

SYNTHESIS AND CHARACTERISATION OF GOLD- RHODIUM NANOCATALYSTS AND THEIR CATALYTIC ACTIVITY ON CARBON MONOXIDE OXIDATION

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A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg,
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DECLARATION

I declare that this is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signature of candidate

_____ day of February 2016

ABSTRACT

Gold nanoparticles are ideally suited as catalysts for selected low temperature reactions such as CO oxidation for catalytic convertors in the motor industry due to their high activity. But they are prone to sintering at high temperatures. Platinum-group-metal based catalysts are efficient at elevated temperatures and generally inactive at lower temperatures. This study explored the CO oxidation efficiency of gold nanoparticles and of a combination of gold and rhodium nanoparticles. Variables such as pH, loading concentration and type of support were varied to control the final properties of the Au based catalysts. Possible bimetallic systems of gold and rhodium were explored for wider temperature range activity than gold alone. All catalysts were characterised using Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-Ray Diffraction (XRD). Activity was measured using a temperature controlled, custom-built reactor linked to a gas chromatograph.

The conditions yielding the smallest gold nanoparticles were established by adding 5, 8 or 10 wt.% loadings of chloroauric acid to aqueous suspensions of either TiO₂ or SiO₂ at pH 5, 7 or 9 and at 70-75 °C over 60 minutes. Each preparation was sealed in parafilm, aged in the dark at room temperature for 3 days, vacuum-filtered and subsequently calcined at 300 °C. Gold nanoparticles were smallest when deposited onto TiO₂ instead of SiO₂, at pH 7 and at a loading of 5 wt. %. A combination of gold and rhodium catalysts were subsequently prepared using these conditions, with the simultaneous addition of rhodium at 1, 3, 5 or 10 wt. % loading.

Hydrolysis of gold is highly dependent upon pH, resulting in the synthesis of smaller particles under alkaline conditions. Catalytic activity of samples analysed at 70 and 150 °C was highest for gold nanoparticles below 5 nm, in agreement with previous studies. In the proposed bimetallic catalysts, it was difficult to distinguish gold and rhodium nanoparticles in TEM images, although EDS confirmed their combined presence on the TiO₂ support. Particle sizes remained below 5 nm, appearing monodispersed on the TiO₂ support except at 10 % rhodium loading where some nanoparticle aggregation was observed. CO oxidation activity showed an apparent temperature-dependent shift in the optimal rhodium loading. Au-TiO₂ catalysts with a 5% loading showed the highest activity up to 350 °C for a period of 10 hours and the catalyst deactivated due to sintering. At 150 and 200 °C the Au/Rh-TiO₂ catalyst remained active for more than 12 hours. It was concluded that the inclusion of rhodium is a potentially-favourable method for stabilising the activity of gold catalysts.

DEDICATION

I dedicate this whole project to my father (Madala Sam Rikhotso), my mother (Khensani Evelyn Rikhotso), my siblings (Ntshembo, Nkateko and Mahluri Rikhotso) who have been supporting me throughout every trial, sadness and joy that I have gone through. I thank my grandparents, The late Joel Makhubela and Louise Makhubela who have passed on a lot of their wisdom to me throughout my growing years....also to all my cousins and friends who have supported me though every struggle that I have fought during my university years...I love you all and may God bless you...

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PUBLICATIONS AND PRESENTATIONS

Posters

1. Title "*Synthesis and Characterisation of Au-SiO₂ and Bimetallic Au/Rh Nanoparticles*" authors: Rirhandzu S.Rikhotso, Paul J.Franklyn and Michael S.Scurrrell. The poster was presented at the international SACI conference that was held at the University of the Witwatersrand in January 2011
2. Title "*Synthesis and Characterisation of supported gold-rhodium nanocatalysts and catalytic activity for carbon monoxide oxidation*" authors: Rirhandzu S.Rikhotso, Paul J.Franklyn and Michael S.Scurrrell. The poster was presented at the international MSSA conference that was held at the Protea Hotel, Stellenbosch in December 2014

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Abbreviations

MEMS/NEMS -Microelectromechanical systems/Nanoelectromechanical Systems
PGMs -Platinum Group Metals
CO - Carbon Monoxide
CO ₂ - Carbon Dioxide
Au - Gold
TiO ₂ - Titanium Dioxide
TEM - Transmission Electron Microscope
BET - Brunauer, Emmett, Teller theory
XRD - X-Ray Diffraction
HRTEM - High Resolution Transmission Electron Microscopy
EDX - Energy-Dispersive X-Ray Spectroscopy
SERS - Surface Enhanced Raman Scattering
AuNPs - Gold Nanoparticles
WGS -Water Gas Shift
Mo - Molybdenum
XPS - X ray Photoelectron Spectra
LEIS - Low Energy Ion Scattering Spectroscopy

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Chapter 1

Introduction

Clean, fresh air is an essential part of our everyday survival. But this essential entity is greatly compromised by pollution of different magnitudes. One of the biggest pollutants in this world is carbon dioxide which is detrimental to the human species as it can damage organs with excessive inhalation as well as increasing global warming ^[1].

Global warming has become increasingly serious and environmentalists push industries to work on creating better processes that result in reduced pollutant production. Examples of such processes include the use of Syngas for the production of liquid transportation fuels rather than biofuels that require new refining methods for them to be used in energy conversions ^[2].

Nanotechnology could be said to have begun with the story of Maxwell's Demon which was interesting, but not technically correct. It was a thought experiment and there was no size specified for the demon he described. Technically it would be more precise to call what the "demon" supposedly did, but nonetheless the work began the route to nanotechnology for scientists ^[3].

Nanotechnology was further brought to light by Richard Feynman in his talk: "There's Plenty of Room at the Bottom" in the 50's that described a process by which the ability to manipulate individual atoms and molecules might be developed. The idea was to use one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale to bring about better properties within the new material ^[3].

Many materials, experiments and almost every area of science is starting to focus on these new tiny materials that often exhibit amazing characteristics, such as a large surface area, excellent mechanical, optical properties, etc. that are essential for the growth of the world ^[4].

It has been argued that nanotechnology does not guarantee our safety and could be potentially dangerous to our health as the effects of exposure of these materials are not completely known ^[5]. There have also been arguments that areas such as biomimetics are not ethical as

they mimic natural biological processes with nanotechnology and reproduce the same things on a nanoscale, e.g. gecko tape being mimicked from gecko feet ^[6].

Nanotechnology is divided into four main areas, namely:

1. Nanostructured e.g., nanoscaled microstructures in bulk or thin films, nanograins, nanocrystalline materials and nanocomposites.
2. Nanotools e.g. Fabrication techniques, analysis, software for nanotech.
3. Nanodevices e.g. Electronic MEMS/NEMS, biodevices/Lab-on-a-chip, biosensors, drug delivery/therapeutics, data storage, catalysis, nanoscaled machines.
4. Nanoparticles e.g. Fullerenes, nanotubes, nanowires, nanofibers, quantum dots and nanospheres ^[7].

Nanoparticles are the areas of interest for this project. These are particles with at least one dimension less than 100 nm and they are a bridge between bulk materials and atomic or molecular structures. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant ^[8].

Scientists have developed the study of material science to new levels over the ages through the Stone Age, Bronze Age, and Steel Age. Examples of this are when people used to make clay pots, ceramics without really noticing that it was some form of science. This science is one of the oldest forms of engineering and applied science and it involves understanding materials so that new materials with the desired properties can be created instead of looking for and discovering materials and exploiting their properties. The field has changed since then as materials need no longer be discovered by accident with properties that are mysterious. Technology has allowed scientists to understand how materials form and how their structure dictates the bulk properties of the materials.

The fundamentals of material science involve looking into the desired properties in a material together with its relative performance. These are related to the arrangement of the atoms and various phases by characterizing and relating these to the laws of thermodynamics. This leads to discovery of a material's microstructure and hence its properties. No perfect crystal of a material exists, so scientists manipulate particular faults of that material to create new

materials with better properties ^[9].

Catalysts are commonly used materials in chemical processes to help increase the rate of chemical reactions without being consumed by the reaction itself. This is achieved by providing an alternative route for a specific reaction to reach its end products. This makes them economically viable even when using expensive metals as the active components as they improve efficiency in multiple chemical transformations ^[10]. Catalysts must meet chemical, financial, environmental, health and safety targets in order to be viable for use and still produce products of highest quality ^[11].

Work on carbon monoxide chemistry and catalysis has become of great interest, most of it leading to the manipulation of platinum group metals (PGMs) and investigating how each metal can be used for this new technology ^[12]. Their catalytic activity makes them more viable for certain catalytic activities than all the other elements in the periodic table, while their poor selectivity makes them inert to competition. One of the mostly used elements for research purposes is Au, as it is more accessible and cheaper than the platinum group metals that currently dominate the metals used for catalysis ^[13].

1.1 Problem statement

Carbon monoxide (CO) is produced by devices amongst others such as propane powered machinery (forklifts, floor polishers and space heaters), gasoline machinery (concrete cutters and pressure washers). Households also produce quantities of CO through gas and camp stoves, ovens, furnaces, burning coal for fireplaces and a large amount of CO can be found in homes with tobacco smokers.

Another source of CO pollution is through car engines, trucks or any other hydro-carbon based fuel vehicle. A typical vehicle combustion reaction in a vehicle will be:



CO is then released through incomplete combustion of hydro-carbon based fuels. Therefore catalysts that oxidize CO to CO₂ most efficiently are desirable. CO₂ is less harmful to human species but also a greenhouse gas. Human health is considered of greater importance than

global warming that has a long term effect on the survival of human species.

CO is known to be a colourless gas without odour and taste. This can kill if inhaled in fairly small quantities. It has been known to go undetected into the atmosphere and high levels of inhalations can cause severe health complications. The division of environmental health in Washington also releases some general effects of CO on healthy adults as seen in the table 1.1 below:

Table 1.1: General effects of CO on healthy adults

PPM CO in air	Percent CO in air	Symptoms experienced by healthy adults	Comments
Less than 35 ppm	0.0035%	No effect in healthy adults	35 ppm is WISHA 8-hour average permissible limit
100 ppm	0.01 %	Slight headache, fatigue, shortness of breath, errors in judgment	
200 ppm	0.02%	Headache, fatigue, nausea, dizziness	200 ppm is Short Term Exposure Limit (STEL)
400 ppm	0.04%	Severe headache, fatigue, nausea, dizziness, confusion, can be life-threatening after 3 hours of exposure	
800 ppm	0.08%	Headache, confusion, collapse, death if exposure is prolonged	
1500 ppm	0.15%	Headache, dizziness, nausea, convulsions, collapse, death within 1 hour	Levels greater than 1500 ppm are considered "immediately dangerous to life or health" (IDLH). This is the ceiling limit.
3000 ppm	0.3%	Death within 30 minutes	
6000 ppm	0.6%	Death within 10-15 minutes	
12,000 ppm	1.2%	Nearly instant death	

ppm - parts per million

1.2 Objectives

The major aim of this project was to investigate the effect of promoting gold supported catalysts with rhodium metal for the oxidation of CO. The hope was to increase the stability while keeping, or hopefully improving, the activity of the catalyst.

Various factors were investigated including:

1. The effects on activity due to the support used, the synthetic methods used as well as the conditions the catalysts endure.
2. The effect of adding Rh to Au on the activity and structure of the catalysts.
3. The factors that promote deactivation of the catalysts.

1.3 Hypothesis

Is it possible for catalytic activity be improved by varying the synthesis method used for depositing Au onto the appropriate support as well as promoting it with a platinum group metal, specifically Rh in this case, to increase the activity for carbon monoxide oxidation.

1.4 Research approach

Experiments were conducted to investigate the influence of varying the following factors on activity of the catalysts for CO oxidation reaction:

1. pH during deposition of the Au onto TiO₂
2. Deposition duration of the Au onto TiO₂
3. Loading concentrations of the Au catalysts on titania and silica supports
4. Calcinations temperatures of the catalysts
5. Duration of ageing the Au-TiO₂ catalysts after synthesis
6. Storage conditions of all the synthesized catalysts (under vacuum and in the fridge)
7. Promoting the Au-TiO₂ catalysts with different rhodium loadings

All prepared catalysts were characterized using analytical techniques (transmission electron microscopy, BET and powder X-Ray diffraction) obtained within the University of Witwatersrand while data from High Resolution Transmission Electron Microscope and EDX was obtained from The University of the Western Cape by Dr Paul Franklyn.

1.5 Thesis outline

Chapter 2: Literature review

This chapter gives a comprehensive study on the background of gold catalysts as well as the research that has been done in the pursuit of the metal combination that improves catalysis performance in different reactions. In line with the thesis, the focus will be on carbon monoxide oxidation.

Chapter 3: Methodology

This chapter outlines the methods used for the synthesis of different catalysts and the different conditions that were used in pursuit of a catalyst that will have a longer lifetime for CO oxidation as well as high activity.

Chapter 4: Characterization of catalysts

The focus is on the data obtained from the different analytical techniques used as well as a discussion on which catalyst proved to have improved activity. This activity was related to the synthetic conditions used for synthesis as well as the addition of rhodium to the gold catalysts supported on titania.

Chapter 5: CO Oxidation measurements

This chapter focuses mainly on CO oxidation measurements carried out during the course of the project on the catalysts. Variations in synthesis methods, pre-treatment of catalysts as well as other factors are discussed.

Chapter 6: Overall conclusions and future work

The final chapter draws conclusions to the work and wraps up the study. The objectives are critically analysed and proposals are made for future work.

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Chapter 2

Literature Review

2.1 Introduction

CO and CO₂ are introduced into the environment through anthropogenic sources such as humans, human machinery i.e. industries, and through natural sources. These two pollutants are detrimental to earth and all its habitants if released in large amounts. This chapter aims at looking at all the work that researchers have done on creating catalysts to convert CO into CO₂ most efficiently, at the lowest cost and with the greatest durability.

2.2 Gold

For years Au was found to be completely inactive in reactions and only used to make items such as jewellery, electronics, etc. This changed after the discovery of Haruta *et al.* when it was found that Au in its nanoparticle form can exhibit some catalytic activity for certain reactions when supported on selective oxide based supports such as Fe₂O₃, TiO₂, SiO₂ and several others ^[1]. This discovery then opened doors towards the study of Au containing catalysts due to their high activity in a number of reactions that involve oxygen at low temperatures. This was an important discovery as a common problem to most CO catalysts was that they only become active at higher temperatures ^[2].

2.2.1 Bulky gold

Haruta reported that, of the whole periodic table, only twelve metals have shown to be usable for catalysis. This was due to their optimum degree of d-band valence. However this was not the case for Au ^[3]. Au has fully occupied d-bands and hence it is hard for it to lose electrons. It also has a large ionization potential, making it catalytically inactive compared to other metals, at least in the bulk form ^[3].

Au has been purified as a pure metal as early as 5000 BC as reported by an Australian paper and applications have increased since its initial use as a decorative material ^[4]. It has always been regarded as a precious metal that possesses many properties for different uses such as those outlined by the paper in Table 2.1

Table 2.1: A list of some applications of bulky Au in different fields as obtained from Minerals council of Australia ^[4]

USE	DESCRIPTION
Money	Gold has been used as coins since early times, but very few coins are made from gold today. More than half the world's gold is stored by governments and banks. One ounce of gold is worth about US\$280, although the price of gold varies from day to day.
Jewellery	Although pure gold (24 carat) is rarely used as it is too soft, gold is often mixed (alloyed) with other metals such as copper, silver or nickel for jewellery (18 carat gold means 18 parts gold and 6 parts other metals).
Decoration	As gold is malleable and durable, it is often used to coat metal or glass objects. Small sheets of 'gold leaf' are often used for decorative letters, gilding book edges and picture frames, and to coat religious statues.
Electronics	As it conducts electricity and is ductile, gold is used for wiring in computers - from digital radios to microwaves, from telephone system to rocket launchers. Gold is very useful for wiring that is difficult to repair, such as under water and in outer space, because it does not corrode or wear out quickly
Shielding	Rays of light do not easily pass through gold so it is useful as a protective shield against heat and light. Buildings in tropical countries sometimes have a transparent film of gold on the windows. Jet engines, space suits and space craft are often coated in gold to reduce heat and glare.
Health	Gold is used to replace or repair teeth and in the treatment of arthritis and other diseases. Lasers in industry and medicine use gold coated reflectors to focus light.

Many aspects of the catalysis industry are currently dominated by studies of Platinum Group Metals (PGMs) as they have shown to be more catalytically active than Au in its bulk form ^[5]. Au is more easily accessible than these as well as cheaper than most of the PGMs. The result is an increased focus in Au in its nano form as it was discovered to be active when it is smaller than 10 nm ^[3].

When a surface of a metal has the ability to bind to a gas it is known to be noble and thus measuring the nobility of the surface of the metal is done by observing whether it chemisorbs oxygen dissociatively on the surface ^[6]. The inertness of bulk Au is shown on in Figure 2.1 as

it is known to have endothermic chemisorption energy. Hence it is unable to bind any oxygen while its neighbouring metals have large chemisorption energies and can thus bind oxygen weakly ^[6].

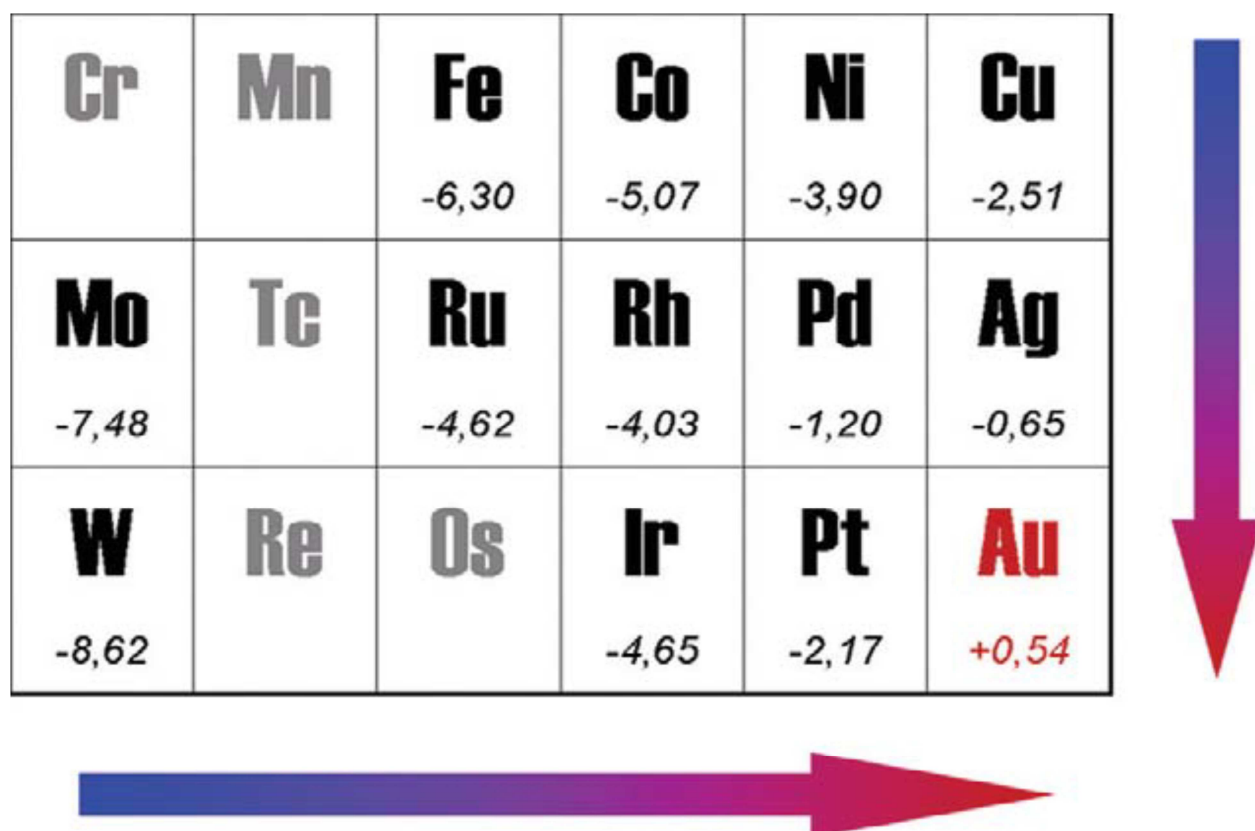


Figure 2.1: The dissociative chemisorption energies for oxygen on metal surfaces with respect to a molecule in vacuum (calculated by DFT) ^[6].

Au has low energy d-bands and thus it repulses the oxygen 2p-states. It is therefore unable to be a catalyst for any oxidation reaction in a bulk material ^[6]. The interesting phenomena of Au being catalytically active when it is smaller than 10 nm for the oxidation of CO ^[3] has then been of great interest to scientists. The main challenge has been to understand what causes this effect and what possible factors could affect the activity of the nanoparticles.

2.2.2 Gold Nanoparticles

The study of nanomaterials and their applications and properties has attracted many scientists throughout the years ^[7]. The applications of these materials range among others in electronics, ceramics, magnetic storage, catalysis, etc. because they show structural, optical, magnetic as well as electronic properties ^[7].

Au nanoparticles have special features such as being highly stable and being biologically compatible. In addition their surface can easily be functionalized. It is also possible to control the morphology and size dispersion of the particles ^{[8] [9]}. Cai *et al.* reported that there are different subtypes of Au nanoparticles according to the different shapes and sizes that give them the properties that they possess to work in different categories in life as seen on figure 2.2 ^[10].

The group reported that the earliest studied gold nanoparticles are gold nanospheres and they continue to dominate in the scientific research. Even though they are referred to as spherical they are rarely observed as perfectly round. Nanorods, nanoshells and nanocages have all been reported ^[10]. These different shaped nanoparticles have found excellent use in the biomedical industry in the different areas due to their excellent biological compatibility properties as shown in Figure 2.2.

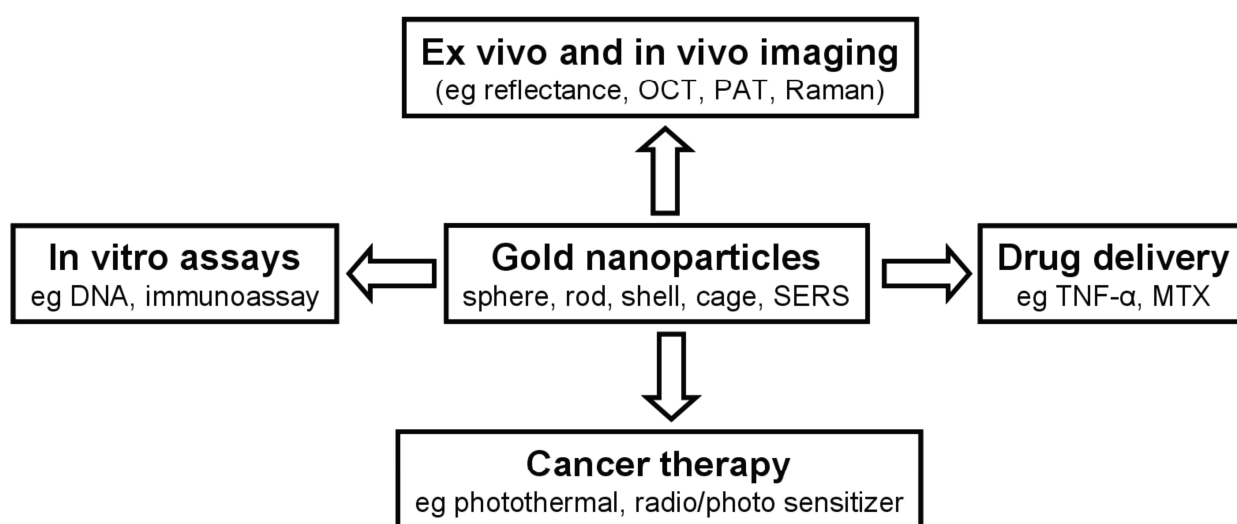


Figure 2.2: Applications of Au nanoparticles in the biomedical industry ^[10]

Grzelczak *et al.* investigated how the growth of Au nanoparticles could be controlled to give different morphologies that could be useful. Tailored shapes can be used for different applications such as making artificial bones, teeth as well as cartilages, sensors as well as nanowires for the electronic industry ^[11].

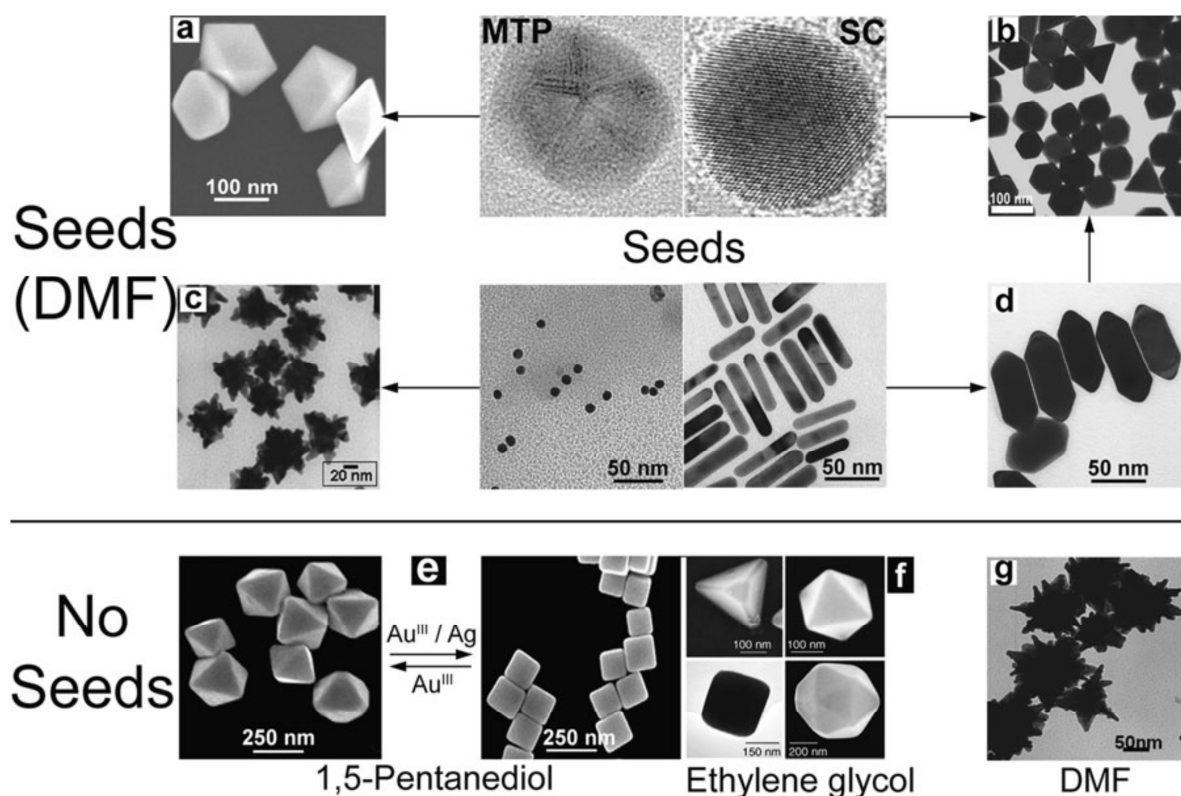


Figure 2.3: Findings by Grzelczak showing electron micrographs of Au nanoparticles with various shapes, synthesized under different conditions ^[11]

The sizes of monodispersed Au nanoparticles can be readily controlled by using the right synthetic method and conditions and can be conjugated with a binding moiety. This means gold nanoparticles can be tailored to detect specific targets in the medicine area. An example is the work done by Yang *et al.* who developed a Au nanoparticles based live cancer cell detector that is able to detect and quantify live epithelial cells in the body by utilizing optical imaging ^[12]

Zhou *et al.* found an application for Au nanoparticles using click chemistry for the visual detection of highly toxic Copper (II). This is highly toxic to organisms (e.g. many bacteria and viruses, fungi and algae) ^[13]. By functionalizing Au nanoparticles with azides- and alkynes and they could visually observe the aggregation of the Au nanoparticles and thus causing their solutions to go colourless and hence detect the presence of the copper. The extinction efficient of the Au nanoparticles was significantly larger than that of the usual organic chromosomes and the smallest concentration observable by the eye was 50 micromolar ^[13].

Au nanoparticles have found many applications in different fields of science: from physics, biology, medicine, chemistry etc. There is still growth in the industry for many more applications. One of the most studied applications of Au nanoparticles is in catalysis.

