Aberration Corrected Analytical Electron Microscopy Studies of Nanometallic Catalysts

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Aberration Corrected Analytical Electron Microscopy Studies of Nanometallic Catalysts

by

Sultan M. Althahban

A Dissertation

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Sultan M. Althahban

Aberration Corrected Analytical Electron Microscopy Studies of Nanometallic Catalysts

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Dedication

I would like to dedicate my thesis to my beloved parents, brothers, sisters and friends.
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Abstract

Catalysis by nanoscopic metal structures, ranging from nanoparticles to sub-nm clusters and even individual atoms, is amongst the most intensely studied topics in nanoscience. The catalytic performance of supported metal nanoparticles is governed by their crysallographic structure, shape, size, composition and interaction with the support. Aberration-corrected scanning transmission electron microscopy (AC-STEM), with its ultra-high spatial resolution for imaging and compositional analysis, is an ideal tool for characterizing such features in metallic nanocatalysts. In this thesis, five case studies are presented where AC-STEM has been invaluable in elucidating synthesis route - structure - performance relationships in some technologically important catalyst systems.

Firstly, high angle annular dark field (HAADF) imaging has been utilized to gain an improved mechanistic understanding of how the Au/CeZrO₄ catalyst system, which shows high initial activity for the low temperature water gas shift (LT-WGS) reaction, rapidly deactivates under typical reaction conditions. It was discovered that a combination of particle agglomeration and substrate de-wetting effects contribute to the instability of the Au/CeZrO₄ system. More importantly, a ‘stop-start’ STEM-HAADF imaging experiment, where the exact same area of catalysts was viewed at different stages of its lifetime, revealed the presence of highly active, but very unstable, ultra-small species (i.e., Au atoms and sub-nm clusters) that were responsible for the high initial activity. Modification of the supported Au by alloying with Pd was attempted in an effort to improve the stability of the catalyst. Unfortunately, the AuPd/CeZrO₄ material was a poorer LT-WGS catalyst, which
complementary AC-STEM, XPS, XRD and CO-DRIFTs studies revealed to be due to larger metal particles with non-ideal CO binding characteristics.

Secondly, a new modified impregnation method has been employed to prepare a highly selective PdZn/ZnO catalyst for the methanol steam reforming (MSR) reaction. Compared to conventional impregnation techniques, this new method, which involves adding excess chlorine anions along with the metal chloride precursors, improves mixing and dispersion of the metal components. The resultant catalyst contains supported highly ordered intermetallic Pd-Zn particles, whose presence correlates well with CO₂ selectivity. In addition, during use it is shown that nanoscopic ZnO patches form on the surface of the PdZn particles, further improving the catalytic performance. Furthermore, the PdZn particle size, which can be varied by altering the surface area of the ZnO support material, can be tuned to improve the level of methanol conversion.

Thirdly, nanoalloy catalysts that that are effective for converting methane directly to methanol have been investigated by AC-STEM. It demonstrated that in the presence of H₂O₂ and molecular O₂, and using unsupported colloidal AuPd nanoparticles as a catalyst, methane can be oxidized to methanol with high selectivity (>90%) in aqueous solution at mild temperatures (50°C). Interestingly when the AuPd nanoparticles were supported on TiO₂, the consumption rate of H₂O₂ during the reaction increased dramatically and consequently the methane activity and selectivity to methanol were notably diminished. STEM analysis has revealed that the peripheral sites at the support/metal interface are the underlying cause of undesirable high H₂O₂ degradation rate in this instance.

Fourthly, a complementary AC-STEM, XPS and XAFS characterization study of Pt/TiO₂ catalysts prepared by an incipient wet impregnation route has been carried out to understand
the preparation-structure-performance relationships that exist in this system. By systematically varying the Pt-content and heat treatments given to the material, a highly effective catalyst for the selective hydrogenation of 3-nitrostyrene to 3-vinylaniline has been developed. We demonstrate that catalysts which have higher Pt loadings require a multi-step heat treatment \textit{(i.e., calcination followed by reduction)} to reach their best performance, while in the case of lower metal loadings the reduction process alone is sufficient to reach optimal performance. The target Pt morphology to achieve was found to be small particles of PtO in the 1-2 nm size range.

Finally, systematic characterization studies have been carried out on PVA stabilized Au and Au-Pd alloy nanoparticles which were produced and immobilized on TiO$_2$ in a continuous manner using a novel 3D printed millifluidic reactor system. AC-STEM investigations reveal that the supported metal nanoparticles generated using the millifluidic reactor system are smaller on average and have a narrower particle size distribution, in comparison to materials synthesized by a conventional batch sol-immobilization method. More importantly, in the case of the PVA- stabilized AuPd bimetallic system, the alloy particles generated have a much more uniform alloy composition as a functions of size compared to their conventional sol-immobilized counterparts.
Chapter 1

Introduction
1.1. Catalysis: definitions and concepts

By simple definition, a catalyst is any substance added to a chemical reaction that lowers the activation energy barrier, as shown in Figure 1.1, to that reaction and accordingly allows it to proceed toward equilibrium more quickly and under milder conditions (e.g., of temperature or pressure). Three distinct types of catalysts exist and are defined as enzymatic, homogeneous, and heterogeneous catalysts.

![Potential energy profile for the reaction with and without catalysts.](image)

**Figure 1.1.** Potential energy profile for the reaction with and without catalysts.¹

Enzymes are natural catalysts existing in living systems which allow biological reactions to occur at rates necessary to maintain life in the organism. Homogeneous and heterogeneous catalysts, on the other hand, are catalysts used in chemical and energy industries. In a typical homogeneous catalysis process, the reactants and catalyst exist in the same phase form (usually in the liquid phase) while in a heterogeneous catalysis process, the reaction usually occurs between gases or liquids (or both) at the surface of a solid catalyst (i.e., reactants are in in a
different phase from catalyst). Heterogeneous catalysis in practice is more popular than homogeneous catalysis because the catalyst can be readily separated from the products and recycled.\(^2\) While homogeneous catalysis is in itself an enormously important field, for the purpose of this thesis, the focus will be on heterogeneous catalysis.

In heterogeneous catalytic processes, the catalyst material is typically a high surface area metal\(^3\), metal oxide\(^4\) or metal sulfide.\(^5\) In this doctoral research project, the focus is on heterogeneous catalysis by both supported and unsupported metal nanoparticles. Elements from groups VIII and IIB of the periodic table are the most common metals used as industrial catalysts. Their unique catalytic behavior can be attributed to three main physical characteristics, namely: (i) these elements have unfilled d orbitals; (ii) they can exist in different oxidation states; and (iii) they can absorb other molecules onto their surface and activate them in the process.\(^6\) Their catalytic performance is typically characterized by three main factors: namely (a) their activity, or ability to convert most reactants to products; (b) their selectivity to the desired products; and (c) their stability under reaction conditions. In many cases, metals from those two groups are intimately mixed to form alloys, thus taking advantage of so-called synergistic effects which can serve to improve their overall catalytic performance.\(^7\)

As stated previously, in the heterogeneous catalysis process, molecules react with each other on the exterior surface of a solid catalyst. Two possible mechanistic scenarios for heterogeneous catalysis on the surface exist. The first one is known as the Langmuir-Hinshelwood mechanism in which all molecules are adsorbed onto the surface and react to form the final product (Figure 1.2(a)). The second scenario is the Eley-Rideal mechanism
where the reaction occurs between an adsorbed molecule and other ones in the gas or liquid phase (Figure 1.2(b)).

Figure 1.2. Two possible mechanistic scenarios for heterogeneous catalysis processes on a solid surface: (a) the Langmuir-Hinshelwood mechanism and (b) the Eley-Rideal mechanism.

It should also be noted that molecules can attach to the catalyst surface via two different type of adsorption process, namely physisorption and chemisorption. Physisorption processes usually occur via low energy Van Der Waals interactions, while chemisorption is occur due to changes in the electronic structure within a molecule resulting in the formation and dissociation of chemical bonds.

The sites on the surface of the catalyst at which the adsorption and reaction happen are usually referred to as active sites. These active sites, especially under harsh reaction conditions, are often not stable. Hence, in practice, catalytic materials are frequently
supported on a second, more refractory material such as activated carbon, alumina, titania or ceria. Although the support itself in many cases may be catalytically inactive, it can provide a high surface area matrix over which the catalytically active sites can be widely spread. In addition, the peripheral sites at the interface between the support and catalytic material may also serve as active sites.\textsuperscript{10,11} In other instances, the catalyst support material may take part in the reaction process. One such example could be that Au catalyst supported on TiO\textsubscript{2} (\textit{i.e.}, a catalyst used in the methanol oxidation reaction), in which the TiO\textsubscript{2} acts not only as catalyst support, but also as a methoxy species reservoir for the reaction.\textsuperscript{12}

In summary, heterogeneous catalysts play a key role in the chemical and energy industries, and without them, many industrial processes would be technically impossible or uneconomical to operate. Currently more than 85\% of industrially operated chemical processes make use of catalysts. Furthermore, the global market for catalyst materials and catalyst regeneration totaled nearly $24.6 billion and this market was expected to grow at an annual rate of 4.0\% reaching $29.9 billion in 2019.\textsuperscript{13} The vast scale at which catalysts are utilized industrially emphasizes the importance of performing fundamental catalytic research to improve existing catalyst systems as well as developing new ones.

### 1.2. Preparation of metal catalysts

The exact preparation method used for synthesizing a metal catalyst plays a pivotal role in determining the properties of the final catalyst. It has been reported that the nanostructural features of the catalyst such as particle size, morphology, composition, distribution and dispersion depend markedly on the preparation method. Metal catalysts may be synthesized as unsupported and supported catalysts (Figure 1.3). Numerous catalyst preparation
methods have been described in detail in the literature,\textsuperscript{14} therefore, only those specific preparation techniques utilized to prepare materials studied in this thesis will be discussed in detail here.

1.2.1. Chemical reduction method

Several methods (see Figure 1.3), which are discussed in detail in the literature review by Poncelet \textit{et al.},\textsuperscript{14} can be used to prepare unsupported metal catalysts (\textit{i.e.} metal colloids). Among these methods, chemical reduction features strongly because of its simplicity and widespread use to prepare colloidal nanoparticles, which are stable and can be easily isolated in dry powder form. Metal alloy nanoparticles may also be synthesized by the chemical reduction method and it has been used extensively to prepare AuPd colloids for some of the reactions of interest in this thesis. In this process, a metal precursor, typically a metal salt, is dissolved in aqueous or non-aqueous solution. It is then chemically reduced with a strong reducing agent such as sodium borohydride (NaBH\textsubscript{4}), hypophosphorous acid (H\textsubscript{3}PO\textsubscript{2}), or alcohols (\textit{e.g.,} ethylene glycol). This procedure is often carried out in the presence of a stabilizing agent (\textit{e.g.,} polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), or citrate ions) which helps to control the particle size and limit the aggregation behavior of clusters and nanoparticles.\textsuperscript{15}

1.2.2. Impregnation method

Impregnation is one of the most widely used methods for the preparation of supported heterogeneous catalysts due to its simplicity and cost-effectiveness. In impregnation,
typically, a pre-formed support material is impregnated with a solution containing the active catalyst precursor components, and then dried and calcined. Impregnation processes are often classified into two main types, namely dry impregnation and wet impregnation. In dry impregnation, the solution of the metal precursor added is exactly enough to fill up the pore volume of the support particles. In the case of wet impregnation, the support is immersed into an excess quantity of solution containing metal precursor(s). The structure and performance of the final supported metal catalysts can be tuned via several processing parameters such as the calcination temperature, the rate of heating, solution pH and obviously, the identity of the support material. When two or more metal precursors are present concurrently in the impregnation solution, the process is referred to as co-impregnation. In the co-impregnation process, it is quite difficult to control the particle size distribution and the composition from particle-to-particle. Such disadvantages make it an imprecise method for synthesizing bimetallic catalysts.

However, due to the simplicity of the methodology, and its suitability for large-scale production, numerous studies have been devoted to improving the impregnation method. For instance, Qing et al.\textsuperscript{16} developed a two-step impregnation procedure to prepare a highly active supported Au catalyst for CO oxidation. They showed that washing-off the excess Au precursor (step one) and then treating the solid with a strong acid (step two) promoted a high dispersion of Au and imparted some additional stability to thermal sintering. The co-impregnation approach has also recently been developed into a more advanced variant called \textit{“modified co-impregnation”} for making alloy nanoparticles with more uniform compositions.\textsuperscript{15} Here the idea is that excess chloride anions are added along with metal chloride precursors to promote alloy formation by providing better mixing between metals,
and further to prevent agglomeration of particles by enhancing their dispersion on the support. Sankar et al.\textsuperscript{17} showed that modified co-impregnation was an efficient way to prepare AuPd/TiO\textsubscript{2} catalysts having high selectivity, stability and re-usability for the oxidation of alcohols.

1.2.3. Sol-immobilization (SI) method

The immobilization of pre-formed metal colloids onto a refractory ceramic support powder has become a wide-spread methodology for preparing supported metal catalysts, because it provides a much better control over the particle size distribution and nanoparticle morphology.\textsuperscript{18} The sol-immobilization (SI) method is based on the preparation of colloidal metal nanoparticles by chemical reduction (Section 1.1.1) and their subsequent immobilization on a support. Typically, metal precursor salts in solution are reduced to the metallic state using a strong reducing agent (\textit{e.g.} NaBH\textsubscript{4}) in the presence of a protecting ligand (\textit{e.g.} polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP)), which acts to passivate the surface of the particle and by steric hindrance prevents them from aggregating. For anchoring the resultant colloidal NPs onto the solid support powder, the pH of the value of the colloidal solution has to be adjusted to keep it below that of the iso-electric point of the support, so as to enable sufficient interaction between the particles and support. It should be noted that the properties of pre-made metal colloids can be finely tuned prior to their immobilization by adjusting the chemical reduction preparation conditions (\textit{i.e.} metal concentration, identity of reductant and solvent, stabilizer/metal ratio, temperature, \textit{etc.})\textsuperscript{19}

However, the conventional sol-immobilization method has been shown by Hutchings and Kiely,\textsuperscript{20,21} to have rather poor control over the particle composition as a function of size when preparing colloidal alloys such as Au-Pd.
1.2.4. Deposition-precipitation (DP) method

The deposition-precipitation (DP) method is one of the most effective routes that can be used to obtain a high dispersion and homogeneous deposition of small metal particles (< 5nm) onto a support. It is based on the addition of the metal precursor(s) to an aqueous suspension of the support, and the subsequent precipitation as a metal hydroxide by increasing the pH, which is typically accomplished by adding a precipitating solution (e.g. Na$_2$CO$_3$, NaOH or CO(NH$_2$)$_2$). The support surface can act as a nucleating agent and consequently most of the active metal will be attached to the support. After the deposition-precipitation step, the product is calcined and reduced to form the final catalyst.\textsuperscript{22} One of the major disadvantages of the DP technique is that the support material needs to have a very low iso-electric point (c.a. <5), because metal hydroxides cannot be deposited on their surfaces.\textsuperscript{23} The deposition-precipitation approach has been reported to provide excellent control over the composition, size, morphology and surface properties of the metal nanoparticles.\textsuperscript{24–26}

![Diagram of Preparation methods of metal nanocatalysts](image)

**Figure 1.3.** A chart showing some popular techniques for preparing unsupported and supported metal catalysts (adapted from Ref.\textsuperscript{27})
1.3. Characterization of catalyst structure and composition via analytical electron microscopy

The catalytic performance of a heterogeneous catalyst system, measured in terms of its activity, selectivity and stability, significantly depends on the surface area, structure, morphology and chemical composition of the material. For a better understanding of the correlation between these parameters and catalytic behavior, many chemical and physical characterization methods are usually used to study the catalyst.\textsuperscript{28} Since the dimensions of the structural features determining their catalytic properties are almost always at the nanometer scale, specialized characterization techniques are required that are capable of revealing the structural and compositional details of catalysts on the nanoscale.

Electron microscopy has been used to explore heterogeneous catalysts since its advent in the early 20\textsuperscript{th} century. Over the past 70 years, the resolution and analytical capabilities of electron microscopes have been significantly improved, and today we are able to obtain fundamental structural and chemical information on the catalyst materials with very high spatial resolution – even down to the atomic level.\textsuperscript{29} Furthermore, the relatively recent development of systems which can effectively correct the spherical aberration ($C_s$) of such instruments provides a superior means for the characterization of materials in general and supported metal catalysts in particular.

The scanning transmission electron microscope (STEM) is one of the most advanced analytical electron microscopes that has been developed. The so-called aberration-corrected analytical electron microscope (AC-AEM) is usually equipped with a probe-corrected illumination system and ancillary spectroscopy techniques such as X-ray energy dispersive spectroscopy (XEDS) and electron energy loss spectroscopy (EELS). Scanning transmission
electron microscopy involves using a high accelerating voltage (60 - 200 kV) and highly focused electron beam to analyze an ultra-thin specimen in a scanning raster manner (Figure 1.4). The interaction between the specimen and the high energy electron beam generates different signals (electrons & X-rays) which are collected and analyzed simultaneously via a variety of recording devices to form an image or compositional map. Depending on which electron signals are collected and displayed, several imaging modes can be accomplished in the STEM as illustrated schematically in Figure 1.4.

![Figure 1.4](image_url)  
Figure 1.4. Schematic diagram showing a BF detector, an ADF detector and an HAADF detector and their respective collection angles in a typical STEM instrument. (after Kumar)

The first important imaging mode is called bright field (BF)-STEM in which near-axis electrons (<10 mrad) are collected via a line-of-sight bright field detector. It should be noted that BF-STEM images are equivalent, but not completely identical, to conventional BF-TEM images. The second STEM imaging mode is known as annular dark field (ADF) imaging
whereby electrons that are deflected further away from the optic axis (i.e. 10-50 mrad) are collected on an annular ring detector. Finally, if an annular detector with a very large inner collection angle (> 50 mrad) is used, so-called high-angle annular dark field (HAADF) images can be formed. The large angle scattered electrons used to form HAADF-STEM images mainly arise from the high angle, incoherent, Rutherford scattering of electrons by the atomic nuclei in the sample. This type of scattering depends strongly on the atomic number of the scattering atom as shown in equation 2.1:

$$\frac{d \sigma}{d \Omega} = \frac{4\gamma^2}{a_0^2} \frac{Z^2}{q^4}$$

Eqn (2.1)

where \((d \sigma)/(d \Omega)\) is the differential scattering cross-section, \(Z\) is the atomic number, \(a_0\) is the Bohr radius, \(q\) is the scattering wave vector, and \(\gamma\) is a relativistic factor. Therefore, HAADF-STEM images are often referred to as Z-contrast or mass contrast images. Figure 1.5 shows an example of a complementary pair of HAADF- and BF-STEM images collected from the same area of a Au/MgO catalyst in which the Au islands can be clearly discerned by mass contrast in the HAADF image, while the support lattice structure in more dominant in the BF-image.
The ability to combine BF and HAADF imaging with highly localized spectroscopy techniques such as XEDS and EELS makes the scanning transmission electron microscope ideally suited for the study of catalyst materials. When the high energy electron beam interacts with atoms in the specimen, an inner orbital electron can be ejected leaving an electron vacancy. An electron from a higher energy shell fills the hole by lowering its energy; a relaxation process. The excess energy can be released through the emission of a characteristic X-ray, as illustrated in Figure 1.6, which is collected by an XEDS detector and used for elemental identification. Electron energy loss signals (Figure 1.6) which are generated by the incident energy losing some energy during the initial ionization process can be collected via a suitable EELS spectrometer. Compared to XEDS, the EELS technique is more sensitive to lighter elements and can provide more chemical information (e.g. elemental composition, oxidation state, dielectric constant, band structure, and specimen thickness).
**Figure 1.6.** Schematic illustration of the generation of characteristic X-rays and energy loss electrons (after Williams and Carter).\(^{33}\)

In STEM, the ability to interrogate the specimen with a sharp and intense electron probe (c.a. ideally half the size of an atomic dimension) is essential not only to obtain atomic-resolution images but also to generate enough signal intensity for spectroscopic analysis. Until relatively recently, achieving atomic resolution performance from the STEM instrument was almost impossible as the electron probe size was broadened by the third order spherical aberration of the objective lens (Figure 1.7). However, the invention and development of aberration corrector systems to effectively sharpen up the electron probe to sub-atomic dimensions has effectively overcome this limitation and atomic resolution imaging and chemical analysis has now become almost routine.

The electromagnetic lenses in the STEM behave as convex lenses by nature and this makes \(C_s\) correction rather difficult. Scherzer, early in the 20\(^{th}\) century, proposed a clever way to break the rotational symmetry of electromagnetic lenses in order to correct the \(C_s\) aberration.
He postulated that the $C_s$ aberration can be corrected by utilizing non-round magnetic lenses such as quadrupole, hexapole and octapole lenses.\cite{34}

![Figure 1.7](image)

**Figure 1.7.** Schematic diagram showing an electron lens (a) with spherical aberration ($C_s$) in which electron trajectories at different angles are focused at different points on the optical axis, and (b) without spherical aberration in which electron trajectories at different angles are all focused at the same point on the optic axis.\cite{35}

It was shown that such non-rotationally symmetric lenses can create a *negative* $C_s$ value to offset the *positive* $C_s$ of the conventional round lenses. Nowadays, based on Scherzer’s idea (*i.e.* using multipole lenses) two commercial aberration corrector systems have been developed and are currently available on the market. The first is the quadrupole-octupole (QO) system developed by Nion Inc.\cite{36} specifically for a dedicated STEM. As can be seen in Figure 1.8, Nion’s corrector consist of four quadrupoles and three octupoles which are placed between the scan coils and the second condenser lens in the STEM instrument. The second aberration correction system is based upon a hexapole corrector geometry. This corrector, consisting of two hexapoles and additional four transfer lenses (Figure 1.9), was developed by Corrected Electron Optical Systems (CEOS) GmbH and can fit in most TEM/STEM
The Lehigh JEOL JEM-ARM 200CF microscope used extensively in this project was equipped with one of the latest CEOS correctors which can correct aberrations up to the 4th order and allows image acquisition with resolutions as high as 0.07 nm.

**Figure 1.8.** Schematic design of the quadrupole-octupole spherical aberration corrector developed by Nion Co.\textsuperscript{36}

**Figure 1.9.** Schematic diagram of the double hexapole corrector developed by CEOS GmbH.\textsuperscript{38}
During catalyst synthesis processes, it is essential to find procedures that generate a homogeneous distribution of active species over the surface of the support. It is also important when multi-component metals are used to check if the components are properly mixed (i.e., if alloy formation has occurred). During the utilization stage, catalysts may suffer from rapid deactivation caused either by morphological changes, sintering, poisoning or phase transformations. A clear understanding of the correlation between these processes and catalyst performance is often a daunting challenge from a characterization viewpoint because they typically occur at the nanometer length scale. AC-STEM, by the virtue of its ability to provide information on morphology and composition of the catalyst at the atomic level, is therefore a powerful catalyst characterization tool. The following sections present a number of studies where different STEM-based techniques have been employed to investigate catalysts.

1.4. Application of aberration-corrected STEM imaging and spectroscopy techniques in studies of heterogeneous catalysts.

1.4.1. Imaging techniques

Most industrial catalysts are multi-component systems (e.g. small active metal nanoparticles homogeneously dispersed on chemically inert support material). Since the catalytic performance of such catalysts greatly depends on the shape, size and size distribution of the supported nanoparticles, the comprehensive determination of these parameters is of vital importance in catalysis research. However, metal nanoparticles having sizes below ~ 1 nm when supported on a crystalline material might hardly be visible in conventional HR-TEM images because of the lack of sufficient mass-thickness and diffraction contrast. In this case, HAADF imaging in aberration corrected STEM is the most appropriate technique to resolve
sub-nm particles and even single atoms and to generate a reliable particle size distribution.\cite{39,40} He et al.\cite{32} used the HAADF-STEM imaging to determine the various Au species co-existing in a co-precipitated Au/FeO\textsubscript{x} catalyst and to identify which one of the Au species is responsible for the high catalytic activity (Figure 1.10(a)). It was found that in the most active catalysts, the majority of Au species present were sub-nm particles, which they proposed to be the dominant active sites for CO oxidation. By using a similar approach, Li-Wen et al.\cite{41} studied Au nanoparticles immobilized on ceria nanorods (Figure 1.10 (b)) and found that Au clusters and particles were more active for CO oxidation than single-atom Au species.

![Representative HAADF-STEM images revealing Au particles, sub-nm clusters and single- atoms presented in (a) Au/FeO\textsubscript{x} and (b) Au/CeO\textsubscript{2} catalysts.\cite{32,42}](image)

**Figure 1.10.** Representative HAADF-STEM images revealing Au particles, sub-nm clusters and single- atoms presented in (a) Au/FeO\textsubscript{x} and (b) Au/CeO\textsubscript{2} catalysts.\cite{32,42}

### 1.4.2. Spectroscopy techniques

The XEDS and EELS spectroscopic techniques play a very important role in catalysis research. They are especially useful for studying the elemental distribution in bimetallic nanoparticles. Practically, the spectroscopy analysis can be performed using four distinct collection modes, namely *spectrum only*, *point analysis*, *line-scan* and *spectrum imaging*.
(or mapping). The spectrum only is the most basic collection mode used for detecting the elemental content within the entire sample. The point analysis mode is mainly used for revealing the elemental identity and composition at a user-defined point within the sample. Moreover, it is used for doing the quantification analysis as will be described later in Chapter 7. The line-scan analysis, on the other hand, shows how the distribution of elements changes as the beam tracks along a set path. This involves doing a linear sequence of point analyses to show composition gradient changes. Finally, spectrum imaging mode, also known as elemental mapping, is used to visualize the spatial distribution of each element within the sample. In this mode of analysis, the data acquisition time is relatively long as the analysis process has to be performed in a point by point in an area scan. Because valuable compositional information can be obtained from these four analysis modes, they have been extensively used in the characterization of heterogeneous catalyst systems. For example, Figure 1.11 shows an example where STEM-EELS spectrum imaging (mapping) was used to visualize the core-shell elemental distribution present in Pt-Co nanoparticles.\(^{43}\) In another example, Heggan \textit{et.al.},\(^{44}\) used EELS line scans (Figure 1.12) to study the mechanism formation of ZnO patches on the surface of PdZn alloy particles prepared by an impregnation method. Herzing \textit{et.al.}\(^ {45}\) identified core-shell morphologies in Au-Pd nanoparticles prepared by conventional impregnation method utilizing STEM-XEDS mapping combined with multivariate statistical analysis MSA). Finally He \textit{et.al.}\(^ {32}\) recently used XEDS-STEM point spectra to quantify the composition varies with particle size (Figure 1.13) in the bimetallic AuPd system prepared by a sol-immobilization method.
Figure 1.11. STEM-EELS spectrum imaging showing the core-shell elemental distribution in Pt-Co nanoparticles.\textsuperscript{43}

![Fig. 1.11](image)

Figure 1.12. (A) HAADF-STEM image of a PdZn alloy particle showing non-uniform contrast. An EELS line-scan across the particle was performed along the track of the white arrow. (B) EEL spectrum profiles for Pd, Zn, and O and the HAADF intensity profile along this line.\textsuperscript{44}
**Figure 1.13.** A set of HAADF images (a and c) and corresponding XEDS point spectra (b and d) showing the composition variation with size in a AuPd/C sample.\textsuperscript{32}

### 1.4.3. *In-situ* (S)TEM

Although *ex-situ* (S)TEM provides valuable information about the structure and chemistry of the catalyst, the observations may necessarily not be entirely representative of the catalyst in its real working state. Catalytic materials during utilization are prone to undergo dynamic structural changes when they make contact with the surrounding environment (*i.e.*, exposure to reactant gases and high temperatures). Moreover, when the catalyst is transferred after use from the reactor system to the electron microscope for structural examination, the material may become hydrated or oxidized due exposure to air. Hence, the microscopy results obtained can be misleading or open to various interpretations. This problem has triggered interest in *in-situ* (S)TEM, where catalysts can be directly imaged under controlled gas and
temperature environments. The technique of exposing the TEM specimen to a controlled gas and temperature environment is also frequently referred to as environmental transmission electron microscopy (ETEM).\textsuperscript{46} Such \textit{in-situ} experiments in the (S)TEM however can be carried out by using either the differential pumping approach (Figure 1.14 (a)) or the window cell approach (Figure 1.14 (b)).

