Preparation and Characterisation of Gold Nanocomposites for use as Heterogeneous Catalysts in Green Chemistry.

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Preparation and Characterisation of Gold Nanocomposites for use as Heterogeneous Catalysts in Green Chemistry.

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A Thesis Submitted to the Dublin Institute of Technology for the Degree of Doctor of Philosophy (PhD)

Supervised by Prof Hugh J. Byrne, Prof. Mary McNamara and Dr. James A Sullivan (UCD)

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May 2013
Abstract:

Three supported gold nanocomposites, gold on titanium dioxide (Au/TiO₂), gold on single walled Au/SWCNT and gold on carbon black (Au/P90) were prepared and systematically characterised using Scanning Electron Microscopy/Scanning Transmission Electron Microscopy/Transmission Electron Microscopy (SEM/STEM/TEM), Energy Dispersive X-Ray Analysis (EDX), X-Ray Diffraction Spectroscopy (XRD), Atomic Absorption Spectroscopy (AAS), (Nitrogen) N₂ adsorption, Ultra Violet-Visible (UV-Vis) absorption spectroscopy and Raman spectroscopy to probe the nanoparticle and support physical and chemical characteristics as well as the metal-support interactions. For all composites, the Au nanoparticles were found to be crystalline with a well-defined and narrow particle-size distribution centered between 4-10nm.

EDX analysis provided the initial confirmation of the presence of gold in the composite samples and XRD provided evidence of the formation of metallic gold nanoparticles on the surface of the supports. AAS was used to determine the % gold by weight in each of the three composites. N₂ adsorption analysis showed an increase in surface area of the supports both before and after deposition of gold, indicative of deposition of crystalline nanoparticles. UV-Vis absorption spectroscopy showed the existence of a gold plasmon resonance bond in the composite samples and by using the absorption maximum allowed estimation of the gold particle sizes to be determined. Raman spectroscopy showed the dampening in intensity of the characteristic bands in each sample due to the deposition of gold nanoparticles on the surface of the supports. In addition, evidence of changes in the
characteristics of the single walled carbon nanotube support spectrum was seen, most specifically charge transfer which lends some insight into the behaviour of the Au/SWCNT composite.

The activity and selectivity of the composites as heterogeneous catalysts for solventless aerobic selective oxidations of aromatic alcohols were examined in three reactions, firstly the aerobic oxidation of 1-phenylethanol as a probe reaction. For this reaction, both Au/TiO$_2$ and Au/SWCNT catalysed the reaction with $>95\%$ conversion and 100\% selectivity, whereas the Au/P90 resulted in a side reaction attributed primarily to the surface carbon acting as a reductant. Au/SWCNT gave the highest reaction rates. All composite materials were shown to be recyclable and the Au/P90 showed improved selectivity after the 2$^{nd}$ cycle of use. With these initial results, it was necessary to expand the activity and selectivity testing to more challenging reactions.

For the second reaction, selective oxidation of 2-phenylethanol, all three composites catalysed the reaction to the corresponding aldehyde all with a $\%$ conversion of $\approx 25\%$ and 100\% selectivity. However the aldehyde spontaneously trimerises to 2,4,6-tribenzyl-s-trioxane and requires an additional clean up step to distill the aldehyde. Again, the Au/SWCNT gave the fastest reaction rates. Finally, for the aerobic selective oxidation of benzylalcohol, all three composites catalysed the reaction to the corresponding aldehyde with $>99\%$ conversion. There are no other products formed which shows all three catalysts to be 100\% selective. The Au/SWCNT showed superior reaction rates in this reaction also.

Overall the novel composite material shows good initial promise for use as a heterogeneous catalyst in green reactions of importance in synthetic chemistry compared to the more typical industry standard catalysts based on these preliminary studies.
Declaration

I certify that this thesis, which I now submit for examination for the award of PhD, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award in any other Institute or University.

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Signature ___________________________ Date ____________

30/7/13
Acknowledgements

Firstly, thank you to my supervisors, Prof Hugh J Byrne, Dr James Sullivan and Prof Mary McNamara for taking the gamble on me. Your patience, time and help throughout the entire process from the conception to the bitter end have been immensely appreciated and I owe you all many beverages.

My gratitude to DIT for providing me with a full fee waiver to allow me to carry out this research part time alongside my full time role as an Instrumentation Support TO in the Focas Research Institute.

Thank you Luke for picking up the slack at work while I tried to get this thesis written but also for your help and friendship throughout my time in Focas so far. Profuse apologies for all the swearing at Sigma Plot and Word! Theresa and Andrew, thank you both for tolerating me in the office for so long. Your advice, chats and general banter helped make the tough times easier to handle.

Thanks to all who have gone before me, Gary, Mim, and the rest of the crazy crew in Focas, you all made the journey a bit more entertaining for sure. To Niina, Jim and the Porterhouse crew, thanks for the laughs at the end of bad days and the Amy Farrah Fowler moustaches!
Dad, you are long since gone but not forgotten. I hope you’d be proud of me making it this far, here’s hoping I can go further. Thank you for your genetics, specifically my stubborn nature! G aka the Mothership, although you have no idea what it is I do, thank you for always attempting to support me in my chosen career and for always being a listening ear. To Aunt Mary, you too are gone and much missed but thank you for having faith in me.

I have to mention my oldest friend, Auds, thank you for the many nights of beer fuelled debate and banter over the last 20 years or more, it’s your round mate 😊. Kudos to Prof Mark Baird from the University of Wales, Bangor for suggesting I pursue Environmental Chemistry back in 1996. Took me a while after the masters, but I did get back to it eventually!

Special thanks must be given to my father in law Buzz aka Mr Bravo Uniform Zulu Zulu. Those early morning mugs of Dean’s Beans and chats about all things science related in your house in woods in NH helped me to keep focused more than you will ever know.

Finally, to my wife Liz, what can I say except thank you for being in my life, for never wavering in your belief that I’d do it (even when I did) and for sticking with me through the peaks and the troughs. So, can we retire now?
Dedication

This thesis is dedicated to my wife Liz aka PVV, it’s all yours dear!
List of Abbreviations

α: alpha
AD: Arc Discharge
Ar: Argon
AAS: Atomic Absorption Spectroscopy
Au: Gold
β: beta
BET: Brunauer–Emmett–Teller
BJH: Barrett–Joyner–Halenda
CNT: Carbon nanotubes
Cu: Copper
CuO: Copper Oxide
CVD: Chemical Vapour Deposition
ddH₂O: doubly distilled water.
EDX: Energy Dispersive X-Ray
Fe: Iron
FT-IR: Fourier Transform Infra Red
He: Helium
HiPCo: High Pressure Carbon Monoxide
λ: Lambda
ml: millilitres
mm: micrometres
nm: nanometres
Ni: Nickel
Pd: Palladium
ppm: parts per million
%: percentage
PSD: Particle Size Distribution
Pt: Platinum
P90: Printex 90 Carbon Black
SEM: Scanning Electron Microscopy
STEM: Scanning Transmission Electron Microscopy
SWCNT: Single Walled Carbon Nanotube
TEM: Transmission Electron Microscopy
θ: Theta (Angle of Diffraction)
µl: microlitres
UV-Vis: Ultra Violet-Visible
XRD: X-Ray Diffraction
Y: Yttrium
Zn: Zinc
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Chapter 1: Introduction
1.1 Introduction:

The world of ‘nano’ has generated enormous excitement in the scientific community in recent years and is the subject of worldwide research across a range of scientific disciplines such as chemistry, physics, material science, biology and engineering. In essence, nanoscience is the study of the preparation, modification, characterisation and assembly of nanoscale materials and the exploitation of their properties for novel technological applications. Several well known scientists and professionals have tried to capture the essence of the impact of nanoscience [1, 2]. The engineer Ralph Merkle summed it up in his article in MIT’s Technology Review in 1997 called ‘It’s a small, small, small, small world’;- ‘What would it mean if we could inexpensively make things with every atom in the right place? For starters, we could continue the revolution in computer hardware right down to molecular gates and wires -- something that today's lithographic methods (used to make computer chips) could never hope to do. We could inexpensively make very strong and very light materials, such as shatterproof diamond in precisely the shapes we want, by the ton, and over fifty times lighter than steel of the same strength. We could make a Cadillac that weighed fifty kilograms, or a full-sized sofa you could pick up with one hand. We could make surgical instruments of such precision and deftness that they could operate on the cells and even molecules from which we are made -- something well beyond today's medical technology’ [3].

Materials are considered to be nanoscale if they have at least one dimension that is nanoscale and if their resulting properties are influenced by confinement to this scale. The
prefix nano comes from the Greek word nanos and/or the Latin word nanus, which translate as ‘dwarf’, and are considered to refer to $10^{-9}$ power or one billionth of a unit. As far as range is concerned, nano is considered to be between 1-100nm in size [4]. Figure 1.1 shows the size of several man made materials in direct comparison with nanomaterials.

Figure 1.1: Schematic of nano vs. micro in naturally occurring materials and manmade materials [5]

Richard Feynman is credited with predicting the present day field of nanoscience. In his 1959 lecture “There’s Plenty of Room at the Bottom” [6], he spoke about many fundamental concepts which are prevalent in nanoscience today. He made the suggestion
that the arrangement of materials on a small scale, atom by atom or molecule by molecule should be possible and that the manipulation of materials on a small scale could be used to make highly complex structures possessing many different properties. Despite Feynman’s vision, there was little experimental work in the field of nanoscience until the development of STM in 1981 and work on nanocarbons didn’t begin to take off until the mid 1980’s with the discovery of buckminsterfullerene C_{60} published in Nature in 1985 [7]. The intense interest in nanoscience/materials is generally attributed to the fact that nanomaterials possess unique size dependent optical, electronic, magnetic and catalytic properties in contrast to the bulk material, isolated atoms or molecules that make up the materials [8].

Nanotechnology is sometimes referred to as a general-purpose technology. In its advanced form it will have significant impact on almost all industries and all areas of society. It will offer better built, longer lasting, cleaner, safer, smarter products for the home, for communications, for medicine, for transportation, for agriculture, and for industry in general [8].

The U.S. National Science Foundation described the potential impact of nanotechnology very well in the following three sentences. ‘Imagine a medical device that travels through the human body to seek out and destroy small clusters of cancerous cells before they can spread. Or a box no larger than a sugar cube that contains the entire contents of the Library of Congress. Or materials much lighter than steel that possess ten times as much strength’ [9].

This would lead to the conclusion that nanotechnology will have a domino effect in that with the rapid developments being made in the area on a daily basis, the maturing of the technology will have advantages and unfortunately also some disadvantages.
1.2 Nanocatalysis:

Nanocatalysis is one of the most exciting subfields to have emerged from nanotechnology. The primary aim is the control of chemical reactions by changing the size, dimensionality, chemical composition and morphology of the reaction centre [10]. This approach opens up new possibilities for atom-by-atom design of nanocatalysts with distinct and tunable chemical activity, specificity, and selectivity.

As the primary purpose of a catalyst is to increase the speed of a given reaction, introducing a catalyst to a reaction increases its speed in one of three ways. It can lower the activation energy for the reaction, acts as a facilitator to bring the reactive species together more effectively or create a higher yield of one species where two or more species are formed. Depending on the application, nanocatalysts can be used in all three of these.

1.2.1 Why nanocatalysis?

As can be recognised from the name, a nanocatalyst is a substance or material with catalytic properties that has at least one nanoscale dimension either externally or in terms of internal structures. Specifically catalysts that can function at the atomic scale are designated nanocatalysts [11].

Nanocatalysts are more effective than conventional catalysts for two reasons. Firstly their extremely small size (typically 10-80nm) yields an excellent surface area to volume ratio.
In addition, when materials are fabricated on the atomic scale, they often achieve properties not seen with their macroscopic counterparts. Both of these reasons therefore account for the versatility and effectiveness of nanocatalysts.

1.3 Why SWCNT as supports and why Gold as the catalyst?

Carbon nanotubes have attracted significant interest as the basis for applications to new materials and device concepts in areas such as nanoelectronics and solar cells due to their unique structural, mechanical and electronic properties [12, 13]. For example, both single walled and multi walled carbon nanotubes have been proposed as substrates for biological devices [14]. Metal filled carbon nanotubes have also been shown to have promising applications in heterogeneous catalysis [15] and multi walled carbon nanotubes (MWCNT) have been used as catalyst supports in thermal and electro catalysis [16,17]. In addition, MWCNTs have been successfully used as supports for electrocatalysts [18] and gold nanoparticles supported on SWCNT films have already been shown to be promising electrochemical sensors [19].

However, as is now widely known by researchers in the area, SWCNT are notoriously difficult to solubilise, rendering conventional methods of composite preparation difficult. However, Dai, et al have demonstrated a directed reduction route of Au$^{3+}$ onto the sidewalls of SWCNT without requiring further chemical processing [20]. The downside to this method however is the broad diameter distribution of the gold nanoparticles. By streamlining this method, it is possible to produce Au nanoparticles with a narrow particle distribution. SWCNT as a support, provide a template of narrow diameter distribution
fibres which allow the constrained growth of metal nano-particles to a narrow diameter range.

Several applications for carbon nanotubes have been considered across the scientific disciplines, including catalysis [21, 22]. Au catalysts have been an area of intense research activity in recent times [23-28]. One area in particular where such catalysts have found application is in environmentally friendly oxidation reactions, e.g. in the selective oxidation of CO from H₂-containing streams [29, 30] and in selective oxidations using O₂ as an oxidant [31-36].

In general, oxidation reactions play an important role in the synthesis of pharmaceuticals, bulk and fine chemicals. However, classical oxidation reactions generally involve the use of chemicals and reaction systems that are not environmentally friendly, (e.g. permanganate and other acidified transition metal systems) [37, 38]. The reagents and waste products produced can be toxic and difficult to remove from process streams and are thus undesirable. A “greener” alternative to such processes is aerobic oxidation using a heterogeneous catalyst. This option is preferred as O₂ is inexpensive, non-toxic and produces water as the sole by-product. However, commonly employed catalyst systems are often prepared/operate at high temperatures requiring significant modifications to the synthetic design. Nanoparticulate materials are an alternative to such conventional catalysts. However, their characteristics and activity can further depend on their support substrate. Haruta has demonstrated for example that the catalytic properties of gold are dependent on both the particle size and the support [39].
Au particles of diameter range ~7.5 nm – 350 nm supported on carbon have been investigated previously in the oxidation of glycerol [40] and the system was shown to be selective for the formation of glyceric acid. Prati, et al [41] were able to improve this selectivity (defined in this case as the ability of the catalyst to promote the formation of a particular compound from a reaction when several products are feasible) considerably by optimizing both the catalyst preparation method and the reaction conditions. Most notable however is that the principle developments were based on control of particle size.

A further area in which supported gold catalysts have been used is in environmentally friendly oxidations such as the liquid-phase oxidation of 1-Phenylethanol to Acetophenone. Notably, nano Au has been reported to have superior performance to nano Pd in this reaction [42]. Nano Au supported on mixed metal oxides has also been tested in this liquid-phase oxidation by Baiker, et al [43, 44] and the system has been shown to be somewhat suitable for this type of reaction but the performance appears to be very dependent on Au particle size which in turn is critically dependent on the support mechanism.

The ability to control the size and diameter range therefore has potential to provide routes towards optimisation of the catalytic process.

In this work, gold nanocatalysts (d_{Au} = ~4-15nm) have been prepared on three different supports, SWCNT as a novel support as well as the more classical catalyst scaffold materials carbon black and TiO_{2}. The materials are fully characterised using a number of techniques in an attempt to understand the metal-support interactions and the materials are tested in two reaction systems to determine their suitability as heterogeneous catalysts.
1.4 Aims and Objectives:

The aims of this research are three fold

- To prepare and characterise nanocatalysts using a novel support system (SWCNT)
- To test their suitability as heterogeneous catalysts in environmentally challenging reactions.
- To compare them to classically supported catalysts (C and TiO₂)

1.5 Thesis outline:

In Chapter 2, catalysis will be introduced and discussed in some detail and an introduction to SWCNT and their potential applications is provided. In Chapter 3, a more detailed discussion on heterogeneous catalysis involving selective and aerobic oxidations. Chapter 4 provides details of the preparation of the three nanocomposite materials, information on the spectroscopic, microscopic and analytical methodologies used to characterise the materials and discusses the results of the characterisations in detail. In Chapters 5 and 6, the studies of the suitability of the composites as heterogeneous catalysts in three reactions that are important in organic synthesis but are generally undertaken with non green methodologies are outlined. In Chapter 7, all of the results are brought together in discussion form and several conclusions drawn. Then finally, conclusions and outlines scope for further work that could be carried out in the area.
References:


Chapter 2:

Introduction to Catalysis, Gold and Carbon
2.1 Introduction to Catalysis

It is estimated that approximately 90% of all commercially produced chemicals utilise catalysts at some stage in the production process [1]. There are several areas in which catalysts play an important role including food processing, fine chemicals, bulk chemicals, energy processing and the environment. This means that catalysis is a vital technology in today’s world.

In the early 19th century it was observed that a number of chemical reactions did not occur without the presence of trace amounts of materials that do not appear to be reactants or products. The phenomenon of catalysis occurs very widely across the living world. For example, all living things depend on the action of biological catalysts called enzymes that usually consist of proteins which often contain metal based moieties such as the haem molecule which is found in blood cells [2]. Indeed, it could be proposed that all synthetic catalysts strive to mimic these powerful biological materials. However, we as humans had learned to utilise natural catalytic processes some time prior to the turn of the 19th century, eg natural yeasts were used to ferment fruits to prepare alcoholic beverages several millennia ago, this too is the work of enzymes! Davy and Berzelius carried out more systematic studies in the area during the 1800’s and then in the late 19th century [3] the application of catalysis accelerated (pun intended) in industrial processes. Probably the most well known of these developments is the Haber process for ammonia synthesis which was developed in Germany prior to World War I [4].
2.2.1 What is a catalyst/catalysis?

There have been several definitions of what a catalyst is over the years and in turn several misunderstandings regarding the nature of catalysis. The word catalysis comes from the Greek words meaning ‘a breaking down’ and this term was first used by Berzelius [2]. In its most concise form, a catalyst is a substance that facilitates a chemical reaction without itself being consumed during the reaction. However, this is an oversimplification and the current views will be explained in more detail later in this chapter.

Industrial catalysis is generally divided into two types, heterogeneous and homogeneous. Heterogeneous catalysis is where the catalyst and the reactant are in different physical phases whereas homogeneous is where both are in the same phase [5]. A large number of industrial processes are heterogeneously catalysed. In general in heterogeneous catalysis knowing the nature of the surface/interface is essential. This is important for assessing the efficiency of the process and even the smallest amount of additives can poison or promote the reaction in which the catalyst is used.

A well known example of heterogeneous catalysis is the aforementioned Haber Bosch process of ammonia synthesis from gaseous N\textsubscript{2} and H\textsubscript{2} over a solid Fe-containing catalyst.

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

Figure: 2.1: Production of Ammonia
A simple example of homogeneous catalysis is the destruction of ozone by Cl radical atoms.

\[
O_3 + Cl \rightarrow ClO + O_2 \\
ClO + O \rightarrow Cl + O_2
\]

Figure: 2.2: Ozone destruction

In addition to the two main types of industrial catalysts, there are is a ‘third’ group, biocatalysts. A biocatalyst is a substance such as an enzyme or a hormone that speeds up a biochemical reaction. Yeast is an example of such a catalyst and is used amongst other things to convert sugar into ethanol fuel [6] for the biotechnology industry. Mechanistically speaking, biocatalysts are somewhere in between heterogeneous and homogeneous catalysts but because of their use in nature they are categorized in their own group. Biocatalysts are often much more efficient that conventional heterogeneous and homogeneous catalysts. For example, a typical enzyme completes about 1000 catalytic cycles in 1 second compared to between 100-10000 per hour for typical synthetic heterogeneous and homogeneous catalysts.

Further advantages of using a biocatalyst over conventional chemical catalysts include somewhat shorter synthetic routes as well as milder reaction conditions. Many enzymes are now available as isolated products for use in reactions in water and organic solvents [7]. However the stability of these materials tends to be a stumbling block in demanding industrial processes. There is a significant amount of research underway in this area.
especially in genetic engineering and it is probably safe to assume that biocatalysts will be major players in industrial catalytic processes in years to come.

2.2.2 The Catalytic Cycle

The catalytic cycle is defined as a multistep reaction mechanism that involves a catalyst and is used to describe the way in which a reaction progresses. The schematic of Figure 2.3 shows a general representation of a catalytic cycle. This type of cycle is particularly common in biochemical reactions, such as enzyme interactions but can be applied to any catalysed reaction. A more detailed description of the steps involved in a heterogeneous reaction is described in Chapter 3.

Figure 2.3: Schematic of a generic catalytic cycle [5]
2.3 Catalytic Materials

As previously discussed, catalysts can have a number of forms which is thus reflected in the quantity of materials produced, ranging from solid materials to biological enzymes, liquid coatings on surfaces and also gas molecules. The most commonly used materials for solid phase catalysts are metals and oxides of various types. Metals generally have very high surface energy and are therefore very active for specific types of reaction. More often than not, metal based catalysts are a combination of two or more metals combined to make a mixed metal oxide system with improved activity and selectivity for a desired reaction or class of reactions.

In addition, many mixed metal oxides are not thermally stable in the high surface area forms in which they are required for use, and so they are often prepared as small particles attached to a support material. This support material provides the high surface area required and helps to reduce sintering of the metal particles. Sintering is the welding together of small particles by applying heat at temperatures below the melting point [8]. Also in many cases, the size and shape of the particles is important for getting optimum performance from the catalyst for specific reactor types as well as reaction dynamics. These properties along with the high surface area and porosity all have to be taken into account when preparing a catalyst.
2.3.1 What makes a good catalyst?

There are a number of properties that must be considered when designing a catalyst for a particular use [9]. Correct kinetic reaction parameters are considered to be the foundations of catalyst production. This in addition to relatively high surface area for easy exposure to the reactant and durability of the catalyst which in turn is important for the cost effectiveness of the process are vital in catalyst development protocols.

