
CHAPTER 1

GENERAL INTRODUCTION

“.....It has pleased me no less than surprised me that of the many studies whereby I have sought to extend the field of general chemistry, the highest scientific distinction that there is today has been awarded for those on catalysis.”

Wilhelm Ostwald

1.1 CATALYSIS – A HISTORICAL PERSPECTIVE

The phenomenon of catalysis is intricately woven into the fabric of chemistry, and the recognition of its nature and importance is relevant. Catalysis, as well as being the mainstay of the chemical industry, is the means through which many laboratory syntheses are effected. In the present days, it is increasingly implicated in the suppression of atmospheric pollution, in the design of environmentally compatible new technologies and in the pursuit of new ways of generating energy and materials. More than 90% of the chemical manufacturing processes in use throughout the world utilize catalysts in one form or another.¹

The beginning of catalysis dates back to the dawn of civilization at a date lost in time when mankind began to produce alcohol by fermentation. The work done during this first period consists mainly of isolated observations that were sporadically documented without any efforts made to explain these phenomena. The first period of catalysis ended when Berzelius systematically investigated the recorded observations and classified them as catalysts in 1835. The second period of catalysis was therefore characterized by systematic research and the discovery of new catalytic processes. For example, in 1877

Lemoine showed that by applying a catalyst to a chemical reaction the rate at which the equilibrium was reached could be increased, but the position of the equilibrium could not be altered.² During this period it became clear that catalysis was applicable in most chemical processes and that by implementing catalysis in an industrial process there could be significant financial gains. This new perception of catalysis was clearly formulated by Wilhelm Ostwald, who once wrote that “there is probably no chemical reaction which cannot be influenced catalytically”.³

The point in time when the shift from the second to the third period occurred is not as clear as between the first and the second. The third period of catalysis began sometime during the end of the nineteenth century, when the growth of academic knowledge translated into industrial applications. At this point the number of catalytic processes that had been developed had grown into hundreds and the economic potential of some of these processes were highly feasible. For example the first small scale catalytic production of ammonia began in 1905, when Haber used an iron-based catalyst.⁴ There was also a general growth in the demand for bulk chemicals and therefore the minimization of by-products by catalysis had evident economic advantages. The industrial production of bulk chemicals of this period was at an all time high during World War I,⁵ when the demands on explosives based upon nitric acid reached preposterous proportions.

The fourth period of catalysis began at the end of the First World War, when the demand for explosives diminished, and the industrial production shifted towards the manufacturing of synthetic fuels and new innovative processes such as Fischer-Tropsch where in 1922, Franz Fischer and Hans Tropsch managed to synthesize hydrocarbons from carbon monoxide and hydrogen from coal gasification. The most significant new process innovation of this period was the FCC (Fluid Catalytic Cracking) process, developed by Lewis and Gilliland, at MIT, for the Standard Oil Company, which enable the Allied forces to provide fuel to its fighters during World War Two. When the war ended there was a notable change in the trend of the catalytic industry and thus the end of the fourth period.

The fifth period, which lasted to some undefined point at the beginning of the 1970s, was strongly characterized by the petrochemical industry and various catalytic processes for the manufacturing of synthetic polymers. For example in 1953, there were two major catalytic discoveries; the discovery of the Ziegler-Natta catalytic system for polymerizing ethylene to linear crystalline polyethylene and the stereo-specific polymerization of propylene to form crystalline polypropylene. The dominating role of the petrochemical industry was the result of the explosive automotive market that had developed in Europe and North America after World War Two. In 1949 the first organized catalysis meeting took place at the University of Pennsylvania. At some point during the early 70s the world started to become aware of the impacts that industry had on the environment. This new trend of thought gave birth to the discipline of environmental catalysis. Environmental catalysis was the first step towards the modern chemical industry where catalysis is applied to almost every process, including the production of fine chemicals for pharmaceutical applications to the production of bulk chemicals and exhaust gas catalysts. The sixth period which started in the seventies, and that can only be characterized by continuous invention of new catalytic processes, has not yet clearly passed into a seventh stage. The point in time when the transition into a new era will take place is today impossible to predict. What we can however say with certainty is that the future of catalysis will be exciting tomorrow as it was during the early years.⁶