\textbf{Figure 1.14.} Schematic diagrams of the two main types of ETEM systems for imaging under gas environments; (a) the differential pumping system, (b) the windowed cell system.\textsuperscript{47}

The differential pumping approach involves confining the gas around the sample utilizing several small apertures have been inserted in the bores of the pole pieces, and evacuating the gas using additional pumps in sequential steps to maintain high vacuum in the electron gun area. With differentially pumped systems relatively low gas pressures (< 3 KPa) near the sample area can be achieved. In this system also, gas molecules are the only entities besides the sample that may interact with the electron beam. Therefore, low and medium atomic number materials, even graphene, can be observed with high resolution and good contrast under low gas pressure.\textsuperscript{48} The major disadvantage of this approach is that a dedicated
microscope is required in which modifications to the microscope column are needed in order to integrate the differential pumping system, which can be very expensive.

The closed-cell approach (i.e. window cell approach), on the other hand, involves using a specially designed holder enclosing the sample between two electron-transparent windows (e.g., C or SiN) whose thicknesses are about 10-50 nm. The cell windows often have high fracture strength; thus, they can be used for both liquids and gaseous atmospheres at differential pressure up to 1 bar. In addition to the high pressure, the main advantage of closed-cell system is that the holder is compatible with most of the current (S)TEMs which means the microscope does not need any modification to its column. The major disadvantage of this approach is that the interaction between the electrons beam and cell windows has a tendency to distort images and hinder reliable XEDS spectroscopy. However, thanks to significant developments in thin-film technology and imaging techniques, the closed-cell system now provides the possibility of imaging catalysts at atmospheric pressure and high temperature with a high spatial resolution.49

There are many nice examples in the literature where in-situ (S)TEM has been employed to study catalysts under more realistic environmental conditions. For example, Hansen et.al.50 have conducted an in-situ TEM experiment using the differential pumping system to determine the sintering mechanism in Au nanoparticles supported on BN in 130 Pa of H2 at 400 °C (Figure 1.15). They demonstrated that two sintering mechanisms can take place under the same conditions - one based on the migration of particles over the support surface and subsequent coalescence when they are in close proximity, and the other based on Ostwald ripening, which involves mass transport from smaller to larger particles by the diffusion of adatoms. By using a window-cell approach, Creemer et.al.51 have carried out an
in-situ TEM experiment to directly observe the growth and mobility of Cu nanoparticles over a ZnO support when they exposed the material to 1.2 bar of H\textsubscript{2} at 500 °C.

Ultimately, aberration-corrected analytical electron microscopy is a fast-growing technique. Suffice it to say that the significant improvement in imaging and analytical capabilities it offers, as evidenced in the afore-mentioned examples, gives us the ability to directly observe the response of the catalyst to the surrounding environment at the atomic level and provides potential for exciting new discoveries in the field of heterogeneous catalysis.

Figure 1.15. A sequence of in-situ bright-field TEM images showing sintering of Au particles in the presence of 130 Pa of H\textsubscript{2} at 400°C. The numbers refer to particles that undergo different sintering mechanisms. Between (a) and (b), particles 1 and 2 coalesce. Between (b) and (c), particle 3 coalesces. In contrast, particle 4 becomes smaller between (c) and (f), consistent with Ostwald ripening.\textsuperscript{50}
1.5. Aims of this dissertation

The main goal of my research project has been to characterize several types of industrially important metal catalysts using state-of-the-art aberration-corrected analytical electron microscopy facilities available at Lehigh. The metal catalysts (supported and unsupported) have been prepared and catalytically tested by our collaborators from the Cardiff Catalysis Institute in the UK led by Prof. Graham J. Hutchings. Under the supervision of Prof. Christopher J. Kiely, I have been performing analytical electron microscopy studies on their catalyst materials and relating the microstructural results obtained to catalytic performance data and other complementary characterization data (e.g., XRD, XPS and EXAFS). The specific objectives of this research project can be summarized as follows:

1.5.1. Specific objectives of the project

1. Gold-based catalysts for the Water Gas Shift (WGS) reaction. The application of gold-based catalysts in the water gas shift reaction has been studied for decades. Recently gold nanoparticles supported on ceria-zirconia (CeZrO$_4$) prepared by deposition-precipitation are beginning to receive some attention from research groups due their promising performance in the low temperature (LT)-WGS reaction. These materials show very high initial levels catalytic activity but rather low stability. In Chapter 3, aberration corrected electron microscopy in conjunction with several other characterization techniques has been used (i) to achieve an improved mechanistic understanding of how the Au/CeZrO$_4$ catalyst system deactivates under typical LT-WGS reaction conditions; and (ii) to determine the underlying reasons why alloyed AuPd/CeZrO$_4$ catalysts do not make good LT-WGS shift catalysts.
II. **Optimization of PdZn/ZnO catalysts for the Methanol Steam Reforming (MSR) reaction.** Owing to their superb performance in the MSR reaction, Pd-based catalysts, especially Pd supported on ZnO, have been widely studied. In Chapter 4, we will discuss the possibility of optimizing the PdZn/ZnO system for the MSR reaction by utilizing a new modified impregnation-based method to synthesize the catalyst. Through this study, in particular, we compare the structures and catalytic performances of ZnO supported PdZn alloy catalysts prepared by conventional impregnation and by the new ‘modified impregnation’ technique.

III. **Unsupported AuPd catalysts for the direct conversion of methane to methanol.** In Chapter 5, aberration corrected analytical electron microscopy is used to develop an understanding of why unsupported AuPd colloidal particles out-perform sol-immobilized AuPd particles on TiO$_2$ for the direct production of methanol from methane. Through a microscopy directed catalyst design study we aimed to optimize the AuPd alloy size distribution, particle morphology and compositional homogeneity for this challenging reaction. New methods of creating core-shell AuPd nanoparticles by selective leaching and roto-evaporation methodologies are also explored.

IV. **Optimizing Pt/TiO$_2$ catalysts for the selective hydrogenation of nitrostyrene to 3-vinylaniline.** Supported Pt nanocatalysts have been reported as an efficient catalytic system for the selective hydrogenation of nitro- groups. The work presented in Chapter 6 has been designed to optimize a Pt/TiO$_2$ catalyst prepared by the impregnation method for the selective hydrogenation of nitrostyrene to vinylaniline. During the study, the structural evolution of nanoscopic Pt particles supported on TiO$_2$ has been followed as a function of various heat treatment conditions using a combination of AC-STEM and XAFS analysis.
The aim is to identify the optimum size, morphology and loading of the Pt on TiO\textsubscript{2} for application in the selective hydrogenation of nitrostyrene.

**V. Immobilized Au and AuPd sol catalysts prepared in novel 3D printed millifluidic reactors.** Recently, automated reactors such as microfluidic and millifluidic reactors have received a great deal of attention as they permit the continuous production of nanomaterials on a large scale. In Chapter 7, we describe a study to explore the applicability of such a synthesis methodology to continuously produce sol-immobilized colloidal Au/TiO\textsubscript{2} and AuPd/TiO\textsubscript{2} catalysts. In particular, a critical microstructural comparison is made between supported monometallic Au and bimetallic AuPd colloidal particles prepared in a conventional batch reactor with those made in a continuous manner using novel 3D printed millifluidic reactors. The aim is to see if improved control over particle size distribution and composition can be achieved using this new reactor technology.

**More detailed literature reviews for each of these specific topics and catalyst systems are presented at the beginning of the relevant chapters.**
References


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Chapter 2

Experimental Methods
This chapter describes the various experimental procedures employed throughout the course of this work to structurally and compositionally characterize the catalyst systems under investigation. It covers some practical details of the general electron microscopy approaches employed in this project, including sample preparation and image processing methods. Complementary characterization techniques such as BET surface area measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and diffuse-reflectance fourier-transform infrared spectroscopy (DRIFTS) are also briefly described in this chapter.

2.1. Electron microscopy characterization

The electron microscopy investigations presented in this thesis were mainly performed by the author using facilities available at Lehigh University. The stop-start ‘anaerobic transfer’ STEM experiments presented in Chapter 3, Section 3.2.2, was carried out in collaboration with Dr. Xi Liu in Synfuels China Technology Co. Ltd. Beijing, China. Some additional STEM-XEDS analysis presented in Chapter 7, Section 7.3, was carried out by Dr. Qian He.

Conventional transmission electron microscopy (TEM), aberration-corrected scanning transmission electron microscopy (AC-STEM) and stop-start scanning transmission electron microscopy (stop-start STEM) form the underlying basis of much of the experimental work described in this thesis.

Samples for examination by transmission electron microscopy were prepared by dry dispersing the catalyst powder onto a holey carbon film supported by a 300-mesh copper TEM grid. Conventional TEM studies were performed with a JEOL 2000FX TEM equipped with a LaB₆ thermionic gun operating at 200kV. The instrument also had an Oxford Si(Li)
X-ray energy dispersive X-ray spectrometer (XEDS) having a 0.1 Sr. collection solid angle, which can be used for chemical analysis.

STEM imaging experiments \textit{i.e.}, bright field (BF) and high angle annular dark field (HAADF) imaging) were performed on an aberration-corrected JEM ARM-200CF microscope (Figure 2.1) operating at 200kV. The AC-STEM instrument was equipped with a cold field emission gun and a CEOS C\textsubscript{s} corrector (fourth order). The inner collection angle typically of the high angle annular dark field (HAADF) detector is between 45 and 200 mrad at a camera length of 10 cm. For BF and HAADF-STEM imaging experiments, the probe current was set to between 26-40 pA, with a typical probe size 8C and a dwell time of 31 µs per pixel. This instrument was also equipped with a JEOL Centurio silicon drift detector having a 0.13 Sr. collection solid angle for X-ray energy dispersive spectroscopy. For XEDS analysis a larger probe current, typically about 80 pA, was used to scan over the catalyst particle, with a total live time of about 100-300 s. During acquisition of XEDS data, the specimen was usually tilted 15° towards the X-ray detector to maximize the collection efficiency. The XEDS quantification presented in Chapter 7, Section 7.3, was performed in conjunction with Dr. Qian He, using the Cliff-Lorimer method. During STEM experiments, carbon contamination build-up in the area under the scanning probe can be a serious issue. To minimize such problems, before any experiment, the sample holder was cleaned for about 15 min in a Fischione plasma cleaner. This process can help to remove dust and remains of other users’ samples. In some cases, especially when plasma cleaning did not seem to help, we performed a beam shower on the sample for about 10 min. During the beam shower process, the sample is illuminated with a defocused beam. This pre-treatment process in fact helps to ‘bake’ the C in place so it does not accumulate under the probe. However, extra
caution should be paid of the beam shower current and exposure time when studying a sensitive material, as it is possible to induce changes in the microstructure of the sample due to electron beam damage.

**Figure 2.1.** The JEOL JEM-ARM200CF aberration-corrected microscope.

The *in-situ* scanning transmission electron microscopy (*i.e.*, stop-start STEM) study discussed in Chapter 3, section 3.2.2, was carried out using an FEI Talos F200X STEM equipped with a Super-X EDS system, operating at 200kV. Catalyst particles were supported on inert silicon nitride finder TEM grids and were exposed to the following low-temperature water gas shift reaction conditions: the catalyst was heated in N\(_2\) at 8 °C min\(^{-1}\) from RT to 150 °C before the introduction of reaction gases (2% CO, 2% CO\(_2\), 7.5% H\(_2\)O, 8.1% H\(_2\) + N\(_2\) to balance). Using this methodology, the TEM grid supporting the sample was anaerobically transferred from the electron microscope to a cell that exposes gas phase reactants at reaction temperature to the sample at atmospheric pressure. When re-inserted
into the microscope, the exact same location on the sample grid could be found and re-examined. By repeating this procedure multiple times, the same region of the catalyst can be analyzed at various stages of its lifetime. The fresh sample was examined by STEM, exposed to N₂ and heated to reaction temperature before being returned to the microscope and re-examined. This process was then repeated for samples after 5 min on-stream and 12 h on-stream, giving snapshots of the same area of catalyst at four different stages of its lifetime.

2.1.1. Software used in microscopy analyses

**Digital Micrograph**

Digital Micrograph is a software package provided by Gatan Inc., which was used to acquire, process, analyze and present image and spectrum data in TEM and STEM.¹ It was also used to acquire Fourier Transforms (FTs) from digital HR-TEM and STEM images via a Fast Fourier Transform (FFT) function. The FFTs obtained were compared to electron diffraction patterns of a given structure in order to facilitate phase identification of materials. Additionally, noise in HAADF-STEM images could be reduced using the low-pass filtering function in Digital Micrograph.

**ImageJ**

ImageJ is a free of charge, java-based image processing program developed at the National Institute of Health. More information about how Image J works, and its capabilities can be found at [https://imagej.nih.gov/ij/index.html](https://imagej.nih.gov/ij/index.html). All particle size distribution (PSD) histograms in this study were generated by analysis of representative HAADF-STEM micrographs using ImageJ. The PSD evaluation process was carried out as follows:

   (i) Multiple HAADF images were obtained from the sample of interest.
(ii) Using imageJ, we converted the images to binary black and white and then measured the 2D projected area of the 3D nanoparticles from the HAADF images. To simplify the PSD measurements, the particles were assumed to be spheres and were described in terms of a projected circular diameter even though they could sometimes be more irregular in shape. The measured areas were then used to calculate the particle diameters. More than 200 particles were measured to obtain a statistically relevant PSD.

(iii) Finally, by using Excel or OrigionLab the PSD data was plotted as a histogram showing the number fraction of particles falling within certain size ranges.

**Vesta**

VESTA (Visualization for Electronic and Structural Analysis) is a multi-dimensional (2D and 3D) visualization system for structural models, volumetric data and crystal morphologies. In this project, VESTA was used to render 2D atomic models, in particular directions, of Pd-Zn alloy phases as described in Chapter 4.

**EDS analysis and quantification software**

The spectra collected by the EDS measurements (i.e. by pointanalysis) were quantified by the Cliff-Lorimer k-factor method to obtain the relative concentrations between two elements (Au and Pd) from the integrated EDS peak intensities. This method is only applied when a specimen thickness is 10 nm or less where any absorption or fluorescence effects can be negligible. However, the Cliff-Lorimer k factor was estimated from a sputtered standard 60wt%Au-40wt%Pd thin film. The detail of this quantification process can be found in Chapter 7, Section 7.3.
2.2. X-Ray Diffraction

All the X-ray diffraction (XRD) experiments presented throughout this thesis were performed by our collaborators from the Cardiff Catalysis Institute (CCI) in the UK led by Prof. Graham J. Hutchings. XRD was used extensively to identify the crystalline phases present in our catalyst samples. In a typical powder X-ray diffraction experiment, a powder sample is irradiated with a monochromatic beam of X-rays (e.g., Cu Kα) and the acquired diffractogram shows the diffracted X-ray intensity as function of diffraction angle. The positions of diffraction peaks can then be analyzed using Bragg’s law (Eqn. 2.1)

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

Eqn. (2.1)

In equation 2.1, \( \lambda \) is the wavelength of the incident X-ray, \( d_{hkl} \) is the spacing between the specific \( hkl \) planes and \( \theta \) is the scattering angle. Through comparison of the position and relative intensity of peaks in the diffraction pattern with those in the XRD database, the phases that are present within the examined sample can be identified. In addition, from the peak width, the average grain size of the sample can be estimated using the Scherrer equation (Eqn. 2.2)

\[ D_{\text{average}} = \frac{K\lambda}{\beta \cos \theta} \]  

Eqn. (2.2)

In equation 2.2, \( D_{\text{average}} \) is the mean grain size in the sample, \( K \) is the shape factor, which is about 0.94 for spherical crystals, \( \beta \) is the full-width-at-half-maximum (FWHM) of the peak being measured and \( \theta \) is diffraction angle.\(^3\)

The X-ray diffraction (XRD) analysis was conducted using a (θ-θ) PANalytical Xpert Pro powder diffractometer using a Cu Kα radiation source (\( \lambda = 0.154 \) nm) operating at 40 keV and 40 mA. A typical standard analysis took about 40 mins. In the case of \textit{in-situ} XRD,
catalyst samples were heated to 500 °C under a constant flow of 5% H₂/N₂ (20 mL/min) and scans were taken at 100 °C temperature intervals. Phase identifications from the XRD patterns were performed by comparison with the ICDD data base.

2.3. X-ray photoelectron spectroscopy

All the X-ray photoelectron spectroscopy (XPS) experiments described in this thesis were performed by Dr. D. Morgan in the CCI at Cardiff University.

XPS is reliable technique for analyzing the surface chemistry of materials. In an XPS experiment, a monochromatic soft X-ray source is used to irradiate a sample, which results in the ionization of surface atoms within the material and the ejection of photo-electrons. The kinetic energy \( E_k \) of the ejected photoelectrons are measured by a suitable spectrometer. The binding energy of the ejected electron can be calculated using equation 2.3:

\[
E_k = h \nu - E_b - \varphi
\]

Eqn. 2.3

where \( h \nu \) is the energy of the incident X-ray photons, \( E_b \) is the binding energy of the emitted photoelectron and \( \varphi \) is the work function of the material under investigation. The binding energy reflects the electronic structure of the material and thus carries information about the surface composition and oxidation state of surface elements.\(^4\)

The XPS spectra presented in this thesis were recorded using a Kratos Axis Ultra-DLD photoelectron spectrometer, using monochromatic Al K\(\alpha\) radiation at 144 W (12 mA \times 12 kV) power. High resolution and survey scans were performed at pass energies of 40 and 160
eV respectively. Magnetically confined charge compensation was used to minimize sample charging and the resulting spectra were calibrated to the adventitious C(1s) line at 284.8 eV.

2.4. Diffuse-Reflectance Fourier-transform Infrared Spectroscopy (DRIFTS)

DRIFTS is a well-established spectral method used to study the surface chemistry of solid catalysts. Recently, it is received much interest as an in-situ characterization technique for studying reaction mechanisms.\textsuperscript{5,6} It can be used to directly monitor the interaction between the adsorbed molecules and the catalyst surface, and the tracking intermediates and products that can form during the catalytic reaction. DRIFT analysis is typically carried out by focusing infrared (IR) light onto the surface of the specimen and the scattered light is collected and sent to an IR detector. The resultant spectrum carries chemical and structural information for the material under investigation.

The CO-DRIFTS measurements presented in this thesis were performed at Cardiff University on a Bruker Tensor 27 spectrometer fitted with a mercury cadmium telluride (MCT) detector and ZnSe windows. A sample was loaded into the Praying Mantis high temperature (HVC-DRP-4) in-situ cell before exposure to N\textsubscript{2} and then 1\% CO/N\textsubscript{2} at a flow rate of 50 cm\textsuperscript{3} min\textsuperscript{-1}. A background spectrum was obtained using KBr and measurements were recorded every minute at room temperature. Once the CO adsorption bands in the DRIFT spectra ceased to change, the gas feed was changed back to N\textsubscript{2} and measurements were made until no change in subsequent spectra was observed. A more detailed description of the DRIFTS technique can be found in a book authored by Mitchell.\textsuperscript{7}
2.5. X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy, including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), plays a pivotal role in catalysis research as it can provide important information on the electronic and structural properties of a catalyst under reaction conditions. The XAS technique involves using a synchrotron X-ray source to irradiate the material of interest and the incident and transmitted X-ray flux is recorded and analyzed by a fluorescence detector to generate the final XAS spectrum (Figure 2.2).

![X-ray absorption spectroscopy spectrum illustrating the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions.](image)

**Figure 2.2.** X-ray absorption spectroscopy spectrum illustrating the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions.8

The XAS spectrum is divided to two main parts called the XANES and EXAFS regions. The XANES region typically carries valuable information about the identity and oxidation state of atoms in the material under investigation while the EXAFS provides quantitative data of bond length and coordination number. A detailed description of the X-ray absorption
spectroscopy technique and its crucial role in the field of catalyst characterization can be found in a book authored by Imelik and Vedrine.  

X-ray absorption spectroscopy measurements presented in this thesis were performed at Stations B18 and I20 at the Diamond Light Source (Harwell, Oxfordshire, UK) operating at 3 GeV in multi-bunch mode with a current of 200 mA. Both stations are equipped with a Si (111) double crystal monochromator, ion chambers for measuring incident and transmitted beam intensities and/or a multi-element Ge (fluorescence) detector for recording X-ray absorption spectra. The measurements were carried out in air on catalysts dispersed on self-supporting wafers (approximately 100 mg) at the Pt L₃ edge, with the respective foils (10 μm) used as a calibrant for the monochromator. Measurements were performed at room temperature in normal step scanning mode. To improve the signal-to-noise ratio, multiple scans were taken. All data were subjected to background correction using Athena (i.e. IFEFFIT software package for pre- and post-edge background subtraction and data normalization). XAFS spectra were normalized from 30 to 150 eV above the edge energy, while the EXAFS spectra were normalized from 150 eV to the last data point using the Autobk algorithm. Normalization was performed between \( \mu(E) \) and \( \mu_0(E) \) via a line regression through the data in the region below the edge and subtracted from the data. A quadratic polynomial is then regressed to the data above the edge and extrapolated back to \( E_0 \). The extrapolated value of the post edge polynomial at \( E_0 \) is used as the normalization constant. This threshold energy (\( E_0 \)) is normally determined using either the maximum in the 1st derivative, approximately 50 % of the rising absorption edge, or immediately after any pre-edge or shoulder features. The isolated EXAFS spectra were analyzed using the DL-EXCURV program. Data were analyzed using a least squares single or dual shell EXAFS
fitting analyses performed on data that had been phase corrected using muffin-tin potentials. Amplitude reduction factors ($S_o^2$) of 0.94 obtained from fitting a Pt metal foil, was also used in the analysis.

2.6. BET surface area measurement

The surface area of a solid catalyst has a significant impact on its activity. Therefore, measuring the surface area of a given catalyst material is extremely important when evaluating its performance. The most widely used method of measuring the surface area of powders is the BET method which was developed by Brunauer, Emmett and Teller in 1938 and further optimized by Ross and Olivier. BET measures the surface area ($S_{BET}$) based on gas adsorption. More specifically, it allows the determination of specific surface area by measuring the amount of physically adsorbed gas such as nitrogen according to the BET equation (Eqn.2.4)

$$\frac{P}{v(P_0-P)} = \frac{1}{v_mC} + \frac{C-1}{v_mC} \frac{P}{P_0} \quad \text{Eqn. 2.4}$$

where $C$ is a constant, $v$ is the adsorbed gas volume and $v_m$ is the monolayer adsorbed gas volume. The linearity $P/P_0$ of this BET equation is maintained between 0.05 and 0.35. By calculating $v_m$, the surface area can be determined from equation 2.5:

$$\text{Surface area, } S_{BET} = \frac{v_m*N_A}{M} \quad \text{Eqn. 2.5}$$

where $N_A$ is Avogadro’s number and $M$ is the molar volume of the adsorbate gas. The BET surface area analysis presented in this thesis was carried out using a Quantachrome
Quadrasorb evo system. A 5-point analysis was performed using N2 as the adsorbate gas. Samples were degassed in vacuum for 1 h at 120°C prior to analysis.

2.7. **Thermo-gravimetric analysis (TGA)**

TGA is a widely used characterization technique in which the mass of a sample is measured as it is exposed to a specific environment (e.g., gases, elevated temperatures, ). For instance, the change in the physical or chemical state of a sample can be measured as temperature is increased under an oxidizing environment. This type of analysis can be used to model calcination procedures and establish when the decomposition of a particular phase has taken place. Typically, the data is represented as mass loss as a function of temperature, allowing us to identify the temperatures at which processes such as water desorption, complete decomposition or sample reduction occur. In some applications, TGA can be coupled with IR spectroscopy or mass spectrometry to identify and quantify specific desorption products. Figure 2.3 shows a typical set-up for a TGA instrument.
2.8. Microwave plasma atomic emission spectroscopy (MP-AES)

Microwave plasma atomic emission spectroscopy (MP-AES) is a powerful tool for conducting high precision elemental analysis of catalyst samples. In this technique, a nitrogen plasma is used to excite and vaporize the atoms in a liquid sample. This causes the electrons in the sample to go from a ground state to an excited state. When the atoms relax, a specific quantum of energy is released, in the form of photons. These transitions have energy, and hence wavelengths, that are characterized by the element of origin. The photons are detected by a charge-coupled device (CCD). Each wavelength is analyzed sequentially, which increases the time needed to analyze a sample, but also achieves p.p.m. level chemical sensitivity.

The MP-AES method also allows multiple wavelengths pertaining to the same element to be quantified – this reduces the possibility of interference from other elements that have
similar emission wavelengths. Figure 2.5 shows a schematic depiction of the MP-AES methodology.

**Figure 2.4.** A schematic showing processes involved in the MP-AES (after Dr J. Carter)\textsuperscript{13}
References


Chapter 3

Gold-based Catalysts for the Low Temperature Water Gas Shift (LT-WGS) Reaction
3.1. Introduction

The water gas shift (WGS) reaction is one of the most viable processes for the \textit{in-situ} production of hydrogen, which is then subsequently utilized in the synthesis of ammonia and hydrocarbons or as a feed in fuel cell applications.\textsuperscript{1} The WGS process involves the reaction between water and carbon monoxide, in the presence of a suitable catalyst, to produce hydrogen and carbon dioxide (Eq.1).