The most essential of all of the overall catalyst properties are surface area and its close relative porosity. There are three types of pores defined by IUPAC [10] as follows:

- Macropores – pores of ≥ 100nm
- Mesopores – pores of ≥ 2nm and ≤100nm
- Micropores – pores of ≤ 2nm

2.3.1.1 Catalyst Poisons and Inhibitors

It is worth noting at this stage some of the problems that can occur during catalytic processes. A material that blocks active sites on the surface of a catalyst, thus reducing the reaction rate or the ‘usefulness of the catalyst is known as a poison. Poisons are generally electron accepting elements such as C and S which react with another compound that bonds chemically to its active surface sites. An example of this is when in the Raney Ni catalyst which has reduced activity when in combination with mild steel [11].
In contrast, an inhibitor can reduce the effectiveness of a catalyst in a catalysed reaction (either a non-biological catalyst or an enzyme). For example, if a compound is so similar to (one of) the reactants that it can bind to the active site of a catalyst but does not undergo a catalytic reaction then that catalyst molecule cannot perform its job because the active site is occupied [12]. When the inhibitor is released, the catalyst is again available for reaction. Inhibition should be distinguished from catalyst poisoning. An inhibitor only hinders the working of a catalyst, whilst in poisoning the catalyst is destroyed by an irreversible reaction with a chemical substance (the active catalyst in the latter case may be regained by a separate process).

2.3.1.2 Catalyst Promoters

A material that enhances the activity of the catalyst by improving reactions at adjacent sites is known as a promoter. Promoters are generally electron donating elements such as La, Cs and K. Promoters can cover up surface to prevent production of a mat of coke, or even actively remove such material (e.g. rhenium on platinum in platforming). They can aid the dispersion of the catalytic material or bind to reagents [13].
2.4 Preparation of Catalysts

There are several types of preparation methods for catalysts and all of these are thoroughly referenced in the literature [14, 15]. The final catalytic properties of materials are strongly affected by every step of their preparation as well as the quality of the raw materials. Choosing a method for preparation of a catalyst is entirely dependent on the physical and chemical characteristics required in its final composition. In order to define a method for catalyst preparation, it is often useful to use the ‘unit operations’ classifications [16]. These operations are usually classified in three broad categories, bulk catalysts and supports, impregnated catalysts and mixed agglomerated catalysts.

Bulk catalysts are generally comprised of active substances, an example of which is silica-alumina for hydrogen cracking. Impregnated catalysts are usually attained from preformed supports by impregnation with the active phase. Finally mixed agglomerated catalysts consist of catalysts obtained by mixing active substances with a powdered support or precursor and then agglomerating the mixture.

In order to give a more detailed breakdown of these broad categories, the use of the ‘unit operations’ classifications is very helpful. In essence, a unit operation is a basic step in a process. A good example of this is in milk production [17]. Homogenisation, pasteurisation, chilling and packaging are all unit operations connected to make the overall process. Using this type of naming system provides an easy manner by which to detail the various steps involved in each catalytic preparation method.
The most commonly used methods of production for catalysts are described next, which are mainly support based catalysts.

2.4.1 Preparation Methods

Impregnation

Preparation of a supported material can be carried out using a high surface area porous material, for example alumina and then dosing it with the active phase precursor. Impregnation can be done in a number of ways such as adsorption of an active phase from solution by adding the support to a solution of the active constituent. Modifications to this method can be made by for example adjusting the pH, but in general the catalyst has to be separated by filtering which can lend to wastage [18].

In order to control this type of method, the incipient wetness technique can be utilised. In this case, the active phase in solution form is added to the dry powdered support until the mixture becomes tacky, whereupon the pores of the support are filled with the liquid [19]. The material is then dried and calcined at a required temperature which allows decomposition of the precursor active phase to occur leaving behind the final active phase. Depending on the desired material, there can be a number of washing and drying steps added at this stage.

Slurry Precipitation

The catalyst can be directly prepared from the active components by mixing. An example of this is the addition of MoO_3 to water to make slurry before impregnating it onto the
support, drying and calcining at a high temperature which allows ionic interdiffusion to produce a rutile mixed metal oxide [20].

**Deposition-Precipitation**

In this method, the support material is exposed to a solution of the precursor material which is generally in salt form. The pH is then increased by the addition of a base and in some cases the mixture is heated to allow deposition of the oxidised precursor onto the support [21]. This type of method is often used to make highly active Au/TiO$_2$ catalysts and is utilised in this body of work.

**Fusion**

The best known version of this method of production is the ammonia synthesis catalyst for which magnetite, potash, lime and alumina are fused at high temperature (~1800K/1527°C) in a melt. The melt is then cooled and broken into irregular pieces of ~5mm diameter which produces a low surface area material with no obvious pore structure. Development of the material then occurs by reducing the Fe$_2$O$_3$ *in situ* in a reactor to produce metallic Fe which subsequently develops pores where the H$_2$ penetrates the material in the reduction process [22].

**The Raney Method**

This is a very famous method developed in 1926 by Murray Raney, an American engineer and has been widely used across mainly industrial processes but most specifically for hydrogenation reactions. In this method, two metals are mixed by melting the active metals...
or alloys, in this case Ni and Al in a crucible and treating them with concentrated sodium hydroxide which dissolves most of the Al out of the alloy leaving behind a highly porous large surface area material which gives high catalytic activity [23]. This methodology is also applied to other metal alloys.

*Physical mixing*

This involves dry powders of the desired materials being mixed and calcined to high temperature [24]. This can often form a mixed phase by ionic interdiffusion (as in the slurry precipitation method). However, more often than not, this method, despite its crudeness, will produce materials with decent characteristics although not as good as more carefully designed methods.

*Washcoating*

This is the largest scale industrial catalyst preparation method and is used in the automotive industry for car catalysts. A monolith support is the component of these catalysts which provides good thermal shock resistance but allows the exhaust gases to flow at extremely high velocity [25]. The active phase only coats the exterior area of this support but a large area is coated by a first coating of what is usually a highly porous alumina called a ‘washcoat’ layer. The final catalyst is produced by dipping the monolith into a mix of active components, for example Pt, Rh and Pd salts followed by drying and calcining.
**Pelleting**

This is generally the final step in the production of the macroscopic forms, used on the plant floor, of many industrially based heterogeneous catalysts. This is ordinarily done in one of two ways, either by high pressure compaction in a pelleting machine or alternatively by extrusion of a plasticised version of the catalyst powder [26, 27]. Various shapes and sizes can be made by engineered designed extrusion formers. This type of engineering is utilised in the manufacture of automotive extrusion for door seals, bonnets, etc.

Following on from this general introduction to catalysis, there now follows a further short discussion on the use of gold as an active ingredient, a general overview of the elements gold and carbon Then the final sections provide an introduction to single walled carbon nanotubes and a short discussion of the use of carbon in catalysis.

2.5 Why use Gold as an active ingredient?

Since gold is considered to be one of the most unreactive metals, it would seem counterintuitive to try to use it as a catalyst. Yet thankfully many well respected scientists thought otherwise. In the past, it has been studied extensively for catalytic potential by Bond [28, 29], Parravano [30], then reviewed by Wachs [31] and Schwank [32, 33]. Following on from this, Haruta and his co workers [34] made a significant breakthrough in the area when they successfully deposited ultra fine Au particles onto the surface of select metal oxides and noted the dramatic change in the chemistry of the material.
Subsequent research in this area has led to a number of publications showing the highly reactive nature of Au in the area of catalysis [35-38]. However in order to understand why Au is such a powerful active ingredient in this area, it is necessary to understand the properties of gold.

2.5.1 The Chemical and Physical Properties of Gold

Prior to discussing the catalytic abilities of gold, it is imperative to understand the significance of its properties. It has been known for a long time that there is a significant relationship between chemisorption of simple molecules on metals and the stability of the analogous bulk compounds [39]. This is due to the physical property, the latent heat of sublimation. In order for catalysis to take place, chemisorption must occur in advance and so it is recognised that many properties of the metal are intrinsically related. Thus catalytic activity cannot be attributed to one single metallic property so this in turn means that all of the properties of Au must be taken into consideration.

2.5.2 General Physical Properties of Gold

Gold (Au) occurs at levels of approximately 0.004ppm of the Earth’s crust both in its elemental state and in telluride (calaverite) ores. It is extracted via the formation of the linear anion \([\text{Au(CN)}_2]^-\). It is yellow in colour, is soft, ductile, malleable and resists atmospheric oxidation by almost all acids [40]. It is generally combined with other metals to provide alloys of increased strength. Its main uses are in the manufacture of jewellery
and coins. In latter years, it has been used in the electronics industry and in the chemical industry and also as a microbiological stain. As far as aqueous solutions are concerned, gold is generally utilised in salt form, typically HAuCl$_4$ which is then reduced from its typical Au$^{3+}$ state to Au$^0$ and it is in this nanoparticulate form that it is at its most active. The electronic configuration of Au is [Xe] 4f$^{14}$ 5d$^{10}$ 6s$^1$ and its ground state electron configuration is shown in Figure 2.4 [41].

![Figure 2.4: Electronic configuration of elemental Au [41].](image)

The chemistry of gold is determined by two factors, firstly the relative ease of activation of the 5d electrons and secondly its need to acquire a further electron to complete the 6s$^2$ level and thus not lose the one it already possesses. These in turn ensures that Au has a larger electron affinity and higher 1$^{st}$ ionisation potential than copper and silver and additionally accounts for the ease of formation of the Au$^{-1}$ and Au$^{III}$ states respectively. Gold’s electronegativity is not too dissimilar to that of the halogens, sulphur and iodine so it has
some properties of the halogen group [42]. In addition its electrode potential is very high for a metal ($E^0 = +1.691V$). All of these properties ensure that Au is quite a unique element in its own right.

2.5.3 Bulk Properties

Gold crystallises in an fcc (faced centred cubic) lattice form. This means it has lattice points on the faces of the cube that each gives exactly one half contribution in addition to the corner lattice points, giving a total of 4 atoms per unit cell ($\frac{1}{8} \times 8$ from the corners plus $\frac{1}{2} \times 6$ from the faces) [43]. In complexes and compounds, Au$^+$ atoms are smaller than those of Ag$^+$. In some cases, for example, density the properties of gold reflect its higher atomic mass compared to Cu and Ag, but in several, this trend is reversed. Examples of these include melting point and heat of sublimation which are almost the same as those of Cu. There is only one naturally occurring isotope of gold and thus its atomic mass is very precisely known (196.9665). It also has a stronger M-M bond owing to its shorter than expected length in comparison to Ag and Cu which is of advantage when studying the coordination state of Au in complexes.

In addition, the optical absorption of Au occurs in the visible region of the spectrum which is due to the lowering of the gap between the 5d band and the Fermi level. Au is also very pliable; ~1g can be pressed into an area of ~1m$^2$ and it forms intermetallic compounds with many other elements [44].
2.5.4 Single Crystal Surface Structure

If a single crystal of a metal is cut parallel to one of the atomic layer, it exposes a surface that contains atoms and their locations are defined by a Miller Index. For an fcc metal such as Au, there are 3 low index planes, Au (100), Au (110) and Au (111).

![Structures of the surfaces of gold](image)

Although the surface of bulk gold does exhibit some catalytic properties, highly dispersed forms will tend towards more effective and specific activity which will quite clearly increase when the mean particle size decreases. Small particles tend to be very energetic and thus when their sizes are reduced, the proportion of atoms at or close to the surface that are not completely bound to their neighbours increases. The lower the mean coordination number of atoms in a particle, the more idle orbitals there will be and therefore the greater their effect on the properties of said particles [45].

There are several ways of preparing small particles of gold. Some of these include deposition of clusters onto a support, formation of clusters in the gas phase, chemical vapour deposition (decomposition of a volatile compound at or near the surface of a support), decomposition of atoms onto a support where they aggregate and form a model
catalyst, preparation of colloidal gold and the traditional methods of preparing supported metal catalysts as discussed in section 2.4.1 [18-27].

This part of the chapter has introduced catalysis and use of gold as an active ingredient. The next section will introduce carbon and Single Walled Carbon Nanotubes and an introduction to explain why they were chosen as supports for making catalysts. Following on from these, in Chapter 3, there is more discussion on gold nanoparticles in catalysis, focusing specifically on oxidation reactions.

2.6 The element carbon

Carbon is considered to be one of the most versatile elements in the periodic table. This is due to its strength and the number of bonds it can form with many other elements. The wide diversity of the bonds and subsequent geometries allow for the existence of structural and geometric isomers as well as enantiomers. These are found in a significant number of large and complex structures that permit an endless number of organic molecules to be formed [46].

The properties of carbon are a direct result of its electronic configuration. There are six electrons in a carbon atom shared evenly amongst the 1s, 2s and 2p orbital’s (shown in Figure 2.6). Because the 2p atomic orbitals can hold up to six electrons, carbon can make up to four bonds but the valence electrons involved in the bonding occupy the 2s and 2p orbitals. Covalent bonds are formed mixing of the 2s orbital with one or more of the p orbitals to form hybrid sp orbitals. This can happen in three different ways depending on
the number of orbitals involved. In the initial type sp\(^1\), the 2s orbital mixes with one of the 2p orbitals and form two singularly occupied sp orbitals in a linear geometry, and two singularly occupied, orthogonal 2p orbitals. In the second type, the 2s orbital hybridises with two 2p orbitals and forms three singularly occupied sp\(^2\) orbitals on the same plane, but separated by a 120° angle and the remaining singularly occupied p orbital projects above and below the plane. The final type sees the 2s orbital hybridise with all three 2p orbitals, resulting in a tetrahedral arrangement of the sp\(^3\) orbitals with a separation angle of 109.5° [47]. A graphical representation of each of these hybridisation types is shown in Figure 2.7.

Figure 2.6: Electronic configuration of carbon [40]

Figure 2.7: Hybridisation types in carbon [48]
Carbon can bind in a pi (π) bond and a sigma (σ) bond when forming a molecule. The molecular structure will depend on the level of hybridisation of the carbon orbitals. An sp¹ hybridised carbon atom can make two σ bonds as well as two π bonds, sp² hybridised carbon forms three σ bonds and one π bond, and an sp³ hybridised carbon atom forms four σ bonds. These variations in hybridisation allow carbon to adopt a range of shapes from tetrahedral to planar to linear [48].

2.6.1 Allotropes of carbon

There is significant debate about the number of allotropes of carbon that exist, the literature stating anywhere between three and eight. Regardless of the ongoing discussion on this topic, there are three definitive allotropes accepted by the scientific community [49]. They are graphite, diamond and buckminsterfullerene (C₆₀) also incorporating its close relatives (C₇₀, C₇₆, C₈₂, C₈₄, etc). It also appears from recent literature, that it is also well accepted that carbon nanotubes are a fourth allotrope of carbon [50-52]. Regardless of this current lack of formal acceptance, the study of CNT has become more and more independent from the fullerenes.
Diamond has a crystalline structure in which each sp\(^3\) hybridised carbon atom is bonded to four others in a tetrahedral geometry. This crystalline network gives diamond its hardness and very good heat conduction properties. The sp\(^3\) arrangement also accounts for its insulation abilities and its optical transparency [54]. Graphite is made up of layered planar sheets of sp\(^2\) hybridised carbon atoms bonded together in a hexagonal network. The geometrical arrangement of graphite changes its properties significantly from those of diamond. In addition, each carbon atom in a graphite sheet is bonded to three other atoms allowing the electrons to move freely from an unhybridised p orbital to another forming an endless delocalised π bond network which thus provides the conductive property of graphite [55]. Graphene is the sheet form of graphite which is considered to be the building block for many of the allotropes of carbon.
Fullerenes are another allotrope of carbon that consist of a group of spherical or cylindrical molecules with all sp$^2$ hybridised carbon atoms. The cylindrical form of the fullerene family, carbon nanotubes are now considered to be a fourth allotrope of carbon because of their mixed hybridisation [56].

2.7 Introduction to Single Walled Carbon Nanotubes

Carbon nanotubes were discovered in multiwall form by an electron microscopist Sumio Iijima in 1991 and then two years later he discovered that they exist in single walled form [57]. A single walled carbon nanotube (often abbreviated to SWNT or SWCNT) can be considered to be a rolled graphene sheet, capped at each end by a hemispherical fullerene and the way in which it is rolled determines its fundamental properties. [58]. Figure 2.9 shows the three forms a SWCNT can take, depending on its chiral angle.
The chiral angle is used to classify carbon nanotubes as it determines the electronic properties. All armchair nanotubes are expected to be metallic, whereas one third of zig-zag and chiral nanotubes should be metallic and the remainder semi-conducting. A combination of different chiralities and diameters will result in hundreds of differing nanotubes, all with their own distinct properties. SWCNT are a very distinctive class of molecules that are known to exhibit unique properties [60]. For this reason, since their discovery, SWCNT have been proposed and used for a number of applications across a wide range of scientific disciplines including electronics, optics and nanotechnology [61-65].
2.7.1 Synthesis of Single Walled Carbon Nanotubes

There are several ways in which single walled carbon nanotubes can be synthesised and the next section gives an overview of the synthetic methods.

2.7.1.1 Arc discharge synthesis

This method was the first one to be recognised for the production of both multi walled and single walled carbon nanotubes [66]. Essentially it uses a low voltage (~12-25V), high current (~50-120 amps) power supply to create an arc across a gap between two graphite electrodes of ~5-20 mm in diameter. An inert gas, He or Ar is used as the atmosphere for the reaction at a pressure of between ~100-1000torr. By adding a catalyst (modern methods employ Ni:Y as a precursor mixed metal alloy applied to the band), SWCNTs are the predominant materials formed on the cathode whereas the initial methodology produced large percentages of soot and fullerenes [68]. The gas ratio can be modified to control the diameter of SWCNTs [67]. Several metal catalyst compositions produce SWCNTs, but the most widely used current method (Ni:Y) and has been shown to produce up to 90% SWCNT with average diameters between 1.2-14 nm [68]. SWCNTs made using this method are relatively inexpensive compared to other synthesis techniques, which is a distinct advantage. Figure 2.10 shows a schematic for the arc discharge method.
2.7.1.2 Laser ablation synthesis

This technique involves using a 1.2% ATM Co/Ni catalyst with a graphite composite target housed in a 1200 °C quartz tube furnace with an inert atmosphere of ~500 torr of He or Ar. The target is vapourised by a laser pulse which is usually either a pulse-pumped or a continuous-working laser [70]. The metal particles catalyse the growth of the SWCNTs in the plasma plume and the nanotubes and by-products are formed. They are all then collected by condensation on a cold finger at the end of the furnace. Figure 2.11 shows the set up for this type of synthesis. The yield using this method varies from 20-80% of SWCNTs by weight with by-products including amorphous carbon and various members of the fullerene family. The diameter distribution of SWCNTs is generally between 1.0-1.6 nm [71].
2.7.1.3 Thermal synthesis

Thermal synthesis is a generalised term for a number of medium temperature production methods [73], the two most common of which are chemical vapour deposition (CVD) [74] and high pressure carbon monoxide synthesis (HiPCo) [75]. In its simplest form, this method utilises carbon feedstock which is flowed over transition metal nanoparticles at a temperature between ~500-1200 °C and the resulting reaction produces SWCNTs. Figure 2.12 shows a schematic of a CVD furnace [76]. With this method, diameters of between ~0.4-5 nm can be produced and the yield can exceed 99% depending on the feedstock, catalyst and operating conditions [77]. Owing to this, this method is being researched more extensively and there are several off shoot methods directly related to it. However, it is...
beyond the scope of the work in this thesis so therefore is not discussed in any further detail.

Figure 2.12: Schematic of a CVD furnace [76]

In contrast, the HiPCo process, although related to the CVD method, has become well known worldwide for production of narrow diameter range carbon nanotubes [78]. It operates on the basis of in situ formation of a metal catalyst when Fe(CO)$_5$ or Ni(CO)$_4$ are injected into a reactor at a temperature between ~900°-1100 °C at a pressure of ~30-50 ATM in the presence of a stream of carbon monoxide gas (CO). Yields of ~97% have been reported and the diameter distribution is ~0.7-1.1 nm. Just as with the CVD method, reactor conditions can be tuned to modify the nanotube diameter distribution [79]. Figure 2.13 shows a schematic of this process.
2.8 Properties of Single Walled Carbon Nanotubes

There has been much discussion on the exceptional properties of SWCNT some of which were predicted theoretically before their discovery [80, 81]. Since then, there has been a large volume of papers published providing detailed analysis and discussion of their properties. Most of these have focused on their physical and electronic properties [82-85]. For the focus of this work, a discussion on their basic properties is provided but with a more detailed spotlight on their chemical properties in the next section.
2.8.1 General Properties of Carbon Nanotubes

Carbon nanotubes have a high content of sp$^2$ hybridised carbon which leads to the two dimensional order in its structures. As previously mentioned, SWCNT can be considered to be rolled graphene sheets that look not unlike chicken wire. When graphene is folded, along the cylinder wall, the $\sigma$ bonds form the hexagonal network and the $\pi$ bonds point perpendicular to the nanotubes surface [86, 87]. The latter are responsible for the weak van-der-Waals interaction between different tubes. The in plane $\sigma$ bonds are too energetically too far away from the Fermi level (defined as the energy that pertains to higher energy electrons in a semiconductor) to participate in electronic transport or optical absorption in the visible energy range [88].

However, the bonding and anti bonding $\pi$ band cross over at the Fermi level. It is this bonding that makes graphene and one third of carbon nanotubes metallic in nature. Figure 2.14 shows a representative lattice structure of graphene and Figure 2.15 shows an energy level diagram for carbon. Thus the way in which graphene layers are arranged governs the physicochemical properties of SWCNT.
Basal and edge carbon atoms are considered to be two different sites and distinguish between their interactions with other molecules, as well as their ability to undergo chemical reactions. The reactivity of a carbon surface is also linked to the amount of disorder, *e.g.* imperfections, structural carbon vacancies and non aromatic rings. These defects along the
edges of graphene layers are the most active sites on the surface, due to the high number of unpaired electrons [90]. Heteroatoms such as O, H, S and N can all be chemisorbed, forming stable surface compounds [91]. In terms of their mechanical properties, carbon nanotubes are the stiffest materials known to man. Their Young’s modulus has been measured to be 0.64TPa [92], which is approximately five times that of steel. They are known to be relatively flexible and can return to their original shape after buckling and bending [93]. In terms of optical properties, carbon nanotubes were expected to show very structured optical spectra because they are one dimensional materials. However, this is not the case when they are in their as synthesised bundled form.