A number of reactions have found use of Au nanoparticles as catalysts to speed up and ensure the right products are obtained. Au has been studied for a range of reactions from the oxidation of nitrogen oxides, carbon monoxide and hydrogen, the selective oxidation of organic compounds by nitrogen dioxide, hydrogenation of alkenes, photocatalytic degradations and low temperature water-gas shift reaction to propylene epoxidation reactions amongst others ^[14].

2.2.2.1 Water Gas shift Reaction

The water gas shift reaction is one of the reactions occurring in the fuel cell process and it produces hydrogen by preferential oxidation with the aim of reducing the levels of carbon monoxide in the reaction ^[15]:



This reaction also involves the adjustment of the CO/H₂ ratio during methanol synthesis thus producing more H₂ for the production of ammonia ^[16]. This helps with the reduction of harmful CO in the atmosphere during industrial processes. A number of catalysts have been used for this reaction and all produce a range of different results.

Sakurai *et al.* proposed the use of Au deposited on TiO₂ for this reaction at low temperatures as opposed to the conventional catalysts of iron oxide promoted with chromium oxide or the copper, zinc oxide and alumina catalysts that required higher temperatures to function (583-723 K and 483-513 K respectively) ^[16].

From the findings of Sakurai *et al.* it was evident that for forward and reverse water gas shift reactions, Au supported on titania and prepared using deposition precipitation showed high activity as compared to the conventional Cu/ZnO/Al₂O₃ catalyst and they attributed this to the crystalline nature of support and how exposed the gold particles were on the surface ^[16].

Au catalysts supported on ceria supports were investigated by Andreeva for the WGS reaction and results showed that activity was higher and more stable for the catalysts when the support (ceria-alumina) was prepared by mechanochemical activation compared to those

prepared by co-precipitation and wash coating ^[17]. This proved that the preparation method for the catalysts plays a major role in determining the activity of the Au catalysts in reactions. Alumina used with the support increased the thermal stability of the catalyst as well as adding oxygen vacancies on the support for the reaction ^[17].

Andreeva proposed a mechanism highlighting the effect of the alumina on the cerium support. Her theory was that the alumina increased the number of oxygen vacancies on the support and thus increased activity as depicted in Figure 2.4 as the Au cluster is deposited on (001) plane of oxygen deficient CeO_y ($y < 2.0$) that contains Ce^{4+} and Ce^{3+} ions ^[17].

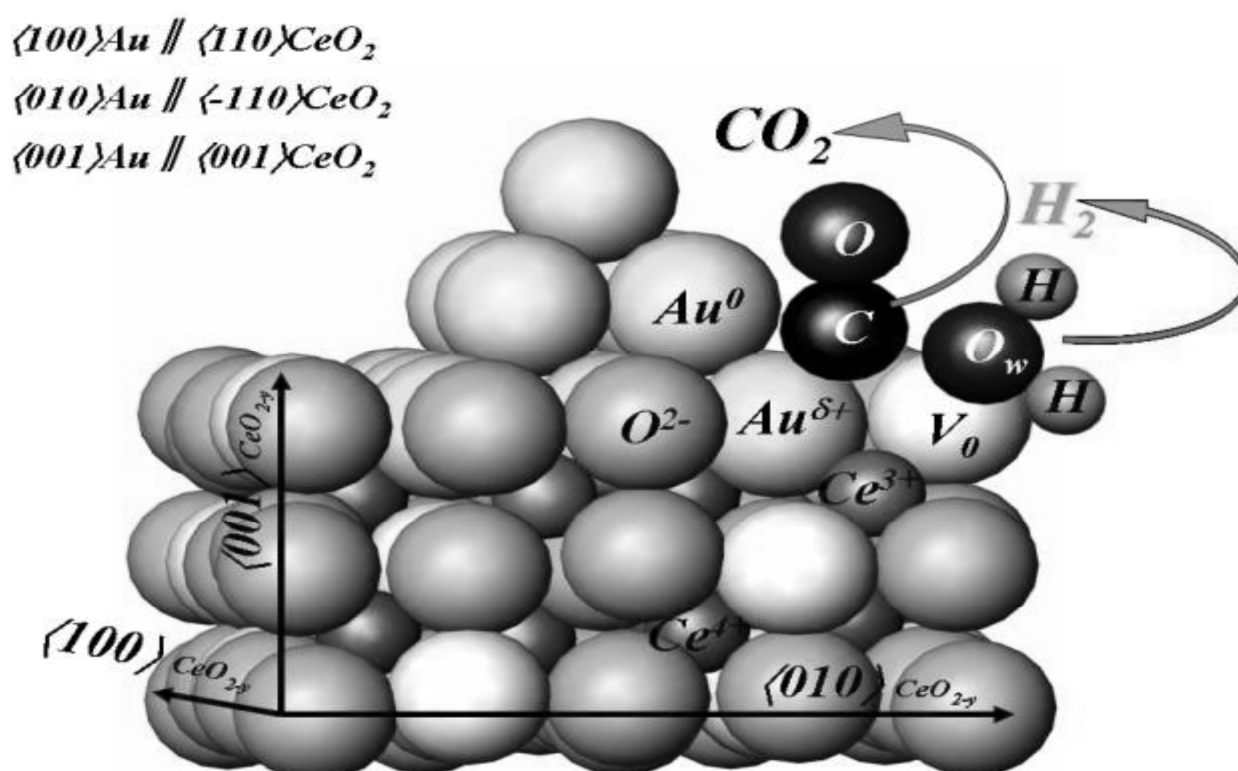


Figure 2.4: Andreeva's proposed model for WGS reaction on gold/ceria catalyst.

V_0 - oxygen vacancy; Au^0 - neutral Au atom; O_w - water oxygen atom.

Another study by Fu *et al.* showed that Au supported on ceria is active and stable at temperatures between 150- 350°C for WGS. They attributed it to the crystal size of the ceria support as they deduced that it controls the amount of surface oxygen available for reduction on the catalyst ^[18]. Increases in the crystallite size of the ceria weakened the interaction between ceria and the gold and hence affected activity. Their study showed that the presence

of gold on the catalyst weakened the oxygen bonds and controlled its interaction with CO at very low temperatures. The group argued that the preparation method of the catalyst had no influence on the enhanced reducibility of the cerium oxide by the Au that increased activity [18].

Deng *et al.* reported that during the WGS reaction the cationic gold changed to a partially reduced state at temperatures as low as 100°C. The research theorized that the oxidation of Au during the reaction was controlled by the composition of the reactant gases and even at different states the Au was active [19]. The catalyst that was fully dispersed on the support and fresh showed the highest activity. It was discovered that the surface lost oxygen due to Au aggregation while the catalyst was in use. The group reported that at temperatures above 673K the Au re-dispersed and was re-oxidized on the support and activity was recovered that could lead to better gold-ceria catalysts being designed [19].

Hurtado-Juan *et al.* reported that bimetallic Au catalysts supported on ceria gave the best catalytic activity as compared to their monometallic counterparts [20]. The Au catalysts were promoted with nickel, calcium, tungsten, palladium as well as platinum and the gold-palladium catalyst reported the best catalytic activity over the other catalysts and they attributed this to the promoter being the palladium altering the local band structure of the ceria support and hence overlooking the redox properties at low temperatures [20].

2.2.2.2 Propylene Epoxidation

Propylene epoxidation involves the oxidation of propene into the desired propoxide under a gas stream of oxygen and hydrogen with very high selectivity as reported by Hayashi *et al.* [21]. Propene oxide is used for the production of polyurethane and polyols. Research into finding the best catalyst for the production of this chemical has long been studied as most major industrials produce propylene oxide via a two stage process and a direct method for the process has been of great interest to scientists [21].

A direct vapour-phase oxidation of propylene to propylene oxide was reported by Hayashi *et al.* and it was in the presence of oxygen as well as hydrogen with gold supported on titania catalyst:

for the oxidation of CO ^[26].

The results obtained by Al-Sayari *et al.* were quite interesting in the sense that the catalysts were observed to be quite sensitive to slight changes to the preparation methods. For example when the group changed the precipitation temperature to higher than 80°C and they noted a decrease in catalytic activity for the catalysts. The study also noted that a difference in the time it took to age the catalysts before filtration also played a role in the activity of the catalysts at the beginning of the CO oxidation reaction. Activity was observed to be low at the start of the time on stream for catalysts that were aged for a short period of time ^[26].

Au nanoparticles are active for solid-gas reaction systems as reported by a number of researchers but recently these catalysts have also been shown to be highly active for electrochemical oxidation of CO as reported by Diao *et al.* in their work ^[27]. The group discovered the potential future use of Au nanoparticles for fuel cells as well as AuNP-based electrochemical sensors as they observed high activity due to the large perimeter-to-surface ratio caused by the relation between the Au and its support being Indium tin oxide as the Au nanoparticle-support perimeters are known to be very active for CO oxidation in solid-gas reaction systems ^[27].

Studies showed that for Au catalysts supported on oxides to be highly active for CO oxidation, a number of factors came into play and these contributed towards the high activity of Au for the reaction and the active sites present on the support also played a vital role in the activity of Au based catalysts ^[27].

Remediakis *et al.* outlined a number of mechanisms as a dependence of different factors. Au based mechanisms are an example whereby the Au atoms that have low coordination act as the active sites while the under coordinated atoms are the centres for the process of adsorbing ^[28]. Support induced mechanisms are also another example whereby the Au nanoparticles are charged by the support or put under strain by the support in order to start the reaction. Mechanisms driven/assisted by the support whereby the oxygen needed for the reaction is provided by the support and the supports also provide stability for the reactants as well as the intermediates involved in the reaction ^[28].

A number of mechanisms have been proposed for the oxidation of CO highlighting the active sites responsible for the high activity of the Au based catalysts, among others Costello *et al.*

proposed that the catalytic activity depended on a number of factors such as the type of support, the preparation method, the Au crystallite size amongst others the nature of the active site on the catalyst played a role ^[29].

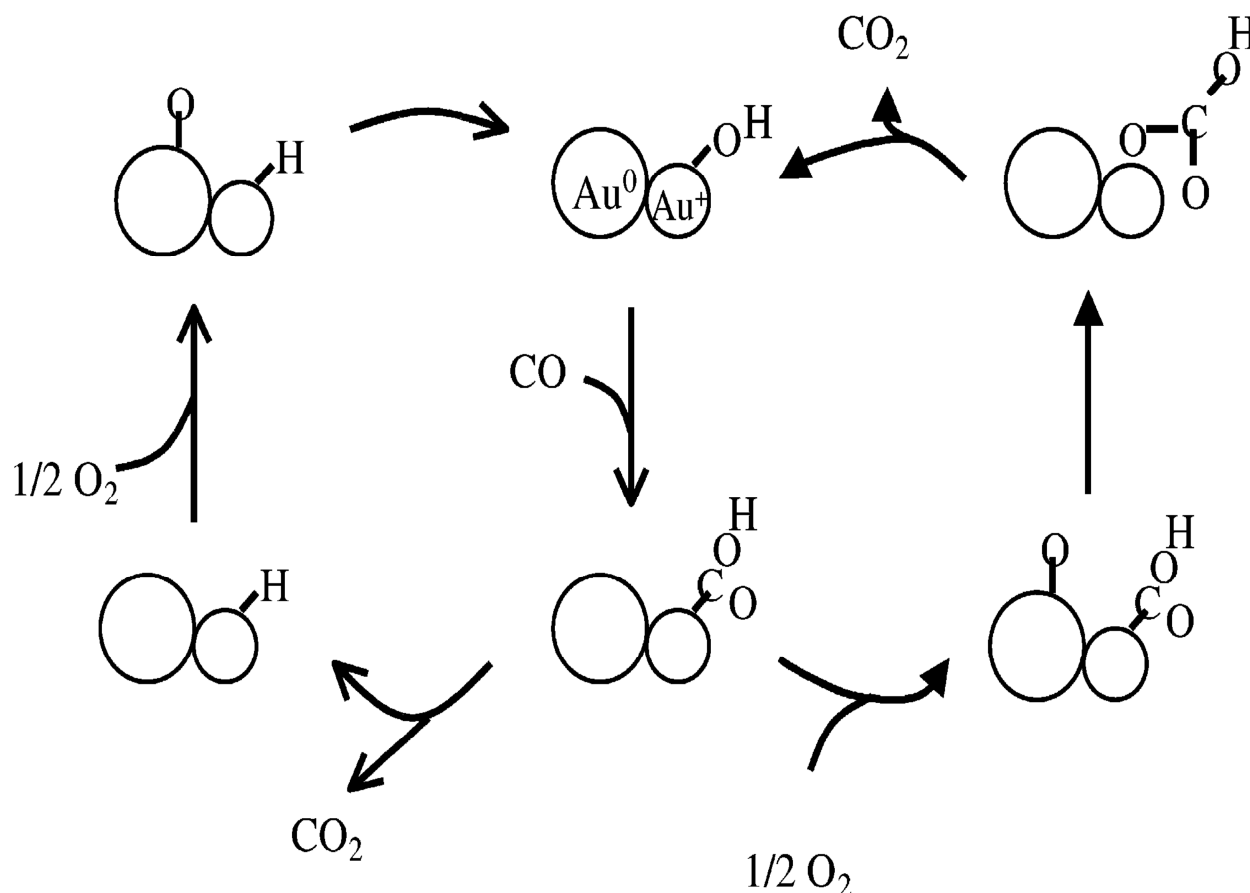


Figure 2.5: Costello *et al.*'s proposed CO mechanism with a Au based catalyst

Costello *et al.* proposed a model as seen in Figure 2.5 in which metallic Au is vital for the activation of the oxygen molecule. From the model they concluded that a positively charged Au molecule with a hydroxyl ligand caused the conversion of CO to CO₂. Their findings proved that for such a reaction mechanism to occur it's highly dependent on the preparation methods as well as pre-treatment conditions of the catalyst ^[29].

Costello *et al.*'s mechanism showed a positively charged Au atom together with an OH- group being present at the edge of the Au particle. An adsorbed CO was then introduced into the Au⁺-OH- bond to form a hydroxycarbonyl with an already adsorbed oxygen molecule. A carbon dioxide molecule is then formed ^[29].

Fujitani *et al.* indicated that there's much debate as to a mechanism for the CO oxidation reaction concerning the active site and how the oxygen molecules become activated as well as the role of moisture on the activity. They went on to prove that under low temperatures of 300K water is the driving force of CO oxidation ^[30]. From their calculations during the study they determined that the oxygen molecules interact with the water to form hydroperoxide species.

A small activation barrier is then applied to promote the interaction of CO with the O-O bond within the hydroperoxide species for CO₂ to be formed ^[30]. In the absence of moisture at those reaction temperatures no CO₂ was observed by quadropole mass spectrometry but contrast to that at 400K CO₂ was observed and they attributed this to the role of reaction temperatures whereas at low temperature moisture played the vital role ^[30].

The role of particle size was also examined by Fujitani *et al.* and their discoveries also showed that with a decrease in particle size there is an increase in catalytic activity at both temperatures of 300 and 400K as previously reported by a number of researchers. Their conclusions for the active sites were that they are present on the gold atoms that are at the periphery of a Au particle on a TiO₂ support ^[30].

Amongst others, different factors affect the activity of Au for CO oxidation and some are highlighted below showing different findings by researchers throughout the years ever since the discovery by Haruta.

2.2.3 Factors that affect activity of gold for CO oxidation

There are various factors that have been reported to affect the catalytic activity of gold nanoparticles supported on some form of support, from the particle size, the type of support used, the reaction conditions, the synthesis method, the metal loading as well as a whole range of factors that contribute to the phenomena of Au catalyst activity ^[6].

Different studies have shown that slight variations in the synthesis methods as well as the reaction conditions for Au based catalysts can play a major role in the activity as well as deactivation of the catalysts ^[26].

2.2.3.1 Effect of Support

In the late 70s and 80s synthesized Au was supported on inactive ceramic oxides such as those of SiO_2 , MgO , unsupported Au filaments as well as powder, sponges, etc. and Haruta *et al.* synthesized Au nanoparticles supported on either single or binary oxides ^[14].

It was clear from the results that the combination of metal oxides gave the best results in terms of catalytic activity for the oxidation of hydrogen. Contrary to the oxidation of hydrogen, oxidation of CO had low activities due to the different oxide supports and the obtained particle sizes, which are both important parameters for a Au catalyst to have high activity ^[14].

Lihui *et al.* reported that if Au was finely dispersed with particle sizes smaller than 10 nm on oxide supports such as Fe_2O_3 , TiO_2 , SiO_2 , Al_2O_3 and so on it was most likely to be chemically active ^[1]. Their findings were that mesoporous silica was an ideal support for Au nanoparticles because it had regular pores and the ability to modify its surface. The research showed that by using the chemical modification synthesis method they were able to obtain highly dispersed and active Au nanoparticles on the mesoporous silica. Contrary to that data the deposition precipitation gave them aggregated Au nanoparticles on the outsides of the support with big particle size above 10 nm ^[1].

Bogdanchikova *et al.* proposed the possibility of using both silica and titania as supports for Au nanoparticles using the sol gel synthesis method. Their findings revealed that the chemical mixture of the two supports gave a larger specific area compared to those of the single supports. Rietveld XRD refinement showed that the majority of the gold particles were large (about 90 nm) and found supported on the TiO_2 while only a quarter of these particles were on the SiO_2 support. Only a tiny amount of Au was observed on the mixed oxide support even with the increased surface area highlighting that activity of these catalysts would be low as particle size has been proven to affect activity ^[31].

Table 2.2: Effect of mixed oxides on surface area of Au catalysts by Bogdanchikova *et al.* [31]

Support	Surface area, m ² /g	Pore volume, cm ³ /g	Pore radius, Å°	Au concentration, wt. %
SiO ₂	426	0.162	<10	3.1
TiO ₂	40	0.046	35	1.2
TiSi ₅	1154	0.415	<10	9.4
TiSi ₁₀	800	0.291	<10	4.0

A paper by Bocuzzi *et al.* reported their findings of Au supported on TiO₂ to be a good catalyst for CO oxidation and observed 100 percent conversions at temperatures below 240K with particle sizes as small as 2.4 nm utilizing the deposition precipitation method at calcination temperatures of 473 and 573K [2]. Above these calcination temperatures they observed an increase in particle sizes for the catalyst and hence lower activity [2] which brings about the other important factor that influences activity being calcination temperature.

2.2.3.2 Effect of Calcination temperature

For the preparation of finely dispersed and small nanoscale Au particles the deposition precipitation method is highly favoured. With this method one is able to control the parameters of the synthesis such as pH and calcinations temperature which play a vital role in creating the best catalytically active nanoparticles [22].

Akita *et al.* prepared Au/TiO₂ nanoparticles and calcined them at different temperatures from room temperature to 873K. They proposed a growth mechanism for the nanoparticles with relation to the change in temperature and observed that below 473K the Au nanoparticles formed on particles as small as 1 nm and grew on the edges of the surface. At temperatures above 573K the particles were trapped on the interface of the support particles and above 673K the sizes of the particles grew rapidly which in turn affected catalytic activity [22]. According to work done by Quin *et al.*, the catalyst that had the best catalytic activity was the one that had particle sizes smaller than 5 nm and had strong interactions with the support [32].

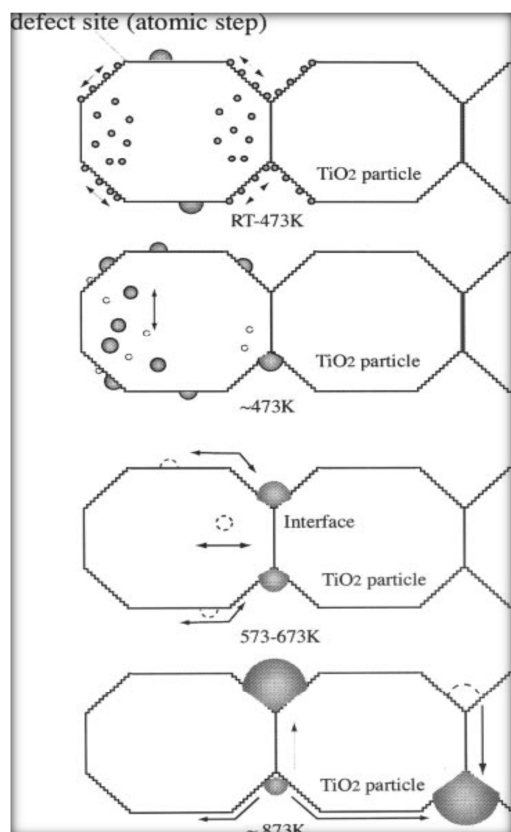


Figure 2.6: Akita *et al.*'s schematic drawing of their proposed growing process of Au particles with calcination temperature increase ^[22]

Contrary to the last two authors Zanella *et al.* proposed that was not the case but that instead the drop in activity for the catalysts calcined at different calcinations temperatures was due to a change of the shape of the particle with the calcination temperature instead of the increase of the particle size ^[33].

Zanella *et al.* stated that after the preparation of their catalysts the Au species were in the oxidic state, III and the transformation to metallic Au occurred in air at 373K utilizing the deposition precipitation method with NaOH as the base and at 423K utilizing the deposition precipitation method with urea as the base. Above 473K all the Au species were metallic for both methods and the particle sizes increased with an increase in the calcination temperature. They recorded that the CO oxidation activity increased with an increase in the number of metallic Au. At higher temperatures a decrease in activity was observed due to pre-treatment at higher temperatures which caused a large amount of low-coordinated sites to be truncated octahedral with smooth facets instead of round ones ^[33].

2.2.3.3 Effect of synthesis methods

Much research has gone into the discovery of the best synthesis method for the preparation of gold based catalysts as they are highly sensitive to certain factors such as temperature, pH, deposition time as well as ageing time.

The different preparation methods for Au based catalysts have been suggested to be ^[34]:

1. **Deposition precipitation**-This method has been used widely because it can be manipulated in different ways to obtain finely dispersed gold particles on any form of support mostly oxide supports. A gold chloride solution is slowly immersed into a support solution under a certain temperature with a control of pH and then followed by ageing, vacuuming and drying as well as calcination.
2. **Impregnation**- This method works by filling the pores of the support with a gold salt or the support can be mixed into a solution of the Au salt in which the solvent will later be removed. This method has been known not to be effective as large Au particles are synthesized that are not highly active
3. **Co-precipitation**- An aqueous solution of HAuCl_4 and a metal nitrate are mixed into an aqueous solution of Na_2CO_3 . The problem with this method is that it is not easy to control and the Au particles tend to get mixed into the support matrix and hence inaccessible for catalytic reaction which makes it unsuitable for high activity CO oxidation.
4. **Other methods**- Chemical vapour deposition, ion exchange, Iwasawa method, suspension spray reaction method, grafting and other methods that are not as effective as the deposition precipitation method.

A study by Wolf and partner showed results indicating that the preparation method of Au catalysts played a major role in the activity of the catalysts. They reported an increase in CO oxidation activity as the pH of the synthetic method increased and when the calcination temperature was decreased ^[34]. Their findings were that with a decrease in particle size the

catalysts became highly active. They concluded that SiO_2 is not suitable for this method and instead TiO_2 was a better suited support for the catalysts which was also better than Al_2O_3 proving that the support does help with more than stabilization of the catalyst ^[34].

Bamwenda *et al.* did a study between Au and Pt catalysts on a TiO_2 support; they supported Wolf *et al.*'s statements by proving that the Au based catalysts were remarkably more sensitive to the preparation method conditions which was not the case with the Pt catalysts ^[35]. They attributed these findings to the assumptions made in literature that the reaction between CO and O_2 takes place on the surface of the Pt for the Pt based catalysts, which is different for the Au based catalysts as they have been said to have the CO oxidation occurring between the Au and support interface hence the sensitivity to the way the catalysts are prepared ^[35].

2.2.3.4 Effect of loading concentrations

Throughout the years much research has been done on the effects of Au loading concentrations on Au based catalysts. This has shown that the loading percentage is inversely proportional to the catalytic activity of Au nanoparticles meaning that the higher the loading the lower the catalytic activity as the particles get bigger with increased loading.

Dobrosz *et al.* did a study on the influence of preparation methods of highly dispersed Au nanoparticles by varying the synthesis method, the concentration of the Au precursor (HAuCl_4), the washing procedure, pre-treatment temperatures and a number of factors that showed that the synthesis of finely dispersed and highly active Au nanoparticles depended mainly on the preparation methods ^[36]. The intended loadings of the Au were 2 and 5 % and the washing procedures were also varied. With unwashed samples they did not notice any increase in the Au particle size between the two loadings as well as no change in activity and they attributed this to the presence of chlorides in the samples which inhibit activity. The washed samples did however show an increase in activity with a decrease in the intended Au loadings ^[36].

Another study was done on Au supported on Y-type Zeolites whereby they observed that higher Au concentration, higher pH of the solution as well as lower temperatures produced big sized Au particles which in turn gave very low catalytic activity due to the now reduced surface area on the catalyst ^[37].

With the variation of the preparation conditions differently dispersed gold particles on the support can be obtained. With an increase in Au loading a decrease in activity for CO oxidation can be observed and hence careful consideration and research was done to ensure the synthesis of highly monodispersed Au nanoparticles that are highly active for CO oxidation.

2.3 Platinum Group Metals

Platinum Group Metals (PGMs): ruthenium, rhodium, palladium, osmium, iridium, and platinum. These metals possess similar chemical as well as physical properties and they are mostly found in the same mineral deposits ^[38].

2.3.1 Applications of PGM's

PGMs have found excellent applications in industry as they possess some excellent properties ^[39]. They have shown to possess outstanding catalytic properties ^[40]. PGMs are highly resistant to chemical attack, work well in high-temperature reactions and are highly stable when it comes to their electrical properties ^[40]. All these properties have been exploited for industrial applications such as the production of nitric acid in the form of gauzes for the oxidation of ammonia, systems designed to oxidize undesirable or harmful organic odours, etc. ^[40]. Au nanoparticles combined with platinum group metals (PGM's) have shown to produce bimetallic systems that show a d-band shift of the PGM in the nanocrystal causing a synergy of properties ^[40].

A catalyst can have good catalytic activity for low temperature reactions such as the case of gold nanoparticles, or a catalyst can have good thermal activity at high temperatures but not that great catalytic activity such as the case of PGMs. Our goal was to combine metals to find a suitable catalyst to work in high temperatures without sintering.

Taking the study done by Zanella in mind where it was discovered that Pt/SnO catalysts that had not been pre-treated exhibited similar overall reaction profiles for different loadings which were maximum at the onset of CO oxidation reaction but readily decayed with time [33]. Au/MnO catalysts that had not been pre-treated exhibited remarkable CO oxidation activity which was approximately an order of magnitude greater than that of the Pt/SnO sample after 6000 min of reaction as reported in the research [33]. In the same study it showed that an increase in the temperature of the reactions gave the reverse of the results, showing the Pt/SnO catalyst working better than the Au/MnO catalyst as they sinter with temperatures above 400K [33].

The use of binary metals in catalysis to combat different problems has been in the increase of late. In electrocatalysis the issue of obtaining a CO tolerant catalysts for the use in solid polymer fuel cells is investigated by Avgouropoulos *et al.* as the already commercialized Pt catalysts are highly deactivated by CO during the operation of the H₂ fuel cell as slight traces of CO are present in the H₂ gas stream [41]. What the group investigated was the effect of adding another metal to the Pt catalyst and observed whether the activity is improved. The data indicated that the addition of Sn and Ru to Pt supported on Carbon support greatly had a promoting effect to the monometallic catalyst. The activity increased by almost 60 times higher for the bimetallics than the monometallic catalyst [41].

With Kiss *et al.* they claimed that introducing a second metal to a monometallic catalyst greatly improved the performance/activity of the catalyst and they attributed these changes to ensemble or ligand effects [42]. Kiss *et al.* characterized Au-Rh and Au-Mo catalysts supported on TiO₂ (known to have great properties as a support to metals in catalysis as it affects catalytic activity due to metal-support interactions) and found that for the Au-Rh catalysts gold clusters were found to be large when rhodium was deposited which was in contrast with that of Mo deposition [42].

The Rh was reported to have a shadowing effect on the Ti and O peaks detected by LEIS analysis but instead the Au peaks were enhanced meaning that more Au atoms on the top most layer were increased. Kiss *et al.* reported that most of the rhodium attached onto the support surface first and then the Au atoms on top as detected by LEIS and XPS analysis. The Au-Mo catalysts showed that Mo instead disrupted the Au nanoparticles forming on the TiO₂ catalyst and they concluded that it was due to Mo reacting strongly with titania and hence the

now introduced reduced centres of titania then caused Au dispersion ^[42].

