H\textsubscript{2} present in the feed should be consumed during the reduction process.\textsuperscript{30,34,36} Reduction of supported reducible species are very complex and so the assumption is accepted that the kinetics of the reaction are first-order with respect to the catalyst and the reducing gas.\textsuperscript{30}

P. Malet and A. Caballero later adapted this equation to include the heating rate, defining a new characteristic parameter, \(P\) (\textit{Equation 2.7 (b)}).\textsuperscript{34} Here they demonstrated that a value of \(P < 20 \text{ K}\) delivered greater resolution of the optimised reduction profile, showing multi-step reduction mechanisms in some cases.\textsuperscript{30} By increasing the ratio of \(\beta/C_0\), the \(T_m\) is shifted to higher temperatures (while maintaining the same profile shape); however, the profile shape is actually dependent on the mass of catalyst – if the catalyst sample size is too large, the resolution is lost.\textsuperscript{34} S. J. Gentry \textit{et al.} surmised that this was due to mass-transfer limitations causing non-homogeneous reduction of the catalyst bed.\textsuperscript{37}
\begin{align*}
K &= \frac{S_0}{F C_0} \\
P &= \frac{\beta S_0}{F C_0}
\end{align*}

Equation 2.7: Operating variable calculations for TPR; (a) D. A. M. Monti and A. Baiker’s characteristic number, \( K \), (b) P. Malet and A. Caballero’s characteristic number, \( P \).  

Where
\begin{itemize}
    \item \( S_0 \) = initial amount of reducible species / \( \mu \text{mol} \)
    \item \( F \) = reducing gas flow rate / \( \text{cm}^3 \text{ min}^{-1} \)
    \item \( C_0 \) = \([\text{H}_2]\) concentration in gas feed / \( \mu \text{mol cm}^{-3} \)
    \item \( \beta \) = heating ramp rate / \( \text{K min}^{-1} \)
\end{itemize}

2.4. Surface Area and Porosity Techniques

When determining the viability of a catalyst, the surface area is investigated as, in general, high specific surface area correlates to an active catalyst. This differs from the porosity which is the ratio of the pore volume compared to the volume of the catalyst granule/pellet. Alongside this, pore size distribution is also a necessary factor to consider to ensure no potential deactivation processes, e.g. pore blocking, occur.  

Pore structures in heterogeneous catalysts are a result of the preparation methods used, with specific surface areas typically being in the range of \(0.01 \text{ - } 10 \text{ m}^2 \text{g}^{-1}\).  
Pores are classified depending on their internal pore widths: ultramicropores (< 0.7 nm), micropores (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm).  

Of the available methods to measure surface area and porosity (see Figure 2.10), gas adsorption (\( \text{N}_2 \) BET) and mercury (Hg) intrusion porosimetry will be evaluated.
2.4.1. BET

The Brunauer-Emmett-Teller (BET) method is the most widely used technique to determine the surface area and texture of porous catalysts.\textsuperscript{42} The theory of N\textsubscript{2} adsorption revolves around the physisorption of a gas (the adsorptive) to the surface of a solid (the adsorbent) at a temperature of 77 K, forming the adsorbate through weak van der Waals forces.\textsuperscript{38} Nitrogen is traditionally used as a probe molecule for gas adsorption (BET) due to its low cost, efficiency and reliability; however, the quadrupole momentum of N\textsubscript{2} has been known to interact with functional groups on the surface of the catalyst, e.g. hydroxyls, so argon or krypton can be used as an alternative.\textsuperscript{43}

The BET method is a multilayer continuance of Irving Langmuir’s concept (for which he won the Nobel Prize for Chemistry in 1932): he specified that only a monolayer of adsorbate can be formed on the surface of the catalyst where active sites are occupied by a single species. As opposed to treating the catalyst surface as an array of identical sites where only a monolayer of adsorbate forms, BET theory considers the possibility of infinite adsorbed layers of the adsorbate ($p/p^0 = 1$) which interact only with the adjacent layers.\textsuperscript{38} Equilibrium is achieved when the rate of adsorption is equivalent to the rate of desorption which can be expressed as Equation 2.8.\textsuperscript{38}

\[
p \left( \frac{1}{v (p^0 - p)} \right) = \left( \frac{1}{v_m C} \right) + \left[ \frac{(C - 1)}{v_m C} \right] \left( \frac{p}{p^0} \right)
\]

*Equation 2.8: BET equation*\textsuperscript{42}
Where \( p/p^0 \) = relative equilibrium pressure
\( v \) = volume of adsorbed gas molecules
\( v_m \) = monolayer capacity
\( C \) = BET constant (Equation 2.9)

As Equation 2.9 shows, the BET method assumes that the heat of adsorption differs between the initial monolayer, \( E_1 \), and the subsequent layers, \( E_L \). This is because the multilayers are treated as a bulk fluid and \( (E_1 - E_L) \) is considered the net heat adsorption.\(^{38,43}\)

\[
C = \exp \left[ \frac{(E_1 - E_L)}{RT} \right]
\]

Equation 2.9: BET constant\(^{42}\)

The BET equation (Equation 2.8) allows a straight line to be plotted with the equation
\[ y = mx + c \]
where the slope, \( m \), is equivalent to \((C - 1)/(v_m C)\) and the y-intercept is \(1/(v_m C)\). From this, the monolayer capacity and the BET constant can be evaluated.\(^{42}\) Interestingly, the calculated value for the BET constant \( C \) appears to elucidate the type of isotherm generated by the adsorbent-adsorbate interactions. However, the linear range of the plot is limited to a \( p/p^0 \) range of 0.05-0.3 for \( \text{N}_2 \) BET which corresponds to the region of point B in Figure 2.11.\(^{38}\)

There are six IUPAC classifications of physisorption isotherms (Appendix 7.2.3.1), but only three are common in catalyst characterisation (depicted in Figure 2.11).\(^{44}\) The shape of the isotherm is dictated by the porous texture of the catalyst.\(^{41}\)

![Figure 2.11: Typical types of \( \text{N}_2 \) isotherms exhibited by (Type I) microporous materials, (Type II) non-porous and/or macroporous materials, and (Type IV) mesoporous materials\(^{39}\)](image)
Type I: Due to strong interactions between the adsorbate and the pore walls, the majority of the adsorption occurs at low relative pressure \((p/p^0 < 0.3)\). However, higher pressure is required to fill all the pores of the microporous materials because of the interactions between the adsorbed molecules, hence the plateau. Of all the types, this reversible isotherm is the most similar to the Langmuir theory as it appears to form a monolayer \((p/p^0 \neq 1)\).

Type II: Both macroporous and non-porous materials are characterised by a reversible isotherm showing monolayer formation at low relative pressure. However, the inflection point B depicts the point at which a multilayer of adsorbate begins to form at higher relative pressure; the thickness of the multilayer is limited by the condensation pressure.

Type IV: The initial isotherm follows the same trend as macroporous materials at low relative pressure. Once adsorption in the mesopores occurs, multilayer formation is evident at high \(p/p^0\) which results in a sharp adsorption volume increase (the larger the mesopore, the higher the relative pressure at which condensation takes place). Type IV isotherms are generally characteristic of most catalytic materials. The desorption of the adsorbate occurs at a \(p/p^0\) below that of the capillary condensation creating an hysteresis, the shape of which is dependent on the pore shape present in the catalyst (Appendix 7.2.3.2).

To calculate the specific surface area of a catalyst, \(S_{\text{BET}}\), the total surface area \((v_m N_A \sigma_m)\) is divided by the mass of the material being analysed, \(m\) (Equation 2.10). A potential source of error lies in the derived \(v_m\) value as it is assumed that the formation of the monolayer is equivalent over a variety of surfaces, which is particularly untrue for heterogeneous catalysts. This method is best applied to evaluate mesoporous materials as the values are only accurate until capillary condensation occurs in the pores \((p/p^0 < 0.4)\). Microporous materials can also be studied, but the measured \(S_{\text{BET}}\) is accepted only as an “equivalent surface area”.

\[
S_{\text{BET}} = \frac{v_m N_A \sigma_m}{m}
\]

*Equation 2.10: BET specific surface area*

Where \(N_A = \text{Avogadro’s constant} / 6.022 \times 10^{23} \text{ mol}^{-1}\)

\(\sigma_m = \text{molecular cross-sectional area of N}_2 / 0.162 \text{ nm}^2\)

2.4.2. Mercury Porosimetry

An advantage of mercury intrusion porosimetry is its ability to accurately evaluate a wide range of mesopore-macropore sizes (0.003-400 µm). It involves the intrusion at high pressure of Hg, a non-wetting liquid, into the pores of the catalyst using a porosimeter. Mercury is considered a non-wetting liquid because its solid-liquid contact angle, \(\theta\), is greater than 90 ° with respect to most catalytic solids (see Appendix 7.2.3.3). Therefore, only when forced, can the Hg
access the interconnected pore structure of the material in question, generating a $\theta$ which is intrinsically negative.\textsuperscript{39}

Pore size can be determined using the Washburn equation, which typically describes long cylindrical pores.\textsuperscript{46} It also assumes that the contact angle and the surface tension are not derived from the pore size or, in the case of heterogeneous catalysts, the surface chemistry.\textsuperscript{47}

\[ d_p = -\left(\frac{4\gamma}{p}\right) \cos \theta \]

*Equation 2.11: Washburn equation*\textsuperscript{48}

Where $d_p$ = pore diameter  
$\gamma$ = surface tension of Hg at 298 K / 484 mN m\textsuperscript{-1}  
$p$ = applied pressure / 0.003-400 MPa

Historically, the literature has been focused on characterising micro- and mesopores as they contribute largely to the overall surface area. However, it is essential to be able to characterise the channels by which these pores are interconnected; these are considered to be the macropores.\textsuperscript{46}

The intrusion-extrusion cycle is illustrated in Figure 2.12 and shows that, initially, if analysing a powder, region (A) corresponds to rearrangement of the particles before the Hg is intruded into the interparticle voids (B). Region (C) is characteristic of the pores filling and, for some materials at higher pressures, continues to (D), which signifies (reversible) compression. Extrusion (E) occurs at lower pressures than intrusion, creating an open hysteresis (F) as some of the Hg is retained in the catalyst’s pores. The intrusion-extrusion process is repeated (at least twice) until the loop closes (G), showing that no further entrapment of the mercury occurs.\textsuperscript{38,46}

*Figure 2.12: General characteristics of mercury porosimetry curves; image taken from J. Rouquerol et al., Pure Appl. Chem., 2012, 84, 107-136.*\textsuperscript{46}
It is essential to understand the relationship between the hysteresis loop and Hg entrapment to achieve accurate pore size measurements. Mercury appears to rupture in ink-bottle shaped pores and junctions, therefore causing entrapment. This is believed to be a result of one of two mechanisms: (1) a single-pore mechanism in which the hysteresis is a result of either a difference between the contact angles from the Hg advancing and receding into the pores or formation of a vapour-liquid interface during extrusion, or (2) a network model which considers ink-bottle pores and pore blocking (percolation) effects. The final hysteresis loop obtained is a similar shape to that from gas adsorption studies, indicating that both capillary condensation and Hg intrusion occur via similar pathways.

2.5. Bibliography


Chapter 3: Preparation and Characterisation of Binary, Ternary, and Cs-Promoted Catalysts

3.1. Introduction

This section will look at preparing and understanding the characteristics associated with promoted and unpromoted CuO/ZnO/Al₂O₃(-Cs₂O) low-temperature water-gas shift catalysts that are comparable to those currently used in industry. The aim is to develop a synthesis method that will be applied across all catalyst syntheses for this thesis, in the hope that the resultant catalysts mimic the behaviour of industrial catalysts during activation (Chapter 4) and failure mechanisms (Chapter 5). Not only will this benefit industry in understanding/exploring the behaviour of these systems, but also elucidate early onset deactivation mechanisms which will drive future academic research.

To accomplish this, pellets of two commercially available catalysts have been investigated, a standard unpromoted catalyst and a Cs-promoted low methanol catalyst, to act as benchmarks during the synthesis process. These have been characterised to determine their chemical composition, phase identification, and surface area in order to guide the synthesis of the synthetic ternary LTS catalysts. Model binary precursor catalysts are also considered to fully elucidate how the differing Cu:Zn ratios affect the chemical nature of the catalysts.

3.2. Experimental Details

3.2.1. Catalyst Preparation

All catalyst preparations (except for CZA1) utilised a Metrohm 902 Titrand to ensure any source of human error was eliminated during the reactant addition and pH maintenance of the coprecipitation process. This computer-controlled, intelligent potentiometric titrator consists of two dosing units and a pH meter, as shown in Figure 3.1. A huge benefit of using this titration instrument is that it records the temperature, pH and amount of precipitating agent added throughout the entire synthesis. Temperature is not controlled through the Titrand, this is done by a stirrer hotplate with a thermocouple control heating circuit. The methods were built using the tiamo™ 2.5 software package and it is evident that the pH was carefully controlled as during the precipitation stage, the pH remained within ±0.12 of the desired pH 7 and within ±0.03 during ageing; evidence of this is supplied in Appendix 7.3.1.
Ternary Catalysts

A variation on the C. Baltes et al. coprecipitation method was used to prepare the low-temperature water-gas shift catalysts. A mixed solution of Cu, Zn and Al nitrates (0.6:0.3:0.1 M of Cu(NO$_3$)$_2$·3H$_2$O:Zn(NO$_3$)$_2$·6H$_2$O:Al(NO$_3$)$_3$·9H$_2$O) was used as well as a precipitating agent (Na$_2$CO$_3$, 1.2 M). The main differences occurred during the precipitation in which the stirring implement and method for dispensing the reactants was altered. The following methods were employed to carry out the coprecipitation:

1. Whilst stirring with a stainless steel pitched blade propeller stirrer shaft, the metal nitrate solution (40 mL) and Na$_2$CO$_3$ (aq) (55 mL) were added dropwise to deionised water (200 mL, 18.2 MΩ cm$^{-1}$, 65 °C), sustaining pH 7. (CZA1)

2. Initially, the solution of metal nitrates (20 mL) and deionised H$_2$O (200 mL, 18.2 MΩ cm$^{-1}$) were heated to 65 °C and brought to pH 7 via addition of the basic precipitating agent (Na$_2$CO$_3$). Following this, the Titrando dosed the metal nitrate solution (20 mL, 1 mL min$^{-1}$) and Na$_2$CO$_3$ into the reaction mixture, whilst maintaining pH 7. Throughout, the precipitate slurry was stirred with a PTFE magnetic stirrer bar. (CZA2)

3. The Titrando dispensed the Cu, Zn, Al nitrate solution (40 mL, 2 mL min$^{-1}$) and precipitating agent (45 mL) into deionised water (200 mL, 18.2 MΩ cm$^{-1}$, 65 °C) whilst being stirred by a PTFE screw propeller stirrer shaft at constant pH 7. (CZA3-CZA13)

Following each of these synthesis methods is the ageing process. The precipitate slurry was aged for 1.5 h at 65 °C and pH 7 in the mother liquor (via metal nitrate addition). The precipitate was then filtered, washed several times with deionised water (3 × 500 mL, 18.2 MΩ cm$^{-1}$) to remove...
residual sodium, dried in air at 80 °C for 15 h and, finally, calcined in air at 300 °C (2 °C min⁻¹) for 5 h.

3.2.1.2. Binary Catalysts

Using the Titrando, the CZ hydroxycarbonate precursor standards were prepared by dosing (40 mL, 2 mL min⁻¹) a mixed solution of Cu and Zn nitrates (1 M, concentration dependent on desired CZ ratio) and an aqueous solution of Na₂CO₃ (1.2 M) into deionised water (200 mL, 18.2 MΩ cm⁻¹) at 65 °C, pH 7 and stirred with a PTFE screw propeller stirrer shaft. The mother liquor was aged for 1.5 h at 65 °C and pH 7 (maintained via metal nitrate addition). Following the ageing process, the precipitate was filtered, washed several times with deionised water (3 × 500 mL, 18.2 MΩ cm⁻¹) to remove residual sodium, and dried in air at 80 °C for 15 h. All precursors were calcined in air at 300 °C (2 °C min⁻¹) for 5 h.

3.2.1.3. Promoting the Ternary Catalysts

The promoted catalysts were prepared via incipient wetness impregnation. The hydroxycarbonate CZA precursor, as prepared following method 3.2.1.1 (3), was impregnated with an aqueous solution of Cs₂CO₃ (the concentration of the Cs salt added was dependent on the desired weight loading), the amount of which was determined by the precursor’s pore volume (ca. 0.6 mL g⁻¹). Once impregnated, the impregnated precursors were dried in air at 80 °C for 15 h.

3.2.2. Ex situ Characterisation

Chemical compositions of the catalyst samples were determined by X-ray fluorescence (XRF). This was measured using a PANalytical Epsilon 3-XL spectrometer at ISIS Materials Characterisation laboratory, Harwell, UK, and analysed using Epsilon 3 software.

A Quantachrome Instrument FloVac Degasser sample preparation unit was implemented to degas the samples overnight at 80 °C.² The BET surface area and BJH surface area and pore volume (N₂ desorption) of the catalyst samples were measured using a Quantachrome Instrument Quadrasorb evo gas sorption surface area and pore size analyser. The data was analysed using QuadraWin.

X-ray diffraction measurements were collected with Cu-Kα₁ (λ = 1.5406 Å) radiation using an accelerating voltage/current of 40 kV/40 mA respectively on a D8 Advance Bruker powder diffractometer equipped with a Vantec-1D-Linear detector. The diffractograms were recorded using DIFFRAC+ XRD Commander software in a locked coupled continuous mode between 5-60 °2θ with a step size of 0.017 °. 1.0 mm divergence and 0.6 mm detector slits were used for all scans. All samples were mixed with an internal standard (quartz, 20 wt.%, see Appendix 7.3.2) using a pestle and mortar and pressed into polymethylmethacrylate (PMMA) sample holders (see Appendix 7.3.3), creating a compact powder to optimise the intensity of the
diffraction patterns. Phase identification of the patterns was carried out using PANalytical X’Pert
HighScore Plus.

Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS 10 FT-IR
spectrometer at a spectral resolution of 2 cm\(^{-1}\), accumulating 64 scans. Prior to loading a sample,
32 background scans were collected. Subsequent spectra were annotated using ACD/Spectrus.

Temperature-programmed reduction (TPR) experiments were carried out in a ChemBET
Pulsar TPR/TPD instrument, which is a Quantachrome automated chemisorption analyser. As
stated in Section 2.3.2, reduction profiles are known to be heavily influenced by the experimental
conditions; therefore, the operating variables (\(S_0, F, C_0\) and \(\beta\)) were chosen to ensure
0.9 < \(K\) < 2.3 min and \(P < 20\) K were satisfied.\(^3\) Each sample was heated to 400 \(^\circ\)C (10 \(^\circ\)C min\(^{-1}\))
in 30 mL min\(^{-1}\) of 10 \% H\(_2\)/Ar. The amount of sample reduced was dependent on the [Cu] in the
investigated catalyst.

Using a TA TGA Q50, the thermogravimetric analysis (TGA) and differential
thermogravimetry (DTG) profiles were measured in a flow of air at a heating rate of 20 \(^\circ\)C min\(^{-1}\)
from room temperature to 900 \(^\circ\)C, with an isothermal time of 90 min. The sample holder was
made of platinum, and brass tweezers were used when handling it. TA Universal Analysis
software was used to view and analyse the results.

3.3. Results and Discussion

3.3.1. Industrial Catalysts

The commercial catalysts investigated are referred to as the Standard LTS
(CuO/ZnO/Al\(_2\)O\(_3\)) and the Cs-promoted LTS (CuO/ZnO/Al\(_2\)O\(_3\)-Cs\(_2\)O) catalysts. Unfortunately,
the author is not able to disclose any characterisation data associated with these.

3.3.2. Model Binary Systems

A collection of single-phase Cu/Zn (denoted CZ) samples were prepared in order to
understand how the morphology affects the catalysts’ properties during activation of the LT-WGS
catalysts. Their compositions have been determined via XRF analysis and are given in Table 3.1.

\(\textbf{Table 3.1: XRF analysis of the model binary CZ catalysts}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CZ 100/00</td>
</tr>
<tr>
<td>CuO</td>
<td>100.00</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
</tr>
</tbody>
</table>

Initially, the binary precursor phases will be considered (Figure 3.2). As previously
mentioned, the characteristic peaks for each precursor phase, binary and ternary, are located in
the 2θ-range 31-33 °; it is here that the (20-1)- and (21-1)-reflections are located, which are heavily influenced by changes to the unit cell parameters. The pattern for malachite (CZ 100/00) has been included to illustrate how zinc incorporation into the malachite structure decreases the crystallinity of the phases and shifts the (20-1)- and (21-1)-reflections to lower d-spacings; this is evident when considering the CZ samples 90/10 through to 60/40 as they transform from malachite, to zincian malachite, and finally to rosasite. The malachite precursor phase that has been prepared is considered a reliable reference material as the diffraction pattern is comparable to that in the literature for the mineral. The sharp, defined peaks also indicate its crystallinity and purity and help highlight that the higher the concentration of zinc present, the broader the reflections and thus the less crystalline.

As stated in Section 1.6.1, for rosasite to form there must be a zinc content between 33-50 wt.% which is why it can be seen in the CZ 70/30 and CZ 60/40 precursors, though to varying degrees. It is formed in preference to aurichalcite because the CZ ratio is more favourable for the rosasite phase. As the copper content increases, malachite-like structures become the dominant phase. This is further evidenced in the CZ 80/20 and CZ 90/10 samples in which a clear phase-pure zincian malachite diffraction pattern is observed.

The least crystalline sample of the model binary CZ hydroxycarbonate precursor phases is CZ 50/50, which possesses the broadest reflections. It can be seen that aurichalcite is the dominant phase formed in this diffraction pattern as reflections associated with a malachite-like structure are very weak. The presence of aurichalcite is confirmed by the characteristic (121)-reflection at 34 °2θ, which does not overlap with the pattern for hydrozincite. As opposed to malachite, the concentration of aurichalcite increases with increasing amounts of zinc; therefore, aurichalcite is first seen to form very weakly in CZ 70/30 and is present in CZ 60/40 as well.

The pure Zn precursor (CZ 00/100) has also been prepared for reference. The pattern is dominated by a mixture of a zinc carbonate hydroxide hydrate phase, Zn$_4$CO$_3$(OH)$_6$·H$_2$O, and hydrozincite, Zn$_3$(CO$_3$)$_2$(OH)$_6$.7,9,11
Figure 3.2: Diffraction patterns of the model binary CZ hydroxycarbonate precursor phases; the dashed grey lines, from left to right, signify the (110)-, (120)-, (200)-, (220)-, (20-1)-, (21-1)- and (240)-reflections of the malachite phase, and the reference patterns for malachite and quartz are given below.

The infrared spectrum of CZ 100/00 contains two bands in the O-H region (see Figure 3.3 (a)) at 3314 and 3400 cm⁻¹; these correspond to two crystallographically different hydroxyl groups whose modes are characteristic of malachite.⁷,¹² As the zinc content increases, the splitting of the O-H bands increases as the predominant phase transitions from malachite, to zincian malachite, to rosasite. The shoulder that is first visible in the CZ 90/10 at 3460 cm⁻¹ is also indicative of zincian malachite and can be seen in the CZ 80/20 spectrum, and weakly in the CZ 70/30 spectrum. The presence of aurichalcite is determined in this region by the presence of a broad band around 3250 cm⁻¹ accompanied by a single sharp band at higher wavenumbers, ca. 3363 cm⁻¹, which is predominantly seen in the CZ 50/50 spectrum.⁷

Figure 3.3 (b) depicts the carbonate ν₃ (asymmetric C-O stretching) modes associated with each precursor phase. The literature states that there should be four bands present in the malachite spectrum as the correlation field splitting is resolved, which are weakly seen at 1513 (shoulder), 1491, 1424 and 1381 cm⁻¹ in the CZ 100/00 spectrum. The two bands at higher wavenumbers become a single broad band as a result of zincian malachite, and the other bands
are shifted slightly to higher wavenumbers as a result of zinc incorporation. As the concentration of aurichalcite in the sample increases, four bands of near equal intensity are exhibited in the region 1600-1300 cm\(^{-1}\), most clearly seen for CZ 50/50.\(^7\)

Three O-H libration bands in the region 1200-850 cm\(^{-1}\) are assigned to malachite. The first two bands of this set are shifted to higher wavenumbers as a result of zincian malachite; this relationship is immediately evident between CZ 100/00 and CZ 90/10. Aurichalcite is easily identified in the infrared spectrum of the CZ hydroxycarbonate precursors as it has two characteristic bands: an M-OH deformation band around 1200 cm\(^{-1}\) and an OH libration band around 970 cm\(^{-1}\). These bands are seen in the spectra for CZ 50/50, CZ 60/40, and faintly in the CZ 70/30 spectrum.\(^7\) Additional bands associated with the \(v_2\) (out-of-plane \(\text{CO}_3^{2-}\) bending) and \(v_4\) (in-plane \(\text{CO}_3^{2-}\) bending) modes are also visible here. For malachite, the \(v_2\) modes are visible at 816 cm\(^{-1}\), with a shoulder at 830 cm\(^{-1}\); these are shifted to higher wavenumber as the [Zn] increases and Zn-OCO\(_2\) bonds are formed. The four bands at 771, 749, 732 (shoulder) and 712 cm\(^{-1}\) correspond to malachite’s \(v_4\) components, which shift to lower wavenumber and their intensity decreases as the copper ions are substituted by zinc ions; as can be seen in Figure 3.3 (c), the band at 771 cm\(^{-1}\) is no longer visible in the CZ 60/40, CZ 50/50, or CZ 00/100 spectra.\(^{13}\)
Figure 3.3: IR spectra for the binary CZ hydroxycarbonate precursor phases in the ranges: (a) 3700-3100 cm$^{-1}$, (b) 1700-1100 cm$^{-1}$ and (c) 1200-650 cm$^{-1}$

The thermal properties of the mixed CZ hydroxycarbonate precursors were investigated to fully elucidate the slight physical and chemical changes seen in the synthetic ternary zincian malachite catalysts.

Unique to malachite (CZ 100/00) is the single decomposition step that occurs at 348.5 °C according to Equation 3.1.

$$\text{Cu}_2\text{CO}_3(\text{OH})_2 \rightarrow 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$$

*Equation 3.1: Decomposition of malachite*\(^6\)

This is associated with the simultaneous decarbonation and dehydroxylation of the precursor, resulting in the bulk of its weight being lost. Interestingly, there appears to be minimal
presence of surface water molecules as only 0.2 % of its weight is lost below 200 °C. Similarly, CZ 90/10 also has a dominant decomposition step at 377.4 °C; however, other decompositions are evident at higher temperatures. This is due to the presence of high-temperature carbonates (HT-CO$_3^{2-}$).\textsuperscript{7}

The presence of high-temperature carbonate species is a direct result of the Cu:Zn ratio; the closer it is to an even ratio (1:1), the more HT-CO$_3^{2-}$ species are present, stabilizing the precursor phase and increasing its decomposition temperature. This has been reported to have a beneficial influence on the ensuing catalysts’ performance.\textsuperscript{7,14,15} As Table 3.2 shows, the pure malachite precursor phase has minimal weight loss between 400-600 °C as compared to when zinc is incorporated into the malachite lattice. M. Behrens \textit{et al.} observed this characteristic of malachite and suggested that HT-CO$_3^{2-}$ are only present at the ZnO-CuO interface due to becoming trapped which is consistent with the results.\textsuperscript{7}

Additionally, the singular weight loss moment for CZ 100/00 and CZ 00/100 is characteristic of the samples being monophasic, whereas the mixed CZ hydroxycarbonate samples experience multiple decomposition steps, indicating that there is a combination of phases present.\textsuperscript{8,11} This is most evident in the DTG profiles shown in Figure 3.5.

\begin{table}[h]
\centering
\caption{TGA summary for the model CZ precursor phases weight loss up to 900 °C}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Cu/Zn ratio} & \textbf{≤ 200 °C} & \textbf{200-400 °C} & \textbf{400-600 °C} & \textbf{600-900 °C} & \textbf{Total} \\
\hline
100/00 & 0.22 & 28.56 & 0.15 & 0.13 & 29.05 \\
90/10 & 1.45 & 24.94 & 2.44 & 6.19 & 35.02 \\
80/20 & 1.17 & 16.14 & 10.54 & 0.67 & 28.51 \\
70/30 & 5.31 & 13.67 & 8.11 & 4.84 & 31.93 \\
60/40 & 4.21 & 16.59 & 6.93 & 4.18 & 31.90 \\
50/50 & 3.30 & 16.79 & 6.91 & 3.45 & 30.45 \\
00/100 & 1.87 & 23.06 & 0.13 & 0.07 & 25.13 \\
\hline
\end{tabular}
\end{table}
Figure 3.4: Thermogravimetric analysis for the model CZ precursor phases up to 900 °C
As expected, the monometallic CZ 100/00 and CZ 00/100 samples have a defined decomposition peak in their DTG profiles (Figure 3.5) because they are monophasic. When zinc is incorporated into the malachite lattice, the peak shifts to higher temperatures which is evidence of the malachite structure being stabilized. As more zinc is introduced, a broadening of the peaks can be seen which is a result of the phases becoming inhomogeneous, and so undergoing a second decomposition step. It is the presence of aurichalcite in the CZ 70/30, CZ 60/40 and CZ 50/50 samples that leads to more complex decomposition patterns.

In terms of LT-WGS catalysts, the observed species decomposing in the DTG profiles occur at greater temperatures than the activation/operation of the commercial catalyst (300 °C/200 °C); therefore, depending on the expressed precursor phase, these species would contribute to the overall performance of the catalyst. Interestingly, B. Bems et al. observed that precursors aged at constant pH had a greater crystallite size compared to those left to free age, causing them to have higher decomposition temperatures.

Figure 3.5: Differential thermogravimetry for the model CZ precursor phases up to 900 °C

Once calcined, it is very hard to determine the initial precursor phase by considering the diffraction pattern alone (see Figure 3.6). For the 100 wt.% Cu and Zn samples, the precursors clearly decompose to afford either phase pure CuO (CZ 100/00) or ZnO (CZ 00/100); however, for the CZ mixtures, the zincite phase is not very pronounced as it is dispersed within the CuO matrix. It can also be seen that the tenorite crystallite size decreases with increasing Zn content as a result of this.
Figure 3.6: Diffraction patterns of the calcined model binary CZ oxidic phases; the reference patterns for tenorite, zincite and quartz are given below.

As detailed in Section 2.3.2, the TPR runs were collected according to the instructions given by both D. A. M. Monti and A. Baiker, and P. Malet and A. Caballero. In order for the runs to be comparable, calculated values of P and K were kept constant depending on the amount of reducible species in the samples of interest. This then elucidated how the ZnO support affected the reducing conditions of the Cu active component.

The shape of the TPR profiles in Figure 3.7 suggests that reduction occurs in two, maybe three, steps. The former is the most widely reported, where the two steps are believed to correspond to (1) the reduction of CuO (Cu$^{2+}$) to Cu$_2$O (Cu$^+$), and then (2) the reduction of cuprite to metallic copper (Cu$^0$). Typically, the TPR profiles overlap as can be seen for the prepared samples, with the second peak appearing as a shoulder to the first. The additional peak(s) may signify that there is a variation in tenorite crystallite size, with the smaller CuO crystallites reducing first, hence the shoulder at lower temperature.

For CZ 100/00, the most intense peak is located at 198 °C, with a higher temperature shoulder at 214 °C; this serves as the standard reduction behaviour of unsupported CuO in this study. In comparison, reduction occurs at 190 °C (shoulder at 208 °C) for CZ 90/10, suggesting
that CuO dispersion is enhanced by incorporating 10 wt.% ZnO, facilitating its reducibility.\textsuperscript{23} However, the catalysts with a greater [ZnO] behave contrarily to this. Not only are the profiles for the TPRs of CZ 70/30 and CZ 50/50 dominated by a single reduction event, they also occur at similar temperatures, with the main peaks centred at 214 °C and 211 °C, respectively. This may imply that the CuO crystallite sizes are larger, but more uniform in the model binary catalysts with a [ZnO] of ≥ 30 wt.%. Nevertheless, a definite correlation between the reduction behaviour and precursor phase has not been observed.\textsuperscript{24}

As expected, no reduction of the CZ 00/100 catalyst is witnessed as ZnO requires temperatures above 700 °C for activation to occur.\textsuperscript{23}

![Figure 3.7: TPR profiles comparing the binary CZ calcined catalysts.](image)

**3.3.3. Prepared Ternary Catalysts**

Preparing LT-WGS catalysts involves coprecipitating the hydroxycarbonate precursor phases, ageing in the mother liquor, washing, drying, and calcining. To synthesise the low methanol catalyst, an additional step is required to impregnate the precursor phase with the alkali metal promoter (explored in Section 3.3.4).\textsuperscript{25,26} As the synthesis method for each catalyst requires the initial preparation of the precursor phase, this section will focus on generating a realistic precursor phase to compare to the industrial catalysts.

Multiple synthesis methods were attempted in order to determine a reproducible method to prepare a catalyst comparable to the presumed zincian malachite-derived industrial catalysts. Due to the sensitive chemical memory of the system, this proved to be a difficult precursor phase to reproduce. In this section, three (Cu,Zn)\textsubscript{2}CO\textsubscript{3}(OH)\textsubscript{2} precursor phases will be fully characterised and compared to the Standard LTS and the Cs-promoted LTS catalysts.
Successful syntheses were determined by their diffraction patterns; Figure 3.8 clearly shows that zincian malachite is the dominant precursor phase in the CZA1, CZA2 and CZA3 catalyst patterns. However, there is also a very small amount of aurichalcite present, which can be seen at 13.1 °2θ. Another common phase found in ternary zincian malachite samples that have been coprecipitated and aged at constant pH is a hydrotalcite-like compound (HTLC).\textsuperscript{10,27} Peaks associated with this HTLC are evident at 11.7 °, 23.6 ° and 34.6 °2θ corresponding to the (003)-, (006)- and (012)-reflections;\textsuperscript{28} the reference patterns for a Cu HTLC and a Zn HTLC have been provided (determined from Section 3.3.5), though it is possible a mixed Cu/Zn HTLC has formed. This does not account for all the aluminium, however, as the rest is poorly crystalline and therefore not visible in the diffractograms. There is also a weak malachite profile visible beneath the zincian malachite reflections of the CZA3 precursor, and a weak profile of a Zn-rich zincian malachite precursor for the CZA1 and CZA2 precursors.

When comparing the diffraction patterns of the prepared precursors, a slight shift to lower d-spacings can be seen in the malachite (20-1)- and (21-1)-reflections for CZA1 and CZA2 as compared to CZA3. This is most likely due to the known difference in zinc content in the samples as determined by XRF (see Table 3.3). Alternatively, as each of the samples were prepared via different coprecipitation methods, this may be evidence of the chemical memory of the system affecting the final properties of the precursor phase. The prepared precursors also differ in their crystallinity: the CZA3 precursor pattern displays more pronounced/sharper reflections highlighting larger crystallite sizes whereas broader/less defined reflections are present in the CZA1 precursor pattern, suggesting smaller crystallite sizes.
Figure 3.8: Diffraction pattern of the synthetic ternary zincian malachite catalysts; the dashed grey lines, from left to right, signify the (110)-, (120)-, (200)-, (220)-, (21-1)- and (240)-reflections of the malachite phase, and the reference patterns for malachite, aurichalcite, a Cu HTLC\textsuperscript{29}, a Zn HTLC\textsuperscript{30} and quartz are given below.

The chemical compositions of the ternary CZA hydroxycarbonate precursor phases show that, empirically, CZA2 and CZA3 possess similar compositions whereas CZA1 contains a higher ratio of CuO:ZnO (2.8:1). The CuO:ZnO ratios of CZA2 and CZA3 (2.3:1) are also comparable to those of the industrial samples. The XRF analysis also confirms that all sodium impurities were removed from the precipitate, proving the washing method during catalyst preparation to be effective.
Table 3.3: XRF analysis of the synthetic zincian malachite catalysts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
<th>CZA1 precursor</th>
<th>CZA2 precursor</th>
<th>CZA3 precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td></td>
<td>65.32</td>
<td>64.66</td>
<td>63.91</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>23.58</td>
<td>27.98</td>
<td>27.86</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>11.10</td>
<td>7.36</td>
<td>8.22</td>
</tr>
</tbody>
</table>

IR spectroscopy is an essential characterisation technique for phase identification as it is capable of identifying key functional groups present in both crystalline and amorphous samples. The IR spectra for the synthetic zincian malachite precursors are very similar indicating that their phase compositions are comparable. Nevertheless, there is a slight discrepancy in the O-H region as displayed in Figure 3.9 (a). Zincian malachite typically displays three O-H bands in this range: two strong bands assigned to malachite seen at 3407 and 3318 cm⁻¹, as well as a characteristic shoulder at 3459 cm⁻¹. These O-H bands are clearly assigned in the CZA2 and CZA3 precursors spectra, however, are very weak in the CZA1 precursor spectrum which may be a result of the smaller crystallite size.

As can be seen in Figure 3.9 (b), there is a weak splitting of the second band visible for each of the synthetic zincian malachite samples, which may indicate that there is some malachite present. This is because for the asymmetric C-O stretching (ν₃) mode of the carbonate anions in malachite, a correlation field splitting effect is seen. For pure zincian malachite, there would be a singlet ca. 1500 cm⁻¹. No aurichalcite can be seen in these spectra, possibly because there is only a small amount present. Evidence of the HTLC assigned in the diffractograms is corroborated by the weak band at ca. 1650 cm⁻¹, which corresponds to interlayer H₂O molecules, and the shoulder at 1350 cm⁻¹, which is assigned as the carbonate ν₁ mode.

Finally, three strong OH libration bands can be seen at 1100, 1050 and 875 cm⁻¹. As the first two band positions are at slightly higher wavenumbers than those quoted for malachite, these bands are also indicative of zincian malachite. Additional carbonate modes are seen at 820 cm⁻¹ (out-of-plane O-C-O bending) and a triplet centred at 740 cm⁻¹ (asymmetric O-C-O bending).
Figure 3.9: IR spectra for the ternary zincian malachite precursor phases in the ranges: (a) 3700-3100 cm\(^{-1}\), (b) 1700-1100 cm\(^{-1}\) and (c) 1200-600 cm\(^{-1}\)

The profiles of the calcined zincian malachite catalysts’ patterns are given in Figure 3.10 and mimic those of the industrial catalysts. Interestingly, there is still evidence of a malachite-like structure present in CZA3 which is very similar to the industrial catalysts investigated. All prepared catalysts were calcined following the same procedure; it can therefore be concluded that the precursor phase present in CZA3 does not fully decompose into its corresponding oxides as it does for CZA1 and CZA2 which could be a result of the larger crystallite size present in this sample affecting its rate of decomposition. The broad overlapping CuO and ZnO peaks in the Standard LTS, Cs-promoted LTS, and CZA3 catalysts are also both centred around 35.4 ° and 38.8 °/θ. Additionally, the HTLC that was present in the precursor phases has fully decomposed.
Figure 3.10: Diffraction patterns of the prepared calcined zincian malachite catalysts (a) stacked and (b) overlapping; the reference patterns for tenorite, zincite, malachite and quartz are given below.

Following the initial activation step, the chemical compositions of the calcined zincian malachite catalysts were re-examined and it was found that the CuO:ZnO ratios for each sample remained unchanged (Table 3.4).
Table 3.4: XRF analysis of the calcined zincian malachite catalysts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
<th>CZA1</th>
<th>CZA2</th>
<th>CZA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>66.36</td>
<td>64.65</td>
<td>64.14</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>24.25</td>
<td>27.74</td>
<td>28.32</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.40</td>
<td>7.61</td>
<td>7.55</td>
<td></td>
</tr>
</tbody>
</table>

The surface area of the final prepared catalysts was also measured (Table 3.5). When compared to the N₂ adsorption results for the Standard LTS catalyst, CZA3 has the most similar properties due to the high surface areas for BET and BJH desorption. It should be noted that the pore volumes of the prepared catalysts are larger than those of the industrial catalysts, but it is presumed this is because the commercial catalysts were provided as pellets, therefore their pore structure, even after being ground into a fine powder for the measurements, differs from that of a freshly prepared powder.

Table 3.5: Nitrogen adsorption results for the calcined zincian malachite catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area / m² g⁻¹</th>
<th>BJH Desorption Surface Area / m² g⁻¹</th>
<th>Pore Volume (N₂ desorption) / mL g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA1</td>
<td>82.5</td>
<td>88.3</td>
<td>0.39</td>
</tr>
<tr>
<td>CZA2</td>
<td>74.0</td>
<td>71.5</td>
<td>0.40</td>
</tr>
<tr>
<td>CZA3</td>
<td>88.1</td>
<td>94.3</td>
<td>0.42</td>
</tr>
</tbody>
</table>

The thermal decomposition properties of the calcined zincian malachite catalysts are compared in Figure 3.11. Once the sample begins heating, there is a continuous weight loss up to 200 °C, mainly due to the loss of surface water molecules, though some CO₂ also evolves at this temperature. Between 200-400 °C, the rate of weight loss increases and peaks around 350 °C for each sample; this is associated with both a dehydroxylation and a decarbonation step of water vapour and carbon dioxide. The weight loss between 400-600 °C is attributed to the very stable, strongly bonded high-temperature carbonate (HT-CO₃²⁻) species associated with water-gas shift catalysts.⁷,₈,3₂
The thermal properties of the industrial catalysts proved to be very similar, meaning they decompose at comparable temperatures.

When the TGA results are considered for the prepared catalysts (Figure 3.11 and Table 3.6), it can be concluded that CZA3 again appears to be the most closely related sample to the industrial catalysts as a similar TGA profile is sustained throughout the temperature ramp. In comparison, CZA1 differs greatly in these respects. However, on closer inspection of the DTG thermograms, CZA3 appears to contain an extra component as an additional peak is visible ca. 460 °C.

Table 3.6: TGA summary for the calcined zincian malachite catalysts’ weight loss up to 900 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight loss / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>≤ 200 °C</td>
</tr>
<tr>
<td>CZA1</td>
<td>3.68</td>
</tr>
<tr>
<td>CZA2</td>
<td>5.97</td>
</tr>
<tr>
<td>CZA3</td>
<td>5.01</td>
</tr>
</tbody>
</table>
Figure 3.12: Differential thermogravimetry profiles for the calcined synthesised catalysts up to 900 °C

The IR spectra of the calcined CZA1, CZA2 and CZA3 catalysts, as shown in Figure 3.13, are comparable to those of the industrial catalysts. Interestingly, all spectra have a weak band at ca. 1640 cm\(^{-1}\), which was previously assigned as evidence of the HTLC.\(^{31}\) However, on closer inspection, CZA3 is the only prepared catalyst that has similar O-H libration bands (1100, 1050 and 875 cm\(^{-1}\)) to the Standard LTS and Cs-promoted LTS catalysts following calcination. This further suggests that the coprecipitation method employed to prepare CZA3 is the most successful at producing catalysts with an industrially relevant morphology.

Interestingly, there appears to be a weak characteristic aurichalcite band present in CZA1 at 1236 cm\(^{-1}\) which was not previously seen.
Figure 3.13: IR spectra of the calcined zincian malachite catalysts in the ranges: (a) 3700-3100 cm$^{-1}$, (b) 1700-1100 cm$^{-1}$ and (c) 1200-600 cm$^{-1}$

3.3.4. Cs Series

Promoting LT-WGS catalysts with a caesium promoter has been shown by P. Kowalik $et al.$ to inhibit methanol production.\cite{P.Kowalik25, P.Kowalik26} In order to investigate the impact the Cs-loading has on the resultant catalyst properties, a zincian malachite precursor (prepared via method 3.2.1.1 (3)) has been impregnated with varying [Cs$_2$CO$_3$]. The composition of the resultant precursors are given in Table 3.7, and though they have been assigned names, e.g. CZA-Cs1, from here on they will be referred to by their [Cs$_2$O].
Table 3.7: XRF analysis of the prepared standard CZA and Cs-promoted zincian malachite catalysts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CZA</td>
</tr>
<tr>
<td>CuO</td>
<td>62.48</td>
</tr>
<tr>
<td>ZnO</td>
<td>28.19</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>-</td>
</tr>
</tbody>
</table>

As shown in Figure 3.14 (a), on first inspection, the diffraction patterns of the Cs-promoted precursors do not differ from that of the unpromoted (0.00 wt.% Cs₂O). The spectral lines for zincian malachite have been superimposed onto the figure in order to highlight that the expressed precursor phase composition is not affected by the impregnation method (additional hydrothermal ageing step) or [Cs₂O]. However, when the hydrotalcite-like compound is considered, two changes are apparent: (1) the crystallinity of the HTLC phase improves from the fresh dried precursor to the impregnated, and (2) it appears that the type of HTLC expressed may transform from a Cu HTLC, to a mixed Cu,Zn HTLC. It was first thought this may be a result of either the Cs-promoter or the presence of CO₃²⁻ anions in the impregnating solution, but when the unpromoted precursor was subjected to the impregnation method, sans the promoter, a similar pattern was obtained.³³,³⁴ This is better realised in Figure 3.14 (b). Here, the (003)- and (006)-reflections associated with the initial HTLC basal planes in the unpromoted precursor at 11.73 °2θ and 23.61 °2θ have shifted slightly to 11.66 °2θ and 23.52 °2θ in the hydrated sample; these changes indicate that zinc ions may have been incorporated into the structure.³⁵ Alternatively, a different type of Cu HTLC may crystallize. This contradicts some of the literature in which it is reported that the structure of the initial HTLC does not change during reconstruction (memory effect, see Section 3.3.5).³³,³⁴,³⁶

It should be noted that F. Cavani et al. specify that the large ionic radius of caesium inhibits it from entering the hydrotalcite framework, which is why this has not been considered.²⁷
Figure 3.14: Diffraction patterns of the (a) Cs-promoted series precursor phases and (b) comparison of the fresh and hydrated unpromoted precursor; the dashed grey lines, from left to right, signify the (110)-, (120)-, (200)-, (220)-, (20-1)-, (21-1)- and (240)-reflections of the zincian malachite phase, and the reference patterns for zincian malachite, a Cu HTLC$^{29}$, a Zn HTLC$^{30}$ and quartz are given below.
The infrared spectra for the Cs series precursors are very similar to that of the standard unpromoted CZA zincian malachite precursor (Figure 3.15). As expected, in the OH region, the two different OH groups present in malachite are visible at 3404 and 3314 cm\(^{-1}\), as well as the characteristic zincian malachite shoulder at 3455 cm\(^{-1}\), highlighting the intended precursor is present.\(^7,12\) There is also a weak shoulder at ca. 3050 cm\(^{-1}\) that is indicative of H-bonding in the HTLC interlayer region between H\(_2\)O and CO\(_3^{2-}\).\(^37\) The additional bands seen in the 1.57 wt.% Cs\(_2\)O IR spectrum, for example in the range 3010-2860 cm\(^{-1}\), are assigned to the asymmetric CH\(_3\) and CH\(_2\) stretching modes of an intercalated alkyl impurity.\(^37,38\)

The only anomalous band, not associated with an impurity, is present in the 1700-1100 cm\(^{-1}\) range (Figure 3.15 (b)). Here, a shoulder at ca. 1360 cm\(^{-1}\) is visible which is attributed to the \(v_1\) (symmetric C-O stretching) mode assigned to either a Cu, Zn, or Cu,Zn HTLC (see Section 3.3.5).\(^29\) It is only expressed in the Cs-promoted samples, therefore appears to be a result of the impregnation method which enhanced the crystallinity of the expressed HTLC.

Furthermore, in Figure 3.15 (c), the positions of the OH libration peaks (1101, 1050, 879 (shoulder) and 862 cm\(^{-1}\)), and \(v_2\) (831 (shoulder) and 818 cm\(^{-1}\)) and \(v_3\) (742 and 707 cm\(^{-1}\)) bending modes of the carbonate ions do not change across the samples.\(^13\) This reinforces that the presence of caesium does not cause major structural changes to the hydroxycarbonate precursor.
Figure 3.15: IR spectra of the Cs-promoted precursor series in the ranges: (a) 3700-2700 cm⁻¹, (b) 1700-1100 cm⁻¹, and (c) 1200-650 cm⁻¹

Calcination of the Cs series precursors affords their oxide intermediates (Figure 3.16 (a)). Interestingly, the precursor phase does not completely decompose in the standard catalyst (0.00 wt.% Cs₂O), but does in the Cs-promoted catalysts. The crystallinity of the tenorite phase increases following Cs-incorporation, which is clearly illustrated in Figure 3.16 (b) and resembles the difference in crystallite size seen for the Standard LTS and Cs-promoted LTS catalysts. This is most likely a result of the hydrothermal treatment the Cs-promoted catalysts received during incipient wetness impregnation as it is reported that phase segregation of the CuO results from the recrystallization of the HTLC; this process does not appear to affect the ZnO support which correlates with the literature for mixed Cu,Zn HTLCs. There are no additional peaks visible to indicate the presence of the Cs-promoter, suggesting that it is highly dispersed throughout the sample, making it poorly crystalline.
Figure 3.16: Diffraction patterns of the calcined Cs-promoted catalysts (a) stacked and (b) overlapping; the reference patterns for tenorite, zincite, zincian malachite and quartz are given below.

There does not appear to be an obvious trend in the surface area measurements collected for the promoted series (Table 3.8), so no definitive conclusions can be drawn. However, it is
clear that the presence of the promoter, even in small quantities e.g. 0.15 wt.%, has a detrimental impact on the overall surface area.