Carbon nanotubes are generally formed or grown in bundles. The way in which they are manufactured can determine the bundle size, which is generally anywhere between 5-40nm [94]. Adsorption studies have been carried out on partially debundled and isolated tubes [95, 96] and Raman spectroscopy has also be used extensively to study the properties of carbon nanotubes [97-100]. Both of these characterisation techniques will be discussed in more detail in Chapter 4.

2.8.2 Solubilisation and Functionalisation of Carbon Nanotubes

It was quickly discovered that SWCNTs were not easy to solubilise in conventional solvents. As previously mentioned, in their natural state they are in bundled form which partially results in to their inability to be dissolved in liquids. Thus, the research of chemical solubilisation and modifications of carbon nanotubes is continuously evolving. Several research groups have reported successful functionalisation of both SWCNTS and
MWCNTs [101-104]. In addition, a lot of work has been carried out on solubilisation and characterisation of SWCNTs in various solvent and aqueous media, such as dimethylformamide (DMF), chloroform and dichloroethane (DCE). More recently the use of surfactants has being explored in more detail [105-108] despite them being used to successfully debundle MWCNTs and SWCNTs back in the late 1990s [109, 110]. Utilising these media types can allow partial or total debundling of the SWCNTS and subsequently investigation of their optical and vibrational properties has become more refined [111]. In addition to using the aforementioned media, the way in which carbon nanotubes and their composites are characterised has improved significantly. A large amount of work has been carried out using a number of spectroscopic and microscopic methods, some of which have been employed in this body of work and will be discussed in more detail later in this thesis.

2.8.3 Nanotube Composite Materials

SWCNTs generally agglomerate into 5-100 nm diameter bundles forming hexagonal lattices within the bundle with resultant binding energies of the order of 900 meV/nm [112]. The length of a SWCNT typically ranges between 200 nm to >10 μm. Thus, overcoming the van der Waals interaction is the main challenge in dispersing SWCNTs. In addition, SWCNT bundles/ropes have a very intricate network structure. Physical and chemical approaches are being adopted to untangle and disperse nanotubes and are these are described briefly here.
A lot of work has been done on polymer/SWCNT composites and a number of the techniques employed use sonication to disperse the SWCNT. However sonication can introduce defects and dislocations in the carbon structure which, if the treatment is prolonged, can reduce the carbon nanotube length and thus result in the formation of amorphous carbon. Subsequently work in this area moved on to in-situ electrochemical techniques and several materials have been successfully made including SWCNT/PMMA [113] and CNT/polypyrrole composite [114]. As far as dispersion is concerned, several solvents have been proven to be able to debundle SWCNT, including chloroform, N,N-dimethylformamide (DMF) and 1,2-dichlorobenzene [115]. Good SWCNT solvents have also been characterised by high electron pair donicity and low hydrogen bond donation parameters [116]. Furthermore, a detailed study of the liquid phase exfoliation of nanotubes by dispersing and stabilising them in a variety of liquids to examine the properties of isolated tubes has been reported in recent years [117]. SWCNT can be dispersed in water but only with the assistance of surfactants [118]. Sodium dodecyl sulphate (SDS) is reported to be one of the most efficient for this [119].

In addition, oxidation in nitric acid for example, can be used to introduce oxygen containing functional groups such as –COOH and –OH onto the surface of the nanotubes [120]. The nanotubes can have their end caps removed during oxidation allowing access by small metal particles and oxidised tubes can form well dispersed stable colloids in both water and ethanol [121, 122]. As mentioned earlier, these materials as well as the precursor SWCNT can be characterised using many techniques and the use of these is discussed in more detail in Chapter 4.
2.9 Use of Carbon in Catalysis

In addition to SWCNT, amorphous and activated carbon have both been used as amongst other things, catalyst supports and so for the purposes of this work, Printex 90, a carbon black or amorphous carbon has been used as a comparative support material. Porous carbon materials are well documented as supports for heterogeneous catalysts [123-124]. This is because their surface properties can be tailored to provide large surface areas to successfully disperse the active phases. They also show some advantages over traditional catalyst supports [125,126] which make them attractive for this application. Some examples include resistance to acidic and basic media, structural integrity at high temperatures and they are cheaper than other conventional catalyst supports. The surface functionality of these materials will directly affect the catalytic behaviour of the active phase.

The preparation of carbon supported catalysts is much the same as for generic oxide supported systems, as previously discussed but the most commonly employed methods are incipient-wetness impregnation and excess solution impregnation. Electrostatic interactions between the carbon surface and the active phase precursors have to be taken into account when preparing carbon supported catalysts as well as the chemical composition of the surfaces.

In most catalysts, the active phase is deposited on a support in order to keep the active phase stable and highly dispersed during use of the catalyst. A lot of the theories on impregnation and ion adsorption are based on Brunelle’s paper [127], which notes that the
Coulombic interaction between support and active phase precursor is vital for obtaining a good distribution of the precursor over the support. There have also been several other models reported describing the adsorption of ions on carbon supports, eg, Regalbuto, et al’s proposed adsorption of a metal precursor on a given support as a function of ionic strength and pH [128, 129]. In contrast, others claim the formation of an inner shell complex during the adsorption of metal precursor complexes on carbon [130] sometimes along with the reduction in the metal precursor complex by the support [131]. An example of this is H₂PtCl₆ on active carbon. Prado-Burguete, et al showed that after impregnating H₂PtCl₆ on heat treated carbon black, a 5.1 nm Pt particle size can be achieved [132]. However after oxidation of the heat treated support, oxygen groups were introduced and after impregnation and reduction, a particle size of 2.4nm was obtained. This was attributed to enhanced interaction of the precursor salt H₂PtCl₆ with the oxidised support and the increased wettability after oxidation. Other theories conflict regarding the ways in which metal precursors strongly adsorb on oxygen containing groups [133, 134]. With all of these considerations in mind, several techniques are utilised in an attempt to understand the metal-support interaction. The results are discussed in detail later in this thesis in Chapter 4.

2.9.1 Carbon as a standalone catalyst

In addition to its use as a catalyst support, carbon can be used as a catalyst in its own right. Activated carbon catalysts have been used in the production of phosgene [135] and sulphur halides [136] as well as in flue gas cleaning, eg the Sumitomo process for simultaneous SO₂/NOₓ removal with active coke which was developed in Japan in the 1980’s. In the
latter process, the active carbon acts as both an absorbent and as a solid phase reductant in a specific temperature range [137].

2.9.2 Carbon nanotubes in catalysis

As discussed earlier, carbon nanotubes have a tubular morphology with one or several graphene layers and have been extensively researched for a wide range of applications. The first results published on use of carbon nanotubes for heterogeneous catalysis supports appeared in 1994 [138] and these were swiftly followed by the preparation of metal particles on CNTs and the determination of the catalytic properties of these systems [139]. There has been a steady stream of work on CNTs in catalysis published since the mid 1990’s owing to their extraordinary properties as discussed earlier and the possibility of macroscopic shaping of the materials have made them very attractive competitive catalyst supports in comparison with activated carbons [140-142]. Specifically they can replace activated carbons in liquid phase reactions as the properties of the latter cannot be easily controlled and their microporosity can slow down or inhibit the catalysts potency. In this work, the problems of using activated carbon in these types of reactions are highlighted and discussed as well as the advantages of using SWCNTs as a catalyst support material.

The next chapter expands on recent developments in heterogeneous catalysis and the move to greener methodologies. Specific examination will be given to the use of Au nanoparticles in oxidation reactions. In addition there is some discussion on carbon supports vs traditional support systems and why catalytic supports are so vital to the success of the catalyst itself.
References:


[89] http://cnx.org/content/m29187/latest/, accessed 19/11/12.


Chapter 3

Importance of Heterogeneous Catalysis and Supported Systems: Application to Green Chemistry
3.1 Importance of Heterogeneous Catalysis

Heterogeneous catalysts are responsible for a large number of chemical transformations of fossil fuels such as methane, coal and liquid petroleum into useful products [1, 2]. In accordance with a 2002 article that highlights the impact of catalysis on the United States economy, “one-third of material gross national product in the US involves a catalytic process somewhere in the production chain” [3]. The manufacture of catalysts alone accounts for over $10 billion of sales revenue in four major sectors, refining, chemicals, polymerisation and emission. Catalysts are responsible for production of over 60% of all chemicals and are utilised in ~90% of all chemical processes worldwide [4]. Nevertheless, the currency generated due to catalyst sales is enormously outweighed by the overall value of the generated products. Examples of said products include pesticides, antibiotics, cosmetics, polymers, paints, plastics, cleaning products and chemical intermediates. In 1998, the annual global impact in the area of catalysis on the whole was estimated to be in excess of $10 trillion [5]. It would be highly likely that in the present day, this figure is significantly higher.

As heterogeneous catalysis has evolved, it has become more apparent that it has a large part to play in ‘green chemistry’ and thus removing or substantially reducing the pollution and undesirable by-products from both chemical and refining processes [6]. This means that these by-products don’t end up as either harmful emissions or nasty waste materials that are dangerous and detrimental to the ecosystems and the environment the world over.

As the majority of industrial catalysts contain an active ingredient in nanoparticulate form (typically in the order of <20 nm in size) dispersed onto high surface area materials,
continual efforts are being made to improve these composites for use across many reaction types. This in itself makes catalysis an integral part of nanoscience and nanotechnology [7].

3.2 Heterogeneous Nanocatalysis in Green Chemistry

It is generally recognised that the ultimate goal in catalytic studies is to be able to develop a detailed understanding of the catalyst systems to allow tuning of the design of nanoscale materials to create new heterogeneous catalysts and thus green catalytic processes [8]. One of the major issues in this area is catalyst performance (e.g. activity and selectivity) which is affected by shape, size, composition and structure of the active ingredient as well as the support material used. There are four major classes of organic reactions in which heterogeneous catalysts are used; dehydrogenation, alkylation, hydrogenation and selective oxidations [9].

The first of this reaction type dehydrogenation is a well established method for production of simple and thermally resistant aldehydes and ketones mostly because these reactions are reversible [10-13]. Alkylation reactions [14-16] are important for the production of gasoline that meets current stringent environmental standards and so researchers are seeking to develop solid-catalyst processes for alkylation technology [17, 18]. Hydrogenation reactions [21, 22] are commonly used in the food industry to make spreads and margarines from liquid oils [23] and so are vital to this industry. Finally, selective oxidations [24-27] are extensively used in organic synthesis for the formation of many important compounds and intermediates to branch in other areas. However, a great deal of these selective catalytic oxidations rely on the use of high valence bimetallic catalytic systems [28-30].
In recent times, the use of supported single metal systems has been highlighted in the literature, which includes some initial studies using carbon nanotubes as both catalysts in their own right and as supports for heterogeneous catalysts [31-40].

3.3 Green Methodologies in Heterogeneous Catalysis

The development of methodologies for green chemistry is a continual challenge, guided by the framework of the ‘Twelve Principles of Green Chemistry’ [41]. These principles specify catalysis as one of the most important methods for implementation of green chemistry. Indeed, catalysis provides many benefits befitting green chemistry, for example, lower energy requirements, increased selectivity and fewer requirements for toxic materials.

Heterogeneous catalysis expressly tackles the aims of green chemistry by permitting easier separation of product and catalyst. Also, environmentally benign catalysts can be used to replace more hazardous catalysts in a range of reaction types. The knock on benefits to health and the environment through the use of catalysis in manufacturing/processing are demonstrated by making the catalyst design and catalyst applications the focal point of current research in this ever changing field.

3.3.1 Selective Oxidations in Catalysis

The selective oxidation of alcohols to aldehydes by heterogeneously catalyzed routes still presents a great challenge in the fine chemical industry [42]. The application of stoichiometric inorganic reagents such as KMnO₄ or K₂CrO₄ still occurs although to a lesser extent. Therefore considerable effort has been made in the past years to develop “green”
oxidation technologies [44]. Though homogeneous catalysts often have high activity, homogeneous processes suffer from the drawback of corrosion, and difficulty in catalyst recovery and reuse. Hence, the most attractive but often limited route concerning large scale industrial application is heterogeneous catalytic oxidation with molecular oxygen. Application of solid catalysts for the gas-phase oxidation of structurally simple and volatile alcohols has been investigated in significant detail [45]. In fact, the liquid-phase oxidation under mild conditions has major practical importance [46]. There are several solid (supported metal) and heterogenized (immobilized metal complex) catalytic materials applicable for the liquid-phase transformation of alcohols to carbonyl compounds and carboxylic acids [47, 48]. The catalytic systems become more attractive from the environmental point of view when molecular oxygen is utilised as an oxidant [49, 50].

There are several catalytic materials that show good performance under close to ambient conditions and fulfill the requirement of low ecological impact. For example, the effectiveness of supported Au and Pt-group metals (ranging from mono to multimetallic promoted systems) is well established in selective oxidation of alcohols to carbonyl compounds or oxidation of sugars without onward further oxidation [51-54]. Nowadays, investigations are mostly in the oxidation of diols, even using supported gold catalysts, although the requirement of aqueous alkaline medium is a severe limitation of the method [55]. Very recently, a bimetallic Pd–Au/C catalyst has been reported to be efficient in the selective oxidation of glyoxal to glyoxalic acid [56]. Silver-based catalysts are used in the gas-phase oxidation of alcohols and diols using O₂ [57]. Several Ru-containing oxides and mixed oxides, hydrotalcites and various metal substituted zeolites have also been tested in
alcohol oxidation, but, in many cases, leached Ru, Mn, or Cr compounds are the real active species. Some supported metal complexes (particularly Ru-and Pd-based catalysts) are also not truly heterogeneous and the active species are dissolved metal complexes, or the oxidative stability of the support is inadequate [58]. A great number of new catalysts have been suggested in recent years for environmentally benign oxidation methods [59]. However, considering high yield and selectivity as well as stability against oxidation and leaching, the conventional Au and Pt-group metal based catalysts represent the best choice in many reactions from an industrial point of view, as indicated by the great number of patents [60, 61].

By noting the continuing challenges in development of new materials in this sub sector of catalysis and specifically the improvements in green technologies, the experimental work in this thesis focuses on the preparation and characterisation of supported gold catalysts for use in selective oxidation reactions. However it is firstly imperative to understand how a heterogeneous reaction takes place as well as the importance of selective oxidations and catalyst supports.

3.4 The steps in a heterogeneously catalysed reaction

Any heterogeneous catalytic reaction involves at least two phases (liquid and solid or gas) and the reaction occurs on the surface of a solid catalyst. Heterogeneous catalytic reactions by their very nature involve a combination of reaction and transport stages. The process of heterogeneously catalysed reactions can be described in seven distinct steps [62-64]. Figure 3.1 shows a schematic of the steps involved in heterogeneous catalytic reactions and highlights steps 1 through 7 respectively for illustration purposes [64]*.
1. Transfer of reactant ($A_1$) from the bulk to the outer surface of the catalyst particle.

2. Diffusion of the reactant/substrate through the catalyst pores to a catalytically active site.

3. Adsorption of reactants (reactant surface).

4. Transformation of reactant to product ($A_2$) by chemical reaction.

5. Desorption of the product

6. Diffusion of the product through the pores to the outer surface.

7. Transfer of the product from the outer surface into the bulk of the fluid.

Figure 3.1: Steps involved in heterogeneous catalytic reaction [64]

*Schematic adapted from source.
Any catalytic reaction will have a minimum of three steps, adsorption of the reactant, surface reaction and finally desorption of a product and Figure 3.2 shows a general representation of these steps. The kinetics of catalysis is such that the catalyst itself needs to be included in the kinetic equation as a participant [65].

\[
A_1 + * \xrightarrow{\text{k}_1} A_1^* \quad \text{Reactant adsorption/desorption}
\]

\[
A_1^* \xrightarrow{\text{k}_2} A_2^* \quad \text{Surface reaction}
\]

\[
A_2^* \xrightarrow{\text{k}_3} A_2 + * \quad \text{Product desorption/adsorption}
\]

Figure 3.2 Kinetic Equations for Basic Heterogeneous Reactions

To describe the kinetics of heterogeneous reactions, Langmuir adsorption isotherms are commonplace, but they do work under assumptions, the main one being that the solid surface is uniform and contains a number of equivalent sites, each of which can only be occupied by one adsorbate species [66]. However, they are often used in conjunction models such as the Langmuir-Hinshelwood [67] or Eley-Rideal [68].
Depending on the treatment of these theories alongside the reaction type, the mathematical derivations vary considerably so this type of study involves a great deal of complex calculations the discussion of which is beyond the scope of this work. It is however touched on in more detail in Chapter 4 as surface area and pore size measurements are used as a characterisation tool.

The focus now shifts to the importance of selective oxidations in green chemistry before moving on to talk about the importance of support systems.

3.5 Green Chemistry and Selective Oxidations

Green or sustainable chemistry, as it has become known, is the design of chemical processes and products that either eliminate or reduce the use or generation of hazardous materials [69]. There has been considerable development in this area recently due to the detrimental effects of greenhouse gases, automotive emissions and toxic waste generation.

One of the areas in which there are sustained challenges to strive for improvements in green chemistry is in the area of selective oxidations. Ideally, a green catalysed oxidation process should consist of a highly active, selective and recyclable catalyst that works at atmospheric pressure, in the presence of oxygen and without the presences of acids or bases. The difficulty is in designing a system that allows for all of these.

Because the oxidation of alcohols to their corresponding aldehydes, ketones and/or carboxylic acids is such an important transformation in organic synthesis, there has been significant research in this area. The application of heterogeneous catalysis and
molecular oxygen to oxidation reactions proffers a green substitute to conventional, toxic oxidants [70]. Platinum-group metals (specifically Pt and Pd) are known to be active catalysts in liquid-phase oxidation of alcohols with O₂ under conditions close to ambient [71, 72]. Au has been demonstrated to selectively oxidise alcohols and diols [73, 74]. In addition, the use of Au catalysts for selective oxidation of sugars and alcohols have been demonstrated [75, 76]. However, the substantial amount of the published work to date requires either the addition of a base [77], raises concerns over oxidation, eg selectivity problems [78] or has need for mixed metallic catalysts [79,80]. The aim of this work is to demonstrate that Au is an active catalyst which can be used in this area of heterogeneous catalysis.

3.5.1 Gold as an active catalyst for selective oxidations.

Gold was for a long time considered to be a poorly active catalyst. Early studies by Hutchings showed that cationic gold was the choice catalyst for acetylene hydrochlorination [81]. However, Haruta, et al made the discovery that when Au is deposited in nanoparticle form onto metal oxides either by co-precipitation or deposition-precipitation methods, it exhibits surprisingly high catalytic activity for CO oxidation at temperatures as low as 200 K [82]. These findings paved the way for further study of Au in heterogeneous catalysis from the 1990s onwards. Early debate on this topic was fuelled by the reviews of Bond and Thompson [83, 84]. Since the turn of the century, several groups have carried out work using gold as an oxidation catalyst. For example, Prati, et al demonstrated the use of Au(0) catalysts for the oxidation of diols [85] and Qi, et al showed that Au can catalyse the
selective oxidation of cyclohexane [86]. More recent work has shown gold is an
excellent catalyst for liquid phase oxidation of alcohols and aldehydes either by
itself as an active ingredient [87-89] or within a bimetallic catalyst [90-92].

3.5.2 Carbon nanotubes in catalysis
Carbon nanotubes have attracted significant interest as the basis for applications in
terms of new materials, due to their unique structural, mechanical and electronic
properties. [93,94]. Metal filled carbon nanotubes have been shown to have
promising applications in heterogeneous catalysis [94] and MWCNTs have been
used as catalyst supports in thermal and electrocatalysis [95, 96]. In addition, Au
nanoparticles supported on SWCNT films have already been shown to be promising
as selective oxidation catalysts in conjunction with acid/water media [97]. However,
as is now widely accepted, SWCNTs are notoriously difficult to solubilise without
using harmful solvents or surfactants which causes problems with conventional
composite preparation. Conversely, Dai, et al have shown a directed reduction of
Au$^{3+}$ on the sidewalls of SWCNTs to form Au nanoparticles without the need for
further chemical processing [98]. The downside to this method however, is the
broad diameter distribution of the Au nanoparticles. By modifying this method, it
was hoped that Au nanoparticles with a narrow diameter particle size distribution
could be produced. The scaffolds on which the Au nanoparticles are deposited were
chosen to enhance the catalytic properties of the gold and protect against denaturing
during the reaction processes. There now follows a brief discussion on catalyst
supports and why they are so important in heterogeneous catalysis.
3.6 The importance of catalyst supports

The main purpose of applying a catalytically active component to a support is to obtain the catalyst in a highly dispersed and hence highly active form when expressed as a function of the weight of the active component [99]. This is particularly important when using precious metal catalysts, as it allows more effective and thus cost-effective usage of the metal than bulk-metal systems. However, in the case of base-metal catalysts, the use of the support is generally aimed at improving the stability of the catalyst. This is usually achieved by interaction between suitable active material and support [100]. An example of this is unsupported CuO which is a very active oxidation catalyst but is thermally unstable at high temperatures [101]. Contrastingly, when the CuO is supported on a high surface area alumina, its thermal stability is improved [102].

In the case of gold catalysts, most of the literature focuses on depositing nanoparticles on metal oxide supports such as TiO$_2$, CeO$_2$, and Al$_2$O$_3$ [103-105]. There are also some cases in which Au nanoparticles have been supported on C for use in oxidation reactions [106-108]. SWCNT have recently started to be considered for use as support materials because of their tensile strength and large surface area [109, 110]. In addition, the thermal stability of SWCNT makes them ideal candidates as catalyst supports [111].