2.3.2 Rhodium as a catalyst

Rhodium from the other PGMs has shown over the years to have high activity conversion processes for the production of synthetic gas ^[43]. This shows potential for a new route for the conversion of natural gas, coal and even biomass into hydrocarbons as well as other chemicals ^[43], making it a good possible PGM for the combination with Au to form either an alloy or a bimetallic system.

Unique to Rh being good in the reduction of nitrogen oxide to nitrogen and oxygen ^[44], they are also good reducing agents of benzene to cyclohexane ^[45]. Rh metal is known to possess characteristics that make it ideal to combine with those of gold to produce a "super" catalyst that can work in high temperatures without sintering as well as be a very good catalyst.

A recent study done on the acetonitrile adsorption of Au/TiO₂, Rh/TiO₂ and Au-Rh/TiO₂ catalysts revealed an electron interaction between TiO₂ and the metallic particles. It was found that the electron flow was directed from TiO₂ to the metal ^[46]. The electron flow then caused the formation of strong Lewis acid sites on titania with Au/TiO₂ and Rh/TiO₂. The study further proved that the strength of Lewis acid sites weakened with the increase of Rh content in bimetallic Au - Rh catalysts, which predicted a special electronic interaction between the two metals ^[46]. This same study further proved particles containing both Au and Rh atoms formed on the titania surface and the size of these bimetallic particles was greater than the particle size of monometallic catalysts and this was seen by Rh enrichment in the outer layers of the catalyst ^[46].

These catalysts could then work with the combination of the two metals on a suitable support. The gold nanocatalysts could be a good source of catalytic activity while the Rh will provide for a good thermal stability and can bond strongly to the support hence producing a bimetallic/alloy of Au and Rh that can endure high temperatures with an increase in lifetime.

2.4 Conclusions

From literature highlighted in this chapter it is evident that the activity of gold nanoparticles strongly depends on a number of factors such as the effect of support interactions with the metal, the effect of the preparation method being the DP most favoured, the calcination temperatures that the catalysts are exposed to, the pH of the reaction solution as well as the pre-treatment that a catalyst endures before catalytic tests are done.

This project will aim to investigate and characterize differently prepared catalysts to determine what effect the preparation conditions can have on the particle sizes of the obtained nanoparticles as well as on the activity of some of the catalysts as not all will be tested for catalytic activity.

The work by Haruta has indeed opened a new field of possibilities in the work of Au nanoparticles catalysts and then the introduction of platinum group metals to these Au nanoparticles is a new field altogether for the improvement of these Au nanoparticles that seem to segregate and deactivate with time and wear.

2.5 References

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Chapter 3

Experimental Procedures

3.1 Introduction

This chapter outlines the procedures that were carried out during the process of acquiring data in this study. Stepwise explanations of the different synthetic conditions that were carried out for the different studies that were conducted on the catalysts as well as their preparation conditions is explained thoroughly in this section. The chapter also outlines the analytical techniques that were used to characterize the catalysts.

3.2 Materials

3.2.1 Chemicals used

The chemicals used in this study were obtained from various manufacturers with different compositions and purities as outlined below

Table 3.1: Percentage purities/composition of chemicals used in the study

Chemical/Gas	Percentage purity/composition	Manufacturer
NH ₃	99+ % NH ₃	Sigma-Aldrich
TiO ₂	80% of anatase, 20% of rutile	Degussa
SiO ₂	99.8 %	
RhCl _x .xH ₂ O	38-40% Rh	Sigma-Aldrich
HAuCl ₄ .xH ₂ O	50.0 ± 0.5% by weight of Au	Next Chimica
CO	10%	Afrox
O ₂	5%	Afrox

3.3 Methodology

This section details the methods applied to study the effects that different synthesis conditions had on the particle sizes of the prepared catalysts as well as the catalytic activity and deactivation of the catalysts. The addition of Rh to the Au catalysts is also outlined in this section. Reproducibility of the results was tested by running the experiments more than one time.

3.3.1 Preparation of catalysts using the deposition precipitation method

A 500 mL Beaker was placed into a water bath and 200 mL of deionised water was added into the beaker. Silica/titania, the metal support, was added to the water. A stirrer bar was placed into the beaker along with a thermocouple to allow for the solution to be heated to 70-75°C. While the reaction took place the temperature was maintained at 70-75°C.

Two burettes were then filled (three in the case where Rh is added). One burette was filled with chloroauric acid, such that the ratio of the acid to the silica/titania used had varying Au loadings. The other burette was filled with ammonium hydroxide of a certain concentration. A third burette with rhodium salt was used in some experiments where rhodium was added to the Au loadings. The beaker was then covered with parafilm. A calibrated pH meter was inserted into the solution to monitor the pH level of the reaction as it progressed.

The chloroauric acid solution was then added drop wise over a certain period. As the Au solution was added the pH steadily declined thus the addition of the Ammonium base was needed in order to control the pH to the desired level for that catalyst. The beaker was then allowed to slowly cool down to room temperature over several hours. Stirring was continued while the solution cooled down. The beaker was then covered in parafilm and placed into a dark cupboard and left to age. After the days of ageing the solution had silica/titania with Au/Rh precipitate on it formed at the base of the beaker. The solution was then filtered via vacuum filtration and rinsed through with enough deionised water until the eluent reached neutrality. The resulting precipitate was then dried and calcined at varying temperatures.

3.3.1.1 Effect of pH

The Au/TiO₂ and Au/SiO₂ catalysts were synthesized using the DP method as it can be done at various pH values to investigate the effect that pH has on the particle sizes and activity of the catalysts. Akita *et al.* reported in their paper that pH does influence the activity of gold catalysts ^[1]. The operating pH had to be higher than the isoelectric point of the support. The isoelectric point is the pH at which the support surface carries no net electrical charge ^[2]. The degrading point of the catalyst was also closely observed. These two parameters had to be within the range that the catalyst would be most effectively operational in.

For titanium dioxide the isoelectric point lies above 7 and hence a pH greater than that will have to be utilized to ensure the binding of the support with the nanoparticles ^[3]. The phase of the TiO₂ is also of importance as it helps ensure adequate uniformity of the nanoparticles on the support surface ^[3]. The isoelectric point of silicon dioxide lies between 1.7 and 3.5 which means that the operational pH is best above those points.

Table 3.2: The different pH levels tested on the catalysts and other synthesis conditions

Catalyst	Theoretical Au loading percentage	Au Concentration	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au/SiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/SiO ₂	5	0.005 M	9	60 minutes	3 days	300°C	70°C
Au/SiO ₂	8	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/SiO ₂	8	0.005 M	9	60 minutes	3 days	300°C	70°C
Au/SiO ₂	10	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/SiO ₂	10	0.005 M	9	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	5	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	9	60 minutes	3 days	300°C	70°C

3.3.1.2 Effect of Deposition duration

Studies have shown that the preparation method together with the synthesis conditions can play a vital role in the synthesis of highly dispersed Au nanoparticles on an oxide support as they are highly sensitive to these ^[4].

The effect that the time taken to deposit Au onto the support under the set temperature of 70°C was also investigated on the Au on titania catalysts under the conditions below utilizing the DP method.

Table 3.3: The deposition durations tested on the catalysts and other synthesis conditions

Catalyst	Theoretical Au loading percentage	Au Concentration	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au/TiO ₂	5	0.005 M	7	15 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	30 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C

3.3.1.3 Effect of loading concentrations

The gold loadings were varied between 5 and 10% and the catalysts were prepared using the DP method and characterized using the characterization methods listed in section 3.4 of this chapter of our work. As outlined by Wolf *et al.* the Au loadings played a vital role in ensuring the synthesis of highly active Au nanoparticles as the loading controlled the sizes of the particles which in turn affected the activity of the catalysts ^[4].

Table 3.4: The varied Au loading percentages tested on the catalysts and other synthesis conditions

Catalyst	Theoretical Au loading percentage	Au Concentration	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au/SiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/SiO ₂	8	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/SiO ₂	10	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	8	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	10	0.005 M	7	60 minutes	3 days	300°C	70°C

3.3.1.4 Effect of ageing duration

The duration a catalyst is allowed to age can determine how well the particles attach to the support. This affects that stability of the support that may deactivate slightly slower than when aged for a shorter period. The catalysts were varied between 24 hours of ageing and 144 hours of ageing in a dark cupboard before the washing and drying as outlined below:

Table 3.5: The ageing durations tested on the catalysts and other synthesis conditions

Catalyst	theoretical Au loading percentage	Au Concentration	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au/TiO ₂	5	0.005 M	7	60 minutes	1 day	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	6 days	300°C	70°C

3.3.1.5 Effect of support

Preparation of the catalysts was done using the DP method with variations in the supports, Titanium P25 Degussa was used, SiO₂ pellets were used as well as a mechanical mixture of the two oxides was used at standard conditions as outlined below:

Table 3.6: The supports used for the catalysts and other synthesis conditions

Catalyst	Theoretical Au loading percentage	Au Concentration	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au/SiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/TiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/5%TiO ₂ -100%SiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C
Au/10%TiO ₂ -100%SiO ₂	5	0.005 M	7	60 minutes	3 days	300°C	70°C

3.3.1.6 Effect of Rhodium loadings

The gold catalysts were synthesized using the traditional DP method but this time with the addition of another metal as a promoter. The Rh solution was added drop wise from a separate burette but at the same pace as the gold solution with the conditions outlined on table 3.7:

Table 3.7: The different Rh loadings tested on the Au based catalysts and other synthesis conditions

Catalyst	Theoretical Au loading percentage	Theoretical Rh loading percentage	pH	Deposition duration	Ageing Duration	Calcination temperature	Reaction temperature
Au-Rh/TiO ₂	3	1	7	60 minutes	3 days	300°C	70°C
Au-Rh/TiO ₂	3	3	7	60 minutes	3 days	300°C	70°C
Au-Rh/TiO ₂	3	5	7	60 minutes	3 days	300°C	70°C
Au-Rh/TiO ₂	3	10	7	60 minutes	3 days	300°C	70°C

3.4 Analytical Techniques

3.4.1 pH meter

Hanna HI pH meter was used to measure the progress of the experiments by measuring pH of the solution as we mixed. The pH meter was calibrated for the measurements using fresh buffers of pH 4 and 7 for the pH ranges being measured.

3.4.2 Surface Area Determination (BET)

A Micromeritics TRISTAR 3000 analyser was used for the measurements of the Nitrogen adsorption-desorption isotherms. About 0.25 g of the sample was placed in the sample holder and degassing of the sample was done by passing N₂ for approximately 4 hours at 150°C for the removal of any moisture in the samples before the measurements were conducted. The samples were allowed to cool down to room temperature while a stopper was in place before starting the measurements. The specific surface areas and pore volumes were determined by the Brunauer-Emmett-Teller (BET) method.

3.4.3 Transmission Electron Microscopy (TEM)

All TEM images were obtained using the Tecnai Spirit Twin TEM from the Wits university microscopy unit operating at the voltage of 120 kV. A small spatula tip sample was placed in a reactor tube and mixed with about 5 mL of acetone and stirred for approximately 15 minutes. The slurry was then pipette into a copper grid and allowed to dry before placing it in the microscope for measurements.

3.4.4 High resolution Transmission Electron Microscopy (HRTEM)

All HRTEM images were obtained using the FEI Tecnai F20 at 200 kV from the University of the Western Cape Physics microscopy unit and at magnifications as high as 800 K. Images were recorded by Paul Franklyn. A small spatula tip sample was placed in a reactor tube and mixed with about 5 mL of acetone and stirred for approximately 15 minutes. The slurry was then pipette into a copper grid and allowed to dry before placing it in the microscope for measurements.

3.4.5 X-Ray Diffraction (XRD)

Data on the structure and composition of the supports and catalysts were obtained by the measurements of their XRD patterns. A small amount of ground powder sample was placed on a sample holder and inserted into the Diffractometer. The measurements were done on a D2 Diffractometer and the particle sizes were measured using POF software utilizing the Scherrer equation below:

$$\text{Particle Size} = 0.94 \times \lambda / (\text{FWHM} - \text{SFWHM}) \times \cos \theta \dots\dots\dots 4$$

3.4.6 Energy Dispersive X-ray Spectroscopy (EDX)

All EDX experimental data was obtained from the HRTEM microscope at the University of the Western Cape to monitor and confirm the presence of rhodium in the gold.

3.5 CO oxidation measurements

All activity measurements were done on a catalytic rig designed for CO oxidation measurements. About 0.1 g of catalyst was charged into a U shaped reactor along with SiC and was pre-treated by passing H₂ through the catalyst at different temperatures depending on what was being observed. The reaction was also carried out at different temperatures between 30 and 350°C while passing 10% CO and 5% O₂. The flow rate was set at 60 ml/min for each gas. The outlet gas was analysed by a GC attached to the reactor, Atmospheric pressure was set for all measurements.

3.6 References

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Chapter 4

Results and Discussion

4.1 Introduction

This chapter aims to present and discuss the results obtained during the experimental work conducted in the previous chapter. The focus area will be the characterization of the prepared mono and bimetallic catalysts due to the following effects: the effect of pH will be discussed, the effect of the ageing duration of the catalysts, the deposition time will also be discussed, the effect of percentage loadings of the Au catalyst, the effect of the support as well as the change in behaviour of the catalyst as the addition of Rh is introduced.

4.2 Characterization of Au/TiO₂ catalysts

4.2.1 Effect of pH

The activity and deactivation of Au based nanoparticles depends strongly on the preparation method of the catalyst. The high activity of nanosized Au catalysts deposited on semiconductor oxides such as TiO₂ can be attributed to the conditions at which these catalysts are prepared ensuring well dispersion on the surface of the support ^[1]. The discussion by Konova *et al.* shows that the control of the shape and sizes of the gold particles on the support is done by monitoring the calcination temperatures, the Au solution concentration as well as controlling the pH of the reaction whilst using the deposition precipitation method ^[1].

Table 4.1 shows the BET surface areas of the different catalysts prepared at pH 5, 7 and 9. There is a big difference between pH 5 and 9 to that of pH 7 which is known to be the optimum pH for the synthesis of highly active and well dispersed Au nanoparticles on a TiO₂ support as this is above the isoelectric point of the oxide support meaning that there are significant interactions between the support and the Au, hence leading to better activity. pH 7 had a higher surface area than the other two showing small mono dispersed particles on the surface.

Table 4.1: BET results on various catalysts with varying pH

Catalyst	BET surface area(m ² /g) (%error)	Pore volume(m ³ /g)	Pore diameter(nm)
5%Au/TiO ₂ (pH 5)	48.38 (2.02)	0.28	23.14
5%Au/TiO ₂ (pH 7)	65.98 (2.01)	0.38	32.96
5%Au/TiO ₂ (pH 9)	50.59 (2.01)	0.34	27.07

Yazid *et al.* reported that when Au based nanoparticles are synthesized at a pH lower than 7 the particles tend to be larger and less mono dispersed than at pH 7 as observed in figures 4.1, 4.2 and 4.3 TEM micrographs and particle size histograms ^[2].

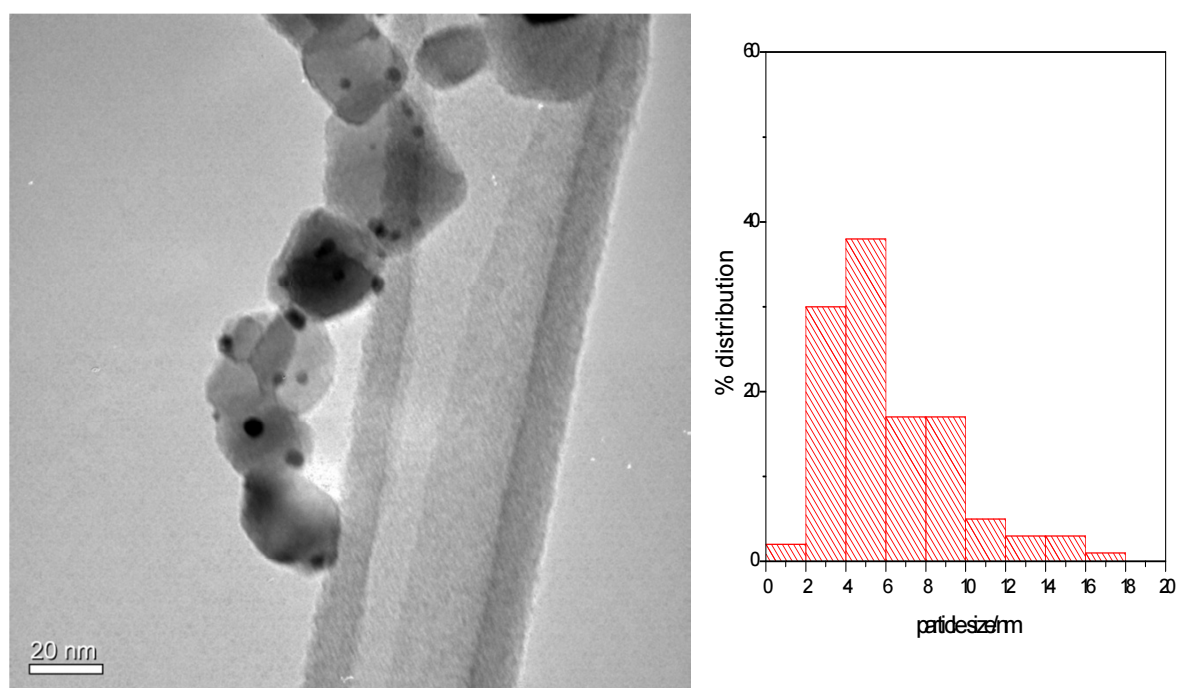


Figure 4.1: TEM micrograph and particle size distribution histogram of TEM image depicting particles synthesised at pH 5 (5% Au/TiO₂)

The Au particles synthesized at pH 5 prove to be in the range of 6-10 nm mostly and as explained by Yazid *et al.* this could be due to the hydrolysis of the AuCl₄ precursor present in the solution ^[2]. Hydrolysis of the Au species is highly dependent on the pH and hence at lower pH more of the Chlorine species are present which also affects aggregations of the particles into bigger particles. At a pH above 7 the particles are observed to become smaller

and better mono dispersed as observed on figure 4.2, at this point Yazid *et al.* explains that this is due to more fully hydrolysed Au species being present ^[2].

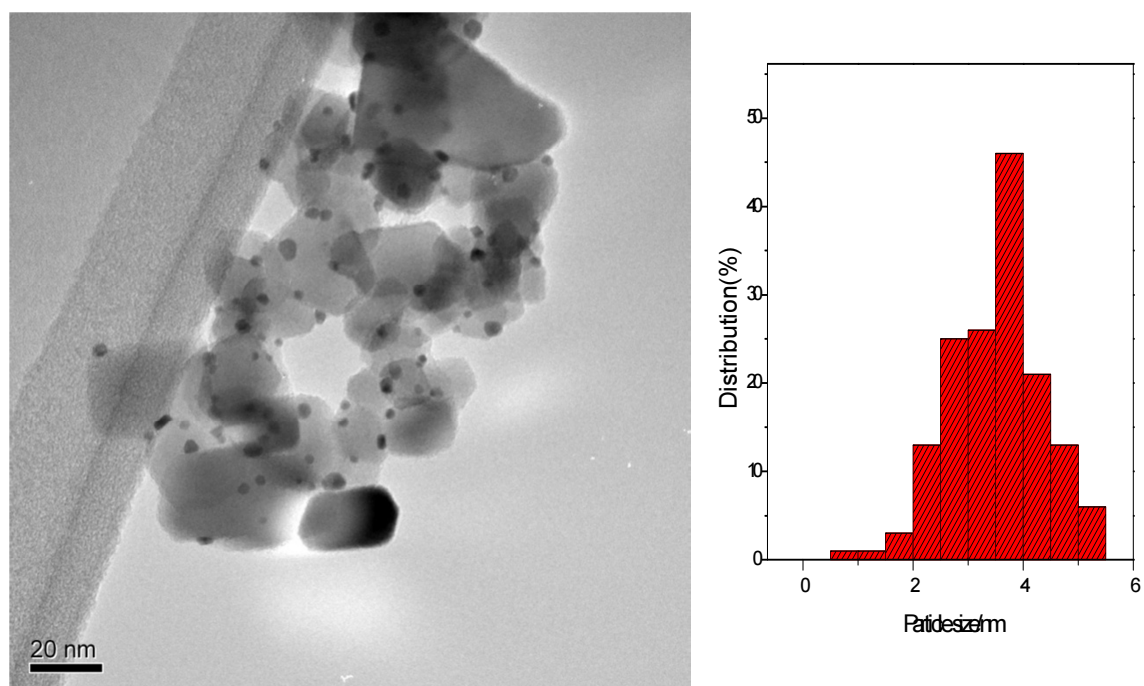


Figure 4.2: TEM micrograph and particle size distribution histogram of TEM image depicting particles synthesised at pH 7 (5% Au/TiO₂)

As reported by Hvolbaek *et al.* the most important parameter in the activity of Au based catalysts is the size of the particles, the most active catalyst are those below 5 nm and these are mostly evident in figures 4.2 and 4.3 at pH 7 and 9 ^[3]. For the catalysts at pH 9 it's evident that the size becomes smaller and more particles are in the same range of 2-4 nm as above this pH more fully hydrolysed species are present in the solution and hence the Au can bind to the support more distinctly and mono-disperse.

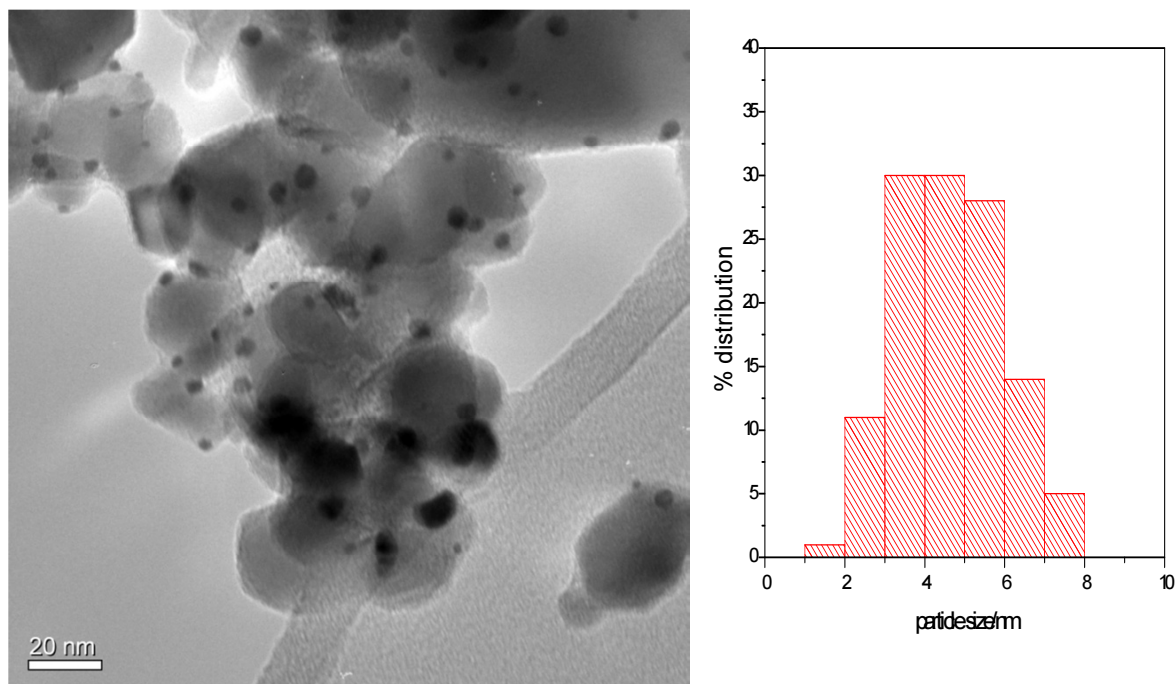
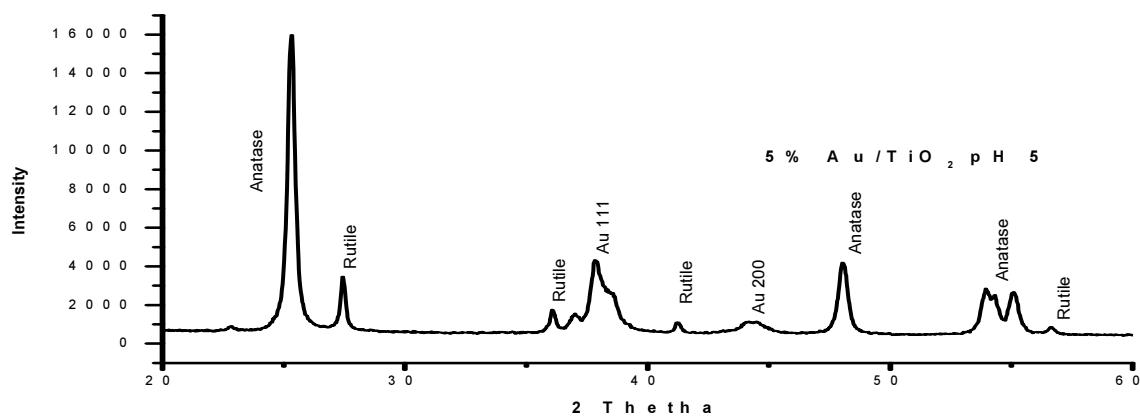


Figure 4.3: TEM micrograph and particle size distribution histogram of TEM image depicting particles synthesised at pH 9 (5% Au/TiO₂)

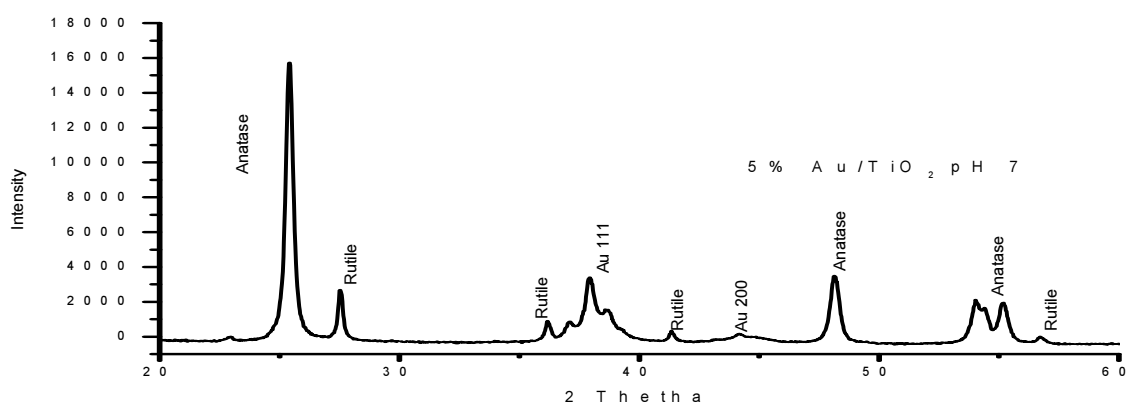
XRD patterns of the catalysts show to agree with the obtained TEM results as its observed that with the low pH larger Au particles are observed as seen by the Au peaks at $2\theta = 38$ and 44° representing the Au (111) and (200) orientation while for pH 7 and 9 the peaks are observed to be more broader and less intense showing that the particle sizes of the Au are small ^[2].

With the careful control of the pH around 6-10 the hydrolysed Au species, Au(OH)₃ can be deposited onto the surface of the support without any present precipitations in the liquid phase and the chloride ions are removed during the washing period before any drying occurs insuring the synthesis of mono dispersed nanometre sized Au particles ^[4].