Table 3.8: BET surface area (SA) results for the zincian malachite catalysts promoted with varying concentrations of caesium

<table>
<thead>
<tr>
<th>[Cs₂O] / wt.%</th>
<th>0.00</th>
<th>0.15</th>
<th>0.55</th>
<th>0.81</th>
<th>0.98</th>
<th>1.57</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET SA / m² g⁻¹</td>
<td>79.273</td>
<td>73.450</td>
<td>63.536</td>
<td>66.129</td>
<td>64.467</td>
<td>67.574</td>
</tr>
</tbody>
</table>

3.3.5. Cu and Zn HTLCs

Unfortunately, there are not many/any reliable reference diffraction patterns available in the ICSD database for Cu and Zn HTLCs. In an attempt to work around this, samples were prepared using equivalent amounts of the starting material to verify the HTLC phases; each sample contains x/Al in the atomic ratio 90/10, where 90 wt.% is composed of x = Cu or Zn, and the remaining 10 wt.% is composed of the Al support (Table 3.9). The synthesis conditions were not altered from those used to prepare the LT-WGS catalysts (65 °C, pH 7, 1.2 M Na₂CO₃, 2 h ageing, dried for 15 h at 80 °C) as the aim was not to intentionally yield the HTLC, but investigate the phases that formed when either Cu or Zn were not included in the ternary mother liquor. The prepared samples were also subjected to the incipient wetness impregnation method, sans the Cs-promoter, which are referred to as ‘Hydrated’ (later as ‘Rehydrated’).

Table 3.9: XRF analysis of the prepared x/Al samples, where x = Cu or Zn

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/Al</td>
</tr>
<tr>
<td>CuO</td>
<td>90.95</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.05</td>
</tr>
</tbody>
</table>

The diffraction patterns of the prepared sample precursors are shown in Figure 3.17 and Figure 3.18; a quartz internal standard (20 wt.%) is included to verify peak position.

From Figure 3.17, it is evident that the main crystalline phase present in the Dried and Hydrated Cu/Al precursor sample is malachite. As the synthesis conditions were not altered from those used for the binary, ternary and promoted catalysts, this is expected. Also present is a hydrotalcite-like compound which corresponds to a Cu HTLC, assigned as Cu₂.₅Al₂C₁.₇O₈.₉5H₂O.²⁹,³⁹ This was assigned according to the (200)-peak at 11.7 °2θ and the (400)-peak at 23.6 °2θ, visible as a shoulder to the malachite (220)-peak at 24.1 °2θ. M. Behrens et al. stated that when pure Na₂CO₃ was employed as the precipitating agent, the formation of
carbonate-rich species occurred, in this case malachite. To avoid this and favour HTLC formation, a mixture of NaOH (0.6 M) and Na$_2$CO$_3$ (0.09 M) could have been used, as well as maintaining a pH of 8. A lower reaction temperature would also have to be employed to ensure oxolation of the Cu(OH)$_2$ species to tenorite did not take place due to the higher pH.$^{27,40}$

The crystallinity of both the malachite and Cu HTLC phases are unaffected by the additional hydrothermal treatment.

![Diffraction patterns](image)

**Figure 3.17:** Diffraction patterns of the Dried and Hydrated Cu/Al precursors; the reference patterns for malachite, a Cu HTLC$^{29}$ and quartz are given below.

The diffraction patterns for the Dried and Hydrated Zn/Al precursors are not easily assigned due to the poorly crystalline nature of the phases present (see *Figure 3.18*). The main identifiable peaks are associated with the quartz internal standard. However, there is evidence of a (003)-Zn HTLC peak, visible as a shoulder at 11.6 °2θ in the hydrated sample, but it appears that growth of the HTLC phase does not form as readily as in the Cu/Al precursor during coprecipitation.
The remaining peaks did not sufficiently match any phases in the database of the phase identification program used. The hydrozincite pattern has been included as the peaks located at 12.8 °2θ, and the weaker peak at 29.7 °2θ, could be indicative of the (200)- and (401)-reflections, although the broadness suggests the presence of another phase. The second broad peak at 19.3 °2θ is probably representative of another form of zinc hydroxycarbonate that is as yet unknown; interestingly, similar peaks were visible in a zinc-rich CZA catalyst pattern prepared by F. Stone and D. Waller.41

Figure 3.18: Diffraction patterns of the Dried and Hydrated Zn/Al precursors; the reference patterns for hydrozincite, a Zn HTLC30 and quartz are given below.

The IR spectra of the prepared Dried and Hydrated precursors have been compared in Figure 3.19 to highlight any functional groups that are characteristic of the phase pure HTLCs.

For the Cu/Al sample, besides the typical bands seen for malachite (CZ 100/00), the only unaccounted-for bands are visible at 1353 cm⁻¹, which has been assigned in the literature as the ν₁(-O-CO₂) symmetric stretching component of Cu₂.5Al₂.5C₁₆.₉₂O₈.₉₂5H₂O, and a weak band at 1650 cm⁻¹, which is indicative of H₂O molecules present in the HTLC interlayer region.²⁹
Alternatively, the Zn/Al Dried and Hydrated precursor spectra are quite dissimilar to the CZ 00/100 spectrum. It is supposed that the additional band in the OH region (3570 cm\(^{-1}\)) is attributed to the Zn-OH stretching vibrations from the HTLC structure, despite it not being identified in both XRD patterns.\(^{42}\) The weak band at 1650 cm\(^{-1}\) is, again, assigned to the interlayer H\(_2\)O molecules (H-O-H bending), while the bands at 1475 and 1428 cm\(^{-1}\) are ascribed to the \(v_3\) modes of the carbonate anions.\(^{42,43}\) However, it is clear from Figure 3.19 (b) that the carbonate symmetry is different between the Cu/Al and Zn/Al precursors.

Again, bands associated with the asymmetric CH\(_3\) and CH\(_2\) stretching modes of an intercalated alkyl impurity are visible in the 3010-2860 cm\(^{-1}\) range.\(^{37,38}\)

![Image](image_url)

**Figure 3.19:** IR spectra for the prepared Cu/Al and Zn/Al precursors in the ranges: (a) 3700-2700 cm\(^{-1}\), (b) 1700-1100 cm\(^{-1}\) and (c) 1200-650 cm\(^{-1}\)

The thermogravimetric analysis of the prepared Cu/Al and Zn/Al samples has been separated into 4 stages to easily compare the two samples.
The amount of weight loss for each sample below 200 °C is comparable as it relates to the amount of surface water molecules; as the samples are heated, the surface is dehydrated. The other decomposition stages present in this temperature range are also attributable to those of the HTLCs present. It has been suggested that this is when dehydroxylation of the brucite layers takes place. From the TGA curve, it is evident that this occurs at a lower temperature for the Zn HTLC than the Cu HTLC, indicating that the H-bonding between the interlayer water molecules in the Cu HTLC are stronger. The suspected reactions associated with these thermal decompositions are stated in Equation 3.2.\textsuperscript{44}

\[
\begin{align*}
\text{Cu}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 & \rightarrow y\text{Al}_2(\text{CO}_3)_3 + (1 - y)\text{Al}_2\text{O}_3 + (6 - x)\text{CuO} + x\text{CuCO}_3 + 8\text{H}_2\text{O} \\
\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 & \rightarrow y\text{Al}_2(\text{CO}_3)_3 + (1 - y)\text{Al}_2\text{O}_3 + (6 - x)\text{ZnO} + x\text{ZnCO}_3 + 8\text{H}_2\text{O}
\end{align*}
\]

Equation 3.2: Thermal decomposition reactions that occur below 200 °C for phase pure Zn HTLCs and Cu HTLCs\textsuperscript{44}

The largest mass loss occurs between 200 and 400 °C for both samples. It is anticipated that the malachite present in the Cu/Al sample dictates the profile of the TGA curve in this temperature range. This is because, as shown in Section 3.3.2, malachite only has one decomposition stage;\textsuperscript{7} however, rather than being at 348.5 °C, it occurs at a higher temperature of 368.1 °C as shown in Figure 3.21. A similar decomposition stage is seen in the Zn/Al sample at 273.7 °C, which is at a slightly higher temperature than for CZ 00/100 (261.1 °C).\textsuperscript{11}

Between 400 and 600 °C, it is understood that high-temperature carbonates readily decompose from CuCO\textsubscript{3} and ZnCO\textsubscript{3} (see Equation 3.3 (a)). For the Cu/Al samples, the weight loss in this temperature range is negligible, whereas a ca. 3 % mass loss is observed for the Zn/Al sample, suggesting HT-CO\textsubscript{3}\textsuperscript{2-} species favour the presence of Zn. At higher temperatures (600-900 °C) we see the carbonate species decomposing from Al\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} (see Equation 3.3 (b)), which is most evident in the Cu/Al sample due to the increased weight loss and the peak evident in the DTG profile.\textsuperscript{44}

\[
\begin{align*}
\text{(a)} & \quad x\text{CuCO}_3 \rightarrow x\text{CuO} + x\text{CO}_2 \\
& \quad x\text{ZnCO}_3 \rightarrow x\text{ZnO} + x\text{CO}_2 \\
\text{(b)} & \quad y\text{Al}_2(\text{CO}_3)_3 \rightarrow y\text{Al}_2\text{O}_3 + 3y\text{CO}_2
\end{align*}
\]

Equation 3.3: Evolutions of CO\textsubscript{2} from the (a) Cu, Zn and (b) Al carbonate species\textsuperscript{44}
Figure 3.20: Thermogravimetric analysis of the Dried and Hydrated (a) Cu/Al and (b) Zn/Al samples

Table 3.10: TGA summary of the Cu/Al and Zn/Al samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss / %</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>≤ 200 °C</td>
<td>200-400 °C</td>
<td>400-600 °C</td>
<td>600-900 °C</td>
<td>Total</td>
</tr>
<tr>
<td>Cu/Al Dried</td>
<td>4.367</td>
<td>22.170</td>
<td>0.865</td>
<td>1.235</td>
<td>28.637</td>
</tr>
<tr>
<td>Cu/Al Hydrated</td>
<td>4.298</td>
<td>22.410</td>
<td>0.842</td>
<td>1.187</td>
<td>28.737</td>
</tr>
<tr>
<td>Zn/Al Dried</td>
<td>4.386</td>
<td>20.720</td>
<td>2.410</td>
<td>0.636</td>
<td>28.153</td>
</tr>
<tr>
<td>Zn/Al Hydrated</td>
<td>3.782</td>
<td>19.170</td>
<td>3.063</td>
<td>0.446</td>
<td>26.461</td>
</tr>
</tbody>
</table>
Following calcination of the Cu/Al and Zn/Al samples, it is evident that the HTLCs (as well as all other hydroxycarbonate phases present) have decomposed to tenorite and zincite, respectively (see Figure 3.22 and Figure 3.23). The Calcined samples were then hydrated to afford the Rehydrated samples which clearly show that the HTLC phases have readily reformed, which have again been assigned as Cu$_{2.5}$Al$_2$C$_{1.7}$O$_{8.9}$·5.2H$_2$O and Zn$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O.\textsuperscript{29,30} The diffraction patterns of the Calcined and Rehydrated Cu/Al and Zn/Al samples have been overlapped in Figure 3.22 (b) and Figure 3.23 (b) to highlight that the CuO crystallinity is unaffected, whereas growth of the ZnO crystallites is apparent by the sharp ZnO/Zn$_6$Al$_2$O$_9$ reflections.\textsuperscript{36,43,45} This is an unusual result as in the CZA catalysts, phase segregation of the CuO occurs; A. J. Marchi and C. R. Apesteguía suggest that this is because Cu$^{2+}$ cations preferentially occupy the octahedral sites in the metal-oxygen framework (Cu$^{2+}$ > Zn$^{2+}$).\textsuperscript{34}
Figure 3.22: Comparison of the Calcined and Rehydrated Cu/Al samples (a) stacked and (b) overlapping; the reference patterns for tenorite, a Cu HTLC\textsuperscript{29} and quartz are given below.
Figure 3.23: Comparison of the Calcined and Rehydrated Zn/Al samples (a) stacked and (b) overlapping; the reference patterns for zincite, a Zn HTLC\textsuperscript{30}, a Zn spinel\textsuperscript{13} and quartz are given below.
The ability for the HTLCs to regenerate in the Calcined Cu/Al and Zn/Al samples is considered a memory effect, which is reported to depend on the parent hydrotalcite formulation, the calcination temperature, and the regeneration conditions (medium, temperature and time).\textsuperscript{27,46}

The samples were calcined at 300 °C which, as seen in the TGA profiles of the samples and Figure 3.24, dehydroxylated the vicinal OH groups within the brucite layer, preserving the close-packed cubic lattice by creating oxygen vacancies amongst the O\textsuperscript{2-} anions. During the collapse of the hydrotalcite (lamellar) structure, carbonate anions were occluded in the oxycarbonate interlayer region.\textsuperscript{34,36} This topotactic transformation also retained the metal-oxygen framework, though the coordination of the Al\textsuperscript{3+} cation changes from octahedral to tetrahedral.\textsuperscript{34,36,46}

Recrystallizing the HTLC occurred via a retrotopotactic transformation when the samples were rehydrated in water and dried at 80 °C for 15 h. The H\textsubscript{2}O molecules were able to diffuse into the oxycarbonate structure, reconstructing the original layered structure.\textsuperscript{27,46} In order to prevent the HTLC from reconstructing, the calcination could be carried out above 700 °C to favour growth of the spinel phase; however, this is not feasible for the type of catalyst currently being investigated.\textsuperscript{27,45}

\textbf{Figure 3.24: Graphical representation of the decomposition-reconstruction process, aka memory effect, of hydrotalcite-like compounds; image adapted from A. J. Marchi and C. R. Apesteguia, Appl. Clay Sci., 1998, 13, 35-48.}\textsuperscript{34}

All the literature suggests that the hydrotalcite must be expressed in the initial precursor for it to be regenerated following calcination.\textsuperscript{34,36,46-48} However, this relies on the HTLC being visible in the precursor diffraction pattern; the results for the Calcined Zn/Al sample thus contradict this as the Zn HTLC was not visible in the Dried Zn/Al diffractogram. It is presumed
this is because it was poorly crystalline/amorphous to XRD as bands assigned to the Zn HTLC are visible in the Dried Zn/Al infrared spectrum.

When the infrared spectra of the Calcined and Rehydrated Cu/Al and Zn/Al samples are compared, the bands associated with the phase pure HTLC phases are more evident. For Zn/Al Rehydrated, the presence of surface water, interlayer H$_2$O, and ZnO-H species are highlighted by the band at 3466 cm$^{-1}$ in Figure 3.25 (a). The weak shoulder ca. 3050 cm$^{-1}$ is attributed to the CO$_3^{2-}$-H$_2$O stretching vibration of H-bonded interlayer H$_2$O and carbonate ions. These bands are seen to a lesser extent in the Cu/Al Rehydrated spectrum, though the OH band is centred at 3391 cm$^{-1}$, presumably as a result of CuO-H species.

The carbonate anion stretches shown in Figure 3.25 (b) highlight the bands associated with the interlayer CO$_3^{2-}$ in the Rehydrated samples, but do not differ greatly from each other. A sharp band associated with the $v_1$ (symmetric C-O stretching) component is visible at 1355 cm$^{-1}$ for Rehydrated Cu/Al, and 1362 cm$^{-1}$ for Rehydrated Zn/Al. Interestingly, $v_3$ modes are weakly expressed in the Cu/Al spectrum, but not the Zn/Al. The spectra of the Calcined samples highlight that, though the diffraction patterns show that the hydroxycarbonate precursors have decomposed to their oxides, there are still carbonate species present due to the appearance of the $v_3$ asymmetric C-O stretching modes at 1495 and 1392 cm$^{-1}$ for Cu/Al Calcined, and 1480 and 1417 cm$^{-1}$ for Zn/Al Calcined. Also, across all samples, the interlayer bending mode of H$_2$O is visible at 1650 cm$^{-1}$.

The band at ca. 680 cm$^{-1}$ in the Zn/Al spectras is either indicative of formation of the spinel or can be attributed to Al$_2$O$_3$; in order to confirm, the recorded wavenumber range would have to be extended to 400 cm$^{-1}$, which was not possible on the instruments available.
Figure 3.25: IR spectra for the Calcined and Rehydrated Cu/Al and Zn/Al samples in the ranges: (a) 3700-2700 cm\(^{-1}\), (b) 1700-1100 cm\(^{-1}\) and (c) 1200-650 cm\(^{-1}\)

3.4. Conclusion

The purpose of this chapter was to determine a reproducible synthesis method to produce catalysts that possessed industrially relevant structural and morphological properties. This was achieved by first characterising two types of LTS catalysts which are commercially available. However, it is commonplace for industry to provide pellets in their calcined form and manufacturing processes are not widely shared. In order to help elucidate the initial precursor phase, XRF analysis was carried out to determine the ratio of CuO/ZnO/Al\(_2\)O\(_3\) (60/30/10); zincian malachite is known to preferentially coprecipitate at these concentrations therefore this was the phase of focus. This was further justified by remnants of a malachite phase present in the Standard LTS and Cs-promoted LTS diffraction patterns.
Initially, binary CZ samples were prepared and characterised. These serve as a reference for assigning diffraction peaks, infrared bands, and TGA/DTG profiles for different precursor phases. The TPRs proved inconclusive, which is in agreement with the literature.  

Three coprecipitation methods were explored to determine their effect on the final ternary catalyst properties. The desired zincian malachite precursor phase was expressed for each, as well as a hydrotalcite-like compound resultant of the Al support. The chemical memory of the system proved sensitive to systematic changes in the synthesis method; despite using equivalent concentrations of the starting materials across each coprecipitation, alterations to the mixing regime and methods for dispensing the reactants led to zincian malachite precursors with varying [Zn] and crystallinity. Following calcination, CZA1, CZA2 and CZA3 were compared to the industrial catalysts; it was determined via N₂ BET, IR, TGA and XRD that CZA3 was the most comparable, due to its high surface area, presence of OH libration bands, similar TGA profile and remnants of the precursor phase in the diffractogram, thus suggesting utilising the Titrando, coupled with a PTFE screw propeller stirrer shaft, produced the most industrially relevant catalysts. This method (3.2.1.1 (3)) was therefore replicated for all further catalyst syntheses within this thesis.

The Cs-promoted catalysts were prepared via incipient wetness impregnation. It was determined that the additional hydrothermal ageing stage in the catalyst preparation method aided crystallization of the HTLC initially expressed in the precipitate. It is also supposed that the composition of the HTLC transforms, facilitating phase segregation of the tenorite as evidenced in the calcined diffraction patterns. Varying [Cs₂O] do not affect this phenomena, though it was found that the promoter presence, even at low weight loadings, decreased the catalyst surface area.

With regards to the assignments of the HTLC phases, this proved difficult as there are no reliable reference patterns available in the ICSD database and the patterns were obscured/dominated by the presence of other phases in the CZA and CZA-Cs diffraction patterns. Therefore, throughout the chapter, the HTLC phases were tentatively assigned as either Cu₂.₅Al₂C₁.₇O₈₉·5.₂H₂O (Cu HTLC) or Zn₆Al₂(OH)₁₆CO₃·4H₂O (Zn HTLC) due to the findings in Section 3.3.5 which were determined using the Search and Match function in the X’Pert Highscore Plus software package.  

The possibility of a mixed Cu,Zn HTLC was also considered, but it was not possible to investigate different compositions experimentally. Other characterisation methods were also investigated, specifically TGA and IR, but these proved to be insufficient diagnostic tools as the resultant measurements were very similar. The only real difference was seen in the DTG thermogram where the Cu HTLC showed a peak at 105 °C which was not seen for the Zn HTLC.

Interestingly, for the Cu/Al and Zn/Al samples, it is only the ZnO that appears affected by the impregnation method (sintering of ZnO crystallites evident), whereas in the CZA and CZA-Cs catalysts, the ZnO crystallites are unaffected and growth of the CuO crystallites is seen.  

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author has not been able to find a conclusive explanation for this which may warrant further investigation.

3.5. Bibliography

2003, 125, 10684–10692.


Chapter 4: Investigating How the Reducing Gas Composition Affects the Microstructure of the LT-WGS Catalysts

4.1. Abstract

Manufacturers of industrial catalysts specify activation procedures to ensure the catalyst’s efficiency and lifetime are optimised. Within this chapter, a standard low-temperature water-gas shift catalyst (sCZA, CuO/ZnO/Al₂O₃ 60/30/10) is investigated in situ under three reducing atmospheres (1 %, 2.5 % and 5 % H₂/Ar) to determine whether the microstructural properties of the FCC Cu⁰ active component can be tailored. These are compared with a high copper loading catalyst (hCZA, CuO/ZnO/Al₂O₃ 80/10/10) reduced under the more forcing 5 % H₂ conditions. As well as this, the incorporation of a caesium promoter (sCZA-Cs and hCZA-Cs), believed to inhibit methanol production during WGS activity, will also be assessed in terms of anisotropy, dislocations, and, finally, stacking fault probabilities.

4.2. Introduction

X-ray diffraction peak analysis is considered a powerful tool when characterising any crystalline material’s microstructure; not only is it sensitive to variations in atomic arrangement, but also to the atomic scattering factors of different elements.¹,² The term ‘microstructure’ encompasses an array of structural characteristics that cause a crystal structure to deviate from that of the ideal; these include compositional inhomogeneity, the distribution and quantity of the phases present, the surface and the grain boundaries of the material, the presence of crystal defects such as dislocations, vacancies, twin and stacking faults, as well as lattice distortions as a result of strain, etc.. A material’s microstructure thus largely determines its properties making it essential to investigate.¹

Lattice defects are classed according to their strain fields, i.e. how they affect the diffraction profile (shape and position), where r is the distance from said defect:²

1. Point defects (interstitials, vacancies and impurities) have short-range strain fields that decay as 1/r². Their diffraction effects differ from the fundamental Bragg reflections, often referred to as Huang scattering.²,³
2. Linear defects (edge and screw dislocations), also known as dislocations, have long-range strain fields that decay as 1/r. As a result, diffraction peaks appear broader as they cause a cluster effect around the fundamental Bragg peak.²
3. Planar defects (grain and twin boundaries) are space independent/homogenous and cause deviations from the fundamental Bragg reflections, realised as shifts in peak position and changes in lattice parameter.²
However, the complex nature of defects means they are not generally confined to solely one category; stacking faults, for instance, cause peak broadening and a shift in peak position as they are both planar and surrounded by partial dislocations. Despite the multifaceted nature of defects, dislocations are always present to some extent in a material, either as the predominant complex lattice defect or as the only type of lattice defect which is evident by line broadening in the pattern. A material that contains defects is defined as anisotropic, as the properties vary along different crystallographic orientations; if a material has the same properties in all directions, it is considered isotropic.

For heterogeneous catalysts, elucidating the microstructure of the catalytically active phases is paramount; in fully characterising these, properties such as surface defects and particle size and shape have been found to contribute towards the overall catalytic performance. For Cu/ZnO/Al₂O₃ catalysts, though almost exclusively reported for methanol synthesis catalysts, it is widely accepted that the Cu microstructure, specifically the defect density and apparent lattice strain, are directly correlated to catalytic performance.

To summarise, broad diffraction peaks are typically an indication of small crystallite size or the presence of lattice defects/anisotropy within the material. These two phenomena can be differentiated by considering the varying diffraction-order dependence of peak broadening, of which there are two main methods: the Williamson-Hall (WH) and the Warren-Averbach (WA) methods. The WH procedure takes into account the integral breadths and full width at half-maximum (FWHM) of the peaks whereas the WA method focuses on the Fourier coefficients of the reflections. However, complications arise if the strain or crystallite shape are anisotropic, as shown in this chapter, though only the WH method is considered.

4.3. Zener constant

An initial calculation which can be carried out to determine if a material has elastic anisotropy is the Zener constant, A₂ (Equation 4.1). The Zener constant, also known as the anisotropy factor, was first introduced in 1947 in a study of β-brass, in which it was determined that β-brass had a high elastic anisotropy of 18. This equation is specific to cubic crystal systems and defines the ratio of orientation-dependent shear moduli. FCC metals have three non-zero, independent elastic components that are each determined by their own individual equation which takes into account volume expansion, pure shearing, uniaxial tension, and three deformation states. If a material has an A₂ of 1, its relationship between strain and stress is not orientation-dependent and it would be considered elastically isotropic, e.g. when \( c_{44} = (c_{11} - c_{12})/2 \), whereas a material with an \( A_2 < 1 \) has moderate anisotropy and an \( A_2 > 1 \) has strong anisotropy. As can be seen from Table 4.1, Cu has an \( A_2 \) of 3.28 and is therefore considered strongly anisotropic.
$$A_z = \frac{2c_{44}}{c_{11} - c_{12}}$$

*Equation 4.1: Zener constant*\(^{10}\)

**Table 4.1: Elastic constants of copper\(^{16}\)**

<table>
<thead>
<tr>
<th>Name</th>
<th>(c_{11})</th>
<th>(c_{12})</th>
<th>(c_{44})</th>
<th>(A_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>1.683</td>
<td>1.221</td>
<td>0.757</td>
<td>3.28</td>
</tr>
</tbody>
</table>

### 4.4. Conventional Williamson-Hall Plot

Though it has already been established that Cu is elastically anisotropic, how that anisotropy affects the microstructure of the Cu/ZnO/Al\(_2\)O\(_3\) unpromoted and promoted catalysts can only truly be evaluated using the conventional Williamson-Hall (cWH) method.

G. K. Williamson and his student, W. H. Hall, were the first to report a method for the separation of size and strain contribution to overall peak broadening.\(^7,17\) The main assumption of the WH procedure is that the investigated material has uniform strain along all crystallographic directions, making it elastically isotropic.\(^{18}\) Within this model, crystallite size, \(D\), and lattice strain, \(\varepsilon\), are described by Lorentzian functions and are considered independent of one another; so the line broadening is a case of adding the two terms together, as shown in *Equation 4.2.*\(^{18}\) The averaging Scherrer factor employed is 0.9 as it is assumed the particles are spherical.\(^4\)

$$\beta \varepsilon \cos \theta_{hkl} = \frac{0.9}{D} \lambda + 4\varepsilon \sin \theta_{hkl}$$

*Equation 4.2: Linear Williamson-Hall equation*\(^{18,19}\)

This equation can be rearranged (*Equation 4.3*) to ensure the desired size and strain information can be extrapolated from the graph of \(2\sin \theta\) vs. \(\beta \cos \theta\) (in nm\(^{-1}\)). Once plotted, it is then possible to derive the crystallite size of the material from the \(\gamma\)-intercept, and the isotropic strain can be extrapolated from the slope of the graph.\(^{18}\) If the cWH plot shows that the FWHM of the reflections does not follow a monotonous trend as a function of \(2\sin \theta\) (in nm\(^{-1}\)), there is anisotropic strain broadening present.

$$\frac{\beta \varepsilon \cos \theta_{hkl}}{\lambda} = \frac{0.9}{D} \left( \frac{2 \sin \theta_{hkl}}{\lambda} \right)$$

*Equation 4.3: Simplified linear Williamson-Hall equation*\(^{18}\)
In this work, the metallic Cu component was analysed via a pattern decomposition method in which each reflection is defined individually. This allowed a crystallite size to be determined based on the broadening of each reflection, therefore, using Equation 4.4, the FWHM can be calculated.

\[ \beta = \frac{0.1 \text{ Rad} \lambda}{D \cos \theta_{hkl}} \]

*Equation 4.4: FWHM as defined by TOPAS*²⁰

Where \( \text{Rad} = 57.2958^\circ \)

4.5. Modified Williamson-Hall Plot

The presence of anisotropic strain broadening in a material suggests there are defects in its microstructure, which may contribute to its overall activity. As line defects are the most prevalent, the modified Williamson-Hall (mWH) method can be employed, which considers parameters such as the average dislocation contrast factor, \( \langle C_{hkl} \rangle \) (see Section 4.5.1).²¹ T. Ungár and A. Borbély suggested that this could be expressed as *Equation 4.5.*²²

\[ \Delta K = \frac{0.9}{D} + \Delta K^D \]

*Equation 4.5: Simplified modified Williamson-Hall equation*²²

Here, \( \Delta K^D \) represents the strain contribution to the overall profile broadening. Where the conventional WH plot treats the strain contribution as a linear/quadratic function of \( K = \frac{2\sin \theta}{\lambda} \), it is stated that for the mWH plot, the presence of dislocations are the cause of the strain and an alternative equation must be used (*Equation 4.6*).²²

\[ \Delta K^D = A(\rho^*)^\frac{1}{2} + A'(Q^*)^\frac{1}{2} \]

*Equation 4.6: Strain contribution to line broadening*²²

Where \( A \) and \( A' = \) parameters determined by the effective outer cut-off radius of dislocations

\( \rho^* = \) formal dislocation density

\( Q^* = \) formal correlation factor
Evidently, there are many variables which must be calculated prior to evaluating any experimental data using the mWH method. The unknown constants, $A$ and $A'$, have been set at 0.1 across all data analysis; this number has been chosen as a variation of *Equation 4.6* multiplies $\rho^*$ by $1/A$ as opposed to $A$, in which $A$ is stated as being equal to 10.\textsuperscript{23,24} In the simplest case, the formal dislocation density can be substituted by the average formal dislocation density, $\langle \rho^* \rangle$.\textsuperscript{25}

$$\rho^* = \rho \left( \frac{\pi g^2 b^2 \langle C_{bkl} \rangle}{2} \right)$$

*Equation 4.7: Formal dislocation density*\textsuperscript{22}

Where $\rho$ = dislocation density

- $g$ = reflection vector
- $b$ = Burgers vector of dislocation (see *Equation 4.13*)

G. K. Williamson and R. E. Smallman demonstrated that the dislocation density could be estimated from strain broadening.\textsuperscript{26} As shown in *Equation 4.8*, the interaction of the dislocations is described by the $F$ parameter; due to the main slip-direction being oriented along the $\langle 110 \rangle$ slip-direction, $F = 1$. The coefficient $k$ is determined by the cubic crystal system of the material of interest and, as Cu is FCC, $k$ is therefore equal to 16.1.\textsuperscript{26–28}

$$\rho = \frac{k \varepsilon^2}{F b^2}$$

*Equation 4.8: Dislocation density*\textsuperscript{26,27}

The strain associated with a given reflection can be calculated if the exact Bragg position is known. For the purpose of this chapter, strain was evaluated using *Equation 4.9*, in which the unstressed lattice spacing, $d_0$, is given in *Table 4.8*, and the experimental $d$-spacing, $d_{exp}$, is calculated via Bragg’s law.\textsuperscript{29}

$$\varepsilon = \frac{d_{exp} - d_0}{d_0}$$

*Equation 4.9: Strain determination per reflection*\textsuperscript{29}

The formal correlation factor, $Q^*$, corresponds to the two-particle correlations in the dislocation structure. Though it is defined in *Equation 4.10*, it can also be related to the fluctuation of $\rho^*$: $Q^* = \langle \rho^* \rangle - \langle \rho \rangle^2$.\textsuperscript{23,25}
\[ Q^* = \frac{Q(\pi g^2b^2\langle C_{hkl}\rangle)^2}{4} \]

*Equation 4.10: Formal correlation factor*\(^{22}\)

The correlation factor, \( Q \), is described as a constant that takes into account the contrast factor that arises as a result of a dislocation.\(^{23}\)

\[ Q = \frac{\pi g^2b^2\langle C_{hkl}\rangle}{2} \]

*Equation 4.11: Correlation factor*\(^{23}\)

By combining *Equation 4.6, 4.7, and 4.10*, the full equation for the modified Williamson-Hall model can be realised. Within this equation, the scaling factor for the FWHM (or breadths) of the reflection profiles is \( K^2\langle C_{hkl}\rangle \) as opposed to just \( K \).\(^{22}\) It should also be noted that there are many variations of the modified Williamson-Hall equation available in the literature.\(^{22,30-33}\)

*Equation 4.12* is cited as the equation to employ when the dislocations are a result of strain, and \( g \) is stated as being equivalent to \( K \) at the exact Bragg position.\(^{22}\)

\[ \Delta K = \frac{0.9}{D} + \left( \frac{\pi A^2 b^2}{2} \right)^{\frac{1}{2}} \rho^{\frac{1}{2}} \left( K\langle C_{hkl}\rangle^2 \right)^{\frac{1}{2}} + \left( \frac{\pi A' b^2}{2} \right)^{\frac{1}{2}} Q^2 \left( K^2\langle C_{hkl}\rangle \right) \]

*Equation 4.12: The modified Williamson-Hall equation*\(^{34}\)

4.5.1. Average contrast factors of dislocations, \( \langle C_{hkl}\rangle \)

When gauging dislocation parameters from broadened diffraction peaks, it is essential to evaluate the average dislocation contrast factor, \( \langle C_{hkl}\rangle \), as it accounts for the slip-system of the dislocations, and the material’s elastic properties and displacement fields.\(^{11}\) In this section, only the dislocation contrast factor for face-centred (FCC) cubic structures will be evaluated as the metallic Cu active component of the LT-WGS catalyst is the structure of interest.

An apt way of visualising the number of slip-systems in an FCC lattice is by embedding a tetrahedron within the cubic lattice. Face-centred cubic materials have 12 slip-systems, i.e. 4 independent, non-parallel slip-planes \( \times \) 3 independent slip-directions which are represented by the 4 faces of the tetrahedron and its 3 edges, respectively; an example of this is shown in *Figure 4.1*, where the \( \{111\} \) slip-plane is depicted along with the \([\overline{1}10], [0\overline{1}1] \) and \([10\overline{1}] \) slip-directions.
Therefore, the primary slip-system in FCC materials for dislocations is \{1\overline{1}1\}〈110〉, which is also related to the Burgers vector, \(\mathbf{b}\).\(^{11}\)

Figure 4.1: A cubic lattice with a tetrahedron embedded in it, illustrating the \{1\overline{1}1\}〈110〉 slip-system in FCC lattices; image taken from N. Armstrong and P. Lynch, Diffraction Analysis of the Microstructure of Materials, eds. E. J. Mittemeijer and P. Scardi, Springer, Berlin, 2004, ch. 10, pp. 249-286.\(^{11}\)

The Burgers vector describes a dislocation in terms of the lattice distortions direction and magnitude. For FCC materials, it can be conveniently calculated according to its unit cell parameter, \(a\), and the crystallographic slip-direction (Equation 4.13), affording a \(\mathbf{b}\) value of 2.56 Å.\(^{35}\) How a dislocation is oriented with respect to \(\mathbf{b}\) and the dislocation line, \(\mathbf{l}\), describes whether the nature of the dislocation is edge, screw, or a mixture of the two linear defects. For edge dislocations, \(\mathbf{b}\) is perpendicular to \(\mathbf{l}\), whereas for screw dislocations, \(\mathbf{b}\) and \(\mathbf{l}\) are parallel, and a mixture of the two has a \(\mathbf{b}\) that is neither perpendicular nor parallel to \(\mathbf{l}\).\(^{36}\)

\[
\mathbf{b}_{\text{FCC}} = \frac{a}{2} \langle 110 \rangle
\]

Equation 4.13: Burgers vector for FCC materials\(^{35}\)

The contrast factors of elastically isotropic materials with screw or edge dislocations are determined analytically. However, those of anisotropic materials must be determined numerically which, for easy understanding, can be separated into 2 parts: the geometric component, \(\mathbf{G} \equiv [G_{KL}]\), and the elastic component, \(\mathbf{E} \equiv [E_{KL}]\). These define the orientation of the diffraction vector, \(\mathbf{g}\), in the dislocation slip-system, and the distortion caused by the dislocation, respectively.\(^{11}\) Both \(\mathbf{G}\) and \(\mathbf{E}\) are 6 x 6 symmetrical matrices.\(^{37}\)
\[
C_{hkl} = \sum_{K,L=1}^{6} G_{KL} E_{KL}
\]

**Equation 4.14: Contrast factor for a single slip-system**  

The above equation describes a single slip-system that is defined by the unit vectors, \(e_1\), \(e_2\) and \(e_3\), and how they are orientated with regards to the normal of the slip-plane, the Burgers vector and the direction of the dislocation, \(l\). To expand, \(e_2\) is normal to the slip-plane, \(e_3\) is parallel to \(l\), and \(b\) is located in the plane formed by \(e_2\) and \(e_1\). This is depicted more clearly in Figure 4.2.  

![Figure 4.2: A representation of a slip coordinate system \((e_k; k = 1, 2, 3)\) and the orientation of the diffraction vector, \(g\): image taken from N. Armstrong and P. Lynch, Diffraction Analysis of the Microstructure of Materials, eds. E. J. Mittemeijer and P. Scardi, Springer, Berlin, 2004, ch. 10, pp. 249-286.](image)

For any dislocation type in an untextured polycrystalline material, the average contrast factor can be calculated according to **Equation 4.15** in which all the slip-systems are averaged.  

\[
\langle C_{hkl} \rangle = \frac{1}{N} \sum_{K,L=1}^{6} \sum_{i=1}^{N} G_{KL}^{i} E_{KL}
\]

\[
= \sum_{K,L=1}^{6} \langle G_{KL}^{i} \rangle E_{KL}
\]

**Equation 4.15: Average contrast factor for a crystal lattice consisting of a single slip-system**

Where \(G_{KL}^{i}\) = geometric component of the \(i\)th slip-system  
\(N = \) total number of slip-systems
This can also be expressed as Equation 4.16 for cubic lattices, where it is described as a linear function in relation to the Miller indices, \( hkl \).\(^{11}\)

\[
\langle C_{hkl} \rangle = A + B \left( \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2} \right)
\]

Equation 4.16: Linear equation for cubic lattice contrast factors

Where \( A \) and \( B \) = constants dependent on \( G \) and \( E \) (see Section 4.5.1.1)

For completeness, T. Ungár et al. developed an alternative equation for calculating the average dislocation contrast factor for cubic crystal systems. Equation 4.17 introduces a new term, \( q \), to assist in determining the dislocation character of the material.\(^{33}\) Assuming pure edge or screw dislocations dominate the Cu material, the \( q \) parameter is equal to 1.7 or 2.4, respectively.\(^{38}\) This is also shown in Section 4.5.1.1.1.

\[
\langle C_{hkl} \rangle = \langle C_{h00} \rangle \left[ 1 - q \left( \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2} \right) \right]
\]

Equation 4.17: T. Ungár’s average dislocation contrast factor for cubic crystals\(^ {33}\)

Where \( \langle C_{h00} \rangle = \) average contrast factor for the \( h00 \)-reflection

\[
q = \frac{B}{\langle C_{h00} \rangle}
\]

It is also important to note, that once the average contrast factors have been calculated for a material containing 100% edge dislocations and 100% screw dislocations, a theoretical average contrast factor can be calculated based on a mixture of the two dislocations. To do this, a weighted sum can be taken of the average edge and screw contrast factors, however, this can only be carried out if the material has one type of activated slip-system, as with FCC-Cu.\(^ {11,39}\)

\[
\langle C_{\text{mix}} \rangle = f \langle C_{\text{edge}} \rangle + (1 - f) \langle C_{\text{screw}} \rangle
\]

Equation 4.18: Average contrast factor for a mixture of edge and screw dislocations\(^ {39}\)
Where \( f = \) fraction of edge dislocations

\[ \langle C_{\text{edge}} \rangle \text{ and } \langle C_{\text{screw}} \rangle = \text{calculated average contrast factors for 100\% edge and 100\% screw dislocations} \]

The next step is to input real values to obtain the calculated contrast factors for the different types of dislocations.

**Table 4.2: Calculated average contrast factors for screw, edge and 50/50 screw and edge dislocations**

<table>
<thead>
<tr>
<th>( g )</th>
<th>( \langle C_{\text{screw}} \rangle )</th>
<th>( \langle C_{\text{edge}} \rangle )</th>
<th>( \langle C_{50/50} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}</td>
<td>0.0614</td>
<td>0.1373</td>
<td>0.0993</td>
</tr>
<tr>
<td>{200}</td>
<td>0.3017</td>
<td>0.3075</td>
<td>0.3040</td>
</tr>
<tr>
<td>{220}</td>
<td>0.1215</td>
<td>0.1798</td>
<td>0.1505</td>
</tr>
<tr>
<td>{311}</td>
<td>0.1885</td>
<td>0.2273</td>
<td>0.2076</td>
</tr>
<tr>
<td>{222}</td>
<td>0.0614</td>
<td>0.1373</td>
<td>0.0993</td>
</tr>
<tr>
<td>{400}</td>
<td>0.3017</td>
<td>0.3075</td>
<td>0.3040</td>
</tr>
<tr>
<td>{331}</td>
<td>0.1040</td>
<td>0.1674</td>
<td>0.1356</td>
</tr>
<tr>
<td>{420}</td>
<td>0.1864</td>
<td>0.2258</td>
<td>0.2057</td>
</tr>
<tr>
<td>{422}</td>
<td>0.1215</td>
<td>0.1798</td>
<td>0.1505</td>
</tr>
<tr>
<td>{333}</td>
<td>0.0614</td>
<td>0.1373</td>
<td>0.0993</td>
</tr>
<tr>
<td>{511}</td>
<td>0.2513</td>
<td>0.2718</td>
<td>0.2610</td>
</tr>
</tbody>
</table>

These were also corroborated using the ANIZC program developed by A. Borbély et al. (accessible via [http://metal.elte.hu/anizc/](http://metal.elte.hu/anizc/)). Here, the type of crystal system is selected and the elastic compliances, diffraction vector and the expected type of dislocation present in the reduced Cu catalyst are added as the input parameters.

### 4.5.1.1. Calculating A and B for the average dislocation contrast factor

When solving *Equation 4.16* for the average dislocation factor, the constants \( A \) and \( B \) can be determined by employing the calculations outlined by J. Martinez-Garcia *et al.*
\[ A = \begin{cases} 
0, & \phi = 0 \\
(1 - \eta_1) \left( \frac{1}{3} \sqrt{2 + \eta_0} \right), & \phi = \pi/2 
\end{cases} \]

\[ B = \begin{cases} 
\frac{2}{3}, & \phi = 0 \\
(\eta_2 - 2) \left( \frac{1}{3} \sqrt{2 + \eta_0} \right), & \phi = \pi/2 
\end{cases} \]

Equation 4.19: Analytic functions of A and B with respect to the Zener constant and Poisson ratio; where \( \phi = 0 \) for screw dislocations and \( \phi = \pi/2 \) for edge dislocations

In which

\[ v = \frac{c_{12}}{c_{11} + c_{12}} \]

Equation 4.20: Poisson’s ratio

\[ \eta_0 = \frac{2(1 - vA_z)}{A_z(1 - v)} \]

\[ \eta_1 = \frac{(1 - 2v) [1 + A_zv(1 - 2v)]}{(1 - v)^2 [1 + A_zv(1 - 2v)]} \]

\[ \eta_2 = \frac{A_z^2 \left( 4v^2 - 4v^2 + 3v - 1 \right) - 2vA_z + 2(1 - v)}{A_z(1 - v)^2 [1 + A_zv(1 - 2v)]} \]

Equation 4.21: Accompanying equations for calculating the average dislocation contrast factor constants A and B

If a material’s elastic constants afford an \( A_z \) of 1 and an \( \eta_0 \) of 2, it is considered isotropic.

4.5.1.1.1. Calculating A, B and q for T. Ungár’s average dislocation contrast factor for cubic crystals

By rearranging Equation 4.17, the average \( q \) parameter can be calculated for each reflection, and thus be averaged in order to gain a value of \( q \) which is representative of the type of dislocation present in the studied material. By inputting the calculated \( \langle C_{hkl} \rangle \) and \( \langle C_{h00} \rangle \) from Table 4.2, the following \( q \) values were calculated, along with the corresponding B constants.
Table 4.3: Parameters q, A and B as calculated from T. Ungár's average dislocation contrast factor for cubic crystals

<table>
<thead>
<tr>
<th>Dislocation Type</th>
<th>q</th>
<th>A ((C_{h00})</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw</td>
<td>2.39</td>
<td>0.3017</td>
<td>0.7208</td>
</tr>
<tr>
<td>Edge</td>
<td>1.66</td>
<td>0.3075</td>
<td>0.5107</td>
</tr>
<tr>
<td>50/50</td>
<td>2.03</td>
<td>0.3040</td>
<td>0.6141</td>
</tr>
</tbody>
</table>

These values can be found experimentally by transforming the modified Williamson-Hall equation into its quadratic form and combining it with T. Ungár's equation for the average dislocation contrast factor for cubic crystals.\(^{33}\)

\[
\frac{(\Delta K)^2 - \alpha}{K^2} \approx \beta(C_{h00})(1 - qH^2)
\]

*Equation 4.22: The experimental determination of the average contrast factors*\(^{33}\)

Where \(\Delta K = \text{FWHM (Equation 4.12)}\)

\[
\begin{align*}
\alpha &= \left(\frac{0.9}{D}\right)^2 \\
\beta &= \frac{\pi A^2 b^2 \rho}{2} \\
H^2 &= \left(\frac{h^2 k^2 + h^2 l^2 + k^2 l^2}{(h^2 + k^2 + l^2)^2}\right)
\end{align*}
\]

The ensuing plot depicts \([(\Delta K)^2 - \alpha)/K \ vs. \ H^2\] in which T. Ungár et al. have determined that the q parameter can be experimentally calculated. This is achieved by extrapolating the line of best fit for the interrogated reflections so that it intersects the x-axis; it is at this point that \(x\) is equal to \(1/q\).\(^{33}\)

4.6. Partial Dislocations

Linear defects, such as dislocations with edge or screw character, within FCC metals are considered perfect dislocations with Burgers vectors \(\frac{a}{2}(110)\). Glide of a dislocation along this lattice translation vector results in a perfect crystal, maintaining the ABCABCA stacking sequence of the (110) planes. However, when a dislocation moves along a Burgers vector that is not a lattice vector, the stacking sequence is disrupted (ABCACABCA), leaving an imperfect
crystal. This creates two partial dislocations and, consequently, a stacking fault (planar defect) is formed.\textsuperscript{41}

For ease of explanation, Figure 4.3 illustrates the \{111\}(110) slip-system for face-centred cubic metals. The three-fold stacking sequence (ABCABCA) of the close-packed \{111\} plane is described by layers of spheres, represented graphically as A, with an identical layer in place of B, and a third in place of C. A perfect dislocation moves atoms within a layer along the $b_1$ vector of type $\frac{1}{2}(110)$, displacing them to identical sites and thus maintaining the perfect crystal’s stacking sequence. However, if a layer, e.g. the $B$ layer of atoms, was first displaced along the $b_2$ vector, and then the $b_3$ vector, both of type $\frac{1}{6}(112)$, the glide occurs as two partial dislocations known as Shockley partial dislocations (ABCACAB).\textsuperscript{41} The resultant stacking fault (SF) formed in the slip-plane between the two partials is considered an intrinsic stacking fault and occurs according to Equation 4.23.\textsuperscript{41–43}

\[
\begin{align*}
(b_1 &\rightarrow b_2 + b_3) \\
\frac{1}{2}(110) &\rightarrow \frac{1}{6}(211) + \frac{1}{6}(12\bar{1}) \\
\frac{1}{2}(\bar{1}01) &\rightarrow \frac{1}{6}(\bar{2}11) + \frac{1}{6}(\bar{1}\bar{1}2) \\
\frac{1}{2}(0\bar{1}1) &\rightarrow \frac{1}{6}(\bar{1}2\bar{1}) + \frac{1}{6}(\bar{1}\bar{1}2)
\end{align*}
\]

Equation 4.23: The dissociation of a perfect dislocation into two Shockley partial dislocations (a) generalised for all FCC metals and (b) within the \{111\} plane.\textsuperscript{41}

The Shockley partial dislocations are associated with slip, and are therefore glissile, but there is another type of sessile partial dislocation which involves the removal/insertion of layers, known as Frank partial dislocations. Again, when considering the \{111\} plane, removal of a plane
disrupts the stacking sequence according to ABCACAB producing an intrinsic SF, whereas insertion of a layer forms an extrinsic fault with the sequence ABCACBC (Figure 4.4). The intrinsic stacking fault generated from a Frank partial dislocation (also referred to as a Frank dislocation loop) differs from that of a Shockley; not geometrically, but in terms of its bounding partial as it does not lie in the plane of the fault. The Burgers vector, $\mathbf{b} = \frac{1}{3}(111)$, is normal to the $\{111\}$ plane and describes an area that cannot move with the dislocation and encloses a SF. These dislocations are a source of strain within the crystal structure, and can be distinguished via elastic diffuse scattering which is sensitive to vacancies (intrinsic SFs) and interstitials (extrinsic SFs).

Another form of stacking fault which may arise is a coherent twin boundary. Here, neighbouring $\{111\}$ planes are shifted sequentially by a vector of type $\frac{1}{6}(11\overline{2})$ forming a boundary layer between the undisplaced and displaced volumes. The resulting stacking sequence is ABCACBA, in which the twin boundary acts as a mirror plane. Twin faults usually occur during growth, therefore they are often considered growth faults.

4.7. Stacking Faults

The elastic strain energy of a material is reduced when a dislocation dissociates into two partial dislocations, enclosing a fault as they separate in the $\{111\}$ planes known as a planar defect (stacking fault). The width of the stacking fault is determined by (1) the repulsion of the partial dislocations due to their stress fields, which decreases as they move apart, and (2) the attractive force applied by the constant surface tension of the SF; the equilibrium at which these repulsive and attractive forces are balanced is partly determined by the material’s stacking fault energy, $\gamma_{SFE}$. Stacking fault energies are the calculated energy difference between an imperfect crystal (fault-affected) and a perfect crystal, normalised by the area of the SF. Whether a material
deforms via cross-slip or twinning is determined by the $\gamma_{SFE}$; the lower the stacking fault energy, the wider the equilibrium partial dislocation separation, making the preferred mode for deformation twinning. Copper possesses a moderate $\gamma_{SFE}$ (Table 4.4), therefore it deforms via slip. However, it is possible to tailor a material’s $\gamma_{SFE}$ through alloying, as can be seen for the 70:30 brass by incorporating 30 wt.% Zn, the $\gamma_{SFE}$ reduces from 78 to 20 mJ m$^{-2}$, decreasing the critical resolved shear stress and promoting deformation via twinning. The strength and ductility of the material is also optimised the lower the $\gamma_{SFE}$.