Utilisation of Au nanoparticle catalysts supported in these ways is an advantage because of the easy of recovery and recyclability, which in turn is important in adhering to sustainable chemistry protocols [112]. These protocols were first
proposed in 1998 by Anastas and Warner in their book Green Chemistry: Theory and Practice [113] and have become the standard guidelines for sustainable chemistry research.

### 3.7 The Principles of Green Chemistry

It is vital to understand why the work that follows is designed to adhere to the principles and so at this point, they are listed in a reworded shortened version for information purposes.

1/ **Prevent Waste:** Design of processes to prevent waste thus leaving no waste behind that requires treatment.

2/ **Maximise Atom Economy:** Design processes that leaves the final product incorporating the maximum amount of raw material used to make it.

3/ **Design Less Hazardous Chemical Syntheses:** Design processes that require the use of little or wherever possible no toxic substances that could be detrimental to human health or the environment.

4/ **Create Safer Chemicals:** Design products that are fully effective and minimise or eliminate toxicity.

5/ **Use Safer Solvents:** Create processes that use environmentally friendly substances such as water as solvents or separation agents.

6/ **Design for Energy Efficiency:** Work at ambient temperature and pressure whenever possible.

7/ **Use Renewable Feedstocks:** Use renewable raw materials and feedstocks wherever possible instead of depleting non-renewable materials.
8/ **Reduce Derivatives**: Avoid or minimise the use of protecting and blocking groups in reactions as they often require additional reagents and generate waste.

9/ **Use Catalysts Instead of Reagents**: Use catalytic reactions that use small amounts of material and thus minimise waste.

10/ **Design for Degradation**: Design chemical products that break down into harmless materials that do not remain in the environment.

11/ **Prevent Pollution in Real Time**: Monitor and control the process to minimise or eliminate the formation of hazardous by products.

12/ **Minimise the Potential for Accidents**: Design chemicals and processes that minimise the potential for accidents such as explosions, fires and toxic releases into the environment.

The primary aim of this work is to adhere as closely as possible to the twelve principles of green chemistry across the entire process from manufacture of the catalysts right through to the testing of them in reactions that are challenging to carry out in an environmentally benign manner. The focus is to prepare then compare gold nanocatalysts supported by more traditional scaffolds, in this case TiO$_2$ and a carbon black, but also with a single walled carbon nanotube support. These composite materials are all tested in three selective oxidation reactions for their catalytic activity. It is believed that this first time that SWCNT have been used as catalyst supports for heterogeneous reactions.
References:


Chapter 4

Preparation and Characterisation of Supported Gold Composites

4.0 Preparation of Au/TiO$_2$, Au/SWCNT and Au/P90 Composites

4.1 Materials

Titanium IV dioxide nanopowder and the SWCNT used in this work were sourced from Sigma-Aldrich. In the case of the SWCNT, prepared by the so-called Arc-Discharge Method [1], the reported composition is ~70% SWCNT (with diameters between 1.2-1.5nm and bundles of lengths in the order of ~20µm), ~30% Amorphous Carbon and ≤ 1% Nickel/Yttrium [2]. The carbon black (P90) whose chemical composition is amorphous carbon was gifted by Degussa. Gold chloride (HAuCl$_4$) and sodium borohydride (NaBH$_4$) were also sourced from Sigma-Aldrich. Finally, doubly distilled water was obtained from a Millipore Elix 5 water purification system.

4.2 Preparation of Composites.

For the preparation of the composites, the required amount of SWCNT, P90 or TiO$_2$ was suspended in double distilled water and stirred vigorously. The necessary volume of 0.02M HAuCl$_4$ solution required to obtain 5% Au by weight on each support material was added dropwise with continuous stirring. The pH of the solution was maintained at ~8.5 by means of addition of 15% NaBH$_4$ [3]. The precipitated solution was aged under stirring for 2hrs. A solution of ice cold 0.02 M NaBH$_4$ was prepared and added as needed to complete the reduction of Au(III) to Au(0) [confirmed by XRD in section 4.4.3] and then the suspended solution was aged while maintaining the pH at 8.5 for a further 2hrs. The suspension was then
filtered using a 0.45 µm nylon filter and washed with 3 times the suspension volume using ddH₂O and then the remaining solid mass was dried in an oven for a minimum of 4hr at ~120ºC prior to characterisation.

4.3 Characterisation Techniques

4.3.1 Scanning Electron Microscopy and Scanning Transmission Electron Microscopy

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern [4]. The electrons interact with the shells in atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity [5].

The types of signals produced by an SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and in some cases transmitted electrons (STEM). Generally the most common or standard detection mode is SE imaging. The spot size in a Field Emission SEM is smaller than in conventional SEM and can therefore produce very high-resolution images, revealing details in the range of 1-5 nm in size [6].

All SEM and STEM images were taken using a Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope with a Schottky field emission electron gun which enables excess of 200nA probe current. The instrument is capable of SE, BSE and STEM imaging. The best attainable SE image resolution is
1.2nm at an operating voltage of 30kV. The TEM image was taken with a JEOL JEL-2000 EX electron microscope with a lattice resolution of 0.14nm and a point to point resolution of 0.3nm operated at an accelerating voltage of 80kV.

**4.3.2 Energy Dispersive X-Ray Analysis (EDX)**

Energy Dispersive X-Ray Analysis (EDX) is a technique used for identifying the elemental composition of a sample or an area of interest within said sample. It is generally coupled with either an SEM or a TEM. During EDX analysis, the sample is bombarded with an electron beam inside the electron microscope and the bombarding electrons collide with the sample atom, freeing them in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher energy electron from an outer shell but for this to happen; the transferring outer electron must give up some of its energy by emitting an X-ray [7].

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferred to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the energies of the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established [8].

EDX was carried out using a Hitachi SU70 Analytical FESEM. It is equipped with an Oxford Instruments 50mm² X-Max silicon drift EDS detector. This detector enables analysis to be performed at high count rates. This analytical component
provides complementary information in terms of elemental analysis, compositional point analysis and mapping.

**4.3.3 X-Ray Powder Diffraction**

About 95% of all materials can be described as crystalline [9] so when X-rays interact with a crystalline substance or ‘phase’, a diffraction pattern is produced. A paper released in 1919 by A.W. Hull entitled “A New Method of Chemical Analysis” pointed out that “every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others”. This in effect means that the X-ray diffraction pattern of a pure substance is like a fingerprint of it [10]. The powder diffraction method is thus ideally suited for characterisation and identification of polycrystalline phases in materials. In addition, the areas under the peaks produced in the diffraction pattern are related to the amount of each phase present in a sample. All X-Ray Diffraction powder patterns were obtained using a Siemens D500 diffractometer with a monochromatic Cu Kα₁ sourced operated at 40KeV and 30mA.

**4.3.4 Atomic Absorption Spectroscopy (AAS)**

AAS is a spectro-analytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state [11]. In analytical chemistry the technique is used for determining the concentration of a particular element (analyte) in a
sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples [12].

AAS was carried out using a Varian Spectr200 with the aid of a standard calibration plot was used to determine the gold loading following acid digestion of the composites. The acid digestion was carried out using mixture of nitric and hydrochloric acid (aqua regia) in a ratio 3:1 HNO₃: HCl which is commonly used for digesting gold and other precious metals [13].

4.3.5 Surface Area Analysis

Adsorption of nitrogen and surface area determination is probably the most widely used method for surface characterisation of many porous materials including catalysts and their supports [14]. There is an inverse relationship between particle size and surface area. For example a cube of edge 10cm has a surface area of 60cm². If the cube was split into smaller cubes with edges of 1cm, there would be 1000 cubes and the total surface area would be 600cm². This of course is in an idealised scenario, as realistically irregular particles would break into smaller particles with a range of sizes and shapes. Real particles of whatever shape or size if studied at the molecular level exhibit planar regions but will also have lattice distortions and cracks. This effectively means that the actual exposed surface of particles is larger than calculated by assuming any one specific geometric shape such as the aforementioned cube [15]. Specific surface area is used to describe more accurately the actual surface area of a body, rather than that of the idealised geometric size. It is measured by monitoring the adsorption of gas molecules to the surface and this
process is described by BET theory which was first determined in 1938 by Stephen Brunauer, Paul Hugh Emmett and Edward Teller [16].

Solid particles that have undergone grinding or crushing operations as well as leaching or weathering are often found to have developed cracks, holes and cavities which are collectively known as pores. In addition, fine particles tend to adhere to each other to form aggregates or large secondary particles, thus producing another level of pore sizes. These pore sizes are expressed either in terms of the diameter (or radius) of the opening (which assumes it is cylindrical) or the width (or half width) of the slit (if it is a slit rather than a hole). Pores with diameters or slits with widths that are less than 2nm are known as micropores and pores with larger diameters between 2-50nm are called mesopores. Thus, the volume of all cracks, holes, etc within the body of the material is the total pore volume. The pore size of a material can thus affect its properties and are known to affect the activity of catalysts [17, 18].

The samples are usually degassed prior to analysis to remove moisture and atmospheric vapours at a specified temperature, generally ~30°C below the melting/decomposition or phase change point. Subsequently the sample temperature is reduced to that of boiling liquid nitrogen. The adsorbing gas is added to the sample and the accumulated gas quantity adsorbed vs. gas pressure at fixed temperature is determined and then graphed to generate an absorption isotherm [19]. These isotherms are generally classified using the IUPAC system for classification which will in turn depend on the type of adsorbent, type of adsorbate and the intermolecular interactions between the gas and the sample surface [20]. The data
generated can also be mathematically analysed to provide other important information about the sample such as pore size and volume [21].

The surface area of the composite materials and their supports were determined by multi point N\textsubscript{2} adsorption using a Gemini VI 2000e Surface Area Analyser at 77K and data analysis was carried out using the multi point Brunauer Emmett Teller (BET) method from the N\textsubscript{2} adsorption isotherms.

4.3.6 UV-Visible Spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface [20]. Absorption measurements can be at a single wavelength or over an extended spectral range. Photons of ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is often applied to molecules or inorganic complexes in solution [12, 22]. UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law [23, 24].

For this work, all UV-Visible absorption spectra were obtained using a Perkin Elmer Lambda 900 Spectrometer which is a double-beam, double monochromator ratio recording system with pre-aligned tungsten-halogen and deuterium lamps as sources. The wavelength ranges from 175 to 3300nm with an accuracy of 0.08 nm in the UV-Visible region and 0.3nm in the NIR region. It has a photometric range of
+/-6 in absorbance mode and is controlled by UV WinLab software. The spectra were all referenced using the appropriate solution background.

4.3.7 Raman Spectroscopy

Raman Spectroscopy is a type of vibrational spectroscopy based on the inelastic scattering of a monochromatic light source usually a laser in the near IR or Vis range. It is used to study the vibrational, rotational and low frequency modes in a system. The laser interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being down or up shifted. These energy shifts provide information about the vibrational modes in the system(s) of interest [25].

Raman spectroscopic analysis of both supports and composites was carried out using a Horiba Jobin Yvon LabRAM HR 800. Light is imaged to a diffraction limited spot (typically 1 µm) via the objective of an Olympus BX50 microscope. The scattered light is collected by the objective in a confocal geometry and is dispersed onto an air cooled CCD array by one of two interchangeable gratings, 300 lines/mm or 600 lines/mm which allows the range from 150 cm\(^{-1}\) to 4000 cm\(^{-1}\) to be covered in a single image or with greater resolution in a combination of images.
4.4 Results and Discussion

4.4.1 Scanning Electron Microscopy and Scanning Transmission Electron Microscopy

The morphologies of the supports and composite materials were investigated using a combination of SEM, STEM and TEM. For SEM imaging, the powders were ground up finely and the smallest possible quantity was placed on a carbon tab mounted on an aluminium sample stub.

For STEM and TEM, samples of the composites and precursor supports were prepared following dispersion in ethanol at a concentration of 0.1 µl/mL and sonication for ~60 secs using a sonic tip (VCX Ultrasonic processor 750W). A drop of the suspension was then placed on a Formvar coated film supported on a 300 mesh copper TEM grid. The size distribution of the Au nanoparticles was evaluated using AxioVision LE software (Carl Zeiss).

Figure 4.1 shows an SEM image of TiO₂ powder which confirms its nano structure and shows mostly spherical particles in the region of 20-100nm with some visible agglomerates which would be expected in a compacted powdered material. Figure 4.2 shows an SEM image of Au/TiO₂ composite taken at a magnification of 200,000x in which the z grey scale contrast is clearly defined distinguishing between the Au nanoparticles (bright particles sitting on the larger TiO₂ particles) and the TiO₂ support network (duller). The Au NPs are of sizes in the order of 10-20nm which is in good agreement with calculations based on the UV-Visible results shown in Section 4.4.6.
Figure 4.1: SEM image and Particle Size Distributions of Nano TiO$_2$ powder
Figure 4.3 shows an SEM image of SWCNT ropes while Figures 4.4, 4.5 and 4.6 show representative samples of the TEM and STEM images from the Au/SWCNT composite as well as the PSD for the Au/SWCNT. Figure 4.3 using a magnification of 30,000x gives an overall indication of the morphology of the composite. The SWCNT are well dispersed and although not fully exfoliated, are present in bundles of diameter significantly less than the rope like structures of the as produced samples, which are several microns in length and have bundles of diameter ~30nm (Figure 4.3). It can be seen that the Au nanoparticles are reasonably homogeneously dispersed and appear to be adhered on the SWCNT surface. Figure 4.6 shows two of the SWCNT structures and shows the Au nanoparticles sitting on the backbone of the SWCNT. The accelerating voltage was reduced to minimize deposition of in-beam contamination onto the sample during imaging at higher magnifications as well as charging effects. The image shows two of the SWCNT structures and both
individual Au nanoparticles as well as agglomerates of predominately amorphous carbon sitting on the backbone of the SWCNT.

In addition, a small proportion of the Au particles on the SWCNT do not appear to be well defined in shape. The Au particle size distribution was estimated using AxioVision LE’s integrated camera controls. After that, the programs interactive histogram and image processing tools allowed optimization of the colour, contrast and brightness of the image as well as image analysis and measurement functions. Although there are some aggregates visible, the particle size distribution is sharply peaked and the average particle size is estimated to be ~7nm for the Au/SWCNT composite which is in relatively good agreement with the calculations performed using the XRD data shown in section 4.4.3.

Figure 4.3: SEM Image of SWCNT ropes
Figure 4.4: TEM Image of Au/SWCNT Composite

Figure 4.5: Au Particle Size Distribution for Au/SWCNT Composite
In contrast, Figure 4.7A shows the Au/P90 composite sample which has a totally different morphology compared to its SWCNT supported counterpart. The Au/P90 has a much more ordered structure than the Au/SWCNT sample. In addition, the Au nanoparticles are much more homogeneously dispersed on the support surface. The particle sizes are centred between 7-9nm in diameter.
Figure 4.7A: SEM Image of Au/P90 Composite

Figure 4.7B: Au Particle size distribution for Au/P90 Composite
4.4.2 EDX Analysis

Energy Dispersive X-Ray Analysis (EDX) of the composites was carried out to verify the presence of gold and all Au containing samples clearly show signals at both 2keV (M Line) and 10keV (L Line) [26]. Figures 4.8, 4.9 and 4.10 show the EDX spectra for the Au composite materials. For clarity, the Y axis units are Counts (a.u.).

Figure 4.8: EDX Spectrum of Au/TiO₂ composite.
Figure 4.9: EDX Spectrum of Au/SWCNT composite

Figure 4.10: EDX Spectrum of Au/P90 composite
4.4.3 X-Ray Diffraction Analysis

The crystallinity of the composites and supports was shown through analysis of their XRD patterns. Figure 4.11 shows the XRD patterns for the nano TiO$_2$ and the Au/TiO$_2$ composite and show that the crystalline phase for both is predominantly of anatase form, i.e. it is the tetragonal phase of the material [27]. Unfortunately, the TiO$_2$ and the Au/TiO$_2$ patterns do not show enough distinguishable differences in their diffraction patterns to accurately calculate the average Au particle size due to the anatase phases overlapping in the areas that Au Bragg reflections would normally be visible, namely ~38.5°, ~45.2° and 65.2° corresponding to Au (111), (200) and (311). This in essence does not allow the estimation of the Au NP sizes using this technique. However, the mode phases are shown to be clearly distinguishable using Raman spectroscopy due to the loading of Au on the surface of the TiO$_2$ as can be seen in section 4.4.7.

![Figure 4.11: XRD Pattern of TiO$_2$ (dots) and Au/TiO$_2$ (dashes)]
The XRD profile of the SWCNT support shows reflections at $2\theta \approx 45^\circ$ [corresponding to CNT (004) and $2\theta \approx 52^\circ$ corresponding to Ni (200)] [27]. There is a broad feature centered at $2\theta \approx 23^\circ$. In contrast the XRD pattern of the composite material shows peaks at $2\theta \approx 38.5^\circ$, $45.2^\circ$ and $65.2^\circ$ which correspond to Au (111), (200) and (311) reflections indicating the formation of Au(0) nanoparticles with a face centered cubic structure [28].

In the XRD profile of the P90 support, there are two fundamental differences. There is no Ni (200) peak present and the CNT (004) peak at $\sim 45^\circ$ is gone also. Contrastingly, the Au/P90 composite shows the same Au (111), (200) and (311) peaks indicating that there is also the formation of Au (0) nanoparticles with an fcc structure [27].
The sizes of the gold nanoparticles were estimated using the Scherrer equation [Equation 4.1] (which assumes the particles are spherical) applied to the Au (111) reflection at 38.5° where \( d \) is the average particle size of the phase under investigation, \( \beta \) is Scherrer's constant (0.89), \( \lambda \) is the wavelength used (1.5405 Å), \( B \) is the width at mean height of the diffraction peak, applied to the principal anatase diffraction peak corresponding to the plane (111) and \( \theta \) is the angle of diffraction [29]. It was found that the Au nanoparticles on SWCNT have an average particle size of 4.7nm, those on P90 have an average particle size of 5.1nm. These values are in some agreement with the STEM particle size distribution values discussed earlier in Section 4.4.1.
Equation 4.1: The Scherrer Equation

\[ d = \frac{B\lambda}{\beta \cos \theta} \]

4.4.4 AAS Analysis

Atomic Absorption Spectroscopy was carried out using a graphite furnace attached to a spectrometer and a calibration plot was used to determine the percentage gold loading following acid digestion of the composites [13, 29]. All of the composite samples were diluted into a calibration range using a dilution of 1 in 1000 that would allow for as close as possible a linear response using an Au lamp (in this case, 0-100ppm where 0ppm is a blank). Figure 4.14 shows the calibration plot and the concentration of the three Au NP composites relative to it using drop lines on the X axis. As can be seen from the graph, the composites are all centred around ~0.6 on the absorbance scale which works out as ~50ppm which in the non diluted range relates to 50000ppm or 5%. The exact calculated values for each of the composites are as follows: Au/SWCNT = 5.21%, Au/P90 = 5.42% and Au/TiO₂ = 5.13%. Accuracy is ~0.01% for [Au] values.
Figure 4.14: AAS Calibration Plot and calculated composite concentrations.

4.4.5 Surface Area Measurements

Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micrometrics Gemini VI Surface Area Analyser. Prior to measurements, the samples were degassed at 200°C at for 3hr under N₂. The Brunauer–Emmett–Teller (BET) surface area was estimated over a relative pressure ($P/P_0$) range of 0.05-0.30. The pore size distribution for both the microporous and mesoporous regions are obtained by analysis of the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method.
4.4.5.1 The BET Method

The BET method is advancement from the original theory that had been proposed by Langmuir regarding the adsorption of gases in one molecular layer on a surface expanding it to cover multimolecular layer adsorption. The fundamental assumption is that the forces active in the condensation of gases are also responsible for the binding energy in the molecular adsorption [15, 30].

4.4.5.2 The BJH Method

The procedure for calculating pore size distributions using the Kelvin Equation [Equation 2] involves the imaginary emptying of condensed adsorptive in the pores in a stepwise fashion while the relative pressure is decreased simultaneously [30]. The mathematics of the technique are equally applicable following either the adsorption branch (low to high pressure) or the desorption branch (high to low pressure). Either way, the condition must be set arbitrarily where all the pores are considered to be filled. This is typically taken at ~99.5% relative pressure (P/P₀ = 0.095) and this calculation is taken from the method described by Barrett, Joyner and Halenda [31].

The data for the TiO₂ and the Au/TiO₂ samples show significantly lower surface areas than those of the carbon based materials discussed later. For the nano TiO₂ a value of 21.93 ± 0.03 m²g⁻¹ was established and the composite Au/TiO₂ yielded a value of 22.79 ± 0.13 m²g⁻¹. These values are to be expected due to the relatively small loading of nanoparticles on a crystalline surface [32]. In addition, there is very little hysteresis visible between the adsorption and desorption branches of the isotherms, which would signify lack of capillary condensation which occurs in
porous solids when multilayer adsorption from a vapour proceeds to the point at which pore spaces are filled with liquid separated from the gas phase by menisci [33].

Figure 4.15 Adsorption/desorption isotherms of TiO$_2$ (dashes) and Au/TiO$_2$ (dots)

All of the carbon based materials, SWCNT and Au/SWCNT, P90 and Au/P90 samples show characteristic Type IV adsorption isotherms (IUPAC classification) which indicate that they have mesoporous regions (shown in Figures 4.16 and 4.17) [34]. Adsorption of N$_2$ at low pressures confirms that both have microporosity also [35]. The specific surface area increases when Au is deposited onto the supports as expected for a relatively small loading of particles on a fibre mesh. The specific
surface area of the SWCNT support was determined to be $249 \text{m}^2 \text{g}^{-1}$ where as for Au/SWCNT it is $265 \text{m}^2 \text{g}^{-1}$. In comparison, the specific surface area of the P90 support was determined to be $275 \text{m}^2 \text{g}^{-1}$ whereas for the Au/P90 it is $293 \text{m}^2 \text{g}^{-1}$. All of the aforementioned values are reproducible to $\sim \pm 2 \text{m}^2 \text{g}^{-1}$. It is important to note at this stage that the results for the SWCNT samples maybe influenced by the natural bundling state of SWCNT and are discussed in further detail in section 4.4.7.