(a)



(b)



(c)

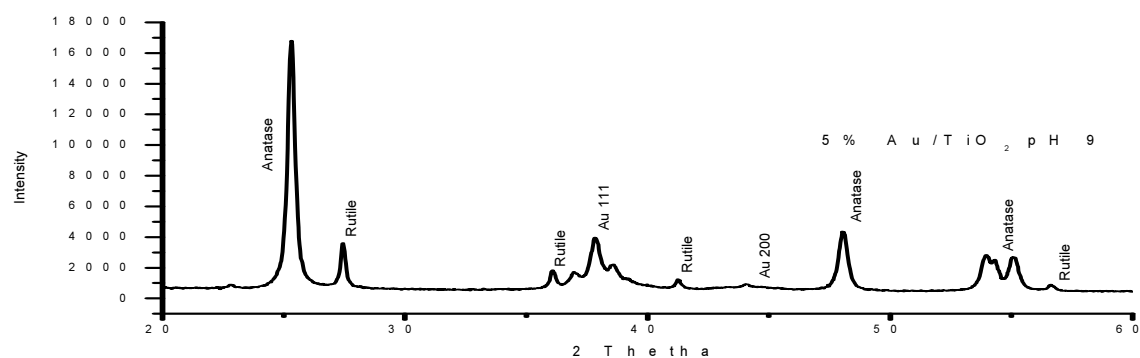
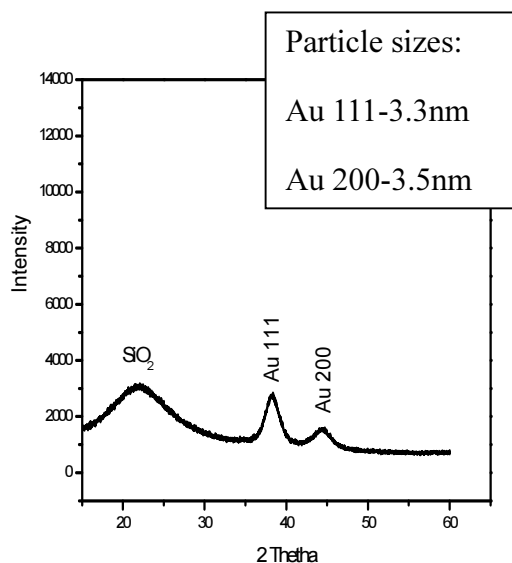


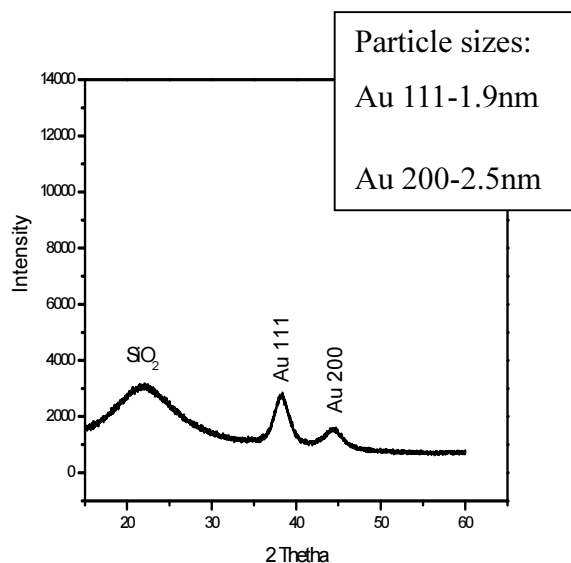
Figure 4.4: XRD patterns of the 5% Au-TiO₂ catalysts prepared at different pH levels (a) pH 5, (b) pH 7 and (c) pH 9

XRD diffraction patterns were obtained for the Au-SiO₂ catalysts as well which were in agreement with those of titania. The silica was tested on different Au loadings and pH and showed the same pattern of a decrease in particle size with an increase in pH within the range of 6-10 but also indicated another trend of an increase in size with an increase in Au loading which shall be discussed in the upcoming subsection.

(a)

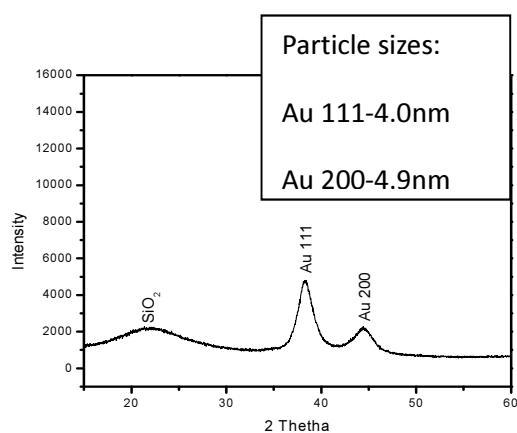


(b)

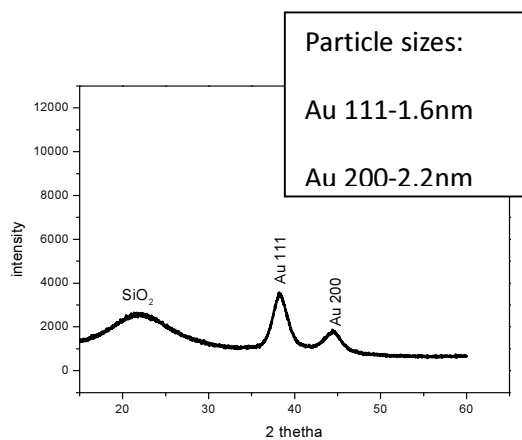


Figures 4.5 (a) and (b) : XRD patterns of the 5% Au-SiO₂ catalysts prepared at different pH levels (a) pH 7 and (b) pH 9

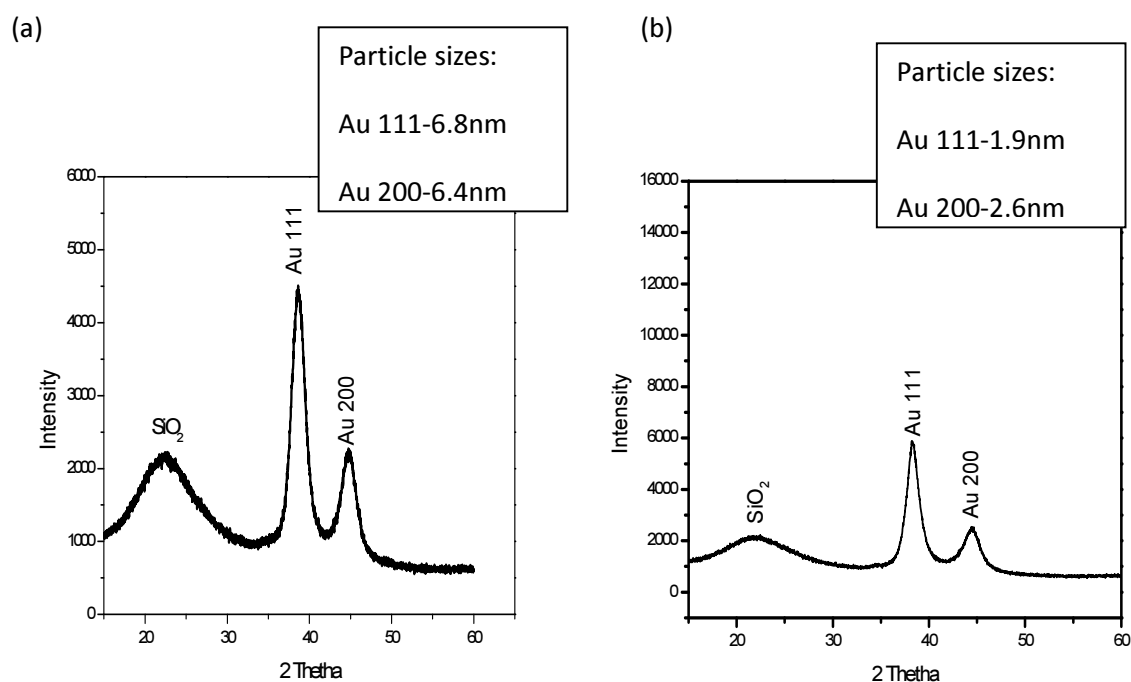
(a)



(b)



Figures 4.6 (a) and (b) : XRD patterns of the 8% Au-SiO₂ catalysts prepared at different pH levels (a) pH 7 and (b) pH 9



Figures 4.7 (a) and (b) : XRD patterns of the 10% Au-SiO₂ catalysts prepared at different pH levels (a) pH 7 and (b) pH 9

The XRD patterns for the silica support show a peak at 22° 2θ typical of amorphous silica and that Au was successfully deposited on the surfaces of the supports as shown by the peaks at $2\theta = 38$ and 44° .

At pH 7 and 9 the two support surfaces are essentially negatively charged and the present species in the solution is the fully hydrolysed Au species, $\text{Au}(\text{OH})_4^-$ which then causes a repulsion between the two ^[5].

The possible explanation as highlighted by Caps *et al.* is the presence of $\text{Au}(\text{OH})_3$ which is neutral and thus there's an equilibrium reaction occurring on the proton deficient support as follows: $\text{Au}(\text{OH})_4^- \leftrightarrow \text{Au}(\text{OH})_3 + \text{OH}^-$, this then forms very small gold particles as research would show ^[5]. The hydroxide particles are the precursor to the final metallic gold particles that are deposited on the surface, and the calcination step is used to convert the hydroxide to the metallic state.

4.2.2 Effect of Deposition Duration

As reported by Wolf *et al.* the preparation method for all gold based catalysts is essential in the production of highly mono dispersed and small nanoparticles for CO oxidation. The time taken to deposit the nanoparticles on the support is crucial because if the time is too short then the Au is simply smeared on the surface without any order and does not bind well to the said surface ^[6].

The experiment conducted was set in all the standard parameters as highlighted in table 3.3 in the previous chapter but with variations in deposition durations of the Au solution onto the support. From TEM observations large particles were observed from the catalysts deposited within 15 minutes which showed that the Au species did not bind well nor disperse on the surface of the support causing them to aggregate into bigger particles on the sizes of the support as seen on figure 4.8

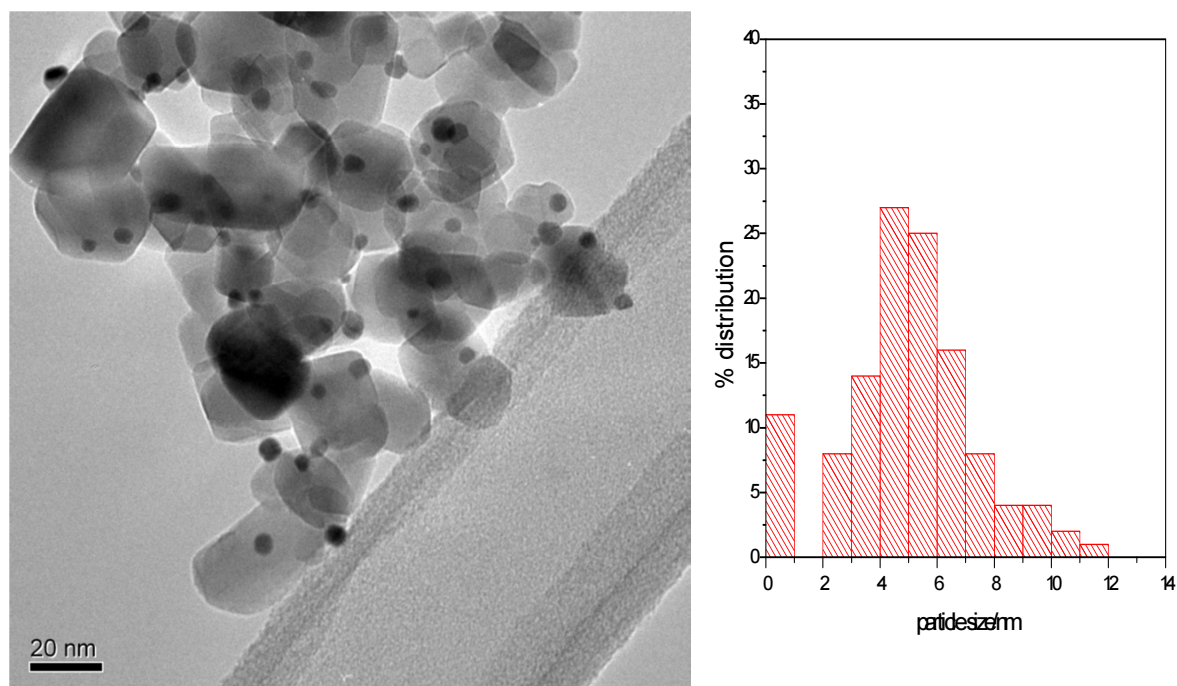


Figure 4.8: TEM micrograph and particle size distribution histogram of TEM image depicting particles deposited within 15 minutes (5% Au/TiO₂)

Figure 4.8 shows the particle size histogram of those shortly deposited Au nanoparticles falling within the ranges of 5-12 nm due to the short period of deposition. With this period the

catalysts doesn't have ample time to settle uniformly onto the surface. As previously discussed by Wolf *et al.* these catalysts are highly sensitive to the method of preparation and hence the deposition precipitation method is highly favoured. The DP method can easily be manipulated to work in the most sensitive of conditions such as careful deposition over a period of 30-60 minutes which shows to be best for the catalysts as observed on figure 4.9 below ^[6].

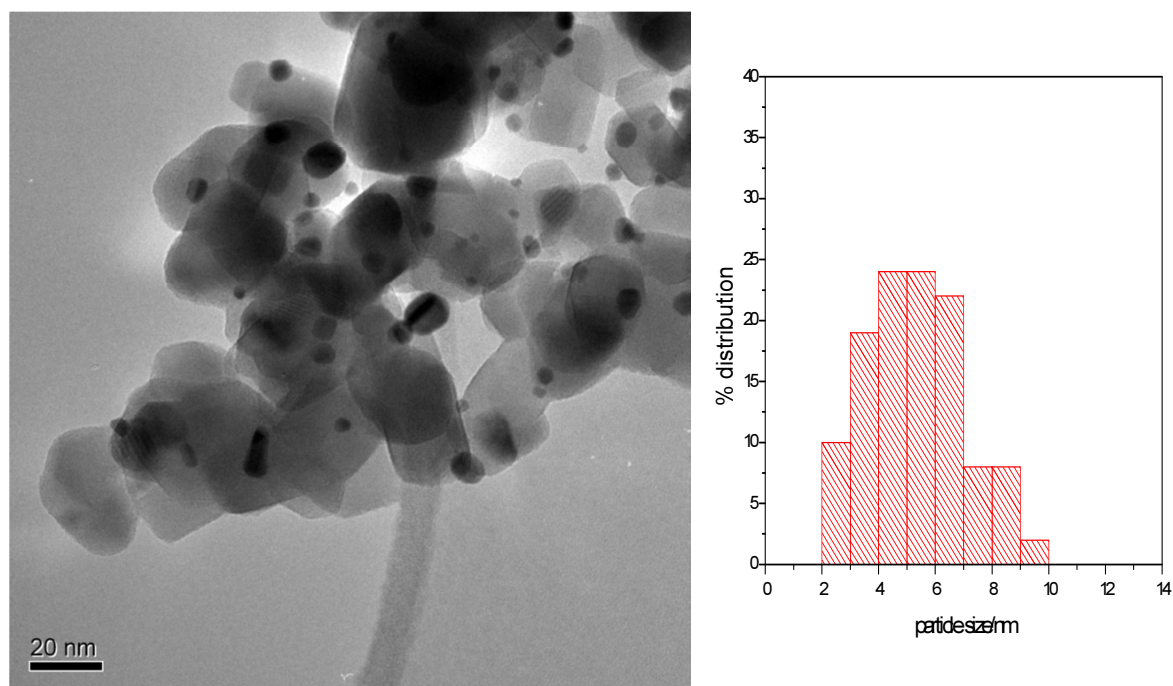


Figure 4.9: TEM micrograph and particle size distribution histogram of TEM image depicting particles deposited within 30 minutes (5% Au/TiO₂)

Several papers have done studies on the effect of preparation methods for the catalysts such as Bamwenda *et al.* who did a study varying the pH of the solution, the concentration of the gold precursor and the amount of the Au and they concluded that the best method for the best and highly active Au nanoparticles would be the deposition precipitation method ^[7].

Figures 4.3 and 4.9 both show that the synthesis of Au nanoparticles at a slower rate gives small spherical Au nanoparticles situated on the support surface as seen by particle sizes histograms indicating that the majority of the Au particles are within the range of 3-5 nm which is ideally the best for active catalysts ^[2].

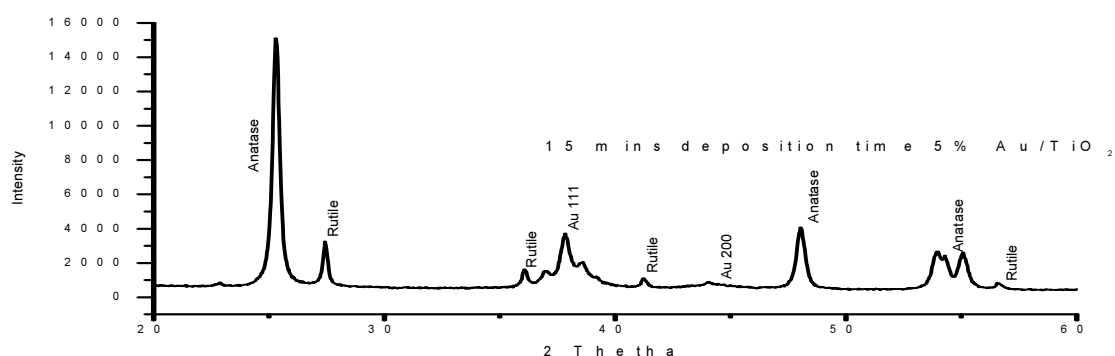
Catalysts prepared with the deposition precipitation (DP) method are easily controllable when it comes to preparation conditions and this method has been duped to be highly preferred for obtaining small nanoparticles, even smaller than 2 nm as reported by Baatz *et al.* [8]. Souza *et al.* reported that many parameters needed to be taken into consideration when utilizing the DP method such as the pH, the support, the percentage loading of the Au as well as the deposition duration of the Au precursor onto the support of which very little research has been done on this last parameter [9].

Table 4.2: BET results on various catalysts with varying deposition duration

Catalyst	BET surface area(m ² /g) (% error)	Pore volume(m ³ /g)	Pore diameter(nm)
5%Au/TiO ₂ (15 minutes)	48.60 (1.91)	0.31	25.65
5%Au/TiO ₂ (30 minutes)	48.19 (1.54)	0.30	24.97
5%Au/TiO ₂ (45-60minutes)	65.98 (2.01)	0.38	32.96

From table 4.2 it is evident that the BET surface area is influenced by the deposition duration for all the catalyst prepared below 30 minutes and for that prepared within an hour. The BET surface area is larger showing that the catalysts are very small and well dispersed on the support showing that ample time for deposition is highly desired for the preparation of small catalysts.

(a)



(b)

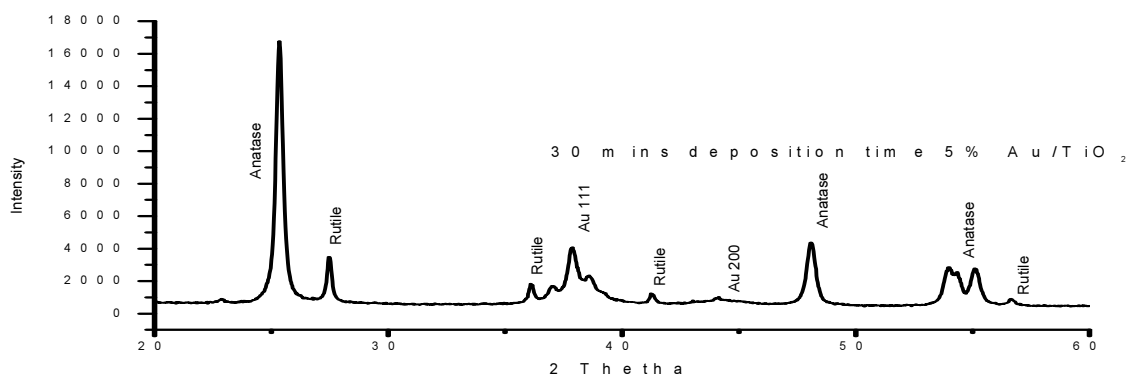


Figure 4.10: XRD patterns of the 5% Au-TiO₂ catalysts prepared at different deposition durations (a) 15 minutes (b) 30 minutes

Figure 4.10 (a) and (b) show that there is a small variation between the catalysts prepared within 15 and 30 minutes while there is a slight variation with that of figure 4.4 (b) whereby the catalysts were deposited over an hour which is in agreement with the TEM images obtained above.

4.2.3 Effect of loading concentrations

When it comes to Au nanoparticles the gold loaded onto the support plays a role on the particle sizes of the obtained NP's. The more gold is loaded on the support is the most likely that the Au will form larger particles than if less loading was used as reported previously in literature.

Figures 4.11,12 and 13 show HRTEM images of Au-SiO₂ samples prepared under the DP standard conditions showing that small gold nanoparticles have deposited uniformly on the silica support and calculated to be smaller than 10 nm making them have lower melting points than Pt and Pd as well as having high catalytic activity^[10]. The results do show that the best loading for Au is 5% as it shows smaller particles than loadings above that.

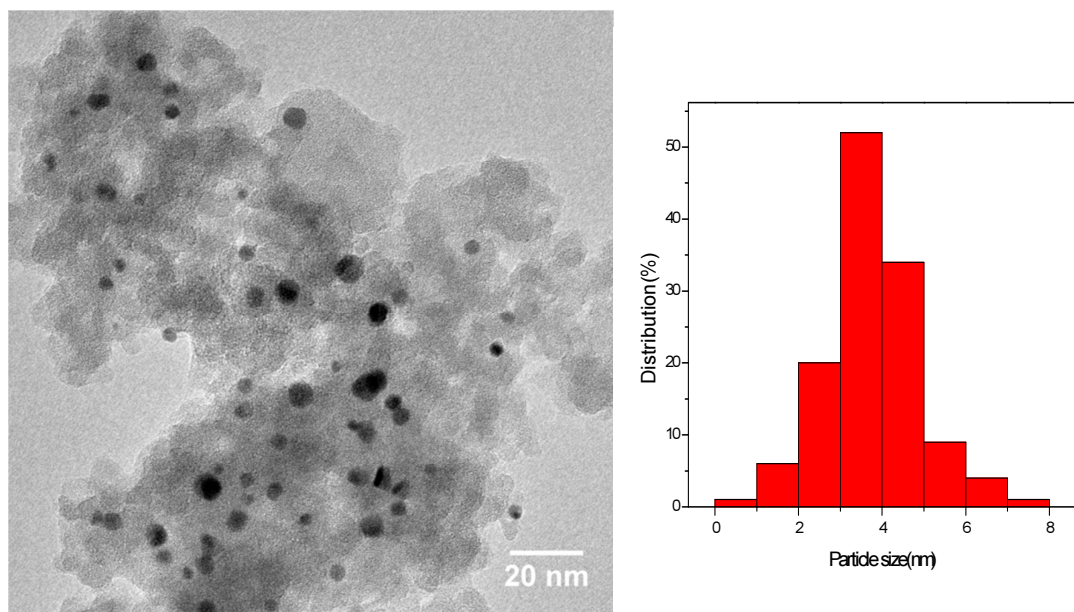


Figure 4.11: HRTEM micrograph and particle size distribution histogram depicting theoretical loading percentages of Au (5% Au/SiO₂)

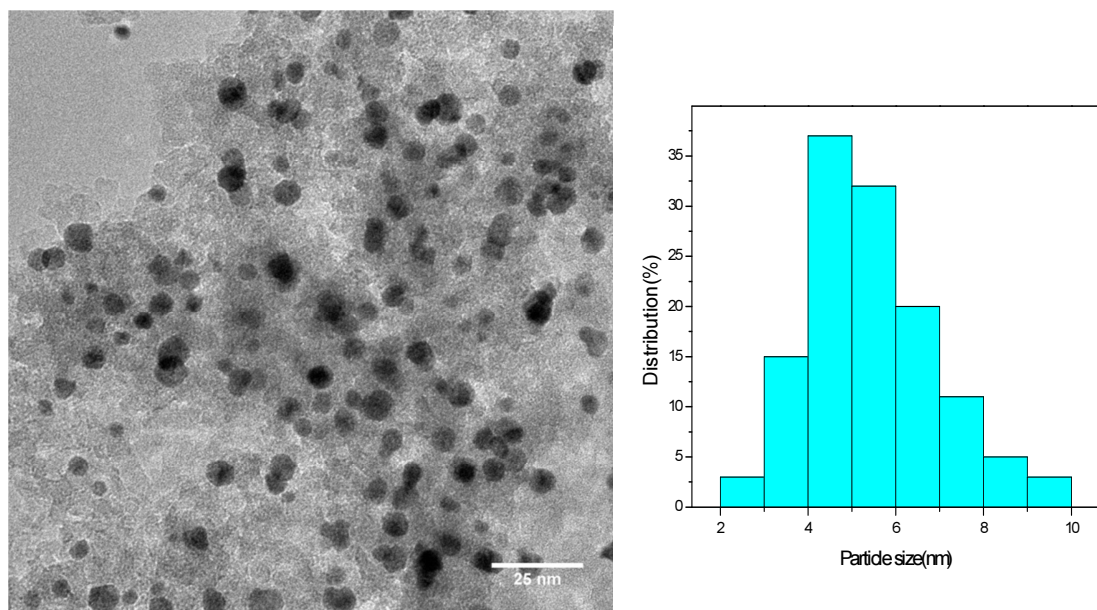


Figure 4.12: HRTEM micrograph and particle size distribution histogram depicting theoretical loading percentages of Au (8% Au/SiO₂)

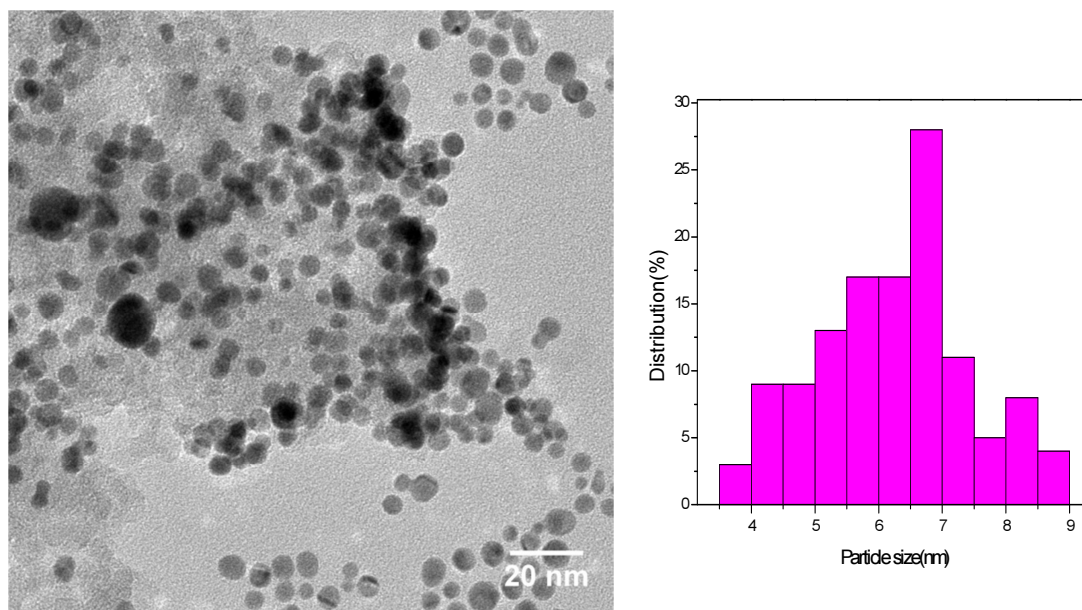


Figure 4.13: HRTEM micrograph and particle size distribution histogram depicting theoretical loading percentages of Au (10% Au/SiO₂)

From the overlay of the XRD data on figure 4.14 below, peaks at $2\theta = 22^\circ$ which is typical of amorphous silica behaviour, as well as a peak at $2\theta = 38^\circ$ showing (111) Au orientations and another peak at $2\theta = 45^\circ$ showing (200) orientations ^[11] were observed throughout the repetitions of the experiments. An intensity increase with Au loadings was observed for all data as well as an increase in particle size with Au loadings.