1.2 CARBON MONOXIDE AND THE ENVIRONMENT

Carbon monoxide (CO) is a colorless, odorless, poisonous gas which is a major product of the incomplete combustion of carbon and carbon-containing compounds. It is a byproduct of vehicle exhausts, which contributes a very large amount of CO emissions in cities, particularly in areas with heavy traffic congestion. Other sources of CO emissions include industrial processes, tobacco smoke and fuel combustion in sources such as boilers and incinerators. It is also present in the atmosphere naturally, chiefly as a product of volcanic activity and natural gases (in coal mines) and forest fires. Carbon monoxide

from automobile and industrial emissions is a dangerous pollutant that may contribute to the greenhouse effect and global warming. Carbon monoxide is dangerous and life-threatening to humans and other forms of air-breathing life, as inhaling even relatively small amounts of it can lead to hypoxic injury, neurological damage, and possibly death. When it enters the body, it combines with haemoglobin to form carboxyhaemoglobin, reducing the oxygen-carrying ability of the blood. Long term exposure to low levels of carbon monoxide may result in heart disease and damage to the nervous system. Exposure of pregnant women to carbon monoxide may cause low birthrates and nervous system damage to the offspring. The concentration of carbon monoxide in the atmosphere varies from one region to another but the levels normally present are unlikely to cause ill effect. The concentration may reach harmful levels in poorly ventilated rooms during operation of unflued gas heaters, or defective non-electric heating appliances, or in the passenger compartment of vehicles with defective exhaust systems.

1.3 CARBON MONOXIDE AND THE FUEL CELL

In the past, the world has widely relied on energy obtained from burning fossil fuels, which are expected to be depleted in the near future. Extensive use of fossil fuels has created air pollution, acid rain, and the greenhouse effect. A lot of research is presently geared towards searching for alternative means of powering vehicles without creating any pollution. Fuel cells extract energy from fuel chemically rather than by burning it, which in general is more efficient and produces less pollution than combustion engines that burn fuel, thereby being more environmentally friendly. Hydrocarbons like fossil fuels and plant matter are widely used as fuel in fuel cells, but they produce carbon monoxide as waste product. The carbon monoxide gets in the way of the fuel cell reaction. Many studies have shown the negative effect of carbon monoxide on the performance of fuel cells. The electrodes of the fuel cell are typically made of platinum which is very sensitive to carbon monoxide poisoning.^{7,8} The absence of carbon monoxide would enable fuel cells to exhibit longer lifetimes and improved efficiency. Carbon monoxide is usually removed using the water-gas shift reaction, which uses water to convert carbon

monoxide to carbon dioxide and hydrogen. The reaction is relatively slow and occurs at temperatures of at least 227 °C, requiring fuel cells to contain heating and cooling equipment and a supply of water. Selective catalytic carbon monoxide oxidation is perhaps the most promising way of removing carbon monoxide in the feed.⁹

1.4 CATALYTIC OXIDATION OF CARBON MONOXIDE

Due to the toxicity of carbon monoxide and its negative effect on the efficiency of the fuel cell, its oxidation to carbon dioxide at lower or ambient temperatures, is a reaction that has engendered a lot of research interest. The reaction using noble metal catalysts normally requires high reaction temperatures above 300 °C and as a result, consumes a large amount of energy to heat the vent stream to the reaction temperature. Metal oxide catalysts require much lower temperatures, yet are readily deactivated by water present in essentially all vent streams containing CO.¹⁰ Vehicle exhaust catalysts,¹¹ carbon dioxide lasers,¹² catalytic combustion¹³ and mine rescue devices¹⁴ are a few of the numerous applications of this reaction. Hopcalite catalysts (mixed oxides composed mainly of Mn and Cu) have been most frequently used for the reaction but they are not water tolerant and easily deactivate at ambient temperatures.¹⁵ A Heterogenized Wacker catalyst (PdCl₂-CuCl₂) has high activity for CO oxidation at temperatures around 60 °C but works only in the presence of water vapor.¹⁶ In the fuel cell technology, the common catalysts that have been used for the selective oxidation of carbon monoxide in the presence of hydrogen are the PROX catalysts which are based on platinum (or other platinum group metals) e.g. Pt/ γ -Al₂O₃. One of the barriers to the commercialization of fuel cells, is the technology advance required to decrease precious metal contents in catalysts and yet still achieve the required output.¹⁷

Until recently, gold was regarded as one of the least catalytically useful metals because of its chemical inertness. However, with the pioneering work of Haruta et al.^{18,19}, in which they showed that if gold is finely dispersed on metal oxide surfaces such as TiO₂, ZrO₂, NiO, Fe₂O₃ and Co₃O₄, it exhibits high catalytic activity in low-temperature CO

oxidation, the metal has been the subject of much interest in the last decade for its catalytic properties. Gold has thus been shown to be a potentially useful system when highly dispersed on a suitable support for various industrial and environmental applications. Such supported gold catalysts are now known to be the most active catalyst systems for CO oxidation. Due to the greater availability and stability of the price of gold compared to the platinum group metals (PGMs), the use of gold in preference to platinum could help to reduce the cost of fuel cell technology.¹⁷ One striking outcome of the discovery of the catalytic activity of gold is the unique nature of its properties when compared with those of its neighbors.