![Adsorption/desorption isotherms of SWCNT (dashes) and Au/SWCNT (dots)](image-url)

**Figure 4.16:** Adsorption/desorption isotherms of SWCNT (dashes) and Au/SWCNT (dots)
The meso and microporosity of the SWCNT supported sample is relatively unchanged following the deposition of the gold nanoparticles. The average pore diameters for both the mesoporous and microporous regions were calculated by the instrumentation’s software taking into account the shape of both the adsorption and desorption branches of the isotherm as well as the hysteresis loops using the BJH method based on the Kelvin Equation [Equation 2] where $p$ is the actual vapour pressure, $p_0$ is the saturated vapour pressure, $\gamma$ is the surface tension, $V_m$ is the molar volume, $R$ is the universal gas constant, $r$ is the radius of the capillary,
and $T$ is temperature [15]. For Au/SWCNT $d_{mes} = 6.3\text{nm}$ and $d_{mic} = \sim 0.8\text{nm}$. In comparison the untreated SWCNT had $d_{mes} = 6.1\text{nm}$ and $d_{mic} = \sim 0.7\text{nm}$.

\[
\ln \frac{p}{p_0} = \frac{2\gamma V_m}{rRT}
\]

Equation 4.2: The Kelvin Equation

4.4.6 UV-Vis Spectroscopy

UV-Vis Spectroscopy is one of the most widely used techniques for characterising the optical properties and electronic structure of nanoparticles, the absorption bands are directly related to the diameter [36, 37].

For UV-Visible spectroscopy of the supports and composites, the samples were prepared by dispersing $\sim 0.4\text{mg}$ of the powders in 15ml of deionised water and sonicating for 60 seconds using a sonic tip (VCX Ultrasonic processor 750W) prior to analysis. The generated UV-Visible absorption spectra are shown in Figures 4.18, 4.19 and 4.20.

Figure 4.18 shows the spectra obtained from the TiO$_2$ and Au/TiO$_2$ samples and the clear difference between the two is the broad absorption band with an absorption maximum ($\lambda_{max}$) at 555nm in the Au/TiO$_2$ which shows the existence of a Au plasmon resonance band in the composite sample. From this absorption maximum,
the average particle size can be estimated to be ≤20nm with the assumption that the particles themselves are spherical [36, 37].

Figure 4.18: UV-Visible spectra of TiO$_2$ (dots) and Au/TiO$_2$ (dashes)

For the SWCNT and the Au/SWCNT, it can be clearly seen that the spectra show the characteristic π plasmon band of SWCNTs at ~270nm [38]. The SWCNT spectrum shows very weak bands at ~700nm and 750nm (Inset in Figure 4.19) that correspond to the electronic transitions between the Van Hove singularities in the nanotube density of states, in these cases the E$_{11}$ transitions for the metallic arc discharge tubes [38]. The Au/SWCNT composite spectrum shows an additional clear broad absorption band at ~560nm which corresponds to an Au surface
plasmon resonance band (see inset) and is characteristic of suspended Au particle sizes of $\leq 15$nm [36].

In addition in the composite material spectrum, the $\pi$ plasmon band is somewhat dampened and red shifted by the presence of the Au nanoparticles. The observed decrease of peak intensity at 270nm in the raw SWCNTs compared to the composite material in addition to a red shift of $\sim 8$nm in this band in the Au/SWCNT composite spectrum suggest that the $\pi$ ion interactions between the SWCNT and the Au contribute to the binding between the Au nanoparticles and the SWCNT surface [39]. The spectra of the aqueous suspensions thus indicate that the nanoparticles remain adhered to the SWCNT template.

![Figure 4.19: UV-Visible spectra of SWCNT (dots) and Au/SWCNT (dashes)](image-url)
The absorption spectra for the P90 and the Au/P90 are shown in Figure 4.20. The obvious difference between the spectra is the absorption band at ~560nm in the Au/P90 sample which corresponds to the Au plasmon band indicative of Au particles of ≤ 15nm also seen in the Au/SWCNT composite sample previously (Figure 4.19). It is also curious to note that in both the P90 and Au/P90 composite there is a clear absorption band at ~490nm which is attributed to the electronic transitions between the Van Hove singularities in the graphite density of states, in this case for S_{22} semi conducting bands in the graphite [38]. In addition, the band at ~390nm is likely to be due to the S_{11} semi conducting band in the graphite and is only visible in the composite sample suggesting that there is a charge transfer in the system [40]. This is explored further in section 4.4.7.

Figure 4.20: UV-Visible spectra of P90 (dots) and Au/P90 (dashes)
4.4.7 Raman Spectroscopic Analysis

Raman Spectroscopy has been used extensively to probe the properties of single walled carbon nanotubes and carbon materials [41, 42] as well as the characteristic bands in TiO$_2$ [43, 44]. However, it is worth noting at this point, that at different laser wavelengths ($\lambda_{exc}$) due to the different resonance conditions there are markedly different spectral profiles [45]. With this in mind, each of the support materials and the corresponding composite materials were studied using two different wavelengths, 473nm (2.62eV) and 660nm (1.88eV). 532nm (2.33eV) was not chosen as it was too close to the point at which the Au NPs in the composites absorbed and subsequently showed too much fluorescence to generate reliable data. Figures 4.21 and 4.22 shows representative Raman spectra of TiO$_2$ and Au/TiO$_2$ composites following irradiation at 473nm and 660nm respectively.

For both irradiation wavelengths in the TiO$_2$ sample, the Raman lines at $\sim$145cm$^{-1}$, $\sim$197cm$^{-1}$, $\sim$395cm$^{-1}$, $\sim$519cm$^{-1}$, $\sim$619cm$^{-1}$ and $\sim$635cm$^{-1}$ can be assigned to the E$_g$, E$_g$, B$_{1g}$, A$_{1g}$, B$_{1g}$ and E$_g$ modes of the anatase phase respectively [3]. In the Au/TiO$_2$ composite sample, the most intense E$_g$ mode at $\sim$145cm$^{-1}$, which arises from the extension vibration of the anatase structure, decreases dramatically in intensity due to the deposition of gold nanoparticles on the surface of the titanium dioxide. This together with the reduction of the intensities of the aforementioned modes indicates that the gold has made a modification to the titania surface [46].
Figure 4.21: Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{\text{exc}} = 473\text{nm}$

Figure 4.22: Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{\text{exc}} = 660\text{nm}$
However, when the areas in which you would expect to see effects from Au phonon resonances are accumulated for a long period and the spectra are expanded, the notable variation in peak ratios can be seen as well as significant adjustments to the peak shape profile. (Figures 4.23 and 4.24 show representative spectra for the TiO$_2$ and Au/TiO$_2$ composite at $\lambda_{\text{exc}} = 473\text{nm}$ and $\lambda_{\text{exc}} = 660\text{nm}$ respectively).

In general these phonon resonances would be visible at various wavelengths depending on the localised environment [47]. In other words, the refractive index near the particle surface. Thus, when the refractive index near the nanoparticle surface increases, the nanoparticle extinction spectrum shifts to longer wavelengths (known as blue-shifting). Practically, this means that the nanoparticle extinction peak location will shift to shorter wavelengths (red-shift) if the particles are transferred from water (n=1.33) to air (n=1.00), or shift to longer wavelengths if the particles are transferred to oil (n=1.5). This would lead one to believe that there should be blue shifts when the Au NPs are deposited on an optically dense material in the solid state as this would surely be considered to be a change in environment. In essence, the vibrations of the Au/TiO$_2$ modes are softened because of an increase of effective mass due to the adhesion of the Au NPs on the TiO$_2$ surface [48].
Figure 4.23: Zoomed Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{\text{exc}} = 473$nm

Figure 4.24: Zoomed Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{\text{exc}} = 660$nm
In general, SWCNT display four clear areas of interest in a Raman spectrum [42, 43]. The Radial Breathing Modes (RBM) in the low frequency region (~100-400cm\(^{-1}\)) are associated with the vibration of carbon atoms in a radial direction in relation to the carbon nanotube axis and are often used to calculate the diameters of isolated SWCNT. The RBM’s are exclusive to SWCNT and are in themselves proof of the presence of SWCNT in a sample [49].

The tangential mode (D and G) incorporates three modes, D at ~1300cm\(^{-1}\), \(G^+\) at ~1590cm\(^{-1}\) and \(G^-\) at ~1570cm\(^{-1}\). D is a phonon mode disorder band that is accepted to be due to defects that break the symmetry of the graphene plane in the sample and tends to increase in intensity with doping [50]. \(G^+\) is associated with carbon atom vibrations along the nanotubes axis. \(G^-\) is associated with vibrations of the carbon atoms along the circumferential direction. The G band frequency and shape is also used to distinguish between semiconducting and metallic SWCNTs. Finally the \(G'\) band at ~2700cm\(^{-1}\) is an overtone of the D band. The peaks at ~580cm\(^{-1}\) and ~1100cm\(^{-1}\) are contributions from the underlying microscope slide.

Figure 4.25 shows the Raman spectra of raw SWCNT and the Au/SWCNT composite following irradiation with a laser at 473nm and Figure 4.26 the same at 660nm.
There are several differences between the spectra shown in Figure 4.25. The G\textsuperscript{+} band has shifted upfield from 1591cm\textsuperscript{-1} to 1597cm\textsuperscript{-1} in the composite sample which is indicative of charge transfer onto the SWCNT [51]. This suggests that the Au nanoparticles have lost electrons to the SWCNT and in the process have become positively charged. In contrast, the G\textsuperscript{-} band at 1577cm\textsuperscript{-1} has become more prominent in the composite sample (inset in Figure 4.25). This suggests the presence of nanotubes of metallic character in the sample. Finally the G\textsuperscript{'} band at 2668cm\textsuperscript{-1} has become less pronounced and has red–shifted in the composite and the D band at \(\sim1337cm^{-1}\) has upshifted to \(\sim1343cm^{-1}\). These types of changes have been attributed
to the presence of metallicity either from doping or might suggest preferential selection of the metallic SWCNT interacting with the Au nanoparticles [52].

However when the laser excitation wavelength is changed to 660nm, there are significant differences in the appearance of the spectrum (Figure 4.26). There have been several theories as to why variations occur in SWCNT Raman spectra, from bundling states to changes in conductivity [51] so in essence it is difficult to be completely precise here. However, the point is that there are modifications to the spectra which can be explained in this case by environmental variations that have manifested themselves in a slightly different manner when irradiated and analysed at 473nm. It has been widely discussed in the literature that at certain irradiation wavelengths, semi-conducting SWCNTs are resonant and in others metallic SWCNTs appear [53, 54]. In the case of the Au/SWCNTs, the entire spectrum signal is dampened which is indicative of surface modifications as was also apparent in the Au/TiO$_2$ composite sample spectrum (Figure 4.22).

There are also some other variations in the spectral profiles. Firstly, the RBM’s have changed their shape and have shifted upfield in the Au/SWCNT composite sample. This can be attributed to debundling due to a change of environment [56]. The intensities of the RBM’s have also decreased which can be attributed to reduction in resonance enhancement of selectively functionalised SWCNTs [57] or charge transfer to the nanotubes causing the previously unoccupied electronic states to be filled [58]. It is also worth noting that the change of transition energies after
bundling or debundling can lead to an apparent shift of peaks in the RBM spectra due to differing SWCNTs being resonant in alternative sample morphologies [59]. In addition, there are significant differences in the G line band shape profile. In the SWCNT, the $G^-$ and $G^+$ bands are prominent and easily distinguishable but in the Au/SWCNT composite, the $G$ band profile has broadened and is asymmetric towards the lower wavenumber side. This broadening is commonly attributed to a Breit-Wigner-Fano (BWF) resonance of metallic SWCNTs induced by a coupling of the phonon excitation to a continuum of plasma states [57]. In addition, the intensity of the D-band increases in functionalised SWCNTs. As the appearance of the D-peak is induced by defects, an increase in the D-band intensity is seen as a fingerprint for successful functionalisation [58].

Figure 4.26: Raman Spectra of SWCNT (black) and Au/SWCNT (green) at $\lambda_{exc} = 660$nm (1.88eV).
For the P90 and Au/P90 samples, in both sets of spectra, the two main peaks at \( \sim 1350\text{cm}^{-1} \) and \( \sim 1600\text{cm}^{-1} \) are characteristic of the crystalline phases in graphite or the D and G modes respectively [60-62]. The main difference is the enormous dampening of the signal following the incorporation of Au NPs across both modes at both laser excitation wavelengths which is indicative of deposition of Au nanoparticles onto the P90 surface.

Figures 4.27 and 4.28 show the Raman spectra of raw P90 and the Au/P90 composite at following irradiation at 473nm and 660nm respectively.

![Raman Spectra of P90 and Au/P90](image)

Figure 4.27: Raman Spectra of P90 (black) and Au/P90 (green) composite samples at \( \lambda_{\text{exc}} = 473\text{nm} \) (2.67eV).
It is also worth noting that the intensities of the ratio of the D band vs the G band switch when the laser excitation wavelength is changed to 660nm (1.88eV) as well as the obvious increase in the D (disorder) band which further accentuates the changes to the P90 surface due to the deposition of the Au NPs [61].

Figure 4.28: Raman Spectra of P90 (black) and Au/P90 (green) composite samples at $\lambda_{\text{exc}} = 660\text{nm (1.88eV)}$. 

4.5 Conclusions:

In this chapter, three support materials have been utilised to prepare Au nanoparticulate composites by utilising a simple redox driven reduction reaction tuned to ensure the formation of nanoparticles with average sizes below 10nm with a view to providing maximum potential activity. In addition, both the precursor supports and the composites have been thoroughly characterised using an array of analytical and spectroscopic techniques.

It has been shown that there are large differences in the spectroscopic profiles of each of the support materials as well as their resultant composites. Perhaps the most significantly obvious of these are the UV and Raman spectroscopic profile differences between the SWCNT and the more standardised supports TiO$_2$ and P90. There is some further discussion on this in the overall conclusions in Chapter 7. It would be expected that these differences would lend to variation in their potential applications so the aim now was to exploit one of these applications and preferably an environmentally friendly one.

Thus, as Au/TiO$_2$ and Au/C have been tested as catalysts before [63-69], it was decided that a preliminary catalytic potential comparison study would be carried out with the aforementioned materials and the new composite Au/SWCNT material to ascertain if the newly made Au NP material could find a promising use in this developing area of environmental interest.

In Chapter 5, each of the composites are put to the test as heterogeneous catalysts in a reaction of environmental interest as a proof of concept before moving on to test them in further, more challenging reactions in Chapter 6.
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Chapter 5

Catalytic Activity Experiments: Part I

5.0 Introduction

The oxidation of alcohols to their corresponding aldehydes or ketones (Figure 5.1) is one of the simplest and most useful transformations in organic chemistry and is the core of many synthetic routes in industrial chemistry [1, 2]. Thus, the ability to catalyse these reactions under more ‘green’ conditions is highly desirable. Of concern is that most of the catalysts or processes that have been identified to date are relatively inactive for primary alkyl or secondary alcohols and those used generate heavy-metal waste and are usually run using chlorinated solvents or acidified systems [3-5]. From a green point of view, using O₂ as an oxidant in place of stoichiometric oxygen donors would be ideal, as water is the only by-product of the process. Nevertheless, using O₂ does raise safety concerns particularly at high temperature and pressure so it is preferable to be able to use oxygen at atmospheric pressure.

Typically, catalyst systems used for these types of reactions require the use of solvents, so it is therefore pertinent that the development of catalysts that can operate in a solventless system be explored, as it is important for improved environmental friendliness. In addition, in order to endeavour to stay within in the rigors of ‘green’ processes, it is necessary to either minimise or where possible eliminate the production of heavy metal or chlorinated waste generated during the reactions. Hence, a system in which the only by product is H₂O would be a significant development to the industrial chemical world.

Figure 5.1: Aerobic oxidation of secondary alcohols
Primary aromatic (benzylic) alcohols can be readily transformed to aldehydes that are relatively resistant to further oxidation at least under mild conditions [6]. An example of this is the oxidation of benzyl alcohol (phenylmethanol), which is the most commonly reported test reaction and has been characterised extensively by excellent selectivities and yields on almost all common catalysts [7,8]. However, there are very few test reactions commonly used to compare different types of catalysts for the selective transformation of alcohol to aldehyde/ketone and/or carboxylic acid. Also, more often than not, further oxidation of aldehydes to their corresponding acids is often considered to be an undesirable side reaction and thus the catalysts and processes are regularly optimised to avoid it.

The object of this work is to compare three supported gold nano composites used to catalyse the aerobic oxidation of alcohols. The first, nano Au/TiO$_2$, is employed as an industry standard catalyst for several reactions including some oxidations [9, 10]. A direct comparison is made with SWCNT supported nano Au particles as a novel material. Finally, the catalytic performance of the Au/SWNT composite system is compared to that of nano Au supported on carbon black (Au/P90), which has also been previously explored for its catalytic potential [11].

5.1 *Aerobic solventless oxidation of 1-Phenylethanol (secondary alcohol)*

The oxidation of 1-Phenylethanol to Acetophenone was chosen for study as it has previously been used as a probe reaction to test gold catalysts and, in this context, it has been reported that gold has a superior performance to palladium [12]. In general, nanoparticulate gold is comparable or superior to platinum and ruthenium catalysts for these types of reactions [13, 14].
The selectivities and activities of three supported gold composites are compared in this work, all of which were prepared by the \textit{in situ} reduction method, previously described in Chapter 4.

5.2 Experimental

Aerobic oxidation of 1-Phenylethanol, which has its functional groups in the alpha $\alpha$ position (the position at which the first carbon attaches to the functional group, shown in Figure 5.2) was performed at atmospheric pressure by bubbling oxygen through 1-Phenylethanol with no solvent. A Dean-Stark trap was used to remove the water formed during the reaction. The following reaction conditions were used: $T = 120^\circ$C, 207 mmol of substrate (substrate to catalyst mass ratio 1 : 0.002) and O$_2$ flow rate of 35 ml min$^{-1}$ The reactions were carried out in triplicate using fresh catalyst to ensure reproducibility.

![Figure 5.2: Aerobic Oxidation of 1-Phenylethanol](image)

5.2.1 Quantification of Product(s)

In order to initially quantify the product(s) from the reactions, Fourier Transform Infrared (FT-IR) adsorption spectroscopy was employed. FT-IR was used during the reaction to monitor the conversion of the substrate 1-Phenylethanol (whose FT-IR spectrum is shown...
in Figure 5.3), at a number of time points during the oxidation process. By looking at the decrease in absorbance of the OH band at $\sim 3300\text{cm}^{-1}$ as the reaction proceeds, in addition to the appearance of the C=O carbonyl stretch at $\sim 1700\text{cm}^{-1}$ (Figure 5.4), characteristic of ketones including in the expected product acetophenone, the $\%$ conversion can be determined. This is quantified using a calibration curve constructed with measured absorbance values at specified percentages for the analyte of interest. The absorbance value at each time point is compared to those of the known percentages of the analyte and the conversion $\%$ calculated accordingly. A point to note here is that the major functional group band assignments not discussed in text or shown in the representative figures for the substrate and product FT-IR spectra are shown in tabulated form in Appendix A1 (Tables 1-3) respectively for reference purposes.

![Figure 5.3: FT-IR Spectrum of 1-phenylethanol (substrate)](image-url)
FT-IR work was carried out using a Perkin Elmer Spectrum 400 spectrometer which is a dual range bench top FT-IR instrument fitted with an MCT (Mercury Cadmium Telluride) detector. Its fully optimized performance is achieved by the provision of dual sources, dual beam splitters and dual detectors. For this work, the MIR configuration was used over a range of 4000cm$^{-1}$-650cm$^{-1}$ with a resolution of 4cm$^{-1}$. The liquid aliquots were dropped onto a UATR (Universal Attenuated Total Reflectance) crystal for analysis.
The % conversion and % selectivity for the aerobic oxidation of 1-phenylethanol to acetophenone are calculated using Equations 5.1 and 5.2 respectively.

Conversion of the 1-phenylethanol is defined based on the initial \( (C_0) \) and final \( (C_1) \) molar concentrations of the substrate:

**Equation 5.1:** \[ \text{% Conv} = 100 \times \frac{(C_0) - (C_1)}{(C_0)}. \]

Selectivity to acetophenone is defined as the ratio of the molar concentration of acetophenone formed during the reaction \( (C_2) \) to the molar concentration of 1-phenylethanol \( (C_1) \) converted in the same time:

**Equation 5.2:** \[ \text{% Sel.} = 100 \times \frac{(C_2)}{(C_0)-(C_1)}. \]

5.2.2 **Confirmation of Product(s).**

\(^1\)H and \(^{13}\)C NMR were also employed to confirm the product(s) and representative NMR spectra for the product(s) using each of the three composites are shown in Appendix 1. \(^1\)H and \(^{13}\)C NMR spectra were measured using a Bruker Avance III (400 MHz). Chemical shifts or bands (\( \delta \)) are expressed in parts per million relative to the residual solvent peak chloroform which in this case is at 7.26ppm for the \(^1\)H spectra and 77.2ppm for the \(^{13}\)C spectra respectively.

The \(^1\)H spectrum of the substrate (shown in Figure 5.5) has 5 clear CH bands representative of the aromatic ring at 7.3ppm, 1 CH band adjacent to the OH group at 4.7ppm, the OH group band at 2.04ppm and finally the CH\(_3\) band at 1.5ppm.
The corresponding $^{13}$C spectrum (Figure 5.6) has 2 CH bands at 129.0ppm and 3 CH bands at 126.5ppm, representative of the aromatic ring, as well as a C band at 38.6ppm. In addition; there is a CH band at 63.6 which is adjacent to the OH functional group.
Contrastingly, the product $^1$H and $^{13}$C spectra are markedly different. In the $^1$H spectrum (shown in Figure 5.7), there are 2 CH bands at 7.95ppm, 1 CH band at 7.54 and 2 CH bands at 7.46ppm, representative of the aromatic ring. There is also a CH$_3$ band at 2.58ppm which is derived from the methyl group at the $\alpha$ position to the C=O group.