Table 4.4: Stacking fault energy of Cu, Zn, Al and 70:30 brass (Cu:Zn)

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\gamma_{SFE} / \text{mJ m}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>78</td>
</tr>
<tr>
<td>Zinc</td>
<td>166</td>
</tr>
<tr>
<td>Aluminium</td>
<td>140</td>
</tr>
<tr>
<td>70:30 brass (Cu:Zn)</td>
<td>20</td>
</tr>
</tbody>
</table>

Generally, the literature does not consider the formation of extrinsic stacking faults within Cu as they give rise to a double discontinuity in the stacking of the planes, therefore their energy is higher. The ABC stacking sequence of a perfect FCC close-packed plane is represented by the triangle $\triangle$; if the stacking sequence of a plane is in the reverse sequence, BAC, this is denoted by an inverted triangle $\triangledown$. Using this notation, atoms in an FCC arrangement follow $\triangle\triangle\triangle\triangle$, as compared to $\triangledown\triangledown\triangledown\triangledown$ for HCP arrangements. An intrinsic stacking fault is thus represented as $\triangle\triangledown\triangle\triangle\triangle\triangle$, and an extrinsic stacking fault as $\triangle\triangledown\triangledown\triangle\triangle\triangle$. This clearly illustrates that two intrinsic stacking faults located on adjacent planes are equivalent to one extrinsic fault, hence intrinsic stacking faults are most likely to form due to their lower $\gamma_{SFE}$.

Unfortunately, when evaluating the propensity of a material to form stacking faults, there is great difficulty in determining $\gamma_{SFE}$ accurately. To overcome this, M. Behrens et al. employed the use of Equation 4.24 to calculate stacking fault probability, $\alpha$. Within an imperfect crystal structure, microstructural defects can affect the resulting diffraction pattern (a generalised overview is given in Table 4.5). Depending on the type of stacking fault, i.e. intrinsic, extrinsic or twin, the peak profiles for FCC crystals vary; peak shifts to smaller and larger scattering angles, $2\theta$, are denoted by $\leftarrow$ and $\rightarrow$, and asymmetry is highlighted depending on the direction the asymmetric tail extends to, also to smaller, $\Delta$, and larger, $\Delta$, scattering angles. The (111)- and (200)-reflections are considered the most reliable peaks to evaluate to determine these properties. It is also interesting to note that stacking fault probability is inversely proportional to the stacking fault energy: the lower the $\gamma_{SFE}$, the greater the $\alpha$. 

133
\[
\alpha = 8.3 \left[ \frac{\sin \theta_{200}}{\sin \theta_{111}} \right]_{\text{ideal}} - \left( \frac{\sin \theta_{200}}{\sin \theta_{111}} \right)_{\text{exp}} \]

*Equation 4.24: Evaluating stacking fault probability*\(^6\)

Table 4.5: Assigning types of stacking faults present in FCC crystals based on their peak profile characteristics in XRD powder patterns\(^{45,55}\)

<table>
<thead>
<tr>
<th>hkl</th>
<th>Intrinsic SF</th>
<th>Extrinsic SF</th>
<th>Twin SF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shift direction</td>
<td>Peak profile asymmetry</td>
<td>Shift direction</td>
</tr>
<tr>
<td>111</td>
<td>→</td>
<td>△</td>
<td>←</td>
</tr>
<tr>
<td>200</td>
<td>←</td>
<td>△</td>
<td>→</td>
</tr>
<tr>
<td>220</td>
<td>→</td>
<td>△</td>
<td>←</td>
</tr>
<tr>
<td>311</td>
<td>→</td>
<td>△</td>
<td>←</td>
</tr>
<tr>
<td>222</td>
<td>←</td>
<td>△</td>
<td>→</td>
</tr>
<tr>
<td>400</td>
<td>→</td>
<td>△</td>
<td>←</td>
</tr>
</tbody>
</table>

4.8. Experimental Details

4.8.1. Catalyst Preparation

Two catalysts are investigated in this chapter: a standard LT-WGS catalyst (sCZA) and a high Cu loaded catalyst (hCZA). To prepare the catalysts, a mixed solution of Cu, Zn and Al nitrates (1 M) were used at molar ratios of 0.6:0.3:0.1 and 0.8:0.1:0.1, respectively. A Metrohm Titrando was used to dispense the mixed metal nitrate solution (160 mL, 5 mL min\(^{-1}\)) and precipitating agent (Na\(_2\)CO\(_3\), 1.2 M) into deionised H\(_2\)O (800 mL, 18.2 M\(\Omega\) cm\(^{-1}\)). The mixture was stirred using an overhead PTFE screw propeller stirrer shaft at 65 \(^{\circ}\)C. The pH was maintained at 7 by adjusting the amount of Na\(_2\)CO\(_3\) added. The pH probe was calibrated at pH 4, 7 and 10 before each coprecipitation. The mother liquor was aged for 1.5 h at 65 \(^{\circ}\)C and pH 7 (*via* metal nitrate addition). The precipitate was then filtered, washed several times with deionised H\(_2\)O (3 × 500 mL, 18.2 M\(\Omega\) cm\(^{-1}\)) to remove residual NaNO\(_3\), and dried in air at 80 \(^{\circ}\)C for 15 h.

The promoted catalysts were prepared *via* incipient wetness impregnation. The hydroxycarbonate sCZA and hCZA precursor were impregnated with an aqueous solution of ca. 1 wt.\% Cs\(_2\)CO\(_3\), the amount of which was determined by the respective precursors’ pore volume. Once impregnated, the sCZA-Cs and hCZA-Cs catalysts were dried in air at 80 \(^{\circ}\)C for 15 h.

Finally, all catalyst precursors were calcined in air at 300 \(^{\circ}\)C (2 \(^{\circ}\)C min\(^{-1}\)) for 5 h. The calcined sCZA, sCZA-Cs, hCZA and hCZA-Cs catalysts were compressed into a 13 mm disc
using a hydraulic press (Specac Ltd., UK) at a pressure of 5 tons for 1 minute. The pellets were then crushed and sieved (125-250 μm).

4.8.2. Ex situ Characterisation

Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS 10 FT-IR spectrometer at a spectral resolution of 2 cm⁻¹, accumulating 64 scans. Prior to loading a sample, 32 background scans were collected. Subsequent spectra were annotated using ACD/Spectrus.

Chemical compositions of the catalyst samples were determined by X-ray fluorescence (XRF). This was measured using a PANalytical Epsilon 3-XL spectrometer at ISIS Materials Characterisation laboratory, Harwell, UK, and analysed using Epsilon 3 software.

Using a Mettler-Toledo TGA/DSC 1 Star TGA at Yara International, Porsgrunn, NO, the thermogravimetric analysis (TGA) was conducted in a flow of air at a heating rate of 20 °C min⁻¹ from room temperature to 900 °C, with an isothermal time of 90 min. The sample holder was made of alumina (900 μL), and brass tweezers were used when handling it. Evolved gas analysis (EGA) was carried out with a Pfeifer Thermostar GSD 320 T2 mass spectrometer (MS). STARe Thermal Analysis Software was used to view the results.

Temperature-programmed reduction (TPR) experiments were carried out in a ChemBET Pulsar TPR/TPD instrument, which is a Quantachrome automated chemisorption analyser. As stated in Section 2.3.2, reduction profiles are known to be heavily influenced by the experimental conditions; therefore, the operating variables (S₀, F, C₀ and β) were chosen to ensure 0.9 < K < 2.3 min and P < 20 K were satisfied. Each sample was heated to 400 °C (10 °C min⁻¹) in 30 mL min⁻¹ of 10 % H₂/Ar. The amount of sample reduced was dependent on the [Cu] in the investigated catalyst.

X-ray diffraction (XRD) measurements were collected with Cu-Kα₁ (λ = 1.5406 Å) radiation using an accelerating voltage/current of 40 kV/40 mA respectively on a D8 Advance Bruker powder diffractometer equipped with a Vantec-1D-Linear detector at Diamond Light Source (DLS), Harwell, UK. The diffractograms were recorded using DIFFRACplus XRD Commander software in a locked coupled continuous mode between 5-60 °2θ with a step size of 0.017 °. 1.0 mm divergence and 0.6 mm detector slits were used for all scans. Phase identification of the patterns was carried out using PANalytical X’Pert HighScore Plus.

4.8.3. AP-XPS measurements at B07, DLS

In situ ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) experiments were performed by Dr. Kanak Roy (DLS, Harwell, UK) on the Versatile Soft X-ray (VerSoX) beamline B07 at Diamond Light Source. The VerSoX endstation is equipped with a differentially pumped PHOIBOS 150 NAP hemispherical electron energy analyzer, which allows in situ measurements of solid samples to be collected, while dosing with a gas/gas mixture in mbar range. In the geometry adopted during the experiments, photoelectrons were detected at an angle of 54.7 ° with
respect to the direction of the surface normal, and linearly polarized light was used throughout the experiments. The spectra were energy calibrated using C 1s at 285.0 eV and were normalised at the maximum intensity.

The author provided the sCZA and sCZA-Cs catalysts in powder form, which were then dispersed as a thin film on a gold coated silicon wafer with an area of ca. 0.5 cm². The wafer was fixed to the sample holder with stainless steel clips. The catalysts were heated (10 °C min⁻¹) in resistive mode, and the temperature was monitored with a Type-K (chromel-alumel) thermocouple integrated into the sample holder. Within the Tea Cup reaction chamber (0.7 L), the catalysts were reduced in H₂ (50 mbar) at 220 °C for 1 h, and then the pressure was evacuated (1 mbar) and spectra were measured with 1700 eV excitation. Following reduction, a 1:3 mixture of CO₂:H₂ (4 mbar) was then dosed at 250 °C for 2 h, and spectra were recorded. Ultrapure gases were utilized, which were introduced through precision leak valves.

4.8.4. XRD and XRD-CT measurements at ID15A, ESRF

The catalytic reactor set-up consisted of the CuO/ZnO/Al₂O₃(-Cs₂CO₃) catalyst (0.3 g, bed length of 1.9 cm) supported on quartz wool in a 4.5 mm quartz capillary. This was then mounted into a gas delivery stub, which was attached to a standard goniometer on a rotation and translation stage. The furnace was lowered to cover the sample tube and heat the catalytic reactor from all directions, from ambient up to 230 °C at atmospheric pressure. As can be seen from Figure 4.5, the gas inlet was placed at the bottom of the bed and the top of the bed was open to the atmosphere. Prior to the beamtime experiments, temperature calibrations were carried out in spare catalyst with a thermocouple embedded in the bed to ensure there was no obvious gradient along the bed; however, the gases were not heated as they were delivered. The hope was that if a gradient developed along the bed it would be seen.

To investigate the impact of the activation procedure on the resultant catalyst microstructure, each sample was first heated to 160 °C (5 °C min⁻¹) in Ar, reduced in flowing H₂ (1, 2.5 and 5 %) in Ar up to 230 °C (1 °C min⁻¹) and held at this temperature until fully reduced (or for as long as possible). The GHSV was 1985 h⁻¹. Two gas bottles were used containing a 5 % H₂/Ar mix and 100 % Ar. The gas flow rate (10 mL min⁻¹) was controlled by two MFCs (Alicat MC-10SCCM-D) that were manually operated. During the activation procedure, the outflow gases were monitored by mass spectrometry using a Hiden Analytical QGA quadrupole mass spectrometer (HAL 201 RC).
In situ synchrotron X-ray diffraction and XRD-computed tomography (CT) measurements were collected at the ESRF on beamline station ID15A using a 70 keV monochromatic X-ray beam with a $30 \times 20 \mu m^2$ ($H \times V$) spot size ($\lambda = 0.17463 \text{ Å}$). The detector used to collect the 2D diffraction patterns was a Dectris Pilatus3 X CdTe 2M ($1475 \times 1679$ pixels, pixel size of $172 \times 172 \mu m^2$) hybrid photon counting area detector. The beam was calibrated using a CeO$_2$ NIST standard.

Point measurements were taken along the catalytic reactor bed at either 3 or 11 positions during the reduction ramp (160-230 °C) and during reduction (230 °C hold). The top, middle and bottoms heights are considered comparable across all measurements; to the best knowledge of the author, the thickness of the quartz wool was the same, the height of the sample bed was constant, therefore the temperature in the reactor cell, as best as the author was able to control it, was the same. This allowed any gradient present in the catalytic bed to be evaluated at either variable position and constant time, or at variable time and constant position (as shown in Figure 4.6); the latter is how the data will be presented in this chapter. The quartz capillary was also recorded in the collected diffractogram and was subtracted prior to analysis (see Appendix 7.4.1).
Figure 4.6: Point measurements set-up; diffraction patterns depict the reduction ramp for the sCZA catalyst at position (g) in a 5 % H₂/Ar environment (0-70 min = 160-230 °C)

XRD-CT measurements of the catalyst bed were collected at 3 positions, the top, middle and bottom (see Figure 4.7), at room temperature, after the reduction ramp (230 °C, 70 min after reducing gas was introduced) and at the end of the reduction run (230 °C). During the measurements, the reduction was stalled by switching the gas flow to pure Ar (10 mL min⁻¹).

Figure 4.7: XRD-CT set-up; the images depict a plane of the catalyst bed at the three investigated positions: top, middle and bottom (the legend shows distribution of Cu⁰ based on peak intensity).
The parameters for the tomographic measurements were a step size of 1.2° to collect 180 translation steps in an angular range of 0-180° (150 line scans/projections), therefore a total of 27000 2D powder diffraction patterns were collected for each XRD-CT scan. The physical area covered by the beam was 5.4 x 5.4 mm². These were radially integrated to give 1D powder diffraction patterns, after applying a filter that removed outliers and single-crystal diffraction artefacts using nDTomo and pyFAI software packages. A filter back projection algorithm was then employed in MATLAB to reconstruct each sinogram. The sinograms consisted of a 3D matrix (200 x 200 x 1990 matrix) in which the 1st dimension illustrates the translation steps, the 2nd the rotation steps and the 3rd dimension shows the channels in the 1D patterns, giving a total of 1990 sinograms.

The instrument parameter file was built from information extracted from Rietveld analysis of the CeO₂ NIST standard reference material that was collected solely for calibration purposes (see Figure 4.8) at ID15A, ESRF. The background was fitted using a Chebyshev polynomial and a modified Thompson-Cox-Hastings pseudo-Voigt (PV-TCHZ) peak type was used to fit the diffraction peaks. For the Rietveld refinement, a CeO₂ CIF file was obtained from the ICSD database (ICSD #: 72155).

Figure 4.8: Rietveld refinement of the CeO₂ NIST diffraction pattern collected during the beamtime on ID15A, ESRF.

Phase composition was determined via Rietveld refinement using the TOPAS5 software package and crystallographic information files (CIFs) taken from the ICSD database. The structures whose CIF files were included in the input file were for cuprite (ICSD #: 172174), tenorite (ICSD #: 16025), zincite (ICSD #: 157724), alumina (ICSD #: 99836), and zincian malachite (ICSD #: 260813)
Once initial Rietveld analysis was carried out on the reduced Cu/ZnO/Al₂O₃(-Cs₂O) catalyst, it was clear that the program was not accurately fitting all the peak profiles for the active component. As can be seen from Figure 4.9 (a), the intensity of the (111)-peak is underestimated, whereas the (200)-, (400)-, and other higher angle peaks are overestimated, and their shape is asymmetrical. This is because the Rietveld refinement program assumes the material will be isotropic by applying isotropic functions to the peak profiles. Deviations in the fit were not resolved by refining temperature factors, it did not appear to be preferred orientation, and contributions from the presence of Cu/Zn alloys was ruled out. However, it was concluded there must be dislocations present in the prepared catalysts as it is known that the 200-reflection is sensitive to line broadening resultant from dislocations.

In order to elucidate the microstructure of the active Cu⁰ component, a pattern decomposition method was employed. This allowed for the Cu⁰ peak profiles to be evaluated individually, affording information about the 2θ-position, width and shape of each peak. Despite structural information (lattice parameters) calculated in this way incurring a larger error, anisotropic effects can be determined from the peak profile parameters allowing full microstructural analysis.

![Figure 4.9: Rietveld refinement of a fully reduced diffraction pattern for the sCZA catalyst using (a) a copper CIF file and (b) a pattern decomposition method for the active Cu component collected on the ID15A beamline at the ESRF](image)

4.8.4.1. Calculating the intensity of diffraction using the structure factor

Copper is the active component present in LT-WGS catalysts, making any deviations from the ideal crystal structure a possible cause for early onset deactivation. Determination of the theoretical diffraction pattern for metallic Cu can be calculated when the relationship between the atom positions in the (hkl) planes and the resulting intensity of the beam diffracting from these
planes is investigated. As previously mentioned in Section 2.1.2, the ability of an atom to scatter X-rays is dependent on the number of core electrons present. The atomic scattering factor, \( f_n \), is described in the classical theory as a ratio between the amplitudes of unmodified scattered radiation by an atom and a single electron under the same conditions; it is expressed in electron units. Radiation is also scattered by the Compton effect; however, it is incoherent and therefore displayed as a diffuse background and can be ignored.

Only the Cu atomic structure is being considered, therefore it is the scattering ability of this atom that is evaluated for the resulting intensity of diffraction. Initially the \( d \)-spacing and \( \sin \theta \lambda^{-1} \) were calculated for the Cu\(^0\) reflections of interest (N.B. for the following calculations, only the workings for the Cu\(^0\)(111)-reflection have been included). At room temperature, Cu\(^0\) has a lattice parameter, \( a \), of 3.61505 Å (ICSD #: 43493).

\[
d_{111} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{3.61505 \text{ Å}}{\sqrt{1^2 + 1^2 + 1^2}} = 2.09 \text{ Å}
\]

\[
\sin \theta \lambda^{-1} = \frac{1}{2d} = \frac{1}{2 \times (2.09 \text{ Å})} = 0.24 \text{ Å}^{-1}
\]

Equation 4.25: Calculation for the ideal \( d \)-spacing and scattering vector length of the Cu(111)-reflection

As can be seen from Figure 4.10, when \( \sin \theta \lambda^{-1} \) is equal to 0, the mean atomic scattering factor of a copper atom, \( f_{\text{Cu}} \), is equivalent to the total number of atoms present (\( Z = 29 \)). The trend is also clear that as \( \sin \theta \lambda^{-1} \) increases, the scattering factor decreases.

![Figure 4.10: Atomic scattering factors of a copper atom as a function of \( \sin \theta \lambda^{-1} \)](image-url)
Table 4.6: The mean Cu$^0$ atomic scattering factors in electrons, as described in the International Tables for Crystallography.$^{68}$

<table>
<thead>
<tr>
<th>$\sin \theta \lambda^{-1}$</th>
<th>0.00</th>
<th>0.05</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{\text{Cu}}$</td>
<td>29.000</td>
<td>28.448</td>
<td>27.084</td>
<td>25.370</td>
<td>23.540</td>
<td>21.687</td>
</tr>
</tbody>
</table>

Free-atom scattering factors for the neutral atom, Cu$^0$, are based on relativistic Hartree-Fock atomic wavefunction calculations, examples of which are shown in Table 4.6.$^{69,70}$ However, to obtain an $f_{\text{Cu}}$ value specifically related to the (111)-reflection of interest, the atomic form factor can be approximated as a function of the length of the scattering vector in the range $0 < \sin \theta \lambda^{-1} < 2.0$ Å$^{-1}$.\(^\text{71}\)

\[
\begin{align*}
\frac{f(\sin \theta \lambda)}{\lambda} &= c + \sum_{i=1}^{4} a_i e^{-b_i (\sin \theta \lambda)^2} \\
\end{align*}
\]

*Equation 4.26: The atomic scattering factor*$^{63,71}$

Table 4.7: Analytical approximation of the Cromer-Mann coefficients $a$, $b$, and $c$ for Cu$^0$.\(^\text{71}\)

<table>
<thead>
<tr>
<th>Element</th>
<th>$a_1$</th>
<th>$b_1$</th>
<th>$a_2$</th>
<th>$b_2$</th>
<th>$a_3$</th>
<th>$b_3$</th>
<th>$a_4$</th>
<th>$b_4$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^0$</td>
<td>13.3380</td>
<td>3.5828</td>
<td>7.1676</td>
<td>0.2470</td>
<td>5.6158</td>
<td>11.3966</td>
<td>1.6735</td>
<td>64.8126</td>
<td>1.1910</td>
</tr>
</tbody>
</table>

Therefore, the calculated atomic scattering factor for Cu$^0$(111) is:

\[
\begin{align*}
\frac{f(\sin \theta \lambda)}{\lambda} &= (13.3380 \ e^{-3.5828(0.24)^2}) + (7.1676 \ e^{-0.2470(0.24)^2}) + (5.6158 \ e^{-11.3966(0.24)^2}) \\
&\quad + (1.6735 \ e^{-64.8126(0.24)^2}) + 1.1910 \\
&= 22.077
\end{align*}
\]

*Equation 4.27: Determining the Cu$^0$(111) atomic scattering factor*

So the value calculated for the Cu$^0$(111)-reflection atomic scattering factor is 22.077 which, when compared with those in Table 4.6, is a reasonable assumption. All calculations for the atomic scattering factor are based on the following two assumptions: (1) the radial distribution of the electron density in the atom of interest has spherical symmetry, and (2) the absorption edge wavelengths for the atom are smaller than the X-ray wavelength used to interrogate it. If the latter condition is not satisfied, a dispersion correction must be performed.$^{66}$
\[ f = f_0 + \Delta f' + i\Delta f'' \]

**Equation 4.28: The dispersion corrected atomic scattering factor**

Where 
- \( f \) = corrected scattering factor
- \( f_0 \) = calculated atomic scattering factor
- \( \Delta f' \) and \( \Delta f'' \) = real and imaginary contributions of the dispersion correction

The amplitude for the Cu atom in the (111) plane has been calculated; however, there are more than one atoms present in the unit cell which must be accounted for. Radiation scattered by these atoms show a phase difference between the waves which is measured by a ‘phase angle’, \( \phi \); if the waves are in-step, \( \phi \) is either equal to 0 or an even multiple of \( 2\pi \), whereas waves which are out-of-step have a phase angle of \( \pi \) or an odd multiple of \( \pi \). As previously stated, the crystal structure of Cu is FCC, making its fractional coordinates \((x, y, z)\) \((0, 0, 0)\), \((\frac{1}{2}, \frac{1}{2}, 0)\), \((\frac{1}{2}, 0, \frac{1}{2})\), and \((0, \frac{1}{2}, \frac{1}{2})\). With this, the structure amplitude, \( F_{hkl} \), for the desired Bragg reflection can then be evaluated in radians as a complex amplitude. A diffraction peak is only visible if \( F_{hkl} > 0 \).

\[
F_{hkl} = \sum_{n} f_n \cos\{2\pi (hx + ky + lz)\} + i \sum_{n} f_n \sin\{2\pi (hx + ky + lz)\}
\]

**Equation 4.29: Equation to determine the structure factor amplitude**

\[
F_{111} = (22.077 \cos\{2\pi ((1 \times 0) + (1 \times 0) + (1 \times 0))\} \\
+ 22.077 \cos\{2\pi ((1 \times \frac{1}{2}) + (1 \times \frac{1}{2}) + (1 \times 0))\} \\
+ 22.077 \cos\{2\pi ((1 \times \frac{1}{2}) + (1 \times 0) + (1 \times \frac{1}{2}))\} \\
+ 22.077 \cos\{2\pi ((1 \times 0) + (1 \times \frac{1}{2}) + (1 \times \frac{1}{2}))\}) \\
+ i(22.077 \sin\{2\pi((1 \times 0) + (1 \times 0) + (1 \times 0))\} \\
+ 22.077 \sin\{2\pi((1 \times \frac{1}{2}) + (1 \times \frac{1}{2}) + (1 \times 0))\} \\
+ 22.077 \sin\{2\pi((1 \times \frac{1}{2}) + (1 \times 0) + (1 \times \frac{1}{2}))\}) \\
+ 22.077 \sin\{2\pi((1 \times 0) + (1 \times \frac{1}{2}) + (1 \times \frac{1}{2}))\}) \\
= 88.309
\]

**Equation 4.30: Calculating the structure factor for Cu(111)**
The intensity, \( I_{hkl} \), of the resultant diffraction waves is proportional to \( |F_{hkl}|^2 \) \((N.B. \ i^2 = -1)\).^53

\[
\therefore |F_{111}|^2 = (88.309)^2 \\
= 7798.47
\]

**Equation 4.31: Intensity calculation reflected from the Cu\(^0\)(111) atoms**

This is also in agreement with the ICSD Cu\(^0\) reference cif file (ICSD #: 43493). The above calculations have been carried out for all reflections of interest, and are given in Table 4.8.\(^67\)

**Table 4.8: Summary for all Cu reflections of interest**

<table>
<thead>
<tr>
<th>( h )</th>
<th>( k )</th>
<th>( l )</th>
<th>( d)-spacing / Å</th>
<th>( \sin \theta \lambda ) / Å(^{-1})</th>
<th>( f_{\text{Cu}} )</th>
<th>( F_{hkl}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.09</td>
<td>0.24</td>
<td>22.077</td>
<td>7798.47</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1.81</td>
<td>0.28</td>
<td>20.724</td>
<td>6871.62</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>1.28</td>
<td>0.39</td>
<td>16.783</td>
<td>4506.61</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1.09</td>
<td>0.46</td>
<td>14.782</td>
<td>3495.99</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1.04</td>
<td>0.48</td>
<td>14.234</td>
<td>3241.68</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0.90</td>
<td>0.55</td>
<td>12.463</td>
<td>2485.29</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
<td>0.83</td>
<td>0.60</td>
<td>11.459</td>
<td>2101.05</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0.81</td>
<td>0.62</td>
<td>11.171</td>
<td>1996.55</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>0.74</td>
<td>0.68</td>
<td>10.195</td>
<td>1662.93</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0.70</td>
<td>0.72</td>
<td>9.612</td>
<td>1478.19</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.70</td>
<td>0.72</td>
<td>9.612</td>
<td>1478.19</td>
</tr>
</tbody>
</table>

Next, in order to calculate comparable powder diffraction intensities to those obtained experimentally, the multiplicity, \( j \), of the reflection must be considered. Within a powder diffraction pattern, multiple reflections with the same \( d \)-spacing are superimposed on each other, affecting the overall peak intensity.\(^72\) This is due to the pattern being 1D, and the reciprocal lattice being 3D.\(^64\) Rather than calculating the intensity of each of these peaks, \( |F_{hkl}|^2 \) can be calculated for a single reflection, and then multiplied by the number of symmetry-equivalent peaks, which is determined by the Laue class. FCC Cu has a Laue symmetry of \( m\)-3\( m \), therefore reflections may have a total multiplicity of 48.\(^72\)
Table 4.9: Multiplicity of equivalent powder diffraction reflections for cubic systems

<table>
<thead>
<tr>
<th>Crystal class</th>
<th>Diffracting plane and multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>h00, 6, hh0, 12, hk0, 24, hhh, 8, hhl, 24, hkl, 48</td>
</tr>
</tbody>
</table>

The other two factors which affect peak intensities are angle, \( \theta \), dependent. The first factor to consider is the polarization of the X-ray beam, \( p \): X-rays do not cause polarization; however, partial polarization occurs when radiation is scattered at any angle, and complete linear polarization is possible when the radiation is scattered at 90°. The second is the Lorentz factor, \( L \), which accounts for two geometrical effects: (1) the finite size and thickness of the reciprocal lattice and the Ewald’s sphere, both of which are inversely proportional to \( \sin \theta \), and (2) the differing radii of the Debye rings which are inversely proportional to \( \sin^2 \theta \). Both the polarization and the Lorentz factors are combined, \( Lp \), as shown in Equation 4.32.

\[
\begin{align*}
(a) \quad p &= \frac{1 + \cos^2 \theta}{2} \\
(b) \quad L &= \frac{1}{\cos \theta \sin^2 \theta} \\
(c) \quad Lp &= \frac{1 + \cos^2 \theta}{\cos \theta \sin^2 \theta}
\end{align*}
\]

Equation 4.32: The (a) polarization factor for unpolarised X-rays, (b) Lorentz factor and (c) Lorentz-polarization factor

The Lorentz-polarization factor is then multiplied by the multiplicity and the squared structure factor to calculate the intensity of diffraction, which the ratio of the predicted peaks was extracted from for the TOPAS input file.
Table 4.10: Summary to calculate the intensity of diffraction for Cu$_0$

| $h$ | $k$ | $l$ | $|F_{hkl}|^2$ | $j$ | $L_b$ | $I_{hkl}$ | $I_{hkl}/I_{111}$ |
|-----|-----|-----|--------------|-----|-------|-----------|-----------------|
| 1   | 1   | 1   | 7798.47      | 8   | 1139.83 | 71111705   | 1.00            |
| 2   | 0   | 0   | 6871.62      | 6   | 854.13  | 35215478   | 0.50            |
| 2   | 2   | 0   | 4506.61      | 12  | 425.57  | 23014747   | 0.32            |
| 3   | 1   | 1   | 3495.99      | 24  | 308.70  | 25900960   | 0.36            |
| 2   | 2   | 2   | 3241.68      | 8   | 282.73  | 7332075    | 0.10            |
| 4   | 0   | 0   | 2485.29      | 6   | 211.31  | 3150944    | 0.04            |
| 3   | 3   | 1   | 2101.05      | 24  | 177.48  | 8949332    | 0.13            |
| 4   | 2   | 0   | 1996.55      | 24  | 168.46  | 8071971    | 0.11            |
| 4   | 2   | 2   | 1662.93      | 24  | 139.89  | 5583150    | 0.08            |
| 3   | 3   | 3   | 1478.19      | 8   | 124.02  | 1466656    | 0.02            |
| 5   | 1   | 1   | 1478.19      | 24  | 124.02  | 4399968    | 0.06            |

4.8.4.2. Theory

Before any testing could take place, a few key experimental parameters had to be calculated and controlled in order to sustain plug flow conditions throughout the catalytic testing cycle.\(^{73}\)

Diffusion and mass transfer limitations must be mitigated by controlling the bed lengths and particle sizes of the catalysts used. Though Equation 4.33 is an approximation of the ratios needed to sustain plug flow conditions, it offers a useful starting point and a way in which to monitor the comparability of the results gained across different catalytic testing instruments. It also controls the particle size of the catalyst used to prevent fine dust accumulating in the reactor. This could cause a pressure drop across the bed which would be highly unfavourable and would not be comparable to industrial conditions.\(^{74}\)

\[
\frac{d_t}{d_p} > 10 \quad \frac{L_b}{d_p} > 50
\]

*Equation 4.33: Plug flow conditions. $d_t$ refers to the tube diameter, $d_p$ is the particle diameter and $L_b$ relates to the bed length.*\(^{73}\)

As well as this, the gas hourly space velocity (GHSV, h\(^{-1}\)) must be calculated. Both calculations have a direct effect on each other; therefore, care has been taken to ensure all requirements are satisfied.
\[ GHSV = \left( \frac{\text{volumetric flow rate} \, \text{cm}^3 \, \text{min}^{-1}}{\text{volume of catalyst} \, \text{cm}^3} \right) \left( \frac{60 \, \text{min}}{1 \, \text{h}} \right) \]

*Equation 4.34: Gas hourly space velocity*

4.9. **Results and Discussion**

4.9.1. **Catalyst preparation**

Two types of catalyst were investigated in this study to determine whether Cs-promotion affected their reduction behaviours: a standard loading catalyst (sCZA) and a high Cu loading catalyst (hCZA). The standard loading catalyst is modelled on those currently employed in industry for low-temperature water-gas shift catalysis, whereas the high Cu loading catalyst was included to determine if the promoter had a significant impact on the active Cu component.

The dependence of the Cu/ZnO/Al₂O₃ catalysts’ activity upon the hydroxycarbonate precursor phase formed during coprecipitation is well documented. For the low-temperature water-gas shift reaction, a Cu:Zn molar ratio close to 2:1 is preferred as a catalyst with high Cu dispersion, and thus higher activity, is achieved. This is because, as mentioned in Section 1.6.1, a maximum of 28 wt.% Zn can be incorporated in the malachite lattice. The precursors of the sCZA and hCZA catalysts are shown in Figure 4.11. Malachite has been included as a reference pattern to, again, show how the (20-1) and (21-1) reflections shift to lower \( d \)-spacings (higher \( \theta^2 \)) as a result of Zn (a non-Jahn-Teller cation) incorporation in the malachite lattice. As expected, the hCZA catalyst has a lower [Zn], therefore its pattern is more crystalline and most similar to that of malachite. There is evidence of pure malachite, \( \text{Cu}_2\text{CO}_3(\text{OH})_2 \), in the hCZA precursor pattern by the (20-1)-shoulder at 31.3\(^\circ\)2\(\theta\). Both patterns indicate an HTLC phase crystallising during the ageing process, which has been assigned as either a Cu HTLC, Zn HTLC or mixed Cu, Zn HTLC. The crystallinity of the HTLC present in the sCZA pattern is greater, which may be due to the larger Zn/Al ratio.
Figure 4.11: Diffraction patterns for the hydroxycarbonate (a) sCZA and (b) hCZA precursors; the dashed grey lines, from left to right, signify the (110)-, (120)-, (200)-, (220)-, (20-1)-, (21-1)- and (240)-reflections of the malachite phase, and the reference patterns for malachite, a Cu HTLC and a Zn HTLC are given below.

The O-H region in the IR spectra shown in Figure 4.12 (a) demonstrates that zincian malachite has been formed by the two strong bands assigned to malachite at 3400 and 3300 cm\(^{-1}\), and the characteristic zincian malachite shoulder at 3460 cm\(^{-1}\). The malachite features are weaker in the sCZA precursor IR spectrum, though this may be due to a more crystalline Cu,Zn HTLC phase which would show a broad band at 3353 cm\(^{-1}\), attributed to the interlayer water molecule’s O-H stretching vibration.

The 1700-1100 cm\(^{-1}\) region contains the carbonate \(v_3\) modes (asymmetric C-O stretching). The four bands in the hCZA spectra at 1520 (shoulder), 1498, 1425 and 1390 cm\(^{-1}\) are assigned to the \(v_3\) of malachite. There is also a shoulder present ca. 1360 cm\(^{-1}\) which is ascribed to the symmetric C-O stretching mode of the interlayer CO\(_3^{2-}\) anions in the HTLC. This band is seen to a greater degree for the sCZA precursor at 1360 cm\(^{-1}\).
Finally, Figure 4.12 (c) shows the O-H libration bands and out-of-plane OCO $v_2$ bending modes associated with the prepared hydroxycarbonate precursor phases. These do not differ from those expected for zincian malachite; however, there is a band present at 778 cm$^{-1}$ for the hCZA precursor which is not expected. It is anticipated that this band is a result of a lattice vibration attributed to metal hydroxide sheets of the HTLC.$^{89}$

![Figure 4.12: IR spectra for the sCZA and hCZA precursor phases in the ranges: (a) 3700-3100 cm$^{-1}$, (b) 1700-1100 cm$^{-1}$ and (c) 1200-650 cm$^{-1}$](image)

Tenorite (3.95, 3.96 and 4.30 $^\circ$2θ) and zincite (3.56, 3.85 and 4.05 $^\circ$2θ) are the only two phases observed in each diffraction pattern of the prepared, calcined standard and high copper loading catalysts. From the Rietveld refinement results (Table 4.11), the zincite crystallite size is so small it is barely visible in the diffraction pattern, suggesting it is completely dispersed in the CuO lattice.$^{16,91,92}$ However, the tenorite crystallite sizes vary depending on the composition of the catalyst; a higher concentration of zinc affords smaller CuO crystallites, therefore the peaks appear broader in the patterns. There also appears to be size and/or strain anisotropy present for the CuO phase, more prevalent in the high copper loading hCZA and hCZA-Cs catalysts, as evidenced by the difference from the observed and calculated Rietveld fit.$^{93}$ Complete decomposition of the intended malachite-derived precursor phase, as well as the HTLC, has occurred during calcination.
Figure 4.13: Diffraction patterns collected on ID15A, ESRF of the (a) sCZA, sCZA-Cs, (b) hCZA and hCZA-Cs catalysts; the calculated Rietveld fit is denoted by the dashed black line, the grey difference line, and the reference patterns for tenorite, zincite and malachite are given below.
The apparent crystallite sizes of the tenorite and zincite phases present in the freshly prepared standard (sCZA and sCZA-Cs) and high copper loading (hCZA and hCZA-Cs) catalysts are detailed in Table 4.11. The larger errors associated with the high copper loading catalysts’ tenorite domain sizes are, again, anticipated to be affected by size/strain broadening not being accounted for in the TOPAS-implemented Scherrer equation. With regards to the larger CuO crystallite sizes for the Cs-promoted catalysts, they are prepared via incipient wetness impregnation, which acts as an additional hydrothermal treatment that the promoted catalysts are subjected to. Therefore, the slightly larger CuO domain sizes calculated for sCZA-Cs and hCZA-Cs may be a result of this additional hydrothermal treatment.

Table 4.11: Apparent CuO and ZnO crystallite sizes for the prepared sCZA, sCZA-Cs, hCZA and hCZA-Cs catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size / nm</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO</td>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>sCZA</td>
<td>6.3(1)</td>
<td>1.0(1)</td>
<td></td>
</tr>
<tr>
<td>sCZA-Cs</td>
<td>8.0(2)</td>
<td>1.2(0)</td>
<td></td>
</tr>
<tr>
<td>hCZA</td>
<td>16.0(7)</td>
<td>1.2(0)</td>
<td></td>
</tr>
<tr>
<td>hCZA-Cs</td>
<td>16.3(8)</td>
<td>1.3(0)</td>
<td></td>
</tr>
</tbody>
</table>

The Cu:Zn ratios for sCZA and sCZA-Cs are 2.2:1 and 2.3:1, respectively, and for hCZA and hCZA-Cs are 8.8:1 and 8.9:1, respectively. It is hypothesised that the standard catalysts will be more stable to thermal sintering during activation due to the larger Zn content which is also the more industrially relevant composition.

Table 4.12: XRF analysis of the investigated promoted and unpromoted catalysts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sCZA</td>
</tr>
<tr>
<td>CuO</td>
<td>62.25</td>
</tr>
<tr>
<td>ZnO</td>
<td>28.56</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.19</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>-</td>
</tr>
</tbody>
</table>

Thermal gravimetric analysis for the prepared standard and high copper loading catalysts, accompanied with evolved gas analysis, is presented in Figure 4.14 (and Table 4.13). The evolved CO₂ (m/z ratio of 44) gas between 400-600 °C is associated with the decomposition of high temperature carbonates (HT-CO₃²⁻). It is anticipated that the TGA profiles for sCZA and sCZA-Cs...
Cs will display more dramatic weight loss due to the increased ZnO content, thus possessing a higher concentration of HT-CO$_3^2$ species.\(^{96}\) The large weight loss for the sCZA-Cs catalyst observed below 200 °C is attributed to the loss of water (m/z ratio of 18) remaining from the incipient wetness impregnation method of the Cs-promoter. In comparison, there appears to be less water present on the surface of the high copper loading catalysts.\(^{88}\)

Figure 4.14: Thermogravimetric analysis, with EGA of H$_2$O and CO$_2$, for the (a) sCZA, (b) sCZA-Cs, (c) hCZA and (d) hCZA-Cs catalysts up to 900 °C

Table 4.13: TGA summary for the prepared catalysts up to 900 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>≤ 200 °C</th>
<th>200-400 °C</th>
<th>400-600 °C</th>
<th>600-900 °C</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCZA</td>
<td>6.988</td>
<td>4.622</td>
<td>3.619</td>
<td>1.753</td>
<td>16.982</td>
</tr>
<tr>
<td>sCZA-Cs</td>
<td>18.113</td>
<td>5.838</td>
<td>2.884</td>
<td>5.697</td>
<td>32.532</td>
</tr>
<tr>
<td>hCZA</td>
<td>2.441</td>
<td>1.039</td>
<td>1.678</td>
<td>0.838</td>
<td>5.996</td>
</tr>
<tr>
<td>hCZA-Cs</td>
<td>1.334</td>
<td>1.223</td>
<td>1.962</td>
<td>0.067</td>
<td>4.586</td>
</tr>
</tbody>
</table>
The reduction behaviours of the prepared catalysts are detailed below. The main reduction peak visible for all species is associated with the formation of metallic copper. P. Kowalik et al. reported that alkali metal promotion of the CuO/ZnO/Al₂O₃ catalysts caused a 20-30 °C shift in the maximum reduction peak temperature to higher temperatures. As can be seen from Figure 4.15, the main reduction band occurs at 211 °C for both the promoted and unpromoted standard catalysts, whereas it is offset by 20 °C for the hCZA and hCZA-Cs catalysts with the maximum reduction band occurring at 212 °C and 232 °C, respectively. This perhaps indicates that the Cs promoter does not favour copper reducibility and this effect is offset by the increased Zn content in the sCZA-Cs catalyst.

![Figure 4.15: TPR profiles comparing (a) the sCZA and sCZA-Cs catalysts and (b) the hCZA and hCZA-Cs catalysts](image)

T. Shishido et al. reported a correlation between the amount of zinc and the resultant reduction temperature of the Cu active component: as the zinc content increases, the reduction temperature of the Cu²⁺ decreases because the CuO particles are better dispersed. Therefore, it would be expected that the reduction temperature of the hCZA and hCZA-Cs catalysts would be greater than those of the sCZA and sCZA-Cs catalysts, but this is not the case for the prepared catalysts.

For all prepared catalysts, a small shoulder is visible at lower temperatures to varying degrees. This is typical for supported copper-containing systems, though its origin is disputed. The majority of the literature assigns it as the first step in the reduction of Cu²⁺ to Cu¹⁺; the strong interaction between the oxide matrix and Cu is kinetically favourable to stabilise the Cu¹⁺ intermediate. It has also been suggested that residual (hydroxy-)carbonates from the catalyst precursors are initially reduced. This shoulder is more pronounced in the high Cu loading samples and there is a shift in its position for hCZA-Cs from 194 °C to 205 °C.
4.9.2. Point Measurements

4.9.2.1. Reduction along the catalyst bed

The Rietveld method combined with pattern decomposition of the metallic copper phase was employed for crystal structure refinement and phase analysis of the collected point measurements. This allowed phase diagrams to be constructed of the active copper component showing the evolving reduction behaviour of the investigated catalyst over time, and how this varied along the length of the catalyst bed.

Multi-component Rietveld analysis allows weight fractions of phases, $W_p$, to be calculated by considering that the weight of a phase in the catalyst bulk is proportional to the product of the scale factor. Once all phases present are identified in the diffraction pattern, the $W_p$ is calculated according to Equation 4.35.$^{104}$

\[
W_p = \frac{S_p(ZMV)_p}{\sum_i S_i(ZMV)_i}
\]

*Equation 4.35: Weight fraction of a given phase present in a diffraction pattern*.$^{104}$

Where $S_p$ = Rietveld scale factor of the phase

$Z$ = number of formula units per unit cell

$M$ = mass of the formula unit / g mol$^{-1}$

$V$ = unit cell volume / Å$^3$

This is the basis of a method providing accurate phase analyses without the need for standards or for laborious experimental calibration procedures.$^{104}$

The diagrams shown in this section depict the response of the Cu-containing phases present in the samples from time 0 min when the reducing gas was introduced. The plotted straight line represents the changes the catalyst goes through from 160-230 °C, and the circle-marked line shows the sample at constant 230 °C. The point at which metallic copper became the predominant phase at that position in the bed is marked by the dashed grey line (referred to as the cross-over line). For each activation test, the reduction was ideally left till the sample was completely reduced; however, this was not always possible due to time constraints.

4.9.2.1.1. sCZA and sCZA-Cs

The copper phase diagrams for the standard unpromoted and promoted catalysts activated in 5% H$_2$/Ar (*Figure 4.16* and *Figure 4.17*, respectively) demonstrate that the reduction was run to completion as the only Cu-containing phase present in the final diffraction patterns is of Cu$^0$. However, the rate at which the Cu reduces along the bed varies. For ease of understanding and
comparison, where more than three positions were collected, the top, middle and bottom positions are given.

Figure 4.16: Phase diagram for the active copper component in sCZA during reduction in a 5 \% H₂/Ar environment at the (a) top, (e) middle and (h) bottom of the catalyst bed; the lines represent CuO (red), Cu₂O (blue) and Cu⁰ (black). (0-70 min = 160-230 °C, > 70 min = 230 °C)

Figure 4.17: Phase diagram for the active copper component in sCZA-Cs during reduction in a 5 \% H₂/Ar environment at the (a) top, (b) middle and (c) bottom of the catalyst bed; the lines represent CuO (red), Cu₂O (blue) and Cu⁰ (black). (0-70 min = 160-230 °C, > 70 min = 230 °C)

In order to visualise how the reduction rate varied along the bed, the time it took for Cu⁰ to become the predominant phase present (the dashed grey line) at individual points along the bed have been plotted in Figure 4.18. Despite only 3 positions being interrogated for the sCZA-Cs catalyst, compared to the 8 positions for the sCZA catalyst, the Cs-promoted catalyst appears to take longer to reduce in a 5 \% H₂ atmosphere. This behaviour is noted in the literature as alkali metal incorporation inhibiting reduction of the copper oxide forms (though this effect was not seen in the TPR profiles in Figure 4.15).\textsuperscript{97}
There is a discrepancy in the reduction behaviour from the top of the bed to the bottom. As stated in Section 4.8.4, the inlet was placed at the bottom of the bed for the ID15A set-up and the top of the bed was open to the atmosphere; despite temperature calibrations having been conducted in flowing Ar along the length of the bed, the gases were not heated before encountering the bed. Therefore, there appear to be slower reduction kinetics at the top and the bottom of the bed, but for different reasons: (1) using cold gases at the inlet may have caused a cold front at the bottom of the reactor as the reduction gas heats on contact with the bed, and (2) as water is created as a byproduct of the reduction reaction, it is presumed that a high water partial pressure develops at the top of the bed which inhibits reduction.

Figure 4.18: Summary of cross over lines (the dashed grey line) for sCZA and sCZA-Cs catalysts reduced in 5 % \( \text{H}_2/\text{Ar} \) (0-70 min = 160-230 °C, > 70 min = 230 °C)

The sCZA and sCZA-Cs catalysts’ reduction behaviour were also investigated under lower \([\text{H}_2]\). The 1 % \( \text{H}_2 \) study shall first be considered as the exotherm released during reduction is most controlled, deeming it the most ideal of conditions (as with the 1 % \( \text{H}_2 \) studies in Chapter 5). Unfortunately, it was not possible to wait till complete reduction of the catalyst beds was achieved; however, the results collected are still presented in Figure 4.19 (a). The sCZA catalyst was left to reduce in 1 % \( \text{H}_2/\text{Ar} \) for 225 min compared to the sCZA-Cs catalyst, which was left for 320 min. As only 3 positions were interrogated for the sCZA catalyst, where only the bottom of the bed reached complete reduction, it is hard to draw comparisons between it and the promoted catalyst’s reduction behaviour.

When the catalysts were reduced in 2.5 % \( \text{H}_2/\text{Ar} \), their reduction behaviours proved very similar, as can be seen from Figure 4.19 (b). Both catalysts were reduced for ca. 190 min, but the Cs-promoted catalyst reduced slightly quicker along the length of the bed than the unpromoted.
Figure 4.19: Summary of cross-over lines (the dashed grey line) for sCZA and sCZA-Cs catalysts reduced in (a) 1% H₂/Ar and (b) 2.5% H₂/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)

Whether Cu⁺ is an intermediate in the reduction of CuO in the LT-WGS catalyst is much debated in the literature. The results of the Rietveld refinement show that there is cuprite present when the reducing gas is first introduced into the reactor atmosphere. The time-resolved point measurements collected in the middle of the (a) sCZA and (b) sCZA-Cs catalyst beds in the first 70 min of 5% H₂ being introduced (ramping in temperature from 160 °C to 230 °C) are shown in Figure 4.20. The positions of the expected Cu₂O reflections are denoted by the dashed orange lines in the depicted 2θ-range. Though it is not obvious, evidence of cuprite is most clearly seen when metallic Cu begins to show in the diffraction patterns, which correlates with the corresponding phase diagrams (Figure 4.16 (e) and Figure 4.17 (b)).
Figure 4.20: Time-resolved XRD data for the reduction of (a) sCZA and (b) sCZA-Cs under 5 % H₂/Ar from the middle of the catalyst bed (0-70 min = 160-230 °C); the reference peak position of metallic copper, cuprite, tenorite and zincite are shown on the plots.

It can also be seen from Figure 4.20 that the middle of the (b) Cs-promoted standard catalyst bed takes longer to reduce than that of (a) sCZA. This supports the phase diagram plots. Temperature is not a factor when comparing these two positions as analysis has shown that the temperature is isothermal.