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.2 \text{ kJ mol}^{-1} \quad \text{Eq}(1) \]

Owing to its reversibility and exothermic nature, the WGS process industrially is implemented in two stages, namely a high-temperature shift (310-450 °C) and a low-temperature shift (150-250 °C), with different catalysts to achieve high CO conversion, maximize hydrogen production, and make the process economically viable.\textsuperscript{2,3} In recent years, the low-temperature (LT) WGS process has gained a renewed interest in the application area of fuel cells. It is recognized as an ideal reaction to boost the efficiency of fuel cells by minimizing the concentration of carbon monoxide present while at the same time generating H\textsubscript{2} fuel, as illustrated in Figure 3.1.\textsuperscript{1}

\textbf{Figure 3.1.} A schematic diagram of the water gas shift process integrated with a proton electrolyte membrane fuel cell (PEMFC) (adapted from ref.\textsuperscript{4}).
Unfortunately, conventional industrial catalysts (such as Cu-based catalysts) for the low temperature (LT) WGS reaction are not compatible with fuel cell applications as they are pyrophoric and normally require lengthy and complicated activation steps before utilization.\(^2,^5\) Gold containing catalysts, however, have been shown to have the potential to overcome those problems and be very active for the LT-WGS reaction.\(^6^-^8\) Although the use of gold-based catalysts for the WGS reaction is not new, the nature of the active sites responsible for the observed high catalytic activity remains unclear because the multitude of preparation methods, testing conditions, investigation approaches employed by different research groups. For instance, Mohamed \textit{et al.},\(^9\) studied AuCl\(_3\) supported on zeolites using IR measurements and proposed that gold cations are responsible for the high activity in the WGS reaction. Other researchers, based on FTIR investigations, proposed that small metallic Au nanoparticles (2 – 4 nm) in close contact with oxide supports are responsible for the high WGS activity.\(^10,^11\) Recently, Flytzani-Stephanopoulos \textit{et al} by using a combination of electron microscopy and associated spectroscopic approaches proposed that non-metallic gold species were mainly responsible for the high activity.\(^12\)

Gold supported on ceria-zirconia is one of the most promising catalytic systems that has been developed for the LT-WGS reaction. It is very active for the WGS reaction at temperatures even as low as 100 \(^\circ\)C.\(^13\) The high WGS activity of Au/CeZrO\(_4\) is attributed to the intimate interaction between Au nanoparticle and the mixed oxide support.\(^6,^13\) Goguet and co-workers investigated this catalytic system using DFT and \textit{in-situ} EXAFS techniques to identify the nature of the active sites and proposed that the metallic gold in close contact with the oxide support is responsible for the high WGS activity observed.\(^14\) However, this Au/CeZrO\(_4\) catalyst suffers from rapid deactivation under reaction conditions which
currently makes it economically unattractive. Furthermore, there are conflicting reports about the precise deactivation mechanism, which impedes efforts to design a more stable Au/CeZrO$_4$ system.\textsuperscript{15–18}

Recently a group from Queens University, using a combination of experimental (EXAFS) and theoretical (DFT) approaches proposed a deactivation mechanism for the Au/CeZrO$_4$ system.\textsuperscript{19–21} They suggested that the Au nanoparticles under the WGS reaction conditions, especially in the presence of a high concentration of water vapor, physically changed shape and partly de-wetted from the mixed oxide support (Figure 3.2). This de-wetting phenomenon significantly reduces the interfacial contact between Au and CeZrO$_4$ – which is the proposed active site in this system.

![Figure 3.2](image.png)

\textbf{Figure 3.2.} Schematic diagram illustrating the proposed deactivation mechanism of partial de-wetting of Au on CeZrO$_4$ under WGS reaction conditions (after reference\textsuperscript{21}).

The structural changes associated with deactivation of the Au/CeZrO$_4$ system, however, have not previously been investigated by electron microscopy methods. Such characterization is essential to study any agglomeration or morphological changes that can potentially occur under reaction conditions which might also contribute to the instability of
Au/CeZrO$_4$. Surprisingly, the previous studies done by the Queens University group disregarded the possible role of particle agglomeration and the formation of surface carbonates contributing to the observed instability of the catalyst, even though this has been reported to be the cause deactivation in some supported gold catalysts.$^{16,17}$ Therefore, the careful characterization of Au/CeZrO$_4$ materials before and after use is crucial to rationalize the underlying causes of deactivation in this materials system.

For the LT-WGS reaction, several bimetallic catalysts have been reported to display a better catalytic performance as compared to their monometallic counterparts.$^{8,22}$ However, the paper by Yeung et al.$^{17}$ is the only experimental report on supported AuPd catalysts being used for the LT-WGS reaction. Since Yeung et al used a different support (CeO$_2$) and a different catalyst preparation method ($i.e.$, co-precipitation), the question of whether AuPd/CeZrO$_4$ prepared by the deposition-precipitation (DP) method is a viable catalyst for the LT-WGS reaction remains unanswered.

### 3.1.1. Aims of this study

The aim of this study was to systematically investigate the deactivation mechanism of Au/CeZrO$_4$ via a combination of bulk spectroscopic and local microscopic characterization techniques. The knowledge gained from this work might allow us to re-engineer the Au/CeZrO$_4$ catalyst to improve its stability in the LT-WGS reaction. In this work, the bimetallic AuPd/CeZrO$_4$ system was also evaluated as an alternative for the unstable Au/CeZrO$_4$ catalyst. The study involves using a range of in-situ and ex-situ characterization techniques to understand the structural evolution of the catalyst and to correlate these with catalyst performance measurements at taken as a function of time-on-line.
3.2. Deactivation of gold catalyst supported on ceria-zirconia oxide during the LT-WGS reaction

3.2.1. Catalyst preparation and testing

The CeZrO₄ supported gold catalysts studied in this project were prepared at Cardiff Catalysis Institute using a deposition-precipitation (DP) method. The DP synthesis approach has been reported to give the most active Au/CeZrO₄ catalysts compared to comparable materials prepared using other synthesis methods such as the conventional impregnation route. It has been proposed that this is because the DP method provides superior monodispersity in the final supported metal particle size.

A typical DP preparation sequence for making the 2wt% Au/CeZrO₄ catalyst is illustrated in Figure 3.3. An aqueous solution of HAuCl₄ (0.067 M) was mixed with 0.2 L of deionized water at 60 °C to obtain a total target metal loading of 2wt%. After that, 0.98 g of CeZrO₄...
(supplied by Solvay) was dispersed in the solution and stirred for 15 min. The pH of the solution was then adjusted to 8 by the dropwise addition of Na$_2$CO$_3$ (0.05 M). The reaction mixture was vigorously stirred for 1 h and the solution filtered under vacuum and washed with 0.8 L of deionized water. The final catalyst finally was dried in an oven at 110 °C for 5h.

The LT-WGS activity in terms of CO conversion was evaluated for the 2wt% Au/CeZrO$_4$ catalyst in a fixed bed flow-reactor equipped with an on-line Gasmet FT-IR. Prior to testing, 180 mg of the catalyst was heated to 150 °C under N$_2$ using an 8 °C min$^{-1}$ temperature ramp rate. Following this, the catalyst was exposed to the WGS mixture (2% CO, 2% CO$_2$, 7.5% H$_2$O, 8.1% H$_2$ + N$_2$ to balance) for 48 h at a flow rate of 100cm$^3$ min$^{-1}$ and GHSV of 52,000 h$^{-1}$. During the reaction, an FT-IR spectrum was acquired every minute and the conversion levels at each time interval were calculated based on the consumption of CO.

Figure 3.4 shows the catalytic activity of the 2wt% Au/CeZrO$_4$ catalyst under the aforementioned LT-WGS reaction. Over the 48 h duration of the experiment, the catalyst lost about 40% of its activity as compared to the initial value. It is also worth noting that most rapid deactivation occurred during the first 6 h on-line. After that, the catalyst continued to deactivate at a fairly constant rate until the end of the experiment. The change in the deactivation rate after 6 h could be an indication that multiple physical processes may be occurring during deactivation. The fresh material in Figure 3.4 is labelled ①. Samples of the catalyst were also recovered at various points (labelled ② - ⑥ in Figure 3.4) in this deactivation cycle and characterized using XPS, XRD and AC-STEM.
Figure 3.4. Time-on-line catalytic activity profile of the 2 wt% Au/CeZrO$_4$ catalyst under LT-WGS conditions showing the specific time intervals (1) fresh, (2) heated under N$_2$, (3) after 5 min (4) after 5 h, (5) after 12 h and (6) after 48 h) at which the catalyst was characterized by XPS and AEM (Courtesy of Dr. James Carter).

3.2.2. Ex-situ catalyst characterization

XPS analysis of the Au/CeZrO$_4$ material allowed us to monitor the relative populations and surface concentrations of the various Au species present in both the fresh and various partially used catalysts. It also allowed us to ascertain if any contaminants (e.g., Cl and Na) have been retained from the catalyst preparation process as they could also potentially poison the catalyst and cause the deactivation. The XPS spectra (Figure 3.5) obtained suggested following: (1) no significant contaminants were detected in either the fresh or used samples; (2) all samples display three characteristic features (labelled Au$^0$, Au$^{3+}$ and Au$^{0*}$) corresponding to different Au species. The peaks found at 84 eV and 86.2 eV, respectively were assigned to Au$^0$ and Au$^{3+}$ respectively, while the Au$^{0*}$ signal at 85 eV has previously been assigned to ultra-small Au nanoparticles (Figure 3.5 (a)).$^{25,26}$

The relative concentrations of these various Au species changed after use (see Table 3.1). The decrease in Au$^{3+}$ content that was observed after the heat ramp under N$_2$ was accepted
as evidence of agglomeration of atomically dispersed Au cations into clusters and small (1-2 nm) Au nanoparticles, while the decrease in Au\textsuperscript{0*} content might be attributable to agglomeration of the Au nanoparticle population. The potent correlation between the simultaneous loss of Au\textsuperscript{0*} and Au\textsuperscript{3+} and decrease in catalytic activity could indicate that these species are highly active but unstable in this system.

**Figure 3.5.** Au 4f XPS spectra of the 2wt% Au/CeZrO\textsubscript{4} catalyst at various stages in the LTS reaction: a) fresh \(\textcircled{1}\); b) after N\textsubscript{2} heating \(\textcircled{2}\); c) after 5 h on-stream \(\textcircled{4}\) and d) after 48 h on-stream \(\textcircled{6}\). The samples show the presence of multiple Au species; namely Au\textsuperscript{0} (dotted green line), Au\textsuperscript{0*} (dashed red line) and Au\textsuperscript{3+} (solid blue line). The fresh catalyst contains a high concentration of Au\textsuperscript{3+} and Au\textsuperscript{0*}, which decreases after heating to the reaction temperature in N\textsubscript{2} and even further under reaction conditions. After 5 h of reaction there is no detectable Au\textsuperscript{3+} remaining (Courtesy of Dr. James Carter).
Table 3.1. The evolution of Au oxidation states in the 2 wt% Au/CeZrO₄ catalyst, before, after N₂ pre-treatment and throughout the LTS reaction as monitored by ex-situ XPS measurement and quantified using the Au 4f spectral region²⁷ (Courtesy of Dr. James Carter).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction of different Au species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au⁰</td>
</tr>
<tr>
<td>Fresh ①</td>
<td>67.1</td>
</tr>
<tr>
<td>Heated under N₂ ②</td>
<td>77.9</td>
</tr>
<tr>
<td>5 h ④</td>
<td>85.0</td>
</tr>
<tr>
<td>48 h ⑥</td>
<td>88.5</td>
</tr>
</tbody>
</table>

Initially an electron microscopic analysis was carried out on the fresh and 48 h used samples of 2wt% Au/CeZrO₄ to look for evidence of sintering or changes in particle morphology. Some representative high angle annular dark field (HAADF-) and bright field (BF-) STEM images collected from the fresh sample are shown in Figure 3.6. The mixed oxide support displayed two distinct morphologies (Figure 3.6 (a) and (b)); one had larger 8-15 nm size particles and displayed distinct {111} and {200} surface facets (Figure 3.6 (c)), while the other was less-ordered and nanocrystalline (i.e., 2-3 nm) in character (Figure 3.6 (d)). Selected area diffraction patterns (SADPs) were collected from the two CeZrO₄ morphologies (Figure 3.7). The difference in grain size can be seen obtained diffraction patterns, as the nanocrystalline regions give rise to a more continuous ring pattern (Figures 3.7 (e) and (f)). However, no structural differences were detected between the larger grained and nanocrystalline regions as shown by the overlaid pattern in Figure 3.7 (d).
Figure 3.6. Characterization of the CeZrO$_4$ support. (a, b) Complementary pair of BF- and HAADF-STEM images of the unused 2wt% Au/CeZrO$_4$ catalyst showing two distinct support morphologies (agglomerates of particles > 10nm – red arrows, agglomerates of sub-5 nm particles – green arrows). The Au nanoparticles are preferentially associated with the agglomerates of larger ceria-zirconia grains; (c) BF-STEM lattice image of an [011̅] projection of a tetragonal CeZrO$_4$ grain from an agglomerate of larger grains showing {111} and {200}-type lattice fringes; (d) HAADF-STEM image showing a typical nanocrystalline region of the CeZrO$_4$ support – the brightest particle in the field of view is a Au nanocrystal.
Figure 3.7. Electron diffraction characterization of the two CeZrO$_4$ support morphologies. (a) Bright field TEM image of an agglomerate of CeZrO$_4$ particles that contains (b) a region with relatively larger grains and (c) a region with nanocrystalline grains. The corresponding selected area electron diffraction patterns of the areas (b) and (c) are shown in red in (e) and in green in (f), respectively. (d) Overlapped pattern showing no structural difference between the larger grained and nanocrystalline regions. (g) Simulated diffraction ring pattern of CeZrO$_4$ (Courtesy of Dr. Qian He).
Interestingly, the distribution of Au NPs over the support in the unused catalyst was inhomogeneous, with most of them being found on the larger CeZrO$_4$ particles. Clearly, the smaller Au particles (<3 nm) prefer to sit in the crevices between CeZrO$_4$ support grains (Figures 3.8 (a) and (b)) while the larger Au particles (>5 nm) form planar interfaces with CeZrO$_4$ support grains and display distinct \{111\} and \{200\} surface facets (Figures 3.8 (c) and (d)). A particle size histogram (Figure 3.11(a)) generated from HAADF images of a large number of Au particles (ca. 300 particles) showed them to have a mean size of ~4.5 nm. Complementary XRD analysis, carried out to verify if structural changes to the support had occurred (or if reflections due to Au could be measured), showed only reflections due to the CeZrO$_4$ support, which remained unchanged after 48 h on-stream (Figure 3.9).
Figure 3.8. (a, d) Representative HAADF- and (b, c) BF-STEM images of the unused 2wt% Au/CeZrO₄ catalyst. (a, b) Pair of HAADF- and BF-STEM images illustrating the tendency of small Au NPs to sit in the crevices between CeZrO₄ support grains. (c, d) Pair of HAADF- and BF-STEM image of larger Au particles showing their tendency to exhibit distinct {111} and {200} surfaces and a flat extended interface with the support.

Figure 3.9. Sequence of XRD spectra from the 2wt% Au/CeZrO₄ material at various stages of its lifecycle as a catalyst. (Courtesy of Dr. James Carter)

Although the XPS results suggested the presence of highly dispersed Au atoms and possibly clusters, it was quite difficult to confirm their presence the high magnification HAADF-STEM images. Figures 3.10 (a) and (b) shows two atomic resolution HAADF-STEM images.
of a support particle from a CeZrO$_4$ sample in which no gold has been added and the unused 2wt% Au/CeZrO$_4$ catalyst, respectively. In each case the CeZrO$_4$ grain is viewed along the [001] zone axis. The intensity variations between adjacent atomic columns in (a) arise purely from mass contrast variations arising differing proportions of heavier Ce ($z = 58$) and lighter Zr ($z = 40$) atoms along the projected cationic columns. In (b) very similar intensity variations are observed, but in this case, they can potentially arise from mass contrast differences between Ce, Zr and occasional Au ($z = 79$) atoms dispersed on the CeZrO$_4$ surface. Hence the fact that occasional brighter atomic columns can be seen in the unused 2wt% Au/CeZrO$_4$ catalyst cannot in of itself be taken as unambiguous direct visual evidence of the presence of highly dispersed Au atoms, because the clean CeZrO$_4$ support also shows similar features. However, neither does it rule out the presence of atomically dispersed Au atoms on the support grains in the 2wt% Au/CeZrO$_4$ catalyst.

Figure 3.10. STEM-HAADF image of a representative support particle from (a) a CeZrO$_4$ sample in which no gold has been added and (b) the unused 2wt% Au/CeZrO$_4$ catalyst. In each case the CeZrO$_4$ grain is viewed along the [001] zone axis.
The images presented in Figure 3.11 and 3.12 show that the Au/CeZrO$_4$ material experienced several microstructural changes after being used for 48 h as a catalyst in the WGS reaction. After use, the Au particles preferred to sit on flat surface facets of the support instead of in the crevices formed at the intersection of neighboring support grains (Figures 3.11 (a) and (b)). Additionally, the Au particles appeared to be considerably rounder, and poorly faceted with less interfacial contact compared to their unused counterparts (Figure 3.11 (c) and (d)). This latter observation, however, is consistent with Au de-wetting on the support. The particle size distribution acquired from HAADF-STEM images (Figure 3.13) indicate that mean size of Au particles exposed to WGS reaction conditions for 48 h increased to about 7.5 nm, a sintering effect which was incorrectly discounted by the study of Gouget et al.$^{21}$

![Figure 3.11. Additional HAADF and BF- STEM images of (a, b) the fresh 2wt% Au/CeZrO$_4$ catalyst and (c, d) the catalyst after 48 h of use. In general, the Au particles appear to be more faceted and form intimate contact planes with the support grains in the fresh state, whereas](image-url)
they are more rounded and have less interfacial contact area after use, suggesting a potential de-wetting behavior.

**Figure 3.12.** Electron microscopy characterization of the 48h used Au/CeZrO4 catalyst. (a and b) Lower magnification HAADF- and BF-STEM images illustrating the more rounded nature of the Au nanoparticles; (c and d) Representative higher magnification HAADF- and BF-STEM images of Au nanoparticles showing their tendency to de-wet from the support and exhibit less distinct surface faceting.
Figure 3.13. Gold particle size distribution histograms generated from HAADF-STEM images taken of the (a) unused and (b) 48 h used 2wt% Au/CeZrO$_4$ catalyst samples.
Although the \textit{ex-situ} characterization techniques (EXAFS, XPS and AC-AEM) described above have identified a number of physical changes occurring in the Au/CeZrO\textsubscript{4} catalysts during use it was not possible to evaluate the relative importance of each of these processes (\textit{i.e.}, sintering, morphology change, de-wetting) to the measured loss in activity. Therefore, a systematic ‘stop-start STEM’ study was devised to follow the microstructural development of the catalyst at the various stages (①) through ⑥ in Figure 3.3 of the WGS reaction, and hence determine which process is primarily responsible for the deactivation of Au/CeZrO\textsubscript{4} catalyst. The experimental details for this ‘stop-start’ STEM study have been presented in Section 2.1.

As shown in Figure 3.14 and 3.15, the exact same area of a 2wt\% Au/CeZrO\textsubscript{4} catalyst has been investigated at four stages of its lifetime: namely, a) fresh (①); b) after the heat ramp in N\textsubscript{2} (②); c) after 5 min on-stream (③) and d) after 12 h on-stream (⑤). Stop-start HAADF-STEM images showed that small Au particles (~1 nm in size) formed after heating to reaction temperature. Such particles were not present in the fresh sample. After 5 min on-stream, these smaller NPs agglomerated to form a larger particle having a size of approximately 5 nm (indicated by white arrows in Figure 3.14 (c)). This 5 nm particle was relatively stable in that it didn’t change significantly after 12 h on-stream. In some cases, 5 nm particles, when in close proximity to other smaller particles, conspicuously tend to sinter and form the most stable 10 nm particles (Figure 3.14, inset (a – d)). This was accepted as a reasonable explanation for the loss of a large number of the smaller Au species suggested by XPS analysis. It also should be noted that the larger (~5 nm) Au particles sinter and grow at a lower rate compared to that of the smaller (~1 nm) particles. The sharp decrease in the catalytic activity is concurrent with the agglomeration of atomically-dispersed Au species.
could indicate that ultra-small Au species are responsible for the high activity in WGS reaction as has been already proposed by Flytzani-Stephanopoulos.\textsuperscript{12} However, from our study, it is probable that sub-nm Au clusters are also active and the rapid loss of activity noted could be partly due to clusters present at the start of the reaction that sinter into larger, less active nanoparticles (Figure 3.16), therefore the extent to which the atomically-dispersed Au fraction is catalyzing the LT-WGS reaction is unclear.

**Figure 3.14.** Stop-start STEM HAADF images of the same region in a 2 wt% Au/CeZrO\textsubscript{4} catalyst at different stages of the LTS reaction: a) ① fresh catalyst; b) ② after the heat ramp under N\textsubscript{2}; c) ③ after 5 mins on-stream and d) ⑤ after 12 h on-stream (Courtesy of Dr. Xi Liu).
Figure 3.15. An additional representative set of stop-start STEM-HAADF images of the 2wt% Au/CeZrO$_4$ catalyst at different stages of the LTS reaction, as described in Figure 3. After the heat ramp in N$_2$ (2), a small Au particle <2 nm (arrowed) can be seen to have formed within the area highlighted by white dashed circle; this particle stays largely unchanged throughout the remainder of the process (Courtesy of Dr. Xi Liu).
Figure 3.16. An additional systematic set of stop-start STEM-HAADF images of the same area in a 2 wt% Au/CeZrO₄ catalyst at different stages of the LTS reaction. In this case, the highlighted Au particle (white dashed circle) that originally existed in the fresh catalyst shows significant growth from stage ② to stage ③ and ⑤. (Courtesy of Dr. Xi Liu).
3.3. Investigation of AuPd/CeZrO$_4$ catalysts for low-temperature water-gas shift reaction

In the first part of this study, it has been shown that the deactivation mechanism of the benchmark gold catalyst (2wt% Au/CeZrO$_4$) is related to a loss of active sites through the agglomeration of ultra-small Au species, particle sintering and de-wetting of particles on the support. Here we describe our exploration of one possible strategy that might potentially improve the stability the supported Au on CeZrO$_4$ catalyst system. The idea was the modification of supported metal through alloying, so taking advantage of so-called synergistic effects which can serve to improve catalyst’s overall catalytic performance.$^{28}$ One of the most promising candidate metals to introduce into the gold catalyst is palladium. This is because of the superb performance of this bimetallic system in wide range of oxidation reactions and the facile formation of the Au-Pd alloy.$^{29,30}$ Since Pd has a much higher melting point, adding it to Au is expected to increase the melting point of the nanoparticle relative to pure Au.$^{31,32}$ Our preliminary investigations on this aspect focused on comparing the activity and stability of a bimetallic AuPd catalyst having a 1:1 Au : Pd molar ratio, with some benchmark monometallic Au and Pd catalysts. All three catalysts were prepared using the deposition-precipitation method and tested for the LT- WGS reaction under standard conditions.

3.3.1. Catalytic testing results

As shown in Figure 3.17, the bimetallic AuPd/CeZrO$_4$ catalyst would not be an effective replacement for the benchmark monometallic Au catalyst in the LT-WGS reaction as it shows a significantly poorer catalytic performance. In fact, the bimetallic AuPd system is significantly less active after 1 h on-line as compared to both the Au- and Pd- monometallic
systems supported on CeZrO$_4$ (Figure 3.18). It was observed that as more Pd is added to Au, the poorer the activity becomes (as evident from Fig 3.18). The detrimental effect on LT-WGS catalytic activity of adding Pd to Au is an example of an anti-synergistic effect. Indeed, supported AuPd catalysts have been reported previously to show anti-synergy for the low temperature CO oxidation reaction.$^{33,34}$ However, this is not always the case, as the supported AuPd nanoparticles tend to exhibit excellent synergy for some reactions such as the selective oxidation of benzyl alcohol and the direct production of hydrogen peroxide.$^{35,37}$ However, differences in the nature of supports used, preparation methods, and even the reaction conditions employed makes the direct comparison of other supported AuPd catalysts with our AuPd/CeZrO$_4$ system difficult. By using a combination of in-situ CO-DRIFTs, XPS and AC-STEM, we were able to rationalize the underlying cause for the anti-synergetic catalytic activity trend displayed by this bimetallic AuPd system towards the LT-WGS reaction.

Figure 3.17. The catalytic activity of Au, AuPd and Pd supported on CeZrO$_4$ after 1 h online (bars, left axis) and the rate of deactivation (black diamonds, right axis). Reaction conditions: 150 °C, 0.15 g catalyst, 100 ml min$^{-1}$ Gas feed: 2% CO, 2% CO$_2$, 7.5% H$_2$O, 8.1% H$_2$ and N$_2$.$^{23}$ (Courtesy of Dr. James Carter).
3.3.2. Catalyst characterization

In this study, we prepared a systematic series of AuPd/CeZrO$_4$ catalysts spanning a range of AuPd molar ratios using the deposition precipitation (DP) method. The molar ratio of Au and Pd has been already reported as a critical parameter for tuning synergistic effect of bimetallic AuPd systems.$^{33,38,39}$ A representative sub-set of the prepared catalysts were characterized by AC-STEM to monitor any changes that may occur to the particle structure or size distribution as function of changing metal composition. The specific catalysts analyzed in detail were: i) Au/CeZrO$_4$; ii) Pd/CeZrO$_4$; iii) Au$_{55}$Pd$_{45}$/CeZrO$_4$ and iv) Au$_{95}$Pd$_5$/CeZrO$_4$.

Some microscopic data for the monometallic Au/CeZrO$_4$ catalyst was previously presented in Section 3.2.2. The Au$_{95}$Pd$_5$/CeZrO$_4$ was studied to investigate the effect of introducing
of a small amount of Pd into the Au catalyst and it was found that the mean particle size significantly increased from 4.45 to 6.15 nm (see Figure 3.19). The morphologies of supported AuPd particles were a mixture of cub-octahedral and icosahedral structures in common with those observed in the monometallic Au catalyst.