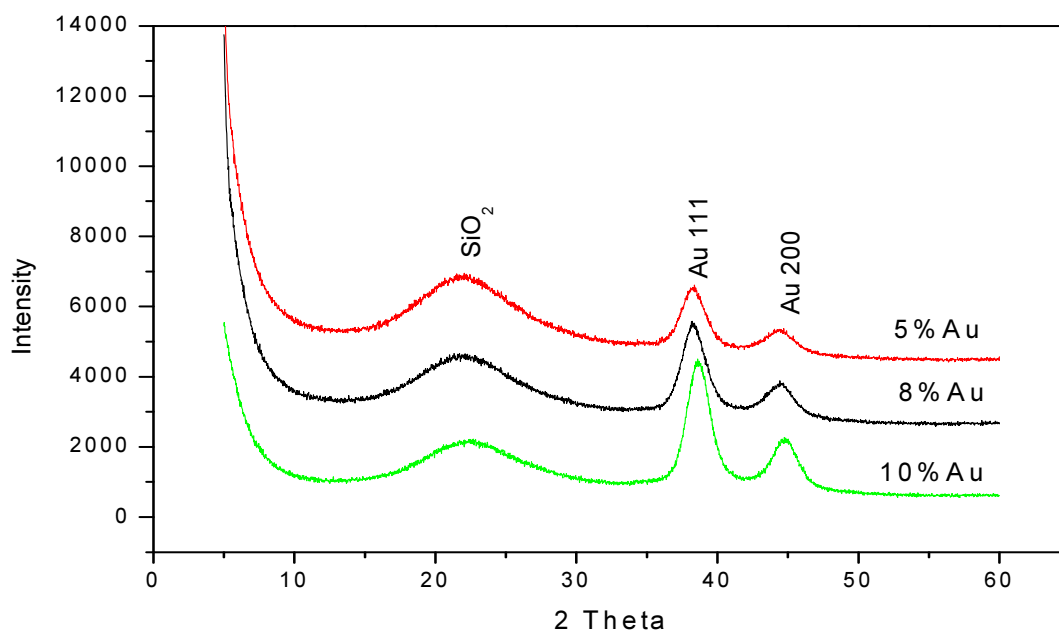


Figure 4.14: Overlay of XRD patterns of the Au-SiO₂ nanoparticles at different Au loadings depicting the amorphous SiO₂ peak and crystalline Au peaks.

4.2.4 Effect of ageing duration

When utilizing the DP method to prepare Au NPs on an oxide support the catalysts are left to age for a certain duration in a dark cupboard to allow complete deposition to take place but as to how long is the ageing period is of little knowledge to researchers as its rarely mentioned or researched in literature. Raphulu *et al.* investigated the deactivation of Au/TiO₂ during storage for CO oxidation and under preparation conditions they mentioned that they left their catalysts to age as prescribed without mention of how long that was ^[12].

With Zanella *et al.* their DP method simply stated that the solution was vigorously stirred for 16 hours and then filtered right after. Ageing time was irrelevant to their research as they were investigating the effect of using NaOH or Urea as precipitating agents varying calcination temperatures as well ^[13].

With optimisation of the catalysts we were able to investigate the effect that ageing had on catalysts stored in a dark cupboard and with figures 4.15 and 4.16 show that there is hardly any difference in the particle size distributions of the two differently aged catalysts.

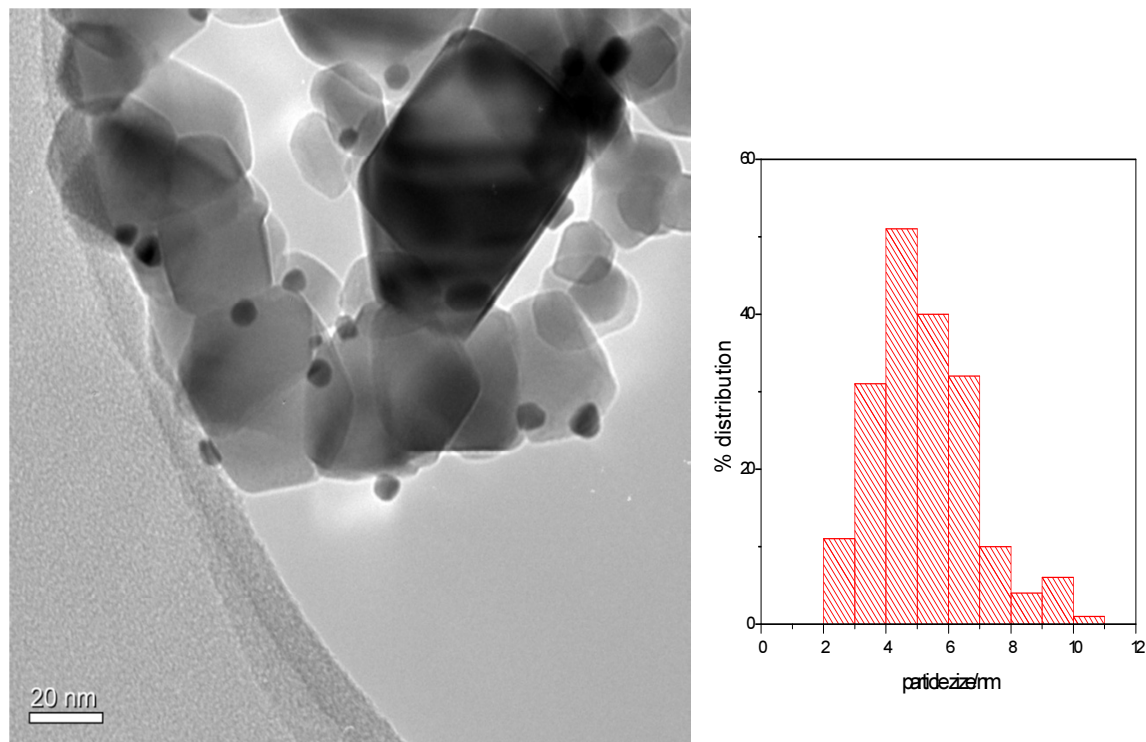


Figure 4.15: TEM micrograph and particle size distribution histogram of TEM image depicting particles left to age for 1 day (5% Au/TiO₂)

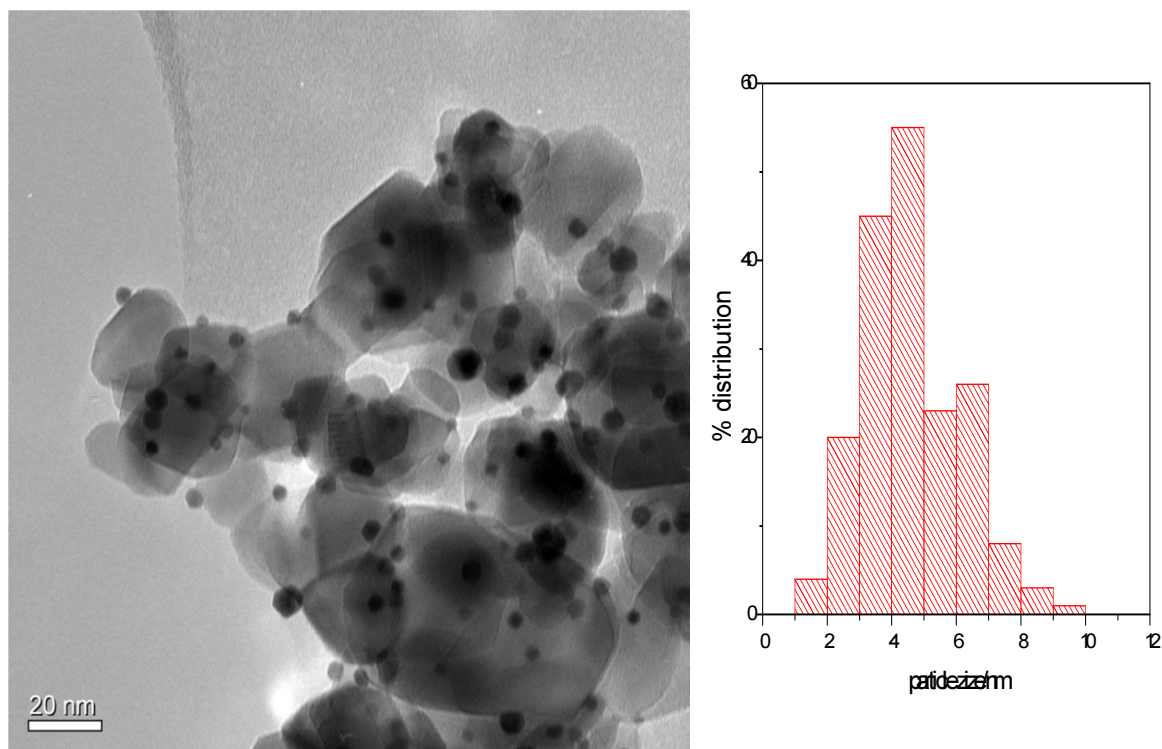
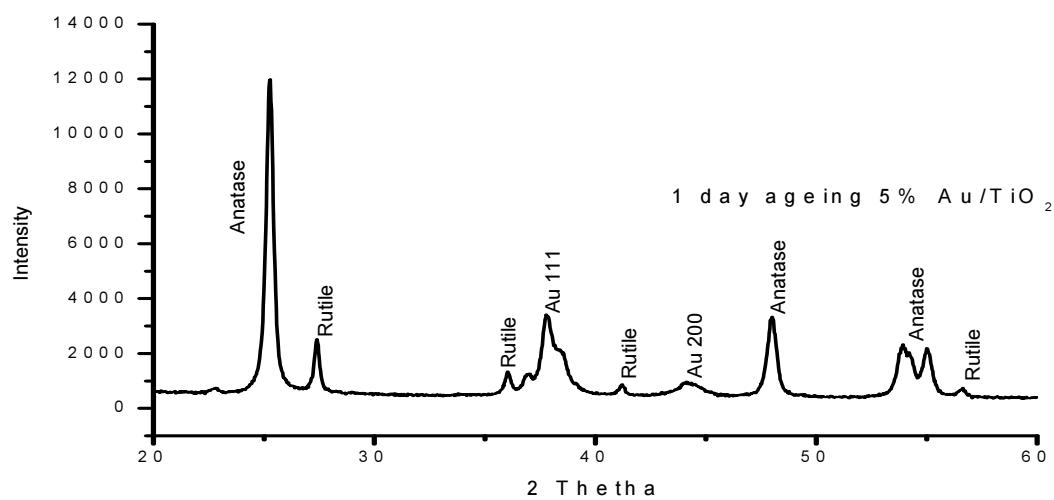


Figure 4.16: TEM micrograph and particle size distribution histogram of TEM image depicting particles left to age for 6 days (5% Au/TiO₂)

XRD data correlates with TEM data as seen on figure 417 (a) and (b), a slight difference in the intensity and peak diameters for the gold peaks at $2\theta = 38$ and 44° . Bamwenda *et al.* prepared their Au and Pt supported on TiO₂ catalysts and left then to age for only an hour and still obtained nanoparticles smaller than 5 nm mostly showing that the ageing period is almost negligible when it comes to obtaining small Au nanoparticles on the oxide support surface ^[7].

(a)



(b)

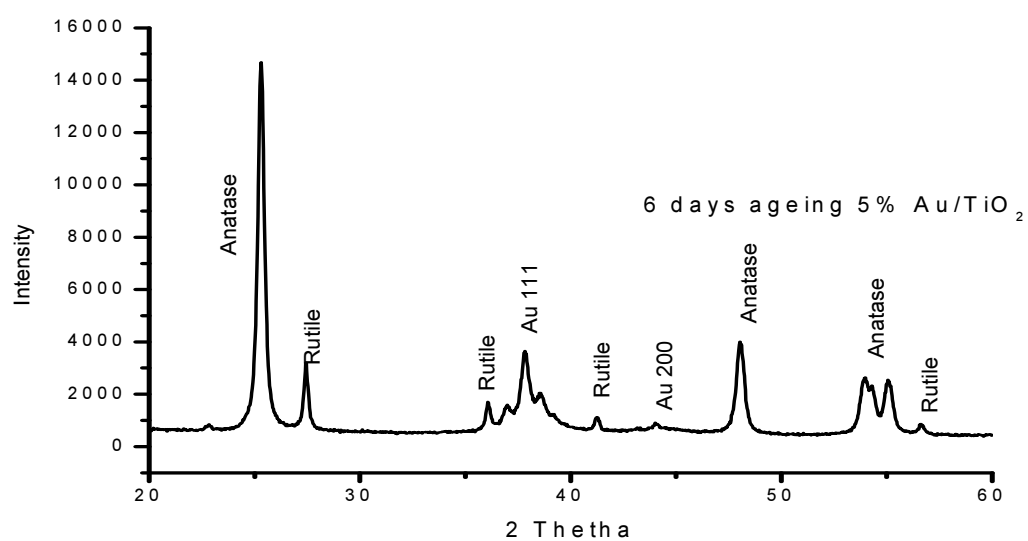


Figure 4.17: XRD patterns of the 5% Au-TiO₂ catalysts prepared with varying ageing days
(a) 1 day aged (b) 6 days ageing

4.2.5 Effect of support

Investigations into supported gold based systems for pollution control has been in the increase in the recent years since the discovery by Haruta ^[10] highlighting how these systems are highly active for various reactions with CO Oxidation being the predominant reaction of note. The key factor reported to be responsible for the high catalytic activity of the Au based catalysts being the size of the nanoparticles. According to Russo *et al.* the deposition of the gold precursor on the support especially oxides such as CeO₂, TiO₂ etc. improved the catalytic properties of the specific oxide such as its selectivity towards certain products, activity as well as the stability of the obtained products ^[14].

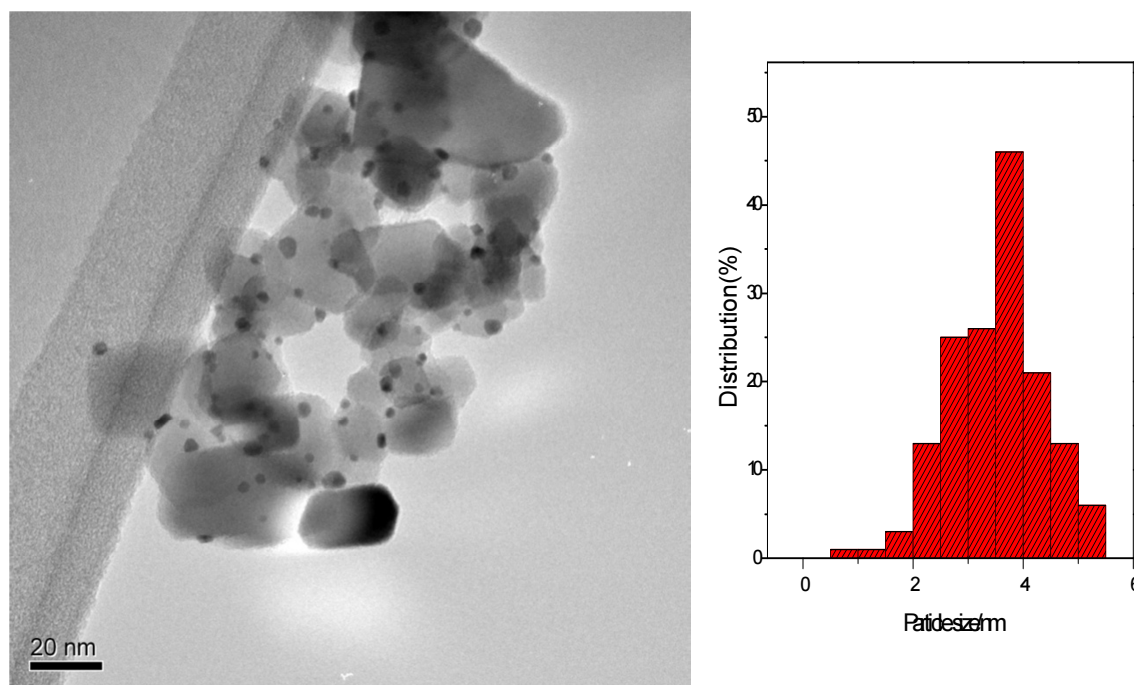


Figure 4.18: TEM micrograph and particle size distribution histogram of TEM image depicting particles supported on TiO₂ (5% Au/TiO₂)

The deposition of Au nanoparticles onto a titania support is shown in Figure 4.18 along with the particle size histogram showing that a large number of particles were within below the 4 nm range which is typical of catalysts synthesized with the conditions outlined in table 3.6 in the previous chapter as reported by Akita *et al.* ^[15].

The study done by Akita and co-workers showed that most of the Au particles occupy the spaces on the interface of the P-25 support for catalysts synthesized using the same parameters as those in table 3.6 ^[15]. The high activity of Au-TiO₂ systems has been reported on reactions such as the selective oxidation of propene, photocatalytic reactions used mostly for pollution control as well as the highly favoured oxidation of CO ^[16].

Special metal-support interactions when there is charge transfer between Au and the P-25 support have been reported to be the cause of the high activity of these catalysts as reported by Rodriguez as they investigate how the interaction between the metal and the support surface could cause the high catalytic activity of the catalysts ^[16].

Studies done by Wolf *et al.* compared the activities of Au/TiO₂, Au/Co₃O₄, Au/Al₂O₃, SiO₂ and Au/ZrO₂ catalysts by varying the preparation conditions using the DP method. Au/TiO₂ and Au/Al₂O₃ differed in catalytic activity even with the same Au particle sizes, Au/TiO₂ having higher activity and they attributed this being due to the nature of the support and the interactions between metal and support (charge transfers). All the catalysts were found to be highly active for CO oxidation except for SiO₂ which was found to be an unsuitable support material for the DP method due to its low isoelectric point ^[6].

The use of SiO₂ has mainly been preferred in the past for depositing metals such as Pt due to the fact that it has a high thermal stability, mechanical strength, high surface areas as well as hard to reduce but has not been preferred for depositing Au nanoparticles onto it as it usually only allows for a very small concentration of Au nanoparticles to adsorb onto the surface ^[17].

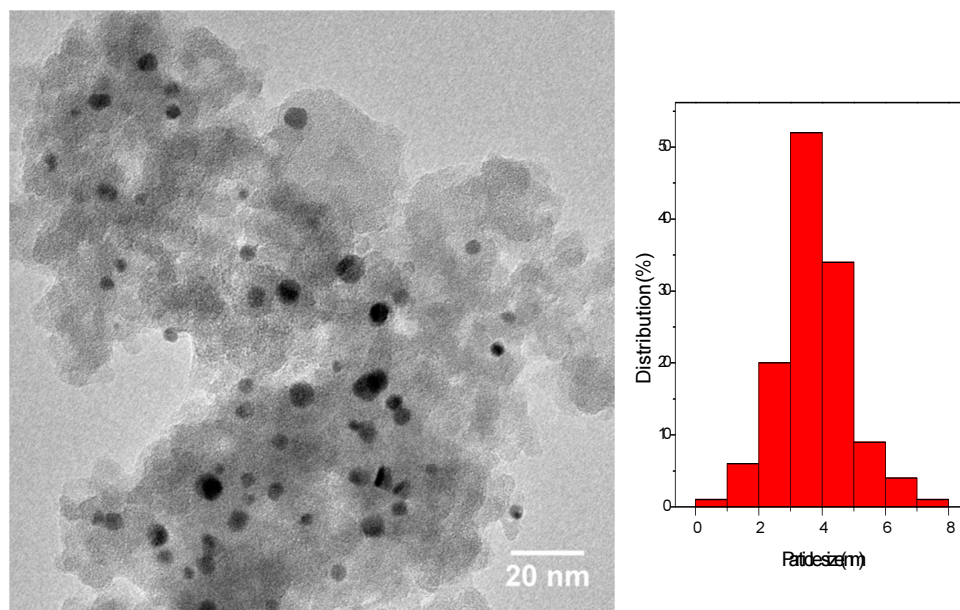


Figure 4.19: HRTEM micrograph and particle size distribution histogram depicting particles supported on SiO₂ (5% Au/SiO₂)

As seen in Figure 4.19 above Au/SiO₂ also gave small Au nanoparticles when compared with those of TiO₂. As reported by a number of publications the resulting catalytic activity is usually low for these catalysts as the IEP of silica is very low (<2) and at the pH of 7 the support is mainly composed of anions that repel the hydrolysed Au(OH)₄⁻ anions that try to deposit onto the support surface hence the Au does not bind well to the support surface ^[17].

The mechanical mixture of TiO₂ and SiO₂ as supports was also investigated in this project as reported by Bogdanchikova *et al.* ^[18]. The group deposited Au onto mixed oxides of titania and silica with ratios of 5 and 10% Titania relative to 100% silica support by weight percentage. The group found that the BET surface area increased with the mixed oxides from 426 and 40 m²/g for silica and titania respectively to 800 and 1154 m²/g for TiSi10 and TiSi5 respectively ^[18].

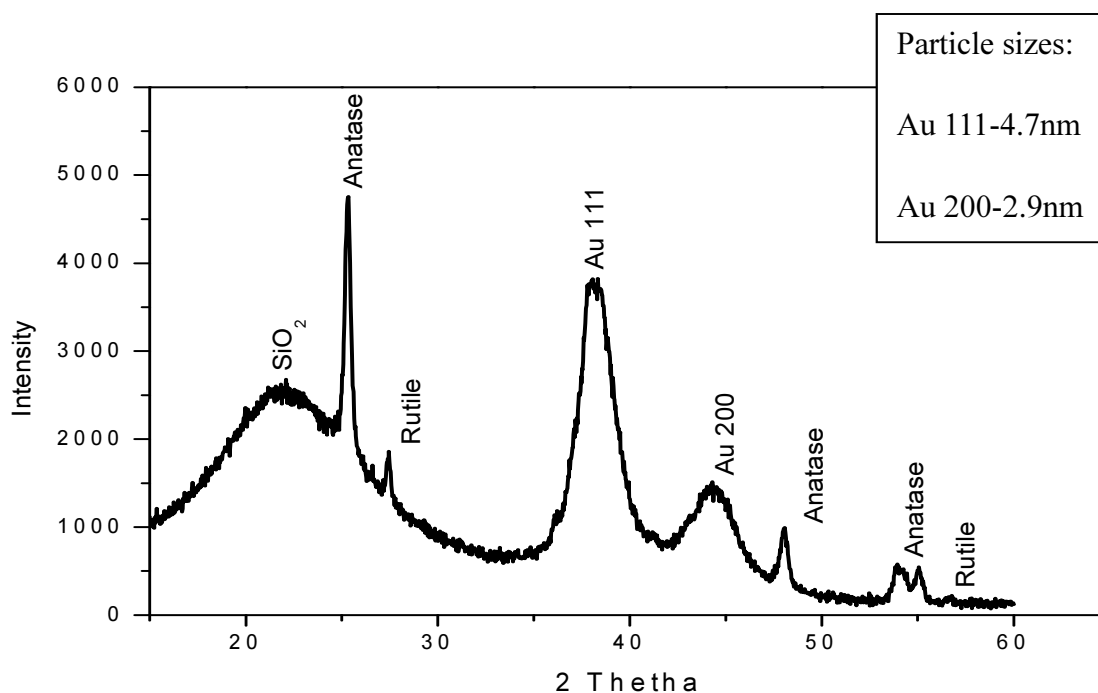
The results obtained by Bogdanchikova *et al.* showed that with a lower titania percentage the surface area increased although titania is known to be a more effective support as compared to silica ^[18]. From the data that was obtained in this project it correlated with that investigated by the group as seen on table 4.3 below

Table 4.3: BET results on various catalysts with varying supports

Catalyst	BET surface area(m ² /g)		Pore volume(m ³ /g)	
	Ref ^[18] data	Our data	Ref ^[18] data	Our data
SiO ₂	426	N/A	0.162	N/A
TiO ₂	40	N/A	0.046	N/A
Au/5%TiO ₂ -100%SiO ₂	1152	312	0.415	0.767
Au/10%TiO ₂ -100%SiO ₂	800	265	0.291	0.723

The data we obtained does correlate with that of Bogdanchkova even though the numbers were further apart and we can theorize that this could be due to the different methods used for the synthesis of the catalysts as we utilized the DP method and the group utilized the sol gel method. The sol-gel method has been known to form big nanoparticles in the ranges of 90 nm in hydrocarbon synthesis and thus the difference with our deposition precipitation method which produces nanoparticles mostly in the 10 nm range or less. XRD data showed that as more titania is used the particle sizes of the Au crystallites decreased from 90 nm for the TiSi5 to 60 nm for the TiSi10. Our data showed that this was indeed the case with more titania being used the particle size decreased but it was a slight decrease as seen on figure 4.20 (a) and (b) of the XRD data.

(a)



(b)

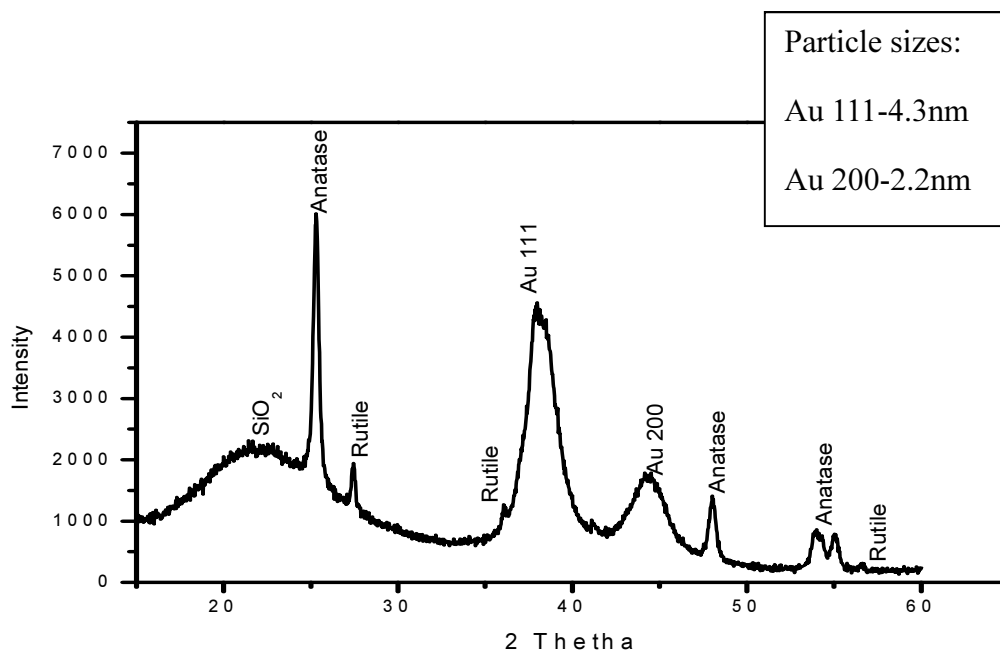


Figure 4.20: XRD data showing Au supported on mixed oxides of silica and titania (a) 5% Au/TiSi5 (b) 5% Au/TiSi10

4.3 Characterization of Au-Rh/TiO₂ catalysts

The characterization of Au-Rh/TiO₂ catalysts by TEM or XRD techniques has not been documented in literature due to the difficulty in distinguishing between the Au nanoparticles and those of Rh in the case of TEM as well as finding a peak for the two in the case of XRD. Raskó *et al.* characterized their Au-Rh/TiO₂ catalysts utilizing XPS data and concluded that the nanoparticles that were present on the titania surface that contained both the Au and Rh were relatively large than those of the corresponding monocatalysts^[19].

The data by Raskó *et al.* does corresponds with that of figure 4.21 whereby it is not distinguishable whether the particles are of Au nanoparticles, Rh nanoparticles or of Au and Rh together as a possible bimetallic on the support surface but the particle size distribution does indicate that the particles have a bigger size distribution and particle sizes than those of a monometallic catalysts such as figure 4.2 as shown above.

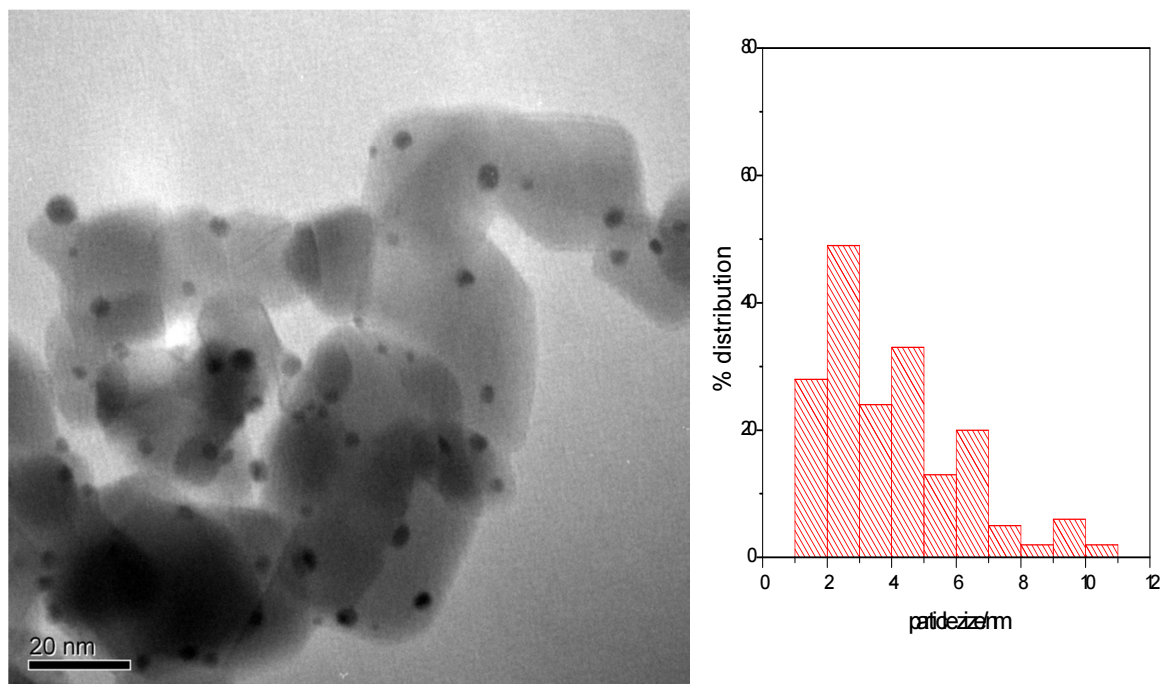


Figure 4.21: TEM micrograph and particle size distribution histogram depicting particles formed with Rh metal addition (3%Au-1%Rh/TiO₂)

Characterization of the then increased percentage loading of Rh was done using TEM and HRTEM together with EDS techniques. Figure 4.22 shows the taken TEM image and particle size histogram of 3% Rh loading that was done and the particle size distribution is quite broad.