1.5 UNIQUE PROPERTIES OF GOLD

The chemical inertness of gold, a diamagnetic metal of extreme nobility, would appear at first sight to render it unsuitable as a catalyst, since catalysis requires the formation at the surface of intermediate species of moderate stability. This expectation is well supported by experience. Gold adsorbs neither hydrogen²⁰ nor oxygen²¹ to any significant extent at ambient temperatures and it cannot therefore act as a hydrogenation or oxidation catalyst in the normal sense. Notwithstanding this unfavorable prognosis, by means of certain procedures, gold has been shown to have some interesting properties.

Gold, found in group 11 in the periodic table, lies between platinum (group 10) and mercury (group 12). Mercury is generally considered to be a poison, except in hydrochlorination reactions, whilst platinum on the other hand is a versatile catalytic metal widely used in chemical processing and in pollution control systems. Gold is also in the same group as copper and silver.²² Figure 1 compares some properties of gold with respect to its neighbors. The absence of a stable oxide is unique to gold: for all other elements, including silver, their oxides have negative free energies of formation. Gold's metallic radius is slightly smaller than that of silver, but the Au^{III} state is more stable than Au^I whilst the reverse is true for silver. Gold has a high electronegativity for a metal as

shown by its high first ionization potential and it can form compounds such as Au^-Cs^+ where it is anionic.²³

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Figure 1.1: Some physical properties of platinum, mercury and the metals of group II. Clockwise from top left: a, metallic radius (nm); b, first ionization potential (kJmol^{-1}); c, melting temperature (K); d, sublimation enthalpy (kJmol^{-1}).

(Source: Based on reference 23).

1.6 RELATIVISTIC EFFECTS AND THE CHEMISTRY OF GOLD

Differences in the chemistry of gold compared with that of silver, particularly the resistance of gold to oxidation can be attributed largely to the impact of a relativistic effect. As the atomic nuclear charge (Z) increases along the periodic table of elements, electrons that penetrate the nucleus (the s electrons) increase their average velocity, which eventually comes close to the speed of light, and as a consequence of relativity,

their mass. This relativistic effect causes the s electrons and to a lesser extent the p electrons to occupy smaller orbitals than if this effect were absent. Therefore, in the heavier elements, the s electrons are more strongly bound and shield the nuclear charge from the other electrons (especially d and f) more effectively than if the relativistic effects were absent. The d and f electrons are therefore less bound and occupy larger orbitals when relativistic effects are large. These effects scale roughly with Z^2 and become important for the elements heavier than the lanthanides. For the elements gold to bismuth the impact on energies is comparable with chemical bond energies. Indeed, gold because it is also at the end of the 5d orbital filling, (third transition series contraction effect) following on the 4f filling (lanthanide contraction) exhibits the maximum impact of this relativistic effect as shown in Figure 1.2.