**Figure 3.19.** (a, b) Representative HAADF-STEM images of the Au95Pd5/CeZrO4 material and (c) the corresponding AuPd particle size distribution derived from analysis of HAADF-STEM images.
As can be seen in Figure 3.20, by further increasing the Pd fraction up to 45% in the alloy, the mean particle size only slightly increased from 6.15 to 6.42 nm and the supported AuPd particles once again exhibited a mixture of cub-octahedral and icosahedral morphologies. The supported metal particles in both samples (Au_{95}Pd_{5}/CeZrO_{4} and Au_{55}Pd_{45}/CeZrO_{4}) were confirmed by XEDS analysis to be intimate AuPd f.c.c. random alloys.

**Figure 3.20.** (a, b) Representative HAADF-STEM images of the Au_{55}Pd_{45}/CeZrO_{4} material and (c) the corresponding AuPd particle size distribution derived from analysis of HAADF-STEM images.
In the case of the monometallic Pd/CeZrO$_4$ material determining morphological and particle size distribution data was technically quite challenging. As evidenced by the HAADF-STEM images presented in Figure 3.21 the supported Pd particles have very low mass contrast against the CeZrO$_4$ support and so were much harder to visualize. The mean size of the Pd containing particles after careful measurement was found to be 1.28 nm (Figure 3.21c). We were unable to verify from HAADF imaging whether the supported metal particles were Pd or PdO$_x$ although the latter seems more likely.

Figure 3.21. (a, b) Representative HAADF-STEM images of the Pd/CeZrO$_4$ material and (c) the corresponding Pd particle size distribution derived from analysis of HAADF-STEM images.
When studying the deactivation mechanism of the benchmark monometallic Au catalyst, an XPS analysis was conducted on the fresh and used Au catalysts to measure the relative fractions of various Au species (Au$^0$, Au$^{3+}$ and Au$^{0*}$) present. A correlation was shown between the concentration of Au$^{0*}$ present, assigned to small Au particles, and good catalytic activity. We therefore decided to repeat the same XPS analysis on the bimetallic AuPd catalysts to study the effect of the addition of Pd to Au catalysts on the relative population of Au species present and correlate it to the catalytic performance. As expected, the Au$^{0*}$ species were present in each of the Au-containing catalysts, but when the Pd was added, the concentration of Au$^{0*}$ progressively decreased (Table 3.2), as did the LT-WGS activity. Again, the loss of Au$^{0*}$ was considered to be due to an increase in particle size with Pd addition to the Au.

Table 3.2: Summary of the XPS analysis of the range of Au$_x$Pd$_y$/CeZrO$_4$ samples showing surface concentration and the binding energies of the different Au and Pd species present.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fraction of different Au species in Au-Pd/CeZrO$_4$ catalysts (%)</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au$^0$</td>
<td>Au$^{0*}$</td>
</tr>
<tr>
<td>Au$_{100}$</td>
<td>65</td>
<td>27</td>
</tr>
<tr>
<td>Au$_{95}$Pd$_5$</td>
<td>76</td>
<td>16</td>
</tr>
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<tr>
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<td>Au$<em>{50}$Pd$</em>{50}$</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>Au$<em>{25}$Pd$</em>{75}$</td>
<td>75</td>
<td>13</td>
</tr>
<tr>
<td>Pd</td>
<td>-</td>
<td>-</td>
</tr>
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</table>
We also carried out an *in-situ* CO-DRIFTS study to determine the mode of CO molecular adsorption in the various supported monometallic and bimetallic catalysts. The CO-DRIFTS spectrum of each catalyst was measured in the 1800-2200 cm\(^{-1}\) range which contains the stretching modes of CO adsorbed on Au and Pd. This technique has been used extensively to probe the surface of supported precious metal catalysts.\(^{40-43}\) The CO-DRIFT data for a selection of catalysts with differing AuPd compositions are presented in Figure 3.22.

The higher wavenumber region of the spectra (2200-2000 cm\(^{-1}\)) has previously been assigned to linearly adsorbed carbonyl species, while features at lower wavenumbers (2000-1800 cm\(^{-1}\)) have been assigned to bridged or three-fold adsorption of CO on Pd or Au-Pd.\(^{40,44}\) For the monometallic Au catalyst, only the CO linear adsorption mode was observed. In such situations, CO molecules are typically adsorbed at the edge or corner sites of the Au nanoparticle.\(^{20}\) For the Pd and AuPd alloy catalysts on the other hand, both linear and bridge-type (non-linear) CO adsorption modes were observed. The non-linear adsorption mode can be attributed to CO molecule adsorption on extended metal surfaces.\(^{45,46}\) Such sites are thought to be less important in the WGS reaction mechanism and are considered to be just spectator sites. Importantly, we found that the catalyst activity increases with an increasing contribution from the linear adsorption mode (Figure 3.23).
Figure 3.22. CO-DRIFTS spectra for selected Au–Pd/CeZrO₄ catalysts: namely (a) Au; (b) Au₉₃Pd₇; (c) Au₆₇Pd₃₃; (d) Au₄₄Pd₅₆; (e) Au₁₂Pd₈₈; (f) Pd (Courtesy of Dr. James Carter).

Figure 3.23. Relationship between the LT-WGS catalytic activity of AuₓPdᵧ/CeZrO₄ catalysts and the linear/non-linear adsorption ratio determined from CO–DRIFTS analysis. Au is not shown, as the CO-adsorption spectrum is dominated by linear CO-Au species (Courtesy of Dr. James Carter).
3.4. Conclusion

The deactivation mechanism of the 2wt% Au/CeZrO$_4$ catalyst in the LT-WGS reaction was probed. Transmission electron microscopy and XPS investigations indicate that in addition to the de-wetting of supported metal NPs, both shape change and sintering of ultra-small Au species contribute to the deactivation Au/CeZrO$_4$ system. The ‘stop-start’ STEM analysis shows that the deactivation during the LT-WGS reaction proceeds primarily through the pre-reaction thermal agglomeration of sub-nm clusters and atomically dispersed Au species. The knowledge gained from this study, however, supports the notion that the strong metal-support interaction is very important to synthesize more active and durable catalyst for the LT-WGS reaction. It also confirms that atomically dispersed Au species are responsible for the high catalytic activity in WGS reaction and this has been already proposed by Flytzani-Stephanopoulos.\textsuperscript{12}

A statistical analysis of the Au particle size distribution (Figure 3.12) shows that significant grain growth has occurred under WGS reaction conditions, with the mean particle size increasing to \~7.5 nm. From our electron microscopy observations, it is clear that use of the Au/CeZrO$_4$ catalyst under WGS reaction conditions causes a combination of effects including (i) Au particles partially de-wetting from the support resulting in less interfacial contact area; (ii) Au particle sintering and growth causing a concomitant loss of surface area; and (iii) a re-structuring of the surface facet structure of the Au grains. All of these nanostructural changes to the material can potentially be detrimental to the catalytic activity. In fact, it is not surprising that \~4.5 nm Au particles are prone to sintering at 150 °C (423 K) under WGS conditions.
Figure 3.24. Theoretical variation of Au melting point as a function of nanoparticle size.

Theoretical estimations of melting point depression (Figure 3.24) show that particles of this dimension would be at ~ 40-50% of their melting temperature and in addition to this, the mildly exothermic nature of the WGS reaction means that localized temperatures in the catalyst bed could be even higher.

In the second part of the study, the viability of using a bimetallic AuPd/CeZrO$_4$ catalyst for the LT-WGS reaction was investigated. It was shown that the introduction of Pd to Au/CeZrO$_4$ catalysts was not beneficial and resulted in a significant decrease in catalytic activity. Moreover, the stability of the bimetallic AuPd system was worse than that of either of the Au- or Pd- monometallic catalysts. The *anti-synergy* between Au and Pd was studied using several *ex-situ* techniques, which all demonstrated an increase in particle size with increasing Pd addition to the Au. The XPS results also indicated the loss of Au$^{0+}$ species which results from the introduction of Pd into the Au catalyst is the underlying reason why
the bimetallic AuPd system exhibited an inferior performance in the LT-WGS reaction. *In-situ* CO-DRIFTs analysis supports the idea that the interfacial sites at the metal-support interface are the most active sites. Maximizing and preserving such active sites are therefore crucial in the design of a more active and robust catalyst for the LT-WGS reaction.

Improving the stability of gold-based catalysts in water gas shift reaction is an ongoing topic of investigation. Recently, Freund *et al.*\(^{47}\) reported the modification of the support as a potential strategy to improve the interaction between Au NPs and the oxide support, which is in fact very important in WGS reaction. By using DFT calculations, they demonstrated that the interaction between Au particles and a doped support (Mo-doped CaO) was much greater than that with undoped support (CaO). This method of stabilization seems to a good potential approach for improved the Au/CeZrO\(_4\) catalyst system because it provides us a unique opportunity to stabilize the Au NPs without modifying the elemental composition of the surface. Rare earth metals such La, Na and Ga can be used as dopants to CeZrO\(_4\). It has been reported that when such elements added to ceria, they provided improved thermal stability and increased activity.\(^{48,49}\)
References


Chapter 4

Optimization of PdZn/ZnO Catalysts for the Methanol Steam Reforming (MSR) Reaction
4.1. Introduction

The onboard production of hydrogen through the reforming of alcohols and hydrocarbons, in an integrated energy system comprising fuel cells has been proposed as an efficient, practical solution to circumvent the drawbacks of hydrogen storage and transport.¹

![Diagram](image)

**Figure 4.1.** Standard set-up for external methanol reforming (after reference ²)

When compared to other feedstocks, methanol (CH₃OH) is inexpensive, liquid under ambient conditions, sulfur-free, possesses a high hydrogen-to-carbon ratio and has a low reforming temperature (200-300 °C) ²–⁴. Such advantages, indeed, make it one of the best candidates as a hydrogen carrier for fuel cells applications.

In a typical methanol reformer (Figure 4.1), methanol reacts with water (steam) to produce carbon dioxide and pure hydrogen (Eqn.4.1).

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2 \quad \Delta H = 49.7 \text{ kJmol}^{-1} \quad \text{Eqn. (4.1)}
\]

The reaction requires the presence of an efficient catalyst which is stable at operating conditions and can suppress the formation of carbon monoxide, a highly detrimental compound in fuel cell technology as it poisons the Pt electrodes. A wide variety of catalytic
systems for the methanol steam reforming (MSR) reaction have been reported in the literature.\textsuperscript{5} Amongst them, intermetallic PdZn catalysts, due to their exceptionally high performance, have been the most frequently studied system.\textsuperscript{5,6}

Iwasa \textit{et al}.\textsuperscript{7,8} were amongst first to study the catalytic performance of Pd/ZnO catalysts for the MSR reaction. They reported that Pd/ZnO catalysts are more stable and selective toward CO\textsubscript{2} in the MSR reaction than conventional copper-based catalysts. Using a combination of XRD and XPS analysis, Iwasa \textit{et al} confirmed that the formation of a PdZn alloy is the key condition for the catalyst to be selective for MSR.\textsuperscript{9} The high selectivity of the Pd/ZnO system has also been associated with the presence of ZnO patches in the near-surface region of the intermetallic alloy.\textsuperscript{10} Armbrüster and co-workers carried out a detailed high-resolution electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and \textit{in-situ} heating experiments to study this phenomenon.\textsuperscript{11} They noticed a significant enhancement in the CO\textsubscript{2} selectivity due to the presence of ZnO patches on the surface of the intermetallic PdZn particles. They suggested that the formation of such surface patches resulted from the partial oxidation of the PdZn particles themselves rather than by transport of material from the ZnO support.

The effect of factors such as (i) the catalyst preparation route, (ii) catalyst pre-treatment conditions, and (iii) the source of ZnO support material on the formation of PdZn intermetallic compounds and their resultant catalytic performance of the Pd/ZnO material have been reported in the literature.\textsuperscript{12-14} It was found that the catalytic function of the Pd/ZnO material increased markedly after a reduction pre-treatment which leads to the formation of the PdZn intermetallic compound. Guangwei \textit{et al}. also showed that Pd supported on a high surface area ZnO material exhibited an activity that was 53\% higher...
than its counterpart supported on commercial ZnO. Chin et al. found that the presence of nitrate anions (NO$_3^-$) during the preparation of Pd/ZnO catalysts may also influence the formation of the PdZn alloy and its final catalytic properties. Taking advantage of the presence anionic species to enhance the degree of mixing between the elemental components of the catalyst during the preparation stage has previously reported by Sankar et al, who prepared a highly selective and stable AuPd/TiO$_2$ catalyst for benzyl alcohol oxidation and H$_2$O$_2$ synthesis using metal chloride precursors along with an excess of chloride anions. Sankar et al inferred that the presence of the additional anions not only provides a better degree of mixing between the metal precursors, but also prevents agglomeration of the alloy particles after formation. However, using such an excess anion method to prepare a supported PdZn catalyst for the MSR reaction has not yet been reported and is worthy of further investigation.

4.1.1. Objectives of this work

In this aspect of my project, a detailed structural study of supported PdZn catalysts prepared by a new modified impregnation-based method ($M_{Imp}$) has been performed. Compared to the conventional impregnation ($C_{Imp}$) technique, this new method involves adding excess chlorine anions (Cl$^-$) along with the metal chloride precursors. These Cl$^-$ ions should facilitate the formation of highly ordered PdZn alloy particles by providing a better mixing between the metal precursor salts, and consequently hopefully producing superior selective catalysts for the MSR reaction. By using a combination of BET, XRD, XPS and AC-STEM, we have compared the structure, composition and catalytic performance of PdZn/ZnO catalysts synthesized by the $M_{Imp}$ and $C_{Imp}$ methods. Also included in this study is an
investigation into whether the choice of the ZnO support material has any significant influence on the catalytic function of the M_{Imp} derived PdZn/ZnO catalysts.

4.2. Experimental

4.2.1. Catalyst preparation

The modified co-impregnation method for making the 3%PdZn/ZnO catalysts used in this study is illustrated in Figure 4.2. A ZnCl₂ (≥98%, Sigma Aldrich) and a PdCl₂ (≥99.9%, Sigma Aldrich) were used as metal precursors without further purification. Additional HCl was introduced in the form of a 0.58 M solution, prepared by the dropwise addition of 5 mL of concentrated HCl (37.2%, 12.1 M) into 95 mL of an PdCl₂ aqueous solution (6 mg Pd/mL) under continuous stirring. The solution was left stirring at 500 rpm for 16 h at ambient temperature. For catalyst synthesis, the requisite amounts of aqueous Zn (6 mg/mL, 3.3ml) and Pd precursor solutions (6 mg/mL, 6.65ml) were charged into a 50 mL round-bottom flask containing deionized water (5 mL); samples with HCl added, were designated as a modified impregnation (M_{Imp}) catalysts, whereas those prepared without HCl are termed as conventional impregnation (C_{Imp}) catalysts. The contents of the flask was stirred vigorously (1000 rpm) and the temperature of the oil bath was raised from room temperature to 60 °C over a period of 10 min. When a temperature of 60 °C was reached, the ZnO support (either 1.94g, Aldrich (referred to as ZnO nanopowder) or Alfa Aesar, 99.9% metal basis) was added slowly over an 8-10 min period with constant stirring. The pH of the solution was analyzed continuously using a Toledo pH meter. When addition of the support material was complete, the slurry was stirred at 60 °C for an additional 15 min and then the temperature of the oil bath was raised to 95 °C, and the slurry was stirred overnight until all the water had evaporated leaving a dry solid. This solid powder was subsequently transferred into a
mortar and pestle and was ground thoroughly. For the preparation of acid treated ZnO support materials, 6.65 ml of 0.58M aqueous HCl was added to a round bottom flask containing 8.3 ml water under vigorous stirring conditions. Next, 1.96g of ZnO was added to the mixture and stirred at room temperature and the subsequent synthesis steps remained the same for the standard preparation procedure described above. Finally, the catalyst was pre-treated in the methanol steam reforming (MSR) reactor under a steady flow of 5% H\textsubscript{2} in Ar for 4 h at 500°C (employing a heating rate of 10°C/min). Catalysts were denoted PdZn/ZnO\textsubscript{nano} for material prepared using ZnO nanopowder purchased from Aldrich and PdZn/ZnO\textsubscript{AA} when the support was purchased from Alfa Aesar.

**Figure 4.2.** Schematic diagram summarizing the synthesis steps in the modified co-impregnation route for preparing the 3wt% PdZn/ZnO catalyst.
4.2.2. Catalyst testing

Methanol steam reforming tests were carried out using powder catalyst samples (150 mg) in a plug flow reactor (inner diameter 7.9 mm, silica coated stainless steel) which was mounted inside a hot box (120 °C) to prevent condensation of liquids (MicroActivity, PID Eng. & Tech). The catalysts were not exposed to air after calcination and reduction treatments. The MSR feed consisted of 0.0325 mL/min liquid (50 mol% MeOH 0.0225mL/min (Sigma-Aldrich, ≥ 99.9%), 50 mol.% deionized water (0.01mL/min), 38.7 ml/min N\textsubscript{2} (99.999%, Praxair) and 4.6 mL/min He (99.999%, Praxair). N\textsubscript{2} was used as a carrier gas, while He was used as an inert tracer gas to calibrate the volumes of the gaseous products, since residual MeOH and H\textsubscript{2}O are not determined in the effluent. The gas composition in the product stream was determined every 4 min by gas chromatography (Varian Micro GC CP4900), which allowed quantitative determination of CO with a detection limit down to 20 ppm. Furthermore, all gaseous reactants and products were monitored by a mass spectrometer (Pfeiffer, Omnistar 300). It was not possible to directly determine the amount of unconverted MeOH or H\textsubscript{2}O by either GC and MS analysis, because the product gas was dried using a cooling trap and a subsequent Nafion® membrane before any gas phase analysis. For the MSR measurements, a maximum reaction temperature of 300 °C was employed. An isothermal test of 10 h duration was carried out directly after a series of temperature dependent measurements including temperature changes from 150 °C to 300 °C and 175 °C to 300 °C (using a heating and cooling rate of 10 °C/min).
4.3. Results and Discussion

4.3.1. Comparison of PdZn/ZnO catalysts synthesized using the modified impregnation (M$_{Imp}$) and conventional impregnation (C$_{Imp}$) methods

Figure 4.3 compares the MSR catalytic performance of the two catalysts, in terms of their methanol conversion and CO$_2$ selectivity. The M$_{Imp}$ and C$_{Imp}$ derived 3%Pd-Zn/ZnO$_{nano}$ catalysts displayed comparable methanol conversion levels (i.e., similar activity) and interestingly, the activity of both catalysts increased gradually over the 10 h duration of the test. These findings suggest that under the MSR reaction conditions both catalysts undergo some beneficial physical changes which enhance the activity of the catalysts.

![Figure 4.3](image)

**Figure 4.3.** Methanol conversion and CO$_2$ selectivity of freshly reduced 3%Pd-Zn/ZnO$_{nano}$ MSR catalysts measured under isothermal conditions at 300 °C. Key: M$_{Imp}$ materials prepared with 0.58M HCl (□); C$_{Imp}$ material prepared without additional HCl (▲). (Courtesy of Dr. Ewa Nowicka).

As shown in Figure 4.3, the selectivity of the M$_{Imp}$ and C$_{Imp}$ derived 3%PdZn/ZnO$_{nano}$ catalysts towards CO$_2$ also increased gradually with time-on-line. Importantly, the catalyst
synthesized by the modified impregnation method displayed a higher CO<sub>2</sub> selectivity than its counterpart prepared by the conventional impregnation route.

4.3.2. **XRD analysis**

The structure of both M<sub>Imp</sub> and C<sub>Imp</sub> derived catalysts during the reduction treatment were studied by *in-situ* XRD measurements (Figures 4.4 and 4.6). The fresh C<sub>Imp</sub> PdZn/ZnO sample prepared by conventional impregnation showed peaks consistent with the hexagonal ZnO phase. In contrast the samples prepared by modified impregnation contained a significant amount of Simonkolleite (ICSD No. 77-2311) in addition to the expected ZnO phase. Simonkolleite is a hydrated zinc hydroxide chloride compound (Zn₅Cl₂H₁₀O₉) which can form when HCl is added to ZnO during the M<sub>Imp</sub> synthesis procedure. Interestingly, no Pd-containing phase was observed in the XRD pattern for the fresh M<sub>Imp</sub> PdZn/ZnO catalyst, which might imply the formation of a Pd-containing Simonkolleite phase, which could act as a single-source precursor phase for subsequent PdZn intermetallic particles.

Heat treatment of these materials under reducing conditions (*i.e.*, heating from 25°C to 500°C in 10% H₂/N₂) led to significant changes in their XRD patterns (Figure 4.6). The reflections at 41.43°, 43.67° and 44.69° that are assigned to the Simonkolleite phase in the M<sub>Imp</sub> 3%PdZn/ZnO catalyst gradually decreased in intensity and eventually disappeared altogether. The final M<sub>Imp</sub> 3%PdZn/ZnO catalyst was found to consist of the ZnO support phase along with some tetragonal PdZn (ICSD 180143) alloy particles as evidenced by very weak 111 and 200 -type reflections at 2Θ = 41.26° and 44.04° respectively. The corresponding XRD pattern for the *in-situ* reduced counterpart C<sub>Imp</sub> 3%PdZn/ZnO catalyst showed the expected ZnO reflections, but also developed weak peaks at 2Θ = 41.42° and 44.31° corresponding the (111) and (200) planes of the tetragonal PdZn alloy phase. It is
therefore postulated that under reducing conditions, Simonkolleite undergoes decomposition, which can then easily lead to the formation of a PdZn alloy. The formation of PdZn alloys when starting from Pd/ZnO requires first the reduction of Pd and then formation of PdHx. It has been reported that the strong interaction between metallic palladium or palladium hydride and the support leads to hydrogen spill-over during reduction.\textsuperscript{17,18} This enables the reduction of the ZnO in the vicinity of the Pd particles and the formation of the intermetallic PdZn compound at lower reduction temperatures.

The XRD analysis revealed that the M\textsubscript{Imp} and C\textsubscript{Imp} derived catalysts had similar crystallographic structures. In the XRD spectra (Figure 4.5), no differences in phase distribution were observed between the two final catalysts, and the presence of the tetragonal PdZn alloy and ZnO was confirmed in both catalysts. From \textit{in-situ} XRD analysis, the PdZn alloy phase was found to form at a reduction temperature somewhere between 300 and 400 °C (Figure 4.6) which is in good agreement with expected literature values.\textsuperscript{19} It should also be noted that no reflections in either sample could be ascribed to the presence of monometallic Pd or Zn.
Figure 4.4. XRD patterns of $M_{\text{Imp}}$ derived 3%PdZn/ZnO$_{\text{nano}}$ (top) and $C_{\text{Imp}}$ derived 3%PdZn/ZnO$_{\text{nano}}$ (bottom) materials in the unreduced state. Legend: ● symbols indicate reflections from Zn$_5$C$_{12}$H$_{10}$O$_9$, while Δ symbols are peaks from ZnO. (Courtesy of Dr. Ewa Nowicka).

Figure 4.5. XRD patterns of $M_{\text{Imp}}$ derived 3%PdZn/ZnO$_{\text{nano}}$ (top) and $C_{\text{Imp}}$ derived 3%PdZn/ZnO$_{\text{nano}}$ (bottom) materials after reduction in 5% H$_2$/N$_2$ at 500 °C. Legend: ♦ symbols indicate reflections from tetragonal PdZn, while Δ symbols are peaks from ZnO. (Courtesy of Dr. Ewa Nowicka)
Figure 4.6. In-situ XRD patterns of the M_{Imp} derived 3wt\%PdZn/ZnO catalyst: in-situ analysis under reducing conditions (5\% H_{2}/N_{2}; 20 ml/min) at several temperatures ranging between 25 and 500 °C (Reflections at 41.43°, 43.67° and 44.69° are assigned to Zn_{5}Cl_{2}H_{10}O_{9}). (Courtesy of Dr. Ewa Nowicka).

4.3.3. XPS analysis

To further understand the role played by the excess Cl⁻ ions on the formation of the PdZn intermetallic compound and subsequently the catalytic properties, XPS experiments were conducted on these materials. XPS analysis (Table 4.1) showed that the apparent surface concentration of Pd for both the M_{Imp} and C_{Imp} 3wt\%PdZn/ZnO catalysts decreased following the reduction pre-treatment at 500 °C. This change is concomitant with a downward shift in the binding energy of the Pd(3d) peaks from 337.4 eV (characteristic of Pd-Cl) in the fresh samples, to ca. 336 and 335 eV in the reduced ones (Figure 4.7). The binding energy values of Pd (3d_{5/2}) for PdZn alloys have been reported to vary from 335.1
to 336.2 eV\textsuperscript{20,21}; however, it is also accepted that alloying Pd with Zn increases the binding
energy of the Pd (3d\textsubscript{5/2}) as a consequence of charge transfer and rehybridisation.\textsuperscript{22}

**Table 4.1.** XPS analysis of the M\textsubscript{Imp} and C\textsubscript{Imp} derived 3\%PdZn/ZnO catalysts in the fresh
and reduced states. (Courtesy of Dr. D. Morgan).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface concentration (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
</tr>
<tr>
<td>C\textsubscript{Imp} 3%PdZn/ZnO</td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>2.9</td>
</tr>
<tr>
<td>reduced</td>
<td>2.3</td>
</tr>
<tr>
<td>M\textsubscript{Imp} 3%PdZn/ZnO</td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td>5.4</td>
</tr>
<tr>
<td>reduced</td>
<td>3.8</td>
</tr>
</tbody>
</table>

In addition, we investigated the Zn(LMM) X-ray excited Auger emission spectra (XAES) for the fresh and reduced variants of the M\textsubscript{Imp} derived 3\%PdZn/ZnO sample. The difference spectrum between the fresh and reduced sample is also plotted to improve the visibility of the weak shoulder feature (Figure 4.8). Despite no observable broadening of the Zn(2p\textsubscript{3/2}) core-level, alloying of Pd and Zn is supported by the emergence of a new state in the Zn(LMM) XAES spectrum, characterized by a major peak at 992.1 eV, which corresponds to a modified Auger parameter of \textit{ca.} 2014 eV and is characteristic of metallic Zn or Zn-containing alloys.\textsuperscript{23,24}

It is also clear from the XPS data shown in Table 4.1 that the 4 h reduction treatment of the catalyst in 5\% H\textsubscript{2}/Ar at 500 °C did not result in the complete removal of chloride species from the M\textsubscript{Imp} and C\textsubscript{Imp} catalysts, since a detectable amount of Cl remained. The apparently
slighter higher concentration of Cl present after reduction could be due to strong anchoring of Cl to the substrate, resulting in a higher apparent dispersion of Cl after alloying and the associated particle size changes under the reductive atmosphere. This can be supported by analyzing the binding energy of ca. 199 eV, that is typical for metal-Cl bonds.24

Figure 4.7. The Pd(3d) XPS spectra obtained from the reduced MImp derived (above) and CImp derived (below) 3%PdZn/ZnO catalysts. (Courtesy of Dr. D Morgan).