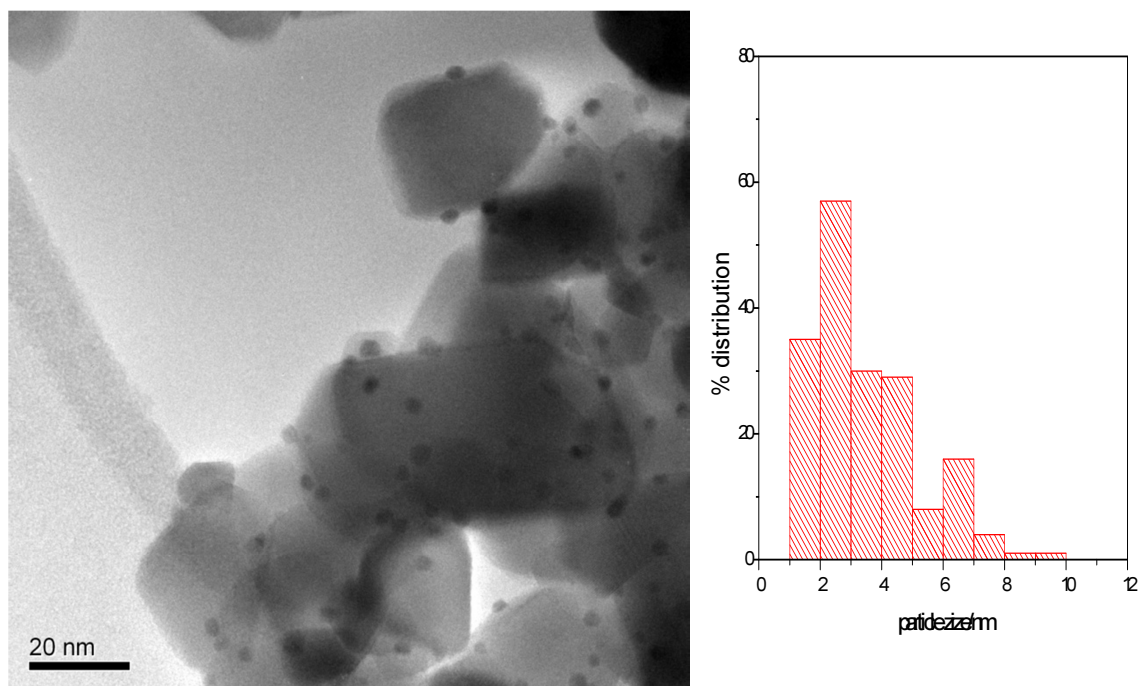


Figure 4.22: TEM micrograph and particle size distribution histogram depicting particles formed with Rh metal addition (3% Au-3% Rh/TiO₂)

From figure 4.22 one is able to observe how most of the particles are within the 3 nm range as seen on the histogram. The differences between the Au and Rh nanoparticles are again unobservable in the TEM images taken.

The image above does show that the deposited Au and Rh have monodispersed on the titania surface however as to which particle belongs to which metal is not observable. Characterization using EDS could not be done as the particles were very small. One might conclude that from looking at the TEM image the darker small nanoparticles could belong to the Au as it is heavier than Rh and the lighter small particles to the Rh.

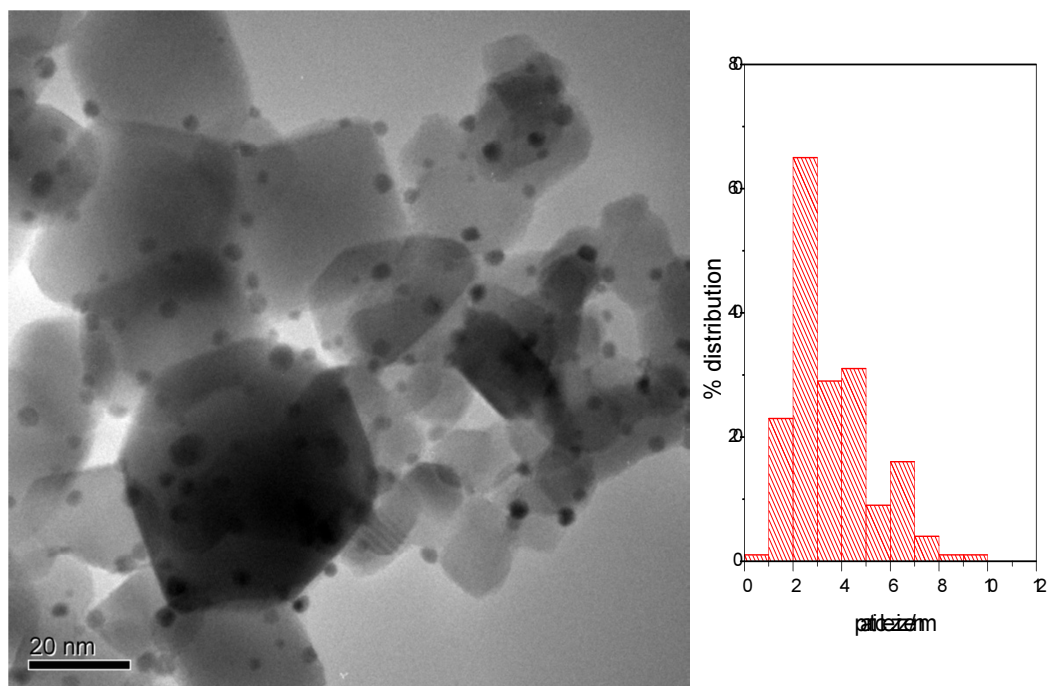


Figure 4.23: TEM micrograph and particle size distribution histogram depicting particles formed with Rh metal addition (3% Au-5% Rh/TiO₂)

On Figure 4.23 the nanoparticles on the support become more distinct and the size distribution becomes more stable and balanced as compared to the previous loadings of Rh.

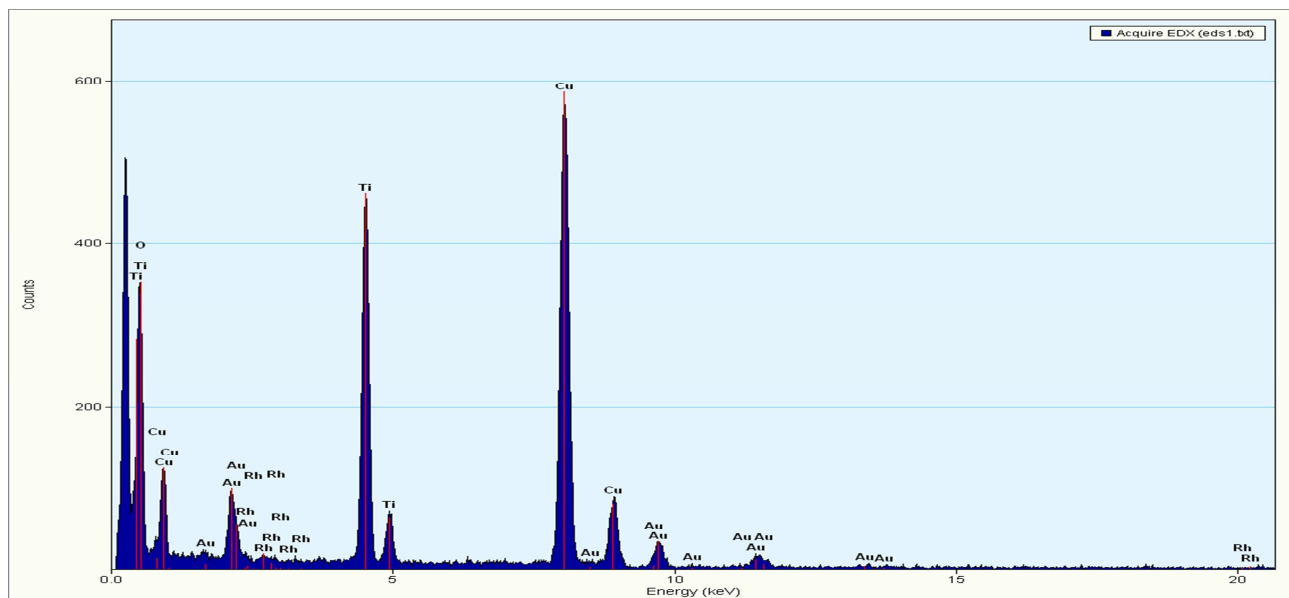


Figure 4.24: EDS spectrum showing bimetallic catalysts for each particles formed with Rh metal addition (3% Au-5% Rh/TiO₂)

On Figure 4.24 above we note that the Au and Rh nanoparticles are both present at particular

spots on the support surface as investigated using HRTEM. EDX data gave sufficient counts to elaborate on the presence of both metals on the support. 5% Rh loading had a narrow range of particle size (2-4 nm mostly) which was then following within the size parameter of 3 nm that has been investigated by Haruta *et al.* to be best for CO Oxidation reactions.

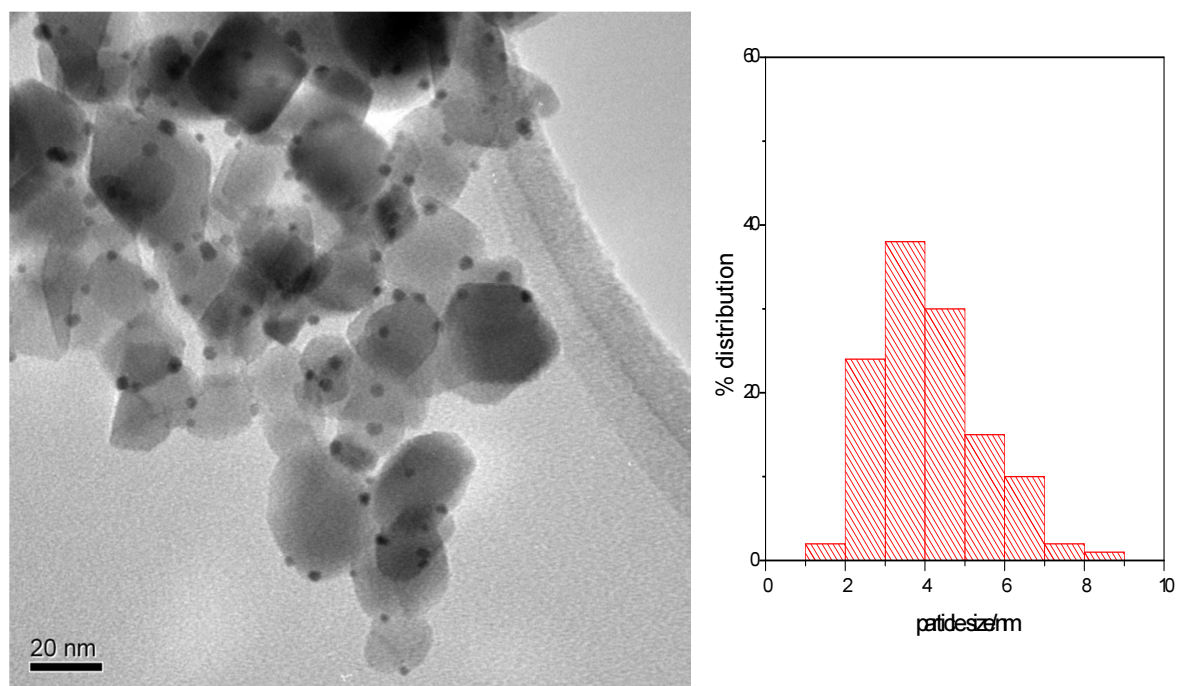


Figure 4.25: TEM micrograph and particle size distribution histogram depicting particles formed with Rh metal addition (3% Au-10% Rh/TiO₂)

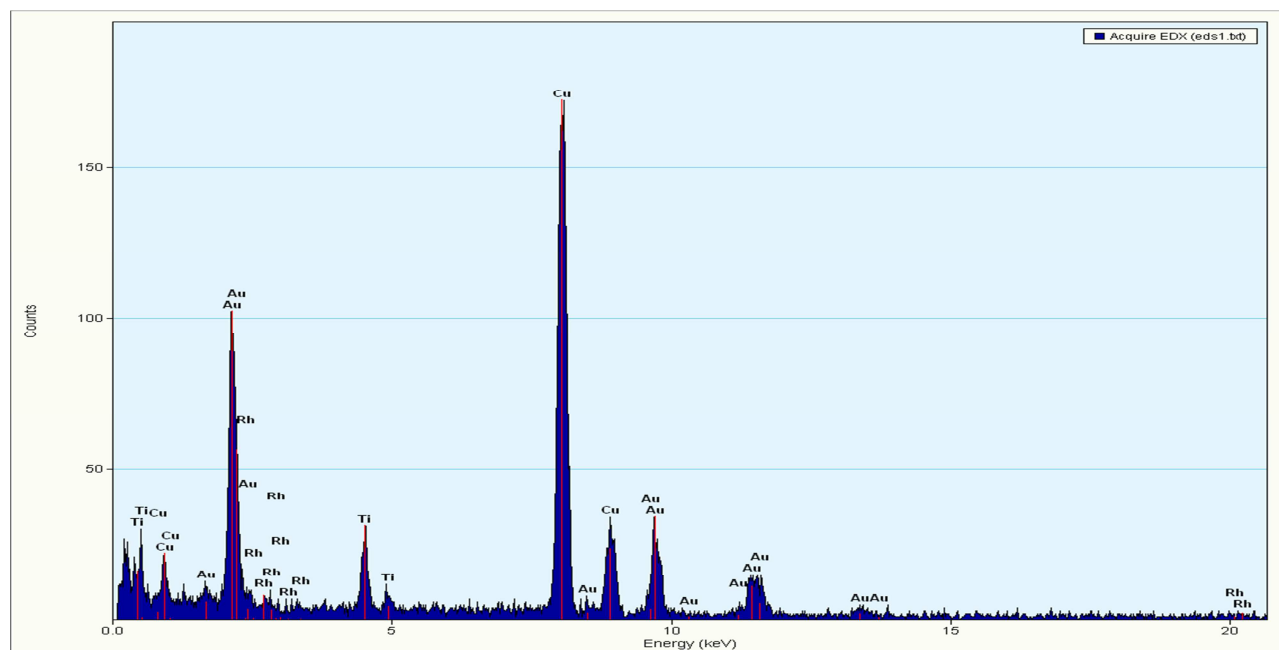


Figure 4.26: EDS spectrum showing bimetallic catalysts for each particles formed with Rh metal addition (3% Au-10% Rh/TiO₂)

Figures 4.25 and 4.26 highlight the increase of loading to 10% and we noted that the sizes of the nanoparticles have grown smaller and the size distribution is much better as compared to the 1% and 3% loadings as those had wider variations in size.

4.4 Conclusions

We set up the deposition precipitation method to determine the optimum deposition duration needed for finely dispersed nanoparticles on the support. The criterion used was 5% Au loading at pH 7 and we tested 15, 30 and 45-60 minutes deposition time. TEM showed that at 15 minutes the range was 5-12 nm sized nanoparticles, at 30 minutes we obtained a sizes distribution of 2-10 nm and at 45-60 minutes we obtained 2- 5nm which is the ideal size for highly active gold nanoparticles for CO oxidation as discussed in Chapter 2. BET data correlated with that of TEM to show that with an increase in deposition time the particles grew smaller and it was shown with an increase from 0.31 m³/g pore volume for 15 minutes to 0.38 m³/g for 45-60 minutes deposition time.

XRD gave a small variation for the 15 and 30 minutes deposition time when it came to the Au peaks differing in size while for the 45- 60 minutes it gave broader Au peaks indicating smaller Au nanoparticles. Activity is meant to be highest when the Au is slowly added over a 45-60 minutes time frame to allow for ample time for metal-support interaction ensuring the production of nanoparticles within the 3nm range.

The pH measurements were done on 5, 8 and 10% theoretically loaded Au onto silica support (SiO₂) as well as 5% Au on Titania support (TiO₂). TEM images showed a difference in Au particle size dependent on the pH that the synthesis was carried under. For pH 5 the size distribution was 2-18 nm, while at pH 7 it was 2-5 nm and pH 9 it was at 2-8 nm and this was for 5% Au-TiO₂.

BET data for pH 5 showed a surface area of 48 m²/g with a pore volume of 0.28 m³/g while at pH 7 the surface area increased to 65 m²/g and the pore volume to 0.38 m³/g which meant that smaller Au nanoparticles were adsorbed onto the surface of the support. An increase of pH led to a smaller surface area with a decrease in pore volume to 0.34 m³/g which indicated an introduction of bigger nanoparticles on the support surface as confirmed with TEM data. This further confirmed pH 7 as the optimum pH for a good size range of the Au nanoparticles

to adsorb on the support surface.

XRD data correlated with TEM results with regards to sizes of the nanoparticles. At pH 5 we obtained narrow Au peaks at $2\theta = 38$ and 44° for Au (111) and (200) respectively while for pH 7 and 9 the peaks grew broader indicating smaller nanoparticles present.

This study was further done with Au-SiO₂ catalysts that were synthesized at different loadings and the Au particle sizes correlated with those of TEM to show that we mostly find nanoparticles smaller than 4 nm for pH 7 and 9. Au loading difference however shows that with XRD at pH 7 there is an increase in size as we increase loading, for the 5% Au-SiO₂ loading we obtained broader (111) and (200) Au peaks with sizes calculated using EVA software to be at 3.3 and 3.5 nm respectively. An increase in loading to 8% gave 4.0 and 4.9 nm while for 10% Au loading we obtained 6.8 and 6.4 nm.

TEM images also show that an increase in Au loading brought about an increase in the particle sizes which plays a crucial role in activity measurements for the catalysts as stated earlier so the optimum loading was set at 5% Au loading.

The choice of support for Au based catalysts depends on various factors as discussed in Chapter 2, we varied TiO₂ against SiO₂ with 5% Au loading at pH 7 at a deposition duration of 60 minutes. TEM and the particle size distribution curves drawn from TEM images gave a size distribution of 2-5 nm for TiO₂ with a majority of the nanoparticles being around 3 nm in size while for SiO₂ under the same conditions we got a range of 2-6 nm. TiO₂ is a reducible support and hence has higher metal-support interaction as compared to SiO₂ which is an insulating material. A mechanical mixture of the two supports yielded on XRD data, an increase in particle size with a decrease in TiO₂ weight percentage.

After synthesis of the 5% Au-TiO₂ using the deposition precipitation method at pH 7 over 60 minutes deposition time the catalysts were filtered and then rinsed to reach neutrality and washed with deionised water to remove all chlorine contaminants that could be present in the sample. The catalysts were covered in parafilm and left to age over different periods of 1, 3 and 6 days. The observations were that at 1 day ageing the catalysts were identified to range between 2-12 nm in size on TEM, 3 days they were between 2- 5 nm in size while for 6 days we obtained 2-10 nm in size.

Addition of Rhodium metal as a promoter to the Au catalysts was done to investigate the effect that the Rh would have on the catalysts with regards to activity for the selected reaction. Characterisation on HRTEM showed that the nanoparticles were present on the support surface with 1% Rh at 1-11 nm wide range, 3% Rh at 1-8 nm range, 5% Rh at 1-7 nm short range and 10% at 2-8 nm range with 3% Au loading. EDX data was unable to pick up any Rh for the 1 and 3% Rh loadings but with the 5 and 10% Rh was present on the surface of the support but there was no differentiation between that and Au.

4.5 References

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Chapter 5

CO oxidation measurements

5.1 CO Oxidation measurement

As discussed in the previous chapters of this work, carbon monoxide is a problem to the environment as well as to humans. The most efficient way that has been developed for the removal of this poisonous gas, is by CO oxidation into less harmful carbon dioxide using metal supported on oxides as catalysts in, for example motor catalytic converters^[1]. This section aims at highlighting the results obtained while co oxidation measurements were conducted with different conditions for the catalysts.

5.1.1 Au/TiO₂ catalysts

Au/TiO₂ nanocatalysts are known to be highly active and favour the CO oxidation reaction when the gold is smaller than 4 nm. Additionally, such catalysts can operate at temperatures below 0°C ^[2]. However, the catalysts rapidly deactivate and so further research has been required to improve the lifespan and temperature activity range of the catalysts. The most efficient method for the deposition of these highly active metals on semi-conductor oxides such as TiO₂ is known to be deposition precipitation. The temperature of reaction, the pH of the solution (modified depending on the IEP of the support), the concentrations of the Au solution as well as the calcination temperatures of which are applied to the catalysts can all be controlled ^[2]. All these factors ensure that the correct sized nanoparticles are obtained as well as mono dispersed particles on the support as discussed in Chapter 2 of this work.

One of the papers by Haruta and co-workers investigated the effect that the preparation method has on the activity of gold and platinum nanoparticles supported on a TiO₂ support ^[3]. Their investigations revealed that Au and Pt are deposited in hemispherical morphologies, leading to strong interaction with the support. This is required for the proposed CO oxidation mechanism and this in turn affects the activity.

Utilization of photochemical deposition (FD) and the impregnation method (IMP) results in the formation of spherical nanoparticles on the support, causing no interaction between support and metal which in turn affects the activity for the Au based catalyst. In contrast to this, the Pt catalysts were not affected by this change instead the activity remains the same ^[3].

In our studies all these factors were studied and the activity trends were observed as well as the average CO conversion percentage that a catalyst was able to obtain over a certain period of time on the catalytic rig. The catalysts were subjected to different parameters to obtain a baseline for optimum oxidation conditions for comparison with those of the Rh promoted catalysts.

5.1.1.1 Effect of pH

pH has been shown to affect the activity of Au based nanocatalysts by determining the size of the nanoparticles on the support ^[4]. The research showed that Au-TiO₂ catalysts have a metal nanoparticle size distribution centered at smaller than 5 nm when they are subjected to a pH between 6 and 10 (This correlates with our results in Chapter 4: Figures 4.2 and 4.3).

0.1 g of the 5% Au/TiO₂ catalyst was added to a U shaped reactor along with SiC and was pre-treated by passing H₂ through the catalyst at different temperatures. The reaction was carried out at 70°C while passing 10% CO and 5% O₂ at a flow rate of 60 ml/min for each gas. The outlet gas was analysed by a GC attached to the reactor, Figure 5.1 below shows the average CO conversion percentage achieved when comparing catalyst prepared between pH 5-9.

From the data, the catalyst with the highest CO conversion within the four hour period on the CO and O₂ gas stream was that prepared at pH 7. The one deposited at pH 9 also showed good conversion. Uphade *et al.* also found that when pH was increased from 6 during deposition, the conversion also increased and reached its optimum at pH 7 and then decreased. This correlates with observations shown on Figure 5.1 ^[5]. This data then correlates with that obtained by Wolf *et al.* who reported that the highly active catalyst in their research was that at pH 8. Catalysts prepared at pH 5 had lower activity. This could be attributed to the

pH being only slightly above the IEP of P25, meaning that a majority of the support surface was still composed of anions that repel the anionic Au precursor ^[6].

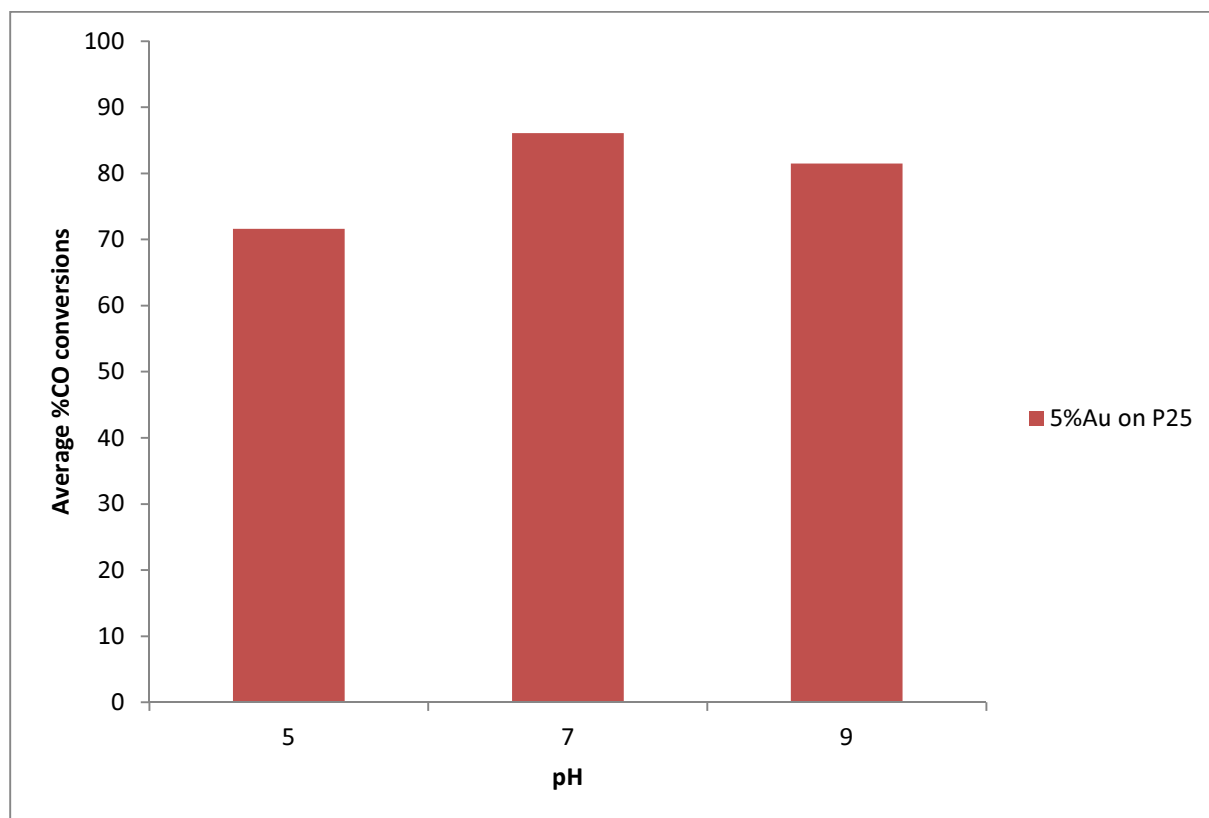


Figure 5.1: Average CO conversion percentage of 5% Au/TiO₂ at different pH (No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

The effect of pH was also observed by XRD in Figure 4.4 where broadening of the Au (200) and Au (111) peaks with an increase in pH was observed, meaning that smaller Au nanoparticles were being synthesized. Smaller nanoparticles imply higher activity should be observed as described by Lee *et al.* ^[7].

It can be deduced that the optimum pH for the deposition of Au species on a P25 support was at 7 and those slightly above 7, but nothing below pH 6 as that gave slightly bigger Au nanoparticles and less active catalysts for CO oxidation.

5.1.1.2 Effect of ageing duration

For Au nanoparticles supported on a reducible support such as TiO_2 , the time taken to age the catalysts has been a controversial issue as some researchers found that catalysts that are aged tend to be less active than those that have not been left to age. Kang *et al.* did an electrocatalytic study of Au nanoparticles and showed that the most electrocatalytically active samples were those that were not left to age ^[8]. This change in activity was attributed to structural reorganization during the ageing period which then caused a decrease in catalytic activity ^[8].