4.9.2.1.2. hCZA and hCZA-Cs

The copper phase diagrams for the high copper loading unpromoted and promoted catalysts reduced in 5 % H₂/Ar are illustrated in Figure 4.21 and Figure 4.22, respectively. Full reduction is not achieved along either catalyst bed as there is ca. 10 wt.% tenorite remaining at the interrogated position. Again, the reduction behaviour is variable along the bed.
Figure 4.21: Phase diagram for the active copper component in hCZA during reduction in a 5% H₂/Ar environment at the (a) top, (b) middle and (c) bottom of the catalyst bed; the lines represent CuO (red), Cu₂O (blue) and Cu⁰ (black). (0-70 min = 160-230 °C, > 70 min = 230 °C)

Figure 4.22: Phase diagram for the active copper component in hCZA-Cs during reduction in a 5% H₂/Ar environment at the (a) top, (f) middle and (k) bottom of the catalyst bed; the lines represent CuO (red), Cu₂O (blue) and Cu⁰ (black). (0-70 min = 160-230 °C, > 70 min = 230 °C)

After plotting the time during reduction at which Cu⁰ becomes the predominant phase, it appears the reduction of the hCZA-Cs catalyst follows a very similar reduction profile to that of the standard catalysts reduced in a 2.5% H₂/Ar atmosphere (Figure 4.23). Unfortunately, only 3 positions were collected along the hCZA bed, but it can still be concluded that the reduction profiles differ along the middle and top of the bed; the unpromoted high copper loading catalyst reduced faster at these positions than the promoted. This could be due to water having a greater effect on hCZA-Cs than hCZA.
Figure 4.23: Summary of cross over lines (the dashed grey line) for hCZA and hCZA-Cs catalysts reduced in 5% H2/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)

The microreactor set-up and environment (e.g. catalyst sieve fraction, bed length and gas flow rate) employed to carry out these activation procedures has been designed to mimic plug flow reactor (PFR) conditions. An ideal packed-bed tubular reactor is considered plug flow when, under continuous flow conditions, mixing occurs solely in the radial direction, not the axial.\textsuperscript{108,109} However, PFRs can be operated in two types of mode: differential or integral. Differential reactors are ideal to ascertain reaction kinetic data as the conditions (e.g. concentration, temperature, pressure) are uniform along the length of the bed, despite the low conversion rates. In comparison, a reactor operated in integral mode has high conversion rates, but these incur significant concentration gradients which lead to axial dispersion and mass transfer limitations. This makes it very hard to maintain isothermal operation of the PFR.\textsuperscript{110} From the reduction behaviours established from the phase diagrams in this section, it appears the microreactor is best described as an integral reactor that is operated under plug flow conditions. There is no variability in the set-up of each measurement, therefore it can be concluded that any variability seen in the performance of the investigated catalyst activation behaviour is due to their composition, making bed heights (specifically top, middle and bottom) comparable.

4.9.2.2. Crystallite Size

Typically, crystallite size in powder-diffraction Rietveld software is calculated using the Scherrer equation, which relates the mean apparent size of coherently diffracting domains to the physical broadening, $\beta$ (\textit{Equation 4.4}).\textsuperscript{94,111} The instrument parameter file is built using a calibration standard that affords suitable approximation of isotropic crystallite sizes, in this case CeO$_2$. This isotropic approach only evaluates one crystallite size contribution for all
corresponding Bragg reflections within the phase of interest’s crystal structure.\textsuperscript{94} Therefore, this assumes all line broadening contributions (peak shape and width) vary as a function of the $hkl$-reflections diffraction angle.\textsuperscript{112}

Apparent crystallite sizes of the active Cu$^0$ and supporting zincite phases during activation are detailed in this section. The above application of the Scherrer equation is accepted to assess ZnO (anisotropy of wurtzite zincite is not explored here);\textsuperscript{113} however, due to the pattern decomposition method employed to evaluate the metallic copper microstructure, each individual $hkl$-peak defined within the TOPAS input file affords a range of calculated domain sizes for Cu$^0$ (N.B. the outputted crystallite sizes for the catalysts reduced in 5\% H$_2$/Ar range are given in Appendix 7.4.2). This result is further evidence of the presence of peak broadening anisotropy. In order to reflect the investigated Cu$^0$ microstructure in the apparent crystallite size, an average has been taken to yield the effective crystallite size, $D_{\text{eff}}$.\textsuperscript{4,52,112}

The cross-over lines determined in \textit{Section 4.9.2.1}, are used to reflect the point in time at which metallic copper is the predominant Cu-containing phase and, thus, the effective crystallite sizes are most reliable.

\textit{4.9.2.2.1. sCZA and sCZA-Cs}

Despite analysis of the expanded copper lattice parameters suggesting the temperature gradient present along both standard catalyst beds is non-uniform and non-linear (Appendix 7.4.3.1), there is a definite trend present in the effective crystallite sizes shown in Figure 4.24; Cu$^0$ $D_{\text{eff}}$ increases towards the top of both standard catalyst beds (with the exception of sCZA position (h)). For the sCZA catalyst, the average domain size increases from 6.0(4) nm to 7.2(4) nm, as compared to the sCZA-Cs bed, which ranges from 6.1(4) nm to 7.7(5) nm from bottom to top. It appears the Cs-promoted catalyst incurs a greater rate of sintering along the length of the bed. This suggests there is another mechanism at play influencing the lattice parameters which is discussed in \textit{Section 4.9.2.8}. 

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Reduction of the standard catalysts in 1 % and 2.5 % H2/Ar are shown in Figure 4.25. Initially, the lowest hydrogen partial pressure study will be considered. The reduction behaviour at the bottom of the sCZA bed reduced in 1 % H2 more closely resembles that of the unpromoted bed reduced in 5 % H2 as the Cu0 effective crystallite sizes are comparable (5.7(2) nm and 5.8(4) nm, respectively). This is not the case for the Cs-promoted catalyst, as growth of the copper crystallites exceeds that of the equivalent position reduced in 5 % H2 (6.8(4) nm and 6.1(4) nm, respectively).

Reduction of the standard catalyst beds under 2.5 % H2 again illustrates Cu0 grain growth from the bottom of the bed to the top. The bottom of the sCZA and sCZA-Cs beds maintain a copper crystallite size of 5.7(2) nm and 6.5(4) nm, respectively. This grows to 8.1(3) nm and 9.2(5) nm, respectively, at the top of the bed, further reinforcing that the sintering effects of the active component are seen to a greater extent in the promoted catalyst.
Figure 4.25: Mean Cu\(^{0}\) crystallite sizes for (a) sCZA and (b) sCZA-Cs during reduction in (i) 1 % and (ii) 2.5 % H\(_2\)/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)

At the start of reduction (time 0 min), when the reducing gases are introduced, the ZnO apparent crystallite size is moderately larger across the standard promoted catalyst bed than the unpromoted; this corresponds with the Rietveld refinement analysis of the fresh standard catalysts (Table 4.11) and is the result of the incipient wetness impregnation of the Cs-promoter.\(^{114}\) Once reduction of the copper-containing phases begins, a gradual increase in the zincite domain size is seen. Interestingly, the most significant grain growth visible in Figure 4.26 occurs simultaneously with the cross-over line specified in Section 4.9.2.1; it is at this point during the reduction of copper oxides that a molecule of hydrogen is consumed and a water molecule is released into the reactor atmosphere.
Figure 4.26: Apparent ZnO crystallite sizes for (a) sCZA and (b) sCZA-Cs during reduction in (i) 1 %, (ii) 2.5 % and (iii) 5 % H₂/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)
The susceptibility of wurtzite ZnO to sinter in the presence of high partial pressures of steam is documented in the literature.\textsuperscript{115–118} In the presence of H\textsubscript{2}O, the electrostatically stable, nonpolar (10\bar{1}0) wurtzite-type surface is selectively hydroxylated, producing a layer of bridging and terminal hydroxyl groups as a result of the amphoteric nature of ZnO.\textsuperscript{115,119,120} This hydroxide layer further interacts with other water molecules in the atmosphere, establishing a structured H\textsubscript{2}O layer into which Zn\textsuperscript{2+} ions can dissolve into. Therefore, hydroxylation of this ZnO surface enhances surface diffusion through chemical interactions with the water, causing sintering of the support via Ostwald ripening.\textsuperscript{117,120,121}

It is anticipated that the water produced during reduction of the active component, selectively adsorbs on the ZnO(10\bar{1}0) surface. The hexagonal close packed (HCP) structure of zincite is composed of three types of surfaces: a polar Zn-terminated(0001) surface, a O-terminated (000\bar{1}) surface and the nonpolar (10\bar{1}0) surface, the latter of which constitutes \textit{ca.} 80\% of available ZnO surfaces.\textsuperscript{122} Therefore, it is highly likely any water present in the reducing gas atmosphere interacts with this surface, promoting surface diffusion and resulting in grain growth of the zincite.

However, the sintering behaviour of zincite is different for the unpromoted and promoted catalysts. Irrespective of the [H\textsubscript{2}(g)], sintering of ZnO is more pronounced along the standard promoted bed than the unpromoted. There are two possible rationalisations for this: (1) the incipient wetness impregnation method employed promotes segregation of ZnO via HTLC formation, and/or (2) additional water is held on the surface of the promoted catalyst, facilitating further growth of ZnO.\textsuperscript{114,123} Both scenarios require weak metal-support interactions between Cu\textsuperscript{0}-ZnO and Cu\textsuperscript{0}-Al\textsubscript{2}O\textsubscript{3} as a result of phase segregation; this also accounts for the increased copper crystallite sizes following reduction in both standard catalysts. Compositionally, the main difference between these two types of catalysts is Cs-promotion, therefore the role of Cs in sintering will be considered.

The incorporation of Cs-promoters in copper-based catalysts, such as LT-WGS and methanol synthesis catalysts, has been researched.\textsuperscript{97,124–129} Typically, the rate-determining step (RDS) in the water-gas shift reaction is the dissociation of H\textsubscript{2}O (\textit{Equation 4.36}). However, once the Cu-based catalyst is promoted with 1-1.2 wt.% Cs\textsubscript{2}O, it is reported that the dissociation of water is no longer rate-limiting and methanol formation is inhibited (the latter is not explored further).\textsuperscript{98} Evidence of Cs promoting water dissociation is reported for coverages of $\theta_{\text{Cs}}^*$ > 0.5 (where a saturated monolayer of Cs atoms is described by $\theta_{\text{Cs}}^* \approx 1$), which corresponds to the [Cs] in the prepared catalysts; therefore, it is feasible that Cs-stabilised OH\textsubscript{(a)} species form \textit{in situ} throughout reduction.\textsuperscript{130,131} During operation of the low-temperature water-gas shift reaction, it is also important to note that the optimal Cs coverage is low to prevent inaccessibility of other species to free copper sites, e.g. for CO adsorption.\textsuperscript{130}
\[ \text{H}_2\text{O} \rightarrow \text{H}^{(a)} + \text{OH}^{(a)} \]

Equation 4.36: The rate-limiting water dissociation step in the WGS reaction; the subscript “(a)” refers to an adsorbed species.

When Cs is incorporated into the CuO/ZnO/Al\(_2\)O\(_3\) catalyst, it is presumed that it preferentially chemisorbs to the Cu\(^0\). Though it is possible for caesium to adsorb onto the O-terminated ZnO(0001) and the nonpolar ZnO(10\(\overline{1}\)0) surfaces, when Cu\(^0\) is present, the majority of the promoter migrates to the copper from the alkali-oxide interface (surface free energy Cs = 0.067 J m\(^{-1}\)).\(^{132,133}\) This is because it is more energetically favourable for Cs to donate an electron into the empty Cu(4s,4p) band than the empty Zn(4s,4p) band of ZnO. Concurrently, the valence electron in the half-occupied Cs 6s-orbital has a greater interaction with the occupied Cu\(^0\) s-orbitals than the occupied {Zn 4s + O 2p} band of ZnO. Thus, preferential adsorption of Cs on Cu occurs in the presence of ZnO, increasing the thermal stability of caesium on the surface.\(^{132}\)

4.9.2.2.2. hCZA and hCZA-Cs

The thermal conductivity of copper is 400 W m\(^{-1}\) K\(^{-1}\) at room temperature, compared to 50 W m\(^{-1}\) K\(^{-1}\) for wurtzite ZnO;\(^{134,135}\) as Cu\(^0\) has a relatively high thermal conductivity, it is more susceptible to sintering, and a role of zincite is to act as thermal stabilizer.\(^{95}\) The sintering effects are far more pronounced for the high copper loading catalysts (Figure 4.27). This is most likely due to the concentration of ZnO decreasing by 2/3 (from \(\text{ca.} 30\) wt.% in \text{sCZA/sCZA-Cs to \text{ca.} 10\) wt.\%). As with the standard catalysts, the metallic Cu crystallite size increases from the bottom to the top of both beds; however, due to the reduced [ZnO], the Cu\(^0\) crystallites are more sensitive to sintering.\(^{136}\) Cs-promotion also exacerbates this effect along the hCZA-Cs bed as its incorporation further weakens the SMSI and holds water on the surface of the Cu\(^0\) nanoparticles, facilitating Ostwald ripening of the active component.
Figure 4.27: Mean Cu$^0$ crystallite sizes for (a) hCZA and (b) hCZA-Cs during reduction in 5 % H$_2$/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)

When compared to the standard catalysts reduced under identical conditions, there appears to be a trend across all results (Figure 4.28). The effective Cu$^0$ crystallite sizes increase almost linearly from the bottom of the bed, to the top. Sintering effects are also more evident along the Cs-promoted beds.

Figure 4.28: Effective final Cu$^0$ crystallite sizes, with errors, along the length of the catalyst beds reduced in 5 % H$_2$/Ar; results of the apparent crystallite sizes determined by TOPAS per reflection are given in Appendix 7.4.2.
The dispersion of the zincite prior to reduction of the active component is considered well-dispersed within the CuO lattice, making it amorphous to diffraction (as seen in Figure 4.13).\textsuperscript{16,91,92} The high extent of ZnO dispersion is maintained during the activation procedure until the active Cu component begins reducing, which is when growth of the zincite occurs (Figure 4.29). As previously stated, it is presumed that the water selectively hydroxylates the ZnO(10\bar{1}0) surface once activation of the active component begins, promoting particle growth via Ostwald ripening.\textsuperscript{117,120,121} These sintering effects are seen to a greater extent along the hCZA-Cs bed due to the Cs-promoter also migrating to the surface of the Cu\textsuperscript{0} and facilitating water dissociation on the surface of the catalyst.\textsuperscript{132}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.29.png}
\caption{Apparent ZnO crystallite sizes for (a) hCZA and (b) hCZA-Cs during reduction in 5 % H\textsubscript{2}/Ar (0-70 min = 160-230 °C, > 70 min = 230 °C)}
\end{figure}

When the final measured zincite crystallite sizes are compared following reduction under 5 % H\textsubscript{2} (Figure 4.30), three conclusions can be drawn: (1) the ZnO in the high copper loading catalyst sinters to a greater extent (despite the larger error) due to the decreased [ZnO], (2) the larger amount of water released as a byproduct of the reduction of copper in the high copper loading catalysts facilitates sintering via Ostwald ripening, and (3) the ZnO in the promoted catalyst sinters more than its unpromoted equivalent due to caesium interacting with water on the surface of the catalyst, hydroxylating the ZnO surfaces to a greater extent. It also appears that the particle growth mechanism occurs almost uniformly along the length of the catalyst beds, suggesting there is no obvious water build-up occurring.
Conventional Williamson-Hall Plots

Pattern decomposition was employed to evaluate the Cu⁰ reflections independently to ensure reliable peak intensities and positions were obtained. Despite the elastically anisotropic behaviour of Cu being known, the conventional Williamson-Hall analysis has been carried out in order to describe the active component’s microstructure. For materials that are isotropic, a straight line is afforded from the plot of $2\sin \theta$ vs $\beta \cos \theta$ (in nm⁻¹), from which the crystallite size may be derived from the y-intercept, and the lattice strain from the slope. A crude interpretation of these results suggests both the sCZA and sCZA-Cs metallic copper crystallite sizes increase from the bottom of the bed, to the top. As with the results displayed in Section 4.9.2.2, sintering occurs to a greater extent in the Cs-promoted sample. The
mean residual strain also increases from bottom to top, and is larger for sCZA-Cs. For reference, the interpretations of the cWH plots can be found in Appendix 7.4.4.

Figure 4.31: cWH plot for the final reduced pattern collected of the sCZA catalyst reduced in 5% H₂/Ar at the (a) top, (e) middle and (h) bottom of the bed

Figure 4.32: cWH plot for the final reduced pattern collected of the sCZA-Cs catalyst reduced in 5% H₂/Ar at the (a) top, (b) middle and (c) bottom of the bed

The same deviations are seen in the cWH plots for the sCZA and sCZA-Cs catalysts reduced in 1% and 2.5% H₂/Ar.

4.9.2.3.2. hCZA and hCZA-Cs

Large scattering present in the cWH plots for hCZA and hCZA-Cs illustrates that these catalysts also exhibit size-induced and strain-induced broadening. The extrapolated results from Figure 4.33 and Figure 4.34 suggest the Cu⁰ crystallite size increases from the bottom of the bed to the top, and that the mean residual strain is, again, greater in the Cs-promoted catalyst (Appendix 7.4.4).
The deviations from linear regression displayed in the cWH plots are attributed to defects present in the Cu\(^{0}\) microstructure causing anisotropic strain broadening. By employing the use of the average dislocation contrast factors calculated in Table 4.2, the dislocation affected FWHM $\Delta K$ values can be plotted as a smooth curve according to the modified Williamson-Hall equation (Equation 4.12). It is assumed that the 12 slip-systems in the Cu FCC crystal are equally populated, and that both screw and edge dislocations occur with equal probability; therefore, the average contrast factors employed in the mWH plot take this into account.\(^{138}\)

As explained in Section 4.5, there is some uncertainty concerning the values calculated for $A$ and $Q^*$ which would impact the results gleaned from the following mWH plots. As a result of this, the analysis will be treated as representative of the catalysts’ anisotropic behaviour, and any interpretations will not be considered quantitative.

4.9.2.4. sCZA and sCZA-Cs

The modified Williamson-Hall plots for the sCZA and sCZA-Cs catalysts reduced in 5 % H\(_2\)/Ar (Figure 4.35 and Figure 4.36) show that this method of analysing the experimental data is
better suited than the cWH method. This is reflected in the trend line and its associated R² value. The measured data follows the smooth curve of the mWH plot, definitively describing the anisotropic strain broadening present in the active component’s microstructure as caused by structural defects.

Once more, the crystallite sizes obtained from these plots increase towards the top of the bed and the sintering effects are more pronounced in the promoted catalyst. This holds true with the Cu⁰ D_eff presented in Figure 4.24. For reference, the interpretations of the mWH plots can be found in Appendix 7.4.5.

![Figure 4.35: mWH plot for the final reduced pattern collected of the sCZA catalyst reduced in 5 % H₂/Ar at the (a) top, (e) middle and (h) bottom of the catalyst bed.](image1)

![Figure 4.36: mWH plot for the final reduced pattern collected of the sCZA-Cs catalyst reduced in 5 % H₂/Ar at the (a) top, (b) middle and (c) bottom of the catalyst bed.](image2)

The anisotropic strain broadening is also better modelled using the mWH plot for the 1 % and 2.5 % H₂ activation studies of the standard catalysts.

4.9.2.4.2. hCZA and hCZA-Cs

It appears the anisotropy present in the high copper loading catalysts also arises from the presence of line defects as the mWH plot, again, better describes the catalysts’ microstructure. The crystallite sizes extrapolated from the mWH plots for hCZA and hCZA-Cs further suggest
that the Cu\(^0\) crystallites are larger at the top of both beds than at the bottom. Additionally, it appears that the Cs-promoted catalyst incurred more sintering than the unpromoted catalyst activated under the same conditions (Appendix 7.4.5). These results also support that crystallites in the hCZA catalyst are larger than those in the sCZA catalyst, which has already been attributed to the decreased [ZnO], making the Cu\(^0\) crystallites more susceptible to sintering.\(^{136}\)

![Figure 4.37](image)

**Figure 4.37:** mWH plot for the final reduced pattern collected of the hCZA catalyst reduced in 5 % H\(_2\)/Ar at the (a) top, (b) middle and (c) bottom of the catalyst bed.

![Figure 4.38](image)

**Figure 4.38:** mWH plot for the final reduced pattern collected of the hCZA-Cs catalyst reduced in 5 % H\(_2\)/Ar at the (a) top, (f) middle and (k) bottom of the catalyst bed.

### 4.9.2.5. FWHM

It can be seen from the mWH plots that the catalysts investigated possess anisotropic strain broadening; however, it has been assumed that each material contains screw and edge dislocations in equal proportions. To determine the type of linear defects present along the catalyst beds, *Equation 4.22* is employed.\(^{33}\) Again, these values are representative, not quantitative.

\[
\frac{[\Delta K]^2 - a}{K^2} \cong \beta(C_{400})(1 - qH^2)
\]

*Equation 4.22: The experimental determination of the average contrast factors*\(^{33}\)
4.9.2.5.1. sCZA and sCZA-Cs

The plot of the FWHMs for the standard unpromoted and promoted catalysts reduced under 5 % H₂ are shown in Figure 4.39 and Figure 4.40. From these, the q parameter values for sCZA and sCZA-Cs can elucidate whether the activation environment impacts the dislocation character of the active component. The intercept of $H^2$ is given on the plots and corresponds to $1/q$. $q$ values of 1.66 and 2.39 correspond to pure edge and pure screw dislocations, respectively, in the {111}{110} slip-systems. The extrapolated $q$ values for the sCZA catalyst bed range from 2.126-2.136 (≈ 63.9-65.2 [screw] %), and 2.131-2.136 (≈ 64.5-65.2 [screw] %) for the sCZA-Cs bed. Therefore, the standard catalyst beds overall possess more screw character than edge character, with the promoted beds expressing a slightly larger concentration.

![Figure 4.39](image1)

*Figure 4.39: The FWHM of sCZA activated in 5 % H₂/Ar, according to Equation 4.22, at the (a) top, (e) middle and (h) bottom of the bed*

![Figure 4.40](image2)

*Figure 4.40: The FWHM of sCZA-Cs activated in 5 % H₂/Ar, according to Equation 4.22, at the (a) top, (b) middle and (c) bottom of the bed*

Interestingly, a predominance of screw dislocations present in a material’s microstructure has been linked to a particle growth mechanism. Particle growth occurs as follows: (1) adatoms populate the terraces between step sites, (2) the flux of adsorbed atoms migrates to the steps via surface diffusion, and (3) adatoms are incorporated into kinks along the steps, resulting in growth along the crystallographic direction normal to the crystal surface. This
mechanism is limited by the formation of steps; however, a high concentration of screw dislocations ensures the presence of step sites with kinks along them for particle growth to take place.\textsuperscript{140} Consequently, all types of analysis preceding this section suggest the Cu\textsuperscript{0} crystallite size increases towards the top of the catalyst bed, thus the [screw dislocations] would be expected to be greater at the top of the bed.

The FWHMs for the sCZA and sCZA-Cs catalysts reduced under 1 \% and 2.5 \% H\textsubscript{2} also conform to these plots and their associated \( q \) parameter values are listed in Appendix 7.4.6. They too suggest the catalyst beds have greater [screw dislocations], as shown in Figure 4.41. For the unpromoted standard catalyst, the greater the [H\textsubscript{2}], the more edge character along the length of the catalyst bed following activation. This differs from the dislocation behaviour of the standard promoted catalyst bed which does not seem as affected by the reduction environment. A clear outlier is the calculated [screw dislocation] in the middle of the sCZA-Cs bed reduced under 1 \% H\textsubscript{2}; here, the [screw dislocations] greatly exceed those determined for the bottom of the bed. Pure copper (deformed at temperature) is reported to have a \( q \) value of 2.15, which is equivalent to 70.3 [screw] \% (pure dislocations were given as \( q_{\text{edge}} = 1.63 \) and \( q_{\text{screw}} = 2.37 \)).\textsuperscript{31,33} It may be that, as the bed has not reached complete reduction, the Cu\textsuperscript{0} has not yet interacted with the ZnO or the Cs\textsubscript{2}O which may afford slightly more edge character. (N.B. When copper is cold-worked, the resulting material is dominated by dislocations with edge character as screw dislocations are annihilated at low temperature.\textsuperscript{2,141})

It could be that, for the sCZA catalyst bed, ZnO is more likely to partly reduce under the more forcing reducing conditions (5 \% H\textsubscript{2}) making it partly migrate onto the surface of the Cu\textsuperscript{0} due to the Cu-ZnO synergism, which is reflected in the lower [screw dislocation]. The same effect would not necessarily be seen in the promoted catalyst bed as here the promoter must also be contended with; Cs has low surface free energy and so migrates to the Cu\textsuperscript{0} surface under any reducing conditions.

![Figure 4.41](image.png)

\textbf{Figure 4.41:} Graphical representation of the concentration of screw dislocations along the (a) sCZA and (b) sCZA-Cs catalyst bed reduced in different [H\textsubscript{2}]/Ar
4.9.2.5.2. hCZA and hCZA-Cs

The plots of the FWHM according to Equation 4.22 for the hCZA and hCZA-Cs catalysts reduced under 5 % H\textsubscript{2}/Ar are shown in Figure 4.42 and Figure 4.43. A good linear regression is achieved, and the average \( q \) parameter can be derived from the \( x \)-intercept (all calculated \( q \) parameters can be found in Appendix 7.4.6). The resultant experimentally determined \( q \) values along the length of the hCZA bed range from 2.152-2.156 (\( \equiv 67.4-67.9 \) [screw] %), and 2.150-2.153 (\( \equiv 67.1-67.5 \) [screw] %) for the hCZA-Cs bed, again both displaying screw character.

![Figure 4.42](image1)

**Figure 4.42:** The FWHM of hCZA activated in 5 % H\textsubscript{2}/Ar, according to Equation 4.22, at the (a) top, (b) middle and (c) bottom of the bed.

![Figure 4.43](image2)

**Figure 4.43:** The FWHM of hCZA-Cs activated in 5 % H\textsubscript{2}/Ar, according to Equation 4.22, at the (a) top, (f) middle and (k) bottom of the bed.

These results suggest there is a predominance to dislocations with screw character in these LT-WGS materials, though the higher copper loading catalysts seem to have more than the standard catalysts (Figure 4.44). Following activation under 5 % H\textsubscript{2}, the high copper loading catalysts gave \( q \) parameters of 2.150-2.156 (\( \equiv 67.1-67.9 \) [screw] %), whereas the standard catalysts yield \( q \) values in the range 2.126-2.136 (\( \equiv 63.9-65.2 \) [screw] %). It is hypothesised that this is due to the differing [ZnO] affecting the nature of the catalyst surface, i.e. the higher the [ZnO], the more dislocations with edge character.

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Figure 4.44: Graphical representation of the concentration of screw dislocations along the sCZA, sCZA-Cs, hCZA and hCZA-Cs catalyst beds reduced in 5% H₂/Ar

4.9.2.6. Peak broadening and asymmetry as a result of stacking faults

Phase defects visible in powder-diffraction arise from global shifts in a crystal’s structure induced by both stacking faults and dislocations. However, where dislocations are caused by long-range heterogeneous strain fields, stacking faults are induced by elastic strain, affecting only the reflections within range of the fault. It is shown in Section 4.8.4.1 that the intensity distribution of a given Bragg reflection in a powder-pattern is dependent on its multiplicity, \( j \). For an ideal crystal, each peak is comprised of a number of symmetry-equivalent subreflections, equal to \( j \), that contribute to the observed profile in the diffraction pattern. However, for materials affected by stacking defects, specific selection rules determined by the \( hkl \) indices of the subreflections elucidate their influence on the resulting diffraction line profile.

The work of M. S. Paterson, and later B. E. Warren and E. P. Warekois, describes the effects of stacking faults in FCC powder-diffraction using hexagonal coordinates. Here, the indices \( H_0K_0L_0 \) respectively correspond to the hexagonal axes \( A_1A_2A_3 \), where \( A_1A_2 \) are in the plane, and \( A_3 \) is normal to the plane (Equation 4.37). They found that the relationship of \( H_0 - K_0 \) determined whether stacking faults influenced a given reflection’s peak profile; where \( M \) is a positive or negative integer, including zero, planar faults do not have an effect when \( H_0 - K_0 = 3M \) (\( u \)), whereas when \( H_0 - K_0 = 3M \pm 1 \) (\( b \)), broadening and shifts in the subreflection position (direction dependent upon \( \pm \)) are seen as a direct result of stacking faults. The \( u \) and \( b \) variables represent the number of unbroadened and broadened subprofiles, respectively.
\[ A_1 = -\frac{a_1}{2} + \frac{a_2}{2} + 0 \quad \quad H_0 = -\frac{h}{2} + \frac{k}{2} + 0 \]
\[ A_1 = 0 - \frac{a_2}{2} + \frac{a_3}{2} \quad \quad K_0 = 0 - \frac{k}{2} + \frac{l}{2} \]
\[ A_3 = a_1 + a_2 + a_3 \quad \quad L_0 = h + k + l \]

**Equation 4.37:** Transformation equations to describe the FCC crystal system by hexagonal coordinates.\(^{46,143}\)

These selection rules are more readily implemented when \(L_0\) is considered. By substituting \(H_0 - K_0\) into the equation for the third index, we get \(L_0 = 3k - 2(H_0 - K_0)\), hence if \(L_0 = 3M \pm 1\), the Bragg reflection will be affected by stacking faults due to a phase shift, \(\Delta \varphi\), of \(\pm 2\pi/3\) (Equation 4.38).\(^{42,46,143}\) When \(L_0 = 3M\), the stacking fault is not visible in the Bragg peak profile as the phase jump between two parts of the crystal is a multiple of \(2\pi\), diffracting as if there are no faults present.\(^{42,144}\)

\[ \Delta \varphi = 2\pi \left( \frac{h}{k} \right) \cdot \frac{n_{111}}{3} \left( \frac{1}{1} \right) = \frac{2\pi}{3} n_{111}(h + k + l) \]

**Equation 4.38:** Calculation for the phase jump across a stacking fault in the (111) plane, where \(n_{111}\) is equivalent to the number of fault-affected planes.\(^{42}\)

Within this section, the peak broadening and profile will be evaluated for the first five \(Cu^0\) reflections. The fault-unaffected and affected subreflections are detailed in Table 4.14 in terms of \(|L_0| = 3M\) and \(|L_0| = 3M \pm 1\), along with the number of subreflections that satisfy these specific \(hkl\) selection rules. For \(|L_0|\) which are multiples of 3, the subreflection intensity distribution is described by a Dirac delta-function centred around the exact Bragg position. The profiles of the fault-affected subreflections are Lorentzian, and the \((\pm)\)-sign signifies the direction, in \(^*2\theta\), that the centre of the subreflection is displaced by.\(^{11,44,145}\)
Table 4.14: Summary for the first five Cu⁰ reflections subprofiles\textsuperscript{144}

<table>
<thead>
<tr>
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<th>Unaffected subreflections</th>
<th>Fault-affected subreflections</th>
</tr>
</thead>
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<td>(</td>
<td>L_0</td>
</tr>
<tr>
<td>{111}</td>
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<td>2</td>
</tr>
<tr>
<td>{200}</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>{220}</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>{311}</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>{222}</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

It should be noted that the \{311\}-reflection is the only investigated reflection which contains two fault-affected subreflections as well as an unaffected subreflection. The broadening, and thus the asymmetry, of said peak is dominated by the subreflection with the greatest value for \(|L_0|\); hence, the \{311\}-peak profile is most sensitive to \(|L_0| = 5\), which for intrinsic stacking faults is displaced to lower scattering angles (2\(\theta\)) and \textit{vice versa} for extrinsic SFs.\textsuperscript{44,144}

4.9.2.6.1. sCZA and sCZA-Cs

When broadening results solely from the presence of planar defects, harmonic reflection pairs (e.g. 111/222) exhibit the same profile shape with opposite asymmetry.\textsuperscript{44} The normalised peak profiles for the first five Cu⁰ reflections at the top, middle and bottom of the sCZA and sCZA-Cs catalyst beds are compared in Figure 4.45 and Figure 4.46, respectively. Peak asymmetry is not easily evaluated when the reflection profiles are considered in this way; however, it is evident from these figures that the peak broadening has a non-monotonous behaviour with respect to the order of reflections.\textsuperscript{138} This is further evidence of the broadening resulting not only from a size effect (cWH), but from anisotropic strain (mWH).\textsuperscript{44,138,145}
Figure 4.45: Comparison of the line profiles for the \{111\}, \{200\}, \{220\}, \{311\} and \{222\}-reflections of Cu$^0$ in the 5% H$_2$ reduced sCZA catalyst bed at the (a) top, (e) middle and (h) bottom; the intensities have been centred and normalised to the reflection maxima.

Figure 4.46: Comparison of the line profiles for the \{111\}, \{200\}, \{220\}, \{311\} and \{222\}-reflections of Cu$^0$ in the 5% H$_2$ reduced sCZA-Cs catalyst bed at the (a) top, (b) middle and (c) bottom; the intensities have been centred and normalised to the reflection maxima.

The following plots (Figure 4.47 and Figure 4.48) study the \{111\}, \{311\} and \{222\}-reflections individually. In OriginPro, a symmetric Lorentzian-type distribution has been fitted to the peak to highlight any asymmetry present. It is understood that the Rietveld refinement fitted the peak as a pseudo-Voigt function (which has a Gaussian and a Lorentzian contribution); however, as it is known that the subprofiles are of Lorentzian-type and that it is impossible to describe crystallite size and shape distribution by a solely Gaussian profile, this is only representative.\textsuperscript{112} All three of these peak profiles include a contribution from an unfaulted subprofile (Table 4.14), as well as at least one faulted component. L. Balogh \textit{et al.} have shown that if these unfaulted subprofiles dominate the peak profile, the resulting asymmetry is consequential of the faulted subprofiles, indicating the presence of intrinsic or extrinsic stacking
faults; if the peak broadening appears symmetric, twin faulting is concluded as the most prevalent type of stacking fault.145

Figure 4.47: Line profiles of the final sCZA pattern reduced in 5 % H$_2$ highlighting the asymmetry of the {111}-, {311}- and {222}-reflections at the (a) top, (e) middle and (h) bottom of the bed; the dashed line is placed in the centre of the peak.
Figure 4.48: Line profiles of the final sCZA-Cs pattern reduced in 5% H₂ highlighting the asymmetry of the \(\{111\}\), \(\{311\}\) and \(\{222\}\)-reflections at the (a) top, (b) middle and (c) bottom of the bed; the dashed line is placed in the centre of the peak.

The extrapolated peak asymmetry is summarised in Table 4.15 and Table 4.16 for the unpromoted and promoted standard catalysts reduced under 5% H₂. When compared to the predicted influence of stacking faults on peak asymmetry (Table 4.5), it appears that the asymmetry mimics that of intrinsic stacking faults. As introduced in Section 4.6, this corresponds to the removal of a \(\{111\}\) plane, disrupting the normal FCC stacking sequence of ABCABCA to form the fault, ABCACAB. Here, a B layer has been removed; if a C layer is removed, the
resulting stacking sequence is ABCABABC. This rearrangement causes a local isostructural phase transformation from FCC to HCP (a vacancy), which is possible due to both structures having close-packed planes with six-fold symmetry.  

Table 4.15: sCZA {111}-, {311}-, and {222}-peak asymmetry reduced under 5 % $H_2$

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<tr>
<th>$hkl$</th>
<th>Position in bed</th>
<th>Top</th>
<th>Middle</th>
<th>Bottom</th>
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<tbody>
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<td>△</td>
<td>△</td>
<td>△</td>
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</tr>
<tr>
<td>222</td>
<td>△</td>
<td>△</td>
<td>△</td>
<td>△</td>
</tr>
</tbody>
</table>

Table 4.16: sCZA-Cs {111}-, {311}-, and {222}-peak asymmetry reduced under 5 % $H_2$

<table>
<thead>
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<th>Position in bed</th>
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4.9.2.6.2. hCZA and hCZA-Cs

As for the standard catalysts reduced under 5 % $H_2$, broadening of the hCZA and hCZA-Cs Cu$^0$ {111}-, {200}-, {220}-, {311}- and {222}-reflections does not increase regularly with the order of reflections. Therefore, it can be concluded that the line broadening is dependent on $hkl$ (due to the selection rules), and independent of the order of reflection.  

Figure 4.49: Comparison of the line profiles for the {111}-, {200}-, {220}-, {311}- and {222}-reflections of Cu$^0$ in the 5 % $H_2$ reduced hCZA catalyst bed at the (a) top, (b) middle and (c) bottom; the intensities have been centred and normalised to the reflection maxima.
Figure 4.50: Comparison of the line profiles for the \{111\}-, \{200\}-, \{220\}-, \{311\}- and \{222\}-reflections of \(\text{Cu}^0\) in the 5\% H\(_2\) reduced hCZA-Cs catalyst bed at the (a) top, (f) middle and (k) bottom; the intensities have been centred and normalised to the reflection maxima.

The asymmetry of the \(\text{Cu}^0\) \{111\}-, \{311\}-, and \{222\}-reflections in the final measured hCZA and hCZA-Cs diffraction patterns following activation can be found in Appendix 7.4.7. The characteristics of the peak profiles for both the high copper loading catalysts (Table 4.17 and Table 4.18) differ from those predicted for FCC crystals affected by SFs; the direction of the asymmetry for all investigated reflections extends to smaller scattering angles (\(\Delta\)). However, the calculated skewness (asymmetry) of the Lorentzian distribution was smaller for the hCZA and hCZA-Cs peak profiles of interest, which may be indicative of twinning being the predominant type of SF present.

Table 4.17: hCZA \{111\}-, \{311\}-, and \{222\}-peak asymmetry reduced under 5\% H\(_2\)

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<td>{311}</td>
<td>(\Delta)</td>
</tr>
<tr>
<td>{222}</td>
<td>(\Delta)</td>
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</tbody>
</table>

Table 4.18: hCZA-Cs \{111\}-, \{311\}-, and \{222\}-peak asymmetry reduced under 5\% H\(_2\)

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<tr>
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<td>(\Delta)</td>
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4.9.2.7. Peak displacement as a result of stacking faults

In order to determine the type of stacking fault formed in the slip-plane as a result of either Shockley or Frank partial dislocations, the \{111\}-, \{200\}-, \{222\}- and \{400\}-reflections are considered. Table 4.19 evaluates the subreflection profiles for each reflection in terms of \(u\) and \(b\), and these values are then put into Equation 4.39 to determine the direction of the peak shift when the deformation fault is intrinsic; the calculated constants for a given \(hkl\) plane, \(X_{hkl}\), due to
faulting are given in Table 4.20. For extrinsic stacking faults, the observed peak shifts occur in opposite directions, whereas the displacements of the subreflections affected by twin SFs are negligible.\textsuperscript{44–46}

Table 4.19: Components of the \{111\}-, \{200\}-, \{222\}- and \{400\}-reflections\textsuperscript{46}

<table>
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<tr>
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<th>$L_0$ (±)</th>
<th>hkl</th>
<th>$L_0$ (±)</th>
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<td>222</td>
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<td>222 -6 - 0</td>
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</tbody>
</table>

(a) $\Delta(2\theta)^0 = \frac{90\sqrt{3}\alpha \tan \theta X_{hkl}}{\pi^2}$

(b) $X_{hkl} = \frac{1}{h_0^2 (u + b)} \sum (\pm) L_0$

Equation 4.39: (a) Fault effected peak displacement calculation for intrinsic stacking faults, where (b) determines the direction of the peak shift\textsuperscript{46,55}

Where $\alpha =$ stacking fault probability

\[ h_0^2 = h^2 + k^2 + l^2 \]

Table 4.20: Determining $X_{hkl}$ for the \{111\}-, \{200\}-, \{222\}-, and \{400\}-reflections\textsuperscript{42,46,55}

<table>
<thead>
<tr>
<th>{hkl}</th>
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<th>{222}</th>
<th>{400}</th>
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<tbody>
<tr>
<td>$X_{hkl}$</td>
<td>+ \frac{1}{4}</td>
<td>- \frac{1}{2}</td>
<td>- \frac{1}{8}</td>
<td>+ \frac{1}{4}</td>
</tr>
</tbody>
</table>

The shift in peak position due to faulting is typically quite small; evaluating single peaks thus incurs more errors, making it advisable to evaluate a pair of reflections with opposite displacements; as shown in Table 4.5 (and Table 4.20), the (111)-(200) pair and (222)-(400) pair are ideal. However, despite the calculated $\Delta(2\theta_{200}-2\theta_{111})$ being smaller than the $\Delta(2\theta_{400}-2\theta_{222})$, it is considered more accurate to use the first order reflection pair. This method is usually employed to determine the deformation (intrinsic) fault probability for $\alpha$-brass (Cu/Zn 70/30); as the \{111\}-
and \{200\}-reflections move towards each other, the SF probability increases.\textsuperscript{46,143,147} Generally, as mentioned in Section 4.7, intrinsic SFs are solely considered for these systems as it is possible to produce vacancies following heating of the sample. In order to obtain a catalyst with a sufficient concentration of interstitials, external work must be done on the crystal, which has not been explored.\textsuperscript{54}

4.9.2.7.1. sCZA and sCZA-Cs

In order to determine the stacking fault probability along the length of the standard unpromoted and promoted catalyst beds, the positions, and thus displacements, of the \{111\}- and \{200\}-reflections are investigated. From the time-resolved \((111)-(200)\) peak separations displayed in Figure 4.51, it appears that as the bed reaches complete reduction (the data has been displayed either from the point at which the reduction temperature is isothermal, or from the predetermined cross over lines in Section 4.9.2.1), the \(\Delta(2\theta_{200}-2\theta_{111})\) deviates further from the ideal difference, eventually plateauing when complete reduction is achieved. The ideal peak position of the \{111\}- and \{200\}-reflections are determined by the Rietveld calculated lattice parameter, \(a\), for Cu\textsuperscript{0}; this suggests that initially the active Cu\textsuperscript{0} component does not contain defects from SFs, it is only as the reduction continues that intrinsic stacking faults appear. Perhaps this is a result of the zincite partially reducing and migrating onto the Cu\textsuperscript{0} nanoparticle’s surface.\textsuperscript{6} Across both the sCZA and sCZA-Cs beds, the difference in peak separation between the \{111\} - and \{200\}-reflections is smallest at the bottom. This suggests that the concentration of SF increases from the top of the bed, to the bottom.

![Figure 4.51: Time-resolved (111)-(200) peak separations for (a) sCZA and (b) sCZA-Cs activated in 5 % H\textsubscript{2}/Ar; where the dashed line represents the ideal and the solid line represents the experimentally derived difference in peak position.](image-url)
The time-resolved change in peak separation between the {111} - and {200}-reflections for the sCZA and sCZA-Cs catalyst beds reduced in 1 % and 2.5 % H₂ are given in Appendix 7.4.8. They too show that as the bed reduces, the stacking fault probability increases from top to bottom. The trend in SF probability along the length of all investigated activated standard catalyst beds is better graphically presented in Figure 4.52. From first inspection, it seems the higher the [H₂], the greater the fault probability; however, the time-resolved (111)-(200) peak separations decreased before plateauing once reduction was complete, and as lower hydrogen partial pressure studies were either not left long enough to fully activate the length of the bed (1 % H₂) or the formation of stacking faults was still occurring as the experimental ∆(2θ_{200}−2θ_{111}) continued to decrease (1 % and 2.5 % H₂), this trend must be verified.

Figure 4.52: Distribution of stacking fault probabilities along the (a) sCZA and (b) sCZA catalyst beds following activation

From Figure 4.52, the inverse of the stacking fault probability affords the frequency of a SF once every \(x\) layers in the [111]-direction.\(^{46}\) The variable ‘\(x\)’ has been calculated for the top, middle and bottom of the sCZA and sCZA-Cs beds and is presented in Table 4.21 and Table 4.22, respectively. It appears that SFs appear more frequently throughout the standard unpromoted catalyst bed when compared to that of the promoted equivalent. The more forcing reducing atmosphere of 5 % H₂ also seems to promote partial dislocation formation, and consequentially SFs.
Table 4.21: Frequency of SFs per x layers for the sCZA catalyst following activation\textsuperscript{46}

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>[H\textsubscript{2}] / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>59 40</td>
</tr>
<tr>
<td>Middle</td>
<td>41 27</td>
</tr>
<tr>
<td>Bottom</td>
<td>42 29 27</td>
</tr>
</tbody>
</table>

Table 4.22: Frequency of SFs per x layers for the sCZA-Cs catalyst following activation\textsuperscript{46}

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>[H\textsubscript{2}] / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>67 44</td>
</tr>
<tr>
<td>Middle</td>
<td>157 48 34</td>
</tr>
<tr>
<td>Bottom</td>
<td>37 37 29</td>
</tr>
</tbody>
</table>

4.9.2.7.2. hCZA and hCZA-Cs

A similar trend is visible for the \{111\}- and \{200\}-reflections in the high copper loading catalysts, as shown in Figure 4.53. It can be seen that the difference between the ideal $\Delta(2\theta_{200} - 2\theta_{111})$ and the experimentally derived $\Delta(2\theta_{200} - 2\theta_{111})$ is slightly smaller along the high copper loading catalyst beds.

![Figure 4.53](image)

Figure 4.53: Time-resolved (111)-(200) peak separations for (a) hCZA and (b) hCZA-Cs activated in 5 % H\textsubscript{2}/Ar; where the dashed line represents the ideal and the solid line represents the experimentally derived difference in peak position.

B. E. Warren and E. P. Warekois show that as the [Zn] in $\alpha$-brass increases, so does the stacking fault probability. They supposed that this results from zinc incorporation reducing the energy difference between FCC and HCP packing.\textsuperscript{443} As shown in Figure 4.54 (and Table 4.23), a greater [Zn] leads to a greater concentration of intrinsic stacking faults (which may also be related to dislocations with more edge character).
Cs-promotion appears to reduce the stacking fault probability along the length of the standard and high copper loading beds. This may be due to the body-centred cubic (BCC) arrangement of Cs, which does not possess close-packed planes.\textsuperscript{146}

![Graph showing stacking fault probability along the length of catalyst beds](image)

*Figure 4.54: Comparison of the calculated stacking fault probabilities along the standard and high copper loading catalyst beds reduced under 5\% H\textsubscript{2}/Ar*

*Table 4.23: Frequency of SFs per x layers for the catalysts reduced under 5\% H\textsubscript{2}/Ar\textsuperscript{146}*

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>Type of catalyst</th>
<th>sCZA</th>
<th>sCZA-Cs</th>
<th>hCZA</th>
<th>hCZA-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>sCZA</td>
<td>40</td>
<td>44</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>sCZA-Cs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>hCZA</td>
<td>27</td>
<td>34</td>
<td>38</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>hCZA-Cs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom</td>
<td>Top</td>
<td>27</td>
<td>29</td>
<td>29</td>
<td>34</td>
</tr>
</tbody>
</table>

4.9.2.8. Lattice Expansion

Following examination of the evolution of the Cu\textsuperscript{0} and ZnO crystallite sizes throughout the various activation studies, it appears the calculated temperature profiles from the extrapolated copper lattice constants (Appendix 7.4.3) may be influenced by a factor not yet considered. The presence of lattice strain and dislocations in the Cu\textsuperscript{0} nanoparticles of the standard and high copper loading catalysts have been identified and discussed. So, too, has the prevalence of intrinsic stacking faults, most prominently within the standard catalysts. However, of the possible types of lattice point defects, substitutional impurities have not been taken into account (Figure 4.55). Not to be confused with extrinsic point defects (interstitials), a substitutional solid solution is formed when a solute atom occupies the site of a host atom.\textsuperscript{148}
Though the synergistic relationship between Cu\textsuperscript{0} and ZnO has been alluded to, its impact on the resulting diffraction pattern, and thus the calculated lattice parameters, has not been considered. For methanol synthesis catalysts, the strong metal-oxide interactions (SMSI) are well documented in the literature\textsuperscript{6,81,149,150}. It is known that during activation, this synergistic relationship facilitates reduction of the zinc to a partially oxidised Zn\textsuperscript{δ+} state; this Zn\textsuperscript{δ+} species is stabilised on defective copper sites, creating a ZnO\textsubscript{x} overlayer where 0 < x < 1\textsuperscript{6,151}. Under strong reducing conditions, this overlayer can result in a CuZn surface alloy\textsuperscript{136,152}.

In order to determine if the calculated experimental lattice parameters are a consequence of solute atoms dissolving into the copper matrix, Vegard’s law may be employed\textsuperscript{153}. When a solvent atom, r\textsubscript{1}, is replaced by a solute atom, r\textsubscript{2}, the lattice will either contract (r\textsubscript{2} < r\textsubscript{1}) or expand (r\textsubscript{2} > r\textsubscript{1}); for the investigated LT-WGS catalysts, the potential solute atoms considered are Zn and Cs whose Seitz radii both exceed that of Cu\textsuperscript{0} (Table 4.24), therefore only lattice expansion will be considered (which also aligns with the measured diffraction data). In general, it is assumed that the solvent and solute atoms are spherical and that the included solute atoms possess elastic properties equivalent to that of the solute in bulk\textsuperscript{154}. Vegard’s law predicts a linear change in lattice constant between pure solvent and pure solute materials according to Equation 4.40\textsuperscript{155}.