Figure 4.8. Zn(LMM) X-ray excited Auger electron spectra for the fresh and reduced variants of the MImp derived 3%PdZn/ZnO catalyst. The difference spectrum between the fresh and reduced sample is also plotted. (Courtesy of Dr. D. Morgan).
4.3.4. **Electron microscopy analysis**

The physical structure and local chemical composition of the unused $M_{Imp}$ and $C_{Imp}$ 3%PdZn/ZnO catalysts were evaluated using STEM-HAADF imaging and X-ray energy dispersive spectroscopy (XEDS) in order to develop morphological correlations with their catalytic performance measurements.

HAADF-STEM images were taken from the unused $M_{Imp}$ and $C_{Imp}$ derived catalysts, as represented in Figure 4.9 (a) and (b), respectively. In both samples, the ZnO support grains, because they were of the same origin, were very similar and ranged anywhere in size from 0.05 - 0.2 µm. The dispersion of metal particles over the ZnO nano support grains was homogeneous in both cases, but the particle size distributions acquired from HAADF images indicate that mean supported metal particle size (~7.5nm) in the $M_{Imp}$ sample was slightly smaller than that in the $C_{Imp}$ sample (~8.8 nm). XEDS elemental mapping studies (Figures 4.10 and 4.11) confirmed that the metal particles on both catalysts were PdZn alloys. Furthermore, analysis of interplanar spacings and intersection angles in atomic resolution HAADF-STEM images such as those shown in Figure 4.10 (e) and 4.11 (e), confirmed that the supported alloy particles had a tetragonal structure consistent with the $\beta$-PdZn phase (ICSD 180143). These findings, in fact, are consistent with XRD analysis which also confirmed the presence of tetragonal PdZn in both the $M_{Imp}$ and $C_{Imp}$ derived catalysts.

In the $M_{Imp}$ derived catalyst the PdZn particles when viewed along certain crystallographic projections, such as [010] shown in Figure 4.10 (f), showed distinct periodic mass contrast in HAADF images that are consistent with $L1_0$ type ordering of Pd and Zn atoms on alternate atomic columns. To illustrate this atomic ordering more clearly, Figure 4.10 (f) shows a magnified [110] HAADF projection view of the atomic structure in Figure 4.10 (e) with the
theoretical atomic structure projection of L1₀ type PdZn superimposed on top of the experimental image. A distinct difference noted in the C_imp derived 3wt% PdZn/ZnO catalysts was that the vast majority of the PdZn alloy particles, while showing a tetragonal structure, did not show the high degree of ordering on the Pd and Zn sub-lattices that was found for the M_imp derived materials (Figure 4.10 (f)). These observations, indeed, demonstrated the beneficial role of Cl⁻ ions in promoting the formation of highly ordered Pd-Zn alloy particles which seems to be key for the catalyst to be selective for MSR.

The gradual improvement in catalytic performance with time-on-line for both catalysts might be related to a structural modification of the materials under reaction conditions. Therefore, we also examined the M_imp 3wt%PdZn/ZnΟnano catalyst after 10 h of use as an MSR catalyst. As shown in Figure 4.12, the catalyst structure was significantly modified during the activation and use process. The supported PdZn alloy particles were no longer atomically clean but became decorated with a 1-2 nm thick patchy over-layer whose average mass is less than that of the PdZn particle (Figures 4.12(a, b and c). The XEDS line-scan shown in Figure 4.12 (c) acquired from the particle in Figure 4.12 (b), shows that the surface is enriched in Zn and deficient in Pd, implying the formation of a ZnO-like overlayer. It is unclear if this overlayer originates from (i) preferential Zn oxidation in the PdZn particle surface or (ii) ZnO migrating from the support over the PdZn particle via a strong metal support interaction (SMSI) effect. The existence of nanoscopic ZnO islands on the PdZn particle surface is consistent with previous reports from Armbruster et al. who associated this particular morphology with fully active catalysts. The time needed to develop this partial overlayer also seems to correlate well with the induction period required for the PdZn/ZnO catalyst to reach its full activity. However, the formation of too many ZnO islands
on the surface of supported particles is likely be detrimental to the catalytic activity. For instance, if PdZn particles get completely covered with ZnO where molecules cannot be absorbed to the PdZn/ZnO periphery sites and then the catalytic activity will turn off.

Figure 4.9. Representative STEM-HAADF images and the corresponding particle size distributions (PSDs) of (a) the CImp 3%PdZn/ZnOnano catalyst, (b) the MImp 3%PdZn/ZnOnano catalyst, and (c) the MImp 3%PdZn/ZnOAA catalyst.
Figure 4.10. STEM-XEDS elemental maps and STEM-HAADF imaging of the M_{imp} 3\% PdZn/ZnO_{nano} catalyst. A lower magnification STEM-HAADF image of the catalyst is shown in (a) along with the corresponding XEDS elemental maps of (b) Zn, (c) Pd and (d) O. The intermetallic particles in profile indicated by arrows in (a-d) show the presence Zn and Pd but not an O signal. (e) A higher magnification STEM-HAADF image of a tetragonal \( \beta \)-PdZn particle, showing characteristic L1_0 ordering of Pd and Zn atoms. This can be better seen in the magnified view in (f), which is overlaid with the atomic structure of PdZn (ref ICSD 180143) viewed along the tetragonal [110] projection.
Figure 4.11. STEM-XEDS elemental mapping and STEM-HAADF imaging of the C_{imp} 3\%PdZn/ZnO\textsubscript{nano} catalyst. A lower magnification STEM-HAADF image of the catalyst is shown in (a) along with the corresponding XEDS elemental maps of (b) Zn, (c) Pd and (d) O. The intermetallic particles in profile indicated by arrows in (a-c) show Zn and Pd signals but not any O. (e) A higher magnification STEM-HAADF image of a rare PdZn particle, showing the (L1\textsubscript{0}) tetragonal \(\beta\)-PdZn phase. (f) A higher magnification HAADF image of a [111] projection of a PdZn crystal in which no atomic ordering can be discerned.
Figure 4.12. (a, b) Representative HAADF images of PdZn intermetallic particles in the M_{Imp} derived 3\%PdZn/ZnO_{nano} catalyst after use, showing that they are no longer atomically clean, but are now decorated with a 1-2 nm thick patchy overlayer whose average mass is less than that of the PdZn particle. The XEDS line-scan in (d) was acquired along the blue line shown on the particle in (c) and shows that the surface is enriched in Zn and deficient in Pd, implying the formation of a ZnO-like overlayer. The schematic diagram at the top shows how the additional PdZn/ZnO interface periphery created by the patchy ZnO islands might improve the overall catalytic activity.
4.4. Comparison of $M_{\text{Imp}}$ derived PdZn/ZnO materials prepared on different ZnO supports.

So far, we have demonstrated that the modified impregnation technique can be utilized to improve the mixing between the precursors and also enhance the CO$_2$ selectivity, yet it did not affect the overall activity as compared to the $C_{\text{Imp}}$ material. However, there have been a few reports regarding the important role of the surface area of the support in promoting the activity of Pd/ZnO MSR catalysts$^5$. For example, Guangwei et al. showed that Pd supported on high surface area ZnO exhibited activity 53% higher than its counterpart supported on commercial ZnO.$^{15}$ This triggered our interest to investigate the influence of the choice of ZnO support on the activity levels displayed by the $M_{\text{Imp}}$ catalysts. Hence, the modified impregnation procedure was utilized to prepare another 3%PdZn/ZnO catalyst on a commercial, lower surface area ZnO (denoted hereafter as $M_{\text{Imp}}$ 3%PdZn/ZnO$_{\text{AA}}$). This catalyst was assessed for the MSR reaction under the same isothermal conditions (300 °C, 10 h) as previously described.

As shown in Figure 4.13, the nature of the ZnO support had limited influence on the selectivity of the catalyst towards CO$_2$. The MeOH conversion, on the other hand, was greatly affected by the choice of support. The $M_{\text{Imp}}$ 3%PdZn/ZnO$_{\text{AA}}$ catalyst exhibited a methanol conversion level significantly lower than that showed by the 3%PdZn/ZnO$_{\text{nano}}$ catalyst. Two things can be inferred based on these observations. The first is that similarly active PdZn alloy particles should be present in both catalysts. Secondly, the nature of the support must be in one way or another be affecting the number of active sites present for methanol decomposition.
The observed activity difference between these two catalysts could be attributed to the support surface area being different. BET surface area analysis showed that the fresh ZnO\textsubscript{nano} material had a significantly higher surface area (10.8 m\textsuperscript{2}g\textsuperscript{-1}) compared to the fresh ZnO\textsubscript{AA} material (3.2 m\textsuperscript{2}g\textsuperscript{-1}). These results were consistent with the catalytic data presented above. However, to gain more insight into the effect of the nature of the support on the PdZn catalyst performance, we studied the structure of the M\textsubscript{Imp} 3\%PdZn/ZnO\textsubscript{AA} catalyst by XRD and STEM and compared it with the structure of the M\textsubscript{Imp} PdZn/ZnO\textsubscript{nano} catalyst investigated previously.

4.4.1. XRD, XPS and TPR analyses

XRD was used to determine the crystal structure of the M\textsubscript{Imp} 3\%PdZn catalysts prepared on ZnO\textsubscript{AA} and ZnO\textsubscript{nano} supports. From the resultant XRD spectra (Figure 4.14), we noticed no
significant difference between the two materials. Both catalysts displayed reflections which could be fully assigned to the ZnO and tetragonal $\beta$-PdZn alloy phases.

A significant difference was observed between the TPR profiles of the M$_{\text{Imp}}$ catalysts prepared with ZnO$_{\text{nano}}$ or ZnO$_{\text{AA}}$ supports (Figure 4.15). Reduction peaks were found at 136°C, 185°C, 230°C & 258°C for PdZn/ZnO$_{\text{nano}}$, and at 121°C, 210°C, 263°C & 293°C for PdZn/ZnO$_{\text{AA}}$. The systematic slight shift to lower reduction temperatures for the PdZn/ZnO$_{\text{nano}}$ material relative to those in the PdZn/ZnO$_{\text{AA}}$ catalyst, suggests a stronger interaction between Zn and Pd in the PdZn/ZnO$_{\text{nano}}$ material. This implies that any Zn which is in close proximity to Pd, is more readily consumed in forming PdZn particles on the ZnO$_{\text{nano}}$ support than on the ZnO$_{\text{AA}}$ support.

We also carried out XPS analysis on the M$_{\text{Imp}}$ 3%PdZn catalysts prepared on ZnO$_{\text{AA}}$ and ZnO$_{\text{nano}}$ supports to determine the underlying reasons behind the difference in their catalytic activity (Table 4.2). Figure 4.16 shows Pd (3d) region of the XPS spectra for both materials. The M$_{\text{Imp}}$ 3%PdZn/ZnO$_{\text{AA}}$ catalyst has two Pd (3d$_{5/2}$) peaks at 335.1 and 336.1 eV, corresponding to Pd$^{+2}$ and Pd$^{0}$ respectively. When we used the commercial support (ZnO$_{\text{AA}}$) having lower surface area, these two peaks were shifted to 335.4 and 336.4 eV. The 0.3 eV shift in binding energy between the two materials is attributable to particle size effects. However, the signals observed at ca. 335 and 336 eV are interpreted as arising from either discrete PdZn alloy particles of differing composition, or due to surface enrichment of the PdZn nanoparticles by one of the metal constituents caused by interaction with the atmosphere as the samples were exposed to air prior to analysis.
4.4.2. *Electron microscopy characterization of the 3%PdZn/ZnOAA catalyst*

The 3%PdZn/ZnOAA catalyst sample was subjected to detailed electron microscopy analysis (Figures 4.9 and 4.17). HAADF-STEM images (Figure 4.8 (c)) showed that most of the ZnOAA support grains appeared to be polygonal, and they were in the 0.1 – 0.5 µm size range, which is substantially larger than that for the ZnO纳米 support material. The supported metal nanoparticles were homogenously dispersed on the ZnOAA support grains, albeit with a broader size distribution and considerably larger mean size (~12.5 nm) than the corresponding Mi材料 on the ZnO纳米 support. Atomic resolution HAADF-STEM images, such those presented in Figure 4.17 (e) and (f), in conjunction with the XEDS mapping data (Figures 4.17 (b), (c) and (d)) demonstrated that metal particles on the ZnOAA were once again highly ordered intermetallic \( \beta \)-PdZn alloys having the characteristic tetragonal \( L1_0 \) structure.

From the detailed structural study, we can conclude that the parameter which mostly affects methanol conversion is the PdZn particle size, which seems to be determined in this case by the surface area of the ZnO material used as the support.

![Figure 4.14. Powder XRD analysis of the reduced Mi材料 3%PdZn/ZnO纳米 (top) and Mi材料 3%PdZn/ZnOAA (bottom) catalysts reduced in-situ at 500 °C. (Courtesy of Dr. Ewa Nowicka).](image-url)
Figure 4.15. TPR profiles for $M_{\text{Imp}}$ 3%PdZn supported catalysts prepared on a) ZnO$_{\text{AA}}$ and b) ZnO$_{\text{nano}}$. (Courtesy of Dr. Ewa Nowicka)

Table 4.2. XPS analysis of the $M_{\text{Imp}}$ derived 3%PdZn catalysts on ZnO$_{\text{nano}}$ and ZnO$_{\text{AA}}$ supports in the fresh and reduced states. (Courtesy of Dr. D. Morgan).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (at %)</th>
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<tr>
<td></td>
<td><strong>Pd</strong></td>
<td><strong>Zn</strong></td>
<td><strong>Cl</strong></td>
<td><strong>O</strong></td>
</tr>
<tr>
<td>$3% \text{PdZn/ZnO}_{\text{AA}}$</td>
<td>fresh</td>
<td>7.1</td>
<td>22.7</td>
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<tr>
<td></td>
<td>reduced</td>
<td>4.4</td>
<td>34.5</td>
<td>4.07</td>
</tr>
<tr>
<td>$3% \text{PdZn/ZnO}_{\text{nano}}$</td>
<td>fresh</td>
<td>5.4</td>
<td>34.9</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>3.8</td>
<td>39.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Figure 4.16. The Pd(3d) XPS spectra for the M_{imp} derived reduced (a) 3\%PdZn/ZnO_{nano} and (b) 3\% Pd-Zn/ZnO_{AA} catalyst materials. Note the binding energy for both Pd species shifts downward by 0.3 eV for the different ZnO supports. (Courtesy of Dr D. Morgan).

Figure 4.17. STEM-XEDS elemental mapping and STEM-HAADF imaging of the M_{imp} 3\%PdZn/ZnO_{AA} catalyst prepared on the Alfa Aesar sourced ZnO support. A lower magnification STEM-HAADF image of the catalyst is shown in (a) along with the corresponding XEDS elemental maps of (b) Zn, (c) Pd and (d) O. The intermetallic particles in profile indicated by arrows in (a-d) show Zn and Pd signals but not O. (e) A higher magnification STEM-HAADF image of a PdZn particle, showing L1_0 type-atomic ordering of Pd and Zn. This can be better seen in the magnified view in (f), overlaid with the atomic structure of the ordered PdZn (ref ICSD 180143) viewed along the [100] projection.
4.5. Conclusion

A novel 3% PdZn/ZnO catalyst was synthesized using a modified impregnation-based method in which excess Cl⁻ ions were introduced along with the metal chloride precursors. The catalyst was highly selective for the MSR reaction. The origin of the high CO₂ selectivity lies in the efficient formation of homogeneously distributed and structurally ordered PdZn intermetallic particles. The presence of chlorine anions during preparation process as indicated by spectroscopy and microscopy investigations facilitates the formation of such intermetallic phases by providing a better mixing between the metal precursor salts, and perhaps by facilitating the formation of a mixed cation compound resembling a Pd-containing Simonkolleite phase. This is further supported by comparisons with the corresponding catalyst prepared by a more conventional impregnation method which was comprised of larger random alloy PdZn particles and exhibited a lower selectivity towards CO₂. The gradual improvement in catalytic performance with time-on-line in terms of both conversion and selectivity was attributed to the formation of ZnO patches on the surface of the supported PdZn intermetallic metal particles during catalyst operation. The formation mechanism of the ZnO patches is still unclear. Moreover, due to the differences in preparation method used, direct comparison with previous report published by Armbruster et al. is difficult. However, two studies could be carried out as future work to determine the formation mechanism of these ZnO patches. The first one is an in-situ heating experiment with the electron microscope to directly study the (i) of the formation of PdZn particles during heat pre-treatment typical and (ii) the nucleation and growth of the ZnO surface patches on the PdZn during the MSR reaction. The second study is based on supporting the
PdZn particles on a different support (e.g. TiO$_2$) rather than on ZnO and investigating if ZnO surface patches still form on the PdZn particles after use in the MSR reaction.

It was also found that the nature of the ZnO support has a significant influence on the activity of the catalyst. This has been associated with the reducibility and surface area of the ZnO, which are crucial parameters to consider when designing the MSR catalyst. Furthermore, a correlation was evident between the resultant PdZn particle size distribution and the type of ZnO support used in the catalyst preparation. Modified impregnation of Pd and Zn precursors on the nanopowder ZnO$_{nano}$ material resulted in smaller ordered PdZn particles having narrower particle size distribution compared to those supported on the lower surface area ZnO$_{AA}$ support. Since both M$_{imp}$ catalysts displayed a high selectivity to CO$_2$ in the MSR reaction, we concluded that the parameter which mostly affects methanol conversion is the PdZn particle size, which is primarily determined by the surface area of ZnO used as the support.
References


Chapter 5

Unsupported AuPd catalysts for the Direct Conversion Methane to Methanol
5.1. 5.1. Introduction

The selective oxidation of hydrocarbons is a process of considerable industrial importance. It involves the reaction between a hydrocarbon and an oxidant, in the presence of a suitable catalyst, to form many useful chemicals, such as alcohols, carbonyl compounds, and epoxides\(^1\). Valuable products form only when the hydrocarbon is partially oxidized, hence total oxidation of the hydrocarbon to \(\text{CO}_2\) needs to be avoided. The choice of oxidant and catalyst, therefore, plays a critical role when complete oxidation needs to be suppressed. This Chapter examines the pivotal role played the oxidizing agent and catalyst material in the selective oxidation of methane to methanol.

Methanol, \(\text{CH}_3\text{OH}\), is one of the most important intermediary feedstock compounds and is also a potentially clean fuel. It is produced industrially via the indirect conversion of methane, \(\text{CH}_4\), to methanol. The indirect process (Figure 5.1) involves the production of synthesis gas (\(\text{CO} + \text{H}_2\)) which is then subsequently catalytically converted to methanol.\(^2\)

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2\text{O}(g) \quad \Delta H^\circ = +49.3 \text{ kcal mol}^{-1}
\]

\[
\text{CO}(g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(g) \quad \Delta H^\circ = -21.7 \text{ kcal mol}^{-1}
\]

overall \(\Delta H^\circ = +27.6 \text{ kcal mol}^{-1}\)

**Figure 5.1.** A typical indirect process to convert the methane to methanol.

This reaction is usually carried out at elevated temperature and pressure which makes it an expensive and energy-intensive process. Hence, the direct selective oxidation of methane to
methanol (Figure 5.2) is highly desirable as an alternative production approach. However, this direct process remains a challenging problem for catalytic science as over-oxidation of CH$_3$OH to the most thermodynamically favored oxidation product, namely CO$_2$, must be avoided.

\[
\text{direct}
\]
\[
\begin{align*}
\text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) & \rightarrow \text{CH}_3\text{OH}(g) \\
\Delta H^o &= -30.7 \text{kcal mol}^{-1}
\end{align*}
\]

**Figure 5.2.** A direct oxidation process of methane to methanol.

In the last century, due to the increase demand for methanol, developing the direct process for the commercial production of methanol has been the subject of numerous studies. The direct conversion of methane to methanol can occur in both gas and liquid phases. The gas-phase oxidation typically operates, in the absence of a catalyst, at elevated temperatures up to 500 °C and under fuel-rich conditions to suppress the over-oxidation of methanol. The main drawback of this process is that improving the selectivity to methanol usually comes at the expense of methane conversion rate. The gas-phase reaction can also be carried out in the presence of a catalyst. Unfortunately, neither the methanol yield nor the methane conversion is much better than those obtained by uncatalyzed reaction. The catalytic liquid-phase oxidation of methane has been developed as an alternative approach to the gas-phase reaction. Olah *et al.* reported that methane can be directly converted to methanol with selectivities up to 95% in liquid super-acidic conditions. There are several studies reported in the literature which use various metals, metal oxides, zeolites and homogeneous complex catalysts as potential catalysts for the direct oxidation of methane to methanol. Although a few of these systems have displayed some promising results, an efficient catalyst
still needs to be developed which produces a reasonable methanol yield under mild reaction conditions.

In the literature, there is a great deal of interest in the direct oxidation of methane to methanol with different oxidants such as SO$_3$, and H$_2$O$_2$.\textsuperscript{1,13} Periana and co-workers\textsuperscript{12} studied the direct conversion of methane to methanol in a strong acid media, using SO$_3$ as an oxidizing agent. They found that in the presence of electrophilic metals such as Hg or Pt complexes, methane was oxidized with SO$_3$ only to the methyl bisulfate, which is very stable against over-oxidation, with a yield greater than 70% at 81% selectivity. The methyl bisulfate was then hydrolyzed to form methanol. More benign oxidants, such as hydrogen peroxide (H$_2$O$_2$), have also been demonstrated to oxidize methane to methanol.\textsuperscript{14} The Pd$^{2+}$ cation was also reported to catalyze CH$_4$ oxidation to methyltrifluoroacetate using peroxytrifluoroacetic acid generated by H$_2$O$_2$ and trifluoroacetic anhydride.\textsuperscript{15} Similarly, heterogeneous catalysts based on Fe-ZSM-5 and Cu-modified ZSM-5 have been used for methane activation to methylhydroperoxide (CH$_3$OOH), CH$_3$OH, and formic acid (HCOOH) in aqueous media at 50 °C.\textsuperscript{16} Kao \textit{et.al}\textsuperscript{15} previously reported that by using Pd$^{+2}$ as the catalyst and H$_2$O$_2$ as the oxidant, it is possible to achieve the selective oxidation of methane under mild conditions. H$_2$O$_2$ is considered a desirable benign oxidant, second only to molecular O$_2$ for this reaction, as the decomposition product is water. Ab Rahim and co-workers\textsuperscript{15} have also reported methane oxidation using supported gold-palladium nanoparticles under mild aqueous conditions with H$_2$O$_2$ as an oxidant at 50 °C. The reaction proceeded through a radical mechanism, as both methyl (•CH$_3$) and hydroxyl (•OH) radicals were observed by electron paramagnetic resonance (EPR) spectroscopy. However, the relatively high cost of H$_2$O$_2$ for
even stoichiometric oxidation of methane makes it difficult to envisage an economically viable process based on this chemistry.

Incorporation of molecular O\textsubscript{2} into the primary oxidation products would represent substantial progress toward a feasible methane-to-methanol process. In a recent publication\textsuperscript{19}, we have reported that this demanding reaction can occur under mild conditions, using colloidal AuPd nanoparticles in the presence of both H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2}. We demonstrate here that by removing the support material from the catalyst, a significant improvement in activity can be achieved and O\textsubscript{2} is directly incorporated into the primary products, with the selectivities reaching >90% and with minimal CO\textsubscript{2} being produced.

5.1.1. Aims of the project

In this chapter a detailed microscopic study using aberration-corrected STEM is presented to uncover the underlying reasons for the superb performance of unsupported colloidal AuPd and inferior performance of AuPd/TiO\textsubscript{2} when they were used as catalysts for the selective oxidation of methane to methanol. Through a microscopy directed catalyst design study we aim to optimize the AuPd alloy size distribution, particle morphology and compositional homogeneity for this challenging reaction.

5.2. Experimental details

5.2.1. Catalyst synthesis and testing

Colloidal bimetallic Au-Pd catalysts were prepared by a standard colloidal method illustrated in Figure 5.3. An aqueous solution of the metal precursor HAuCl\textsubscript{4} (Sigma Aldrich) and acidic solution of PdCl\textsubscript{2} in 0.5 M HCl (Sigma Aldrich) were dissolved in 800 mL of de-ionized water. Polyvinyl pyrrolidone (PVP, average molecular weight 1,300,000, Sigma
Aldrich) was added as a stabilizer to give the required metal-to-PVP ratio (typically 1:1.2). After 2-3 min of stirring, freshly prepared 0.1 M sodium borohydride (NaBH₄, Sigma Aldrich) solution was added such that the molar ratio of NaBH₄-to-metal was 5 : 1. This produced a dark brown colloid which was left for stirring for 30 min to ensure all the metal precursor material was reduced to metal nanoparticles. The colloid was concentrated using rota-evaporation to a give nominal metal loading of 6.6 µmol per 10 ml.

**Figure 5.3.** Schematic diagram of the preparation method used to synthesize AuPd colloids and sol-immobilized AuPd/TiO₂ catalysts.

For TiO₂ supported catalysts, the sol prepared above was immobilized onto the support material. For a 1wt% metal loading, 1.98g of TiO₂ (P25, Degussa) was added to of the aforementioned colloid and the solution was acidified to pH 1 using sulphuric acid to aid better deposition. The supernatant solution became clear over 1 h of stirring as the nanoparticles attached onto the TiO₂ support material. The final catalyst was then recovered
by filtration, washed thoroughly with distilled water and left to dry in an oven at 110 ºC overnight.

Both catalysts were assessed for the liquid phase oxidation of CH₄ using H₂O₂ and molecular O₂ as shown in Table 5.1. The reaction was carried out in a 50 mL glass-lined stainless-steel Parr autoclave reactor. The reactor was charged with 10 mL of colloidal catalyst (6.6 µmol metal equivalent) and different amounts of H₂O₂ (Sigma Aldrich, 50% wt in water). The charged autoclave was sealed and purged three times with CH₄ (99.999%, Air Products). It was then pressurized with CH₄ (30 bar) and O₂ (5 bar, BOC) to remain within oxygen lean limits. It was stirred at 1500 rpm and heated to the desired reaction temperature, (usually 50 ºC) and maintained at the reaction temperature for a fixed time (30 min). At the end of reaction, the autoclave was cooled in ice to a temperature below 10 ºC to minimize the loss of volatile products. The reaction gas was then removed for analysis in a gas sampling bag. In some instances, with supported catalysts, the reactor was charged with 100 mg of catalyst in 10 mL solution of de-ionized water and H₂O₂. At the end of the reaction, the reaction mixture was filtered to recover the catalyst before analysis.