Contrary to Kang *et al.*'s results, Figure 5.3 below showed that as the ageing period increased so did the activity of the studied catalyst prepared. If aged for more than 3 days however, the activity decreased again. Factors influencing this include solution state equilibria (whereby all reactants have completely dissolved and formed nanoparticles at a certain point during aging), optimum particle size being reached over 3 days (as observed on Figure 5.2), and that longer than this the particles started growing through the phenomena of ripening vs nucleation.

The probable explanation for the increase in activity at 3 days as compared to 1 day could be because as the ageing period increased, more of the gold particles were able to deposit onto the support and more of the chloride ions were able to be hydrolyzed out of the solution and hence more $\text{Au}(\text{OH})_3$ could form and interact with the support more strongly. After 1 day most of the gold was unable to deposit onto the support and hence it was lost during the filtration process.

Changes in particle sizes were observed on TEM images as seen on Figure 5.2. Particle growth was observed at 6 days of aging. After 3 days and beyond that, particles begin to grow again as supersaturation decreases and thus the nucleation barrier and nucleus size of the nanoparticles increases for the particles ^[9]. Activity data (shown in Figure 5.3) corresponds directly to particle size data.

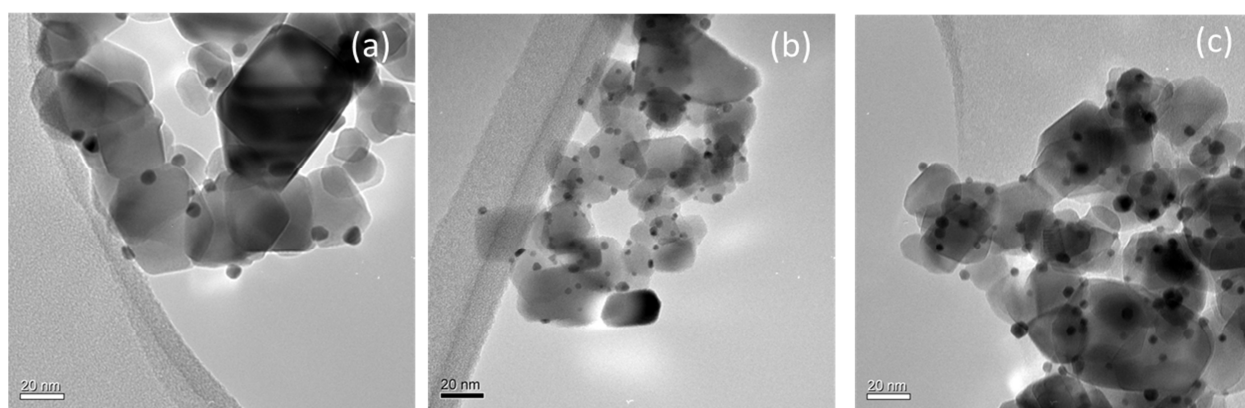


Figure 5.2: TEM micrographs showing comparison between 5% Au/TiO₂ particles left to age for (a) 1 day (b) 3 days and (c) 6 days

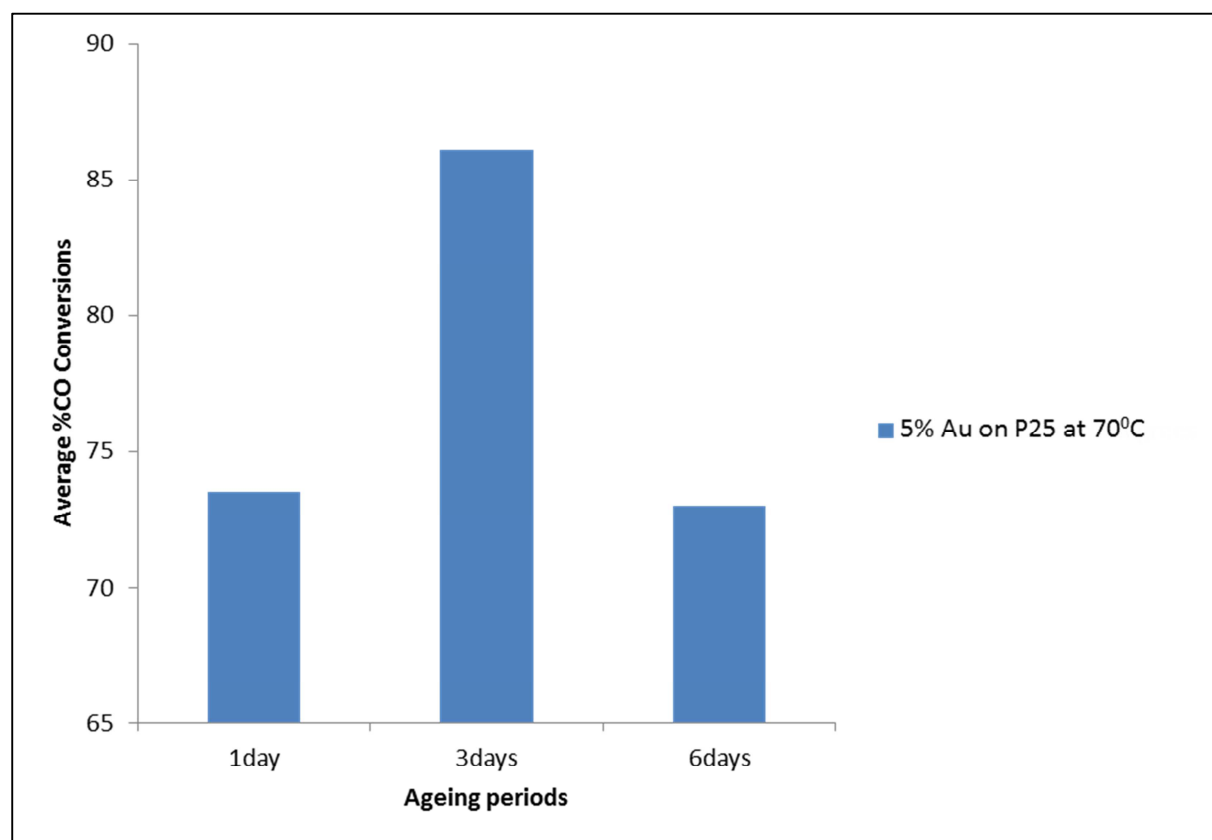


Figure 5.3: Average CO conversion percentage of 5% Au/TiO₂ at different ageing periods (No pre-treatment, flow rates: 10% CO-60ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

Figure 5.4 below showed the dependence of CO conversion on the ageing period, this time at a higher temperature of 150°C. There is not much change in activity compared to Figure 5.3 where the catalyst runs at 70°C. The catalysts left to age for 6 days showed a higher conversion percentage as compared to those left to age for 1 day which showed a drop in activity.

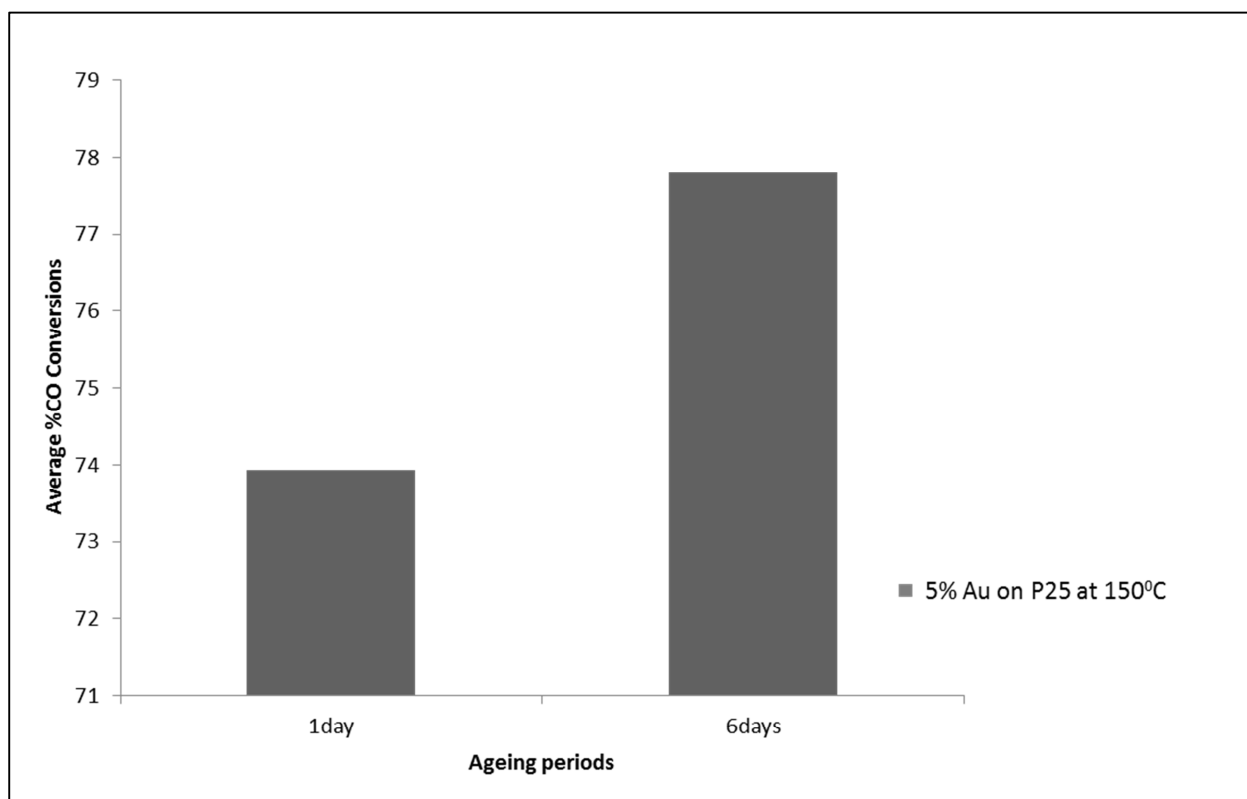


Figure 5.4: Average CO conversion percentage of 5% Au/TiO₂ at different ageing periods (No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 150°C)

The drop in activity for the catalysts left to age for 1 day could also be due to most of the Au being lost during filtration, as explained previously, and that some of the Au was not attached strongly to the support. An increase in temperature could cause the loss of attachment of some of the Au on the support as most of the Au was forming as metal in the solution instead of in ionic form as well as the possibility of Au sintering with an increase in temperature.

Table 5.1 gives BET results obtained for the measurements of catalysts aged for 1 day and 6 days. Surface area decreased for catalysts aged for 6 days as compared to those aged for a day as larger nanoparticles were formed after the optimum aging period was reached. The pore volume and diameter decreased as aging increased, showing the presence of bigger particles adsorbed on the surface of the catalyst and hence narrowing the pore diameter and volume.

Table 5.1: BET results on various catalysts with varying aging hours

Catalyst	BET surface area(m ² /g) (% error)	Pore volume(m ³ /g)	Pore diameter(nm)
5%Au/TiO ₂ (1 day)	49 (0.71)	0.37	31
5%Au/TiO ₂ (6 days)	48 (1.75)	0.36	29

5.1.1.3 Effect of Deposition Duration

The time taken to deposit gold onto a support using deposition precipitation method is a crucial element for an active catalyst. Fast deposition of the Au onto the support can result in loss of Au during filtration as most of it could be in the suspension instead of adsorbed onto the support.

The Au concentration, calcination and reaction temperatures were constant for all the prepared catalysts as highlighted in chapter 3 of this work. The duration of deposition was the parameter that was varied in determining the time over which the addition of Au to the support suspension was carried out. Three catalysts were prepared with deposition durations of 15 minutes, 30 minutes and the last one being between 45 and 60 minutes spent on deposition that has become the optimum time as reported in most research papers.

The observations (as seen on Figure 5.5) were that there was an increase in catalyst activity for CO oxidation as the deposition durations increased. The longer the time taken to deposit the Au onto the surface of the support, the more active the catalyst was observed to be over a 4 hour run on the catalytic rig. There was a significant increase in the catalytic activity as more time and patience was taken to load the gold concentration on the support. Bamwenda

et al. previously reported the importance of careful preparation conditions whenever utilizing the deposition precipitation method for gold catalysts preparation [3]. Variables such as the temperature of the reaction, the extent of mixing out the compounds involved, order of mixing, washing methods, etc all play a crucial role in the preparation of active Au catalysts as described by Wolf *et al.* [6].

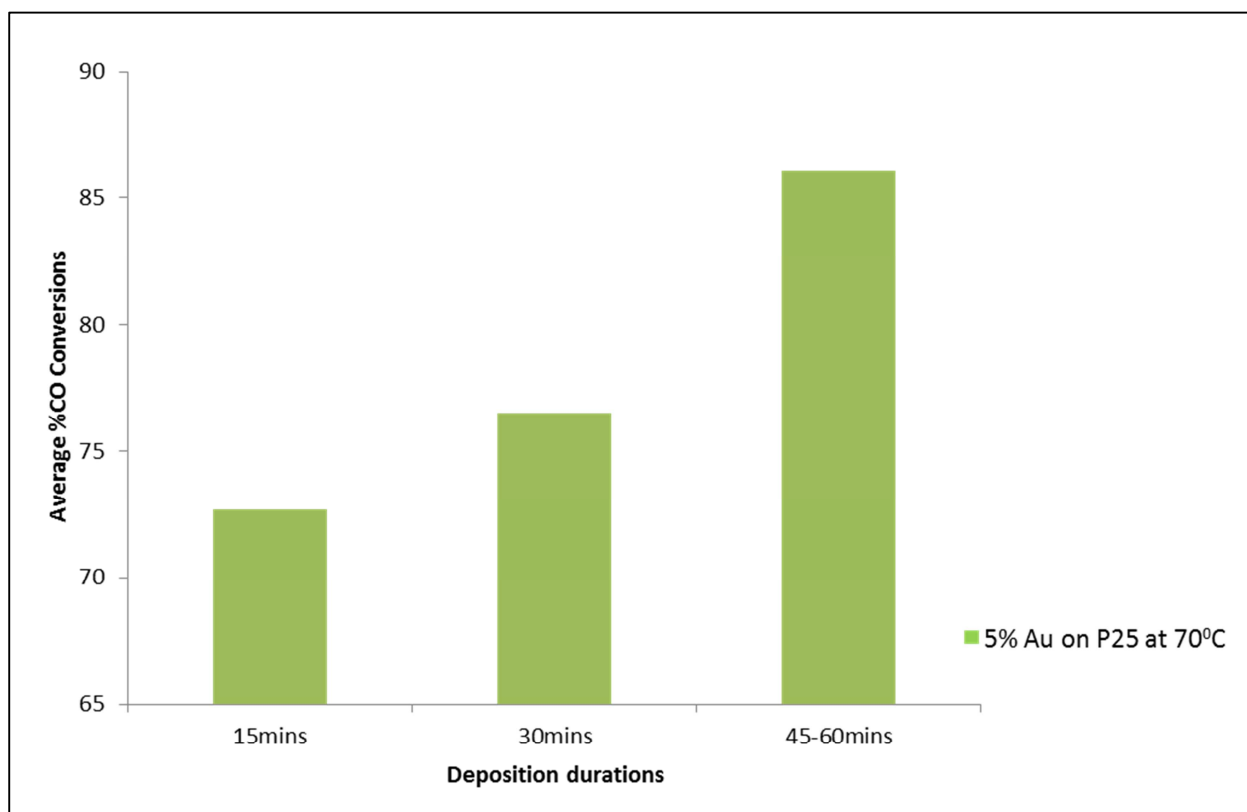


Figure 5.5: Average CO conversion percentage of 5% Au/TiO₂ at different deposition durations (No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

Looking at Figure 5.5 above it was evident that the activity of Au nanoparticles was influenced by a variety of factors; this included the duration spent on deposition of the Au solution into the support solution. From the data it was evident that the more time spent on deposition, the better for the catalyst activity as that meant that the Au solution was given ample time to mono-disperse on the support surface.

Using a deposition time of 15 minutes, it was found that catalysts the average CO conversion into CO₂ was found to be at 73%, using 30 minutes it was observed to increase activity to

about 76% while deposition over a longer period of 45-60 minutes was found to increase activity around 85%. The increase in activity can be attributed to changes in particle sizes as seen in Figure 5.6 below. The longer the catalyst was allowed to deposit onto the support (30 and 45-60 minutes) which is (Figure 5.6 a and b) the more uniformly dispersed were the particles with a smaller range of particle size as compared to those at 15 minutes that had a larger particle size distribution range (Figure 5.6 a).

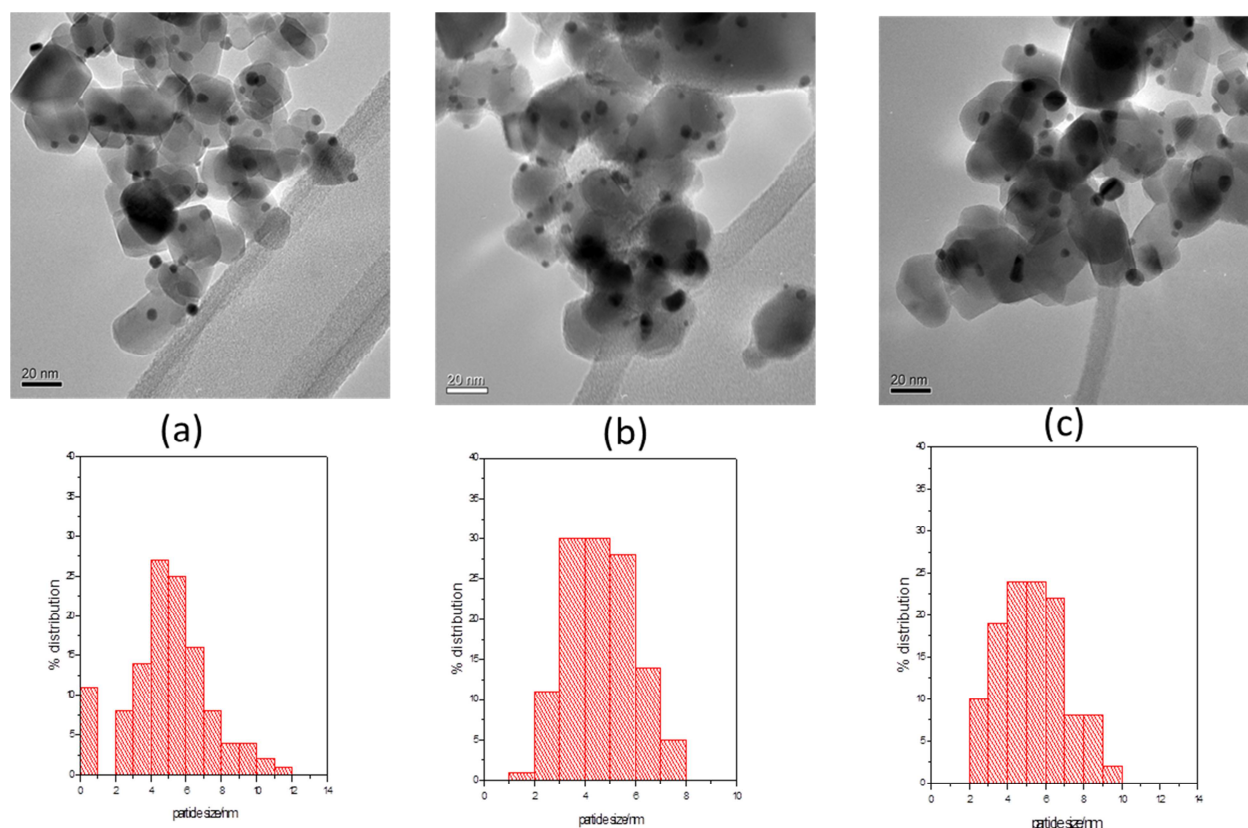


Figure 5.6: TEM micrographs showing comparison between 5%Au/TiO₂ particles with different deposition durations with their corresponding particle size histograms (a) 15 minutes (b) 30 minutes and (c) 45-60 minutes.

Careful and slow addition of Au onto the support ensures ample time for the pH of the solution to reach its equilibrium point set by the synthesis procedure. As the Au is slowly added to the support, ample time is required for the pH of the support solution to reach equilibrium with the pH of the Au and be maintained at that point throughout the synthesis for better preferable particle size distribution.

A slow intake of OH⁻ anions is assumed to be the cause for the low activity as the pH decreased with more addition of Au onto the support even with the addition of ammonium

hydroxide for control. At 15 minutes and 30 minutes the ideal pH of 7 could not be reached with sufficient adsorption of anions. The slow intake meant that longer deposition time was needed to reach equilibrium for the overall reaction taking place in the vessel.

5.1.1.4 Effect of Support

The oxidation of carbon monoxide into carbon dioxide has been known to be catalyzed most effectively by Au based catalysts supported on particular oxide supports such as $\text{Mg}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, TiO_2 , Fe_2O_3 , NiO as well as SiO_2 ^[10]. The most popular oxide used is the semi conducting TiO_2 as P25 Degussa, as it appears to possess high oxygen storage capacity as well as highly favoured catalytic and redox properties ^[10].

Alkali earth metals such as $\text{Mg}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are known to be active for CO oxidation when gold is supported on them, at temperatures as low as 196K however, these catalysts have a short life span. Studies have shown them to be active for a few months (not lasting more than four months) ^[11].

Au supported on semi conducting oxides such as TiO_2 , Fe_2O_3 and NiO are known to be highly catalytically active. These supports provide more stability as compared to insulating oxides such as Al_2O_3 and SiO_2 . SiO_3 - Al_2O_3 and activated carbon are known to be bad supports for CO oxidation as they are highly acidic ^[11].

Alumina, silica and titania all seem to have the same turn over frequencies for CO oxidation when gold is supported on them. The difference is the water concentration needed by alumina and silica to be effective at room temperature as compared to titania, titania requires a minimal amount as compared to the two ^[12].

Research has shown that when Au is deposited on titania using deposition precipitation, gold sits on the support surface hemispherically with the flat sides of the particles attached strongly onto the support. These studies have shown that the strong contact between the

support and the Au ensures the high activity of the catalyst as there is easy charge transfer between the two materials ^[13].

Another factor in ensuring the preparation of highly active Au catalysts is size. This is of particular importance for a reaction like CO oxidation. For gold catalysts supported on silica they tend to form very small uniform particles that should be very active for this reaction, however because silica is an insulating material and gold doesn't bind strongly to it, activity tends to be very low hence the semi conductive titania is preferred.

Bogdanchikova's study as investigated in Chapter 4 demonstrated the mixture of both titania with silica to make a support using the deposition precipitation method. This yielded much smaller particles compared to their sol gel method that gave them much larger particles which would not be as effective for the oxidation of CO ^[14].

For this section we set out to replicate the research conducted by Bogdanchikova *et al.* The results obtained at a reaction temperature of 70°C showed that for the samples with a ratio of 10% of titania to 90% silica gave the highest average percent CO conversion as compared to the mixture containing approximately 5% of titania to 95% silica. More titania composition in the mixed support increased the total metal-support interaction during the reaction. In the literature it was reported that utilizing the sol gel method gave a general trend of an increase in the surface area as well as the pore volume showing that the two oxides mixed together had a synergistic effect on the material ^[14]. This BET data correlates with that obtained in our research as shown in Table 4.3.

Figure 5.7 below highlights the difference in average percent CO oxidation occurring on the surfaces of the mixed oxide supports. The data obtained showed a slight difference between the two differently mixed oxides when mechanically mixed during the synthesis stage. The paper stipulates that the mixture of these two oxides could have given rise to a new chemical compound all together and shows that SiO₂ and TiO₂ have good contact between them when synthesized using the sol-gel method but with significant sintering of the catalyst with time on stream ^[14].

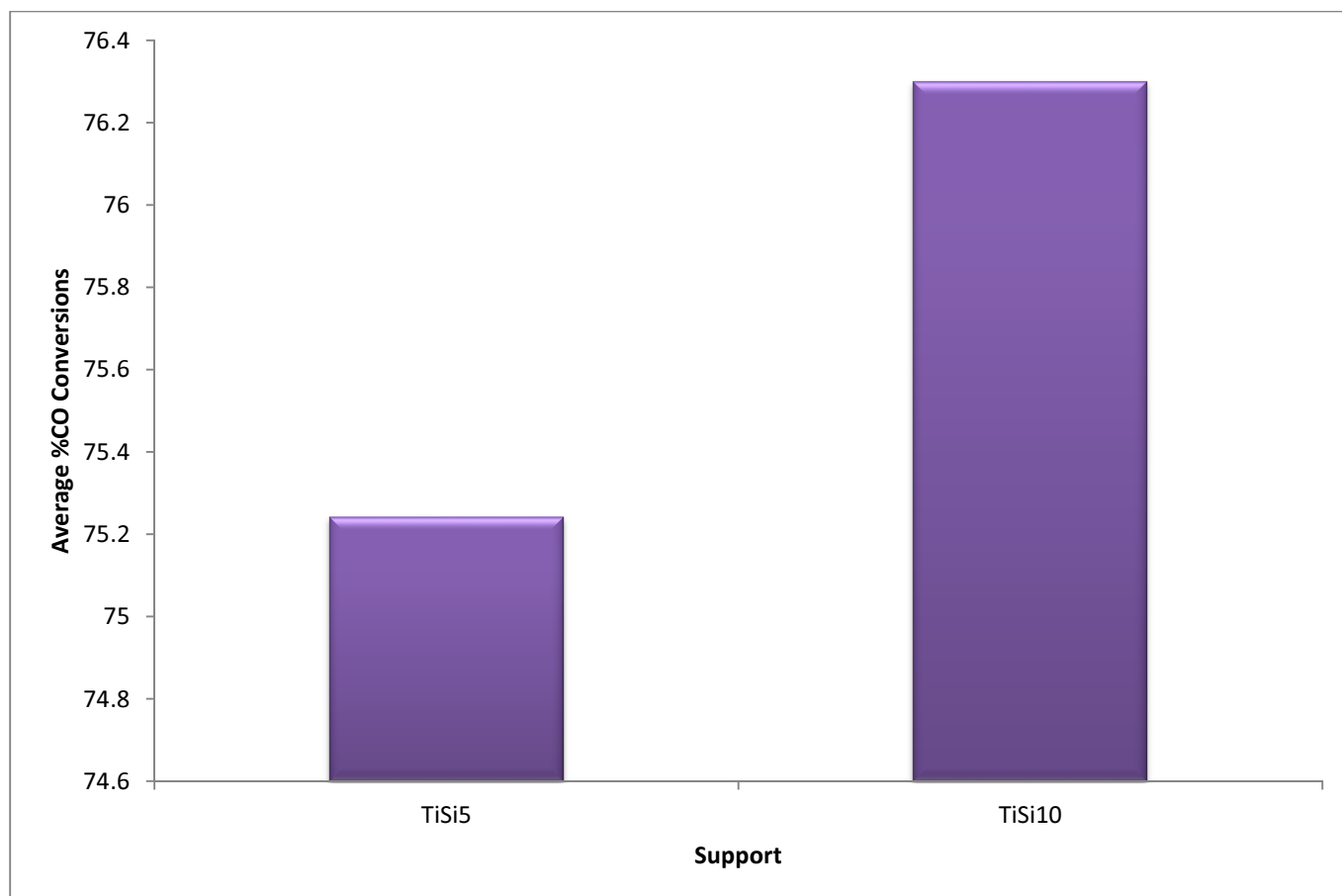


Figure 5.7: Average CO conversion percentage of 5% Au on mixed oxides supports (No Pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

Figure 5.7 shows the average % CO conversion for TiSi5 at 75.3% while that of TiSi10 averaged to 76.3% which shows a slight increase with an increase in the titania concentration to the mixed supports. The surface area for the mixed oxides with titania at 5% was found to be 312 and 265 for 10%.

The drop in surface area is known to be a phenomenon of the addition of a material with lower surface area to that of high surface area. Activity of these catalysts could then be dependent on the concentration of the titania and showed an increase in activity with an increase in titania. Addition of titania concentration to the mixed oxides resulted in a positive shift on activity of the Au based catalysts as titania is known to be a reducible support that has good contact with Au ^[10].

5.1.1.5 Effects of gold loading

Au is highly sensitive to certain parameters with regard to the properties it can exhibit during CO oxidation. One of those crucial parameters is metal loading. As discussed in Chapter 4.2.3, an increase in the loading of Au onto the oxide support resulted in the increase of particle size. According to literature, this should lead to a decrease in activity of the particular catalyst. Figure 5.6 below shows the activity of different Au loadings on P25 over duration of 4 hours. The graphs indicate a slight decrease in the conversion of CO into CO₂ with an increase in the loading of Au over time.