\textbf{Table 4.24: Seitz radii (r\textsubscript{0}) and atomic volumes (Ω) of Cu, Zn and Cs at room temperature}\textsuperscript{154,156}

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>r\textsubscript{0} / Å</th>
<th>Ω / Å\textsuperscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>29</td>
<td>1.413</td>
<td>11.82</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>1.538</td>
<td>15.24</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>4.865</td>
<td>482.32</td>
</tr>
</tbody>
</table>
\[ a_{A-B} = a_A + k_{A-B} c_B \]

*Equation 4.40: Vegard’s law to determine the lattice parameter, a, dependence on solute concentration in binary alloys* \(^{157}\)

Where  
\( a_{A-B} \) = binary A-B solid solution lattice parameter, \( a / \text{Å} \)  
\( a_A \) = solvent lattice parameter, \( a / \text{Å} \)  
\( k_{A-B} \) = characteristic parameter of the A-B solid solution / Å  
\( c_B \) = atomic fraction of the solute / at.%

First, the possibility of Zn dissolving into the Cu\(^0\) matrix will be discussed. The solubility limit of Zn in Cu is ca. 38.95 wt.% at high temperature; however, the compositional range at which stable Cu-Zn solid solutions are formed is \( 5.4 \leq [\text{Zn}] \) / wt.% \( \leq 37.5 \) (5.3 \( \leq [\text{Zn}] \) / at.% \( \leq 36.8 \)). Interestingly, the enthalpy of mixing for these materials is negative, \( \Delta H_{\text{Cu-Zn}} = -6 \text{ kJ mol}^{-1} \). \(^{158}\) The compositional maximum concentration of ZnO incorporated into the investigated catalysts (standard) is close to 30 wt.%; for a Cu-Zn alloy with < 35 wt.% Zn a stable FCC \( \alpha \)-brass phase is exhibited, whereas above this the \( \beta \)-brass phase (CsCl type) is formed. The \( k_{A-B} \) constant for Cu-Zn solid solutions is cited as 0.2265 Å which can be substituted into *Equation 4.40*; \(^{157-159}\) the solutions for the possible resultant expanded Cu\(^0\) lattice parameters at room temperature are represented graphically in *Figure 4.56*. Furthermore, *Equation 4.41* can then be employed to calculate the thermal expansion of the differing Cu-Zn standard solutions at the temperature of activation (230 °C). From this, it can be extrapolated that the TOPAS limit placed on the Cu\(^0\) lattice parameter, \( a \), corresponds to a maximum of 4.27 at.% Zn. Despite this being below the stable compositional range stated by H. Hong *et al.*, this analysis has been applied to the experimental results.

\[ \frac{l_f - l_0}{l_0} = a_l (T_f - T_0) \]

\[ \therefore l_f = l_0 (1 + a_l \Delta T) \]

*Equation 4.41: Thermal expansion of a solid material* \(^{160,161}\)

Where  
\( l_0 \) = initial length / Å  
\( l_f \) = final length / Å  
\( a_l \) = linear expansion coefficient / K\(^{-1}\)  
\( \Delta T \) = change in temperature (\( T_f - T_0 \)) / K
Figure 4.56: The effect of Zn-incorporation on the Cu lattice constant, $a$, at room temperature and 230 °C; the dashed grey line signifies the TOPAS limit set for the Cu$^0$ unit cell parameter, $a$

As the temperature along the bed is not monitored in situ, it is not possible to quantitatively evaluate the Cu$^0$ unit cell parameters for Zn-incorporation; however, assuming the temperature of the final measured diffraction pattern is 230 °C, the calculated lattice expansion and experimental lattice parameters have been plotted for the unpromoted and promoted standard catalysts in Figure 4.57. The outlier at the bottom of the sCZA bed reduced under 5 % H$_2$ corresponds to a [Zn] of 2.64 at.%. Other than this result, sCZA and sCZA-Cs activated under 5 % H$_2$ suggest < 1 at.% Zn has dissolved into the Cu$^0$ lattice. The 2.5 % H$_2$ activation results differ depending on the presence of Cs-promoters, with the sCZA-Cs bed suggesting a maximum [Zn] of 1.76 at.% (position (c)) compared to 1.03 at.% (position (e)) for the sCZA bed. Though the 1 % H$_2$ studies have been included, their results are not necessarily indicative of the composition of a fully reduced catalyst bed under these conditions.
Figure 4.57: Graphical representation of the final calculated Cu\(^0\) lattice parameters along the (a) sCZA and (b) sCZA-Cs beds; the dashed grey line represents the calculated Cu\(^0\) unit cell parameter, \(a\), at 230 °C, and the subsequent dashed blue lines correlate with the atomic \([\text{Zn}]\).

For the high copper loading catalysts, the calculated atomic \([\text{Zn}]\) exceeds that of the equivalent standard catalysts. The maximum \([\text{Zn}]\) incorporated into the hCZA Cu\(^0\) lattice is 2.60 at.%, compared to 1.62 at.% for the hCZA-Cs catalyst. There does not appear to be an obvious relationship between Cs-promotion and the substitutional alloy formation; however, as previously introduced, these catalysts are more sensitive to changes in temperature due to their thermal conductivities which may be reflected in these results.

Figure 4.58: Graphical representation of the final calculated Cu\(^0\) lattice parameters along the hCZA and hCZA-Cs beds; the dashed grey line represents the calculated Cu\(^0\) unit cell parameter, \(a\), at 230 °C, and the subsequent dashed blue lines correlate with the atomic \([\text{Zn}]\).
Lattice expansion as a result of Zn-incorporation, even at 1 at.%, distorts the host lattice quite considerably, despite the Seitz radius of zinc being comparable to copper (Table 4.24). Caesium has a Seitz radius 216 % larger than Zn, therefore it has been concluded that Cs does not dissolve into the Cu⁰ matrix.¹⁵⁶ There is also no evidence in the literature that Cs forms an alloy with Cu under the investigated reducing atmospheres.¹³²,¹⁶²

4.9.2.8.1. AP-XPS of the standard catalysts

Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was employed to interrogate the surface of the sCZA and sCZA-Cs catalysts during reduction. In particular, the behaviour of the zincite support was investigated in order to determine whether evidence of surface alloying could be detected under activation conditions.

M. S. Spencer stated that the formation of dilute α-brass proceeds via the following mechanisms: (1) reduction of the zincite to afford Zn⁰ atoms, (2) transport of the reduced zinc atoms to the copper crystallite surface, and (3) zinc diffusion into the copper matrix (a schematic model is given in Figure 4.59 depicting this behaviour in terms of activation atmosphere). The latter stage determines the amount of α-brass formed and is highly dependent on the temperature of reduction/reaction for LT-WGS and MeOH synthesis catalysts; at temperatures < 227 °C, the maximum Zn-incorporation is limited to ≤ 1 at.%, even under strong reducing conditions, whereas between 227-277 °C, bulk diffusion is limited, and it is only at temperatures > 277 °C that the rate of diffusion favours equilibrium α-brass formation. This was written in terms of methanol synthesis and low-temperature water-gas shift catalysts, however, the equilibrium bulk and surface zinc concentrations in LT-WGS catalysts (0.005 at.% Zn) were deemed negligible.¹⁶³–¹⁶⁵

![Figure 4.59: Graphical representation of the wetting/non-wetting of Cu⁰ crystallites supported on ZnO: (a) Cu⁰ crystallite under oxidising syngas conditions, (b) under more reducing conditions the Cu⁰ particle becomes disk-like, (c) stronger reducing conditions leads to surface Cu-Zn alloying and (d) severe reducing conditions cause brass alloy formation, where ■ symbolises the oxygen vacancies, and ○ denotes reduced Zn species; image taken from J.-D. Grunwaldt, A. M. Molenbroek, N.-Y. Topsøe, H. Topsøe and B. S. Clausen, J. Catal., 2000, 194, 452–460.¹⁶⁶](image)
It is believed that Zn is incorporated into the copper matrix via step sites. These surface steps are generated at the intersection between Cu\(^0\) nanoparticle surfaces and stacking faults (or twin boundaries). \(^{167}\) As previously discussed, a prevalence for screw dislocations also ensures the presence of step sites. \(^{140}\) Once the Zn atom is at the Cu step, it is stabilised by bulk defects in the host matrix, allowing for alloying to take place. \(^{170}\) This behaviour is facilitated by SMSI via the formation of oxygen vacancies at the Cu/ZnO interface. \(^{166,171}\)

As introduced in Section 1.7.4, the Hüttig, \(T_{HH}\), and the Tammann, \(T_{TAM}\), temperatures predict the onset of surface mobility and bulk diffusion, respectively; \(^{172,173}\) for copper, the temperatures corresponding to these phenomena are ca. 179 °C and ca. 405 °C. Therefore, the mobility of copper atoms on the surface would be expected. By comparison, Zn\(^0\) has a much lower melting point (693 K), which may account for the migration of the reduced Zn species to the surface of the Cu\(^0\) crystallites. \(^{174}\)

The XPS results of the Cu 2p and Zn 2p regions for the sCZA and sCZA-Cs catalysts following reduction are shown in Figure 4.60 (a) and (b). The XPS spectra appear to show that the copper is completely reduced following activation due to the absence of satellite peaks ca. 945-940 eV corresponding to either Cu\(^{2+}\) or Cu\(^{1+}\); \(^{175}\) the binding energy (BE) of Cu 2p\(3/2\) is ca. 932.7 eV and for Cu 2p\(1/2\) is ca. 952.5 eV for both catalysts. This is further evidence that Cs adsorbed on the surface of the sCZA-Cs catalyst does not form an alloy during reduction as the Cu 2p\(3/2\) features remain the same. \(^{132}\) The Cu LMM Auger spectra for the standard catalysts can be found in Appendix 7.4.9.1 and confirms that the active component is reduced.

From Figure 4.60 (b), the BE of Zn 2p\(3/2\) is ca. 1022.3 eV and for Zn 2p\(1/2\) is ca. 1045.5 eV for both the unpromoted and promoted standard catalyst. Unfortunately, it is harder to evaluate the oxidation state of zinc via XPS as for Zn\(^0\) and ZnO, the Zn 2p\(3/2\) lines appear at 1021.4 eV and 1021.7 eV, respectively. However, the Zn 2p\(3/2\) peak for sCZA-Cs appears broader than that of sCZA, which may indicate the presence of additional Zn species. In order to definitively determine whether any reduction of zinc occurs, the binding energy of the Zn LMM Auger peak must be considered, as a 3 eV downward shift of BE is observed on reduction. \(^{170}\)
Figure 4.60: (a) Cu 2p and (b) Zn 2p core levels for sCZA and sCZA-Cs following reduction

The Zn LMM Auger lines, shown in Figure 4.61, suggest that the majority of the zinc remains in the Zn$^{2+}$ state (Zn LMM peaks at ca. 987.0 eV in kinetic energy); however, there is evidence that a fraction of the zincite is reduced to metallic Zn by the appearance of the shoulder at ca. 990.5 eV. S. Kuld et al. published similar data for these systems and attributed the Zn Auger shoulder feature as evidence for Cu/Zn alloy formation.\textsuperscript{170} It appears the Cs-promoted sample contains a larger portion of metallic zinc than sCZA; it has been reported by S. Chaturvedi et al. that caesium cannot achieve bulk reduction of ZnO to Zn$^0$, but it is able to form a substoichiometric zincite, ZnO$_{\chi}$.\textsuperscript{132} Therefore, it is proposed that the Cs-ZnO relationship paired with the Cu-ZnO synergism promotes reduction of zincite.
The Cs 3d region was also recorded for the promoted standard catalyst and can be found in Appendix 7.4.9.2. The appearance of the Cs 3d$_{5/2}$ (ca. 725.0 eV) and Cs 3d$_{3/2}$ (ca. 739.0 eV) signals in the sCZA-Cs spectra following reduction confirm the presence of the Cs-promoter on the catalyst surface.\textsuperscript{132}

It is important to note that the presented XPS spectra were collected following activation in a 100 \% $\text{H}_2$, strongly reducing atmosphere (at 220 °C). Under the investigated LT-WGS reduction environments ([H$_2$] = 1 \%, 2.5 \%, 5 \%), zincite reduction would not be expected to such a large extent; however, these measurements confirm the synergistic relationship between copper and zinc as it proves substitutional alloy formation is possible, making the lattice expansion attributed to the dissolution of zinc in the copper matrix more likely.

Most of the research conducted for this type of catalyst on the role of ZnO is focussed on methanol synthesis.\textsuperscript{136,150,170,176,177} For methanol synthesis, it is believed there is a shape-activity relationship in place for the active Cu$^0$ component: the greater the wetting of the copper nanoparticles on the ZnO support, the more active for MeOH production.\textsuperscript{178} However, for LT-WGS catalysts, formation of an \(\alpha\)-brass alloy has been reported to cause deactivation due to the high temperatures required to get alloy formation.\textsuperscript{177,179} This highlights the main discrepancies between the LT-WGS and the MeOH synthesis reaction: the temperature and pressure at which they are operated.\textsuperscript{136}

4.9.3. XRD-CT

As for the analysis of the point measurements, the same Rietveld analysis data processing strategy was applied across all X-ray diffraction computed tomography (XRD-CT) data sets. The
results presented in this section were collected at the end of reduction, at 230 °C, and were taken at the top, middle and bottom of the activated catalyst beds. As a reminder, each image consists of 27000 pixels per XRD-CT image, each corresponding to a unique diffraction pattern. These spatially-resolved XRD patterns offer more information concerning the microstructure of the active Cu component across the plane of the catalyst bed when compared to the point measurements, which consider an average of the particles at varying bed heights.

For conciseness, the XRD-CT results for the crystallite sizes can be found in Appendix 7.4.10. They too suggest growth of the metallic copper crystallites from the bottom of the bed to the top, and that the zincite particle sizes remain fairly uniform throughout the bed; as for the point measurements, the Cs-promoted catalysts incur more growth/sintering of these components than the unpromoted catalysts. It is important to note that the crystallite sizes remain fairly uniform across the planes of the catalyst beds, suggesting that the furnace heated the bed efficiently.

4.9.3.1. Intensity

Deviations from the ideal intensity distributions are indicative of imperfect crystal structures, and thus the presence of lattice defects. The initial results from the Rietveld refinements indicated the anisotropic behaviour of the investigated materials and called for the pattern decomposition method to be employed. As shown in Section 4.8.4.1, the ideal intensity ratio of the (111)- and (200)-peaks is equal to 2.0 for isotropic Cu$^0$, therefore, any $I_{111}/I_{200}$ that are greater than or less than 2.0 are indicative of microstructural defects.

Following analysis of the point measurements, it appears that the most likely stacking faults in these materials are intrinsic faults (vacancies) due to the decreased $\Delta(2\theta_{200}-2\theta_{111})$ presented in Section 4.9.2.7. It has been proposed that as the concentration of vacancies increases, the $I_{111}/I_{200}$ decreases.$^{180,181}$ As can be seen in the following figures, not much information can be gleaned from the intensity ratio of the (111)- and (200)-reflections across and along the sCZA, sCZA-Cs, hCZA and hCZA-Cs catalyst beds.

4.9.3.1.1. sCZA and sCZA-Cs

Across the planes of the standard unpromoted and promoted catalyst beds, a deviation from the ideal $I_{111}/I_{200}$ ratio is observed (see Figure 4.62 and Figure 4.63). However, the intensity deviations are uniformly distributed along the lengths of both catalytic beds making it hard to draw any conclusions.
4.9.3.1.2. hCZA and hCZA-Cs

There is a visible difference between the intensity distributions of the (111)- and (200)-reflections for the high copper loading catalysts when compared to those of the standard. Figure 4.64 and Figure 4.65 suggest that hCZA and hCZA-Cs possess a larger concentration of vacancies than their standard composition counterparts due to the decreased intensity ratio.\[180,181\]
Figure 4.65: Intensity ratio of the (111)- and (200)-reflections across the (a) top, (b) middle and (c) bottom of the hCZA-Cs catalyst bed reduced under 5 % H₂

### 4.9.3.2. d-spacing

It has already been established that the most reliable reflections to elucidate microstructural defects are the (111)- and (200)-peaks. For an ideal FCC material, where \( h = 1,2 \), the \( d_{hhh}/d_{2h0} \) ratio is anticipated to remain constant at \( 2/\sqrt{3} \), which is equal to 1.1547. Intrinsic stacking faults present in the Cu⁰ microstructure cause the (111)- and (200)-peaks to move towards each other, thus the \( d_{111}/d_{200} \) ratio is expected to decrease with increasing planar defects. Within this section, how the d-spacing ratios deviate across the plane of the catalyst beds at the top, middle and bottom is discussed.

#### 4.9.3.2.1. sCZA and sCZA-Cs

The distribution of the \( d_{111}/d_{200} \) ratios are depicted in Figure 4.66 and Figure 4.67 for the standard unpromoted and promoted catalysts, respectively. As previously determined, the d-spacing ratio decreases from the top of the bed to the bottom, with increasing intrinsic stacking faults. It is therefore expected that WGS activity would be greatest at the bottom of the bed as the closer the values are to the ideal, the more inactive the catalyst is suspected of being during LT-WGS operation. Cs-promotion does not seem to have a great effect on the positions of these reflections.
Figure 4.66: \(d\)-spacing ratio of the (111)- and (200)-reflections across the (a) top, (b) middle and (c) bottom of the sCZA catalyst bed reduced under 5 % \(H_2\)

Figure 4.67: \(d\)-spacing ratio of the (111)- and (200)-reflections across the (a) top, (b) middle and (c) bottom of the sCZA-Cs catalyst bed reduced under 5 % \(H_2\)

It should be noted that T. Kandemir et al. found that during reduction and throughout methanol synthesis conditions (250 °C), the \(d\)-spacing ratio of the (111)- and (200)-reflections for their investigated catalyst (CuO/ZnO/\(\text{Al}_2\text{O}_3\) 60/30/10, as with sCZA) remained below the ideal \(\frac{2}{\sqrt{3}}\). It was only following annealing of the defects at 330 °C that the ratio returned to that of an ideal Cu\(^0\) crystal.\(^{174}\)

When evaluating these figures, previous analysis should be considered to explain the trends in \(d\)-spacing ratio. It has been shown extensively that the Cu\(^0\) and ZnO crystallite sizes increase from the bottom of the bed to the top across both the unpromoted and promoted catalyst beds. This has been ascribed as a sintering phenomenon, either as a result of the microreactor set-up, or due to the exotherm released on reduction of tenorite (however, there are many other variables which may have affected this). The Cs-promoted samples also incur more grain growth than their unpromoted counterparts which has been attributed to both the incipient wetness impregnation method employed and the interaction of zinc and caesium with the water produced on reduction of copper enhancing early onset phase segregation and growth of the active component.
Crystalline solids do not typically possess smooth surfaces, they are rather populated with defects such as vacancies, adatoms, steps and kinks.\textsuperscript{182} During sintering, the surface free energy of particles is minimized \textit{via} surface-mediated Ostwald ripening: small particles dissolve into the copper matrix and are deposited on larger particles, causing growth.\textsuperscript{183,184} Surface diffusion is expected to proceed \textit{via} the following mechanism: (1) atoms break away from the lattice, e.g. at a defect site, (2) migrate across the catalyst surface with random motion, and (3) reattach at a site of equilibrium e.g. another defect site.\textsuperscript{182} As previously stated, the Hüttig temperature for copper is below the temperature of reduction, therefore the mobility of copper atoms on the surface is expected.\textsuperscript{172} The chief motive for particle rearrangement during sintering is to minimise the excess surface free energy:\textsuperscript{184} as the surface defects are consumed, surface diffusion decelerates.\textsuperscript{182} However, the final sintered product does not possess a perfect FCC crystal structure, as some defects are retained.\textsuperscript{185}

Densification also results from sintering: grain growth occurs which increases the number of inter-particle bonds.\textsuperscript{184} The presence of vacancies reportedly facilitates the transport of atoms \textit{via} surface/lattice diffusion; however, the overall vacancy concentration diminishes as they are annihilated when they diffuse from the pore-solid interface to the grain boundaries.\textsuperscript{184,186,187} This would also lead to a return to the ideal $d_{111}/d_{200}$ ratio.

4.9.3.2.2. hCZA and hCZA-Cs

Where the $d$-spacing ratios across the positions of the standard catalyst beds were comparable, the high copper loading beds, hCZA-Cs in particular, have a $d_{111}/d_{200}$ ratio very close to that of the ideal (see Figure 4.68 and Figure 4.69). Cs-promotion appears to, again, have a larger impact on the phase segregation of Cu$^0$ and ZnO in these systems causing the FCC crystal structure to become more ordered following activation. Greater variation in the $d$-spacing ratio of the (111)- and (200)-peaks are seen along the hCZA catalyst bed, following the suspected thermal effect, suggesting it would be more active for WGS activity.

\textit{Figure 4.68:} $d$-spacing ratio of the (111)- and (200)-reflections across the (a) top, (b) middle and (c) bottom of the hCZA catalyst bed reduced under 5 \% $H_2$
Stacking Fault Probability

Within an FCC crystal structure, if the periodic arrangement of atoms is disrupted, the resulting defect is referred to as a stacking fault. The stacking fault probability, $\alpha$, is calculated according to Equation 4.24 and differs from the method employed in Section 4.9.2.7. To the best knowledge of the author, this is the first example of this type of analysis being applied to time-resolved XRD, as well as spatially-resolved XRD-CT, of copper-based LT-WGS catalysts.$^6,^{103,174}$

\[
\alpha = 8.3 \left[ \left( \frac{\sin \theta_{200}}{\sin \theta_{111}} \right)_{\text{ideal}} - \left( \frac{\sin \theta_{200}}{\sin \theta_{111}} \right)_{\text{exp}} \right]
\]

*Equation 4.24: Evaluating stacking fault probability* $^6$

It is proposed that, as for methanol synthesis catalysts, the microstructure of the catalyst determines its intrinsic activity: $^6$ the greater the stacking fault probability, the more active for catalysis.

**4.9.3.3. sCZA and sCZA-Cs**

The distribution of stacking fault probabilities across the three interrogated planes of the sCZA and sCZA-Cs catalyst beds are shown in Figure 4.70 and Figure 4.71, respectively. The bottom of both beds contains a much larger $\alpha$ than the middle and top positions; Cs-promotion appears to decrease $\alpha$ here. However, this behaviour is reversed in the middle of the catalyst beds with sCZA-Cs exhibiting greater $\alpha$. For the beds reduced in 1% and 2.5% H$_2$, $\alpha$ decreases from the bottom of the bed to the top, with the sCZA beds appearing more active (refer to Appendix 7.4.11).
Sintering plays a key role here, as with the \(d\)-spacing ratio: the smaller the Cu\(^0\) crystallite size, the greater the stacking fault probability. If the temperature profile follows the grain growth behaviour – increases from the bottom of the bed to the top – it appears the formation of SFs favours lower temperatures. It would thus be expected that the bottom of both standard beds would have greater WGS activity as a result of this.

Dissolution of zinc into the copper host matrix is known to be possible for catalysts of these compositions (see Section 4.9.2.8.1). Paired with the top of the bed (outlet) being open to the atmosphere, it is possible these stacking fault probability plots would also correlate with stacking fault energy.\(^{51}\) The larger oxygen content at the top of the reactor would inhibit partial reduction of the zinc, minimising the available oxygen vacancies, and increasing the Cu-ZnO interface free energy (reduced SMSI). In comparison, the bottom of the bed receives the reducing gas free of any oxidants, allowing partial reduction of the zinc to occur, decreasing the interface energy and promoting substitutional surface-alloy formation.\(^{188}\) Along the length of the bed, water released during activation hydroxylates the ZnO(10\(\overline{1}0\)) surface promoting grain growth of the zincite support, further reducing the \([\alpha]\).\(^{117,120,121}\)
The average stacking fault frequency per x layers have also been calculated and displayed in Table 4.25 to highlight the amount of information shown across the XRD-CT planes. For reference, M. Behrens et al. found that an active CuO/ZnO/Al₂O₃ (60/30/10) catalyst for MeOH synthesis had an \( \alpha \) of ca. 0.018, which corresponds to a SF in the stacking of the (111) layers once every 56 layers.6,46

Table 4.25: The average frequency of SFs per x layers, as calculated from the XRD-CT, for the standard catalysts reduced under 5 % H₂/Ar46

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>Frequency of SFs per x layers</th>
<th>sCZA</th>
<th>sCZA-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td></td>
<td>72</td>
<td>69</td>
</tr>
<tr>
<td>Middle</td>
<td></td>
<td>60</td>
<td>49</td>
</tr>
<tr>
<td>Bottom</td>
<td></td>
<td>38</td>
<td>38</td>
</tr>
</tbody>
</table>

4.9.3.3.2. hCZA and hCZA-Cs

On first inspection of the distribution of stacking fault probabilities across the unpromoted and promoted high copper loading catalyst beds (see Figure 4.72 and Figure 4.73), the higher [Cu⁰] (or the lower [ZnO]) is detrimental to the formation of SFs. Following the explanation for the standard catalysts, this appears to be a result of weak metal-support interactions between Cu⁰ and ZnO reducing SF formation. The bottom of the hCZA bed contains the greatest stacking fault density suggesting that Cs has a greater effect on these systems. Interestingly, the \( \alpha \) appears quite uniform across the bottom and middle of the hCZA-Cs bed, perhaps indicating that the maximum number of SFs have been formed.

Figure 4.72: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the hCZA catalyst bed reduced under 5 % H₂
Figure 4.73: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the hCZA-Cs catalyst bed reduced under 5 % H₂

Table 4.26: The average frequency of SFs per x layers, as calculated from the XRD-CT, for the high copper loading catalysts reduced under 5 % H₂/Ar

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>Frequency of SFs per x layers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hCZA</td>
</tr>
<tr>
<td>Top</td>
<td>76</td>
</tr>
<tr>
<td>Middle</td>
<td>59</td>
</tr>
<tr>
<td>Bottom</td>
<td>48</td>
</tr>
</tbody>
</table>

4.10. Conclusion

In summary, it has been shown that smaller Cu⁰ (and ZnO) crystallite size and increased [ZnO] (30 wt.%, sCZA) afford catalysts with greater edge character of dislocations and stacking fault probability; it is expected that these microstructural properties would increase their water-gas shift activity. Cs-promotion of these catalysts does not appear to impact the microstructure of the active Cu⁰ component greatly; however, it does promote sintering, and may inhibit the promotional effects of the zincite.

Anisotropic strain broadening was visible in the diffraction patterns, which called for a pattern decomposition method to be used to evaluate the peaks individually. The modified Williamson-Hall method confirmed this and, thus, the presence of microstructural defects (Section 4.9.2.4). In order to characterise the type of linear defects/dislocations, Equation 4.22, as determined by T. Ungár et al., was employed. Here, the high copper loading catalysts served as a comparison for the role of the zincite support; it was hypothesised that increased [ZnO] promoted the formation of dislocations with more edge character which was favoured during activation under the more forcing 5 % H₂ atmosphere (most evident for the unpromoted catalysts, see Section 4.9.2.5). The line profiles of the Cu⁰ reflections were also interrogated (Section 4.9.2.6 and 4.9.2.7); more specifically the positions of the (111)- and (200)- reflections, highlighting the presence of intrinsic stacking faults in all investigated systems, though most prevalent in the
standard catalysts. During reduction, these peak positions shifted towards each other, implying that the microstructural properties of the active component evolve as full reduction is achieved. Initial calculations of the stacking fault probabilities along the length of the catalyst beds were also conducted; it was found that the unpromoted catalysts contained more stacking faults following activation than their promoted equivalents, and greater stacking fault probability favoured higher $[\text{H}_2]$ at the bottom of the catalyst beds, as well as smaller Cu$^0$ size due to decreased temperature.

Following analysis of the Cu$^0$ crystallite sizes (Section 4.9.2.2), it is supposed that a temperature gradient is present along the length of the microreactor set-up (i.e. from the cold delivery of gases, and the open reactor outlet). In an attempt to affirm this, the calculated Cu$^0$ unit cell $a$ parameters were extrapolated to derive the temperature (see Appendix 7.4.3), but these proved unreliable. Consequentially, the possibility of substitutional impurities had to be considered (Section 4.9.2.8). It was deemed unlikely that a Cs/Cu alloy could have formed, but possible that zinc dissolved into the copper matrix. Probing of the catalyst surface using AP-XPS showed that brass alloy formation occurs under severe reducing conditions for the sCZA and sCZA-Cs systems, therefore it is not unreasonable to assume that, in less reducing atmospheres, partial reduction of the zinc could occur, forming a surface-alloy due to SMSI. This lends itself as an explanation as to why the dislocations in the 5% H$_2$ studies have greater edge character in the unpromoted standard studies, and so a greater concentration of stacking faults (alloys possess lower $\gamma_{\text{SFE}}$).

When the impact of the caesium promoter is considered, its role as an electronic promoter appears to have the most dominant effect on early onset deactivation. Incorporating caesium as a promoter increased the sintering effects of the active component. It was determined that this was due to Cs preferentially chemisorbing to the surface of the Cu$^0$ and promoting water dissociation on the catalyst surface. It then also became clear that the water produced during reduction interacted with the zincite support, facilitating surface diffusion and causing growth of the ZnO crystallites via Ostwald ripening. Despite the AP-XPS studies suggesting reduction of the zincite support is facilitated by the addition of Cs, the electronic properties of the Cs-promoter ultimately dampen the promotional effects of the zincite.

The above analyses and conclusions were drawn from the point measurements collected along the length of the bed, which correspond to the most common way of conducting research, using bulk averaging techniques. The XRD-CT data served to act as both a reliability test of the data, and to highlight any spatial variation in the particles across the planes of the interrogated catalyst beds. This was done in three stages: (1) the intensity was first plotted to show that the strain induced anisotropy of the copper microstructure was uniform across and along the length of the bed (Section 4.9.3.1), (2) the $d$-spacings ratios of the (111)- and (200)-peaks were consulted to help elucidate the effect sintering has on the FCC crystal structure (Section 4.9.3.2), and finally, (3) the stacking fault probability was then graphically represented across the top, middle, and
bottom of the catalyst beds (Section 4.9.3.3). It was determined that $\alpha$ increases with increasing zinc content, and that Cs-promotion impacts this, not only by causing sintering of the active component and thus reducing the stacking fault probability, but also by inducing growth of the zincite crystallites, reducing any SMSI which inhibits formation of the ZnO$_x$ overgrowth.

Within this chapter, only the microstructure of the active copper component has been considered. This is because planar defects are most prominent in FCC materials; however, stacking faults are also prevalent in HCP materials, such as wurtzite ZnO, and would warrant further investigation.\textsuperscript{189–192}

4.11. Bibliography


86. U. Costantino, F. Marmottini, M. Sisani, T. Montanari, G. Ramis, G. Busca, M. Turco and


1720–1730.


Chapter 5: **Industrial Scale-Up and Testing of the Effects the Activation Procedure Has on Catalyst Pellet Composition**

5.1. **Introduction**

Industrial Cu-based LTS catalysts purchased from a manufacturer are typically supplied in their oxidic form and therefore require activation via in situ reduction on installation in the reactor to complete catalyst preparation.\(^1,2\) The activation procedure is stipulated by the manufacturer depending on the customer’s intended reactor set-up.\(^2\) It is exceptionally important to carry out the reduction gradually as the process is highly exothermic e.g. CuO/ZnO/Al\(_2\)O\(_3\) catalysts with 30-35 wt.% CuO evolve 340 kJ of heat per kg of catalyst, which can cause a temperature fluctuation of 500 °C;\(^1,3\) hence care must be taken to ensure the heating ramp rate is slow and controlled as Cu metal particles sinter at elevated temperature.\(^3,4\) Of all industrial processes requiring catalytic reduction, those listed in Table 5.1 are considered most important and each requires different activation procedures.\(^2\)

*Table 5.1: Industrial processes which require catalyst activation via reduction*\(^2\)

<table>
<thead>
<tr>
<th>Catalytic process</th>
<th>Catalyst reduction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming of hydrocarbons</td>
<td>NiO → Ni(^0)</td>
</tr>
<tr>
<td>High-temperature shift (HTS) reaction</td>
<td>Fe(_2)O(_3) → Fe(_3)O(_4)</td>
</tr>
<tr>
<td>Low-temperature shift (LTS) reaction</td>
<td>CuO → Cu(^0)</td>
</tr>
<tr>
<td>Methanation</td>
<td>NiO → Ni(^0)</td>
</tr>
<tr>
<td>Ammonia synthesis</td>
<td>Fe(_3)O(_4) → Fe(^0)</td>
</tr>
</tbody>
</table>

* Reduction of the active component is solely reported here

Water presence in the reactor is known to facilitate sintering, not only of the active component, but also of the support. D. Dollimore and P. Spooner found that ZnO sintered in the presence of H\(_2\)O\(_(g)\) at ca. 450 °C and increased with rising pressure due to excess Zn on the oxide surface.\(^5\) Though this temperature is greater than the LTS reactor conditions, it is still a possible source of deactivation that must be considered.

\[
\text{Zn + H}_2\text{O}_(g) \rightarrow \text{ZnO}_((s)) + \text{H}_2(g)
\]

*Equation 5.1: Reaction between excess zinc on the catalyst surface with H\(_2\)O*\(^5\)
Despite it being well documented that the presence of water in the reducing gas mixture can accelerate the sintering process, it is of particular interest how H₂O provokes structural changes within the catalyst pellets. Understanding this may elucidate early onset deactivation mechanisms that have not previously been taken into account. During a full-scale plant reduction, there are three possible sources of water:

1. The final CuO/ZnO/Al₂O₃ catalysts generally contain a small amount of precursor. Therefore, water is already present in the catalysts in the form of hydroxides or hydroxycarbonates or, in the case of hydrotalcites, co-intercalated water is present prior to activation. During catalyst pellet production, water is also added as a binding agent and lubricant which is discussed in Section 5.1.4.

2. Water is a by-product of the reduction of CuO by hydrogen and the amount produced correlates directly to the [H₂] in the reducing gas stream. Consequently, the reduction of a commercial catalyst is run in a dilute [H₂]/inert atmosphere over the course of a few days as it is known that water generated in situ can lead to sintering of the Cu₀ and ZnO components.

3. The third source of water is added up-stream of the low-temperature shift reactor. The active phase of the HTS catalyst is magnetite, Fe₃O₄, which requires steam to be added in order to prevent the catalyst from over-reducing to Fe₀ during reduction; the H₂O/H₂ ratio must surpass 0.18 to ensure Fe₃O₄ is stable. Before the feed gas enters the LTS reactor from the HTS reactor, it is cooled to ca. 200 °C via indirect or direct heat exchange (depending on the reactor set-up), but the water is not removed.

5.1.1. **The Role of the Cs-Promoter**

Promoting the active copper component in low-temperature CuO/ZnO/Al₂O₃, water-gas shift catalysts with Cs has proven to increase the rate of the forward WGS reaction by, essentially, removing the rate-determining step of dissociative water adsorption. It is suggested by C. T. Campbell et al. that this proceeds via Equation 5.2 (a) and (b), then (c):¹¹

\[
\begin{align*}
\text{(a)} & \quad 2\text{H}_{(a)} \rightarrow \text{H}_2 \\
\text{(b)} & \quad \text{OH}_{(a)} \rightarrow \text{H}_{(a)} + \text{O}_{(a)} \\
\text{(c)} & \quad \text{H}_2\text{O} + \text{O}_{(a)} \rightarrow 2\text{OH}_{(a)}
\end{align*}
\]

*Equation 5.2: Proposed mechanisms for the dissociation of adsorbed water over Cs-promoted Cu-based LTS catalysts during the forward WGS reaction; the subscript “(a)” refers to an adsorbed species.*¹¹

It is not likely that CsOH_{(a)} would form in situ due to the highly endothermic nature of the reaction at room temperature (ΔG^{298K} = 128.5 kJ mol⁻¹), and a Cs coverage of θ^CS_{(a)} ≥ 0.5 is needed (where θ^CS = 1 describes a saturated monolayer of Cs atoms). Typically, in industrial Cs-
promoted LTS catalysts, the Cs coverage is better described as $0 \leq \theta_{\text{Cs}}^* \leq 0.5$ which corresponds to the range Cs-stabilised $\text{OH}_{(a)}$ species rather than $\text{CsOH}_{(a)}$, instead more readily form.$^{11}$

Cs promoters (in the form of Cs$_n$ or in complexes with O$_n$ and OH$_n$) have been shown to cause a marked decrease in the work function of Cu complexes, improving their catalytic activity. The Cs and its surface complexes adsorb to the surface via strong dipole moments, where the negative end points towards the surface of the Cu, allowing Cs to stabilise $\text{O}_{(a)}$, $\text{OH}_{(a)}$ and $\text{H}_2\text{O}_{(a)}$. Stabilization of these species thus decreases the water dissociation activation barrier, which is one of the rate-determining steps.$^{12}$

The interactions between Cs/Al$_2$O$_3$ and Cs/ZnO have been previously investigated under UHV.$^{14-16}$ It is known that Cs atoms wet the Al$_2$O$_3$, forming strong chemisorption bonds, as Cs$_2$O is thermodynamically stable (Figure 5.1).$^{14}$ The adsorption of caesium on zincte via the non-polar (10\overline{1}0) and the O-terminated (000\overline{1}) faces is also well established; superstructures formed on the ZnO(000\overline{1})-O surface are strongly bound and can only be removed from the surface when exposed to temperatures ca. 730 °C, whereas adsorbed Cs can be removed from the ZnO(10\overline{1}0) surface at temperatures $< 380$ °C.$^{15}$ When caesium is adsorbed on the surface of both Al$_2$O$_3$ and ZnO supports, a significant increase in the binding energy of the support is seen showing that Cs acts as an electron donator to the oxides.$^{14,16}$

Despite ZnO and Cs$_2$O possessing similar stabilities to form oxides, zinc does not suitably wet the alumina surface to have a substantial impact on the oxides’ electronic properties; this behaviour has also been seen for copper.$^{14}$ However, it has been shown by Chaturvedi and Rodriguez that when Cu is introduced to a Cs/ZnO system, Cs migrates to the surface of the Cu overlayer from the alkali-oxide interface. Caesium has a very low surface free energy (0.067 J m$^{-2}$) which promotes this migration, making it feasible to form strong Cs-Cu bonds.$^{16,17}$ On average, the bonds between Cs-Cu are stronger than Cs-ZnO as it is more energetically favourable for Cs to donate into the empty Cu(4s,4p) band than the empty Zn(4s,4p) band of ZnO. Therefore, Cs prefers to be bonded to Cu in the Cs/Cu/ZnO system.$^{16}$

5.1.2. Ellingham Diagram

Ellingham diagrams allow the stability of compounds to be evaluated at different temperatures according to their standard Gibbs free energy change, $\Delta G^\circ$. This type of plot can be used to determine the conditions at which oxides, nitrates, sulphides, chloride, etc., will form, though the oxide diagram is most common. Ellingham diagrams can be used to investigate an array of heat treatments but, for the purpose of this chapter, will only be considered to determine whether a metal oxide will reduce at differing $[\text{H}_2:\text{H}_2\text{O}]$ at a given temperature.$^{18}$

$\Delta G^\circ$ is calculated according to Equation 5.3; unless a phase change occurs, both the standard enthalpy and entropy of a reaction for a given compound, $\Delta H^\circ$ and $\Delta S^\circ$ respectively, do not vary with temperature, therefore the Ellingham diagram consists of a series of straight lines. Each reaction presented on the Ellingham diagram is normalised to consume one mole of O$_2$ to
ensure easy comparison.\textsuperscript{18} The standard enthalpies and entropies used can be found in Appendix 7.5.1.

\[ \Delta G^\theta = \Delta H^\theta - T \Delta S^\theta \]

Equation 5.3: The standard change in Gibbs free energy

An example of an Ellingham diagram concerning activation of the LT-WGS catalyst is detailed in Figure 5.1. The reactions that may occur during activation by reduction of hydrogen have been included. The position of the lines in the graph dictate the stability of the resultant oxide as a function of temperature. For example, the \( 2\text{Cu}(s) + \text{O}_2(g) \rightarrow 2\text{CuO}(s) \) reaction at the top of the diagram is considered the least stable oxide and is therefore easily reduced. Towards the bottom of the diagram, the oxides are harder to reduce due to the more reactive nature of the metals. \( \text{Al}_2\text{O}_3 \) is barely visible on this graph as it is exceptionally stable, especially in the given temperature range. A useful piece of information that can be gleaned from this diagram is that Zn metal has the capability to reduce the metal oxides whose reaction lines occur at higher \( \Delta G^\theta \).\textsuperscript{18}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ellingham_diagram.png}
\caption{Ellingham diagram exhibiting free energy changes for the oxidation of H\(_2\)O, CuO, Cu\(_2\)O, ZnO, Cs\(_2\)O and Al\(_2\)O\(_3\) with varying temperature}
\end{figure}

\subsection{Plug Flow Reactors}

When deciding the type of catalytic reactor to utilise, the desired reaction and fundamental reaction variables must be considered; these include temperature, pressure, residence time, reactant properties, mass transfer between phases, and the type of catalyst.\textsuperscript{19} Plug flow reactors (PFRs) are generally used in industry when investigating systems which employ a solid
catalyst. The catalyst is installed in the cylindrical reactor, either inside tubes (within a reactor vessel) or as a bed, and the fluid is passed through the catalyst.\textsuperscript{20,21} When discussing PFRs, it is common to refer to the reactants as a fluid; this term encompasses gases, liquids and slurries.

Tubular reactors describe any reactor with a large length to diameter ratio (L/D); the term is also used synonymously with fixed bed reactors which are comprised of a bed of pellets (typically 3-50 mm diameter) and are predominantly used for gas-solid homogeneous and heterogeneous catalytic reactions.\textsuperscript{19,22} Due to the continuous operation of most tubular reactors, the impact of the fluid flow on the rate of reaction and the extent of the chemical reactions occurring inside must be modelled. This is done by considering the velocity distribution within the reactor; as fluid flows through a tube, the position of the highest velocity is located at the centre and the lowest at the wall, making the radial velocity distribution nonuniform.\textsuperscript{22}

The plug flow reactor model consists of three assumptions for continuous flow operation: (1) the reactor is run at steady-state, (2) plug flow is achieved when the fluid progresses in a flat velocity profile through the bed, and (3) at any cross-section in the reactor perpendicular to the flow, there is no temperature variation or spatial variation in species concentration.\textsuperscript{23} To summarise, all fluid particles have the same velocity and so remain in the PFR for equal duration, and only radial mixing occurs (no axial mixing). However, in reality, a flat fluid velocity profile is rare and, especially for reactors with large diameters, a temperature gradient is present and species composition varies throughout the bed, making the model only representative of industrial reactors.\textsuperscript{23}

\subsection*{5.1.4. Granulation and Pelletizing}

Commercial CuO/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts can be installed in industrial reactors in the form of pellets, extrusions or spheres, depending on the type of reactor.\textsuperscript{24} The low-temperature water-gas shift catalyst is, however, supplied as a cylindrical pellet for adiabatic plug flow reactors, therefore, this is the only type of pellet considered in this chapter.\textsuperscript{5} It is important to reinforce that the purpose of this study is not to design an optimum catalyst pelletizing procedure, rather the aim is to reproduce pellets that are comparable to those used in industry. Despite the global catalyst market being valued at 25.0 billion USD in 2018, and projected to grow to 34.1 billion USD in 2025, there remains a gap in knowledge transfer between industry and academia.\textsuperscript{25,26} This is most likely due to commercial reasons, thus industry specifications and precise methodologies for pellet manufacture are not shared.

Once the LT-WGS catalyst has been coprecipitated, filtered, dried and calcined, the next stage is to manufacture the catalyst pellets. Catalyst powders as produced cannot be installed in industrial reactors as it would cause huge pressure drops to occur across the bed, therefore, a high-pressure agglomeration/shaping technique, known as pelletizing, is employed.\textsuperscript{27-29} Pelletizing requires a punching tool to compress the powder in a die, applying forces in the range of 100-4000 atm, producing catalyst particles with high shape accuracy.\textsuperscript{27,29} Though the compression
operation is detrimental to the activity of the catalyst, it is essential to install a hard catalyst particle for vapour- or liquid-phase fixed bed reactors, typically in the range of 3-6 mm, with a narrow particle size distribution to reduce the void fraction of the packed bed, and thus the pressure drop.\textsuperscript{30,31}

A pellet can either be produced by direct compacting of the catalytic powder or by converting the powdered material into granules prior to pelletizing. The latter method is most commonly employed to ensure even distribution of the active component throughout the pellet. It can also improve flow properties by increasing the density of the powder and decreasing the total surface area of particle-particle contacts, thus reducing friction between particles. This results in a more uniform filling of the die, resulting in the production of pellets with optimum strength.\textsuperscript{8,31}

Granulation produces larger aggregates, or granules, \textit{via} dry granulation, in which powders are compacted to form the granulate, or by wet granulation, where the powder is agglomerated using a liquid binding agent (water is used for the majority of catalysts).\textsuperscript{8,31} For CuO/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts, it is typical to pelletize with a dry-produced granulate, though there is a need for a lubricant to improve its mechanical strength.\textsuperscript{8}

Literature concerning the use of lubricants states that the amount of lubricant required is between 0.5-3 wt.\%, and is dependent on the material’s tensile strength, moisture content and mesoporosity.\textsuperscript{29,30} Examples of lubricants include graphite, water, talc, stearic acid, magnesium oxide, polyethylene, waxes and greases.\textsuperscript{27,29,30} As the LT-WGS reaction is carried out at relatively low temperature, organic lubricants are not utilised as they oxidise and burn out of the pellet during reaction, compromising the integrity of the pellet. For this reason, graphite is incorporated as it only begins decomposing at temperatures above 787 °C; however, all graphite contains a small amount of ash (a silicate mineral) as an impurity which is catalytically harmful.\textsuperscript{30,32} Nevertheless, it is the most widely used lubricant as its benefits in the manufacture of abrasion-resistant, hard pellets outweigh its negative effects on overall catalytic activity.\textsuperscript{30}

The final pellets’ mechanical strength is dependent on the punch motion rate of the press and the pressure applied. Too high a compacting pressure causes wear of the machine, generating pellets with cracks. Ideally, the pellet would be formed with a slow pressure growth resulting in total deaeration of the catalyst powder and reducing pellet heating effects. Incorporating small quantities of water (1-3 wt.\%) as a binding agent allows lower pressure to be used as it promotes
particle adhesion. The exact amount is determined experimentally, depending on the resultant average mechanical strength of the pellet.\textsuperscript{8}

Any pelletizing conducted in an academic lab is typically carried out batchwise using a benchtop single punch-and-die pellet press. This is manageable when working with small amounts of catalyst (< 50 g); however, for industrial scale-up a continuously run rotary machine is used (Figure 5.3).\textsuperscript{27} Maintenance of the rotary pellet press is essential to ensure reproducibly strong pellets are produced. Wear of the pellet dies can cause disking and cracking of the pellets on ejection, rendering them useless. Prior to total failure, pellets may be generated that do not show obvious signs of strain but, when employed, cause the pellet to disintegrate into powder.\textsuperscript{30} Therefore, in this study all pellets were meticulously checked before installing in the flow reactor.

![Schematic of an industrial pelletizing machine](image)

*Figure 5.3: Schematic of an industrial pelletizing machine; image of a Stokes-Merrill pelletizing machine taken from A. B. Stiles and T. A. Koch, Catalyst Manufacture, CRC Press, 2\textsuperscript{nd} edn., 1995, ch. 9, pp. 85-98.\textsuperscript{30}*

5.1.4.1. Mechanical Strength Testing

In typical academic studies, as in Chapter 4, catalyst sieve fractions are utilised as the reactions investigated are carried out either in a microreactor in a lab or using a synchrotron-based technique. This only requires small amounts of catalyst; therefore, the structural integrity of the sieve fraction is not evaluated. This chapter not only considers the effect of the activation procedure on the phase composition of the pellets, but also on the pellets’ mechanical strength.
Before a catalyst can be installed in an industrial reactor, the mechanical strength of the solid catalysts must be investigated. If a catalyst were to fail due to decreased pellet strength, a large pressure drop could develop across the catalyst bed, causing a maldistribution of fluid flow. Not only would this inhibit the installed catalyst’s performance, but it could lead to further issues causing the plant to shutdown, with detrimental economic consequences.  

When assessing the structural integrity of pellets, pre- and post-reaction, it is essential to evaluate the probability of the pellet fracturing under a stress event. As shown in Figure 5.4, there are three possible outcomes of applying pressure to pellets: (1) some surface breakage and weakening occurs within the pellet, (2) shows a transition from surface to body breakage, and (3) all pellets undergo complete body breakage due to the increased stressing intensity. By studying these properties, mechanical degradation as a result of the activation procedure can be assessed.  

![Figure 5.4: Typical sigmoid plot depicting the probability of pellet breakage; image taken from L. M. Tavares, P. P. Cavalcanti, R. M. de Carvalho, M. da Silveira, M. Bianchi and M. Otaviano, Powder Technol., 2018, 336, 546-554.](image)

5.1.4.2. Capillary Condensation

A catalyst pellet’s pore structure is determined by the manufacturing process, in this case fine microporous particles are compacted to form a pellet. Once the granulate has been pressed in the rotary press, the void space between the catalyst particles creates an irregular pore network structure (Figure 5.5 (a)). Most catalysts’ porous structure can be described as polydisperse, though it is common to consider industrial supported alumina catalyst pellets as having bidisperse globular structures composed of micro- and macropores. In this model, the micropores are contained within a globule, and the macropores are between the globules. It is within the microporous particles that the majority of the nanoparticles of the active component (Cu⁰) are located. Therefore, the bulk of the reaction is undertaken in the micropores, and the macropores
are responsible for transporting the reactants to the active sites. Under reaction conditions, a complex array of diffusion/reaction processes occurs simultaneously, for example, adsorption-desorption, gas-liquid phase change, surface-catalysed reaction and capillary condensation.