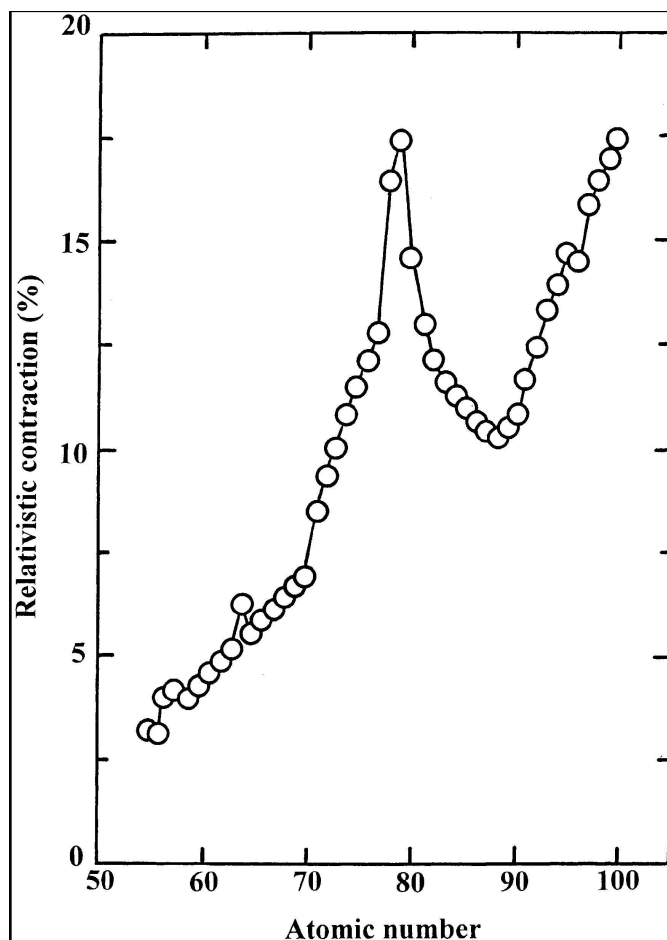


Figure 1.2: Calculated relativistic contraction of the 6s level as a function of atomic number. (Source: Based on reference 23).

As a consequence of the lanthanide contraction and the relativistic effect, we expect that the effective size of the gold atom will be comparable with that of silver. The relativistic effect in gold enhances the binding of the s electrons relative to those of silver and accounts for the smaller size established by Schmidbaur and his coworkers²⁴ for Au(I) versus Ag(I); the high electron affinity of gold relative to silver, and for the existence of aurides (e.g. Cs^+Au^-) which are non-metallic semiconductors. It is also why the first ionization potential of gold (removing the s electron from the $5d^{10}6s$ configuration) is so much higher than that of silver.

Table 1.1: Comparing gold with silver.

		Au	Ag
Ionization potentials (eV)	1 st	9.225	7.576
	2 nd	20.5	21.49
Electron affinity (eV)		2.039	1.202
Heats of atomization (kJmol^{-1})		368	285
Melting point ($^{\circ}\text{C}$)		1063	961
A-A distance in f.c.c. cells (\AA), 25°C		2.8840	2.8894

The tighter binding of the valence s electrons of gold also contributes to the higher melting point, and smaller atom to atom close contact in the metal. The raising of the Au 5d electron energies and the lowering of the valence 6s also accounts for the yellow color of gold (absorption beginning at about 2.38eV) associated with transitions from 5d band to the Fermi level (largely 6s in character). The related absorption in silver (4d band to the Fermi level of $\sim 5s$ character) is in the ultraviolet, at $\sim 3.7\text{eV}$.

The consequences of the relativistic effect have prime impact in causing metallic gold to be more resistant to oxidation than silver. If a sufficiently potent oxidizer is available however, gold can be oxidized to a higher oxidation state than silver. For example, when metallic gold is exposed to elemental fluorine at room temperature in the presence of

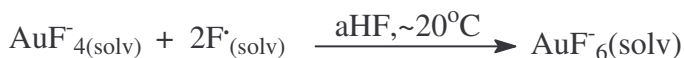
ionizing solvent liquid anhydrous hydrogen fluoride (aHF) containing an alkali fluoride, the metal is quickly dissolved to give the alkali salt of the anion AuF_4^- .



Under similar conditions silver is oxidized only to the +2 oxidation state, the ultimate product being AgF_2 , which is not soluble in aHF. If however the F_2 is photo-dissociated to atoms, the AgF_2 is further oxidized and dissolves in the aHF made basic with alkali fluoride.



Under such conditions of photo-dissociated F_2 , AuF_4^- is oxidized further to AuF_6^- .



These reactions clearly indicate how much more easily the 5d electrons of gold can be involved in bonding than can the 4d electrons of silver.²⁵

1.7 GOLD CATALYSIS

As for many aspects of gold science and technology, gold catalysis has unique features. Many early studies have shown gold to be a useful promoter of other more active metals for some reactions, and to influence selectivity of the reaction at the expense of activity. Gold had thus been generally regarded as the least useful of the noble metals for catalytic purposes. However, the 80s and 90s saw a huge growth an interest in gold as a catalyst. Firstly, Hutchings used a gold-on-carbon catalyst for the conversion of ethyne into vinyl chloride by the addition of hydrogen chloride, a reaction important for the manufacture of polyvinyl chloride (PVC).²⁶ The activity of the catalyst was shown to be about three times higher than the commercial mercuric chloride used at the time. This was the first example of a reaction for which gold exhibited the highest activity and is the catalyst of

choice. Haruta then showed that gold catalysts could be effective for the oxidation of carbon monoxide at and below ambient temperatures, thus making them unique.¹⁹ It was demonstrated that gold is better than conventional Pd and Pt catalysts and the way gold acts catalytically is substantially different from other metals from the Pt group. It is now known that gold can catalyze a wide variety of reactions under comparatively mild conditions. Nowadays gold catalysis is receiving increasing attention from a number of research groups around the world and the subject has been reviewed by Bond and Thompson.^{27,28} This relatively new field of gold catalysis has very promising applications but amongst them, CO oxidation is the reaction that has received the most attention. Table 1.2 shows some of the potential applications of gold catalysis.