The catalytic data revealed that using colloidal AuPd nanoparticles rather than TiO₂ supported AuPd nanoparticles led to a significant enhancement in activity and selectivity to primary products (namely CH₃OOH, CH₃OH and HCOOH) reaching more than 90%. Furthermore, a correlation was noticed between the amount of H₂O₂ consumed and the amount of products generated. The more H₂O₂ consumed, the fewer products were formed. It was determined that a high rate of H₂O₂ degradation is prejudicial to the reaction either by (i) the termination of reactive radical chains caused by radical concentrations being too high, or (ii) by consumption of H₂O₂ at such a high rate that it does not allow sufficient interaction
with the low amount of solubilized CH$_4$. Experiments were performed to investigate which part of the catalyst was responsible for the high H$_2$O$_2$ degradation rates and noted that this phenomenon was only observed when AuPd nanoparticles were supported on TiO$_2$ (Figure 5.4). Previously a high H$_2$O$_2$ degradation rate was attributed either to the interfacial sites at the support/metal interface$^{16}$ or subtle morphological changes that occurred in the alloy nanoparticles during the immobilization stage$^{17}$. To investigate this effect further, a comparative study has been carried out, before and after use, of the structure, size distribution and composition of the nanoparticles present in these colloidal AuPd and sol-immobilized AuPd/TiO$_2$ catalysts.

**Table 5.1.** Comparison of catalytic activity of TiO$_2$ supported and unsupported colloidal AuPd catalysts for the liquid phase oxidation of CH$_4$ using H$_2$O$_2$. Test conditions: Reaction time = 0.5 h; Stirring speed = 1500 rpm; Pressure CH$_4$ = 30 bar; Reaction temperature = 50 °C with stirred heating ramp rate of 2.25 °C/min. (Courtesy of Dr. Nishtha Agarwal).

<table>
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<tr>
<th>Entry</th>
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<th>Amount of Product (µmol)</th>
<th>Primary Oxygenate Selectivity / %</th>
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Degradation of hydrogen peroxide as a function of reaction time for various catalyst. Hydrogen peroxide degradation was carried out at ambient pressure and temperature. 1000 µmol H₂O₂ was added to 10 mL of colloidal catalyst or water containing 100 mg of sol immobilized supported on TiO₂ catalyst or bare TiO₂ in a glass vial. The H₂O₂ concentration was measured every 10 min. (Courtesy of Dr. Nishtha Agarwal).

5.2.2. Catalyst characterization

Figure 5.5 shows some representative HAADF images (a, b, d, e) and particle size distributions (c, f) obtained from the unsupported AuPd-PVP sol in the fresh (a, b, c) and used (d, e, f) states. In the fresh sample, the HAADF images reveal that AuPd particles primarily have multiply-twinned icosahedral structures, although some cub-octahedral NPs were also detected (Figures 5.5 (a) and (b)). The particle size distribution of the fresh AuPd-PVP particles derived from HAADF images showed them to range in size between ~1 and 10 nm and have a mean diameter of 3.7 nm (Figure 5.5 (c)). In the used sample as expected, no significant morphological changes were noted. The AuPd NPs still exhibited structures that were seen in the fresh sample (Figures 5.5 (d) and (e)). The AuPd NPs after use, as shown in the corresponding particle size distribution presented in Figure 5.5 (f), ranged
anywhere in size from ~2-10 nm and had a mean diameter of ~4.5 nm. In both catalysts (unused and used) neither sub-nm clusters nor dispersed atoms were found indicating that the catalyst was stable against leaching under reaction conditions. Additionally, STEM-XEDS compositional analysis showed the AuPd-PVP NPs to have a similar Au: Pd ratio irrespective of their size. The resultant XEDS spectra (Figure 5.6) can be considered as representing the average composition of the entire particle. By comparing the relative intensities of the Pd L line series and Au M line series in Figures 5.6 (b), (d) and (f), a relatively uniform ratio was found irrespective of particle size, with all particles from ~1nm up 10 nm having a composition close to the nominal composition. These findings however seem to be unique to PVP, since PVA shows definite composition variation with particle size.\textsuperscript{18}
Figure 5.5. Representative HAADF images and particle size distributions for the unsupported AuPd-PVP sol in the fresh (a to c) and after a CH$_4$ oxidation reaction (d to f).
Figure 5.6. Representative XEDS compositional analysis from individual AuPd-PVP nanoparticles of varying size before use.
A detailed electron microscopy study was also carried out on the PVP-AuPd/TiO₂ sol-immobilized catalysts in the fresh and used states (see Figures 5.7). TEM analysis showed the AuPd NPs to have a similar size range and morphology to their colloidal counterparts. Based on these findings, the undesirable high H₂O₂ degradation rate, in this case, was attributed to the interfacial sites at the support/metal interface. Consuming a large amount of H₂O₂ during the reaction could likely terminate the formation of 'CH₃ radicals which are very important for the reaction to proceed. Simply removing the support from the catalyst formulation effectively solves this problem.

Figure 5.7. Representative BF-TEM images and particle size distributions for the AuPd-PVP/TiO₂ sol-immobilized catalyst in the fresh (a, c) and used (b, d) states.
5.3. Possible new techniques for making core-shell nanoparticles

Bimetallic core-shell nanoparticles are a class of nanostructured materials which have recently received much interest due to their unique catalytic properties.\textsuperscript{19} The sequential colloidal growth method is the most common way to prepare core-shell particles. This technique is based on deposition one metal on top of the other where the core particle serves as a seed or nucleation center when reducing a second metal precursor.\textsuperscript{19} Even though this method has been used for many decades to prepare core-shell nanoparticles, controlling the core size and shell thickness as well as the formation of uniform shell are difficult to achieve. Ferrer and co-workers found that initial variations in core size give rise to shells of different thicknesses.\textsuperscript{20} Furthermore, the secondary nucleation of second metal which cannot be avoided in the sequential method gives rise to a population of monometallic clusters of the second metal. This problem has been previously reported by Toshima and co-workers\textsuperscript{21} when they tried to prepare Au(core)/Pd(shell) particles via the successive reduction route. Tiruvalam \textit{et al.}\textsuperscript{22} also prepared Pd (core)/Au (shell) particles by sequentially reducing Pd\textsuperscript{2+} and Au\textsuperscript{3+} ions, using poly vinyl alcohol (PVA) as the stabilizing agent. They studied the as-prepared material by the aberration corrected analytical microscopy and confirmed the presence of the following structures: (i) Pd cores with complete Au coverage; (ii) particles with off-center Pd cores and incomplete Au coverage; and (iii) Pd particles with no Au coverage. All these reports, in fact, indicate that the sequential colloidal growth method for preparing core-shell nanostructures synthesis has many limitations and may not produce the expected core-shell morphology.

In this project, it was found that during the preparation of the supposed random AuPd alloy colloids in this study, a Au-Pd alloy (core)/Pd-rich (shell) structure developed if a rota-
evaporation step was employed (see Figure 5.9(a)). Apparently, during the roto-evaporation process Au species were preferentially depleted from the surface of the particle and this leads to the formation of the core-shell structure. It was also found that if random alloy AuPd particles were exposed to too high a H$_2$O$_2$ concentration (>1000µmol) during the methanol synthesis reaction, then a similar Au-Pd alloy (core)/Pd-rich (shell) structure was developed (Figure 5.9(b)). It was noted in both cases that all core-shell particles irrespective of their size had very similar shell thicknesses and this is a good thing as it is difficult to active this by sequential sol methods.

Interestingly, Au species leached out during the roto-evaporation process formed a thin film coating on the wall of the vessel maybe due to the synergistic action of the centrifugal force and migration and coalescence process. In the case of H$_2$O$_2$ post-treatment the depleted Au species were found in the reaction solution as single atoms and sub-nm clusters (Figure 5.10). The monometallic Au and Pd colloids as well as the metal chloride precursors showed no activity for methane oxidation (Table 5.1. entry 5-9). Therefore, the development of AuPd (core)/Pd (shell) structure should be detrimental to the catalytic activity in the direct formation of methanol.

However, a more detailed and systematic study is required to further understand the formation mechanism of the core-shell structure during the rota-evaporation and H$_2$O$_2$ post-treatment processes and to assess their relative advantages and disadvantages compared to the more commonly used sequential deposition method of forming core-shell structured colloids. In the case of rota-evaporation process, the correlation between the shell thickness and vacuum pressure, temperature and time period of the rota-evaporation process should be studied. In the case of the H$_2$O$_2$ post-treatment process, a systematic study of how the shell
thickness changes as a function of (i) time of exposure to hydrogen peroxide and (ii) hydrogen peroxide concentration should be undertaken.

Figure 5.8. Representative HAADF-STEM images reveal that a AuPd (core)/Pd (shell) structure is developed if (a) the roto-evaporation step was employed; or (b) random alloy AuPd particles were exposed to a high concentration of H₂O₂ during the methanol synthesis reaction.

Figure 5.9. HAADF-STEM images collected from AuPd colloid catalyst when (a) the roto-evaporation step was employed showing no evidence of Au atoms or clusters on the C support.; or (b) random alloy AuPd particles were exposed to a high concentration of H₂O₂ during the methanol synthesis reaction showing Au atoms and sub-nm clusters on the C support.
5.4. Conclusions

We have developed a feasible process for transforming methane directly to methanol under mild reaction conditions. It has been demonstrated that in the presence of H₂O₂ and molecular O₂, and using colloidal AuPd nanoparticles as the catalyst, methane was oxidized to methanol with high selectivity (>90%) in aqueous solution at mild temperature (50 °C). The presence of H₂O₂ in the reaction mixture facilitated the formation of CH₃ radicals, which are important for the reaction to proceed. Surprisingly, when the AuPd NPs were supported on TiO₂, the formation of CH₃ radicals was suppressed and therefore the activity and selectivity was notably diminished. It was observed that with the supported catalyst the consumption rate of H₂O₂ was high which was previously reported to cause termination of reaction and limiting the formation of products. Electron microscopy (TEM and STEM) investigations unambiguously indicate that the interfacial sites at the support/metal interface were responsible for the undesired high rate H₂O₂ degradation.

In this study, it also has been found that rota-evaporation or H₂O₂ post-treatment processes can selectively leach out gold, leading to particles with a AuPd alloy (core)/Pd (shell) morphology. The exact formation mechanism of this core/shell structure in each case remains unclear. The development of the core/shell structure is not beneficial for this reaction since it is known that monometallic Au and Pd nanoparticles are not active for methane oxidation. However, these two processes, if developed further, may represent interesting new methods of fabricating core-shell structured particles with uniform shell thicknesses irrespective of particle size variations.
References


Chapter 6

Optimizing Pt/TiO$_2$ Catalysts for the Selective hydrogenation of Nitrostyrene to 3-Vinylaniline

5.5.
6.1. Introduction

The selective catalytic hydrogenation of nitro groups represents a type of reaction that is of high interest as the resulting functionalized aniline products are important in the fine chemical and pharmaceutical industries\(^1\). Industrially, the hydrogenation of nitro groups are performed over various commercial catalysts (e.g., Cu and Ni)\(^2,3\) using a stoichiometric reducing agent such as sodium hydrosulphite (or H\(_2\)S), iron in acidic media (Bechamp process), stannous chloride, samarium iodide or zinc in ammonium hydroxide.\(^4-6\) Unfortunately, these methods are not effective since they are unselective and generate a huge amount of waste. The selective reduction of a nitro group with H\(_2\), in contrast, is a preferred methodology because it is environmentally friendly and generates only water as a by-product.\(^7,8\) However, when there are other reducible groups (e.g., C=C, C=O, C≡C and C≡N) present in the same molecule, the reduction of nitro groups, especially with H\(_2\), is much more challenging. In any case, an issue which frequently emerges is that conventional catalysts are usually not chemoselective and their selectivity is usually only improved at the expense of their intrinsic activity. Therefore, the development of new catalysts for this process is a subject of considerable interest.

Supported Pt-based catalysts, amongst all the homogeneous and heterogeneous catalysts tested to date for the selective hydrogenation of nitro groups, appear to be the most promising candidate materials since they combine good activity with a reasonable degree of selectivity. Improving the chemoselectivity of Pt catalysts has been the subject of many studies in literature. For example, Lioubov et.al.\(^9\) showed that introducing a second metal such Zn to the Pt catalyst significantly increased the yield of the desired product (i.e. selectivity) in the hydrogenation of 3-nitrostyrene reaction. Alloying Pt catalysts with metal oxides or organic
thiols to improve their chemoselectivity has also been reported.\textsuperscript{10–13} Hiroshi \textit{et al.}\textsuperscript{14} demonstrated that the support structure is a very important factor for controlling and improving the catalytic properties of Pt nanoparticles for the hydrogenation of nitro groups. They found that the catalytic efficacy, is dependent on the size of support crystallites. Corma \textit{et al.} recently reported that the support material used and the details of the synthesis method for preparing for Pt catalysts are important parameters in determining their final catalytic performance during the hydrogenation of nitrostyrene.\textsuperscript{15} The majority of catalysts used in the hydrogenation of nitro groups are often prepared using the impregnation method which involves some heat treatment processes (\textit{i.e.}, calcination followed by reduction process) to form the most active metal nanoparticles before reaction.\textsuperscript{15,16} Many literature reports have shown that the performance of calcined and reduced catalysts was much better than that of reduced-only catalysts.\textsuperscript{17–19} However, even though much work has been devoted to improving the overall performance of supported Pt-based catalysts for this process,\textsuperscript{20} the nature of the active sites in this catalytic system is still unclear and is worthy of further investigation.

6.1.1. \textit{Selective hydrogenation of nitrostyrene to 3-vinylaniline using a Pt/TiO\textsubscript{2} catalyst}

\textbf{Figure 6.1.} Schematic representation of the chemoselective hydrogenation of 3-nitrostyrene (3-NS) to form 3-ethyl nitrobenzene (3-ENB), 3-vinylaniline (3-VA) and 3-ethylaniline (3-EA).
The catalytic hydrogenation of 3-nitrostyrene to 3-vinylaniline is an important process in the manufacture of fertilizers, pharmaceuticals, dyes and plastics. Supported Pt nanoparticles tends to be the catalyst of choice for this particular reaction. Here we report the catalytic activities of 0.05 wt. %, 0.08 wt.%, 0.2 wt.% and 0.5 wt.% Pt on TiO$_2$ for the chemoselective hydrogenation of 3-nitrostyrene (3-NS) to 3-vinylaniline (3-VA) (Figure 6.1). We have fine-tuned the active sites by studying the effect of three different high temperature heat treatments (namely (i) reduction-only, (ii) calcination-only and (iii) calcination followed by reduction) to this systematic set of Pt/TiO$_2$ catalysts.

6.1.2. The aim of the project

The focus of this aspect of my work is to follow the structural evolution of Pt catalysts of varying loading supported on TiO$_2$ supports under various heat treatment conditions. Moreover, our aim is to identify the optimum morphology and active sites in the Pt/TiO$_2$ system for the selective hydrogenation of 3-nitrostyrene to 3-vinylaniline. By correlating our STEM results with complementary XPS and EXAFs characterization data, we should be able to gain more detailed insight into the various nanostructural characteristics which affect the performance of Pt/TiO$_2$ catalysts.

6.2. Experimental Details

6.2.1. Catalyst preparation

Supported Pt catalysts on TiO$_2$ were prepared by a standard wet-impregnation method. A systematic set of catalysts with different nominal Pt loadings (i.e., 0.05, 0.08, 0.2 and 0.5 wt% Pt) were synthesized. For a typical preparation of 2g of the catalyst, the requisite amount of the aqueous Pt precursor solution (9.6mg Pt/ml, prepared from hydrogen
hexachloroplatinic acid solution, assay 30.21%, Johnson Matthey) was added in a 50 ml round bottom flask and made up to 16 ml using de-ionized water. The flask was submerged into an oil bath held at 60 °C under vigorous stirring conditions (800 rpm). When the contents reached 60 °C, the requisite amount of TiO₂ support (Evonik®P25) was added slowly to achieve a complete and homogeneous mixing of the components. After addition of the support, the temperature of the oil bath was raised to 95 °C and the slurry was left to dry overnight (16 h). The dried sample was recovered and ground with a mortar and pestle to obtain a homogeneous dry solid (designated as the fresh ‘dried-only’ sample). A 500mg portion of the dried-only sample was then transferred in a glass calcination boat (20 cm in length) for high temperature heat treatment either in static air (for calcination treatments) or under a steady flow of 5% H₂/Ar (for reduction treatments). All the heat treatments were carried out at 450 °C for 4 h with a heating rate of 10 ° min⁻¹. Samples that underwent (i) reduction-only were coded as “red”; (ii) calcination only as “calc” and (iii) calcination followed by reduction treatment as “calc+red.” All these catalysts were used without any further treatment unless stated otherwise.

6.2.2. Catalyst testing

Liquid phase selective hydrogenation of nitrostyrene was performed in a 50 ml glass round bottom Colaver® reactor fitted in an oil bath. For each reaction, 0.2ml of nitrostyrene and 8ml of toluene were added to the reactor, together with 50 mg of the catalyst. The reactor was purged three times with N₂ after loading it with reactant, catalyst and solvent to remove traces of air. After that the reactor was submerged into an oil bath maintained at 40 °C, and then the reactor was purged three times with 3 bar of pure H₂ while stirring. Finally, the reaction was commenced after pressurizing the reactor with 3 bar pure H₂. At the end of the
reaction, the reactor was removed from the oil bath and cooled using ice. When the reactor and its contents were completely cooled (ca. <5 °C), the reactor was opened, and small aliquots of the reaction mixture was removed and centrifuged to remove the solid catalyst. The clear reaction mixture (1 ml) along with a fixed amount of external standard (o-xylene) was injected into a GC. The determination of the conversion was performed by GC analysis, using a Varian 450GC gas chromatograph fitted with a HP-5ms boiling point column, a flame ionization detector (FID) and a CP8400 auto-sampler. Quantitative analyses of the substrates and products were performed with the help of suitable calibration plots and response factors.

6.3. Results and Discussion

Figure 6.2 summarizes the catalytic data for the 0.2wt% Pt/TiO₂ catalyst which was our starting point material in this project. We observed that the reduced-only 0.2wt% Pt/TiO₂ sample showed good activity and 100% selectivity to 3-vinylaniline.

![Figure 6.2](image-url)  
**Figure 6.2.** Conversion of nitrostyrene as a function of time-on-line for the 0.2wt% Pt/TiO₂ catalysts subjected to various heat treatments. (Courtesy of Dr. Margherita Macino).
Interestingly the calcined-only 0.2wt% Pt/TiO₂ catalyst did not show any activity in the reaction, suggesting that the catalysis process had been completely switched-off when the Pt was oxidized to PtOₓ. Interestingly, the 0.2wt% Pt/TiO₂ sample which underwent consecutive calcination-then reduction treatments showed an even higher activity than the reduced-only sample while maintaining a very high selectivity.

The remainder of the samples Pt/TiO₂ samples which have higher (0.5wt %) and lower (0.08wt % and 0.05wt %) precious metal loadings were also tested in a similar manner. As expected, only the reduced-only and calcined + reduced catalysts were active. Figure 6.3 (a) summarizes the catalytic data for all the aforementioned Pt/TiO₂ catalysts, whereas in Figure 6.3 (b) the activity is expressed in terms of turnover frequency (TOF). Since the catalysts contain different amounts of metal, the TOF value should give a better comparison of their respective catalytic activities.

We noticed that as the metal loading was varied, the selectivity remains consistently high while the activity changes significantly. For higher metal loadings, the calcined + reduced catalyst was significantly more active compared to the reduced-only variant (Figure 6.2). Interestingly, those catalysts with lower metal loadings exhibited the opposite behavior and the activity of the reduced-only catalyst was higher than that of the calcined + reduced variant. Overall, our catalytic performance data indicate that controlling both the metal loading and treatment conditions are crucial for the optimization of Pt/TiO₂ activity for the selective hydrogenation of 3-nitrostyrene.

Comparison of the TOF values for the various Pt/TiO₂ catalysts suggest that the higher Pt loading catalysts that have undergone a calcination + reduction treatment behave similarly to those with lower Pt loadings that have only been reduced. We hypothesize that these
should have similar nanostructures. To test this hypothesis, a detailed electron microscopy analysis and some complementary XPS and XAFS studies were implemented on the high and low metal loading Pt/TiO$_2$ catalysts. The results should help us to identify the optimum nanostructures in those catalysts displaying high activity.

**Figure 6.3.** (a) Nitro styrene conversion and 3-vinylaniline selectivity for the 0.05, 0.08, 0.2 and 0.5wt% Pt/TiO$_2$ catalysts subjected to various heat treatment protocols. (b) The activity of these same catalysts expressed in terms of turnover frequency (TOF). (Courtesy of Dr. Margherita Macino).
6.3.1. *Electron microscopy analysis*

Presented in Figure 6.4 (a-c) are some representative HAADF-STEM images acquired from the set of 0.5wt% Pt/TiO₂ catalysts. This allowed us to follow how the structure of the Pt nanoparticles changes according to the heat treatment encountered. In the calcined-only sample, most of the Pt species are sub-nm clusters and highly dispersed atoms which are inhomogeneously distributed over the support (Figure 6.4(a)). Interestingly, when the calcined sample is subjected to another reduction step, the Pt nanoparticles become more homogeneously distributed over the support and exhibit a relatively uniform 2 nm size (Figure 6.4(b)). In the reduced-only sample on the other hand, the Pt species exist as a mixture of larger particles (>5 nm) and smaller particles (<1nm) (Figure 6.4(c)).

Catalytic data shows that decreasing the Pt loading from 0.5wt% to 0.2wt% causes a significant improvement in the catalytic activity. The influence of decreasing Pt loading on catalyst structure was also investigated using AC-STEM (Figure 6.5). In the calcined-only 0.2wt% sample, the Pt-containing species once again comprised only sub-nm clusters and single atoms (Figure 6.5(a)). In the case of the consecutive calcination +reduction treatment, the Pt particles were even smaller and very uniformly distributed over the TiO₂ when compared to the corresponding 0.5wt% Pt/TiO₂ calcined-reduced sample (Figure 6.5(b)). The correlation between metal loading and the size of the supported metal particles was obvious in the 0.2wt% reduced-only sample (Figure 6.5(c)). The Pt particles were observed all over the support with sizes ranging from 1- 4 nm, and the larger Pt particles (>5 nm) which were found in the corresponding reduced 0.5wt% Pt/TiO₂ sample did not exist in the 0.2wt% Pt/TiO₂ sample.
Figure 6.4. Representative HAADF-STEM images of the unused 0.5wt% Pt/TiO$_2$ catalysts (a) calcined-only; (b) calcined + reduced; and (c) reduced-only catalyst.
Figure 6.5. Representative HAADF-STEM images of the unused 0.2wt% Pt/TiO₂ catalysts. (a) calcined-only; (b) calcined + reduced; and (c) reduced-only catalyst.

The 0.08wt% Pt/TiO₂ catalyst was one of the lower metal loading samples in our study. Figure 6.6 reveals the structure of the Pt nanoparticles after various heat treatment regimens for this sample. As expected, in the calcined-only sample, the HAADF images show only some sub-nm clusters and single Pt atoms (Figure 6.6(a)). In the 0.08wt% Pt loading sample in particular, the reduced and calcined + reduced catalysts have a very similar nanostructure.
where the Pt particles seem to have relatively uniform size (1-2 nm) and a reasonable dispersion (Figures 6.6(b) and (c)). In fact, this observation is entirely consistent with catalytic data where these two catalysts show very similar activities.

Lowering the Pt content too much might at some point be detrimental for the catalytic activity, but the TOF measurements (Figure 6.3(b)) illustrate that by choosing the right combination of loading and heat treatment conditions, a Pt/TiO$_2$ catalyst which exhibits good activity for the selective hydrogenation of 3-nitrostyrene can be generated. HAADF-STEM images of the very low (0.05wt%) Pt loading catalysts are shown in Figure 6.7. As the density of Pt species is extremely low and we know that the Pt species in all the calcined-only samples were sub-nm clusters and single Pt atoms, we can safely assume this also the case for the 0.05wt% calcined-only sample. Figures 6.7(a) and 6.7(b) are representative HAADF-STEM images acquired from the calcined + reduced and reduced-only variants of the 0.05wt% Pt/TiO$_2$ samples. The Pt species in both cases were ultra-small particles and no single atoms were detected. However, in the reduced-only sample, the Pt particle size distribution is much more uniform compared to that of the corresponding calcined + reduced sample.

To understand in a more quantitative manner the correlation between the particle size and catalytic activities of lower and higher metal loading catalysts, we have measured the particle size distribution from each of our samples from HAADF-STEM images (Figure 6.8). Based on correlating the electron microscopy observations and catalytic results, we can deduce that smaller (< 1nm) or larger (> 3nm) Pt particles are not desirable. Instead samples with Pt particles predominantly in the 1-2 nm size range seem to show the optimal activity.
Furthermore, the final particle size can be tuned by a combination of metal loading and heat treatment.

**Figure 6.7.** Representative HAADF-STEM images of the unused 0.08wt% Pt/TiO$_2$ catalysts (a) calcined- only; (b) calcined + reduced; and (c) reduced-only catalyst.
Figure 6.8. Representative HAADF-STEM images of the unused 0.05wt% Pt/TiO$_2$ catalysts (a) calcined + reduced and (b) reduced-only catalyst.

(a) Calc + red
Mean = 1.6 nm
$\sigma$ = 0.6 nm
Skewness = 0.6

(b) red
Mean = 1.4 nm
$\sigma$ = 0.2 nm
Skewness = 0.5

(c) Cal + red
Mean = 1.1 nm
$\sigma$ = 0.2 nm
Skewness = 0.5

(d) red
Mean = 1.6 nm
$\sigma$ = 0.6 nm
Skewness = 0.4
Figure 6.9. Particle size distributions derived from HAADF-STEM images for the unused Pt/TiO$_2$ catalysts. (a, b) 0.5wt%; (c, d) 0.2wt%; (e, f) 0.08wt%; and (g, h) 0.05wt% Pt/TiO$_2$.