When a single phase (gas or liquid) is fed into a fixed-bed reactor, the catalyst pores typically consist of the same phase. However, it is possible for a liquid-phase to evaporate and a gas- or vapour-phase to condense in the pores, causing a phase transition. The LTS reaction consists of a gas phase; therefore, capillary condensation can occur in pores with radii between 3 and 50 nm, when the vapour pressure is below the dew point due to capillary forces, which is a common pore diameter for industrial catalysts. Capillary phenomena are illustrated in Figure 5.5 (b) in which the larger pores are filled with gas and the smaller pores (capillaries) with liquid.

![Figure 5.5](image)

**Figure 5.5:** (a) Bidisperse globular representation of a catalyst pellet and (b) an illustration of the catalyst pores; images taken from N. M. Ostrovskii and J. Wood, Finely Dispersed Particles: Micro-, Nano-, and Atto-Engineering, eds. A. M. Spasic and J.-P. Hsu, Taylor & Francis, 2006, ch. 23, pp. 601-640.

The nature of capillary condensation is stochastic, but the effects are well known. By partially filling the pellets with liquid, the available surface area and pore volume for the gas-phase reaction to occur is decreased. This causes catalyst poisoning to varying degrees as pores can become blocked or disconnected from the feed gas at the pellet surface. Therefore, the reaction rates are determined by the pore structure’s mass transport limitations and the capillary vapour-liquid equilibria as the reaction kinetics differ between the gas- and condensed liquid-phases. Additionally, under LT-WGS conditions, if capillary condensation occurs and the catalyst pores contain condensed H$_2$O, a sudden change to the reactor conditions, e.g. a spike in temperature, could cause the pellets to fracture if the generated steam cannot escape fast enough.
5.2. Experimental Details

5.2.1. Catalyst Preparation at Yara Technology Centre, Porsgrunn, NO

To prepare the hydroxycarbonate CZA (CuO/ZnO/Al₂O₃) catalyst precursor, a mixed solution of Cu, Zn and Al nitrates (1 M, 10 L) was used at a ratio of 0.6:0.3:0.1, respectively. Two peristaltic pumps (Watson Marlow, 520Di) were used to prime two centrifugal pumps to dispense the mixed metal nitrate solution and precipitating agent (Na₂CO₃, 1.2 M) into H₂O (15 L, 65 ºC). Whereas during the lab-based synthesis the coprecipitation and ageing occurred in the same vessel, here, in order to scale-up the process, the precipitation occurred in a smaller vessel that fed into a larger reaction tank (ca. 50 L). Within the precipitation vessel, the mixture was stirred using a mechanical overhead stirrer (IKA, RW20 digital) at 65 ºC. The pH was maintained at 7 by adjusting the flow of the Na₂CO₃. The pH probe was calibrated at pH 4, 7 and 10 before each coprecipitation. Following precipitation, ageing occurred in the larger reaction tank for 2 h at 65 ºC and pH 7 (via metal nitrate addition) with continuous stirring (IKA, RW28 digital). The precipitate was then split into two batches, filtered (SP Bel-Art, 24” ID vacuum filter), washed with ca. 10 L H₂O several times to remove residual NaNO₃, and dried in air at 80 ºC for 15 h. Following each washing cycle, samples of the precipitate were taken and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES); this was carried out by SINTEF Molab, Porsgrunn, NO and the results are given in Appendix 7.5.2. The dried filter cake was then blended into a fine powder.

The promoted CZA-Cs catalyst was prepared via incipient wetness impregnation. Half of the prepared hydroxycarbonate CZA precursor (1.5 kg) was impregnated with an aqueous solution of ca. 1 wt.% Cs₂CO₃, the amount of which was determined by the precursor’s pore volume. Once impregnated, the CZA-Cs catalyst was dried in air at 80 ºC for a further 15 h.

Finally, the CZA and CZA-Cs catalyst precursors were calcined in (static) air at 300 ºC (5 ºC min⁻¹) for 10 h.

5.2.2. Granulation and Pelletizing

Once the catalytic material was calcined, 1 wt.% graphite was blended in. The catalytic material was then pressed cold isostatically (CIP) at 10,000 psi using a Loomis wet bag isostatic press. These compacts were then crushed and sieved so that the particle size was between 0.2-0.5 mm. The desired particle size range was determined experimentally according to Table 5.2.

Table 5.2: Effect of sieve fraction used on overall radial crush strength of catalyst pellets as determined from a single punch-and-die pellet press at a force of 300 kg for 30 sec; standard deviations are shown in the brackets

<table>
<thead>
<tr>
<th>Sieve fraction / mm</th>
<th>0.2-0.3</th>
<th>0.3-0.4</th>
<th>0.4-0.5</th>
<th>0.2-0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average hardness / N</td>
<td>50(2)</td>
<td>49(4)</td>
<td>47(1)</td>
<td>51(3)</td>
</tr>
</tbody>
</table>

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An additional 3 wt.% graphite was added to coat the particles to act as a lubricant, as well as 1 wt.% H₂O, which was left to equilibrate overnight in an airtight container. The pellets were then pressed in a Kilian Eifel H rotary pellet press, equipped with 20 dies; each containing four 5 mm diameter cavities. The upper and lower punches were concave, so slightly domed pellets were produced.

A Dr Schleuniger Pharmatron SmartTest 50 semi-automatic tablet testing system was employed to evaluate the mass, diameter, height and hardness of each pellet via single particle strength (SPS) testing. It has the capability to test the crush strength of pellets up to 500(1) N. These measurements were carried out by Yara Technology Centre, Porsgrunn, NO. It is widely accepted that in order to reliably evaluate the mechanical strength of pellets, 20-30 pellets should be tested and this has been done where possible.

5.2.2.1. Pre-hydrating pellets

For some tests, the pellets were pre-hydrated with 20 wt.% H₂O; this was achieved by adding the calculated amount of water to the bottom of a vacuum desiccator, placing the pellets on the ceramic metal desiccator plate, sealing it, and then leaving it to equilibrate overnight; therefore, the pellets did not come in contact with the water, only the water vapour.

5.2.3. Ex situ Characterisation

Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS 10 FT-IR spectrometer at a spectral resolution of 2 cm⁻¹, accumulating 64 scans. Prior to loading a sample, 32 background scans were collected. Subsequent spectra were annotated using ACD/Spectrus.

Chemical compositions of the catalyst samples were determined by X-ray fluorescence (XRF). This was measured using a PANalytical Epsilon 3-XL spectrometer at the ISIS Materials Characterisation laboratory, Harwell, UK, and analysed using Epsilon 3 software.

Using a TA TGA Q50, the thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) profiles were measured in a flow of air at a heating rate of 20 °C min⁻¹ from room temperature to 900 °C, with an isothermal time of 90 min. The sample holder was made of platinum, and brass tweezers were used when handling it. TA Universal Analysis software was used to view and analyse the results.

Mercury porosimetry measurements were carried out by Yara Technology Centre, Porsgrunn, NO, using a Micromeritics Autopore IV 9500 in accordance with the ASTM International standard test method for determining catalyst pore volume distributions (D4284-12). Approximately 4-5 pellets were sampled across the catalytic bed for each measurement, allowing pore volume distributions from 450 μm to 4 nm to be determined.

Temperature-programmed reduction (TPR) experiments were carried out in a ChemBET Pulsar TPR/TPD instrument, which is a Quantachrome automated chemisorption analyser. As stated in Section 2.3.2, reduction profiles are known to be heavily influenced by the experimental
conditions; therefore, the operating variables \((S_0, F, C_0\) and \(\beta)\) were chosen to ensure \(0.9 < K < 2.3 \text{ min}\) and \(P < 20 \text{ K}\) were satisfied.\(^{38,39}\) Each sample was heated to 400 °C \((10 \text{ °C min}^{-1})\) in 30 mL min\(^{-1}\) of 10 % H\(_2/\text{Ar}\). The amount of sample reduced was dependent on the amount of Cu present in the investigated catalyst.

X-ray diffraction measurements were collected with Cu-K\(_{\alpha1}\) \((\lambda = 1.5406 \text{ Å})\) radiation using an accelerating voltage/current of 40 kV/20 mA respectively, on a Rigaku Miniflex 600 powder diffractometer equipped with a D/teX Ultra detector at ISIS Materials Characterisation laboratory, Harwell, UK. The diffractograms were recorded using the Miniflex Guidance software in a continuous mode between 3-65 °2\(\theta\) with a step size of 0.01 °. A divergence slit of 1.25 ° was used for all scans. All samples \((100 \text{ mg})\) were mixed with an internal standard \((20 \text{ wt.\%}, \text{quartz, see Appendix 7.5.3})\) using an agate pestle and mortar and pressed into low background silicon sample holders \(\text{(see Appendix 7.5.4 – 4 sample holders were utilised; all position 1 diffraction patterns were measured using sample holder 1, all position 2 patterns were measured using sample holder 2, etc.)}\), creating a compact powder to optimise intensity of the diffraction patterns. Pattern fitting and phase analysis of samples taken from 4 positions in the catalyst bed \((\text{with 1 representing the top, and 4 the bottom of the bed})\) were carried out using the Rietveld method as implemented in TOPAS5.

The instrument parameter file was built from information extracted from Rietveld analysis of the ZnO 674b NIST standard reference material that was collected solely for calibration purposes \(\text{(see Appendix 7.5.5).}\) The background was fitted using a Chebyshev polynomial and a modified Thompson-Cox-Hastings pseudo-Voigt (PV-TCHZ) peak type was used to fit the diffraction peaks. For the Rietveld refinement, a ZnO CIF file was obtained from the ICSD database \(\text{(ICSD #: 157724).}\)

Rietveld analysis is preferred to single peak analysis as its whole-pattern fitting approach allows quantitative phase analysis with minimal errors/inaccuracies associated with preferred orientation, microabsorption, overlapping peaks, particle statistics and the presence of amorphous/trace phases. However, in order to detect amorphous phases, a known amount of a crystalline internal standard \((\text{IS}),\) whose crystal structure is known, must be incorporated. This is known as the internal standard method whereby the amorphous content of a sample is derived from the Rietveld result for the IS compared with the inputted dosage \(\text{(Equation 5.4); this method is suitable if the amount of IS added is} \geq 20 \text{ wt.\%}, \text{as it has been for all catalyst samples investigated in this chapter.}\)^{40}

\[
W_{\text{Amor}} = \frac{1 - \frac{W_{\text{IS}}}{R_{\text{IS}}}}{100 - W_{\text{IS}}} \times 10^4
\]

\textit{Equation 5.4: Weight fraction of amorphous content using the internal standard Rietveld method}
Where \( W_{\text{Amor}} \) = weight fraction of amorphous content / wt.%
\( W_{\text{IS}} \) = amount of added IS / wt.%
\( R_{\text{IS}} \) = Rietveld weight fraction of IS / wt.%

5.2.4. Activation Tests

The 0.06 cm ID (53.5 cm length) stainless steel reactor was loaded with CuO/ZnO/Al\(_2\)O\(_3\)-(Cs\(_2\)O) catalyst (40 pellets, bed length of ca. 16 cm) supported on quartz wool. This was then installed in the commissioned flow reactor set-up as illustrated in Figure 5.6. Once leak checked, the system was flushed at room temperature with Ar, pressurised to 20 bar, before heating to 160 °C (5 °C min\(^{-1}\)) in Ar (100 mL min\(^{-1}\)), and holding for 30 min. If a wet atmosphere (20 vol.% H\(_2\)O) was required, deionised water (0.02 mL min\(^{-1}\), 18.2 MΩ cm\(^{-1}\)) was introduced into the system via an HPLC pump (see Figure 5.6 (a)) at 160 °C. The catalyst was then reduced in flowing H\(_2\) (1 % and 5 %) in Ar (100 mL min\(^{-1}\)) up to 220 °C (1 °C min\(^{-1}\)) and held at this temperature for either 24 h or 48 h. The GHSV was 1233 h\(^{-1}\). The outlet of the reactor was monitored via GC (Shimadzu GC-2014).

Once activated, the catalyst was cooled to room temperature in Ar and then passivated following the protocol outlined in Table 5.3. The two gas bottles used were a 10 % O\(_2\)/He mix and a 100 % Ar. Throughout passivation, the temperature was monitored to ensure no exotherms were triggered.

Table 5.3: Method for passivation

<table>
<thead>
<tr>
<th>[O(_2)] / %</th>
<th>0.2</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>5.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time / min</td>
<td>60</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>60</td>
<td>≥ 150</td>
</tr>
</tbody>
</table>

5.2.4.1. Designing and commissioning the flow reactor set-up

In order to successfully incorporate steam into the pressurised, reducing atmosphere, the set-up of the fixed bed reactor at Research Complex at Harwell needed to be altered.
Figure 5.6: Process flow diagram of the high-pressure microreactor; indicated on the diagram are the (a) high-pressure pump, (b) expansion volume, (c) fixed bed reactor with heating jacket, (d) hot catch-pot, (e) condenser, (f) cold catch-pot

As shown in Figure 5.6 (c), a Parr 5400 tubular reactor system has been commissioned; the tubular reactor was placed vertically within a split tube single zone furnace (Vecstar, VT-SP F3790). The 0.06 cm ID stainless steel reactor (Swagelok, SS-T8M-S-1.0M-6ME-S) was chosen so that the pellets fit snugly, one on top of the other, to ensure any gradient present along the bed would be identifiable on a pellet-by-pellet basis. The thermocouples (TCs) employed in the flow reactor set-up are Parr Type-J (iron-constantan) that are regulated from the set-point temperature by a proportional integral derivative (PID) controller to maintain the furnace temperature. This set-up includes two TCs: TC1, which is an internal thermocouple that is placed after the expansion volume to ensure the water/gases are suitably heated by the heat-tape, and TC2, which is an external thermocouple located in the middle of the heated zone of the furnace close to the reactor. For the purpose of all activation procedures investigated, TC2 was used to monitor/control the reactor temperature (temperature profile can be found in Appendix 7.5.6).

The set-up is equipped with three Brooks SLA5850 Delta Smart 2 mass flow controllers (MFCs). These deliver the inert (Ar), reducing (H₂/Ar) and oxidising (O₂/He) gases to the reactor
and operate with a minimum flow of 3 mL min\(^{-1}\) and a maximum flow of 100 mL min\(^{-1}\). The high-pressure pump which delivers water to the system is a Series III Isocratic HPLC Pump (Scientific Systems) equipped with a 10 mL stainless steel self-flushing pump head (0.01-10 mL min\(^{-1}\)). The flow of deionised H\(_2\)O (18.2 MΩ cm\(^{-1}\)) was calculated according to Equation 5.5.

\[
\text{Required flow of } H_2O = \left( \frac{0.1 \text{ L min}^{-1}}{22.4 \text{ L mol}^{-1}} \right) \left( \frac{20 \text{ vol.}% H_2O}{80 \text{ vol.}% \text{Gas}} \right) \left( \frac{18.015 \text{ g mol}^{-1}}{\text{mol}} \right) \left( \frac{60 \text{ min}}{1 \text{ h}} \right)
\]

\[
= 1.2 \text{ g h}^{-1}
\]

\[
= 0.02 \text{ mL min}^{-1}
\]

*Equation 5.5: Desired flow of H\(_2\)O to achieve a water vapour concentration of 20 vol.\%*

Check valves with low cracking pressure (Swagelok, SS-2C-1/3) were chosen so that low flows could be easily maintained, if need be. The flame arresters are stainless steel in-line 7 μm particulate filters (Swagelok, SS-2F-7). The expansion volume consists of a 440 μm filter (Swagelok, SS-6F-440) packed with 1 mm glass beads (Sigma, G1152-10G) to ensure adequate heat transfer and mixing.

A hot-pot (*Figure 5.6 (d)*) was incorporated to make the flow reactor set-up more versatile for future catalytic testing. A condenser (*Figure 5.6 (e)*) was then implemented before the cold catch-pot (*Figure 5.6 (f)*) to trap all water dosed into the system and produced during activation; this is due to the back pressure regulator (Tescom, 26-1765-24-154A) not being multi-phase, therefore only the gas products were analysed by the GC.

The reactor outlet stream was analysed by a Shimadzu GC-2014 Gas Chromatograph equipped with a temperature conductivity detector (TCD). H\(_2\) and CO\(_2\) were determined on a Restek ShinCarbon ST column (2 m, 0.53 mm ID, mesh 80/100). Argon was used as the carrier gas at a flow rate of 34.9 mL min\(^{-1}\). The column oven temperature program for analysis was as follows: 0-2 min isothermal at 40 °C; 2-7.35 min 40-200 °C with a ramp rate of 30 °C min\(^{-1}\); 7.3-9.3 min isothermal at 200 °C.

An image of the fixed-bed reactor set-up is shown in *Figure 5.7*. A graphical representation of the reactor and catalyst bed has also been included to illustrate how the catalyst bed is separated into four sections for analysis purposes; the top of the bed is denoted as position 1, whereas the bottom of the bed is considered position 4.
5.2.4.1.1. Theory

The PFR model, discussed previously, is described as having a uniform flow. In reality, the flow regime is either described as laminar flow, where the radial distribution is parabolic (L/D > 200), or as turbulent flow, where the radial distribution flattens as the turbulence increases (L/D > 20), as depicted in Figure 5.8. A turbulent flow system is preferred to laminar flow as there is less of a difference in residence time of the fluid between the centre and the wall. The mechanism and degree of how the fluid mixes inside the reactor affect the temperature and species concentration along the length of the reactor. Though industrial reactors do not fully adhere to the PFR model as their conditions stray from the ideal, it is sufficient to help understand this complex physical phenomenon. For the reactor commissioned, the L/D is 86 and, therefore, turbulent.
Figure 5.8: Radial velocity distributions for (a) plug flow, (b) turbulent flow and (c) laminar flow.

Though the L/D ratio approximates the diffusion and mass transfer limitations needed to sustain plug flow conditions, it offers a useful starting point and a way in which to monitor the comparability of the results gained across different catalytic reactor set-ups. As well as this, the gas hourly space velocity (GHSV, h⁻¹) should be calculated according to Equation 5.6.

\[
\text{GHSV} = \left( \frac{\text{volumetric flow rate}}{\text{volume of catalyst}} \right) \left( \frac{60 \text{ min}}{1 \text{ h}} \right)
\]

Equation 5.6: Gas hourly space velocity equation

Another method for determining the conditions the reactor is run under is to calculate the particle Reynolds number, Reₚ. If Reₚ < 10, this represents laminar flow.\(^{41}\)

\[
\text{Re}_p = \frac{\rho_g u D_p}{\mu_g}
\]

Equation 5.7: The particle Reynolds number

Where
- \(\rho_g\) = gas mixture density / kg m⁻³
- \(u\) = superficial velocity / m s⁻¹
- \(D_p\) = catalyst particle diameter / m
- \(\mu_g\) = (dynamic) gas mixture viscosity at operating temperature / kg m⁻¹ s⁻¹

The density of the gases utilised are calculated at activation temperature according to Equation 5.8.
\[ \rho_g = \frac{P M_w}{R T} \]

*Equation 5.8: Density of gases*

Where

\( P \) = pressure / 19.74 atm

\( R \) = ideal gas constant / 0.082 L atm mol\(^{-1}\) K\(^{-1}\)

\( T \) = 493.15 K

*Table 5.4: Densities of the pure gases and gas mixtures*

<table>
<thead>
<tr>
<th>Gas mixture composition / %</th>
<th>( \rho_g ) at 20 bar / kg m(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

The superficial velocity inside the reactor is calculated to be 0.059 m s\(^{-1}\) according to *Equation 5.9*. The flow rate is kept constant at 100 mL min\(^{-1}\) throughout all the activation procedures and the internal reactor radius is 3 mm.

\[ u = \frac{Q}{A} = \frac{Q}{\pi r^2} \]

*Equation 5.9: Superficial velocity inside the reactor*

Where

\( Q \) = flow rate / m\(^3\) s\(^{-1}\)

\( r \) = reactor radius / m

The dynamic gas viscosity of the binary gas mixtures is calculated according to *Equation 5.10*, as developed by J. W. Buddenberg and C. R. Wilke.\(^{42}\) Here, the constant 1.385 is described as dimensionless. The viscosities of pure H\(_2\) and Ar at 220 °C are calculated as 1.23 \times 10\(^{-5}\) kg m\(^{-1}\) s\(^{-1}\) and 3.27 \times 10\(^{-5}\) kg m\(^{-1}\) s\(^{-1}\), respectively.\(^{43}\) The diffusion coefficient for H\(_2)/Ar\) is estimated to be 1.66 \times 10\(^{-4}\) m\(^2\) s\(^{-1}\).\(^{44}\)
\[ \mu_g = \frac{\mu_1}{1 + 1.385 \frac{\mu_1}{D_{12} \rho_1} x_2 x_1} + \frac{\mu_2}{1 + 1.385 \frac{\mu_2}{D_{12} \rho_2} x_1 x_2} \]

*Equation 5.10: Viscosity of binary gas mixtures* \(^{42}\)

Where \( \mu_1 \) and \( \mu_2 \) = viscosity of pure H\(_2\) and pure Ar / kg m\(^{-1}\) s\(^{-1}\)

\( x_1 \) and \( x_2 \) = mole fractions of H\(_2\) and Ar in the gas mixture

Once all parameters have been determined, they can be inputted into *Equation 5.7* to calculate the Reynolds number for the activation procedures under 1, and 5 % H\(_2\)/Ar; these have been calculated as 168.34 and 148.58, respectively. As previously stated, it is known that Reynolds numbers below 10 indicate the gas flow to be laminar flow. Therefore, the flow during activation is determined to be turbulent.

### 5.3. Results

#### 5.3.1. Scale-Up of Catalyst Preparation

In order to successfully manufacture catalyst pellets similar to those produced in industry, it was necessary to scale-up the lab-based coprecipitation method detailed in *Chapters 3 and 4*. Whereas before it was suitable to synthesise and test with 5-20 g of catalyst material, a minimum of 1 kg of each of the CZA (CuO/ZnO/Al\(_2\)O\(_3\)) and CZA-Cs (CuO/ZnO/Al\(_2\)O\(_3\)-Cs\(_2\)O) catalysts was required to ensure enough pellets were produced to adequately investigate how the activation procedure affected the pellet morphology and mechanical strength. All catalysts presented in this chapter were prepared by the author at Yara Technology Centre, Porsgrunn, NO.

#### 5.3.1.1. Determining Ageing Time

Previously, in the lab-based coprecipitations, problems were encountered when attempting to reproducibly prepare the desired zincian malachite precursor phase. This was largely overcome by fine-tuning the time the mother liquor was left to age. Therefore, this synthetic parameter was initially investigated in the industrial set-up by sampling aliquots from the mother liquor after 30, 60, 90, and 120 min.

XRD is used for phase identification of the prepared catalysts. As can be seen from *Figure 5.9*, the morphology of the precursor phase transforms during ageing. Despite the target zincian malachite, (Cu\(_2\)Zn\(_2\))CO\(_3\)(OH)\(_2\), precursor phase being weakly visible in the diffraction pattern after 30 min ageing time, there is evidence of either auralchalcite, (Cu,Zn)\(_3\)(CO\(_3\))\(_2\)(OH)\(_6\), or hydrozincite, Zn(CO\(_3\))\(_2\)(OH)\(_6\), due to the characteristic (200)-reflection visible at 13.1° \(2\theta\). \(^{45}\) The peak at 25.7° \(2\theta\) also corresponds to the (200)-reflection of a Cu or Zn hydroxynitrate impurity. \(^{46-48}\) It is only after 90 min that the unwanted Zn-rich secondary phase re-dissolves and
a crystalline zincian malachite phase remains. After 2 h, there is no clear change in the zincian malachite precursor phase and so the ageing process was stopped here.

![Diffraction patterns for zincian malachite, aurichalcite, and hydrozincite](image)

**Figure 5.9:** Diffraction patterns of aliquots taken from the mother liquor at different stages during ageing; the reference patterns for zincian malachite, aurichalcite and hydrozincite are given below.

The infrared spectra of the CZA precipitate also show the precursor phase evolution during ageing. It could be argued that the 30 min IR spectrum is indicative of a synthetic zincian georgeite phase having been formed; when compared to the literature, however, this is not definitive. From the diffraction pattern it is clear a Zn-rich precursor phase crystallizes during the first hour of ageing, but it is not possible to discern whether it is aurichalcite or hydrozincite. As there are no bands present at 1200 and 970 cm\(^{-1}\), respectively associated with the aurichalcite M-OH deformation band and O-H libration band, it can be concluded that it is a hydrozincite precursor phase that initially precipitates. A shoulder by the asymmetric C-O \(v_3\) stretching mode around 1353 cm\(^{-1}\) is also visible in the first two spectra; this has previously been attributed to Cu-OCO\(_2\) bonds in hydrozincite, further reinforcing this point.

In the region 1200-850 cm\(^{-1}\) (see Figure 5.10 (c)), three O-H libration bands are weakly expressed in the aliquot aged for 30 min and become more dominant as the ageing progresses to
120 min, which is evidence of the zincian malachite phase evolving.\textsuperscript{52} The same trend is seen in the out-of-plane OCO $v_2$ bending modes: their positions remain at 833 and 818 cm$^{-1}$, but their intensity increases as the re-dissolution of the Zn-rich phase promotes the desired zincian malachite.\textsuperscript{53} The bands at 744 and 706 cm$^{-1}$ are caused by the asymmetric OCO $v_4$ bending mode of malachite.\textsuperscript{53} The O-H region (see Figure 5.10 (a)) shows a clear transformation to the target precursor phase \textit{via} the appearance of two O-H bands at 3400 and 3300 cm$^{-1}$ that are attributed to malachite and a shoulder at 3460 cm$^{-1}$ which is characteristic of zincian malachite.\textsuperscript{52} The unresolved, single broad band at 1497 cm$^{-1}$ as well as the two bands at 1424 and 1398 cm$^{-1}$ are also assigned to the $v_3$ mode of zincian malachite.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure_5.10.png}
\caption{IR spectra of aliquots taken from the mother liquor at different stages during ageing in the ranges: (a) 3700-3100 cm$^{-1}$, (b) 1700-1100 cm$^{-1}$ and (c) 1200-650 cm$^{-1}$}
\end{figure}

It was concluded that to ensure the zincian malachite phase is fully formed, with no evidence of other precursors having evolved, the ageing time would be set at 2 h for all syntheses.
5.3.1.2. Batch Precursor Formation

Once the coprecipitation method was tried and tested, the precursor phase could be produced in batches of approximately 250 g. As the batches were prepared, they were assigned numbers 1-13 chronologically.

The diffraction patterns of the batches of precursor show that the mother liquor was left to age long enough for the hydrozincite precursor phase to redissolve into the mixture; however, crystalline zincian malachite is not the only phase present. A hydrotalcite-like compound (HTLC) appears to have formed, identifiable by the presence of the (003)- and (006)-reflections at 11.7 and 23.6 °2θ, respectively; this has been tentatively assigned as a Cu HTLC.
To gain a better understanding of any differences present between the prepared precursor batches, TGA and DTG were carried out in air (Figure 5.12 and Figure 5.13).

As expected, thermal gravimetric analysis shows two defined decomposition stages, with the majority of the weight loss (ca. 20.3 %) occurring before 400 °C, which is attributed to H₂O and CO₂ emission, and the remaining HT-CO₃²⁻ species evolving at higher temperatures. The average total weight loss across all batches of precursor is 28.8 %; this is in agreement with the
calculated total weight loss of 27.9% for mineral rosasite if complete dehydroxylation and decarbonation were to take place.\textsuperscript{52}

Figure 5.12: Thermogravimetric analysis for each batch of the precursor phases up to 900 °C

Table 5.5: TGA summary for the batches of precursor weight loss up to 900 °C

<table>
<thead>
<tr>
<th>Batch number</th>
<th>Weight loss / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>≤ 200 °C</td>
</tr>
<tr>
<td>1</td>
<td>6.746</td>
</tr>
<tr>
<td>2</td>
<td>6.633</td>
</tr>
<tr>
<td>3</td>
<td>6.362</td>
</tr>
<tr>
<td>4</td>
<td>6.479</td>
</tr>
<tr>
<td>5</td>
<td>6.248</td>
</tr>
<tr>
<td>6</td>
<td>5.756</td>
</tr>
<tr>
<td>7</td>
<td>6.103</td>
</tr>
<tr>
<td>8</td>
<td>6.110</td>
</tr>
<tr>
<td>9</td>
<td>5.625</td>
</tr>
<tr>
<td>10</td>
<td>5.430</td>
</tr>
<tr>
<td>11</td>
<td>5.670</td>
</tr>
<tr>
<td>12</td>
<td>4.883</td>
</tr>
<tr>
<td>13</td>
<td>4.866</td>
</tr>
</tbody>
</table>
When considering the general shape of the differential thermogravimetry profile, it too appears that zincian malachite is the predominant phase present in each batch. Here, the two broad decomposition steps are shown to occur around 341 °C and 483 °C, as shown in Section 3.3.3. However, the DTG profiles also show evidence of other phases decomposing, outside of what is expected of zincian malachite.

It is known that surface water molecules and CO$_2$ are lost as the temperature ramps from room temperature to 200 °C; however, it is unclear why there is evidence of a sharp peak in all but two of the DTG profiles around 110 °C (peak not visible for batches 6 and 13). Previously, this peak was seen in Section 3.3.5 for the Cu/Al sample, therefore it may be assumed that it is a result of a Cu HTLC phase decomposing.

It is accepted that any mass loss that occurs above 400 °C is exclusively attributed to the evolution of HT-CO$_3^-$ species. Within the batch precursor DTG profiles a pronounced third peak appears around 563 °C. It is thought that this peak is a result of a potential Zn-rich phase which may be amorphous to diffraction.

![Figure 5.13](image)

*Figure 5.13: Differential thermogravimetry for each batch of the precursor phases up to 900 °C*

The infrared spectra collected for each of the precursor batches also appear to show that zincian malachite is the predominant phase formed in each. Again, there is no evidence of an obvious impurity in any of the batches.
Following characterisation of the precursor batches, all batches were mixed together. This was then separated into 2 halves; one half remained the CZA precursor while the other half was promoted with 1 wt.% Cs₂CO₃ via incipient wetness impregnation, the diffraction patterns of which are shown in Figure 5.15. The CZA precursor phase consists of zincian malachite and what appears to be the Cu HTLC. The promoted precursor pattern is very similar to that of the standard; however, there is a greater contribution from the hydrotalcite phase. With the appearance of a peak at 34.5 °2θ in the promoted pattern, there also appears to be Zn₆Al₂(OH)₁₆CO₃·4H₂O present as this corresponds to the (012)-reflection. Furthermore, the mixed Cu,Zn HTLC has a similar pattern to that of the Zn HTLC, hence it is not possible to assign this phase with any level of certainty. The Cs-promoter is not visible in the CZA-Cs diffraction pattern; therefore, it is either present as an amorphous phase, or the quantity is too small to detect.
Figure 5.15: Diffraction patterns of the final CZA and CZA-Cs precursor; the reference patterns for zinccian malachite and a Cu HTLC$^{54}$ and Zn HTLC$^{57}$ are given below.

The infrared spectra of the final prepared precursors (Figure 5.16) do not differ much from those of the batches – though the band associated with an HTLC ($v_1$ shoulder $ca.1360$ cm$^{-1}$) is again only visible in the spectrum following the incipient impregnation method.$^{54}$ The O-H region for the CZA-Cs precursor is more defined than that of the CZA precursor, suggesting that the crystallinity of this sample is greater which may be as a result of the Cs-promoter.
These are then calcined to afford the catalyst powder ready for granulation and pelletizing.

5.3.2. Granulation and Pelletizing

The method for granulation was determined experimentally, as shown in Figure 5.17. The catalyst powder was pressed cold isostatically (CIP) at 2500, 5000 and 10000 psi prior to crushing and sieving. As it is unknown at which stage graphite is incorporated in industrial production, 1 wt.% was added internally for each test and a control without graphite was prepared at 5000 psi. Additional graphite (1 wt.%) was added to dust the granulate externally for added lubrication between granules, and between granules and the die wall. Mechanical strength tests of the resulting pellets show that the powder CIPed at 10000 psi produced pellets with the highest average radial crush strength, 119(26) N. Though the pellets formed from the powder CIPed at 5000 psi did not show a great difference in radial crush strength as a result of graphite being incorporated in the granulate, it was concluded that the graphite may offer a more reliably strong pellet. Further investigation into the pellets’ surface area, mean pore diameter, and porosity (Table 5.6) demonstrated that this method also produced pellets comparable to those employed in industry (BET area of 70.4 m$^2$ g$^{-1}$, mean pore diameter of 16.8 nm and a total porosity of 51.0 %, respectively); therefore, all catalytic material was CIPed at 10000 psi and 1 wt.% graphite was included internally.
Figure 5.17: Effect of the pressure exerted to form the granulate on the overall pellet strength (standard deviations given in brackets); I. G. represents internal graphite. All granulates were also coated with 1 wt.% graphite before pressing.

Table 5.6 shows that as the isostatic pressure increases, the resultant pellets’ BET area, mean pore diameter and porosity decrease; this is because more particle-particle contacts occur which are inaccessible to the N₂/Hg.

Table 5.6: Effect of the pressure exerted to form the granulate on the overall pellet surface area, mean pore diameter and porosity; I. G. represents internal graphite. All granulates were coated with 1 wt.% graphite before pressing.

<table>
<thead>
<tr>
<th>Pellet</th>
<th>BET Area / m² g⁻¹</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000 psi (0 wt.% I. G.)</td>
<td>72.5</td>
<td>20.8</td>
<td>53.1</td>
</tr>
<tr>
<td>2500 psi (1 wt.% I. G.)</td>
<td>82.8</td>
<td>24.9</td>
<td>64.9</td>
</tr>
<tr>
<td>5000 psi (1 wt.% I. G.)</td>
<td>73.9</td>
<td>19.7</td>
<td>54.1</td>
</tr>
<tr>
<td>10000 psi (1 wt.% I. G.)</td>
<td>70.4</td>
<td>16.8</td>
<td>51.0</td>
</tr>
</tbody>
</table>

As previously mentioned in Section 5.1.4, water can also be incorporated as a binding agent in the industrial manufacturing of pellets. Once all the granulate was produced, a test was carried out in which equal amounts of granulate were separated into sealable containers and a
known quantity of water (1-3 wt.%) was introduced to their atmosphere and left to equilibrate overnight. *Figure 5.18* shows that the granulates were then dusted with either *(a)* 1 wt.%, *(b)* 2 wt.%, or *(c)* 3 wt.% external graphite to also investigate whether this influenced the overall radial crush strength of the resultant pellets. It should be noted that only the CZA pellets were considered in this way. From these results, incorporating 1 wt.% H₂O and dusting with an additional 3 wt.% graphite delivered the narrowest hardness distribution and thus most reliably strong pellets with an average radial crush strength of 92(20) N.

![Graphs showing the effect of water incorporation as a binding agent with different graphite dustings.](image)

*Figure 5.18:* Effect of water incorporation as a binding agent with *(a)* 1 wt.%, *(b)* 2 wt.% and *(c)* 3 wt.% external graphite used to coat the granulate (standard deviations given in brackets)
5.3.3. Final Prepared Catalysts

Once all catalysts were successfully pelleted, they were again characterised to ensure the final product was as expected.

5.3.3.1. Fresh CZA and CZA-Cs pellets

The diffraction patterns of the final CZA and CZA-Cs catalysts are shown in Figure 5.19. The ZnO and CuO peaks are broad and overlap as they are not very crystalline after being calcined at 300 °C, a common observation for these types of catalysts. The zincian malachite precursor phase is still partially visible in both patterns as well, though the HTLC appears to have completely decomposed or is completely amorphous. The Cs-promoter is still either amorphous to XRD or present in too low a quantity to be detectable. The graphite, included as a lubricant, is identifiable in the pattern by the (002)-reflection at 26.6 °2θ.

The CuO:ZnO ratios for the CZA (2.3:1) and CZA-Cs (2.2:1) catalysts are relative to commercially available catalysts (see Section 3.3.3), where the Cu:Zn:Al ratio is approximately 60:30:10.60

Table 5.7: XRF analysis of CZA and CZA-Cs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration / wt.%</th>
<th>CZA</th>
<th>CZA-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>60.97</td>
<td>62.22</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>26.38</td>
<td>27.75</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.65</td>
<td>9.26</td>
<td></td>
</tr>
<tr>
<td>C₂S₅O</td>
<td>-</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.19: Diffraction patterns of the final CZA and CZA-Cs catalysts (a) stacked and (b) overlapping; the reference patterns for tenorite, zincite, zincian malachite and graphite are given below.
To qualify whether the pelletizing procedure was successful, the freshly prepared CZA and CZA-Cs pellets were crushed in the SmartTest (Figure 5.20). Interestingly, the average hardness for the catalyst pellets were very similar, with the CZA pellets requiring an average of 105(38) N to crush them, and the CZA-Cs pellets requiring 106(16) N. The average radial crush strength of the prepared promoted and unpromoted pellets is therefore comparable to the tests performed prior to batch pelletizing. Initially, it appears that Cs-promotion does not affect the mechanical strength of the pellet prior to activation. In fact, the larger range for the CZA mechanical strengths suggests these pellets are less stable than the Cs-promoted ones.

![Figure 5.20: Comparison of the radial crush strength of the prepared CZA and CZA-Cs catalysts (standard deviations given in brackets)](image)

The Hg porosimetry measurements for the prepared pellets, however, differ from the results previously measured in Table 5.6. The mean pore diameter is greater than expected and the porosity less than, but this is the consequence of batch pelletizing methods.

*Table 5.8: Mean pore diameter and porosity as determined by Hg porosimetry for the standard and promoted catalyst*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>17.4</td>
<td>48.9</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>17.1</td>
<td>44.5</td>
</tr>
</tbody>
</table>
Temperature-programmed reduction was then carried out to distinguish any possible differences in the reduction behaviour of the samples as a result of Cs-promotion (Figure 5.21). The main sharp peak visible in the TPR profile coincides with the formation of Cu⁰; reduction occurs at 218 °C for the standard catalyst, and at 210 °C for the promoted. P. Kowalik et al. reported that Cs-promotion should result in a shift of the reduction peak to higher temperatures; however, for the prepared CZA-Cs pellets, it appears the promoter may facilitate copper reducibility.62

![Figure 5.21: TPR profile of the CZA and CZA-Cs catalysts](image)

5.3.3.2. Pre-hydrated CZA and CZA-Cs pellets

The moisture uptake of the prepared CZA and CZA-Cs pellets was also investigated to elucidate whether early onset deactivation could occur prior to installation in the LTS reactor. Pellets were left to equilibrate overnight in a vacuum desiccator with 20 wt.% H₂O. As can be seen from Figure 5.22, the average catalyst mass of the CZA pellets increased by 13.8 % and the catalyst mass of the CZA-Cs pellets increased by an average of 14.6 %. These pre-hydrated (PH) pellets will be referred to as PH-CZA and PH-CZA-Cs.
Figure 5.22: Catalyst mass probability comparison of the CZA and CZA-Cs pellets before and after hydration (standard deviations given in brackets)

The diffraction patterns of the prepared PH-CZA and PH-CZA-Cs (Figure 5.23) catalysts clearly show that a HTLC has reformed after the catalysts were exposed to a wet atmosphere. This is evidenced by the basal planes’ (003)-, (006)- and (009)-peaks at 11.6, 23.4 and 33.8 °2θ, respectively for each catalyst (the (009)-peak is not as well-defined, but still visible). The expressed hydrotalcite closely matches the reference pattern given for a Zn HTLC (Zn₆Al₂(OH)₁₆CO₃·4H₂O), but, again, these reflections can also be assigned as a Cu,Zn HTLC.⁷,₅⁷,₅₈ The tenorite crystallites appear larger following hydration in both catalysts, more so for the Cs-promoted sample, though this profile is also impacted by the HTLC (015)-reflection at 39.2 °2θ.
Figure 5.23: Diffraction patterns of the pre-hydrated CZA and CZA-Cs catalysts (a) stacked and (b) overlapping; the reference patterns for tenorite, zincite, a Zn HTLC, malachite and graphite are given below.
Both the PH-CZA and PH-CZA-Cs catalysts consist of smaller pores and have less porosity than the CZA and CZA-Cs catalysts. This may be due to the reformation of the HTLC blocking the catalyst pores and reducing the void volume present in the pellets, which would also account for the decrease in porosity for both samples. Both of these effects are seen to a greater extent in the Cs-promoted catalyst, possibly due to a larger HTLC content.

Table 5.9: Mean pore diameter and porosity as determined by Hg porosimetry for the pre-hydrated standard and promoted catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH-CZA</td>
<td>16.0</td>
<td>34.2</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>13.9</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Interestingly, when the radial crush strength of the prepared pre-hydrated standard and promoted catalysts is investigated, PH-CZA-Cs affords a stronger pellet, on average. Figure 5.24 shows that the average hardness for PH-CZA is 113(28) N and for PH-CZA-Cs is 128(22) N. This requires 7.6 and 17.9 % more force that the fresh CZA and CZA-Cs, respectively, in order to cause the pellet to fracture. The increase in strength is likely to be a result of HTLCs reforming during the pre-hydration process.

Figure 5.24: Comparison of the radial crush strength of the prepared PH-CZA and PH-CZA-Cs catalysts (standard deviations given in brackets)
Unfortunately, only a TPR profile was collected for the PH-CZA-Cs catalyst, which is shown in Figure 5.25. The maximum reduction peak temperature for the pre-hydrated promoted catalyst has shifted to 216 °C from 210 °C and the peak is broader and more asymmetrical. As the TPR experimental parameters were carefully controlled according to Section 2.3.2, the resolution and peak position should be representative of the investigated sample. Therefore, it is possible that the broad peak is a combination of two reduction events: the first attributed to the reduction of well-dispersed surface CuO, and the second to bulk-like CuO phases. The latter may be related to the presence of the HTLC; Cu$^{2+}$ embedded in the hydroxylated layers increases the temperature of reduction.

Upon calcination at 300 °C for 5 h, Figure 5.26 shows that the hydrotalcite decomposes to give tenorite and zincite. The zincian malachite precursor phase is also still evident, though more so in the unpromoted pre-hydrated pattern. The CuO maintains a high crystallinity throughout these treatments.
Figure 5.26: Diffraction patterns of the calcined PH-CZA and PH-CZA-Cs catalysts (a) stacked and (b) overlapping; the reference patterns for tenorite, zincite, zincian malachite and graphite are given below.
5.3.4. Activation Tests

The following section investigates the effect the activation procedure has on the installed catalysts’ properties throughout the bed. Two $\text{H}_2$ were investigated, 1 % and 5 %, as these are representative of the reducing gas compositions most utilised in industry and academia, respectively. As previously detailed in Section 5.2.4, 40 pellets are loaded into the fixed-bed reactor, flushed with Ar, and then pressurised to 20 bar in Ar. The temperature is then ramped to 160 °C (5 °C min⁻¹) in Ar and maintained for 30 min. During this time, the gas is switched to the reducing gas composition. The temperature is then increased to 220 °C (1 °C min⁻¹) and held for either a dwell time of 24 h (5 % $\text{H}_2$) or 48 h (1 % $\text{H}_2$). Steam incorporated into the reducing gas environment has also been investigated up to 20 vol.% to elucidate if any structural changes are provoked as a result of its presence (this was introduced at 160 °C). Throughout the activation procedure, the temperature of the fixed-bed reactor is monitored and no exotherms were detected.

Following reduction, the reactor was cooled to room temperature in Ar. Once cooled, the catalyst was passivated following the aforementioned procedure (see Table 5.3). The pellets were removed from the reactor in four sets of 10 pellets and stored under N₂ to prevent further oxidation. A diffraction pattern has been collected from the four positions in the bed, with position 1 signifying the top and position 4 the bottom of the bed (illustrated in Figure 5.7), for each investigated activation procedure. It may be useful to restate that the heated inlet is at the top of the bed, and the heated outlet is at the bottom.

Ideally these activation tests would have been monitored in situ to avoid the need to interpret the passivated catalyst results. However, as these experiments were conducted in a laboratory reactor, the surface of the reduced catalysts were passivated via a controlled re-oxidation procedure which ensured a protective oxide layer (scale) formed. This prevented oxidation of the bulk and the pellets were stored under N₂. During analysis of these samples using XRD, the pellets required crushing and loading into the diffractometer which may have caused reoxidation of some of the bulk. This may be evidenced by some of the large [Cu₅O₆].

All of the diffraction patterns associated with this section are located in Appendix 7.5.7. The results of the Rietveld refinements have been displayed graphically for each activation procedure. The errors associated with said fitting are displayed on the bar graphs.

5.3.4.1. Wet, Inert Atmosphere

Initially, steam incorporation was investigated to elucidate any morphological anomalies which resulted solely from being heated in a wet, inert atmosphere for 24 h. Tenorite and zincite are the only phases identifiable in the diffraction patterns (Figure 5.27) for each catalyst, though their peak shapes differ. Visually, the ZnO crystallite size appears to increase towards the bottom of the bed for the CZA catalyst, perhaps as a water gradient forms along the bed. There is no clear difference across each bed position for the ZnO in the CZA-Cs catalyst; the CuO phase also seems unaffected. It is only after Rietveld refinement that more in-depth conclusions can be drawn.
Figure 5.27: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing ‘activation’ in a wet (20 vol.% H$_2$O) inert (Ar) atmosphere for 24 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the reference patterns of tenorite, zincite and quartz are given below.
The bar graphs depicting the weight fractions in Figure 5.28 (a-i) and (b-i) show that the Rietveld refinement requires a contribution from amorphous phases due to the internal standard method employed (see Section 5.2.3). At least 10 wt.% of this amorphous content can be rationalised as an γ-alumina-containing phase due to the absence of any observable reflections pertaining to an Al phase. Interestingly, the bottom of the bed for the CZA catalyst has a greater amorphous content than the equivalent promoted catalyst position. As the ZnO content remains relatively constant throughout both the CZA (21.1(7)-26.5(8) wt.%) and CZA-Cs (22.2(7)-25.0(8) wt.%) catalyst beds, this could be indicative of an amorphous Cu-containing Al phase having formed more readily in the wet atmosphere than for the CZA-Cs catalyst.

It is also evident that the presence of steam accelerates sintering of the ZnO component. The top of the CZA catalyst bed is relatively unaffected by the presence of steam, with the ZnO crystallites remaining < 12.0(2) nm in size. It is only in the third position that growth of ZnO crystallites is significant (32.7(8) nm). Sintering of the zincite support in the CZA-Cs catalyst increases linearly down the bed, also indicating the presence of a water gradient; however, it is far more pronounced, most likely due to the presence of the Cs-promoter (as shown in Chapter 4). This trend is seen to a lesser extent with the CuO crystallite size in both studies.

Figure 5.28: Wet inert (Ar) in 20 vol.% H₂O (a) CZA and (b) CZA-Cs showing (i) the corresponding weight fractions and (ii) crystallite sizes
At this point, these results are not ideal as a role of ZnO as a supporting component for Cu is to prevent sintering during operation, whereas introducing steam to the reactor atmosphere causes growth of the zincite crystallites. This impacts on the structure of the pellet, increasing the average pore diameter for the CZA catalyst by 113% and for the CZA-Cs catalyst by 206%. The increase seen could be the result of water condensation in the pores causing the zincite to agglomerate, culminating in pore expansion.

Table 5.10: Hg porosimetry results for the catalysts treated in a wet (20 vol.% H₂O), inert (Ar) atmosphere for 24 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>0</td>
<td>20</td>
<td>37.1</td>
<td>58.5</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>0</td>
<td>20</td>
<td>52.4</td>
<td>56.0</td>
</tr>
</tbody>
</table>

5.3.4.2. Dry, Reducing Atmosphere

The activation of the CZA and CZA-Cs catalysts has been carried out in a 1% H₂/Ar atmosphere for 48 h and in a 5% H₂/Ar atmosphere for 24 h. This also allows for easy comparison with the wet studies.

5.3.4.2.1. 1% H₂/Ar, 48 h

To begin, the dry reduction in 1% H₂/Ar is presented as the most ‘ideal’ condition investigated as any structural changes will be a result of the reduction itself. For this reason, industry generally carries out their activation procedures at low H₂ partial pressures over a prolonged time period.² As expected, the diffraction patterns (Appendix 7.5.7.2) show evidence of the reduction taking place as Cu⁰ and Cu₂O are visible.

During reduction, a small amount of water will always be present as it is a by-product (i.e. oxygen is removed from the oxides). It appears that the water produced is not significant enough to affect the zincite support (ZnO crystallite size remains ≤ 5.0(2) nm for both catalysts); however, it may still promote formation of HTLCs. As seen previously, the amorphous content increases towards the bottom of the bed for the CZA catalyst and decreases for the promoted one. For the CZA catalyst, this trend may be related to the behaviour of the ZnO where the first 3 positions in the CZA bed contain ca. 30(1) wt.% ZnO compared to 16(1) wt.% in the bottom. The total weight fraction of the Cu-containing phases accounts for ca. 32.0(7) wt.% of Figure 5.29 (a-i), suggesting that the amorphous content is composed of Cu-rich HTLCs in positions 1-3 of the bed and the bottom either consists of Cu and Zn HTLCs and/or of mixed Cu,Zn HTLC. The ZnO weight fractions across the promoted catalyst bed remain constant at ca. 25(1) wt.% ZnO. Interestingly, the Cu⁰ content decreases while the combined cuprite and tenorite weight fractions increase towards the bottom of the bed. If a water gradient is present, the Cs appears to
inhibit formation of a Zn-rich HTLC and may facilitate condensation of water on the surface of the pellet, retarding reduction at the bottom of the bed.