![Figure 5.7: $^1$H NMR spectrum of Acetophenone](image)

The corresponding $^{13}$C spectrum (Figure 5.8) shows 3 CH bands at 128.5ppm, 1 CH band at 133.1ppm and 2CH bands at 137ppm, which are attributed to the aromatic ring. In addition, there is CH$_3$ band at 26.6ppm and finally a C band at 198.1ppm which is derived from the C=O functional group and is indicative of ketones. For reference, the triplet at $\sim$77ppm is the residual chloroform solvent peak.
5.2.3 Determination of Selectivity (for Au/P90 reactions).

In the case of the reactions using the Au/P90 catalyst, a dual product formation is evident in the FT-IR spectra and the corresponding NMR data (this is discussed in more detail in Section 5.3.3). In order to quantify the % conversion to each product under these reaction conditions, High Pressure Liquid Chromatography (HPLC) was used to separate the analytes of interest and a method was developed and validated for this very purpose. Each fraction is injected onto the HPLC column after dilution in the mobile phase and the subsequent percentages of each analyte can be calculated from their respective calibration curves relative to the concentration of the sample.

The validation protocol for the method in essence involved ensuring that the analytes of interest could be separated fully using a stationary phase and mobile phase system. Then the analytes were tested to the lowest level of quantification (LLOQ) so that a calibration
range could be constructed to fit the constraints of the visible concentration for each of the analytes. Once the LLOQ’s had been determined, calibration standards containing known amounts of each analyte were made up in mobile phase over an eight point calibration range from 1ppm-100ppm inclusive. In addition, quality control (QC) samples were prepared at the LLOQ, mid-range and ULOQ (Upper Level of Quantification). The purpose of the QC samples is three fold. Firstly, they are dispersed amongst the ‘live’ fraction samples to ensure that the concentration values remain accurate throughout the reactions. In addition, they are used to ensure there is no sample carry over from the stationary phase as the reaction proceeds. Finally, the peak shapes for the analytes can be monitored at both ends of the sample concentration range as peak shape is vital for the processing of the integrated peaks once the reactions are completed. These peaks are then used for quantification of the products by measuring the areas under the peaks relative to the calibration standards, rather than the FTIR bands used for the Au/TiO$_2$ and Au/SWCNT substrates. This type of protocol is standard in industry to clarify the reproducibility and accuracy of the methodology [15].

For full validation, this procedure has to be repeated in triplicate to confirm the reproducibility of the method as well as ensure that the analyte retention times (RT) on the column are stable. This is vital to the method because often these types of separation systems are used for detailed analyte quantification so it is imperative to know that the RT’s remain stable so that each compound of interest can be confirmed to be present at its known retention time.

HPLC analyte separation was achieved using a Waters 600E Multi-Solvent Delivery System with a dual absorbance UV/Visible Detector. A stationary phase column (Gemini
C18 5µ, 150 x 4.6mm) was used. This column was chose as it is suitable for samples with variation in pH. A mobile phase consisting of acetonitrile and water in a ratio of 60:40 was used. Samples of 10µl in volume were injected onto the column using a Rheodyne 7725i Injection Valve with an internal mobile phase flow switch and data was generated then analysed using Waters Empower II Software.

5.3 Results

5.3.1 Au/TiO₂ Catalyst

The ¹H and ¹³C NMR data from these reactions show, as expected, the formation of acetophenone with no other side products. Figure 5.9 shows an FT-IR spectrum of the product from the reaction, which shows the clear presence of the C=O carbonyl stretch at 1680cm⁻¹ due to conjugation of the carbonyl group with the phenyl group in alpha and beta-unsaturated ketones. In addition, the OH stretch visible at ~3300cm⁻¹ in the secondary alcohol substrate (Figure 5.3) has completely disappeared, which is an excellent indication that the reaction has gone to completion.
Figure 5.9: FT-IR spectrum of product from aerobic oxidation of 1-phenyethanol using Au/TiO$_2$ after 8hrs.

Figure 5.10 shows the % conversion to acetophenone vs time. The use of the Au/TiO$_2$ catalyst gave a conversion of ~95% with 100% selectivity within ~8hrs towards acetophenone when the reaction was conducted under the aforementioned conditions and the only by product was H$_2$O. Note, the error bars in the % conversion graphs in this section are based on the standard deviation of the FTIR measurements and utilisation of Equation 5.1. However, they do neglect any inaccuracies in the automated spectral baseline correction procedure.
Figure 5.10: Conversion of 1-Phenylethanol to Acetophenone using O₂ over an Au/TiO₂ catalyst as a function of time. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.

5.3.2 Au/SWCNT Catalyst

The use of Au/SWCNT as a catalyst results in the expected oxidation to the corresponding ketone acetophenone (confirmed by $^1$H and $^{13}$C NMR – Appendix 1), showing 100% selectivity to the desired product with ~95% conversion and the only by product was H₂O. Compared to the observations using the Au/TiO₂ catalyst, the only variation was the time taken for the reaction to go to completion. Whereas with the former system the reaction took ~8hrs, with the Au/SWCNT catalyst it had reached 95% conversion within ~3hrs. The
time evolution of the % conversion for the Au/SWCNT catalysed reaction is shown in Figure 5.11.

![Figure 5.11: Conversion of 1-Phenylethanol to Acetophenone using O₂ over an Au/SWCNT catalyst as a function of time. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.](image)

5.3.3 Au/P90

Notably, when the Au/P90 catalyst was used, the FTIR profile indicated the presence of a by-product of the reaction. Figure 5.12 shows the FT-IR spectrum for the mixture and initial observations using the FT-IR data show some variations in the fingerprint region of the spectrum confirming more than one product had formed. In addition, the C=O band indicative of ketones is still clearly visible but has red shifted to 1683cm⁻¹ and a peak has appeared at 1495cm⁻¹, which is characteristic of a CH₂ bend in arenes.
The NMR data confirms that there is a second product alongside the acetophenone. Firstly the $^1$H NMR spectrum shows a band at 1.2ppm which is attributed to the CH$_3$ group adjacent to the β positioned (the second carbon which would be attached to the functional group) carbon. In addition, the $^{13}$C NMR spectrum shows the same CH$_3$ band at 15.6ppm. These bands are not visible in the pure acetophenone spectra and are also clear indications that there is a second product formed under these reaction conditions.
Figure 5.13: $^1$H NMR spectrum of acetophenone and by-product for the aerobic oxidation of 1-phenylethanol using Au/P90 catalyst.

Figure 5.14: $^{13}$C NMR spectrum of product(s) of aerobic oxidation of 1-Phenylethanol using Au/P90 catalyst.
Notably, under similar reaction conditions, using Pd/CeO$_2$ and Pd/apatite catalysts, ethylbenzene was reported to be formed as a by-product [12], although no explanation was proposed for this occurrence. With this exception, no other products have been reported for the aerobic oxidation of 1-Phenylethanol other than the expected acetophenone. The structure of ethylbenzene is shown in Figure 5.15 for reference.

![Figure 5.15: Structure of Ethylbenzene](image)

The FT-IR spectrum (Figure 5.16) of ethylbenzene is markedly different to the acetophenone spectrum (Figure 5.4) although similarities between itself and the product spectrum (Figure 5.12) are apparent. Firstly, the detail in the C-H stretches at 3084cm$^{-1}$, 3063cm$^{-1}$ and 3027cm$^{-1}$ for aromatics plus the alkyl C-H stretch at 2932cm$^{-1}$ are all visible in both the product(s) spectrum and the ethylbenzene spectrum, but not in the pure acetophenone spectrum. In addition, the fingerprint region (below 1500cm$^{-1}$) is significantly diminished in spectral detail in the ethylbenzene spectrum, when compared to both the product(s) spectrum (Figure 5.12) and the pure acetophenone spectrum (Figure 5.4). Ethylbenzene is therefore a likely candidate for the by-product of the reaction using Au/P90 as catalyst.
The NMR data confirms this in a couple of ways. Firstly, the $^1$H NMR spectrum shows a band at 1.2ppm which can be attributed to the CH$_3$ group adjacent to the β positioned
carbon bond and a band at 2.6ppm which is a contribution from the \( \text{CH}_2 \) (methylene) \( \alpha \) positioned carbon. The \( \text{CH}_3 \) group in acetophenone (Figure 5.8) is shifted further upfield to 2.6ppm, because of the withdrawing effects of the C=O group adjacent to it.

The \(^{13}\text{C} \) NMR spectrum shows the same \( \text{CH}_3 \) band at 15.6ppm and the corresponding \( \text{CH}_2 \) band at \( \sim 29 \)ppm. It is also clear that there is no band at 199ppm, which is the characteristic C=O signal for ketones. This latter band is plainly visible in the pure acetophenone spectra (Figure 5.4) so its absence is also clear indication that there is a second product formed under these reaction conditions.

![Figure 5.18: \(^{13}\text{C} \) NMR spectrum of ethylbenzene](image)

These observations give a very strong indication that the by product under these reaction conditions is in fact ethylbenzene. Thus, in order to confirm this, it was necessary to employ a further analytical tool to separate the two products. In addition, by separating the
two, it would then be possible to quantify the % conversion to each during the course of the reaction.

For this purpose, HPLC was used as a further confirmation. As detailed in section 5.2.3, aliquots were taken from the reaction at several time points and the two analytes of interest were separated on a stationary phase column by solubilising them in a suitable mobile phase (in this case 60:40 Acetonitrile/H₂O). The areas under the curves for the peaks were then used in conjunction with characteristic calibration curves which yielded average values for their linear regressions of $R^2=0.9986$ for acetophenone and $R^2=0.9987$ for ethylbenzene respectively. The calibration curves are constructed using as-purchased analyte stock solutions that are diluted over the range required to determine the % of each in the aliquots which then permits the calculation of both the % conversions and % selectivity for each product. Figure 5.19 shows a representative chromatogram of the two completely separated analytes at concentrations of 20ppm.

![HPLC chromatogram](image)

Figure 5.19: HPLC chromatogram showing the two separated product analytes acetophenone (red) and ethylbenzene (black) at 20ppm.
It was thus determined using the aforementioned methodology that the use of the Au/P90 composite resulted in a dual product formation with ~60% selectivity with ~65% conversion to acetophenone and ~30% selectivity with 35% conversion to ethylbenzene. The reaction was repeated in triplicate, resulting in the same outcome each time thus verifying it not to be an anomaly. Figure 5.20 shows the averaged % conversion as a function of time.

Figure 5.20: Conversion of 1-Phenylethanol to Acetophenone (dots) and Ethylbenzene (dashes) using O$_2$ over an Au/P90 catalyst as a function of time.
The dual formation of ethylbenzene during the oxidation of a secondary alcohol to its subsequent ketone was unexpected, as it should not be possible under the reaction conditions used. In order for ethylbenzene to be produced under these types of reaction, there would either require the surface carbon to act as a reductant or there be surface H present and these are hard to reconcile without further investigation. These issues are touched on in section 5.4 and then experimental data is presented in section 5.5.

5.4 Proposed Mechanisms

The mechanism for aerobic oxidation of 1-Phenylethanol to Acetophenone is thought to occur in four stages, following a Langmuir-Hinshelwood type mechanism (Figure 5.21) [15]. The initial stage is the adsorption of the reactants followed by breaking of the O-H bond of the alcohol functional group attached to the ring, on adsorption to active sites, forming an alkoxide species and releasing a hydrogen atom. This is then followed by the rate determining step, which is the breaking of the weakest C-H bond, in this case in the β position, due to the electron withdrawing effect of the neighbouring O atom. This would generally be accelerated by the presence of basicity and in this case occurs due to the slightly basic nature of the as prepared catalyst (pH 8.5) in the substrate system [17]. The role of oxygen (or similarly adsorbed OH species in alkaline medium) is to oxidize the co-product hydrogen and thus shift the equilibrium towards the carbonyl compound.
Figure 5.21: Proposed mechanism for the aerobic oxidation of 1-Phenylethanol to Acetophenone using Au/TiO$_2$ and Au/SWCNT catalysts [15].

The variation in time taken for the reactions to go to completion could be potentially attributed to the Au particle sizes which for the Au/TiO$_2$ catalyst are larger (10-20 nm) than those of both the Au/SWCNT and Au/P90 that are between (7-9 nm). As is widely reported in the literature, oxidation over gold is very sensitive to particle size [18-21] so this could go some way to explaining the difference in time taken for the reactions to go to completion.

In addition the Au nanoparticle size distribution on the SWCNT support being more homogeneous than that on the TiO$_2$ support, which could be ascribed to the significantly lower surface area of the TiO$_2$ supported composite (~23 m$^2$ g$^{-1}$) in contrast to that of the SWCNT supported catalyst (265 m$^2$ g$^{-1}$). This in turn would be likely to increase the number of exposed active catalyst sites for the adsorption of O$_2$ which would subsequently be responsible for the increased reaction rate. The surface area of the Au/TiO$_2$ catalyst is
over a factor of ten less than that of the Au/SWCNT catalyst, so this is possibly another contributory factor for the time taken for the reaction to go to completion to reduce from 8hrs to 3hrs.

In the case of Au/P90 catalyst, it is clear that it played an active part in the reaction as the % conversion to acetophenone is 65%. Conversely the production of ethylbenzene under these conditions could be possible with the presence of surface carbon acting as a reductant and producing CO and ethylbenzene alongside oxidation to the ketone (Figure 5.22A).

\[
\begin{align*}
\text{C(s)} + \text{O} & \text{(s)} + \text{H} \rightarrow \text{C(s)} + \text{CO} + \text{H}_2
\end{align*}
\]

Figure 5.22A: Potential pathway for reduction of 1-Phenylethanol to Ethylbenzene

Alternatively, surface H could remain behind on the catalyst after manufacture although this is a less likely scenario. The only way envisaged for surface H to be present in the catalyst is if it were retained within the surface structure during the preparation of the catalyst which is made using the precursor salt HAuCl₄ and using a reducing agent NaBH₄ (section 4.2). It would appear that, despite washing the catalyst as per standard protocol [22], not all of the H⁺ ions are removed, but remain adhered to the catalyst surface during the drying process. In essence, the amorphous carbon support acts as a hydrogen trap.

This would mean that if the active sites on the catalyst are strongly basic when it is in suspension with the substrate and, it is possible that hydrogenation of 1-Phenylethanol could occur if the reactant itself was to behave as a hydrogen acceptor. Bearing this in
mind, it is suspected that the O₂ reduction mechanism would be quite complex, involving competing reaction routes. The most straightforward one in this case would be the stepwise partial oxidation via a phenyethoxy intermediate namely from O₂ to O* and then hydrogenation to ethylbenzene by released H atoms adhered to the surface of the catalyst (Route 2) and, in parallel, the generic oxidation with loss of hydrogen to form acetophenone (Route 1). Figure 5.22B shows the possible mechanistic routes for the dual formation of acetophenone and ethylbenzene using the Au/P90 catalyst.

Figure 5.22B: Proposed mechanism for the aerobic oxidation of 1-Phenylethanol to Acetophenone using Au/P90 catalyst.
5.5 Recycled Catalyst Cycles

In the interests of determining both the catalyst stability and further investigating the nature of the results yielded using the Au/P90 catalyst, it was necessary to repeat the reactions using recycled catalyst for each of the three composites over at least three reaction cycles. Between cycles, the catalyst was collected after filtration, washed thoroughly using acetone which has been reported to promote catalyst regeneration [23] and deionised water, then finally dried at ~120°C overnight prior to redeployment.

5.5.1 Au/TiO₂

Testing the reusability of the Au/TiO₂ illustrates that the catalyst has a moderate decrease in its activity after an additional three reaction cycles which in turn demonstrates the relative stability of the Au/TiO₂ catalyst for this reaction. Figure 5.23 shows the % conversion variation over the three reaction cycles for the Au/TiO₂ catalysts and Table 5.1 shows the % conversion values after each cycle for ease of reference. Note, the error margins are calculated for these and for subsequent data in this section from the standard deviation of the average conversion values for each reaction cycle. This does not take into account the reduction in potency of the catalyst after each use.
Figure 5.23: % conversion vs time for reactions using the recycled Au/TiO$_2$ catalyst.

Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.

<table>
<thead>
<tr>
<th>% Conversion</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Conversion</td>
<td>95.2</td>
<td>94.3</td>
<td>92.8</td>
</tr>
</tbody>
</table>

Figure 5.24: Table of averaged % conversion values for three reaction cycles using recycled Au/TiO$_2$. 

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5.5.2 Au/SWCNT

Similarly, the recycled Au/SWCNT catalyst showed good reusability over three reaction cycles and a selectivity of 100% within the same timeframe with marginal decrease in its activity which would be expected over several uses [24]. Figure 5.25 shows a graph of the % conversion vs time for the three reaction cycles and Table 5.2 shows the maximum % conversion values for each cycle for clarity.

![Graph showing conversion vs time for three reaction cycles using recycled Au/SWCNT catalyst.]

**Figure 5.25:** Conversion of 1-Phenylethanol to Acetophenone using O₂ over a recycled Au/SWCNT catalyst for three cycles as a function of time. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.

<table>
<thead>
<tr>
<th>% Conversion</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>94.1</td>
<td>93.7</td>
<td>93.1</td>
</tr>
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</table>

**Figure 5.26:** Table of averaged % conversion values for three reaction cycles using recycled Au/SWCNT over 3hrs.
5.5.3 Au/P90

Following on from the aforementioned dual product formation using the Au/P90 composite, the reaction was repeated using recycled Au/P90 catalyst material for an extended five full reaction cycles. As mentioned in section 5.4, the production of ethylbenzene under these conditions could be possible with the presence of surface carbon acting as a reductant producing CO and ethylbenzene alongside oxidation to the ketone. As the reaction cycles ensued, the % conversion to acetophenone increased and the by-product ethylbenzene reduced and ceased, as would be expected if the active carbon support P90 acted as a reductant producing CO but once this CO production ceased, the Au/C remaining was now stable as a selective oxidation catalyst.

Alternatively, as discussed for a second hypothesis, if there was excess H on the catalyst surface, the surface H would be removed as the reaction took place over a number of cycles. As the concurrent formation of ethylbenzene decreased and then ceased after the second reaction cycle this could be consistent with a release of trapped hydrogen atoms which in turn are consumed during the repeated reaction process or slowly removed during the washing of the composite material between reaction cycles [17]. This would also be consistent with the reaction mechanism as described by Figure 5.22 (Route 2). There is also an increase in water production as the ethylbenzene production decreases consistent with a shift to Route 1 as the residual surface hydrogen in the composite is consumed. The production of water would be completely normal under these reaction conditions. The ethylbenzene production could possibly be attributed to free radical formation due to reactive oxygen species such as a hydroxyl radical being formed but detailed EPR spin trapping and oxygen monitoring techniques utilised for other oxidation type reactions [25,
26] would be required to attempt to determine and devise a detailed mechanistic pathway which is outside the scope of this work. Figure 5.27 shows the % conversions to acetophenone over the five reaction cycles and Table 5.3 the % conversions to ethylbenzene over three reaction cycles.

![Graph showing % conversion to acetophenone vs time over five cycles using recycled Au/P90 after 4hrs. Cycle 1: Black, Cycle 2: Red, Cycle 3: Green, Cycle 4: Blue and Cycle 5: Pink.](image)

Figure 5.27: % conversion to acetophenone vs time over five cycles using recycled Au/P90 after 4hrs. Cycle 1: Black, Cycle 2: Red, Cycle 3: Green, Cycle 4: Blue and Cycle 5: Pink.
Figure 5.28: % conversion to ethylbenzene over three cycles using recycled Au/P90 after 4hrs. Cycle 1: Black, Cycle 2: Pink and Cycle 3: Green.

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
<th>Cycle 5</th>
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<td>% Conv to Acetophenone</td>
<td>62.5</td>
<td>93.1</td>
<td>88.2</td>
<td>82.1</td>
<td>79.4</td>
</tr>
<tr>
<td>% Conv to Ethylbenzene</td>
<td>32.4</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.29: Table of % conversions to both products using the recycled Au/P90 over five reaction cycles.

These results illustrate the resistance of the Au/P90 catalyst to degradation but also clearly show an overall decrease in activity in direct contrast to both the Au/TiO$_2$ and Au/SWCNT
catalysts. Figure 5.30 shows the highest recorded % conversion for each of the three composites.

Notably, even when the Au/P90 is purged by the first reaction cycle, the conversion rate is significantly lower than that of the Au/SWCNT catalyst, although it is substantially higher than that of the Au/TiO$_2$ counterpart.

Figure 5.30: Summary of % conversions to acetophenone over Au/TiO$_2$ (blue dots), Au/SWCNT (green dots) and Au/P90 (black dots).
5.6 Conclusions:

In this chapter, the three composite materials have been tested for their initial catalytic activity in a probe reaction. While all three catalyse the oxidation to the expected ketone, there are some distinct variations in their performances. The Au/TiO$_2$ catalyst which is 100% selective to the formation of its corresponding ketone within ~8hrs while Au/SWCNT catalyst is 100% selective to formation of the ketone much faster within ~3hrs. The Au/P90 catalyst promotes the production of a secondary product ethylbenzene alongside acetophenone most likely due to either the active carbon support acting as a reductant or its capacity for trapping hydrogen during its synthesis [27]. However, the secondary reaction ceases when the catalyst is recycled which suggests that either the remaining Au/C catalyst has ceased to produce CO and has stabilised or that the hydrogen trapped in the support is either used up as the catalyst is turned over or removed during the washing process between cycles. A detailed investigation into this unusual situation is beyond the limits of this body of work and so it will not be discussed in any further detail in this thesis.