Table 1.2: Potential applications for gold catalysts.

Heterogeneous	
Chemical processing	WGS, hydrocarbon reactions relevant to petroleum reforming; selective oxidation reactions, including some in the liquid phase; hydrogenation and dehydrogenation reactions.
Clean energy generation	Hydrogen purification and electrocatalysis for fuel cells.
Environmental pollution control	Air conditioning in automobiles, aircraft, ships, submarines, trains, office buildings, hospitals etc
Waste incinerators	Removal of dioxins.
Automotive pollution control	For low temperature applications in diesel vehicles and for cold start with gasoline engines.
Sensors	For inflammable and poisonous gases such as hydrocarbons and CO, respectively.
Homogeneous	
Chemical processing	Alkyne reactions and selective routes to specialty chemicals such as pharmaceuticals and fragrances.

Possible applications of gold catalysts for CO oxidation include:

- (a) car exhaust systems for pollution control.²⁹
- (b) fuel cells (CO purification in H₂ + O₂ streams).²⁷
- (c) gas sensing.³⁰
- (d) chemical processing (CO oxidation in reforming gas).³¹
- (e) air purification systems (long term space travel).²⁹

However, any practical application of a catalyst will require a reliable method of manufacture, long-term stability, good response to operating conditions, and more information on the kinetics and mechanism of the reaction. The explanation of the causes and mechanism of this outstanding low temperature activity for CO oxidation on gold catalysts is expected to be important, not only because of the practical applications of this reaction but also because it will surely provide insight into the more general field of heterogeneous catalysis.³²

Notwithstanding the seemingly confused state of literature, there is a large measure of agreement by different researchers to the different factors responsible for the activity of gold catalysts. The following chapter (Chapter 2) reviews some of the work that has been reported in literature on gold catalysis.

CHAPTER 2

LITERATURE REVIEW

“.....I have a goal to double the industrial demand for gold over the next decade. Is that just a silly pipedream or could it be a reality? You can probably guess my answer to that question. Today, I want to show you why I believe it is a reality and how it can be achieved.”

Christopher W. Corti

2.1 INTRODUCTION

Oxidation represents one of the key processes in the functionalization of molecules *via* selective oxidation or the removal of pollutants *via* total oxidation. Oxidation is used in many processes and, therefore, influences everyday life in a way similar to the impact of catalysis in general. The designing of oxidation catalysts is therefore one area of research that has gained a lot of attention in recent times.³³

Gold, as a metal, has fascinated mankind since the dawn of civilization, and as an element it is a component of some of the beautiful pieces of artwork ever produced. One reason for this fascination lies in its qualities of being both a lustrous and beautiful material, as well as being immutable, i.e. it does not corrode under normal conditions and retains its beauty over very long periods of time. Until recently, gold was regarded as one of the least catalytically useful metals because of its chemical inertness. However, with the pioneering work of Haruta et al.^{18,19}, in which they showed that if gold is finely dispersed on metal oxide surfaces such as TiO₂, ZrO₂, NiO, Fe₂O₃ and Co₃O₄, it exhibits

high catalytic activity in low-temperature CO oxidation, the metal has been the subject of much interest in the last decade for its catalytic property. Gold has thus been shown to be a potentially useful system when highly dispersed on a suitable support for various industrial and environmental applications.