A water gradient may have inhibited reduction at the bottom of the CZA bed as well due to the small portion of Cu\textsuperscript{0} present. The metallic copper weight fractions for the first 3 positions are comparable (ca. 15.3(6) wt.%), with full reduction appearing to take place in the 3\textsuperscript{rd} position for the crystalline Cu-containing phases (the presence of Cu\textsuperscript{1+} is a result of the passivation technique) due to the absence of tenorite.\textsuperscript{46} This is likely the result of the temperature gradient, in that copper more readily reduces in the positions 2 and 3 as the temperature is more forcing for reduction to occur.

Figure 5.29: Bar graphs of the (a) CZA and (b) CZA-Cs catalysts exposed to a dry reducing (1 \% \textit{H}_2/\textit{Ar}) atmosphere showing (i) the corresponding weight fractions and (ii) crystallite sizes.

The mean pore diameters for both catalysts have increased from those present in the original catalyst, with the CZA pores growing by 35.6 \% and the CZA-Cs pores by 43.9 \%. This is likely due to the removal of oxygen during reduction.
Table 5.11: Hg porosimetry results for the catalysts treated in a dry, reducing (1 % H₂/Ar) atmosphere for 48 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>1</td>
<td>0</td>
<td>23.6</td>
<td>60.2</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>0</td>
<td>24.6</td>
<td>53.8</td>
</tr>
</tbody>
</table>

5.3.4.2.2. 5 % H₂/Ar, 24 h

When the reducing gas concentration is increased to 5 % H₂, any sintering phenomena would be exacerbated as it is a more forcing condition due to the exothermity of the reaction; the larger the [H₂], the quicker the reduction, therefore the more water produced as a by-product.

The main difference that can be seen from the Rietveld refinements (Figure 5.30) is that there is no tenorite present along the length of the CZA bed after it has been reduced in 5 % H₂. When compared with the Cs-promoted catalyst, CuO is still present. This further implies that Cs promotes water dissociation which would inhibit complete reduction of the active copper component. It is also interesting to note that the amount of reduced Cu (including Cu^{1+}) along the Cs-promoted bed varies. This could suggest a cycle where position 1 partially reduces, then the water produced slightly inhibits position 2, position 3 reduces, and the water produced slightly inhibits the reduction of position 4.

The same trend can be seen for the amorphous content for both catalysts; where the ZnO content remains relatively constant across the CZA-Cs bed (ca. 26(1) wt.%), it decreases at the bottom of the CZA bed by ca. 12(1) wt.% suggesting that the addition of Cs prevents formation of a Zn-rich HTLC in situ.

When the reduction was carried out under the more ‘ideal’ conditions of 1 % H₂/Ar, the crystallite sizes of the active and supporting components were comparable between both datasets. Here, the standard catalyst ZnO and Cu⁰ crystallite sizes are smaller at the top and bottom of the bed compared to the middle, which is a result of the temperature gradient that is known to be present along the bed. This temperature effect is not visible in the promoted catalyst bed. The Cu⁰ and zincite crystallites are, however, larger, highlighting that Cs may also be promoting sintering of the copper.
Figure 5.30: Dry reducing (5% H₂/Ar) atmosphere (a) CZA and (b) CZA-Cs showing (i) the corresponding weight fractions and (ii) crystallite sizes

There is a greater increase in the average pore diameter, with the CZA catalyst pores increasing by 46.0% and the CZA-Cs pores by 62.0%. Again, the promoted catalyst is most affected.

Table 5.12: Hg porosimetry results for the catalysts treated in a dry, reducing (5% H₂/Ar) atmosphere for 24 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>5</td>
<td>0</td>
<td>25.4</td>
<td>60.9</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>5</td>
<td>0</td>
<td>27.7</td>
<td>57.6</td>
</tr>
</tbody>
</table>

5.3.4.3. Wet, Reducing Atmosphere

The next activation procedures investigated are those in a wet atmosphere with 20 vol.% water vapour. As previously mentioned, there are three main sources of water in a full-plant reduction, including steam that may be injected upstream in the HTS reactor which carries through
to the LTS bed. It has already been established that steam incorporation causes sintering of the supporting zincite, evidenced by the wet, inert ‘activation’ studies; however, how this affects the reducing behaviour of the catalyst bed is unclear.

5.3.4.3.1. 1 % H$_2$/Ar, 20 vol.% H$_2$O($g$), 48 h

From the diffraction patterns collected at the four positions along the bed (Appendix 7.5.7.4), there again appears to be a build-up of water towards the bottom of the bed as the ZnO peak profiles become more well-defined. Where the whole of the CZA catalyst bed has not undergone reduction, it is only the bottom of the promoted catalyst bed that does not appear to have reduced as no Cu$^0$ reflections are visible.

There is no evidence of complete reduction having taken place in the CZA catalyst bed, despite the GC data showing consumption of H$_2$ (Appendix 7.5.8). The water may have been acting as an oxidising gas, reoxidising any Cu$^0$ formed and causing slight sintering of the resultant tenorite.$^{67}$ Capillary condensation may have also occurred which will have inhibited CuO reduction.

The ZnO content across both catalyst beds is relatively constant, and behaviour of the crystallites follows the trend seen for ‘activation’ in the wet, inert atmosphere. The zincite crystallite size increases quite dramatically towards the bottom of the CZA bed (from 16.4(4)-36.0(8) nm), whereas it remains equally large across the CZA-Cs bed (from 25.4(5) nm at the top, to 33.0(7) nm at the bottom).

The CZA-Cs catalyst bed clearly has a different reduction behaviour to the CZA bed. Where reduction was inhibited for the unpromoted catalyst, the active component of the promoted bed appears to have agglomerated, forming large ingots of Cu$^0$. Though the mechanism is unclear, Cs-promotion may interfere with the strong metal oxide support interactions (SMSI) that form between the Cu and the ZnO during reduction which prevent the Cu from sintering,$^{68}$ growth of the Cu$^0$ crystallites is evident in Figure 5.31 (b-ii), with the metallic Cu crystallite sizes ranging from 50.8(7)-60.2(9) nm. These effects are not seen at the bottom of the bed, as the water build-up may have prevented reduction from taking place.

No amorphous content is determined for the bottom of the CZA-Cs bed; this is considered an anomaly amongst these results.
Figure 5.31: Wet reducing (1 % \(H_2\)/Ar, 20 vol.% \(H_2O\)) atmosphere (a) CZA and (b) CZA-Cs showing (i) the corresponding weight fractions and (ii) crystallite sizes

By reducing in 20 vol.% water vapour and 1 % \(H_2\)/Ar, the average pore diameters have almost doubled for the CZA catalyst (209 %) and, to a slightly greater degree, for the CZA-Cs catalyst (231 %). This cannot only be attributed to sintering of the ZnO component by steam incorporation, though it clearly plays a key role.

Table 5.13: Hg porosimetry results for the catalysts treated in a wet (20 vol.% \(H_2O\)), reducing (1 % \(H_2\)/Ar) atmosphere for 48 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>([H_2] / %)</th>
<th>([H_2O] / %)</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>1</td>
<td>20</td>
<td>53.7</td>
<td>60.3</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>20</td>
<td>56.6</td>
<td>55.8</td>
</tr>
</tbody>
</table>

5.3.4.3.2. Comparison of 10, and 20 vol.% \(H_2O(g)\)

Sintering phenomena resulting from steam incorporation are more prevalent for the CZA-Cs catalyst during reduction in 1 % \(H_2\)/Ar. As previously mentioned, this is considered the least
harsh reducing atmosphere, therefore any sintering is a direct result of the wet atmosphere. In order to determine whether the sintering behaviour of the Cu\(^0\) and ZnO crystallites changes if the [H\(_2\)O] in the reducing gas feed decreases by 50\%, activation of the promoted catalyst in 1\% H\(_2\)/Ar and 10 vol.% H\(_2\)O\(_{(g)}\) was carried out and the results were compared to the equivalent reduction in 20 vol.% H\(_2\)O\(_{(g)}\).

The diffraction patterns comparing the effects of the two [H\(_2\)O] in a 1\% H\(_2\) reducing atmosphere exhibit the same trends (Appendix 7.5.7.4.1). Reduction is observed to have taken place in positions 1-3 of both catalytic beds, evidenced by the presence of Cu(111)- and (200)-reflections. The bottom of the bed does not show any signs of Cu\(^0\); therefore, the water gradient is still substantial enough to inhibit reduction of/oxidise the active copper component.

The more steam incorporation, the greater effect on the active Cu component with the crystallite sizes increasing by an average of ca. 12.3(8) nm from 10 vol.% H\(_2\)O\(_{(g)}\) to 20 vol.% No clear difference is visible for the ZnO; therefore, it can be concluded that the critical amount of steam that causes sintering of this support is below 10 vol.% [H\(_2\)O].

**Figure 5.32:** CZA-Cs in (a) 10 vol.% H\(_2\)O and (b) 20 vol.% H\(_2\)O wet, reducing (1\% H\(_2\)/Ar) atmosphere for 48 h showing (i) the corresponding weight fractions and (ii) crystallite sizes
It appears the average pore diameter of the promoted catalyst reduced in a 10 vol.% steam atmosphere has a comparable increase (201 %) to that of the unpromoted catalyst reduced in a 20 vol.% H₂O environment (209 %). However, the average pore diameter increases by a further 30 % when the steam concentration is doubled, suggesting capillary condensation occurs to a larger extent.

Table 5.14: Hg porosimetry results for CZA-Cs catalysts treated in a reducing (1 % H₂/Ar) atmosphere with varying steam concentrations (10, and 20 vol.% H₂O) for 48 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>10</td>
<td>52.3</td>
<td>55.7</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>20</td>
<td>56.6</td>
<td>55.8</td>
</tr>
</tbody>
</table>

5.3.4.3.3. 5 % H₂/Ar, 20 vol.% H₂O(g), 24 h

Next, the upper boundaries of the activation parameters were tested, with the CZA and CZA-Cs catalysts being reduced in a 5 % H₂/Ar atmosphere with 20 vol.% H₂O(g). This was performed to understand how the sintering effects observed with a greater [H₂] paired with the increased steam concentration.

As expected, the diffraction patterns show evidence of reduction across all positions of the bed; however, only slight reduction is observed at the top of the promoted catalyst bed (Appendix 7.5.7.5). From the Rietveld refinements, compositionally there is not a huge difference between the [ZnO] in the CZA and CZA-Cs catalysts, therefore any changes seen can be rationalised as being a result of interactions between the Cs promoter and the active Cu component.

A temperature effect is visible in the catalyst bed for CZA; reduction occurs to a greater extent in the middle of the bed (positions 2 and 3) compared to the top and bottom. Where this temperature effect may also be seen at the top of the promoted-catalyst bed, the presence of water/build-up of water combined with the Cs-promoter appears to negate any temperature effects that would be seen at the bottom of the bed.

The ZnO behaves in very similar ways, increasing in crystallite size towards the bottom of both beds. However, the sintering occurs to a greater extent than previously observed, with the largest ZnO crystallites growing to 37.6(8) nm and 41.4(9) nm for the CZA and CZA-Cs catalysts, respectively. This gradient is again attributed to the presence of a water build-up along the bed. The Cu⁰ crystallite sizes also appear to follow this trend, as they increase towards the bottom of the bed and are greater in the CZA-Cs catalyst. This is expected as Cs-promotion appears to facilitate sintering of the active component, as it did in the dry 5 % H₂ activation.

The amorphous content of the bed positions remains relatively constant in the unpromoted bed, whereas there is quite a lot of variation for the Cs-promoted bed. This again
hints at a cycle of the reduction along the bed which may contribute to this effect. However, the calculated weight fractions for Cu are in deficit of what is present in the pellets, therefore it is rationalised there must again be a formation of an amorphous Cu-containing Al phase.

Figure 5.33: Wet reducing (5 % H₂/Ar, 20 vol.% H₂O) atmosphere (a) CZA and (b) CZA-Cs showing (i) the corresponding weight fractions and (ii) crystallite sizes

The mean pore diameters for the catalysts reduced in a wet, 5 % H₂ environment are not as affected as the wet, 1 % H₂ tests; the pore diameter increases by 191 % for the CZA catalyst, and 205 % for the CZA-Cs catalyst.

Table 5.15: Hg porosimetry results for the catalysts treated in a wet (20 vol.% H₂O), reducing (5 % H₂/Ar) atmosphere for 24 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>5</td>
<td>20</td>
<td>50.7</td>
<td>68.7</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>5</td>
<td>20</td>
<td>52.2</td>
<td>50.0</td>
</tr>
</tbody>
</table>
5.3.4.4. Pre-hydrated Catalysts

Pre-hydrating the pellets with 20 wt.% H₂O(g) (PH-CZA and PH-CZA-Cs) caused an increase in the average radial crush strengths (Section 5.3.3.2). It is expected that this is resultant of the HTLC phase, first crystallized in the precursors, reforming following exposure to a wet atmosphere. In this section, the presence of water adsorbed onto the pellets, and thus the presence of the HTLC phase prior to activation, is investigated to determine whether this impacts the overall catalyst morphology and mechanical strength of the pellets.

5.3.4.4.1. 5 % H₂/Ar, 24 h

On first inspection of the diffraction patterns (Appendix 7.5.7.6), it is clear the HTLC that recrystallised during hydration of the pellets decomposes during reduction, as it is known that HTLCs decompose at temperatures above 200 °C.⁶⁹ It also appears that the unpromoted catalyst is able to undergo full reduction as opposed to the promoted catalyst.

Results from the Rietveld refinement again show a similar trend to that of the fresh catalysts reduced in 5 % H₂. The PH-CZA catalyst appears to have undergone complete reduction as there is no CuO present in any position of the bed. However, tenorite is still visible for the PH-CZA-Cs catalyst highlighting that the same phenomena have occurred in this activation test in which Cs appears to inhibit full reduction of the active Cu component through its interaction with the water in the atmosphere. The amorphous content also increases towards the bottom of the bed for the PH-CZA catalyst as the ZnO decreases, whereas it remains quite constant for the promoted catalyst bed. The crystallite sizes for each of the components also follow the same trend, though the Cu⁰ crystallite size is slightly larger in Figure 5.34 (b-ii) compared to those of the CZA-Cs catalyst under the same activation conditions. This may be a result of reforming the HTLC prior to loading the catalyst in the reactor.
Pre-hydrating the pellets with water prior to reducing them in a dry, 5 % H₂ atmosphere, affects the mean pore diameter for both catalysts to a greater extent when compared to the dry reduction of the fresh catalysts. The average pore diameters of the PH-CZA catalyst have increased by 92.0 % and those of the PH-CZA-Cs catalyst have increased by 74.9 %.

**Table 5.16:** Hg porosimetry results for the pre-hydrated catalysts treated in a dry, reducing (5 % H₂/Ar) atmosphere for 24 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH-CZA</td>
<td>5</td>
<td>0</td>
<td>33.4</td>
<td>61.7</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>5</td>
<td>0</td>
<td>29.9</td>
<td>56.8</td>
</tr>
</tbody>
</table>

Despite the catalysts being loaded with water, the difference between the results of the dry reduction in 5 % H₂ for the CZA/CZA-Cs catalysts and PH-CZA/PH-CZA-Cs catalysts were
negligible. Thus, loading the pellets with water does not have the same effect as introducing the pellets to a wet atmosphere.

5.3.4.4.2. 5 % H\textsubscript{2}/Ar, 20 vol.% H\textsubscript{2}O\textsubscript{(g)}, 24 h

Once it was established that the pre-hydrated pellets did not show any differing signs of deactivation in a dry atmosphere compared to the fresh catalyst pellets, it was then time to reduce PH-CZA and PH-CZA-Cs in a wet atmosphere.

Complete reduction is not achieved across both catalyst beds under these conditions, as was seen for the CZA and CZA-Cs catalysts. Where there was a temperature effect visible along the CZA bed activated in 5 % H\textsubscript{2}, this is no longer seen to the same degree. The metallic copper at the bottom of the promoted bed appears to have been oxidised to cuprite during passivation. It seems this process caused sintering of the Cu\textsubscript{2}O; however, it is assumed this is not related to the activation procedure.

There is evidence of how water affects the stability of the Cu-containing phases as the sintering effects are much greater in these studies. The ZnO crystallite size increases drastically towards the bottom of the bed for both catalysts. This trend is also seen for the Cu\textsuperscript{0} crystallites. These phenomena are expected to be a result of the water gradient present.
Figure 5.35: Wet reducing (5 % H₂/Ar, 20 vol.% H₂O) atmosphere pre-hydrated (a) standard and (b) doped showing (i) the corresponding weight fractions and (ii) crystallite sizes.

Once steam was introduced into the atmosphere, the pre-hydrated pellets’ mean pore diameter more than tripled for the PH-CZA (332 %) and PH-CZA-Cs catalysts (385 %). This shows structural changes to the pellet have occurred which would have a detrimental effect on the catalysts’ effectiveness.

Table 5.17: Hg porosimetry results for the pre-hydrated catalysts treated in a wet (20 vol.% H₂O), reducing (5 % H₂/Ar) atmosphere for 24 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH-CZA</td>
<td>5</td>
<td>20</td>
<td>75.2</td>
<td>69.9</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>5</td>
<td>20</td>
<td>83.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

5.3.4.4.3. 1 % H₂/Ar in (a) a dry atmosphere and (b) 20 vol.% H₂O, 48 h

The promoted pre-hydrated catalyst was then investigated under the ‘ideal’ dry, 1 % H₂/Ar reducing atmosphere and in a 20 vol.% H₂O, 1 % H₂/Ar environment.
Previously, it was deduced that water produced as a result of the reduction occurring in 1 % H$_2$ did not have a significant effect on the composition of the catalyst. This was also seen for the PH-CZA-Cs catalyst; the average crystallite size of the zincite increased slightly to ca. 5.7(2) nm, as did the Cu$^0$ to ca. 17.3(3) nm. Where the CZA-Cs catalyst completely reduced exclusively in the 3rd position of the bed, the middle of the PH-CZA-Cs catalyst bed (positions 2 and 3) shows no evidence of tenorite, therefore reduction was able to take place. This may be rationalised as a temperature effect.

The real structural changes to the PH-CZA-Cs catalyst can be seen after it is reduced in a 1 % H$_2$/Ar, 20 vol.% H$_2$O(g) atmosphere. Expectedly, the Cu$^0$ and ZnO phases visibly sinter, but to a much larger extent, much more so than during the 5 % H$_2$ investigations. It appears that the top of the bed was able to begin reducing, but the water build-up at the bottom of the bed has saturated the catalyst, inhibiting reduction.

![Weight Fraction and Crystallite Size](image)

*Figure 5.36: Pre-hydrated CZA-Cs (a) dry and (b) wet (20 vol.% H$_2$O) reducing (1 % H$_2$/Ar) showing (i) the corresponding weight fractions and (ii) crystallite sizes*

Again, when the reduction was carried out under the most ‘ideal’ conditions, the average pore diameter remained relatively unaffected for the PH-CZA-Cs catalyst (increased by 47.4 %), whereas in a wet atmosphere, the mean pore diameter expanded by 337 %.
Table 5.18: Hg porosimetry results for the pre-hydrated catalysts treated in a dry and a wet (20 vol.% $H_2O$), reducing (1 % $H_2$/Ar) atmosphere for 48 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$[H_2]$ / %</th>
<th>$[H_2O]$ / vol.%</th>
<th>Mean Pore Diameter / nm</th>
<th>Porosity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH-CZA-Cs</td>
<td>1</td>
<td>0</td>
<td>25.2</td>
<td>57.2</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>1</td>
<td>20</td>
<td>74.8</td>
<td>63.5</td>
</tr>
</tbody>
</table>

5.3.5. Mechanical Strength Tests

Whilst understanding changes to the catalyst morphology is an important step in characterising possible early onset deactivation mechanisms, the robustness of the pellets is also a major factor to consider for prolonged industrial use.

Following the wet, inert ‘activation’ tests on CZA and CZA-Cs, the average radial crush strengths of the pellets have been severely affected (Figure 5.37). From the Rietveld refinement results discussed in Section 5.3.4, it was clear that sintering of the zincite had taken place; therefore, it appears that dispersion of the ZnO throughout the catalyst pellets has a key role in their structural integrity. There is little difference between the average hardness of the resultant CZA and CZA-Cs pellets (16(14) and 19(5) N, respectively), indicating that Cs-promotion does not negate this obvious mechanical strength failure. The high standard deviation for the mechanical strength of the CZA pellets is due to an outlier with an average hardness of 94 N which has been omitted from the graph.

![Fracture probability for the CZA and CZA-Cs catalyst pellets 'activated' in an inert, 20 vol.% $H_2O$ atmosphere](image_url)

Figure 5.37: Fracture probability for the CZA and CZA-Cs catalyst pellets 'activated' in an inert, 20 vol.% $H_2O$ atmosphere
Table 5.19: Average radial crush strength for catalyst pellets ‘activated’ in a wet, inert atmosphere (standard deviations given in brackets)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H\textsubscript{2}] / %</th>
<th>[H\textsubscript{2}O] / vol.%</th>
<th>Average Hardness / N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>0</td>
<td>20</td>
<td>16(14)</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>0</td>
<td>20</td>
<td>19(5)</td>
</tr>
</tbody>
</table>

The radial crush strength of all catalyst pellets reduced under 1 % H\textsubscript{2} are shown in Figure 5.38 for the (a) standard and (b) promoted catalysts. It is evident that once the catalysts are introduced to a wet, reducing atmosphere, there is mechanical failure, regardless of the Cs-promoter, and the resultant pellets have an average hardness of 11(7) N (Table 5.20). As the effects on the mechanical strength of the wet, reduced catalysts are greater than those seen for the dry, inert tests, this may not be just down to ZnO sintering. The catalyst pellets reduced under dry atmospheres have an increased average pellet strength, and exhibit a broad range of strengths, comparatively. The PH-CZA-Cs pellets reduced solely in 1 % H\textsubscript{2} afforded the highest average radial crush strength, 61(28) N, of all the datasets.\textsuperscript{70}

Figure 5.38: Fracture probability for (a) CZA and (b) CZA-Cs/PH-CZA-Cs catalyst pellets reduced in 1 % H\textsubscript{2}/Ar
Table 5.20: Average radial crush strength for catalyst pellets reduced under 1% H₂/Ar (standard deviations given in brackets)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H₂] / %</th>
<th>[H₂O] / vol.%</th>
<th>Average Hardness / N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>1</td>
<td>0</td>
<td>38(22)</td>
</tr>
<tr>
<td>CZA</td>
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<td>12(5)</td>
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<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>0</td>
<td>47(24)</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>10</td>
<td>11(7)</td>
</tr>
<tr>
<td>CZA-Cs</td>
<td>1</td>
<td>20</td>
<td>11(7)</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>1</td>
<td>0</td>
<td>61(28)</td>
</tr>
<tr>
<td>PH-CZA-Cs</td>
<td>1</td>
<td>20</td>
<td>10(3)</td>
</tr>
</tbody>
</table>

Similar to the above results, the catalyst pellets reduced in 5% H₂ show a marked decrease in mechanical strength when they are introduced to a wet atmosphere (Figure 5.39). The average radial crush strength for all catalyst pellets reduced in a 20 vol.% H₂O atmosphere is 9(3) N (Table 5.21); however, it would be expected that due to the higher [H₂], any morphological changes that lead to decreased mechanical strength would be exacerbated under these conditions. Again, the pre-hydrated catalysts reduced in a dry atmosphere exhibit greater mechanical strength, although this is spread over a wide range. This is also seen for the CZA and CZA-Cs pellets activated in a dry, reducing atmosphere. In general, the Cs-promoted catalysts exhibit greater mechanical strength than the unpromoted catalysts.
Figure 5.39: Fracture probability for (a) CZA/PH-CZA and (b) CZA-Cs/PH-CZA-Cs catalyst pellets reduced in 5% H\textsubscript{2}/Ar

Table 5.21: Average radial crush strength for catalyst pellets reduced under 5% H\textsubscript{2}/Ar (standard deviations given in brackets)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[H\textsubscript{2}] / %</th>
<th>[H\textsubscript{2}O] / vol.%</th>
<th>Average Hardness / N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>5</td>
<td>0</td>
<td>26(12)</td>
</tr>
<tr>
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<td>20</td>
<td>8(2)</td>
</tr>
<tr>
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<td>0</td>
<td>38(14)</td>
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<tr>
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<td>5</td>
<td>20</td>
<td>7(3)</td>
</tr>
<tr>
<td>CZA-Cs</td>
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<td>0</td>
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<td>5</td>
<td>20</td>
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<tr>
<td>PH-CZA-Cs</td>
<td>5</td>
<td>20</td>
<td>9(4)</td>
</tr>
</tbody>
</table>

5.4. Discussion

From the above results, the catalysts activated in atmospheres with high partial pressures of steam undergo severe morphological changes which cause sintering of the active Cu\textsuperscript{0} component and metal oxide phases, leading to mechanical failure of the pellets. The calculated amorphous content appears to contain an unknown X-ray amorphous Cu/Al phase which contributes to the sintering behaviour of the catalysts, though the mechanism is not clear. Caesium
promotion intensifies the sintering phenomena and inhibits complete reduction of the copper. For better understanding, the discussion has been separated into two sections: the effects of sintering and the role of Cs.

Passivation of the reduced catalyst pellets under ambient conditions was required prior to removal from the reactor due to their pyrophoric nature. This was carried out in a very controlled manner to ensure the catalyst morphology was preserved. Due to copper nanoparticles’ large surface area to volume ratio, they are prone to oxidation; however, this behaviour is dependent on their size. For example, small Cu$^0$ nanoparticles (ca. 5 nm) completely and rapidly oxidise to Cu$_2$O, whereas larger nanoparticles (ca. 30 nm) partially oxidise, forming a stable Cu$_2$O shell surrounding the Cu$^0$ core.$^{71,72}$ The presence of cuprite in the final diffraction patterns is most likely a result of the passivation, rather than a preserved intermediate that is observed during reduction. It is possible that as a result of the passivation, the “nanoscale Kirkendall effect” has occurred, where hollow Cu$_2$O shells are formed as a result of the reactive oxygen species diffusing to the Cu$^0$ core slower than the metal atoms diffusing to the surface of the oxide layer. However, K. P. Rice et al., suggest that these hollow shells are formed when passivation is undertaken at elevated temperatures (ca. 100 °C) as complete oxidation can occur. Consequently, at ambient temperature, it is more likely that a core-shell type structure has formed.$^{71}$

It should also be noted that, though not explored in this discussion, the partial pressure of oxygen in the gas feed as a result of the partial pressures of hydrogen and water vapour is not negligible.$^{67}$

5.4.1. The Effects of Sintering

Sintering is one of the main causes of catalyst deactivation for industrial heterogeneous catalysts.$^{73–75}$ Thermodynamically speaking, the driving force of nanoparticle sintering is to reduce the catalyst systems total surface free energy via grain growth.$^{75}$ When sintering occurs of ceramic supports, not only is their density affected, but the size, shape and distribution of their pores change; accordingly, the surface area is reduced.$^{75–77}$ Possible mechanisms of sintering include grain boundary diffusion, lattice diffusion, viscous flow, surface diffusion and evaporation-condensation. It has been established that the first three mechanisms proposed cause densification (pore shrinkage), whereas the latter two cause rounding of the pores (pore growth).$^{76}$ For the purpose of this discussion, only sintering effects which cause pore expansion are considered as this correlates with the Hg porosimetry results reported in Section 5.3.4.

Initially, effects of sintering on the zincite component will be discussed. There is a clear relationship between the sintering behaviour of ZnO with steam which is shown in Figure 5.40 (a-ii) and (b-ii). The CZA and CZA-Cs catalysts ‘activated’ in a wet (20 vol.% water vapour), inert (Ar) atmosphere exhibited high degrees of sintering of the zincite. As no hydrogen was introduced into the reactor atmosphere, it is not possible that an exotherm occurred (none were detected by the fixed-bed thermocouple); therefore, the sintering of the ZnO is attributed to a
water build-up along the bed. The environment wherein sintering arises plays a key role in the pore kinetics. J. A. Varela et al. explored how different pressures of water vapour in Ar affected the sintering behaviour of MgO, finding that sintering and pore growth occurred in 22.7 KPa of steam.\textsuperscript{76} It was concluded that two mechanisms occurred during sintering: (1) particle rearrangement, or coalescence, of ≥ two metal nanoparticles migrating across the catalyst support surface \textit{via} Brownian-like motion to form an aggregate, and (2) Ostwald ripening \textit{via} surface diffusion of metal atoms between the nanoparticle surfaces. Both of these mechanisms are accelerated by the presence of water vapour interacting with the oxide surface.\textsuperscript{75,76} Weak metal-support interactions and close particle proximity promote coalescence.\textsuperscript{75} However, it is the surface diffusion phenomena which cause strengthening of the necks between particles, preventing collapse of the larger pores and thus resulting in both pore and grain growth.\textsuperscript{76} Due to limitations of the HPLC pump used in these studies (see Section 5.2.4.1), the investigated steam partial pressure for the wet, inert investigations is 400 KPa (20 vol.%), which provides some insight into the large rates of sintering achieved of the ZnO in 24 h, and the mechanical failure of the resultant pellets. In the presence of H\textsubscript{2}O\textsubscript{(g)}, hydroxylation of the ZnO takes place, promoting surface diffusion through chemical interactions with the water. Compared to pure ZnO, hydroxylated zincite sinters at a faster rate due to the increased surface diffusion, which would explain why grain growth of the ZnO occurs to a much larger extent across all the wet studies.\textsuperscript{76,77}
Figure 5.40: Summary of the (a) standard and (b) promoted catalysts’ zincite crystallite sizes following reduction in (i) dry and (ii) wet atmospheres, where position 1 signifies the top of the bed, and position 4 the bottom.

A role of alumina in the Cu-based LTS catalysts is to stabilise the Cu\(^0\) nanoparticles from sintering, overall enhancing the catalysts’ stability.\(^{77,79}\) As a consequence of this, any morphological changes that occur to the Al\(_2\)O\(_3\) support can negatively impact the Cu and ZnO sintering behaviour.\(^{77}\) As shown in Section 5.3.3.2, when the fresh catalyst pellets are hydrothermally treated, a retrotopotactic transformation of the HTLC phase first seen after coprecipitation occurs where it is recrystallized. These cycles of HTLC regeneration have been reported to cause segregation of the catalyst components which undesirably result in an inhomogeneous catalyst with low specific area of the Cu, ZnO and Al\(_2\)O\(_3\).\(^{65}\) In Zn/Al systems, reconstruction of the Zn HTLC causes sintering of the ZnO phase, highlighting evidence of induced phase segregation and offering another potential mechanism for zincite crystallite...
growth.\textsuperscript{80} It is important to note that the Cs-promoted catalyst has undergone one more topotactic transformation than the CZA catalyst due to the incipient wetness impregnation method employed.\textsuperscript{81} This offers an explanation as to why the sintering effects are greater in the CZA-Cs catalysts activated under dry, reducing conditions.

Unfortunately, the alumina, and any Al-containing phases, remain poorly crystalline/amorphous to XRD following passivation of the activated catalyst, thus its behaviour must be inferred from the Rietveld refinement analysis. With respect to the amorphous content calculated for each activation procedure, it is expected, from the weight fractions calculated for Cu-containing species and ZnO, that it is most likely that segregation of the Cu component has occurred, and an amorphous Cu/Al phase has formed.\textsuperscript{70} To the best knowledge of the author, such a phase has only been reported by F. Cavani \textit{et al.}, though there has been evidence of an X-ray amorphous CuO/ZnAl\textsubscript{2}O\textsubscript{4}-type material forming, and an amorphous Cu/Zn HTLC (Cu,Zn)\textsubscript{6}Al\textsubscript{2}(OH)\textsubscript{16}CO\textsubscript{3}∙4H\textsubscript{2}O in other literature.\textsuperscript{61,70,82} However, as evidenced by the structural reversibility of these HTLC compounds, it is not unlikely that the [H\textsubscript{2}O], either produced by the reduction of copper and/or added to the reactor environment, allows hydrothermal ageing of the catalyst to take place, regenerating an HTLC. Studies have shown crystalline HTLCs decompose at temperatures > 200 °C, which would also account for the lack of an HTLC phase visible in the final diffraction patterns.\textsuperscript{69,83} Any form of an Al-containing phase would cause segregation of alumina, therefore it would be expected that the Al\textsubscript{2}O\textsubscript{3} would show signs of sintering and pore growth.\textsuperscript{77}

Sintering of Cu\textsuperscript{0} results in loss of surface area of the active component in the LTS reaction and, therefore, is considered a major deactivation mechanism for these types of catalysts.\textsuperscript{84} In the dry studies, the metallic copper crystallite sizes are comparable, with sintering being slightly more prevalent in the Cs-promoted catalyst. This, again, is most likely a result of the extra topotactic transformation of the HTLC phase during impregnation of the precursor. The greatest extent of sintering is prevalent in the wet studies. Segregation of the Cu phase is already expected owing to the HTLC formation. This makes the Cu\textsuperscript{0} more susceptible to sintering due to decreased SMSI between the Cu\textsuperscript{0} and ZnO and Cu\textsuperscript{0} and Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{77} However, the influence of Cs-promotion on the behaviour of the Cu-component in the standard and promoted catalysts will be discussed in Section 5.4.2.

The relationships between [H\textsubscript{2}] and the [H\textsubscript{2}O\textsubscript{(g)}] in the reducing atmosphere with respect to the changes to the pellet’s pore diameter and porosity, and thus sintering, are displayed graphically in Figure 5.41. A clear trend emerges for the pore diameters for all catalysts, under all activation conditions considered, in that introducing steam into the reduction environment causes a substantial increase in the mean pore diameters.\textsuperscript{77} As can be seen in Figure 5.41 (b-i), the critical amount of steam present to cause pore expansion is between 0 and 10 vol.% H\textsubscript{2}O\textsubscript{(g)} as the pore expansion in 10 vol.% water vapour (200 KPa) is comparable to the 20 vol.% study. In the unpromoted catalyst, this effect is not completely caused by sintering of the zincite support,
though this contributes to the larger pore diameter as evidenced by the CZA wet, inert test. However, there appears to be an alternative mechanism at work in the promoted catalyst, potentially as a result of the Cs-promoter. When CZA-Cs is subjected to a wet, inert atmosphere, the mean pore diameters are comparable to those of the CZA-Cs reduced in 5 % H\textsubscript{2}/Ar, 20 vol.% H\textsubscript{2}O.

Interestingly, in the dry reductions, the mean pore diameter increases with rising [H\textsubscript{2}] for the CZA/CZA-Cs and PH-CZA/PH-CZA-Cs catalysts, with a greater increase seen for the pre-hydrated catalysts compared to the as-prepared (fresh) catalysts. Once the catalysts are introduced to the wet atmosphere, it appears the mean pore diameter is then not only dependent on the [H\textsubscript{2}], but also the amount of time it is exposed to the wet atmosphere. The smallest average mean pore diameters are measured for the 24 h (5 % H\textsubscript{2}) activations of the fresh catalysts and increase for the 48 h (1 % H\textsubscript{2}) activations of the equivalent catalysts. However, the pre-hydrated catalysts appear to be more affected by the [H\textsubscript{2}].

The porosity is defined as the fraction of void volume over the apparent total bulk volume of the pellets (in %); therefore, as porosity increases, so does the void volume.\textsuperscript{85} It was expected that with growing pore diameter, there would be an increase in porosity; however, Figure 5.41 (a-ii) and (b-ii) show that this is not the case for all activation studies.
The mechanical strength data for the pellets which underwent the activation procedures is summarised in Figure 5.42. It is evident that reducing in a wet atmosphere is severely detrimental to the average radial crush strength of the resultant pellets. The average hardness of the fresh CZA, CZA-Cs, PH-CZA and PH-CZA-Cs (105(38) N, 106(16) N, 113(28) N and 128(22) N, respectively) have not been shown in the figures.

As expected, it appears that loss of mechanical strength is related to sintering phenomena caused by the presence of water vapour.
The Role of Caesium

First, the dry activation conditions will be considered to elucidate any influence of Cs-promotion on the reducibility of the active copper component. As discussed in the results, the least harsh reduction conditions of the 1 % H\textsubscript{2} studies do not show much difference along the bed to draw a conclusion on how the promoter affects the reduction behaviour. The Cu\textsuperscript{0} crystallite sizes are slightly larger for the promoted catalyst, but this is most likely a result of the retrotopotactic transformation which occurred during incipient wetness impregnation. It is when these conditions are exacerbated under 5 % H\textsubscript{2} that the Cs promoter behaviour can begin to be inferred. Within the standard catalyst bed complete reduction is achieved, and it appears from the trend in metallic copper crystallite size (Figure 5.43 (a)), that they are effected by the temperature gradient present along the bed. This behaviour is also seen for PH-CZA. However, the Cu\textsuperscript{0} crystallites in the promoted catalyst do not appear to be affected by the temperature gradient (Figure 5.43 (b)), suggesting there is a more dominant mechanism underway which negates this.

Complete reduction is also not achieved for CZA-Cs, or PH-CZA-Cs, under 5 % H\textsubscript{2}; therefore, Cs appears to be inhibiting the copper from fully reducing. It is proposed that the water produced during reduction interacts with the Cs on the surface, dissociating via adsorbed hydroxyl species. These species retard the reduction in this manner.\textsuperscript{13} From Figure 5.40 (a-i) and (b-i), there is not sufficient water present to dramatically induce sintering of the ZnO component, therefore any phase segregation phenomena are not as expressed in these studies. This may also account for the similar crystallite sizes between the standard and promoted dry activation investigations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Summary of the (a) CZA/PH-CZA and (b) CZA-Cs/PH-CZA/Cs average pellet mechanical strength following activation.}
\end{figure}
Figure 5.43: Summary of the final (a) standard and (b) promoted catalysts’ metallic copper crystallite sizes following reduction in a dry atmosphere, where position 1 signifies the top of the bed, and position 4 the bottom

In order to try and ascertain the role of Cs under wet activation conditions, the 1 % H₂, 20 vol.% water vapour study will first be considered. On first inspection there is a clear difference in the reduction behaviours of the standard and promoted catalysts: the standard catalyst bed remains almost completely oxidic, whereas the promoted catalyst bed can begin reducing, but with major sintering of the active component occurring. It has already been introduced that it is thought HTLC formation is taking place, especially during the wet activation studies, causing a topotactic transformation which inevitably results in phase segregation of the Cu, ZnO and Al₂O₃. The high [H₂O(g)] in the gas feed appears to saturate the surface of the CZA catalyst which inhibits reduction, therefore phase segregation is only visible through the sintering of the ZnO. By incorporating the Cs-promoter, the effects of phase segregation are dramatic with the average Cu⁰ crystallite size increasing from 15.0(6) nm (CZA-Cs dry 1 % H₂ study) to 55.9(8) nm. It is believed that the phase segregation effects are most prominent in the Cs-promoted catalyst for two reasons:

(1) As seen in the dry 5 % H₂ activation studies, Cs incorporation, even at low weight loadings, promotes water dissociation on the surface of the catalyst. This occurs via stabilised O(ads), OH(ads) and H₂O(ads) species, potentially promoting in situ generation of HTLCs as a by-product of the hydroxylated surface. Therefore further promotion of HTLC formation in the promoted catalyst would see greater effects of phase segregation.

(2) It is believed that within these systems, Cs will preferentially donate an electron into the empty Cu(s,p) band, forming a Cs-Cu bond (Section 5.1.1). The zincite readily agglomerates in a wet atmosphere, as evidenced by the wet, inert studies, which would also reduce the favourable metal-support interactions between Cu-ZnO, leaving Cu⁰ essentially unsupported.
as the Cs ion is large enough to inhibit reincorporation into an oxidic framework. The Hüttig temperature of unsupported copper is \textit{ca.} 179 °C which is below the activation (and operation) temperature of the LTS reactor (\textit{Section 1.2.2}). ZnO and Al\底线{2}O\底线{3} are incorporated as thermal stabilisers to increase this temperature, decreasing the likelihood of sintering by reducing the Cu\底线{0} atoms’ surface mobility.\textsuperscript{86} Therefore, reduced metal-support interactions allow the Cu\底线{0} atoms to move more freely across the surface, forming the large ingots of metallic copper visible in the diffraction patterns.

When the 5 % H\底线{2}, 20 vol.% steam results are considered, a similar trend can be seen. Partial reduction of both the CZA and CZA-Cs beds is achieved, with varying degrees of Cu\底线{0} sintering: the CZA bed’s average Cu\底线{0} crystallite size increases from 13.1(4) nm in the dry study to 28.8(6) nm, whereas the CZA-Cs’s average metallic crystallites during dry activation are 18(1) nm, compared to 48(2) nm for the wet study. It is important to note when interpreting these results, that the 5 % H\底线{2} activation studies were carried out for 24 h compared to 48 h for the 1 % H\底线{2} studies. This means that within the latter tests, the pellets were exposed to a wet atmosphere for double the length of time, so effects of phase segregation are expected to be more extreme.

The pre-hydrated catalysts exhibit similar Cu\底线{0} behaviour to the CZA and CZA-Cs catalysts as shown in \textit{Figure 5.44}. Within the 1 % H\底线{2} study for the PH-CZA-Cs catalyst, the active component begins reducing and the sintering effects are minimal (16.2(4) nm average Cu\底线{0} crystallite size), in comparison to the wet activation which saw the largest Cu\底线{0} agglomerates form (75(5) nm on average). The wet study appears to have a more pronounced water gradient along the bed, with the majority of the reduction occurring in positions 1 and 2. This can be rationalised accordingly: as the gas feed enters the reactor, the hydrogen works to reduce the CuO while the Cs dissociates water on the surface, through adsorbed oxygen-containing species. As the Cs preferentially bonds to the Cu\底线{0} via an electron donation mechanism, the stabilised O\底线{(a)}, OH\底线{(a)} and H\底线{2}O\底线{(a)} species inhibit complete reduction of the copper, therefore the H\底线{2} entering the bed is constantly working to reduce the top of the bed.\textsuperscript{12} This allows the water gradient to build up at the bottom of the bed, saturating the catalyst surface as in the 1 % H\底线{2} CZA study. This effect is also seen to a lesser extent in the wet 5 % H\底线{2} study.
Conclusion

To conclude, activation carried out in the investigated wet atmospheres causes early onset deactivation of the CZA/PH-CZA and CZA-Cs/PH-CZA-Cs catalysts. Phase segregation of the active Cu$^0$ component from the supporting ZnO and Al$_2$O$_3$ (Section 5.4.1) is the greatest cause for deactivation witnessed in these studies, and this process is aggravated by the presence of the Cs-promoter (Section 5.4.2). However, it is proposed that this is not the only effect of the promoter; the following hypothesis for the role of the caesium promoter has been concluded from the results presented in this chapter.

It is known that caesium is an electronic promoter, and it is expected that Cs preferentially donates an electron into the empty Cu($s,p$) band. Thus, when water is present in the reducing gas atmosphere, whether it is added or produced as a by-product of the activation, it interacts with the Cs on the surface of the active component via a dissociation reaction. This results in stabilized oxygen-containing species adsorbed to the Cs surface which inhibit complete reduction of the active copper component. These stabilised O$_{(a)}$, OH$_{(a)}$ and H$_2$O$_{(a)}$ species also promote formation of a HTLC. However, it has been established that the working temperature of the activation (220 °C) is above the decomposition temperature of these hydrotalcite-like compounds, therefore there is a constant rearrangement occurring on the surface. Through this mechanism, phase segregation occurs to a greater extent than the standard catalyst. Therefore, it is proposed that, due to its large ionic radius and low surface free energy, caesium migrates across the surface to the copper during these rearrangements. This inhibits any SMSI between the Cu$^0$ and ZnO and the Cu$^0$ and Al$_2$O$_3$, promoting agglomeration of the unsupported copper. The copper component thus more readily reduces, and sinters, due to Cs inhibiting the support interactions.
Despite the low weight-loading of the promoter, its large ionic radius and low surface free energy, paired with the highly dispersed copper are the reasons this phenomenon is observed.

Other means for deactivation also occur during the wet investigations. Once water vapour is introduced into the reactor atmosphere, sintering of the zincite support is incurred. Not only does this result in another mechanism for segregating a support phase from the active component, but evidence of pore growth, and thus diminished mechanical strength, also lead to failure of the catalyst.

5.6. Bibliography

40. P. Zhao, L. Lu, X. Liu, A. G. de la Torre and X. Cheng, Crystals, 2018, 8, 110.
Chapter 6: SUMMARY AND CONCLUSIONS

6.1. Summary
The work in this thesis has focused on the effects of caesium promotion on the preparation and activation of Cu-based LT-WGS catalysts, highlighting previously unreported areas for early onset deactivation mechanisms to occur.

6.1.1. Preparation and Characterisation of Binary, Ternary, and Cs-Promoted Catalysts
Despite Chapter 3 solely focussing on synthesising LT-WGS catalysts with industrially relevant structural and morphological properties, a potential early onset deactivation mechanism was identified. Here, formation of the hydrotalcite-like compound (HTLC) in the precipitate resulted in phase segregation of the active copper component during incipient wetness impregnation of the Cs-promoter. It was shown that this was a result of the impregnating solution, H$_2$O, not the Cs$_2$CO$_3$, which aided crystallisation of the HTLC and caused growth of the tenorite (evidenced in the calcined catalysts’ diffractograms in Section 3.3.4).$^{1-3}$ This is a well-known issue associated with hydrotalcite-like compounds due to the so-called memory effect; however, it has not been previously discussed in terms of negatively impacting LTS catalyst stability.

6.1.2. Investigating How the Reducing Gas Composition Affects the Microstructure of the LT-WGS Catalysts
Intrinsic activity of CuO/ZnO/Al$_2$O$_3$ methanol synthesis catalysts has been intimately linked to the anisotropic behaviour of copper, and thus the presence of lattice defects.$^{4-6}$ To the best knowledge of the author, this study is the first instance in which this type of analysis has been applied to LT-WGS catalysts, comparable to those employed in industry; high copper loading catalysts were also investigated to verify the role of ZnO. Chapter 4 looks at the influence the activation procedure has on the resultant defect microstructure of the active copper component, as well as the effects of the Cs-promoter and the concentration of [ZnO].

It is well established that strong metal support interactions (SMSI) facilitate the migration of partially reduced zinc oxide species to the surface of the metallic copper nanoparticles, creating the catalytically active sites for WGS activity.$^{5,7,8}$ However, this requires high dispersion of the ZnO to be maintained throughout activation and, subsequently, operation. When the copper begins reducing, the water produced clearly hydroxylates the ZnO surfaces causing growth via Ostwald ripening, and this is exacerbated by the presence of the Cs-promoter (refer to Section 4.9.2.2).$^{9-11}$ It is believed that this is due to Cs facilitating water dissociation on the surface of the copper, enhancing the surface diffusion effects.$^{12-14}$ While this is undesirable for catalyst stability, as weakening the structural promotional effects of the zincite support causes sintering of the active Cu$^0$ component, it is also a direct result of the desired electronic promotional effects of caesium.
Employing Equation 4.22 to evaluate the dislocation character of the unpromoted standard and high copper loading systems in the final measured diffraction patterns suggested that increasing the [ZnO] afforded dislocations with more edge character (refer to Section 4.9.2.5).\textsuperscript{15} It also showed that the standard catalyst beds possessed more edge character following activation in greater [H\textsubscript{2}]; this was rationalised due to the more forcing reducing atmosphere promoting substitutional Cu-Zn surface-alloy formation (aka a substoichiometric ZnO\textsubscript{x} overlayer on the Cu\textsuperscript{0} surface, where 0 < x < 1).\textsuperscript{5,16} This trend was not seen for the standard promoted catalysts; in fact, the presence of the Cs-promoter appeared to dominate the reducing atmosphere effects and afforded catalysts which more closely resembled the dislocation character of the standard unpromoted 5 \% H\textsubscript{2} studies. Interestingly, the AP-XPS measurements collected for the standard catalysts showed that caesium facilitated the partial reduction of the zincite support to a greater extent, therefore both the Cu-ZnO SMSI and Cs-ZnO relationship were determined to favour dislocations with more edge character in these systems (refer to Section 4.9.2.8.1).\textsuperscript{12}

The plotting and mapping of the stacking fault probability, $\alpha$, along the length and across the plane of the catalyst beds have been the culmination of this body of work (refer to Sections 4.9.2.7 and 4.9.3.3, respectively). For the first time, the microstrain present in the active copper component has been mapped across the plane of the catalyst bed, where each pixel of the resultant image corresponds to an individual diffraction pattern as it has been acquired tomographically. The intrinsic activity of the copper is reportedly correlated to increased stacking fault probability, and can be further enhanced through Cu-Zn alloying (low stacking fault energy).\textsuperscript{5,6,17,18} The extent of sintering of the active component in the high copper loading catalysts is believed to occur via a particle growth mechanism, driven by the high [screw dislocation], which consumes the majority of the surface defects and so the resultant catalysts have low $\alpha$.\textsuperscript{19–21} Alternatively, the standard catalysts possess greater $\alpha$, with the unpromoted catalysts appearing more active than the promoted. Despite the presence of Cs (BCC) facilitating partial reduction of the zincite, it is believed it acts as a steric hinderer on the surface of the Cu\textsuperscript{0} (FCC), preventing surface-alloy formation, as opposed to the standard unpromoted catalyst in which ZnO (HCP) can readily be substituted.\textsuperscript{17,22}

### 6.1.3. Industrial Scale-Up and Testing of the Effects the Activation Procedure has on Catalyst Pellet Composition

When steam is incorporated into the reducing atmosphere, there are catastrophic consequences, as shown in Chapter 5. The failure mechanisms identified during catalyst activation in high partial pressures of steam result in severe structural and morphological changes for both the unpromoted and promoted standard catalyst pellets and can be linked to two root causes: hydrotalcite formation and the presence of the Cs-promoter.