While all three composite materials show potential as catalysts in this reaction type, the Au/SWCNT composite in this early test phase has shown the most promise most specifically in terms of time taken for full reactant conversion, i.e. reaction rate. In order to determine the true catalytic potential of each of the composites it is necessary to test them in more than one reaction as well as in a more challenging system [28]. In Chapter 6, the three composites are tested for their activity in the aerobic oxidations of two primary aromatic alcohols and the results are discussed in detail.
References:


Chapter 6

Catalytic Activity Experiments Part II
6.1 Introduction

Catalytic conversion of primary alcohols to aldehydes is essential for the preparation of fragrances and food additives as well as many organic intermediates [1]. Traditional methods for the synthesis of aldehydes generally involve the use of stoichiometric amounts of inorganic oxidants such as Cr$^{VI}$ and generate large quantities of undesirable waste. Thus the development of effective and environmentally benign heterogeneously catalysed oxidations of primary alcohols is an important challenge. Metal catalysed reactions using molecular oxygen instead of mineral oxidizing agents are particularly attractive for environmental reasons. Pd and Pt metals supported on aluminium oxide are among the widely used metal catalysts in the selective oxidation of alcohols. More recently supported gold nanoparticles have been shown to be a versatile catalyst for primary alcohol oxidation addressing the selectivity constraints toward aldehydes in the presence of aqueous alkali [2-5].

It can be seen in the literature that efforts are on going to improve selectivity using catalyst design modifications [6]. However a significant of this is done using computational modelling based on the expected performance of the catalyst or by making the modifications while it is in a reactor system [7]. The preparation of these catalysts is a relatively easy process and the results so far have shown there is no specific requirement for modification in terms of their catalytic activity.

It has been shown in Chapter 5 that the SWCNT supported gold nanoparticle catalyst showed the most promise of the three catalytic systems tested albeit in the less demanding secondary alcohol oxidation. However in order to establish the suitability of this novel
composite material for heterogeneous catalysis, it is necessary to test its ability versus other catalysts in more than one reaction. It has been shown that it is 100% selective to the ketone in the aerobic oxidation of 1-phenylethanol with ≥95% conversion in ~3hrs so it would be of interest to analyse its ability to catalyse the aerobic oxidation of its primary alcohol counterpart.

In the first half of this chapter, the aerobic oxidation of 2-phenylethanol, using the three composites as potential catalysts are shown and the results discussed in detail. The second half of the chapter details the aerobic oxidation of another primary alcohol, benzylalcohol, which is commonly used as a general solvent for inks and coatings [8]. In addition, it is used in the toiletries industries for soap and perfume manufacture and so it is an essential component of multiple organic syntheses. The results for this are also discussed and a direct comparison made for the three composite materials.

6.2. Experimental

6.2.1. Aerobic solventless oxidation of 2-phenylethanol

The oxidation of 2-phenylethanol (which has its functional groups in the β position, as shown in Figure 6.1) is usually carried out with complex catalytic systems, but most of them are fairly acidic and are often selective to the production of the corresponding carboxylic acid [6-8]. Those are mild enough to just go as far as the aldehyde either require solvents [9] or irradiation [10] and are thus not considered to be environmentally friendly. Specific examples of this would be working under acidic or basic conditions by modifying the pH of the substrate/catalyst system prior to the reaction or use of additional solvents or strong oxidising agents alongside the substrate. In this work, a solventless system is used
with three supported gold nanocatalysts which are slightly basic following their preparation protocol (Chapter 4 Section 4.2).

Figure 6.1 Aerobic oxidation of 2-phenylethanol to phenylacetaldehyde.

6.2.2 Reactions using Au/TiO$_2$ catalyst.

Aerobic oxidation of 2-phenylethanol was performed at atmospheric pressure by bubbling oxygen through 2-phenylethanol in a solventless system as carried out for the aerobic oxidation of 1-phenylethanol in Chapter 5. As previously, a Dean-Stark trap was used to remove the water formed during the reaction. The reaction conditions were as follows. T = 120 °C, 208 mmol of substrate (substrate to catalyst mass ratio 1 : 0.002) and O$_2$ flow rate of 35 mL min$^{-1}$ for the required time to go to completion. The reactions were carried out in triplicate using fresh catalyst to verify reproducibility.

The qualitative and quantitative analysis of product(s) was carried out in the same way as described previously in Chapter 5 (section 5.2.1). The partial conversion of 2-phenylethanol (whose FT-IR spectrum is shown in Figure 6.2) to its corresponding aldehyde phenylacetaldehyde, (FT-IR spectrum shown in Figure 6.5) as well as ‘intermediates’ took ~6hrs using the Au/TiO$_2$ catalyst. For clarity, the $^1$H and $^{13}$C NMR spectra for 2-phenylethanol are shown in Figures 6.3 and 6.4 respectively. In addition, for reference, any
of the major band assignments for the FT-IR spectra not discussed or shown in the representative data are shown tabulated in Appendix A1 (Tables 4-6 respectively).

Figure 6.2: FT-IR Spectrum of 2-phenylethanol substrate

Figure 6.3: $^1$H NMR spectrum of 2-phenylethanol.
The $^1$H spectrum of the substrate (shown in Figure 6.3) has 5 clear CH bands representative of the aromatic ring between 7.0 and 7.21ppm, bands at ~2.7ppm as well as ~3.8ppm which are contributions from CH$_2$ and a band at 2.0pm which is indicative of the OH group in an alcohol. In contrast, the $^{13}$C spectrum (Figure 6.4) has 5 clear CH bands representative of the aromatic ring between 126-129ppm, bands at ~39ppm as well as ~62ppm which are CH$_2$ contributions and finally a band at ~140ppm which is representative of C-C at the junction of the aromatic ring and the functional group.
The $^1$H NMR spectrum of the expected aldehyde is shown in Figure 6.6. There are 5 CH bands contributed by the aromatic ring at ~7.1ppm, a CH$_2$ band at ~3.7ppm and finally the CH band at ~9.7ppm which is a contribution from the CHO functionality of the C=O aldehyde stretch.
The $^{13}$C spectrum of the aldehyde (shown in Figure 6.7) has 5 clear CH bands contributed by the aromatic ring between 127-130ppm, a $\text{CH}_2$ band at ~51ppm, a C band at ~136ppm from the junction of the ring and the functionality and a CH band at ~9.8ppm corresponding to the carbonyl functional group.
There are some conclusions that can be drawn from the FT-IR spectra of the substrate (Figure 6.2) and of the reaction mixture (Figure 6.8). Firstly, the characteristic broad alcohol O-H group visible in the substrate spectrum at ~3300 cm$^{-1}$ has completely disappeared in the product spectrum. This strongly suggests that the substrate has reacted fully under the aforementioned conditions.

Also, there is a strong band present at ~1725 cm$^{-1}$ which can be attributed to a C=O stretch for an aldehyde. This band also increases in intensity as the reaction proceeds consistent with conversion from the alcohol to an aldehyde. The position of this band would be expected to be lower (~1700 cm$^{-1}$) if the reaction had proceeded all the way to the carboxylic acid. In addition there are also several variations in the fingerprint region of the substrate compared to the product(s) spectrum which are indicative of changes in the localised environment.
Figure 6.8: FT-IR spectrum of reaction mixture after 360 mins of reaction.

The reaction does not continue to form the carboxylic acid and this is clear from the absence of a carboxylic acid group at 11ppm in the product(s) $^1$H NMR spectrum (Figure 6.10) however, there is evidence of by-product formation during the reaction alongside the formation of the aldehyde, in particular the cluster of bands between 7-7.2ppm which add up to three additional aromatic ring contributions. In addition, there are 3 CH bands between ~4.5-5.5ppm (indicated by black arrows in Figure 6.12) which can be attributed to contributions from linkers in the by product structure (shown in Figure 6.12). There are also 3 CH$_2$ bands which are contributions from the bonds between the linker and the aromatic rings (indicated by red arrows in Figure 6.12).

Initially, it was thought that the presence of the additional features in both the FTIR and NMR spectra may be a contamination issue. However, the observations are consistent in
the FTIR and NMR data from all of the reactions. Despite leaving the reaction to continue on beyond the 5.5hr window, there is no further conversion to the aldehyde or any onward conversion to its carboxylic acid counterpart. The reaction simply stops with yields of ~25% for the aldehyde and ~75% for the by-product. Figure 6.9 shows the % conversion vs time to phenylacetaldehyde as measured using FT-IR. % conversion to the aldehyde was calculated using the absorbance values of the C=O stretch at 1780cm$^{-1}$.

Note, the error bars in the % conversion graphs in this section are based on the standard deviation of the FTIR measurements (specifically the C=O stretch) and utilisation of Equation 5.1 (Chapter 5 Section 5.2.1). However, they do neglect any inaccuracies in the automated spectral baseline correction procedure.

Figure 6.9: % conversion to phenylacetaldehyde vs time using Au/TiO$_2$ catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.
Figure 6.10: $^1$H NMR spectrum of reaction mixture after 6hrs from aerobic oxidation of 2-phenylethanol.

The $^{13}$C spectrum for the products (Figure 6.11) also shows the corresponding CH bands between 126-129ppm which are contributions from the aromatic rings. Also there are 3 CH$_2$ bands at ~49ppm bands which are contributions from the positions between the linker and the aromatic rings. Finally there are CH bands between 95-100ppm which are contributions from the linker.
It is very clear from the huge variation between the substrate spectrum (Figure 6.2) and the reaction mixture spectrum (Figure 6.8) that at least partial conversion to the corresponding aldehyde has occurred. Also as the C=O stretch is such a dominant feature in both the FT-IR and NMR spectra (not shown in Figure 6.11), it is clear that a carbonyl containing species is present. It is also worth noting that the C=O stretch is down shifted ~1780cm\(^{-1}\) down to ~1760cm\(^{-1}\) as the reaction proceeds, as well as between reactions. The vibration of the carbonyl group in the product should be fixed at one wavelength if it is purely a single
carbonyl species so this down shift most definitely points towards the presence of another species.

Considering what the by-product was likely to be, it was noted in literature the fact that phenylacetaldehyde has a tendency to polymerise on standing and that in fact the trimer 2,4,6-tribenzyl-s-trioxane is its common form for long term storage [11]. Phenylacetaldehyde is also polymerised in the presence of acids such as sulphuric acid and hydrochloric acid, so it is safe to assume that a slightly acidic or basic system would provide a similar environment [12]. Figure 6.12 shows the structure of this trimer for clarification.

The structure of the trimer shows the three functionalised aromatic rings with a trioxane linker between all three. A trioxane is a six membered ring with three C atoms and three O atoms interspersed throughout the ring structure. The red arrows highlight the aforementioned positions between the aromatic rings and the trioxane ring and the black
arrows highlight the positions in the trioxane linker. The contributions to the structure are shown and discussed in the $^1$H and $^{13}$C NMR spectra shown earlier (Figures 6.10 and 6.11).

To endeavour to confirm the potential involvement of 2,4,6-tribenzyl-s-trioxane in the reaction, subsequent experimental investigations using Mass Spectrometry were carried out, which confirmed that some of the phenylacetaldehyde product is spontaneously polymerised to its corresponding trimer 2,4,6-tribenzyl-s-trioxane [13] which in turn can be adjudged to account for the apparent presence of three ‘intermediates’ that are visible in the NMR data. Mass Spectrometry was also used to confirm the presence of phenylacetaldehyde. An aliquot of the reaction mixture was injected onto the instrument under the conditions detailed below.

ESI mass spectra were acquired using a Micromass time of flight mass spectrometer (TOF) interfaced to a Waters 2690 HPLC. The instrument was operated in positive or negative mode as required. Leucine Enkephalin was used as an internal lock mass. Masses were recorded over the range 100-1000 m/z. Operating conditions were as follows: ESI capillary voltage 2500V, cone voltage 25V, desolvation temperature 200ºC, source temperature 100ºC. The ESI gas was nitrogen. MassLynx 4.0 software was used to carry out the analysis. EI mass spectra were acquired using a GCT Premier Micromass time of flight mass spectrometer (TOF). The instrument was operated in positive mode. Heptacosa (+) was used as an internal lock mass. Masses were recorded over a range of 100-600 m/z. Operating conditions were as follows: Detector voltage 3000V, source temperature 200ºC, and filament energy 70eV with a trap current 99uA. MassLynx 4.0 software was used to carry out the analysis.
Figure 6.13 shows the compositional report from the reaction mixture for phenylacetaldehyde and Figure 6.14 shows the report for the trimer respectively.

Figure 6.13: Mass Spectral Elemental Compositional Report for Phenylacetaldehyde
6.2.3 Reactions using Au/SWCNT catalyst.

The reactions were carried out in exactly the same manner as in section 6.2.2. The results were strikingly similar to those found over the Au/TiO₂ catalyst, which would certainly suggest that phenylacetaldehyde readily trimerises under the aforementioned aerobic oxidation conditions. The only difference was the time taken for the reaction to occur, which in this case was ~3.5hrs. Figure 6.15 shows the FT-IR spectrum of the reaction mixture after 3.5hrs.
Figure 6.15: FT-IR Spectrum of product(s) from aerobic oxidation of 2-phenylethanol using Au/SWCNT composite.

It is clear from the lack of O-H stretch at ~3330cm$^{-1}$ that the substrate has reacted fully under the aforementioned conditions. However, the spectral profile is identical to that of the product(s) using the Au/TiO$_2$ composite (Figure 6.8). This in itself indicates that the reaction takes the same pathway. It would certainly appear that for this particular substrate under aerobic oxidation conditions that the reactant cannot be completely converted to the corresponding aldehyde because the aldehyde
readily trimerises at the reaction temperature of 120°C at atmospheric pressure and thus prevents formation of the aldehyde in its pure form.

Figure 6.16: % conversion vs time to phenylacetaldehyde using Au/SWCNT catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.

6.2.4 Reactions using Au/P90 catalyst.

The reactions were carried out in exactly the same manner as in section 6.2.2 using the Au/P90 composite as the catalyst, with almost identical results in terms of both the time taken and the yields of the observable products using the Au/SWCNT composite discussed in section 6.2.3. Figure 6.17 shows the FT-IR spectrum for the reaction mixture obtained using the Au/P90 composite after ~4hrs. This product(s)
also has an almost identical spectral profile to the ones from the previous reactions suggesting that this too follows the same reaction pathway as those using the previous catalysts. Figure 6.18 shows the % conversion to the aldehyde vs time using Au/P90.

![FT-IR Spectrum of product(s) from aerobic oxidation of 2-phenylethanol using Au/P90 composite.](image)

Figure 6.17: FT-IR Spectrum of product(s) from aerobic oxidation of 2-phenylethanol using Au/P90 composite.
6.3 Proposed mechanism

The reaction is thought to occur in three stages. The initial oxidation of the alcohol, which is the release of hydrogen to form the aldehyde [14]. Then, under excess O₂ and at the reaction temperature of 120ºC approximately three quarters of the aldehyde spontaneously trimerises to 2,4,6-tribenzyl-s-trioxane [15]. The corresponding trimer is more stable than the aldehyde and thus remains
predominantly in this form when the reaction reaches its natural conclusion. This is in good agreement with the $^1$H and $^{13}$C NMR results discussed in section 6.2.

Figure 6.19: Possible reaction mechanistic pathway for aerobic oxidation of 2-Phenylethanol and subsequent trimerisation of phenylacetaldehyde using Au/TiO$_2$, Au/SWCNT and Au/P90 catalysts.
6.4. Recycling of the catalysts.

In the interests of determining both the catalyst stability and further investigating the nature of the results using each of the three catalysts, it was necessary to repeat the reactions using recycled catalyst for each of the three composites over at least three reaction cycles. Between cycles, the catalyst was collected after filtration, washed thoroughly using acetone, which has been reported to promote catalyst regeneration [23] and deionised water, then finally dried at ~120ºC overnight prior to redeployment.

6.4.1 Reactions using Au/TiO$_2$ catalyst

The reactions were carried out in the exact same manner as described previously in Section 6.2.2.

Testing the reusability of the Au/TiO$_2$ illustrates that the catalyst has a moderate decrease in its activity after an additional three reaction cycles. Figure 6.20 shows the % conversion variation over the three reaction cycles for the Au/TiO$_2$ catalysts. Note, the error margins are calculated for these and for subsequent data in this section from the standard deviation of the average conversion values for each reaction cycle. This does not take into account the relatively minor reduction in potency of the catalyst after each use.
6.4.2 Reactions using Au/SWCNT catalyst

The reactions were carried out in the exact same manner as described previously in Section 6.2.2. Figure 6.21 shows the % conversion variation over the three reaction cycles for the Au/SWCNT catalysts. The catalyst shows a very moderate decrease in activity over the three cycles, which illustrates its stability and the reaction goes to its stopping point within 3.5hrs, just as it did with the fresh catalyst.

Figure 6.20: % conversion vs time to phenylacetaldehyde using the recycled Au/TiO$_2$ catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.
6.4.3 Reactions using Au/P90 catalyst

The reactions were carried out in the exact same manner as described previously in Section 6.2.2. Figure 6.22 shows the % conversion variation over the three reaction cycles for the Au/P90 catalysts. The catalyst shows very moderate decrease in activity over the three cycles which shows its stability and the reaction goes to completion within 4hrs just as it did with the fresh catalyst.
Figure 6.22: % conversion vs time to phenylacetaldehyde using the recycled Au/P90 catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.
6.4.4 Product clean up

As discussed previously, in the aerobic oxidation of 2-phenylethanol the spontaneous trimerisation of phenylacetaldehyde produced a by product (2,4,6-tribenzyl-s-trioxane). In addition, as discussed in Chapter 5, the aerobic oxidation of 1-phenylethanol yielded only the expected ketone so there was no requirement for further product clean up or purification.

In order to produce the aldehyde entirely, it is necessary to rapidly heat the product mixture to ~195°C to allow distillation of the phenylacetaldehyde to occur within its boiling point range. In addition to affect full distillation, the temperature has to be increased to ~230°C to promote decomposition of the trimer to produce the pure aldehyde. The distillation needs to be carried out as quickly as possible to avoid forming further by products, typically higher molecular weight polymers [11, 12].

This is a crude way to produce the aldehyde which is far from ideal when attempting to adhere to the principles of green chemistry. Unfortunately at the reaction conditions chosen and using these catalysts to make the process green, it is not possible to get a 100% conversion to the phenylacetaldehyde under the aforementioned reaction parameters.
6.5 Conclusions

While all three catalysts show some selectivity to the formation of phenylacetaldehyde, the major product using all three is the trimer 2,4,6-tribenzyl-s-trioxane, which was subsequently discovered to be the product of spontaneous polymerisation of the aforementioned product. However, the notable difference between the three catalysts is the time taken for the reaction to reach its completion. The reaction with the Au/TiO$_2$ catalyst takes ~5.5hrs while the Au/SWCNT catalysed reaction takes ~3.5hrs and finally the Au/P90 reaction takes 4hrs. Although the aldehyde trimerises to trimer 2,4,6-tribenzyl-s-trioxane, it does not form the carboxylic acid under the aforementioned conditions. This is significant in that it technically means that the catalysts are 100% selective to the aldehyde as the trimer can be hydrolysed back to the aldehyde should it be required. This is done by rapidly heating the trioxane compound at atmospheric pressure which yields pure phenylacetaldehyde as the distillate. This in essence could be described as a cleanup step post oxidation.

The next section of this chapter details the aerobic oxidation of benzylalcohol utilising the three catalysts as the third and final reaction in the catalytic test series and then some discussion on possible additional reasons for the performance variations of the catalysts in the reactions.
6.6 Aerobic solventless oxidation of Benzylalcohol

6.6.1 Introduction

As discussed earlier in this chapter, the aerobic oxidation of the primary alcohol 2-Phenylethanol using the supported gold nanocatalysts (prepared and described in Chapter 4) to its corresponding aldehyde phenylacetaldehyde can be achieved using all three composites. Thus, in order to attempt to determine whether the composites could catalyse additional reactions successfully, it was decided that using another primary alcohol was a natural progression.

Benzylalcohol was chosen as it is a primary alcohol that naturally occurs in plants, teas and fruits. It is widely used as a solvent in the photographic and paint industries [16]. In addition, its corresponding aldehyde benzylaldehyde is very commonly used as a precursor to other organic compounds ranging from plastics to pharmaceuticals so can be considered to be an important intermediate compound in organic chemical synthesis [17-18]. Figure 6.23 shows a schematic of the reaction and highlights the position of the functional group relative to the aromatic ring.

6.6.2 Experimental

Aerobic oxidation of benzylalcohol was performed at atmospheric pressure by bubbling oxygen through benzylalcohol with no solvent. The following reaction conditions were used. \( T = 120 \, ^\circ\text{C} \), 240 mmol of substrate (substrate to catalyst mass ratio 1 : 0.002) and \( \text{O}_2 \) flow rate of 35 mL min\(^{-1}\) for the required time to go to
completion. The reactions were carried out in triplicate using aliquots of fresh catalyst to ensure reproducibility.

![Reaction diagram](image)

Figure 6.23: Aerobic oxidation of benzylalcohol to benzylaldehyde

### 6.6.2.1 Confirmation of products

The confirmation of the product from the reactions was determined using FT-IR as well as $^1$H and $^{13}$C NMR spectroscopy as described in Chapter 5 Section 5.2.1. Any of the representative FT-IR band assignments not shown in the spectra or discussed in the text are tabulated in Appendix A1 (Tables 7-8 respectively) for reference purposes.

### 6.6.3 Reactions over Au/TiO$_2$ catalyst.

The reaction was carried out as described in section 6.5.2 and the substrate reacted successfully to form the desired aldehyde with >99% conversion and selectivity after 7hrs. Representative $^1$H and $^{13}$C NMR data from these reactions show, as expected, the formation of benzylaldehyde with no other side products and are shown in Appendix A2 for confirmation. Figure 6.24 shows an FT-IR spectrum of
the substrate which shows the clear presence of the OH stretch at ~3300 cm\(^{-1}\) which is indicative of alcohols.

Figure 6.24: FT-IR spectrum of benzylalcohol

Figure 6.25 shows an FT-IR spectrum of the product of the reaction. The two most notable differences are the disappearance of the OH stretch visible at ~3300 cm\(^{-1}\) which is a excellent indication that the reaction has gone to completion and the appearance of the C=O carbonyl band at ~1730 cm\(^{-1}\) which corresponds to the formation of an aldehyde which is clarified by the \(^1\)H and \(^{13}\)C NMR spectra in Appendix A2.
Figure 6.25: FT-IR spectrum of benzylaldehyde from aerobic oxidation of benzylalcohol over Au/TiO$_2$ catalyst.