The three differently loaded catalysts were synthesized using deposition precipitation. It has generally been shown to be the most effective method for the synthesis of highly dispersed mono nano catalysts. All catalysts were subjected to the same conditions before the catalytic runs were done (deposition time: 60 minutes, deposition temperature: 70°C, aging time: 72 hours, calcination temperature: 300°C and reaction temperature on the catalytic rig: 70°C) and the highest conversion observed within 4 hours was that of the lowest theoretical loading which was 5% Au loading on the P25 and it reached a maximum of approximately 75%.

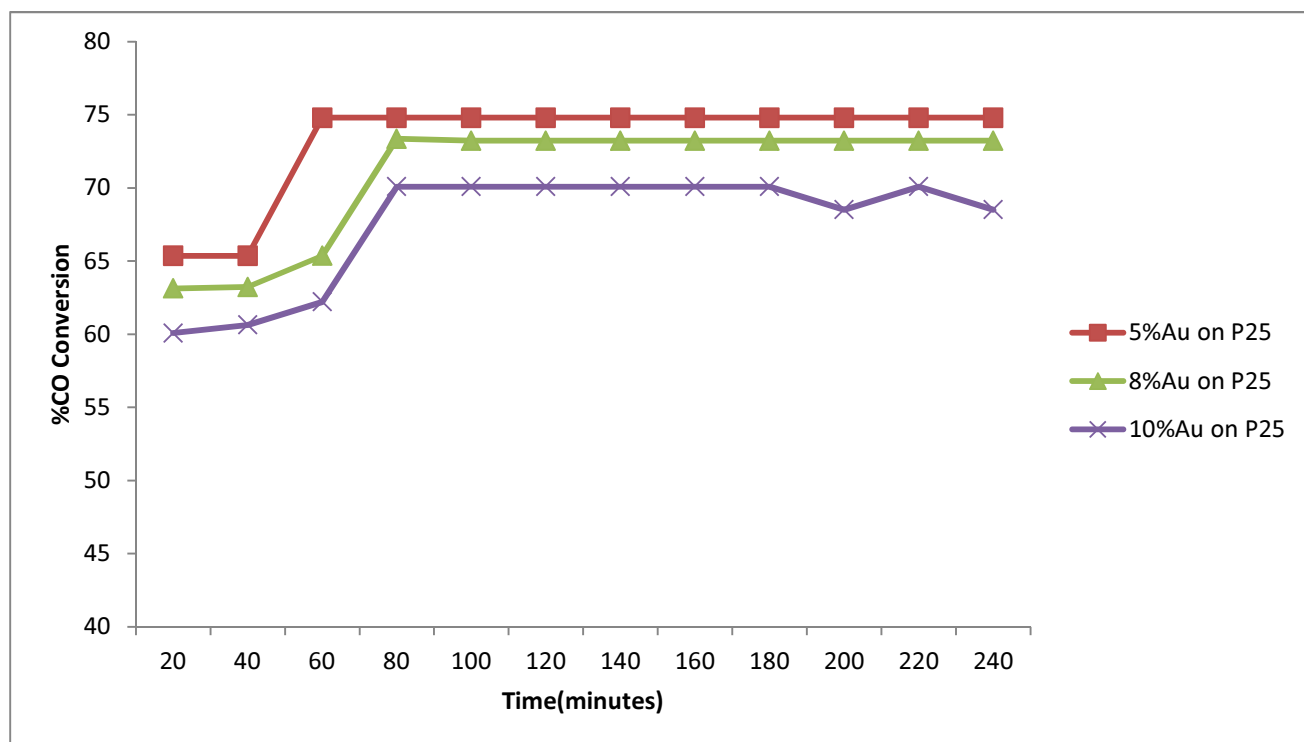


Figure 5.8: CO oxidation reactions highlighting the effect of Au loading (No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

The decrease in activity was attributed to the formation of larger nanoparticles on the surface of the oxide support with an increase in loading as the particles agglomerated on the surface as more Au was loaded ^[4].

Catalysts with a high Au loading were found to exhibit less activity than those at low concentrations. Figure 5.8 above shows activity for 10% Au loading was highest at 68% while at 8% Au loading activity was highest at 73% and 5% Au loading showed highest CO conversion at 75%. The increase was shown over a 4 hour run on the catalytic rig after pre-treatment with hydrogen gas for activation of the catalysts for easy adsorption of CO and O₂ on the Au surface ^[4].

As Au concentration was increased an observed agglomeration of Au on the support is noticed which could explain the observed low activity for the catalysts with the highest Au loading. Less loading was observed to highlight small hemispherical Au nanoparticles (indicated by the arrows) distributed fairly on the surface of the reducible support as seen in in figure 5.9 below.

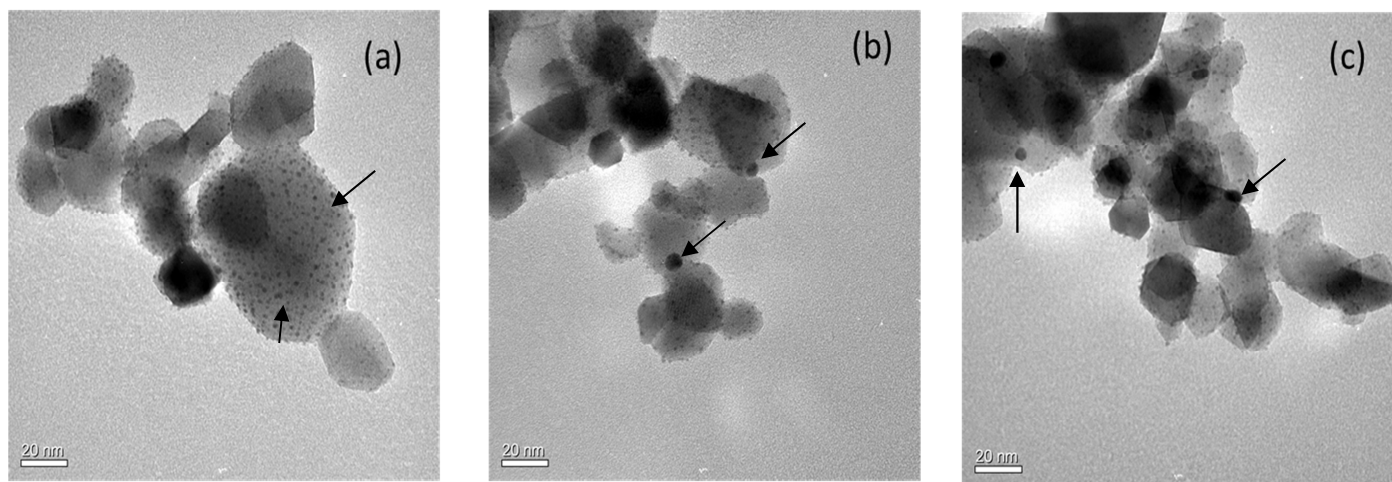


Figure 5.9: TEM micrographs showing comparison between Au/TiO₂ particles with different loadings before CO Oxidation (a) 5% (b) 8% and (c) 10%.

5.1.1.6 Effect of different reaction temperatures

Figure 5.10 below shows the catalytic data from catalysts prepared using the same preparation method as before but differing in reaction temperatures. The catalysts were all pre-treated with 5% H₂ at a temperature of 300°C over a period of an hour and a half as done in literature ^[15].

Pre-treatment of catalysts was done to allow the reduction of the Au nanoparticles from ionic Au to metallic Au. Bond *et al.* proposed that this is the optimum temperature for reduction as most of the ionic Au is converted to metallic and any temperatures above these could result in the sintering of the Au species on the surface as stability would have been lost ^[16].

The trend observed in figure 5.10 amongst the graphs was that the increase in reaction temperatures resulted in the activity of the catalysts to increase with the catalyst reacting at 350°C having the highest CO conversion to CO₂ sitting around 90% conversion as compared to that at 150°C being around 70-100%.

At 200°C and 150°C conversion was observed initially at a maximum of 80 and 70% respectively before a sharp drop at around 105 minutes to 72 and 62% respectively as indicated by the arrow at A in Figure 5.9. The drop in activity could have been stabilization of the catalysts at such low temperatures and within 160 minutes both catalysts seemed to stabilize at around 70% CO conversion.

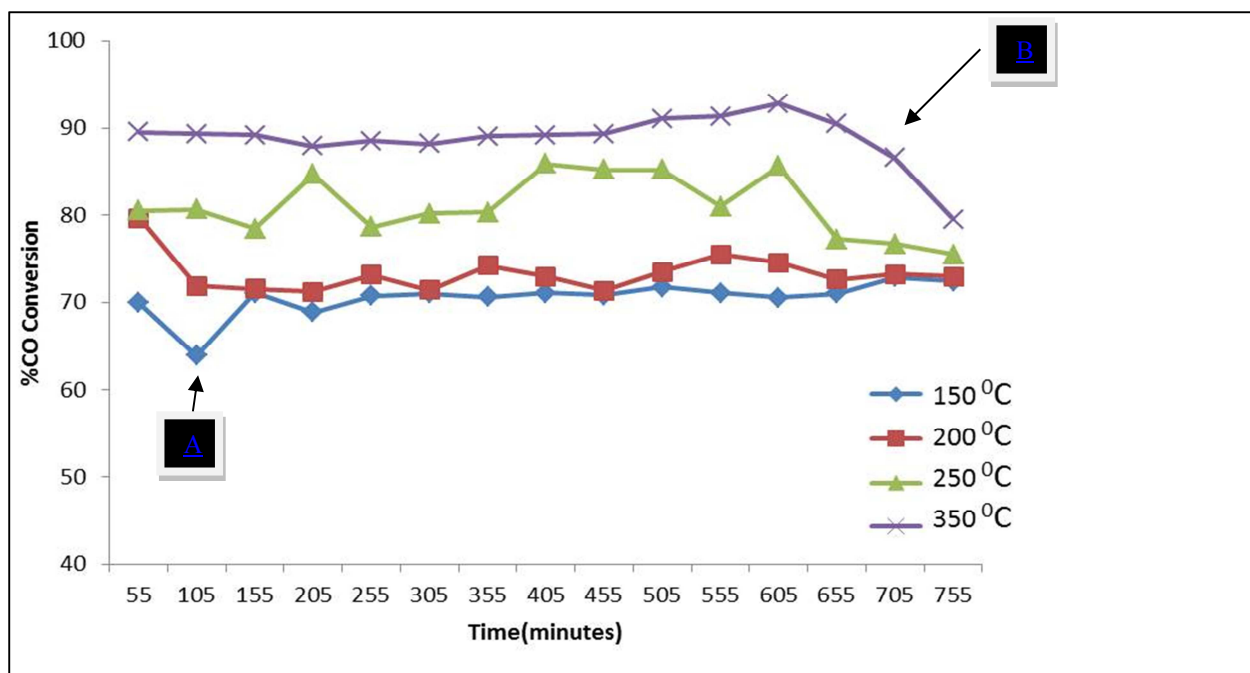


Figure 5.10: CO oxidation reactions highlighting the effect of different reaction temperatures over 5% Au-TiO₂ catalysts (pre-treatment: 300°C in 5% H₂, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 12 hours run, temperature 150-350°C)

Figure 5.9 at point B highlighted with an arrow shows the significant sintering of the catalysts at 250 and 350°C. The sintering is observed after 10 hours of time on stream and could be caused by bigger Au particles having formed (figure 5.11 arrows) and hence a decrease in surface area on the catalyst inhibiting adsorption of CO and O₂ molecules for oxidation as demonstrated in the TEM images on Figure 5.11 below.

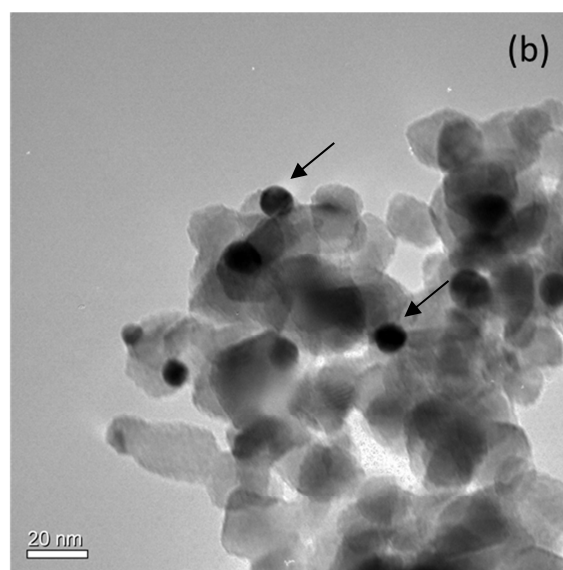
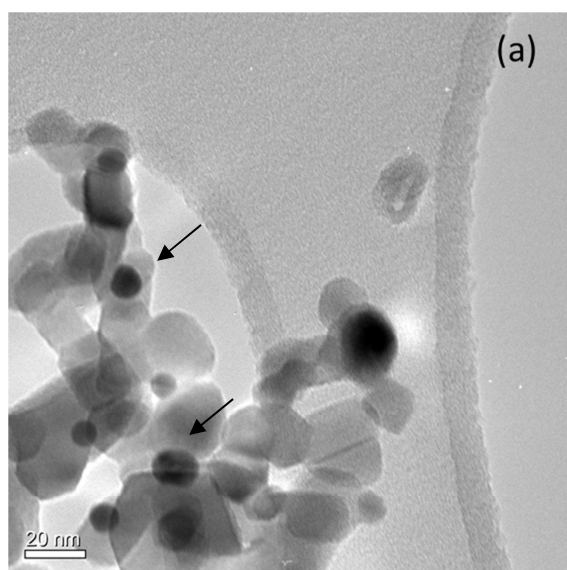


Figure 5.11: TEM micrographs showing the effect of different reaction temperatures between 5% Au-TiO₂ catalysts after CO Oxidation (a) 250°C and (b) 350°C.

5.1.2 Au-Rh/TiO₂ catalysts

According to Carranza, platinum and palladium metals have a strong ability for the oxidation of carbon monoxide as they are able to operate at low and high temperatures of which most metals and oxides are unable to function at. PGMs such as Rh are able to give superior performances for CO oxidation reactions when combined with other PGMs as they can handle high temperatures and concentration ranges of which other metal catalysts are unable [17]. PGMs have been known to survive deactivation in a reaction as compared to Au catalysts that have been known to sinter with time on stream [17].

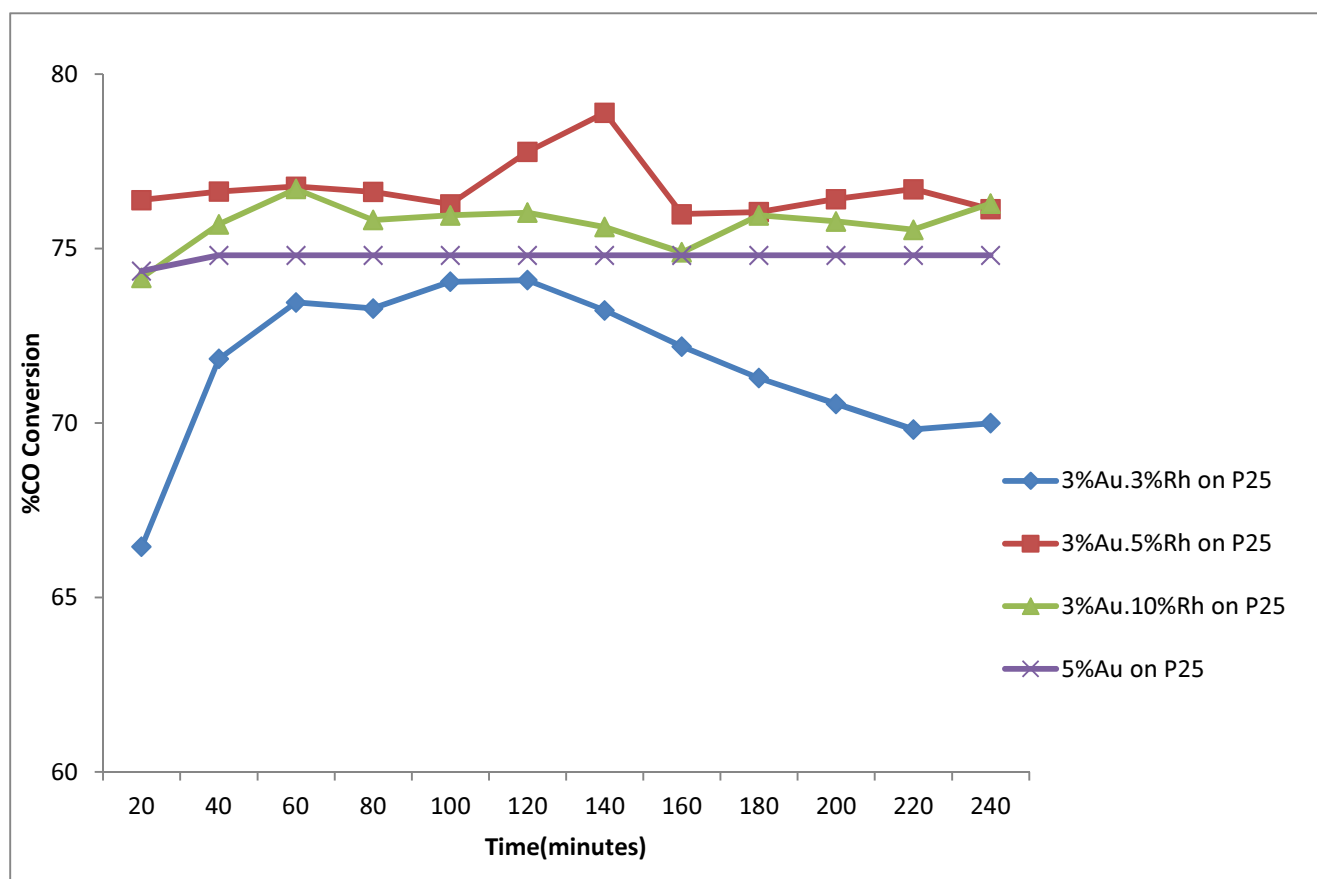


Figure 5.12: CO oxidation reactions highlighting the effect of varying Rh loadings over 3% Au-TiO₂ catalysts (No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 70°C)

Figure 5.12 above shows catalysts prepared utilizing the DP method at a deposition temperature of 70°C and they show an increase with Rh loading until the theoretical loading of 5% Rh onto 3% Au. Loadings above the 5% loading then show a decrease on catalytic activity on the catalytic rig, Raskóá *et al.* theorized that the strength of Lewis acid sites weakened with the increase of Rh content in bimetallic Au – Rh catalysts, which predict a special electronic interaction between the two metals ^[18]. The observed hikes and drops at certain times on figures 5.12 and 5.13 could be due to instrumental fault as they were not reproducible for different runs.

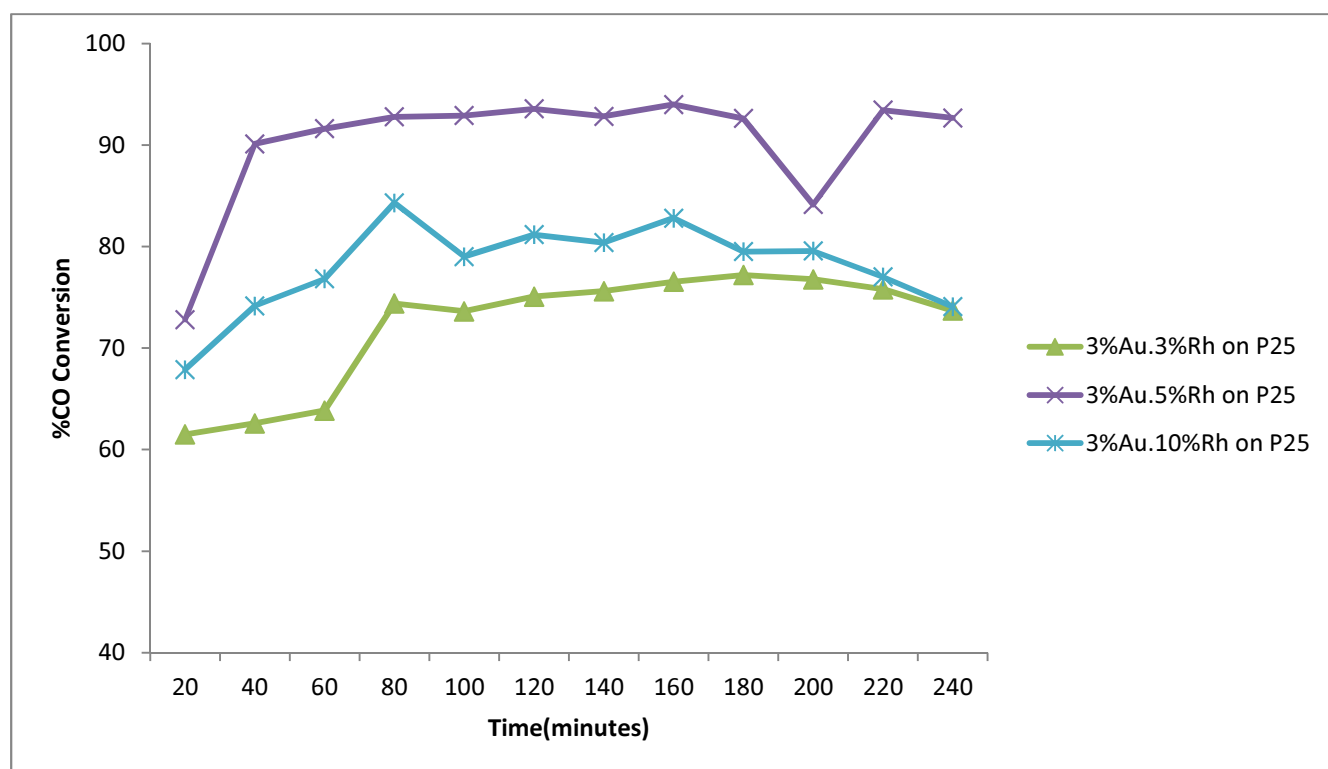


Figure 5.13: CO oxidation reactions highlighting the effect of varying Rh loadings over 3%Au-TiO₂ catalysts No pre-treatment, flow rates: 10% CO-60 ml/min, 5% O₂-60 ml/min, 4 hour run, temperature 150°C)

Figure 5.13 depicts the data as the temperature of the bimetallic was increased to 150°C, the highest conversion was still observed for the Rh loading of 5% while that of 3% loading was the lowest amongst the three different loadings. This in turn shows that the optimum loading for Rh should be 5% because beyond that regardless of temperature the activity is decreased. Another theory for this could be that more of the Rh blocks active sites on the catalyst as they appear as bigger particles when observed on TEM.

Figure 5.14 shows the different sized Au-Rh/TiO₂ when comparing loadings using the HRTEM. The 5% showed slightly uniform sizes for the nanoparticles while that at 10% had slightly bigger particles that could also be seen forming merrier fringes indicating the presence of more than once particle at that point as indicated by point A on (Figure 5.14 b). As noted in chapter 4 of this work the 3% loading hardly showed any signs of Rh on EDX data and that could be the reason for the observed low activity of that catalyst.

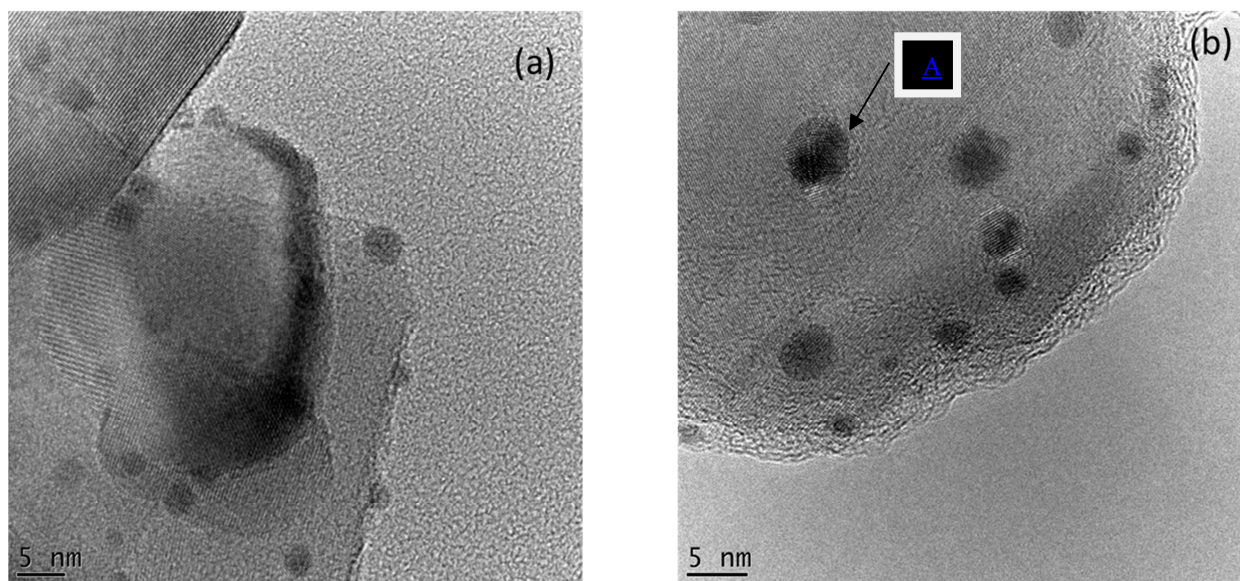


Figure 5.14: HRTEM micrographs showing comparison between Au/TiO₂ particles with different Rh loadings before CO Oxidation (a) 5% and (b) 10%.

From Figure 5.13 it was noted that the 3% Rh loading had a conversion of between 60-75% over the four hour duration that the run was carried through at a higher temperature of 150°C while at a lower temperature of 70°C (Figure 5.12) conversion was between 65 and 75% not showing a major difference. Looking at Figure 5.13 again a shift was observed in conversions for the 5 and 10% Rh loadings.

At 70°C, 5% Rh has a conversion of between 75-80% over the four hour duration constantly while an increase in conversion occurs as the run was carried through at a higher temperature of 150°C going to 75—95% and stays constant throughout the duration of the run.

At a lower temperature of 70°C (Figure 5.12) conversion was between 74-77% for 10% Rh loading onto the gold while at 150°C conversion spiked up from 68% during the early minutes of the run to about 80% conversion after an hour only to drop below 70% conversion

for the rest of the duration of the run which could have been caused by the high loading of the Rh causing agglomeration of particles on the catalyst as seen in Figure 5.14.

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Chapter 6

Overall Conclusions and Future work

6.1 Overall Conclusions

The work covered in our investigations was motivated by the need for a highly active Au based catalyst that can be used for various catalytic processes such as CO oxidation.

Au-Rh catalysts supported on titanium dioxide were also synthesized with the aim of creating a synergy of properties for combating sintering as well as short life span of the Au only based catalysts for CO Oxidation reaction. All these catalysts displayed promising results for the reaction and the Rh promoted Au catalysts showed a higher conversion percentage as compared to the Au only doped catalysts over a certain period of time due to size and morphology control from the synthesis.

We set up the deposition precipitation method to determine the optimum deposition duration needed for finely dispersed nanoparticles on the support. The criterion used was 5% Au (5% as less agglomeration of particles was observed) loaded on TiO₂ (as it has good metal-support interactions due to its reducibility) at pH 7 (as this is above the isoelectric point of TiO₂), 60 minutes deposition time (ample time for the solution to reach the ideal pH) and 3 days of ageing. These optimum conditions were set by the data gathered from TEM, BET and XRD as nanoparticles within the ranges of 2-4 nm could be obtained.

Addition of Rh metal as a promoter to the Au catalysts was done to investigate the effect that the Rh would have on the catalysts with regards to activity for the selected reaction and CO oxidation measurements showed an increase in activity for the bimetallic catalyst in comparison to the mono catalyst. There was an increase in activity with an increase in Rh and this was observed for both 70 and 150 °C temperature runs meaning that Rh does give a synergic effect on the Au catalysts at an optimum loading of 5%.

6.2 Possible Future work

Investigate the cause of the drop in catalyst activity from 85% to 75% activity for 5% Au-TiO₂ synthesized and used for application at different time periods.

Investigate the effects that Rh metal would have on the differently synthesized catalysts as per our variations in synthesis conditions.

Investigate different loadings of Au with Rh and check activity with various other applications.

Characterise Au-Rh catalysts using Scanning Transmission Electron Microscopy for the differentiation between Au and Rh using point and shoot analysis or mapping.

Characterise samples using TEM after catalytic measurements to investigate the effects of time on stream for the all the catalysts.

Utilise XPS and FT-IR to determine if bimetallics were synthesized or not