Further analysis of the particle size distributions reveals that Pt catalysts displaying higher activity have very narrow size distributions. A correlation was detected between the good catalytic activity and an abundance of Pt particles having a size of about 1.2 nm. Specifically, the catalyst which had the narrowest size distribution and the largest population of ~1.2 nm particles showed the highest catalytic activity for this reaction. Calculating the total peripheral line length between the Pt and TiO$_2$ support in each catalyst is another way of analyzing the observed variation in the activity of Pt/TiO$_2$ catalysts when the metal loading
and heat treatment conditions are changed. This can be estimated based on particle size distribution derived from HAADF-STEM images. As shown in Table 6.1, Pt particles were modelled as half-spheres of Mackay icosahedra, so that peripheral sites can be estimated for particles with different sizes.\textsuperscript{21} Boronat \textit{et al.} \textsuperscript{22} suggested that increasing the number of peripheral sites is very important to obtain a highly active and selective Pt catalyst for the hydrogenation of nitro- groups. Calculation of total Pt peripheral line length in our case was consistent with Boronat’s hypothesis (Figure 6.10). We observed a positive correlation between the number of peripheral sites and the catalytic activity. In the case of the 0.08 wt% Pt/TiO\textsubscript{2} sample in particular, the calcined + reduced and reduced-only Pt catalysts display comparable activity levels because they have almost the same number of peripheral sites. However, no such correlation was achieved when the same conversion data was plotted against the total number of exposed surface Pt atoms (Figure 6.11). The combined effect of different heat treatment protocols and the Pt loading determine the final fraction of the peripheral line sites that the Pt makes with the TiO\textsubscript{2} support, which consequently has a profound effect on the resultant catalytic activities.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure610.png}
\caption{The correlation between total peripheral Pt atoms and activity for selective hydrogenation of hydrogenation of 3-nitrostyrene.}
\end{figure}
Figure 6.11. The correlation between the 3-NS conversion and total amount of Pt surface or peripheral Pt atoms for different Pt/TiO$_2$ catalysts as determined from HAADF-STEM analysis. Reaction conditions: 3-NS: 0.2 ml; toluene: 8 ml; pH$_2$: 3 bar; catalyst: 50 mg; temperature: 40 °C; reaction time: 15 min. Key: R: red-only; C+R: calc+red. For this plot 0.05%Pt catalysts were not used because the conversion for this catalyst was very low after 15 min. (Courtesy of Dr. Qian He).

Table 6.1. The Mackay icosahedral model that is used for estimating numbers of surface sites and peripheral sites for Pt/TiO$_2$ catalyst particles of different sizes.

<table>
<thead>
<tr>
<th>Shell no.</th>
<th>Cluster Size (nm)</th>
<th>Number of atoms in the cluster (full sphere)</th>
<th>Number of atoms in the cluster (half sphere)</th>
<th>Peripheral sites</th>
<th>Total number of surface atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.84</td>
<td>13</td>
<td>6.5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>1.43</td>
<td>55</td>
<td>27.5</td>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>2.01</td>
<td>147</td>
<td>73.5</td>
<td>14</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
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<td>309</td>
<td>154.5</td>
<td>18</td>
<td>81</td>
</tr>
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<td>3.75</td>
<td>923</td>
<td>461.5</td>
<td>26</td>
<td>181</td>
</tr>
</tbody>
</table>
6.3.2. XPS characterization

All the Pt/TiO$_2$ catalysts with different loadings and heat treatments have also been characterized by XPS, and the results are presented in Figure 6.12. XPS analysis allows us to determine the nature of the Pt species present on the surface of each sample. At this point, it is important to highlight that very low loading samples, specifically those < 0.1 wt% loadings, have a much lower spectral quality, even after an unusually large number of scans (>100). Hence the exact quantification of these spectra is challenging due to the poor signal-to-noise ratio, and the further complication of an overlapping Ti loss peak at ca. 75 eV.$^{23}$

Generally, regardless of Pt loading all samples were fairly similar in respect to their XPS analysis, therefore for ease of discussion we focus here initially on the 0.5 wt% Pt/TiO$_2$ catalysts. For the ‘dried-only’ sample, the Pt(4f$_{7/2}$) binding energy of 72.2 eV is indicative of a Pt(II) species, presumably associated with residual excess Cl on the sample surface, although the presence of Pt oxides cannot be excluded.$^{24}$ Calcination of this highest loading sample reveals two distinct Pt environments; the first with a binding energy again of 72.2 eV and a second with a binding energy of 74.4 eV. Considering the calcination temperatures and the small concentration of Cl (ca. 0.2 – 0.25 at%), and the Pt concentration (equally ca. 0.2 at%) a bulk PdCl$_2$ species is not the cause of the 72.2 eV signal, therefore this is likely a PtO or Pt-Cl based species. The high energy component at 74.4 eV, is likely to be PtO$_2$ or Pt hydroxide.$^{25}$ The reduced-only and calcined + reduced catalysts both exhibit Pt (0) as indicated by the asymmetric peak shape and a binding energy of 70.6–70.8 eV.$^{26}$

For the lower (0.08 and 0.05 wt% Pt) loading catalysts, depending on the heat treatments, the Pt(4f) signal strength is very weak, especially for the catalysts which have undergone reductive treatments. When we consider the accompanying microscopic data (Figure 6.8),
such poor resolution of the Pt(4f) peaks is attributed to highly dispersed ultra-small Pt particles, and no evidence of TiO$_2$ encapsulation of the Pt is found.

\( (i) \)

\( (ii) \)

\( (iii) \)

\( (iv) \)

**Figure 6.12.** XPS data of (a) dried only, (b) calcined-only, (c) reduced-only, and (d) calcined + reduced samples of Pt/TiO$_2$ catalysts with different Pt loadings (i: 0.5wt% ; ii: 0.2wt.%; iii: 0.08wt.; iv: 0.05wt.%). (Courtesy of Dr D. Morgan).
6.3.3. X-ray absorption spectroscopic studies

Multiple XAFS experiments were performed in order to analyze the 0.05 to 0.5 wt% Pt/TiO$_2$ reduced-only as well as the calcined + reduced samples. The two extreme metal loading samples (i.e., 0.5 and 0.05 wt% Pt) calcined-only samples were also analyzed. The XAS analysis gives the opportunity to collect both XANES and EXAFS information. The Pt L$_3$ edge XANES spectrum is dominated by the dipole allowed 2p$_{3/2} \rightarrow 5d_{5/2}$ transition of a core electron and is known to be sensitive to the oxidation and coordination state of Pt.$^{27-30}$ Complementary information is also given by EXAFS but since this phenomenon occurs due to the ejected photoelectron interacting with the neighboring atoms, information regarding the interatomic distances and the chemical environment of the specific element analyzed can be derived.

In Figure 6.123, both XANES plots show a comparison of the different metal loading samples that underwent the same heat treatment: reduced-only (Figure 6.13 (a)) or calcination + reduction (Figure 6.13 (b)). Figure 6.14 also shows a plot of the XANES for the 0.05 wt% Pt sample and a PtO$_2$ reference material. Already from this overview it is possible to notice the existence of a variety of platinum species and environments present in these samples.

XANES spectra in Figure 6.13(a) appear almost identical for the three lowest loadings (i.e., 0.05 to 0.2 %) with a maximum in the $\mu$(E) trace seen at ~ 11568 eV. It is noticeable however that the maximum of the rising absorption edge of the samples and the edge position is lower (i.e., ‘red’-shifted) than that of the reference PtO$_2$ phase (Figure 6.14). The sample with 0.5 wt% loading is particularly red-shifted and its rising absorption edge possesses the lowest overall intensity, particularly at 11,568 eV. Previously it has been shown that such changes
indicate differences in the extent of reduction/oxidation with all samples possessing a Pt oxidation state < + 4 with the 0.5 wt% sample being more reduced than all the samples with lower loadings which are seen to be the most oxidised.27

Figure 6.13 Pt L3-edge XANES data recorded on Pt/TiO2 samples after (a) reduction-only and (b) calcination + reduction. Note that the dashed arrow indicates the decrease in edge position with increased loading. The solid arrow indicates the increased rising absorption edge. (Courtesy of Dr. Margherita Macino)

Figure 6.4. Pt L3-edge XANES data recorded on the 0.05wt% Pt sample and the PtO2 reference. Note dashed arrow indicates the decrease in edge position with increased loading. The solid arrow indicates the increased rising absorption edge. (Courtesy of Dr. Margherita Macino).

A similar case can be seen for the calcination + reduction samples shown in Figure 6.13 (b) although, based on the intensity of the rising absorption edge, all samples except that
containing 0.08 wt% Pt appear more oxidized than after simple reduction; the 0.08 wt% sample appearing to remain the same. In order to verify and even to extract further information from these samples the EXAFS Fourier Transform (FT) data are plotted and analyzed in Figure 6.15.

Focusing on Figure 6.15 (a) after reduction-only it is clear that all except the 0.5 wt% sample contain a strong peak at ~ 2.0 Å assignable to a Pt-O distance typical of PtO$_2$ species; see Figure 6.17 (a) which illustrates the similarities of the Pt-O distances in the samples that to PtO$_2$.\textsuperscript{31,32} The intensity of the Pt-O contribution with respect to the reference PtO$_2$ is much smaller in all samples and suggests that the Pt-O environments in the samples are more disordered. This can be rationalized as due to static disorder caused by the high dispersion of Pt-O$_2$ species across the TiO$_2$ support and according to the XANES, a partial reduction of the Pt$^{4+}$ to Pt$^{2+}$. Note that since a PtO reference does not exist, it is not possible to unambiguously identify its presence nor rule out its absence. The 0.5 wt% Pt/TiO$_2$ sample also contains a broad peak with a maximum intensity at ~ 2.73 Å typical of Pt metal. Analysis of the EXAFS data (see Table 6.2 and Figure 6.16) for this sample suggests the existence of spherical Pt nanoparticles ~ 1 nm in diameter.\textsuperscript{33} For the 0.05 and 0.2 wt% Pt/TiO$_2$ reduced-only samples, weak peaks at 2.87 and 2.81 Å may also suggest the presence of a small amount of Pt metal in these samples as well as a much more significant Pt-oxide environment.
Figure 6.15. $k^3$ EXAFS FT data recorded on Pt/TiO$_2$ samples after (a) reduction-only and (b) calcination + reduction. Labels above the peaks indicate the scattering pairs that give rise to that contribution. (Courtesy of Dr. Margherita Macino).

Figure 6.16. Fitted FT data (first Pt-Pt shell) for sample 0.5 wt% Pt after reduction. The parameters extracted from the fitting of the data are shown in Table 4.2. (Courtesy of Dr. Margherita Macino).
Table 6.2. EXAFS parameters for the 0.5wt% Pt/TiO$_2$ catalysts determined from an analysis of the Pt L$_3$, K-edge data. (Courtesy of Dr. Margherita Macino).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt-Pt (Å)</th>
<th>(N)</th>
<th>2σ$^2$ (Å$^2$)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>2.76</td>
<td>12</td>
<td>0.009</td>
<td>33.33</td>
</tr>
<tr>
<td>Pt 0.5 wt%</td>
<td>2.76</td>
<td>7.8</td>
<td>0.009</td>
<td>41.38</td>
</tr>
</tbody>
</table>

Figure 6.15 (b) contains FT data after sequential calcination + reduction and are characterized by the presence of a strong Pt-O contribution in all samples although the intensity of this contribution is inversely proportional to the amount of Pt present; see Figure 6.17 (b) which illustrates the similarities of the Pt-O distances in the samples that to PtO$_2$. This is again consistent with the XANES data which suggests the presence of more Pt$^{4+}$ in the samples after the calcination + reduction treatment; the 0.05wt% Pt/TiO$_2$ sample in particular contains Pt-Pt scattering contributions consistent with PtO$_2$ suggesting that some PtO$_2$ nanocrystallites may have evolved in this sample. For the 0.5wt% Pt/TiO$_2$ sample, the Pt-O peak possesses a skew and kurtosis towards higher Pt-O distances and when considered along with the weaker absorption edge intensity for this sample, suggests the presence of more Pt$^{2+}$. Interestingly no real evidence for metallic Pt species could be seen on visual inspection or when attempts were made to fit the data.
Figure 6.17. Fitted FT data for the various Pt/TiO$_2$ catalysts after (a) reduction-only and after (b) calcination + reduction. (Courtesy of Dr. Margherita Macino).

6.4. Conclusions

We have clearly demonstrated that Pt nanoparticles impregnated on TiO$_2$ can be highly active and selective for the selective hydrogenation of 3-nitrostyrene to 3-vinylaniline. It was observed that the catalytic activity is dependent on the Pt-loading and on the heat treatment conditions employed during the preparation stage. According to our results, a catalyst with higher Pt-content (e.g., 0.5wt% and 0.2wt%) requires a multiple heat treatment (i.e., calcination followed by a consecutive reduction at 450 °C) to achieve a high activity catalyst, while in the case of lower Pt loadings the reduction process alone at 450 °C appears to be sufficient to achieve the highest catalytic performance.

The STEM results revealed that a catalyst with narrowest size distribution and largest population of ~1.2 nm particles displayed the highest catalytic activity for this reaction. The fraction of peripheral line sites at the Pt/TiO$_2$ interface, which have previously been reported to be crucial for the selective hydrogenation reactions, was calculated to rationalize the observed variation in the activity of Pt/TiO$_2$ catalysts when the metal loading and heat
treatment conditions are changed. The total number of peripheral sites for all the Pt/TiO₂ catalysts examined were estimated based on the particle size distributions derived from HAADF-STEM images. The number of peripheral line sites that the Pt particles make with the TiO₂ support with different particle sizes were estimated by modelling them as half-sphere Mackay icosahedra (Table 6.1). Our analysis showed a direct correlation between the number of peripheral Pt/TiO₂ sites and the resultant catalytic activity. However, we did not observe such a correlation when we plotted the activity data against the total number of exposed surface Pt atoms. The complementary spectroscopic techniques (XPS, XANES and EXAFS) investigations showed that in the most active catalysts, most of the Pt species were in fact associated with Pt-O bonding. Such species in samples with higher metal loadings were achieved only when the catalyst was subjected to a consecutive calcination then reduction process. However, in the case of the samples with the lower metal loadings, the reduction process alone was enough to achieve the correct oxidation state.

Investigating the inter-dependency of metal loading and the different heat treatment protocols to produce the most active catalyst for other selective hydrogenation reactions would be worthy of further investigations. Jiang et al. recently studied the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde over a supported Pd catalyst. Such reaction is very important in the production of flavors and pharmaceuticals. They demonstrated that Pd particle size is the key factor that has to be finely tuned to achieve most active and selective catalyst for this reaction. In their study to tune the size of Pd particles, they tried several strategies such as using different precursors, changing calcination or reduction temperatures. However, tailoring the Pd particles size using different routes such the one we used in this project is an attractive study.
References


Chapter 7

Sol-Immobilized Au and AuPd Catalysts Prepared using Millifluidic Reactors
7.1. Introduction

Metal nanoparticles, due to their unique optical, electronic, mechanical and chemical properties, are increasingly utilized in different fields, including medicine, electronics, energy, environment, biology and chemistry.\textsuperscript{1–5} The topic of supported nanoparticles is currently an area of intense scientific interest due to their applications in catalysis. For example, small gold and gold-palladium nanoparticles (< 10 nm) are often supported on a high surface area oxide and used to catalyse many reactions such as the hydrogenation of nitro- compounds,\textsuperscript{6} selective oxidation of alkenes to epoxides\textsuperscript{7,8} and alcohol oxidations to aldehydes and acids.\textsuperscript{9,10} It is also well-known that the catalytic properties of nanoparticles are strongly dependent on their size, shape and composition.\textsuperscript{11,12} Therefore, a preparation method that can generate small nanoparticles with a tight size distribution and uniform compositions is highly desirable. As discussed in Chapter 1, there are several methods commonly used to produce supported nanoparticles. Amongst these, the sol-immobilisation method is considered as a promising approach because it provides tighter control over the size distribution of the nanoparticles. However, even at relatively small production scales \textit{(i.e., < 5g of product)}\textsuperscript{13} inhomogeneous mixing of the reactants and inefficient heat transfer can often lead to variances in the resultant nanoparticles from batch-to-batch. This is particularly critical for bimetallic particles, where composition variations can often lead to the formation of nanoparticles rich in one metal, therefore making the production of particles with uniform alloy composition difficult to achieve\textsuperscript{13,14} These challenges currently restrict the adoption of the sol-immobilization method for larger scale operations.\textsuperscript{15,16}

In recent years, there has been a substantial shift towards the synthesis of nanomaterials in automated continuous flow microfluidic or millifluidic reactors instead of using
conventional batch preparation methods. Owing to their large surface area-to-volume ratio, such devices offer several advantages over the complex, multi-step batch procedures, such as superior control over mixing of reagents, high throughput, better safety and the potential for real-time monitoring of material quality.\(^{17}\) By using automated reactors, it may eventually become possible to produce nanomaterials in more reliable, reproducible and scalable manner.

Amongst the automated reactors currently available, *microfluidic* devices are becoming very popular and their utility in nanoparticle synthesis has been studied in some detail.\(^ {18-20}\) Despite their excellent control over the mixing of reagents, their small channels (d < 1mm) make them expensive and usually require sophisticated manufacturing techniques. Furthermore, the small dimension channels during nanoparticle synthesis are more prone to fouling and clogging, a problem which is detrimental to the lifetime of the microreactor. For these reasons, industry is becoming less interested in employing microfluidic technology in nanoparticle production. *Millifluidic* devices, in contrast, offer the same advantages regarding controlling the contact time, flow rate and manipulation of reagents. In addition, their millimeter dimension channels (d > 1mm) makes them easier to manufacture at a lower cost. Furthermore, the larger channel size can withstand higher flow rates and pressures during the synthesis process, are less susceptible to blockage and potentially allow the production of nanoparticles on a larger scale.\(^ {21}\) Surprisingly, there are very few studies reported in the literature which demonstrate the utility of millifluidic systems for nanoparticle or catalyst synthesis.
7.1.1. The aim of this work

In this chapter, we demonstrate for the first time the possibility of utilizing a millifluidic system, created by the 3D printing of the reactor assembly, to continuously produce supported metal nanoparticles. A critical microstructural comparison is made between TiO$_2$ supported Au and AuPd colloidal particles prepared in a conventional batch reactor with those made in a continuous manner using novel 3D printed millifluidic reactors. The aim of the study was to determine if improved control over the nanoparticle size distribution and composition could be achieved using this new type of reactor technology.

Figure 7.1. Schematic representation of the experimental set-ups for (a) semi-continuous and (b) continuous production of Au nanoparticles supported on TiO$_2$. (Courtesy of Dr S. Cattaneo).
7.2. Experimental detail

7.2.1. Synthesis of supported Au nanoparticles

As can be seen in Figure 7.1, two experimental set-ups have been developed by S. Cattaneo at Cardiff University to prepare supported Au/TiO$_2$ catalysts: namely, a semi-continuous process (Fig. 7.1(a)), and a continuous process (Fig. 7.1(b)). In both cases, the method of preparing the Au colloid were identical where a solution containing the Au metal precursor (HAuCl$_4$) and the stabilizing agent (PVA) was mixed with a second solution containing the reducing agent (NaBH$_4$) in a T-type mixer, which was made of perfluoroalkoxy alkane (PFA) using a 3D printer (Figure 7.1(a), red box). The complete reduction of all the Au species present in the solution, and therefore the formation of the Au colloid, was confirmed by the UV-vis spectrometer unit integrated into the system. However, the two approaches differ only in the method of introducing the oxide support suspension into the Au sol. In the semi-continuous process, the mixing of Au colloid and the TiO$_2$ suspension was done in a flask outside the millifluidic system, while in case of the continuous process the mixing and sol-immobilization on TiO$_2$ occurred in another T-type mixer head integrated into the millifluidic system. The final materials in both cases were transformed into active catalysts via subsequent washing and drying steps (120 °C, overnight). The overall flow rate of the metal precursors/stabiliser and reductant, the reactor length, the Au/NaBH$_4$ molar ratio and PVA/Au weight ratio are thought to be critical parameters for controlling the Au particle size distribution and mono-dispersity, hence they have been carefully optimised by S. Cattaneo in this project. The optimised production conditions for the semi-continuous process are summarized below in Table 7.1.
The overall flow rate of the metal precursors/stabiliser and reductant was varied between 1 and 24 mL min\(^{-1}\). It has been reported that higher flow rates tend to increase the degree of mixing in the region of T-shape connectors due to the formation and intensification of Dean vortices.\(^{22}\) This has the potential to cause a faster nucleation step that results in the production of smaller seed particles and narrower nanoparticle size distributions.\(^{23}\) This is consistent with our observations, where the mean size of nanoparticles, determined from STEM analysis decreased from 15.1 nm at 1 mL min\(^{-1}\) to 5.6 nm at 24 mL min\(^{-1}\) (Table 7.1, entries 1-6).

The solution mixing can be tuned via changing the geometry of the connector unit and the millifluidic reactor using a stereo-lithographic 3D printer. It has been previously reported that the tubing material can affect the quality of the metal colloid produced.\(^{24}\) In this work, the default T-shape connector, was compared with alternative Y-shape and I-shape connectors. The Y-shape connection simply allows the two streams to merge with a lower contact angle compared to the T-shape connector, while the I-shape connector unit can be defined as a coaxial mixer where the two solutions make contact in the same flow direction, with the Au\(^{3+}\) solution forced into the NaBH\(_4\) solution for better mixing. Indeed, in our case, a noticeable change in the mean size of nanoparticles was noticed when different connectors were used (Table 7.1, entries 7-9). For instance, a catalyst produced with the standard I-shape connector gives a slightly smaller mean particle size (6.5 ± 1.7 nm) compared to a catalyst produced with a T-shape connection (7.0 ± 1.9 nm).

Specially shaped reactors, having helical or plait-like geometries (Figure 7.5) were also 3D printed and tested in conjunction with a T-shape connector (Table 1, entries 10-11). The helix design is an 8-turn helicoidal shaped reactor that takes advantage of its 3-dimensional
curves to intensify the so-called Dean vortices and thus increase the degree of mixing. The plait-like reactor is a device based on previous reports\textsuperscript{25,26} where the two solutions split and recombine multiple times, using this mechanism to create new heterogeneous interfaces. The results show that amongst the tested geometries, the I-shape connection and the helix reactor produced the smallest and most uniform nanoparticles (6.4 ± 1.5 nm and 6.3 ± 1.3 nm respectively), whereas the plait-like reactor and the Y-shape connection proved to be the least effective configurations (7.4 ± 2.2 nm and 7.5 ± 2.5 nm respectively).

As reported in other studies\textsuperscript{27,28} the reactor length should be optimised in order to achieve complete reduction of the metal precursor whilst avoiding unwanted growth and coalescence of the nanoparticles due to longer residence times. The total reactor length was varied from 80 to 130 cm by changing the length of tubing between the T-connection and the UV-vis cuvette (from 50 to 100 cm), while an even shorter length of 30 cm was achieved by-passing the in-situ cuvette altogether. For this comparison, the flow-rate was maintained at a constant value of 6 mL min\textsuperscript{-1}. At this flow rate, all the metal precursor salt was efficiently reduced in less than 8 s (the time required for the solution to pass through the 50 cm of reactor from the T-connection and the in-line UV-vis cuvette), suggesting that the use of longer reactors should only result in larger nanoparticles with a broader size distribution. Indeed, this was experimentally borne out because increasing the reactor length from 80 cm to 130 cm, caused the mean nanoparticle size to increase from 6.5 nm to 7.2 nm (Table 7.1, entries 12-14), with the corresponding size distributions increasing from ± 1.7 to ± 2.6 nm. Decreasing the total reactor length to 30 cm resulted in a decrease of the mean nanoparticle size to 5.7 ± 1.3 nm (Table 7.1, entry 15) showing the importance of choosing the appropriate reactor dimensions. Finally, the effect of varying the amount of PVA and NaBH\textsubscript{4} used was
investigated as the concentration of both stabilising agent and reducing agent relative to the concentration of metal precursor are known to be critical parameters for controlling the Au particle size distribution in the conventional batch method. The PVA-to-Au weight ratio was varied from 0 to 1.3 (Table 7.1, entries 16-18), while the NaBH₄-to-Au molar ratio was changed from 1 to 7.5 (Table 7.1, entries 19-22). Both of these parameters are expected to affect (i) the reduction rate, (ii) the nucleation and growth process, and (iii) stability and activity of the formed Au nanoparticles. The absence of the stabilising agent, as expected, led to the production of larger nanoparticles with a very broad size distribution (7.9 ± 3.0 nm). On the other hand, when PVA was present in excess, the extent of excess did not significantly change the characteristics of the final Au colloid; small highly uniform Au nanoparticles (6.0 ± 1.4 nm) were efficiently produced with a PVA-to-Au ratio of 1.3. For catalysis applications, however, it is desirable to use the lowest amount of stabilising agent possible since it may block or decrease the accessibility of the metal active sites from the substrate, affect adsorption/desorption of substrates/products and thus decrease the overall activity. The reductant, NaBH₄, is typically used in excess in order to accomplish full and fast reduction of Au³⁺ to produce metallic Au nanoparticles with small mean size and narrow particle size distribution.²⁹ Similarly, in our semi-continuous set-up we investigated a broad range of NaBH₄-to-Au molar ratios from 1 to 7.5 (Table 7.1, entries 19-22) and identified an optimum value below which the NaBH₄ did not efficiently reduce the Au precursor and led to the formation of Au nanoparticles with broader size distribution and larger mean particle size. In particular, when NaBH₄ was added in a stoichiometric amount, less than half of the metal was successfully deposited onto the support leaving the filtered solution still rich in Au³⁺. In contrast, an excess of reducing agent (i.e., NaBH₄-to-Au ratio = 7.5) caused
a destabilising effect due to the excess of electrolytes in solution and PVA hydrolysis, and thus to the formation of larger nanoparticles.\textsuperscript{30}

The catalyst prepared with the most optimised reaction conditions (\textit{i.e.}, an 8 mL min\textsuperscript{-1} flow rate, 50 cm reactor length with a PFA T-shape connection, PVA-to-Au weight ratio of 0.65 and NaBH\textsubscript{4}-to-Au molar ratio of 5) was then compared to the benchmark catalyst prepared via the standard \textit{batch} sol immobilisation method (Table 7.2). It should be mentioned that by using the millifluidic reactor at the optimised conditions, it was possible to produce the 1 wt\% Au/TiO\textsubscript{2} catalyst at a rate of up to 3.6 g h\textsuperscript{-1} per reactor.