The % conversion and % selectivity were calculated using Equations 6.1 and 6.2 respectively. % Conversion of the benzylalcohol is defined based on the initial ($C_0$) and final ($C_1$) molar concentrations of the substrate:

Equation 6.1: $\text{% Conv} = 100 \times \frac{[C_0] - [C_1]}{[C_0]}$.

Selectivity to benzylaldehyde is defined as the ratio of the molar concentration of benzylaldehyde formed during the reaction ($C_1$) to the molar concentration of benzylalcohol ($C_3$) converted in the same time:

Equation 6.2: $\text{% Sel.} = 100 \times \frac{[C_3]}{([C_0]-[C_1])}$. 
Note, the error bars in the % conversion graphs in this section are based on the standard deviation of the FTIR measurements and utilisation of Equation 6.1. However, they do neglect any inaccuracies in the automated spectral baseline correction procedure. Figure 6.26 shows the % conversion to benzylaldehyde as a function of time using the Au/TiO$_2$ composite.

Figure 6.26: % conversion vs time for the aerobic oxidation of benzylalcohol using Au/TiO$_2$ catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3 Green.
6.6.4 Reactions over Au/SWCNT catalyst.

The reaction was carried out as described in section 6.6.2 and the substrate reacted successfully to form the desired aldehyde with >99% conversion and selectivity within ~3.5hrs. The $^1$H and $^{13}$C NMR data from these reactions show as expected the formation of benzylaldehyde with no other side products and are shown in Appendix 1. Figure 6.27 shows the FT-IR spectrum of the benzylaldehyde product from the reaction.

Figure 6.27: FT-IR spectrum of benzylaldehyde from the aerobic oxidation of benzylalcohol over Au/SWCNT catalyst.
Figure 6.28: % conversion vs time for the aerobic oxidation of benzylalcohol using Au/SWCNT catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3: Green.

6.6.5 Reactions over Au/P90 catalyst.

The reaction was carried out as described in section 6.6.2 and the substrate reacted successfully to form the desired aldehyde with >99% conversion and selectivity after ~5hrs. Figure 6.29 shows the % conversion as a function of time using the Au/P90 composite. $^1$H and $^{13}$C spectra for the product are shown in Appendix 1.
Figure 6.29: % conversion vs time for the aerobic oxidation of benzylalcohol using Au/P90 catalyst. Reaction 1: Black, Reaction 2: Pink and Reaction 3 Green.

6.7 Recycled Catalyst Cycles.

The reactions were carried out in the exact same manner as described in Section 6.2.2. However to illustrate repeatability and stability, the recycled catalyst was used in three reaction cycles. In each case, catalyst was treated between each cycle as detailed in Chapter 5 Section 5.5. Representative FT-IR, $^1$H and $^{13}$C spectra for the product from this set of reactions are shown in Appendix A2.
6.7.1 Au/TiO₂ catalyst

Figure 6.30 shows the % conversion variation over the three reaction cycles for the Au/TiO₂ catalysts. Testing the reusability of the Au/TiO₂ illustrates that the catalyst has a moderate decrease in its activity after an additional three reaction cycles. Note, the error margins are calculated for these and for subsequent data in this section from the standard deviation of the average conversion values for each reaction cycle. This does not take into account the reduction in potency of the catalyst after each use.

Figure 6.30: % conversion vs time using the recycled Au/TiO₂ catalyst, Cycle 1: Black, Cycle 2: Pink and Cycle 3 Green.
6.7.2 Au/SWCNT catalyst

Figure 6.31 shows the % conversion variation over the three reaction cycles for the Au/SWCNT catalysts. There is a very slight reduction in the potency of the catalyst over the three reaction cycles which illustrate the stability of the catalyst as well as its reusability in terms of % conversion to the desired product.

Figure 6.31: % conversion vs time for reactions using the recycled Au/SWCNT catalyst Cycle 1: Black, Cycle 2: Pink and Cycle 3 Green.
6.7.3 Au/P90 catalyst

Figure 6.32 shows the % conversion variation over the three reaction cycles for the Au/P90 catalysts. There is a moderate reduction in the potency of the catalyst over the three reaction cycles which illustrate the stability of the catalyst in addition to its reusability with regard to % conversion to the required product.

![Graph showing % conversion vs time for reactions using the recycled Au/P90 catalyst (Cycle 1: Black, Cycle 2: Pink and Cycle 3 Green)]
6.8 Conclusions:

Utilising the recycled catalysts, while there is a moderate decrease in their activity, they still catalyse the reaction to completion within the same timeframe as their fresh counterparts. In addition, they remain stable for the duration of the reaction and are easily regenerated with a simple washing process. This illustrates their reusability which is a vital property for a catalyst.

Overall the Au/SWCNT catalyst is the fastest thus the most efficient catalyst for this reaction also going to completion in ~3.5hrs compared to the Au/TiO$_2$ catalysed reaction which reaches completion after 7hrs and finally the Au/90 catalysed reactions which took 5hrs to reach completion. There are no other products formed which shows all three catalysts to be exclusively selective to benzylaldehyde.

In the literature, there are several mentions of supported Au catalysts being used to successfully catalyse the selective oxidation of primary alcohols however, they all either require longer to reach completion, have significantly lower % conversions or require promoters to be effective [19-25].

In addition, in comparison to other selective primary alcohol oxidations recorded in the literature, for example oxidation of benzyl alcohol over supported Au and Pd catalysts reported by Enache, et al [26] as well as the selective oxidation of benzyl alcohol catalysed by Cu (II) in a solvent system reported by Velusamy, et al [27], the three supported Au catalysts used in this work show excellent potential for faster, more efficient selective aerobic oxidation adhering more closely to the principles of green chemistry.
It is possible that the position of the functional group, in the case of the 2-phenylethanol (β position) and benzylalcohol (α position) plays a part in the substrates ability to be effectively selectively catalysed under these reaction conditions in addition to the differences in the support structures. This is discussed in more detail in the overall conclusions in Chapter 7.
References


Chapter 7:

Conclusions and Further Perspectives
7.1 Summary of Findings:

Novel catalysts based on nanoparticles combined with nanosupports have been synthesised and have been demonstrated to show improved performance over established systems for green reactions. The systems were fully characterised using a range of spectroscopic, microscopic and materials analysis techniques. Their performance was investigated for a range of reactions of industrial relevance.

5% by weight Au catalysts were prepared on TiO$_2$, SWCNT and P90 and thoroughly characterised. A range of techniques were used for this, SEM/STEM/TEM, EDX, XRD, AAS, N$_2$ physisorption, UV-Vis spectroscopy and Raman spectroscopy. The use of the array of techniques allowed for a detailed and systematic characterisation of the Au nanoparticle morphology, particle size distributions and the metal-support interactions. In the first stage of the activity testing work, preliminary studies were carried out using the solventless aerobic oxidation of 1-phenylethanol to its corresponding ketone acetophenone using the three catalysts. This reaction has been used previously as a probe reaction for testing new potential catalysts so it served as an ideal model system for this work [1]. The comparison of the novel material, Au nanoparticles supported by SWCNT in the as synthesised state to more established Au nanoparticle supported catalysts, TiO$_2$ and P90 provided an important initial insight into the ability of SWCNT to provide an effective scaffold to an active ingredient. The use of SWCNT as a catalyst support for a heterogeneous reaction is original work and is published in a peer reviewed journal [2].
The Au/SWCNT system was seen to catalyse the reaction to completion under green conditions in ~3hrs with >95% conversion and 100% selectivity. The Au/TiO$_2$ and Au/P90 systems also catalyse the reaction but at lower rates and/or selectivity. Using the former, the reaction takes significantly longer and, with the Au/P90, the by-product ethylbenzene is formed. This is likely to be due to surface carbon acting as a reductant during the first reaction cycle. When the Au/P90 catalyst is recycled, the % conversion to acetophenone increases as expected and the by-product formation ceases. In order to determine the feasibility of using the three catalysts for selective alcohol oxidations, it was necessary to carry out reactions with additional substrates to ascertain their generic suitability. As they successfully catalysed the oxidation of a secondary alcohol, it was advisable to test them in more challenging reactions. With this in mind, two primary alcohols of industrial importance, 2-phenylethanol and benzylalcohol were chosen.

The selective aerobic oxidation of the 2-phenylethanol yielded some unexpected results. All three composites selectively catalyse the reaction to phenylacetaldehyde which was expected. However, as phenylacetaldehyde tends to trimerises on standing and so 2,4,6-tribenzyl-s-trioxane was formed alongside the aldehyde. All three catalysts produced a very similar reaction profile with the catalysts all being 100% selective to the aldehyde with ~25% direct conversion to same with no further oxidation to the corresponding carboxylic acid. However, the Au/SWCNT again catalysed the reaction with the fastest rate. In addition, the trimer can be converted back to the aldehyde with relative ease by rapidly heating the reaction mixture produced to affect full distillation. Recycling the catalysts made little difference to the conversion profiles and showed very minimal activity decrease thus highlighting the stability of the catalysts in this type of reaction.
In the third and final test reaction, the selective oxidation of benzylalcohol, all three catalysts show excellent % conversion and % selectivities to benzylaldehyde, the Au/SWCNT again proving to be the most efficient with complete conversion within ~3.5hrs compared to ~5hrs for the Au/P90 and 7hrs for the Au/TiO₂ catalysts. No other products were found in these reactions, showing the three catalysts to be exclusively selective to the aldehyde. Recycling the catalysts showed little depreciation in their activity, again illustrating their stability in these reaction styles.

To recapitulate, the results presented in Chapters 5 and 6, yielded from the solventless aerobic oxidations of the three substrates using the three supported Au catalysts have shown their initial promise for use in green reactions. From the three, the Au/SWCNT catalyst has been shown to be the most efficient and shows excellent activity and selectivity for green aerobic alcohol oxidations. The thermal stability, tensile strength and surface area of the SWCNT in particular should lend to them being able to be used as catalyst supports across a range of reaction conditions.

In Chapter 4, SEM showed that Au nanoparticles have a similar size distribution on all supports. XRD confirmed this for the Au/SWCNT and the Au/P90 however it was inconclusive for the Au/TiO₂ because of the overlap of the anatase phase of the TiO₂ support with the Au nanoparticle Bragg reflections. EDX confirmed the presence of Au on each of the composites while AAS determined the % weight of the Au on the support surfaces. The N₂ adsorption isotherms showed increased surface areas of the composite samples which were expected with the deposition of Au nanoparticles onto crystalline substrates. The SWCNT and P90 supports both showed much larger surface areas than the TiO₂ both before and after deposition which could well lend to their ability to catalyse the
oxidation reactions with fast rates alongside the optical and electronic properties of both the supports and the composites.

The UV-Vis characterisation showed that the three composites exhibit the distinct Au nanoparticle plasmon adsorption in the visible region, where as the Au/SWCNT system also has a well defined plasmon adsorption in the UV. The surface plasmon adsorption in the Au nanoparticles arises from the combined oscillations of the free conduction band electron that are generated by incident electromagnetic radiation [3] and, the oscillations are localised on the surface, this plasmon adsorption of Au nanoparticles is both strongly dependent on the nanoparticle size and sensitive to changes in the surrounding environment [4]. The narrower plasmon adsorption band in both the Au/SWCNT and Au/P90 matrices compared to the Au/TiO$_2$ composite may be the result of slightly smaller diameters observed for the nanoparticles in the former two composites. Literature has already shown that smaller Au nanoparticles are more active for catalysis and this suggests that even the subtlest difference in average Au particle size between the composites can have a large reaching effect on their activity [5]. Alternatively, it may suggest an interaction at the particle/matrix interface in these composites which results in a decrease of the free electron density in the Au nanoparticles induced by charge transfer [6]. Either or a combination of these phenomena could result in increased catalytic activity of the Au nanoparticle composites.

Raman analysis of both the SWCNT support and the Au/SWCNT composite also point towards change in the nanotube characteristics as a result of the Au deposition. The G$^+$ band shifts upfield in the composite sample which is indicative of charge transfer in the sample [7]. The RBMs have also changed their shape, shifted downfield and decreased in
intensity. These significant changes can be attributed to debundling due to changes in the environment of the system or to charge transfer to the nanotubes filling previously unoccupied electronic states. The formation of Au nanoparticles onto the sidewalls of SWCNT has been attributed to direct redox reduction between the nanotubes and the metal ions in solution [8]. In effect, this means that the nanotube/Au$^{3+}$ systems can be categorised as redox pairs which would be expected to cause an enhancement in the conduction of the system which could account for the catalytic rate of the Au/SWCNT system being more efficient than that of the traditional TiO$_2$ and P90 supported systems. An example of redox pairs is the galvanic cell in which Zn and a Cu$^{2+}$ solution, spontaneous oxidation of Zn to Zn$^{2+}$ and reduction of Cu$^{2+}$ to Cu occurs [9]. The work function and Fermi levels of SWCNT have been shown to be above the reduction potentials of AuCl$_4^-$ which rationalises the spontaneous electron/charge transfer from the nanotubes to the metal ions and their subsequent reduction [10-12].

Finally it is worth noting that the influence of solution pH on the transport of electrons in an SWCNT system has been shown to directly affect their electrochemical and electrocatalytic properties [13]. This in turn could enhance the selective deposition of the Au NPS onto the SWCNT walls and thus the number of active sites available from the Au/SWCNT system to catalyse the reactions more effectively [14,15].
7.2 Hypothesis of activity testing findings:

As shown in Chapters 5 and 6, the three composites catalyse the three test reactions in a selective fashion as was hoped. However, there are some unanticipated by products formed, and although potential explanations have been furnished, there now follows a short discussion on alternative possibilities.

Considering the structures of the three reaction substrates (Figure 7.1), the most obvious difference between them is the position of the functional group on the carbon linker relative to the aromatic ring. The position of the –OH group could have a more activating affect, as it is closer to the ring which could certainly potentially account for the ease with which the 1-phenylethanol and the benzylalcohol are selectively catalysed to their corresponding ketone and aldehyde respectively.

As a consequence, it is possible that steric hindrance could play some part during the 2-phenylethanol oxidation [16], in which the spontaneous trimerisation of the phenylacetaldehyde product occurred. The 2-phenylethanol substrate is the only one of the three that has its functional group at the β carbon position relative to the ring. Steric effects have also been known to switch the mechanistic pathway in a catalytic reaction [17].

\[
\text{Figure 7.1: Substrate Structures: (i) 1-phenylethanol, (ii) 2-phenylethanol (iii) Benzylalcohol.}
\]
As these reactions are all carried out under mild conditions, perhaps this suggests that there is a strong link between structure and reactivity in these types of compounds under green conditions. This could mean that under these conditions, reactions with substrates having α positioned functional groups are regioselective and not chemoselective, similar to Baeyer-Villiger reactions (oxidation of a ketone to ester or a lactone) and hence the catalysts exhibit higher selectivity because of the position of the migrating group relative to the aromatic ring [18]. In general alcohol oxidations are carried out in solution using reactions in which the hydroxyl hydrogen is replaced by an atom or group that is readily eliminated along with the alpha hydrogen. Examples of these would be Jones’s reagent [19] and pyridinium chlorochromate (PCC) [20]. However, these reactions, although considered mild in terms of how far they take a reaction, are not considered to be green in terms of toxic chemical use and generation. It is likely that a detailed systematic study across a range of aromatic and aliphatic alcohols with substituted functional groups would elucidate more detail regarding these hypotheses.

7.3 Future Perspectives:
So far, it has been shown that Au supported on SWCNT is the most effective catalyst for these selective oxidation reactions compared to Au/TiO₂ and Au/P90. So, bearing this in mind, there are several ways in which this initial study could be expanded in this area. Firstly, it would be prudent to investigate stand alone SWCNT for their potential performance as catalysts in a control study prior to widening the range of reactions they could be applied to as heterogeneous catalysts.
The SWCNT used in this work were utilised as received with no further processing or purification. It would be of interest to purify the SWCNT and use the purified material to prepare supported Au NPs, characterise and test them in the same manner as the as received sample. This would provide information on how the purification procedures might modify the support surface prior to interaction with the Au NPs but also whether the purification of them affects their ability to support the nanoparticles successfully. Several different purification procedures have been shown to ‘clean up’ SWCNT, mostly in terms of removing either amorphous carbon or catalytic particles used in their manufacturing processes [21-23]. Some of the purification processes involve high temperatures, which would also lend some valuable information on their thermal stability. Some purification processes such as high temperature oxidation have been shown to remove the end caps from the SWCNT [24, 25]. This could allow for deposition of NPs inside the tube walls. This in itself would surely change the properties of the SWCNT and thus their catalytic activity. The biggest issue in undertaking this work would be to attempt to find a green process for SWCNT purification. Some initial work has been done using steam [26], which would certainly be an enormous improvement on using acids and solvents [27] or surfactants which can be difficult to remove from the tubes [28] so this is definitely an area that could be investigated further for the purposes of these studies. Detailed XPS studies could also be of use to probe in greater detail the Au-support interaction which in turn would provide valuable information on the surface chemistry of the composite materials.

As discussed in Chapter 2, there are several ways to prepare catalysts. The methodology used for the preparation of the catalysts in this work is relatively straight forward yet still resulted in successful catalysts. The industry standard preparation protocols could be
compared to produce a range of similar catalysts for testing in reactions of environmental concern.

Of course, in order to branch into other areas, the novel Au/SWCNT composite should be further studied and adapted for use in materials science applications such as electronics, solar cells, lithography and biological sensing, as carbon materials and Au are being researched for use in these areas [29-32]. Both of these areas could lend to collaborations with other research groups and could potentially pave the way for new applications for the composite.
References:


Appendix A1: FT-IR Data

Table 1: Band Assignments for 1-phenylethanol substrate:

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Alcohol</td>
<td>O-H stretch</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td>C-O stretch</td>
<td>1250</td>
</tr>
</tbody>
</table>

Table 2: Band assignments for acetophenone:

<table>
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<tr>
<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Ketone</td>
<td>C-C stretch</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>C=O stretch</td>
<td>1700</td>
</tr>
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Table 3: Band assignments for ethylbenzene:

<table>
<thead>
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<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1610 and 1500</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Alkyl</td>
<td>C-H stretch</td>
<td>3050-3000</td>
</tr>
<tr>
<td>Arene</td>
<td>CH₂ bend</td>
<td>1495</td>
</tr>
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</table>
Table 4: Band assignments for 2-phenylethanol substrate:

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Alcohol</td>
<td>O-H stretch</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td>C-O stretch</td>
<td>1250</td>
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Table 5: Band assignments for phenylacetaldehyde:

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<th>Molecular Motion</th>
<th>Wavenumber (cm(^{-1}))</th>
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</thead>
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<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>C-H aldehyde stretch</td>
<td>2850 and 2750</td>
</tr>
<tr>
<td></td>
<td>C=O stretch</td>
<td>1710</td>
</tr>
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</table>

Table 6: Band assignments for 2,4,6 – tribenzyl-s-trioxane:

<table>
<thead>
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<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch (w)</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>750 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>745</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>880, 780 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>825</td>
</tr>
<tr>
<td>Trioxane</td>
<td>C-O stretches</td>
<td>1300, 1250 and 1200</td>
</tr>
<tr>
<td>Linkers</td>
<td>C-H</td>
<td>Overlap of C-H bend (meta)</td>
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<tr>
<td></td>
<td>CH(_2) ring-linker stretches</td>
<td>~1490</td>
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Table 7: Band assignments for benzylalcohol substrate:

<table>
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<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>740 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>735</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>870, 790 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>835</td>
</tr>
<tr>
<td>Alcohol</td>
<td>O-H stretch</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td>C-O stretch</td>
<td>1250</td>
</tr>
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</table>

Table 8: Band assignments for benzylaldehyde:

<table>
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<tr>
<th>Functional Group</th>
<th>Molecular Motion</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>1600 and 1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>740 and 690</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>735</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>870, 790 and 700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>835</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>C-H aldehyde stretch</td>
<td>2850 and 2750</td>
</tr>
<tr>
<td></td>
<td>C=O stretch</td>
<td>1710</td>
</tr>
</tbody>
</table>
Appendix A2: $^1$H and $^{13}$C NMR spectra

Figure 1: $^1$H NMR spectrum of product from the aerobic oxidation of 1-phenylethanol over Au/TiO$_2$ catalyst.

Figure 2: $^{13}$C spectrum of product from the aerobic oxidation of 1-phenylethanol over Au/TiO$_2$ catalyst.
Figure 3: $^1$H NMR spectrum of product from the aerobic oxidation of benzylalcohol over Au/SWCNT catalyst.

Figure 4: $^{13}$C NMR spectrum of product from the aerobic oxidation of benzylalcohol over Au/SWCNT catalyst.
Publications, Conferences and Invitations:

Peer Reviewed Published Papers:


Conference Proceedings:

Proceedings of 5th ICEC Queen's University Belfast 31st August-3rd September 2008.

Presentations:

Poster presented at 5th International Conference on Environmental Catalysis (ICEC) at Queen's University Belfast 31st August-3rd September 2008 entitled:
"Preparation, characterisation and activity testing of Gold catalysts supported on Single Walled Carbon Nanotubes".

Reviewing: Reviewer for the Central European Journal of Chemistry, specifically in the area of carbon supports in catalysis.
Invitations:

Invited to present at 6\textsuperscript{th} International Conference on Environmental Catalysis (ICEC) in September 12\textsuperscript{th}-15\textsuperscript{th} 2010 in Beijing, China.

Invited to speak at the BIT Life Sciences’ 1\textsuperscript{st} Annual World Congress of Advanced Materials (WCAM-2012) Beijing, China, June 6th-8th, 2012 in the New Catalytic Materials track.

Invited to speak at the World Congress of Advanced Materials (WCAM-2013) Suzhou, China, June 5th-7\textsuperscript{th} 2013 in the New Catalytic Materials track.

Invited to speak at the 4th Annual Global Congress of Catalysis (GCC-2013) Dalian, China, June 29th-July 1st, 2013 in the Heterogeneous Catalysis track.