It is believed that the phase segregation effects first seen in Chapter 3 are aggravated in the investigated wet studies; the Rietveld refinement analysis suggests the formation of an
amorphous/poorly crystalline Cu/Al phase which has been assigned as an HTLC. The reactor environment essentially promotes hydrothermal ageing of the catalyst, facilitating the retrotopotactic transformation of the HTLC first expressed in the precipitate, and shown to readily recrystallise in the pre-hydrated samples, consequentially resulting in phase segregation of the active copper component. The subsequent reduced SMSI between the Cu$^0$ and ZnO not only makes the zincite more susceptible to hydroxylation, but both components incur sintering via Ostwald ripening. This also causes pore growth and mechanical failure of the catalyst pellets which has disastrous consequences for industry (refer to Section 5.4.1).

Caesium in the promoted catalyst pellets exacerbates these effects (refer to Section 5.4.2). Its role in water dissociation has already been discussed as well as the negative impacts sustained by the ZnO support. However, as Cs preferentially chemisorbs to the surface of copper via an electron donation mechanism and possesses high surface mobility (low surface free energy), it is anticipated that during reconstruction of the catalyst surface (topotactic/retrotopotactic transformations) it remains on/continually migrates to the Cu$^0$ surface. Its large ionic radius acts as a steric hinderer, inhibiting any promotional interactions between copper and its supports, and thus large agglomerates of unsupported Cu$^0$ are formed.

6.2. Conclusions and Future Work

In conclusion, the effects of caesium promotion on the preparation and activation of LT-WGS catalysts are undesirable. The benefit of the electronic promoter inhibiting MeOH production and facilitating water dissociation on the catalyst surface, which is the rate-determining step of the water-gas shift reaction, is outweighed by the failure mechanisms that are exacerbated by its presence.

The work in this thesis has focussed on recreating industrial LTS activation conditions. It would therefore be expected that, if the promoted catalyst failed in an industrial plant, e.g. pressure drops and reduced/no activity, characterisation of the catalyst would show three things: (1) large ingots of copper would form due to phase segregation effects of hydrotalcite formation in wet atmospheres, (2) sintering of the zincite due to reduced SMSI, intensified by the presence of caesium both as a steric hinderer and due to the excess water held on the catalyst surface, and (3) mechanical failure of the catalyst pellets as a result of steps (1) and (2).

In order to circumvent these disastrous catalyst failure mechanisms, alterations must be made to the catalyst synthesis method and activation environment. Initially, the main obstacle would be to ensure any (amorphous/poorly crystalline/crystalline) HTLCs expressed in the initial precipitate are fully decomposed during calcination to afford stable (crystalline/quasicrystalline) spinel-like phases. These can then act as geometrical spacers to prevent the Cu$^0$ from agglomerating, and also act as heat sinks during reduction.

Furthermore, reducing the steam concentration within the reactor throughout activation, and subsequent water-gas shift operation, is paramount. It is evident in both Chapters 4 and 5 that
the H₂O produced during reduction in a dry atmosphere causes growth of Cu⁰ and the zincite support. Unfortunately, the critical steam concentration in which these effects are fatally exacerbated was not determined in Chapter 5 due to limitations with the HPLC pump used, but the consequence of its presence is clearly seen. Not only does the surface of the ZnO become hydroxylated, incurring sintering via Ostwald ripening, the caesium promoter aggravates these effects, offering an additional mechanism for phase segregation of the copper component. It is expected that any quantity of steam incorporated into the reducing atmosphere would have negative consequences for a Cs-promoted catalyst and should be avoided. This, alas, is unrealistic for the water-gas shift reaction as its reactants include H₂O; perhaps by avoiding HTLC formation these effects can be somewhat mitigated, but for the investigated catalysts, it would be necessary to explore other promoters as extended lifetimes could not be guaranteed under industrial conditions.

The discovery that XRD-CT can also be used to map stacking fault probabilities, as well as other microstructural defects, across the plane of the catalyst bed is ground-breaking. Intrinsic Cu/ZnO/Al₂O₃ catalytic activity is reported as being intimately linked to its defect structure for MeOH synthesis catalysts but has not been explored for LT-WGS systems. Typical studies utilise conventional laboratory- and synchrotron-based X-ray techniques which afford an average assessment of a catalyst bed at a given time and position, but this thesis introduces XRD-CT as a technique which affords far more comprehensive analysis of the microstructural properties most important for catalytic materials (peak asymmetry, strain broadening, etc.) tomographically. Up till now, XRD-CT was solely employed to evaluate phase information and peak widths (Scherrer equation) to give insights into catalyst behaviour. The author has now shown that researchers can obtain more nuanced information from their collected data, to glean information about microstrain, dislocation character, and ultimately, stacking fault probabilities. This study is the first of its kind and has applications across many catalytic systems and materials.

6.3. Bibliography
Chapter 7: APPENDIX

7.1. Chapter 1

7.1.1. Titration curves for the pure and mixed Cu/ZnO/Al$_2$O$_3$ solutions

M. Behrens et al. produced the following titration curves by acidifying either the pure Cu, Zn, Al and mixed Cu/ZnO/Al$_2$O$_3$ solutions with nitric acid and alkalising with Na$_2$CO$_3$ precipitating agent:\(^1\)

![Pure Cu solution titration curve](image1)

**Figure 7.1**: Pure Cu solution titration curve. A clear plateau is reached at ca. pH 3 as the precipitating agent is consumed by the Cu$^{2+}$ until a ratio of 1.5 [CO$_3^{2-}$]/[Cu$^{2+}$] is achieved. Above pH 4, the precipitate has formed. A decrease in pH is evident from pH 10 to pH 9 which corresponds to the formation of tenorite.\(^1\)

![Pure Zn solution titration curve](image2)

**Figure 7.2**: Pure Zn solution titration curve. Precipitation occurs when the ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] is 0.7, which starts at ca. pH 5. The pH then increases to pH 11 until a final [CO$_3^{2-}$]/[Zn$^{2+}$] ratio of 1.6 is achieved.\(^1\)
Figure 7.3: Pure Al solution titration curve. At ca. pH 2.5 there is evidence of an olation process due to the plateau present. This occurs between hydroxyl ions and Al\textsuperscript{3+} centres, forming a bridging ligand. The precipitate only formed at ca pH 5 at a ratio of 4.9 [CO\textsubscript{3}\textsuperscript{2−}] / [Al\textsuperscript{3+}].\textsuperscript{1}

Figure 7.4: Mixed Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} solution titration curve. Both plateaus observed at pH 3 and pH 5 in the titration curve indicate the Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ions are being sequentially precipitated out of solution. This does not reflect a true coprecipitation process. The olation of Al\textsuperscript{3+} was seen to still occur at ca. pH 2.5.\textsuperscript{1}
7.1.2. Crystal Structure of Aurichalcite

Figure 7.5: Various copper coordination environments present in the aurichalcite crystal structure (M1: octahedral, M2: tetragonally elongated octahedral site, M4: trigonal bipyramidal)

Figure 7.6: Coordination environment of zinc in aurichalcite (M3: tetrahedral)

7.1.3. Crystal Structure of Hydrozincite

Figure 7.7: Both the copper coordination environments present in the hydrozincite crystal structure (M1: octahedral, M2: tetragonally elongated octahedral site)
Figure 7.8: Coordination environment of zinc in hydrozincite (M3: tetrahedral)

7.2. Chapter 2

7.2.1. X-ray Techniques

7.2.1.1. Laboratory X-ray Sources

The electron beam, generated by thermionic emission from the cathode, bombards the cooled metal target causing radiation to be emitted through the beryllium (Be) windows in the form of X-ray photons. The windows are composed of Be due to its low atomic number, making it very permeable to X-rays.²

Figure 7.9: Illustration of a conventional sealed X-ray tube; image taken from P. Atkins and J. de Paula, Atkins’ Physical Chemistry, Oxford University Press, Oxford, 9th edn., 2010, ch. 19, pp. 695-742.

7.2.1.2. Scattering Factor

The scattering direction at $\theta = 0$ (and hence $\sin\theta\lambda^{-1} = 1$) is considered to be the ‘forward direction’; here, the scattering factor, $f_n$, is greatest and is equivalent to the number of electrons present in the interrogated atom. It is important to note that the scattering factor is independent of
the atoms’ position in the unit cell. As the angular value increases, the magnitude of the atomic scattering factor decreases, as shown in Figure 7.10. To summarise, the greater the atomic number, the greater the scattering factor.\textsuperscript{2}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_10.png}
\caption{The relationship between the atomic scattering factor and $\sin \theta \lambda^{-1}$}
\end{figure}

\subsection{7.2.1.3. Conventional Computed Tomography}

X-ray absorption computed tomography can only occur if, when a material is interrogated with a monochromatic beam of wavelength $\lambda_0$ and intensity $I_0$, a fraction of the radiation ($I/I_0$) is able to pass through and be detected as depicted in Figure 7.11; the wavelength of the beam does not change, but its intensity does.\textsuperscript{4}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_11.png}
\caption{Possible interactions that occur when X-rays are used to illuminate a material; image adapted from R. Jenkins, Encycl. Anal. Chem. Appl. Theory Instrum., 2006, 13269-13287.\textsuperscript{4}}
\end{figure}
\[ I(\lambda_0) = I_0 \exp^{-\left(\mu \rho x\right)} \]

*Equation 7.1: Beer-Lambert’s law for transmission*

Where \( I(\lambda_0) \) = transmitted intensity of X-ray photon beam
- \( \mu_a \) = absorber mass attenuation coefficient (a.k.a. absorption coefficient)
- \( \rho_a \) = absorber density
- \( x_a \) = thickness of absorber

Once the transmitted intensity is measured, it is evident that a quantifiable number of photons is lost during the absorption process, equal to \((I_0 - I)\). The majority of this loss is attributed to the photoelectric effect;\(^4\) when an X-ray photon is absorbed by the core energy level electrons of the sample/absorber (e.g. 1s or 2p), two possible mechanisms can occur: (1) if the binding energy of the electron exceeds that of the incoming X-ray energy, it is not absorbed or (2) if the electronic binding energy is less than the energy of the X-ray, the electron is excited to either a vacancy or the continuum. The latter results in the X-ray being absorbed and the remaining energy is ejected in the form of a photoelectron.\(^5,6\)

7.2.2. Optical Spectroscopy Techniques

7.2.2.1. Infrared Spectroscopy

In general, the available modes of molecular vibrations can be categorised as in *Figure 7.12*. As depicted, there are two types of stretching modes: symmetric and antisymmetric. Symmetric stretching allows the molecule to move through space, whereas antisymmetric stretching causes either an increase or a decrease in bond length. There are four types of bending vibrations: scissoring, rocking, wagging and twisting. Bending requires less energy than the stretching modes and so occurs more readily. The bond strength is another factor to take into account; single bonds require less energy to stretch/bend than a double/triple bond and so its movement appears at lower wavenumbers.\(^7\)
Figure 7.12: General representation of molecular modes of vibration, the (+) sign illustrates movement towards the reader and the (-) sign moves away from the reader; image adapted from M. El-Azazy, Comprehensive Analytical Chemistry: Modern Fourier Transform Infrared Spectroscopy, ed. M. El-Azazy, IntechOpen, 2018, ch. 1, pp. 1-10.7

7.2.3. Surface Area and Porosity Techniques

7.2.3.1. IUPAC BET Isotherm Types

For completeness, all International Union of Pure and Applied Chemistry (IUPAC) physisorption isotherms have been illustrated in Figure 7.13.8

Figure 7.13: IUPAC classifications of BET physisorption isotherm types; images taken from M. Thommes et al., Pure Appl. Chem., 2015, 87, 1051-1069.8
Type I: Reversible isotherm characteristic of microporous materials with Type I a) majority narrow micropores (pore width < 1 nm) and Type I b) a range of pore size distributions (pore width < 2.5 nm).\textsuperscript{8}

Type II: Reversible isotherm for macroporous materials.\textsuperscript{8}

Type III: There is no point of inflection, B, at low \(p/p^0\) indicating that the monolayer formation is not identifiable for these types of macroporous or non-porous materials.\textsuperscript{8}

Type IV: The difference between these isotherms for mesoporous materials is that Type IV (a) depicts capillary condensation with hysteresis as the critical width for pores is exceeded, and the reversible Type IV (b) isotherm is representative of smaller pore widths.\textsuperscript{8}

Type V: As with Type III isotherms, there are weak adsorbent-adsorbate interactions at low relative pressure; however, pore filling occurs at higher \(p/p^0\) which is indicative of H\(_2\)O adsorbing on microporous/mesoporous surfaces.\textsuperscript{8}

Type VI: Uniform non-porous materials generate a reversible step-wise Type VI isotherm that shows the layer-by-layer adsorption mechanism. To successfully measure these materials, it is best to probe the surface with either krypton (77 K) or argon (87 K) on graphitised carbon blacks.\textsuperscript{8}

\subsection*{7.2.3.2. IUPAC Hysteresis Shapes}

As mentioned in \textit{Section 2.4}, the pore structure present in the catalyst determines the shape of the hysteresis formed, as shown in \textit{Figure 7.14}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{hysteresis_shapes.png}
\caption{Possible N\textsubscript{2} BET hysteresis shapes; images taken from M. Thommes et al., Pure Appl. Chem., 2015, \textit{87}, 1051-1069.\textsuperscript{8}}
\end{figure}

Types H1 and H2: These hysteresis shapes are typically characteristic of catalysts containing either cylindrical pores, consolidated (aggregated) spheroidal particles or
unconsolidated (agglomerated) spheroidal particles. Where Type H1 materials have pores with a uniform shape and size, H2 materials have a non-uniform distribution of pores in which the pores are partly blocked with a narrow (Type H2 (a)) or wider (Type H2 (b)) range of pore necks. Mesoporous catalysts generally give this profile.8,9

Types H3 and H4: Materials consisting of aggregated or agglomerated particles, that form slit shaped pores, generate this type of hysteresis. As above, they are distinguished by their uniform (H3) and non-uniform (H4) pore shape and size and are generally characteristic of zeolites and active carbons.9

Type H5: Although uncommon, this type of hysteresis is characteristic of mesoporous materials with both open and partially blocked pores.8

No hysteresis: This arises when the catalyst contains an irregular array of pore shapes and sizes, e.g. cone-shaped, wedge-shaped and blind cylindrical pores.9

7.2.3.3. Degrees of Wettability

Where N2 adsorption is dependent on capillary condensation in the pores (θ < 90°), mercury porosimetry is a non-wetting technique (θ > 90°), therefore pressure must be applied to determine pore size distribution. In general, Hg exhibits a high contact angle with most solids and, when θ is unknown, it is assumed that the contact angle is 140°.10

![Figure 7.15: Examples of different contact angles depending on the wettability of the fluids on the surface; image adapted from L. M. Anovitz and D. R. Cole, Rev. Mineral. Geochem., 2015, 80, 61-164.](image)

7.3. Chapter 3

7.3.1. Metrohm 902 Titrando Variables

The Titrando is operated through the Metrohm software tiamoTM 2.5. All coprecipitations of catalysts within this thesis were carried out through this software and the method used is shown in Figure 7.16. The first command calls for addition of the metal nitrate solution at a constant rate to be titrated into the heated deionised H2O. As this occurs, the STAT pH command allows the pH to be monitored and controlled by first controlling the amount and speed at which the precipitating agent (Na2CO3) is added along with the acidic metal nitrate solution, and finally it
allows ageing of the mother liquor to be carried out at constant pH through addition of the metal nitrate solution.

Figure 7.16: Screenshot of the tiamo™ 2.5 method used for the coprecipitation of the majority of the catalysts in this thesis

Figure 7.17 and Figure 7.18 are examples of the images generated in the final tiamo™ 2.5 report, detailing how much Na₂CO₃/metal nitrate solution was added to maintain the pH at 7 and how effective it was, respectively.
Figure 7.17: Addition of sodium carbonate to the reaction slurry and control of pH throughout the precipitation

Figure 7.18: Addition of metal nitrate solution during ageing and control of the pH throughout the process
7.3.2. Quartz Internal Standard

![Quartz Internal Standard Diffraction Pattern](image)

*Figure 7.19: Quartz internal standard diffraction pattern; the reference pattern for quartz is given below.*

7.3.3. PMMA Sample Holder

![PMMA Sample Holder Diffraction Pattern](image)

*Figure 7.20: PMMA sample holder diffraction pattern*
7.4. Chapter 4

7.4.1. Subtraction of quartz capillary from raw diffraction data

The subtraction of the collected quartz capillary diffraction pattern from the measured raw data is shown in Figure 7.21. Following this, the background is easier to model/fit during Rietveld analysis.

![Figure 7.21: Example of the quartz capillary subtraction from the measured raw diffraction data of sCZA reduced in 5% H2 (position g, at time 70 min at the end of the reduction ramp)](image)

7.4.2. Temperature Gradient

Within an ideal catalyst bed operating under true plug flow conditions, fluctuations in temperature would not be observed; however, this is not always the case for integral reactors. The set-up of the microreactor (Section 4.8.4) does not include a thermocouple embedded in the bed, and though thorough calibrations were carried out prior to any testing, it is unknown whether the temperature remains at 230 °C throughout each activation procedure. In an attempt to circumvent this, the in situ unit cell parameters determined by the Rietveld method have been evaluated to yield the estimated local temperature at the position of the measured diffraction pattern. It is well known that when most solid materials are heated, their lattice expands to accommodate the increasing interatomic separation. Typically, the expansion of crystals with cubic symmetry is considered isotropic, i.e. expansion occurs equally along each crystallographic orientation, and can be calculated for solid materials according to Equation 4.41.

\[
\frac{l_f - l_0}{l_0} = \alpha_l (T_f - T_0)
\]

\[\therefore l_f = l_0 (1 + \alpha_l \Delta T)\]

*Equation 7.2: Thermal expansion of a solid material*
Where  
\[ l_0 = \text{initial length} / \text{Å} \]
\[ l_f = \text{final length} / \text{Å} \]
\[ \alpha = \text{linear expansion coefficient} / \text{K}^{-1} \]
\[ \Delta T = \text{change in temperature} (T_f - T_0) / \text{K} \]

Despite it being known that metallic copper is anisotropic in nature (refer to Section 4.3), the thermal expansion of face-centred cubic materials is treated as isotropic, as stated above.\(^{13,14}\) Therefore, the ideal Cu\(^0\) unit cell parameters \(a\), or in this case \(l_f\), have been determined at elevated temperatures according to the linear expansion coefficient of copper, which is cited as 17.0 \(\times 10^{-6}\) K\(^{-1}\) (Figure 7.22).\(^{13,16,17}\) A broad temperature range has been plotted in the event the reduction caused a large exotherm in the bed or if the furnace deviated from the set temperature. The results of this were used as the minimum and maximum lattice parameter limits. (The anticipated thermal expansion of zincite was also calculated and the results can be found in Appendix 7.4.2.3).

![Figure 7.22: Temperature dependence of the Cu\(^0\) lattice parameter, a](image)

Equation 4.41 can now be applied to the point measurements collected along the bed under varying reducing atmospheres. The unit cell parameters, and thus the calculated temperatures, have been plotted from the cross-over lines determined in Section 4.9.2.1.

7.4.2.1. sCZA and sCZA-Cs

When the reduction behaviours of sCZA and sCZA-Cs were discussed in the previous section, it was supposed that a temperature gradient was present along the bed. As can be seen along the standard catalyst beds reduced under 5 \% H\(_2\) (Figure 7.23), there is a discrepancy in the temperature along the length of the bed, though its behaviour deviates from what was previously hypothesised.
Due to the set-up of the microreactor, it was anticipated that the bottom of the bed would be at a lower temperature owing to the cold delivery of the reducing gases. However, there is a huge deviation from 230 °C (the dashed grey line) at the bottom of the sCZA bed. It is well known that reduction of the copper-based LTS catalyst is exothermic (Equation 7.3), and, if not properly controlled, the exotherm can exceed temperatures of 500 °C. Therefore, it is possible that, once the reducing gas stream came in contact with the bottom of the sCZA bed, reduction immediately took place. However, this does not explain why the temperature remained elevated.

\[
\text{CuO} + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}_2\text{O} \\
\Delta H_{298\text{K}} = -80.8 \text{ kJ mol}^{-1}
\]

*Equation 7.3: Reduction of tenorite*¹⁸

During the reduction ramp, the bottom and middle of the sCZA bed nearly reached complete reduction (*Figure 4.16*); this is reflected in the unit cell parameters as they remain constant (i.e. the calculated temperature remains constant) during the isothermal period of reduction. This behaviour differs from the top of the bed, where a spike in temperature (expansion of Cu\(^0\) lattice) is observable at *ca.* 88 min. As the microreactor is open to the atmosphere, and the GHSV is relatively low, it is presumed that the exotherm is a result of the top of the bed continuously reoxidising and re-reducing which would cause a rise in temperature. However, evidence of cuprite in the diffraction pattern would be seen, if this were the case. Sintering of the active component would also be incurred and will be explored in later sections.

The behaviour of the standard promoted bed varies from that of the unpromoted. Here, the bottom of the bed is significantly below the desired reduction temperature which can be rationalised due to the cold delivery of the reducing gases. The top of the bed exhibits similar behaviour to that of the sCZA bed, although delayed by *ca.* 27 min, and it appears the exotherm influences the temperature at the middle of the bed.

The reduction data acquired at the middle of the bed for both standard systems reduced in 5% H\(_2\) more closely reflect the intended reduction temperature. Thus, it is expected that this position is least affected by the set-up variables.
Figure 7.23: Calculated temperature along the (a) sCZA and (b) sCZA-Cs catalyst bed reduced under 5% H₂ from the Rietveld Cu⁰ unit cell parameter, a; error bars are shown on the graph and the intended reaction temperature, 230 °C, is depicted by the dashed grey line.

In order to compare how the temperature of the bed varies across all investigated activation procedures for the standard catalysts, Figure 7.24 shows the calculated bed temperature extrapolated from the Cu⁰ lattice parameter of the final measured diffraction pattern. In general, the bottom of the bed is lower in temperature than the middle which is in agreement with the cold gases decreasing the local temperature on contact with the bed. The bottom of the sCZA bed reduced in 5% H₂ appears to be an anomalous result. Throughout the middle of the beds, the temperature is better controlled in the sCZA studies than the sCZA-Cs. Unfortunately, only three positions were examined for the promoted 5% H₂ reduction, therefore any deviations along the bed are not seen. When the 2.5% H₂ results are compared, temperature fluctuations appear more pronounced along the promoted bed.
Figure 7.24: Graphical representation of the temperature gradient present along the (a) sCZA and (b) sCZA-Cs catalysts beds at the end of reduction; the dashed black line represents the intended reactor temperature of 230 °C.

Unfortunately, reduction of the sCZA and sCZA-Cs beds under 1 % H₂ were not left to complete reduction due to time constraints on the beamtime. However, it appears from Figure 7.25 (a-i) and (b-i) that the bottom of the bed is below the desired bed temperature of 230 °C, most likely as a result of the cold delivery of the reducing gases. As the promoted standard catalyst was left to reduce for a longer time, evidence of reduction in the middle of the bed is seen, and the temperature is calculated as closer to that of the intended.

The beds reduced in 2.5 % H₂ follow similar temperature profiles during reduction (Figure 7.25 (a-ii) and (b-ii)). As expected, the bottom of both beds is below 230 °C, the middle is ca. 230 °C, and the top fluctuates, most likely as a result of the microreactor being open to the atmosphere.
Figure 7.25: Calculated temperature along the (a) sCZA and (b) sCZA-Cs catalyst bed reduced under (i) 1 % and (ii) 2.5 % H\textsubscript{2} from the Rietveld Cu\textsuperscript{0} unit cell parameter, a; error bars shown on graph and the intended reaction temperature, 230 °C, is depicted by the dashed grey line.

7.4.2.2. hCZA and hCZA-Cs

The calculated temperature profiles at the top, middle and bottom of the unpromoted and promoted high copper loading catalyst beds during reduction under 5 % H\textsubscript{2} are given in Figure 7.26. It was hypothesised that the local bed temperatures would be greater than that of the equivalent standard catalyst beds due to the decreased zincite content; the thermal conductivity of copper is 400 W m\textsuperscript{-1} K\textsuperscript{-1} at room temperature, compared to 50 W m\textsuperscript{-1} K\textsuperscript{-1} for wurtzite ZnO\textsuperscript{19,20}. Therefore, by reducing the quantity of ZnO in the catalyst composition by 2/3 (from ca. 30 wt.% in the standard catalysts to ca. 10 wt.%), the thermal conductivity of the bed would more resemble that of pure Cu\textsuperscript{0} and there would be evidence of conduction as heat transfer. It could be argued that this effect is seen for hCZA in Figure 7.26 (a); the bottom of the bed is ‘coldest’ out of all positions and the top of the bed shows the largest exotherm; however, all bed temperatures exceed...
230 °C. As the only difference between this study and that of sCZA activated under 5% H₂ is the [ZnO], it is presumed sintering of Cu⁰ has taken place, to a greater extent at the top of the bed, as a result of the decreased zincite content. When Figure 7.26 (b) is considered, the hCZA-Cs bed does not follow the same trend, and the bottom of the bed is again below 230 °C. Perhaps the promoter, though only included in small quantities (ca. 1 wt.% Cs₂O), acts as an additional thermal stabilizer. The thermal conductivity of caesium is 36 W m⁻¹ K⁻¹ at room temperature which may account for this.¹⁹

![Figure 7.26](image_url)

Figure 7.26: Calculated temperature along the (a) hCZA and (b) hCZA-Cs catalyst bed reduced under 5% H₂ from the Rietveld Cu⁰ unit cell parameter, a; error bars shown on graph and the intended reaction temperature, 230 °C, is depicted by the dashed grey line.

When the final calculated temperatures are plotted as a function of bed height, it appears that the hCZA catalyst conducts heat more than the hCZA-Cs catalyst.
Figure 7.27: Graphical representation of the temperature gradient present along the hCZA and hCZA-Cs catalyst beds at the end of reduction; the dashed black line represents the intended reactor temperature of 230 °C.

### 7.4.2.3. Calculated thermal expansion of wurtzite ZnO

The synergistic relationship between Cu$^{0}$ and ZnO is well documented in the literature, therefore it is anticipated that the zincite lattice will expand proportionally to the Cu$^{0}$ lattice.\textsuperscript{21–23} However, wurtzite ZnO is composed of two interpenetrating HCP sublattices, thus making it non-cubic.\textsuperscript{24} Iwana et al. show that the temperature-dependence of the wurtzite ZnO lattice parameters can be calculated by employing the following equations (± 5 × 10^{-4} Å):\textsuperscript{14,24,25}

\[
a(T) = 3.2468 + (0.623 \times 10^{-5})T + (12.94 \times 10^{-9})T^2
\]

\[
c(T) = 5.2042 + (0.522 \times 10^{-5})T + (12.13 \times 10^{-9})T^2
\]

\textit{Equation 7.4: Polynomial anisotropic temperature-dependence of wurtzite ZnO lattice parameters} \textsuperscript{24}

Where \( T = \) temperature / K

In order to ensure the correct limits are fixed in the TOPAS input file, both \textit{Equation 4.36} (linear) and \textit{Equation 7.4} (polynomial) have been evaluated and presented in Figure 7.28.
Figure 7.28: Temperature dependence of the lattice parameters (a) $a$ and (b) $c$ for wurtzite ZnO
### 7.4.3. Effective Crystallite Size

Due to errors associated with the (422)- and (333/511)-crystallite sizes, these reflections have not been included when evaluating the mean apparent crystallite size, $D_{\text{eff}}$.

**Table 7.1:** Apparent crystallite sizes (CS) determined by Topas via the Cu⁰ pattern decomposition method for each reflection in the final measured sCZA and sCZA-Cs powder-pattern reduced in 5 % $H_2$

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>sCZA</th>
<th>Error</th>
<th>CS</th>
<th>Error</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>sCZA-Cs</th>
<th>Error</th>
<th>CS</th>
<th>Error</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<td>9.75</td>
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<td>0.09</td>
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</tr>
<tr>
<td>220</td>
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<td>5.58</td>
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<td>9.07</td>
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<td></td>
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<td>0.45</td>
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<td>0.36</td>
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<td>0.42</td>
<td>6.78</td>
<td>0.39</td>
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<td>0.54</td>
<td>5.04</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.2: Apparent crystallite sizes (CS) determined by Topas via the Cu pattern decomposition method for each reflection in the final measured hCZA and hCZA-Cs powder pattern reduced in 5% H2.

<table>
<thead>
<tr>
<th>hkl</th>
<th>hCZA</th>
<th>hCZA-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) CS</td>
<td>Error</td>
</tr>
<tr>
<td>111</td>
<td>11.57</td>
<td>0.10</td>
</tr>
<tr>
<td>200</td>
<td>7.06</td>
<td>0.10</td>
</tr>
<tr>
<td>220</td>
<td>9.29</td>
<td>0.18</td>
</tr>
<tr>
<td>311</td>
<td>9.43</td>
<td>0.18</td>
</tr>
<tr>
<td>222</td>
<td>10.00</td>
<td>0.49</td>
</tr>
<tr>
<td>400</td>
<td>9.89</td>
<td>1.73</td>
</tr>
<tr>
<td>331</td>
<td>7.77</td>
<td>0.44</td>
</tr>
<tr>
<td>420</td>
<td>8.74</td>
<td>0.50</td>
</tr>
<tr>
<td>422</td>
<td>6.59</td>
<td>0.63</td>
</tr>
</tbody>
</table>
7.4.4. Results of the cWH plots for the 5 % H₂ studies

Despite the large scattering of the cWH plots, the apparent Cu⁰ crystallite size and mean residual lattice strain have been extrapolated and presented in Table 7.3 and Table 7.4, respectively. These are not to be interpreted quantitatively.

Table 7.3: Extrapolated metallic copper crystallite sizes from the cWH plots at the top, middle and bottom of the catalyst beds reduced in 5 % H₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu⁰ crystallite size / nm</th>
<th>Top</th>
<th>Middle</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCZA</td>
<td>8.51</td>
<td>6.79</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>sCZA-Cs</td>
<td>9.80</td>
<td>7.63</td>
<td>6.79</td>
<td></td>
</tr>
<tr>
<td>hCZA</td>
<td>11.35</td>
<td>10.18</td>
<td>9.23</td>
<td></td>
</tr>
<tr>
<td>hCZA-Cs</td>
<td>15.68</td>
<td>14.68</td>
<td>12.08</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4: Extrapolated mean residual strain from the cWH plots at the top, middle and bottom of the catalyst beds reduced in 5 % H₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice strain / nm⁻¹</th>
<th>Top</th>
<th>Middle</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCZA</td>
<td>0.001255</td>
<td>0.00111</td>
<td>0.00053</td>
<td></td>
</tr>
<tr>
<td>sCZA-Cs</td>
<td>0.00161</td>
<td>0.001075</td>
<td>0.00106</td>
<td></td>
</tr>
<tr>
<td>hCZA</td>
<td>0.001295</td>
<td>0.001165</td>
<td>0.001465</td>
<td></td>
</tr>
<tr>
<td>hCZA-Cs</td>
<td>0.00193</td>
<td>0.002235</td>
<td>0.00236</td>
<td></td>
</tr>
</tbody>
</table>
7.4.5. Results of the mWH plots for the 5 % H₂ studies

As the reliability of some of the variables input into Equation 4.12 are not guaranteed, the following effective crystallite sizes derived from the mWH plots are not considered quantitative.

Table 7.5: Extrapolated metallic copper crystallite sizes from the mWH plots at the top, middle and bottom of the catalyst beds reduced in 5 % H₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu⁰ crystallite size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
</tr>
<tr>
<td>sCZA</td>
<td>5.21</td>
</tr>
<tr>
<td>sCZA-Cs</td>
<td>5.41</td>
</tr>
<tr>
<td>hCZA</td>
<td>5.79</td>
</tr>
<tr>
<td>hCZA-Cs</td>
<td>6.28</td>
</tr>
</tbody>
</table>

7.4.6. Calculated q parameters for the investigated activation procedures

The following q parameter values were calculated according to Equation 4.22 and used for all analysis in Section 4.9.2.6.

Table 7.6: Calculated q parameters for the activated sCZA catalysts

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>[H₂] / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1/q</td>
</tr>
<tr>
<td>(a)</td>
<td>0.466</td>
</tr>
<tr>
<td>(b)</td>
<td>0.467</td>
</tr>
<tr>
<td>(c)</td>
<td>0.466</td>
</tr>
<tr>
<td>(d)</td>
<td>0.467</td>
</tr>
<tr>
<td>(e)</td>
<td>0.468</td>
</tr>
<tr>
<td>(f)</td>
<td>0.468</td>
</tr>
<tr>
<td>(g)</td>
<td>0.467</td>
</tr>
<tr>
<td>(h)</td>
<td>0.468</td>
</tr>
<tr>
<td>(i)</td>
<td>0.468</td>
</tr>
<tr>
<td>(j)</td>
<td>0.468</td>
</tr>
<tr>
<td>(k)</td>
<td>0.468</td>
</tr>
</tbody>
</table>
**Table 7.7: Calculated q parameters for the activated sCZA-Cs catalysts**

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>([\text{H}_2]/%)</th>
<th>([1%])</th>
<th>([2.5%])</th>
<th>([5%])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/q</td>
<td>q</td>
<td>[Screw]</td>
<td>1/q</td>
</tr>
<tr>
<td>(a)</td>
<td>0.468</td>
<td>2.137</td>
<td>65.4</td>
<td>0.468</td>
</tr>
<tr>
<td>(b)</td>
<td>0.468</td>
<td>2.137</td>
<td>65.3</td>
<td>0.468</td>
</tr>
<tr>
<td>(c)</td>
<td>0.468</td>
<td>2.138</td>
<td>65.5</td>
<td>0.469</td>
</tr>
<tr>
<td>(d)</td>
<td>0.468</td>
<td>2.136</td>
<td>65.2</td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>0.469</td>
<td>2.134</td>
<td>64.9</td>
<td></td>
</tr>
<tr>
<td>(f)</td>
<td>0.464</td>
<td>2.157</td>
<td>68.1</td>
<td>0.469</td>
</tr>
<tr>
<td>(g)</td>
<td>0.467</td>
<td>2.141</td>
<td>65.9</td>
<td>0.470</td>
</tr>
<tr>
<td>(h)</td>
<td>0.469</td>
<td>2.134</td>
<td>64.9</td>
<td>0.470</td>
</tr>
<tr>
<td>(i)</td>
<td>0.468</td>
<td>2.136</td>
<td>65.2</td>
<td>0.470</td>
</tr>
<tr>
<td>(j)</td>
<td>0.468</td>
<td>2.136</td>
<td>65.2</td>
<td>0.469</td>
</tr>
<tr>
<td>(k)</td>
<td>0.468</td>
<td>2.136</td>
<td>65.2</td>
<td>0.469</td>
</tr>
</tbody>
</table>

**Table 7.8: Calculated q parameters for hCZA and hCZA-Cs activated under 5 % H\(_2/\text{Ar}\)**

<table>
<thead>
<tr>
<th>Position in bed</th>
<th>hCZA</th>
<th></th>
<th>hCZA-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/q</td>
<td>q</td>
<td>[Screw]</td>
</tr>
<tr>
<td>(a)</td>
<td>0.465</td>
<td>2.152</td>
<td>67.4</td>
</tr>
<tr>
<td>(b)</td>
<td>0.465</td>
<td>2.153</td>
<td>67.5</td>
</tr>
<tr>
<td>(c)</td>
<td>0.464</td>
<td>2.156</td>
<td>67.9</td>
</tr>
<tr>
<td>(d)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(j)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.4.7. hCZA and hCZA-Cs $\{111\}$-, $\{311\}$-, and $\{222\}$-peak profiles

A symmetric Lorentzian function has been fit to the $\{111\}$-, $\{311\}$-, and $\{222\}$-reflections at the top, middle and bottom of the high-copper loading catalysts. This was done to highlight any peak asymmetry visible as a result of faulting. The results for these fits are given in Section 4.9.2.7.2.

Figure 7.29: Line profiles of the final hCZA pattern reduced in 5 % $H_2$ highlighting the asymmetry of the 111-, 311- and 222-reflections at the (a) top, (b) middle and (c) bottom of the bed; the dashed line is placed in the centre of the peak.
Figure 7.30: Line profiles of the final hCZA-Cs pattern reduced in 5 % H₂ highlighting the asymmetry of the 111-, 311- and 222-reflections at the (a) top, (f) middle and (k) bottom of the bed; the dashed line is placed in the centre of the peak.

7.4.8. Time-resolved (111)-(200) peak separations for the 1 % and 2.5 % H₂ standard point measurement studies

The experimentally derived $\Delta(2\theta_{200} - 2\theta_{111})$ for the sCZA and sCZA-Cs catalysts reduced in (i) 1 % and (ii) 2.5 % H₂ are shown in Figure 7.31. As with the 5 % H₂ studies, as the bed reaches complete reduction, the $\Delta(2\theta_{200} - 2\theta_{111})$ deviates further from the ideal, increasing the stacking fault probability at the interrogated position in the bed.
Figure 7.31: (111)-(200) peak separations for (a) sCZA and (b) sCZA-Cs activated in (i) 1 % and (ii) 2.5 % H₂/Ar; where the dashed line represents the ideal and the solid line represents the experimentally derived difference in peak position.

7.4.9. AP-XPS supplementary figures

7.4.9.1. Cu LMM Auger spectra

The Cu LMM Auger spectra for sCZA and sCZA-Cs following reduction are displayed in Figure 7.32. There is a main signal at ca. 918.2 eV, reinforcing that the active component is reduced.
7.4.9.2. Cs 3d region for sCZA-Cs

Figure 7.33 depicts the Cs 3d\(\frac{3}{2}\) (ca. 725 eV) and Cs 3d\(\frac{1}{2}\) (ca. 739 eV) signals of the sCZA-Cs following reduction and reaction.\(^{27}\) This serves as evidence of the Cs-promoters presence on the surface of the promoted catalyst.

Figure 7.33: Cs 3d signal of sCZA-Cs following reduction, and under reaction
7.4.10. Cu⁰ and ZnO crystallite sizes as determined from the XRD-CT measurements

Due to the large difference in processing time between the point measurements and the XRD-CT scans, the investigated 2θ-range used for the Rietveld refinement is smaller for the XRD-CT measurements. This means that when the effective crystallite size of the Cu⁰ is calculated, the particle sizes differ slightly, appearing larger in these measurements, but describing the same trend.

7.4.10.1. Copper crystallite sizes

*Figure 7.34: Cu⁰ crystallite sizes across the (a) top, (b) middle and (c) bottom of the sCZA catalyst bed reduced under 5 % H₂*

*Figure 7.35: Cu⁰ crystallite sizes across the (a) top, (b) middle and (c) bottom of the sCZA-Cs catalyst bed reduced under 5 % H₂*

It should be noted that the scale bar for the high copper loading Cu⁰ crystallite sizes has increased from that for the standard catalysts, therefore a visual comparison between the two is not reliable.
Figure 7.36: Cu\(^{0}\) crystallite sizes across the (a) top, (b) middle and (c) bottom of the hCZA catalyst bed reduced under 5 % H\(_2\)

Figure 7.37: Cu\(^{0}\) crystallite sizes across the (a) top, (b) middle and (c) bottom of the hCZA-Cs catalyst bed reduced under 5 % H\(_2\)

7.4.10.2. **Zincite crystallite sizes**

Figure 7.38: ZnO crystallite sizes across the (a) top, (b) middle and (c) bottom of the sCZA catalyst bed reduced under 5 % H\(_2\)
Figure 7.39: ZnO crystallite sizes across the (a) top, (b) middle and (c) bottom of the sCZA-Cs catalyst bed reduced under 5 % H₂

It should be noted that, again, the scale bar for the high copper loading ZnO crystallite sizes has increased from that for the standard catalysts, therefore a visual comparison between the two is not reliable.

Figure 7.40: ZnO crystallite sizes across the (a) top, (b) middle and (c) bottom of the hCZA catalyst bed reduced under 5 % H₂

Figure 7.41: ZnO crystallite sizes across the (a) top, (b) middle and (c) bottom of the hCZA-Cs catalyst bed reduced under 5 % H₂
7.4.11. Stacking Fault Probability XRD-CT Images Across the sCZA and sCZA-Cs Beds Reduced Under 1 % and 2.5 % H₂/Ar

Figure 7.42: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the sCZA catalyst bed reduced under 1 % H₂

Figure 7.43: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the sCZA-Cs catalyst bed reduced under 1 % H₂

Figure 7.44: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the sCZA catalyst bed reduced under 2.5 % H₂
Figure 7.45: Stacking fault probabilities across the (a) top, (b) middle and (c) bottom of the sCZA-Cs catalyst bed reduced under 2.5 % H₂

7.5. Chapter 5
7.5.1. Standard Enthalpies and Entropies of Formation

All standard enthalpies and entropies of formation utilised in Chapter 5 are given in Table 7.9.

Table 7.9: Standard enthalpies and entropies of formation used to generate the Ellingham diagram

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH/ kJ mol⁻¹</th>
<th>ΔS / J K⁻¹ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(s)</td>
<td>0</td>
<td>33.2</td>
</tr>
<tr>
<td>CuO(s)</td>
<td>-157.3</td>
<td>42.6</td>
</tr>
<tr>
<td>Cu₂O(s)</td>
<td>-168.6</td>
<td>93.1</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>0</td>
<td>130.7</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>-241.8</td>
<td>188.8</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>-285.8</td>
<td>70</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>0</td>
<td>205.2</td>
</tr>
<tr>
<td>Zn(s)</td>
<td>0</td>
<td>41.6</td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>-350.46</td>
<td>43.6</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0</td>
<td>28.3</td>
</tr>
<tr>
<td>Al₂O₃(s)</td>
<td>-1675.7</td>
<td>50.9</td>
</tr>
<tr>
<td>Cs(l)</td>
<td>2.1</td>
<td>92.1</td>
</tr>
<tr>
<td>Cs₂O(s)</td>
<td>-317.6</td>
<td>146.8</td>
</tr>
</tbody>
</table>
7.5.2. ICP-OES of Precipitate (SINTEF Molab, Porsgrunn, NO)

7.5.2.1. Method

The hydroxycarbonate precursor (0.5 g) was dissolved in 10 vol.% HNO₃ (50 mL), diluted × 10-50 depending on the Na level, and analysed with ICP-OES. The samples were not dried before dissolution.

7.5.2.2. Results

Where, for the laboratory-based syntheses, the precipitate was generally washed in three cycles with deionised H₂O (3 × 500 mL, 18.2 MΩ cm⁻¹), this translated to a total of ca. 30 L of H₂O used for washing to produce one batch of hydroxycarbonate precursor in the scaled up syntheses. In order to determine whether all washing cycles were necessary, inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed. As can be seen from Figure 7.46, following 2 wash cycles, the [Na] is below 0.01 wt.%.

![Figure 7.46: Consequence of washing procedure on the average [Na] in the resultant precipitate; the dashed grey line is representative of a [Na] < 0.01 wt.%](image)

7.5.3. Quartz Internal Standard

The quartz internal standard used was purchased from Sigma Aldrich (CAS #: 14808-60-7). Unfortunately, it was only realised after incorporating 20 wt.% into all flow reactor samples that its grade is rated purum p.a.. As can be seen from Figure 7.47, there are some impurities present in the standard, the main being visible to the right of the SiO₂ (101)-reflection, therefore, for the sake of the Rietveld refinements of the CZA and CZA-Cs catalysts subjected to activation treatments, the region between 25-28 °2θ was excluded. This significantly improved the pattern fitting and thus delivered more accurate quantitative data.
Miniflex Low Background Sample Holders

The Rigaku Miniflex 600 located at Isis Materials Characterisation Laboratory is equipped with a 6-position automatic sample changer with spinner. However, only 4 positions were utilised and the diffraction patterns of the low background silicon sample holders used are displayed in Figure 7.48. Each measured diffraction pattern at position 1 in the reactor bed (top) was collected using sampler holder 1, for position 2, sample holder 2 was utilised, etc.. However, the diffraction patterns have been superimposed onto each other to highlight that there is not much difference between them, therefore this should not impact the calculated amorphous content following reduction of the CuO/ZnO/Al₂O₃(-Cs₂O) catalysts.

Figure 7.47: Quartz internal standard diffraction pattern; the reference pattern for quartz is given below.
The results of the Rietveld refinement of the ZnO 674b NIST standard reference material are shown in Figure 7.49.

Figure 7.49: Rietveld refinement of the ZnO 674b NIST diffraction pattern collected on the Rigaku Miniflex 600
7.5.6. Temperature Profile for Flow Reactor Catalyst Bed

As stated in Section 5.2.4, the external thermocouple, TC2, was sued to monitor/control the reactor temperature. This was calibrated according to Figure 7.50 using corundum; TC1 was located inside a thermowell that extended along the length of the corundum bed, and the thermocouple was moved to measure the temperature across the bed.

![Temperature Profile for Flow Reactor Catalyst Bed](image)

*Figure 7.50: Temperature profile for catalyst bed length installed in the flow reactor; where the position in the bed is denoted by 1 (top), through to 4 (bottom).*

7.5.7. Diffraction Patterns for Section 5.3.4

All Rietveld refinement results displayed graphically in Section 5.3.4 are derived from the presented TOPAS fits.
7.5.7.1. CZA and CZA-Cs: 0 % H₂/Ar, 20 vol.% H₂O, 24 h

Figure 7.51: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing ‘activation’ in a wet (20 vol.% H₂O) inert (Ar) atmosphere for 24 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.2. CZA and CZA-Cs: 1 % H₂/Ar, 48 h

Figure 7.52: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in a dry, reducing (1 % H₂/Ar) atmosphere for 48 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal), and quartz (dark purple) are shown below.
7.5.7.3. CZA and CZA-Cs: 5 % H2/Ar, 24 h

Figure 7.53: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in a dry, reducing (5 % H2/Ar) atmosphere for 24 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.4, CZA and CZA-Cs: 1 % H₂/Ar, 20 vol.% H₂O, 24 h

Figure 7.54: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in a wet (20 vol.% H₂O), reducing (1 % H₂/Ar) atmosphere for 48 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.4.1. Comparison of 10 and 20 vol.% H$_2$O for CZA-Cs

Figure 7.55: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in (a) a 10 vol.% H$_2$O and (b) a 20 vol.% H$_2$O wet, reducing (1 % H$_2$/Ar) atmosphere for 48 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.5. CZA and CZA-Cs: 5 % H2/Ar, 20 vol.% H2O, 24 h

Figure 7.56: Diffraction patterns taken of the (a) CZA and (b) CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in a wet (20 vol.% H2O), reducing (5 % H2/Ar) atmosphere for 24h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.6. PH-CZA and PH-CZA-Cs: 5 % H₂/Ar, 24 h

Figure 7.57: Diffraction patterns taken of the pre-hydrated (a) PH-CZA and (b) PH-CZA-Cs catalysts, from the (1) top of the bed to the (4) bottom, after undergoing activation in a dry, reducing (5 % H₂/Ar) atmosphere for 24 h; the calculated Rietveld fit for each position is denoted by the dashed black line, the grey line highlights the difference between the observed and calculated fit, and the peak positions of metallic copper (dark red), cuprite (orange), tenorite (red), zincite (teal) and quartz (dark purple) are shown below.
7.5.7.7. PH-CZA and PH-CZA-Cs: 5 % H\textsubscript{2}/Ar, 20 vol.% H\textsubscript{2}O, 24 h

(a)

(b)

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Equation 4.32: The (a) polarization factor for unpolarised X-rays, (b) Lorentz factor and (c) Lorentz-polarization factor

Equation 4.33: Plug flow conditions. $d_\text{d}$ refers to the tube diameter, $d_\phi$ is the particle diameter and $L_\text{b}$ relates to the bed length.

Equation 4.34: Gas hourly space velocity
Equation 4.35: Weight fraction of a given phase present in a diffraction pattern

Equation 4.36: The rate-limiting water dissociation step in the WGS reaction; the subscript “(a)” refers to an adsorbed species.

Equation 4.37: Transformation equations to describe the FCC crystal system by hexagonal coordinates.

Equation 4.38: Calculation for the phase jump across a stacking fault in the (111) plane, where \( n_{111} \) is equivalent to the number of fault-affected planes.

Equation 4.39: (a) Fault effected peak displacement calculation for intrinsic stacking faults, where (b) determines the direction of the peak shift.

Equation 4.40: Vegard's law to determine the lattice parameter, \( a \), dependence on solute concentration in binary alloys.

Equation 4.41: Thermal expansion of a solid material.

Equation 5.1: Reaction between excess zinc on the catalyst surface with \( \text{H}_2\text{O} \).

Equation 5.2: Proposed mechanisms for the dissociation of adsorbed water over Cs-promoted Cu-based LTS catalysts during the forward WGS reaction; the subscript “(a)” refers to an adsorbed species.

Equation 5.3: The standard change in Gibbs free energy.

Equation 5.4: Weight fraction of amorphous content using the internal standard Rietveld method.

Equation 5.5: Desired flow of \( \text{H}_2\text{O} \) to achieve a water vapour concentration of 20 vol.%

Equation 5.6: Gas hourly space velocity equation.

Equation 5.7: The particle Reynolds number.

Equation 5.8: Density of gases.

Equation 5.9: Superficial velocity inside the reactor.

Equation 5.10: Viscosity of binary gas mixtures.

Equation 7.1: Beer-Lambert’s law for transmission.

Equation 7.2: Thermal expansion of a solid material.

Equation 7.3: Reduction of tenorite.

Equation 7.4: Polynomial anisotropic temperature-dependence of wurtzite ZnO lattice parameters.