**Table 7.1.** DLS and DF-STEM particle size measurements and metal loading calculated for the catalysts produced during the optimization of the semi-continuous production experimental set-up. (Courtesy of Dr. Stefano Cattaneo).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Flow rate (mL min\textsuperscript{-1})</th>
<th>Reactor length (cm)</th>
<th>PVA : Au (g : g)</th>
<th>NaBH\textsubscript{4} : Au (mol : mol)</th>
<th>Particle size (nm)</th>
<th>Metal loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>18.3 ± 2.1</td>
<td>15.1 ± 6.2</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.8 ± 2.0</td>
<td>6.7 ± 1.5</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.1 ± 1.6</td>
<td>7.0 ± 2.0</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.5 ± 1.7</td>
<td>6.5 ± 1.7</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.0 ± 1.7</td>
<td>5.4 ± 0.9</td>
</tr>
<tr>
<td>6</td>
<td>24</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.9 ± 1.7</td>
<td>5.6 ± 1.3</td>
</tr>
<tr>
<td>7\textsuperscript{a}</td>
<td>6</td>
<td>60</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.9 ± 1.7</td>
<td>7.0 ± 1.9</td>
</tr>
<tr>
<td>8\textsuperscript{b}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.2 ± 2.1</td>
<td>7.4 ± 2.2</td>
</tr>
<tr>
<td>9\textsuperscript{c}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.6 ± 1.8</td>
<td>6.4 ± 1.5</td>
</tr>
<tr>
<td>10\textsuperscript{d}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.8 ± 1.7</td>
<td>6.3 ± 1.3</td>
</tr>
<tr>
<td>11\textsuperscript{e}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.2 ± 1.6</td>
<td>7.5 ± 2.5</td>
</tr>
<tr>
<td>12</td>
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<td>130</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.8 ± 1.8</td>
<td>7.2 ± 2.6</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>105</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>6.1 ± 1.7</td>
<td>7.0 ± 2.1</td>
</tr>
<tr>
<td>14\textsuperscript{*}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.5 ± 1.7</td>
<td>6.5 ± 1.7</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>30</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.9 ± 1.7</td>
<td>9.4 ± 2.9</td>
</tr>
<tr>
<td>16</td>
<td>6</td>
<td>80</td>
<td>0 : 1</td>
<td>5 : 1</td>
<td>10.5 ± 0.9</td>
<td>14.5 ± 8.7</td>
</tr>
<tr>
<td>17\textsuperscript{*}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.5 ± 1.7</td>
<td>6.5 ± 1.7</td>
</tr>
<tr>
<td>18</td>
<td>6</td>
<td>80</td>
<td>1.3 : 1</td>
<td>5 : 1</td>
<td>7.0 ± 1.3</td>
<td>6.0 ± 1.4</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>1 : 1</td>
<td>50.9 ± 3.0</td>
<td>22.9 ± 8.2</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>2.5 : 1</td>
<td>6.7 ± 1.9</td>
<td>9.0 ± 2.8</td>
</tr>
<tr>
<td>21\textsuperscript{*}</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>5 : 1</td>
<td>5.5 ± 1.7</td>
<td>6.5 ± 1.7</td>
</tr>
<tr>
<td>22</td>
<td>6</td>
<td>80</td>
<td>0.65 : 1</td>
<td>7.5 : 1</td>
<td>16.1 ± 2.2</td>
<td>11.3 ± 4.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Printed T-shape connection. \textsuperscript{b}Printed Y-shape connection. \textsuperscript{c}Printed I-shape connection. \textsuperscript{d}Printed plait-like reactor. \textsuperscript{e}Printed helix reactor. \textsuperscript{*}Same catalyst as entry 4.
7.2.2. Preparation of benchmark sol-immobilized Au/TiO₂ and AuPd/TiO₂ batch samples

The standard Au and AuPd batch benchmark catalysts were prepared by following the procedure described in detail elsewhere.³¹ Briefly, to an aqueous solution of HAuCl₄ (and PdCl₂ in case of bimetallic catalyst) of the desired concentration (typically 0.127 mmol L⁻¹ for Au and 0.165 mmol L⁻¹ for Pd for a AuPd 1:1 molar ratio), the appropriate amount of PVA was added (PVA: metal weight ratio of 0.64 for Au and 1.2 for AuPd respectively) under vigorous stirring. A freshly prepared solution of NaBH₄ was then added to the metal precursor(s) with NaBH₄: metal molar ratio of 5:1 and the sol was left stirring for 30 min. The appropriate amount of TiO₂ (typically 0.495 g for a 0.5 g scale production) was added and the solution acidified with concentrated H₂SO₄ to pH 2. After 1 h of stirring, the slurry was filtered, washed with 1 L of distilled water and dried at room temperature for 48 h. The obtained catalyst was finally crushed with a pestle and mortar and sieved through a 60-mesh (0.250 mm) grid.

7.3. Results and Discussion

The Au/TiO₂ materials prepared by the ‘semi-continuous’ and ‘continuous’ methods were compared against each other (both catalytically and microstructurally) and also to a conventional sol-immobilized Au/TiO₂ catalysts made by the batch process. HAADF-STEM images reveal that, when the support suspension is directly mixed with the Au colloid inside the millifluidic system (i.e., via the continuous process), the particle size distribution was significantly narrower (see Figures 7.2 and 7.3). Furthermore, the supported Au NPs prepared utilizing the continuous set-up were on average much smaller (~ 4.3 nm) than their counterparts (~ 7.6 nm) made by the semi-continuous route. The supported Au nanoparticles
in both continuous and semi-continuous cases comprised a mixture of cub-octahedral and icosahedral morphologies. The supported Au NPs prepared by the batch approach, on the other hand, were found to have a mean size (Table 7.2) which was similar to that obtained by the *semi-continuous* set-up, but larger than that obtained from the *continuous* set-up. However, the *semi-continuous* and continuous methods produced nanoparticles with a slightly narrower particle size distribution (± 0.9 nm for semi-continuous and ± 1.3 for *continuous*) as compared to the *batch* produced materials (± 1.6 nm). Although the partial dispersion of nanoparticles on the TiO$_2$ support in the material prepared by using the *continuous* method is much better compared to that in the material made by the *semi-continuous* route (Figures 7.2 and 7.3), in both cases, it was better than that in the catalyst synthesized by the *batch* route. Considering this, the millifluidic reactor route proved to be a highly effective alternative method for the synthesis of small and uniform supported Au nanoparticles.
Figure 7.2. (a, b, c) Representative HAADF-STEM images of the Au/TiO$_2$ material prepared using the semi-continuous preparation set-up. (d) Particle size distribution derived from such HAADF-STEM images.
Figure 7.3 (a, b, c) Representative HAADF-STEM images of the Au/TiO$_2$ material prepared using the continuous preparation set-up. (d) Particle size distribution derived from such HAADF-STEM images.

In the millifluidic experimental set-ups developed at Cardiff University, the flow characteristic of the sol reactor was initially designed to be laminar in nature. Such a flow regime is almost always associated with a large variation in residence time due to the velocity variance along the cross-section of the channel (Figure 7.4). The distribution in residence time has already been reported to lead to a distribution of particle growth time and consequently poly-dispersity in the final particle size.$^{27,28}$ Such an effect was indeed noted
when we compared our materials to those made by a conventional batch process (Table 7.1). However, in order to limit such problems in our millifluidic system, we modified the continuous process of generating supported metal nanoparticles by introducing different 3D printed mixer and reactor geometries. The new investigated designs were two connections (Y-shape and I-shape) instead of the T-type and two reactors (plait-like and helix) instead of a straight tube which we hoped would introduce a more turbulent flow pattern (see Figure 7.5).

Our HAADF-STEM analysis (Figures 7.6 and 7.7) revealed a strong correlation between the mixer and reactor geometries and the mean metal nanoparticle size and broadness of the size distribution. The results clearly showed that, compared to the initial design (i.e., straight tube with T-shape mixer), with the helical reactor and I-shape connection metal nanoparticles can be generated having relatively similar mean sizes but with narrower particle size distributions (Figures 7.6 (b, d) and 7.7 (b, d). The opposite behavior was observed (i.e., poorer particle size control) when the Y-shape connection and plait-like reactor combination were employed (Figures 7.6 (a, c) and 7.7 (a, c)). We have learned through these experiments that the system design which provides better mixing between reagents will inevitably produce particles with more uniform size characteristics.
Figure 7.4. Diagram illustration of the laminar flow inside the channel of the millifluidic straight tube reactor after leaving the T-type connector.

Figure 7.5. Schematic diagram showing the different perfluoroalkoxy alkane (PFA) 3D printed connection shapes – namely a) T-shape, b) Y-shape, c) I-shape, and reactor types – namely d) helix and e) plait-like.
Figure 7.6. Representative HAADF-STEM images and corresponding particle size distribution histograms of the Au/TiO$_2$ materials prepared using different reactor geometries. [(a, c) - plait like with T-shape connector and (b, d) helix like with Y-shape connector].
Figure 7.7. Representative HAADF-STEM images and corresponding particle size distribution histograms of the Au/TiO$_2$ materials prepared in a straight tube reactor using different mixer geometries [(a, c) I-shape and (b, d) Y-shape].

Diffuse reflectance UV-vis spectroscopy was performed on the three colloids made by the semi-continuous, continuous and batch methods and the results (Figure 7.8) are in general agreement with the electron microscopy analysis. The surface plasmon resonance of the continuous-prepared Au colloid was very weak and broad compared to that of both the batch and semi-continuous derived materials, and the maximum intensity occurred at shorter wavelengths (536 nm for the continuous derived colloid, compared to 540 nm and 543 nm...
of the batch and semi-continuous derived colloids respectively). All the plasmon resonance features in Figure 7.8 (b) were shifted towards longer wavelengths compared to those in the absorption UV-vis spectra derived from the colloidal samples (Figure 7.8 (a)) due to interaction between the Au nanoparticles and the TiO$_2$ support.\textsuperscript{32} XPS analyses were also performed on the Au/TiO$_2$ supported catalysts prepared by the batch, the semi-continuous and the continuous methods (Table 7.2, and Figure 7.9). The Au(4f) spectra showed the presence of metallic Au, with Au4f$_{7/2}$ binding energy (BE) values in the 83.5-83.6 eV range which is in agreement with previous reports.\textsuperscript{33} No significant difference in Au4f$_{7/2}$ BE was detected amongst the three samples analyzed.

**Figure 7.8.** (a) UV-vis analysis showing the plasmon resonance with the batch, semi-continuous and continuous synthesis routes. The inset shows the entire UV-vis spectra. (b) Diffuse reflectance UV-vis spectroscopic analysis of the Au colloids synthesized by the batch, semi-continuous and continuous production methods. (Courtesy S. Cattaneo).
**Figure 7.9.** Au 4f\(_{7/2}\) XPS obtained from the Au/TiO\(_2\) and AuPd/TiO\(_2\) catalyst materials prepared by the batch, semi-continuous and continuous preparation methods. (Courtesy of Dr D. Morgan).

**Table 7.2.** Comparison between batch benchmark, semi-continuous and continuous derived Au/TiO\(_2\) and AuPd/TiO\(_2\) catalysts showing mean particle size, metal loading, and Au 4f\(_{7/2}\) and Pd 3d\(_{5/2}\) binding energies. (Courtesy of Dr D Morgan).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean NP size [nm]</th>
<th>Metal loading [wt%]</th>
<th>Binding energy [eV]</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DLS</td>
<td>DF-STEM</td>
<td></td>
<td>Au 4f(_{7/2})</td>
<td>Pd 3d(_{5/2})</td>
</tr>
<tr>
<td>Au/TiO(_2)-Batch</td>
<td>5.6 ± 1.7</td>
<td>5.6 ± 1.6</td>
<td>0.94</td>
<td>83.6</td>
<td>-</td>
</tr>
<tr>
<td>Au/TiO(_2)-Semi-continuous</td>
<td>6.0 ± 1.7</td>
<td>5.4 ± 0.9</td>
<td>0.92</td>
<td>83.7</td>
<td>-</td>
</tr>
<tr>
<td>Au/TiO(_2)-Continuous</td>
<td>5.4 ± 1.6</td>
<td>4.5 ± 1.3</td>
<td>0.96</td>
<td>83.6</td>
<td>-</td>
</tr>
<tr>
<td>AuPd/TiO(_2)-Batch</td>
<td>7.7 ± 2.1</td>
<td>2.1 ± 0.7</td>
<td>0.95</td>
<td>83.2</td>
<td>334.7</td>
</tr>
<tr>
<td>AuPd/TiO(_2)-Continuous</td>
<td>7.6 ± 2.3</td>
<td>2.0 ± 0.7</td>
<td>0.94</td>
<td>83.0</td>
<td>334.6</td>
</tr>
</tbody>
</table>
7.4. Continuous production of TiO$_2$ supported AuPd nanoparticles

Following the promising results obtained in the continuous synthesis of supported monometallic Au/TiO$_2$ particles utilizing millifluidic reactor technology, it was decided to explore further if the continuous process could be extended to generate supported bimetallic AuPd nanoparticles.

The optimized set-up using the straight tube reactor integrated with T-shape connection used for the continuous production of supported Au colloids was again utilized to prepare supported bimetallic AuPd NPs. The Au and Pd precursors were mixed together immediately before pumping into the apparatus to have a simultaneous reduction of the two metals by the NaBH$_4$ and thus generate alloy nanoparticles. The material obtained was compared against the benchmark AuPd catalyst made by a batch sol-immobilization process. From STEM analysis (Table 7.2), the mean size and particle size distribution were very similar at 2.1 ± 0.7 nm for the batch derived materials and 2.0 ± 0.7 nm for those made by the continuous process.

Both alloy catalysts were characterized by X-ray photoelectron spectroscopy (Table 7.2 and Figure 7.10). No significant surface compositional differences were detected between the two catalysts. The Au (4f$_{7/2}$) peaks were between 83.0-83.2 eV, which were lower than that of bulk gold (ca. 84.0 eV).$^{33}$ This decrease in BE is attributable to particle size effects and electronic interaction between the Au and Pd, confirming the presence of small AuPd alloy nanoparticles.$^{34}$ In accordance with these results, a slight downshift in energy was observed in the metallic Pd (3d$_{5/2}$) peak as well (from 335.0 to 334.6 eV). No Pd$^{2+}$ species were observed at ca. 337.0 eV, confirming the metallic state of the AuPd nanoparticles.
Figure 7.10. Pd 3d5/2 XPS of AuPd/TiO₂ catalyst materials prepared by the batch and continuous preparation methods. (Courtesy of Dr. D. Morgan).

The supported AuPd alloy nanoparticles prepared by continuous method was subjected to further characterization using STEM in order to demonstrate the ability of millifluidic systems to produce supported bimetallic nanoparticles with well-defined size, crystallinity and composition. The XEDS quantification has been achieved using the Cliff-Lorimer method described in detail elsewhere.\textsuperscript{35} Briefly, since the AuPd particles are generally below 10 nm in diameter, the absorption and fluorescence were ignored and therefore the composition can be expressed as eqn. 7.1:

\[
\frac{C_{Au}}{C_{Pd}} = k_{AuPd} \cdot \frac{I_{Au}}{I_{Pd}} \tag{Eqn. 7.1}
\]
where $C_{Au}$ and $C_{Pd}$ are the concentration of Au and Pd in the particle respectively. The $k_{AuPd}$ parameter is the so-called “k-factor” for this pair of elements. The $k$-factor was experimentally calculated from a sputtered standard 60wt%Au-40wt%Pd thin film to be $0.77 \pm 0.03$ with a 95% confidence level. With $k$ factors in hand, the composition can be derived for each spectrum. The error estimation is done using eqn 7.2:

$$
\Delta C_j = \sqrt{\sum_{i=1}^{n-1} [C_j(\Delta k_i) - C_j]^2 + \sum_{i=1}^{n-1} [C_j(\Delta I_i) - C_j]^2} \quad \text{Eqn 7.2}
$$

where $C_j$ is the resultant concentration of element $j$, and $C_j(\Delta k_i)$ is the error caused by $k$-factor estimation, and $C_j(\Delta I_i)$ is the error caused by the X-ray detection process, which can be modeled using Poisson statistics and therefore $\Delta I_i = 2(I)^{0.5}$ at 95% confidence level.

STEM experiments have revealed that all the supported AuPd NPs produced were random alloys with a particle size distribution from 1.5 - 5.0 nm (Figure 7.11). Interestingly PVA capped AuPd colloids prepared by conventional batch methods always showed a systematic composition variation with particle size, with the larger particles being Pd-rich and the smaller ones being Au-rich. However the PVA-capped AuPd particles synthesized by our semi-continuous method show a much more uniform composition irrespective of the particle size (Figures 7.12 and 7.13). The average measured Pd composition of $ca. 35$ wt%, corresponds well to a Au-to-Pd molar ratio of 1:1, which is in excellent agreement with the nominal value. Although several studies have been reported regarding the continuous production of metal nanoparticles, to the best of our knowledge, this is the first time that a supported bimetallic catalyst has been synthesised entirely in a continuous flow system. This new approach provides a reproducible and scaleable synthesis method which provides good
control over alloy particle size and more importantly, a superior consistency in alloy composition with particle size as compared to comparable materials made by the batch protocol. However, the underlying reason for this highly advantageous improvement in composition control still requires further investigation. For example, it was previously reported that the reactant mixing time is a key factor for controlling the composition of bimetallic nanoparticles.\textsuperscript{18} Therefore, perform systematic studies should be performed to investigate the composition of individual particles as a function of size for different residence times inside the reactor.

**Figure 7.11.** (a, b, c) Representative HAADF-STEM images of the AuPd/TiO\textsubscript{2} material prepared using the continuous preparation set-up. (d) Particle size distribution derived from such HAADF-STEM images.
Figure 7.12. Representative XEDS compositional analyses from individual AuPd (PVA) random alloy nanoparticles of different sizes prepared in the straight tube reactor integrated with a (PFA) T-shape connection.
Figure 7.13. STEM-XEDS composition versus particle size analysis for AuPd/TiO$_2$ material prepared using the continuous preparation set-up (blue data points) and by a conventional batch method (green data points).

7.5. Catalyst testing

The catalytic performance of the batch and continuous Au/TiO$_2$ and AuPd/TiO$_2$ materials were evaluated for the hydrogenation of various nitroarenes to aminoarenes. The nitroarenes studied were namely: 4-nitrophenol (4-NPH), 3-nitrophenol (3-NPH), 2-nitrophenol (2-NPH), nitrobenzene (NBZ), 4-nitroaniline (4-NAL), 4-nitrotoluene (4-NTL) and 4-nitrobenzyl alcohol (4-NBA). The hydrogenation of nitroaromatic compounds generates aminoarenes, important chemicals widely used in pharmaceutical industry as analgesics, antipyretics and chemotherapeutics, in agriculture as fungicides and pesticides and as intermediates in the synthesis of polymers (polyurethanes), dyes, pigments, photographic chemicals and corrosion inhibitors. The reduction of 4-nitrophenol (4-NPH) with NaBH$_4$, in particular, is a relatively simple reaction, and is frequently used by the research community as a model reaction to evaluate the catalytic activity of different Au catalysts. UV-vis spectroscopy was used to monitor the consumption of the nitroarenes in a cuvette.
For a typical measurement, the decrease in intensity with time of the substrate peak (typically at ca. 350-400 nm) was used to calculate the rate constant of the reaction (Figure 7.14). Since the NaBH₄ was present in excess, it was assumed that the reaction rate depended only on the concentration of nitroarenes, allowing us to approximate the kinetic data with a first-order rate law (as previously has been reported). This assumption was shown to be valid by the linear correlation achieved between the substrate consumption expressed in terms of \(-\ln(C_t/C_0)\) (where \(C_t\) and \(C_0\) are the concentration at the time \(t\) and the start of the reaction respectively) and the reaction time (Figure 7.15), allowing determination of the reaction constant \(k\) based on the kinetic equation (Eqn. 7.3).

\[
r = -\frac{dC_t}{dt} = kC_t
eqn. 7.3
\]

where \(k\) is the reaction rate constant, and its numerical value is the gradient of the linear correlation.

The catalyst prepared continuously showed higher activity compared to that of the batch produced material (Table 7.3). This increase in activity can be better quantified in terms of percentage difference \(\Delta k\), between the \(k\) values for batch and the continuous derived catalysts and, for the various substrates studied, being in a range of 6 – 50 %, with the 4-NBA and the NBZ respectively being the substrates with the least and the highest measured increase in activity. In the case of Au, the greater activity was attributed to the presence of smaller NPs, while, in the case of AuPd, the more uniform alloy composition and absence of Au-rich and Pd-rich nanoparticles in the catalyst was responsible for the difference in performance.
Figure 7.14. Typical UV-vis spectra of the catalytic 4-NPH reduction reaction (and more generally of NAR reduction reactions) over Au/TiO$_2$ made using the continuous preparation method with an excess of NaBH$_4$ at room temperature. Molar ratios of Au: NAR: NaBH$_4$ is 1: 2.5: 250. (Courtesy of S. Cattaneo).

Figure 7.15. Typical plots of $C_t/C_0$ and $-\ln(C_t/C_0)$ versus the reaction time for the reduction reaction of NAR. (Courtesy of S. Cattaneo).
Table 7.3. The catalytic activity of batch and continuous derived Au/TiO$_2$ catalysts towards the reduction of nitroarenes. (Courtesy of S. Cattaneo).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_{APP}$ [10$^3$ s$^{-1}$]</th>
<th>$\Delta k_{APP}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Batch</td>
<td>Continuous</td>
</tr>
<tr>
<td>4-NPH</td>
<td>12.6</td>
<td>16.8</td>
</tr>
<tr>
<td>4-NPH$^a$</td>
<td>24.4</td>
<td>28.9</td>
</tr>
<tr>
<td>3-NPH</td>
<td>8.9</td>
<td>10.3</td>
</tr>
<tr>
<td>3-NPH$^a$</td>
<td>15.2</td>
<td>17.0</td>
</tr>
<tr>
<td>2-NPH</td>
<td>6.2</td>
<td>11.6</td>
</tr>
<tr>
<td>2-NPH$^a$</td>
<td>11.0</td>
<td>14.1</td>
</tr>
<tr>
<td>NBZ</td>
<td>4.7</td>
<td>9.4</td>
</tr>
<tr>
<td>NBZ$^a$</td>
<td>9.8</td>
<td>13.5</td>
</tr>
<tr>
<td>4-NAL</td>
<td>35.7</td>
<td>42.9</td>
</tr>
<tr>
<td>4-NAL$^a$</td>
<td>38.7</td>
<td>46.2</td>
</tr>
<tr>
<td>4-NTL</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td>4-NTL$^a$</td>
<td>4.6</td>
<td>5.6</td>
</tr>
<tr>
<td>4-NBA</td>
<td>7.4</td>
<td>8.4</td>
</tr>
<tr>
<td>4-NBA$^a$</td>
<td>14.9</td>
<td>15.9</td>
</tr>
</tbody>
</table>

$^a$ bimetallic AuPd/TiO$_2$ catalyst was used for this reaction.
7.6. Conclusions

A very simple and easy to set-up millifluidic reactor has been developed at Cardiff University for the continuous production of supported Au and Au-Pd alloy nanoparticles in a homogeneous and controlled fashion. In this chapter, we have demonstrated the high efficiency of this approach in eliminating detrimental effects related to uncontrolled polydispersity and composition-related processes observed in the conventional batch synthesis of supported gold nanoparticles. To accurately optimize the process and produce Au NPs with small size and narrow particle size distribution, the effect of the method of introducing the oxide support into the Au sol (i.e., effect of using semi-continuous and continuous set-ups) was systematically investigated. STEM analysis reveals that Au NPs produced via the continuous process were smaller and had good mono-dispersity compared to those synthesized using semi-continuous process. STEM-HAADF images also showed that the mean metal nanoparticle size and broadness of the size distribution are dependent on the reactor and mixer geometries. It has been shown that the helical or straight tube reactor designs with an I-shape connector provides better mixing between reagents and will consequently generate metal nanoparticles having smaller mean sizes and even narrower particle size distributions. Importantly, the AuPd alloy nanoparticles prepared utilizing our developed and optimized millifluidic reactor, as confirmed by STEM-XEDS studies, had a much more uniform alloy composition compared to their counterparts made by the conventional sol-immobilization method. It is thought that the short residence time and high heat and mass transfer parameters which we cannot achieve in the conventional batch method were responsible for the superior control over size, particle size distribution and composition that millifluidic reactors display. The better material quality achieved with the
continuous apparatus was further demonstrated applying the catalysts produced in the model reaction of nitroarenes reduction to aminoarenes. With all the substrates tested, the catalyst prepared by the continuous method was more active than the benchmark material made by a conventional batch-type sol-immobilization process (up to 37% in the case of NBZ reduction). Finally, the potential to scale-up the synthesis method to the multi-gram scale is also evident with catalyst material productivities up to 3.6 g h\(^{-1}\) per reactor.

However, this work demonstrates that continuous flow millifluidic reactors represents a promising methodology for the efficient production of uniformly dispersed supported metal nanoparticles with having very reproducible structural and compositional characteristics. Furthermore, this technique should also be feasible for the industrial production of supported catalysts because they are easy to scale-up and cheaper compared to other continuous flow technologies. It can also potentially be applied in the production of a much wider range of supported mono-metallic and bi-metallic nanoparticles with desirable functional properties.

Furthermore, this method can in principle be adapted further for the production of more complicated nanostructures such as core-shell morphology nanoparticles. In Figure 7.16 the results of some of the preliminary STEM investigations are presented that were conducted to explore the ability of such millifluidic technology to generate particles with core-shell type structures. In particular, we were trying to prepare particles with a Au (core)/Pd (shell) morphology. To accomplish this goal, the Pd precursor and pre-made Au colloid were injected into the reactor and mixed inside a T-shape mixer. After that, the colloidal solution was collected for subsequent immobilisation and heat treatment to form the final product. The residence time was changed (by altering the reactor length) during the preparation stage to ensure the complete reduction of the Pd precursor on the surface of pre-formed Au
particles in order to generate Au (core)/Pd (shell) structures. Interestingly, initial atomic resolution HAADF-STEM images (Figure 7.16) show an occasional hint of core-shell structures being formed, although the process still requires considerable optimization. These initial results suggest that the tube length is not necessarily the limiting factor here in making core-shell type nanoparticles. Other factors such as the reducing agent and protecting agent employed should be varied in future experiments of this type.

![Figure 7.16](image)

**Figure 7.16.** Representative atomic resolution HAADF-STEM images acquired from Pd@Au core-shell particles continuously prepared using (a) a shorter length (15m) and (b) a longer length (75m) millifluidic reactor set-ups.
References


27. Gómez-de Pedro, S., Puyol, M., & Alonso-Chamarro, J. Continuous flow synthesis


Appendix A

5.6. Publication lists


Vita

Sultan Althahban was born on Jan 16, 1987 in Khamis Mushait; a city in the southern region of Saudi Arabia. He is the son of Mohammed and Mohmesah. He received his Bachelor of Science degree in mechanical engineering from King Khalid University Saudi Arabia in 2009. In 2010, he joined Jazan University as a teaching assistant in the department of mechanical engineering. Sultan got his Master of Science in Materials engineering from the University of Dayton in 2013. Presently, He is at Lehigh University working for PhD in materials Science and Engineering. Some of his research results have been already published in high profile journals such as Science and ACS Catalysis. After pursuing Doctor of Philosophy degree, he will go back to Saudi Arabia to work as assistant professor at Mechanical Engineering Department in Jazan University.