2.2 REACTIONS CATALYZED BY SUPPORTED GOLD CATALYSTS

Some of the important processes that are catalyzed by supported gold catalysts include the following:

2.2.1 Water-gas shift reaction

The water-gas shift (WGS) reaction may be considered to involve the selective oxidation of carbon monoxide in the presence of water. It is a key reaction in the production of hydrogen for a number of processes, including petroleum refining and chemicals synthesis. Another application is in the production of hydrogen for the proton exchange membrane (PEM) fuel cells as a clean energy source for vehicle propulsion and auxiliary power units³⁴ and also in residential electricity-heat delivery systems.³⁵ This reaction is important because it removes CO, a poison to the fuel cell electrocatalysts, which is produced during the steam reforming and/or partial oxidation reactions. Commercial catalysts used for this reaction based on Ni or Cu operate at 900 K or at 600 K respectively.³⁵ Kim and Thompson³⁶ have also reported the commercial use of copper- and Fe-Cr based catalysts for the reaction but that these are not suitable for portable vehicular applications because of insufficient durability and activities. Consequently, there has been substantial interest in the development of better performing and more durable WGS catalysts.³⁷⁻⁴⁰ Several authors have reported that gold catalysts are highly active for the WGS reaction. Supported gold catalysts are advantageous because they operate at temperatures as low as 473 K.⁴¹ Such supported gold catalysts include Au/ZrO₂,³⁵ Au/TiO₂, Au/Fe₂O₃, Au/Al₂O₃ and Au/ZnO²⁷, Au/CeO₂³⁷, Au/TiO₂⁴².

Au/NaY has also been reported by Mohamed et al⁴³, to be active for the reaction at 373K although it is not very stable. The redox cycle of Au⁺ and Au⁰ is assumed to operate for CO activation, while the NaY support is responsible for H₂O activation.

2.2.2 Reduction of nitric oxide

The catalytic reduction of nitrogen oxides has been one of the most important challenges during the last few decades. Reduction of nitric oxide is one of the reactions occurring in catalytic converters for the purification of engine exhaust gases. The most practical convenient method for removing nitric oxide is the catalytic reduction using unburnt compounds such as carbon monoxide, hydrogen and hydrocarbons contained in exhaust gases. There are two different practical conditions for catalysts to work; i.e. stoichiometric and lean-burn. Under stoichiometric conditions where the amount of air supplied is controlled to a level just sufficient for the complete combustion of the fuel, three-way catalysts are used. These catalysts are made of the platinum group metals usually supported on oxides with oxygen-storage capacity such as CeO₂ deposited on Al₂O₃⁴⁴ and operate at temperatures above 400 K.⁴⁵ Gold supported on a variety of metal oxides shows good low temperature catalytic performance for the reduction of nitric oxide by hydrocarbons such as propene, propane, ethene and ethane. For example, over Au/Al₂O₃,⁴⁴ Au/ α -Fe₂O₃ or Au-NiFe₂O₄⁴⁶ the reaction of NO with CO takes place at 373 K producing nitrogen whilst over Rh/Al₂O₃ it takes place at 573 K. The mechanical mixture of Au/Al₂O₃ with Mn₂O₃ is reported to enhance the activity of Au/Al₂O₃.⁴⁷ Addition of carbon monoxide and hydrogen to the reactant gas improves the conversion of nitric oxide to nitrogen. Reaction temperature regions and nitric oxide conversions are affected by the selection of the metal oxide support. Zinc oxide support makes gold very active at low temperatures. Au(I)/ZSM-5 has also been reported to be active for this reaction at low temperature.⁴⁸ Supported gold catalysts are thus very promising for applications for emission control of stationary and road vehicle engines.⁴⁹

2.2.3 Hydrogenation reactions

Many production processes of unsaturated hydrocarbons lead to a mixture of hydrocarbons, and further hydrogenation is sometimes necessary to obtain the valuable products commonly used in the chemical industry. Selective hydrogenation of dienes is an important reaction in this light. In general, the hydrogenation of hydrocarbons is a structure insensitive reaction over most metal catalysts.³⁵ Bond and coworkers have carried out 1,3-butadiene hydrogenation over Au/SiO₂ and Au/Al₂O₃ and found a very high selectivity for partial hydrogenation of 1,3-butadiene. Although the catalytic activities were low, selectivities to butenes were higher than those of conventional Pt catalysts.⁵⁰ Hydrogenation of dienes and alkenes over Au/ZrO₂ prepared from amorphous alloys with 100% selectivities to monoenes has also been reported.⁵¹ The Au/ZrO₂ catalysts were selective to the C=O bond in the hydrogenation of unsaturated carbonyl compounds.

Hydrogenation of CO and CO₂ using gold supported on ZnO⁴¹ and ZrO₂⁵² prepared by coprecipitation has been reported to yield methanol while other noble metals lead to deep hydrogenation to form CH₄ as the main product. However, Au/ZrO₂ prepared from amorphous alloy mainly produces CH₄ from CO.⁵³ These results indicate prospects for supported gold catalysts to be applied to controlled hydrogenation of unsaturated compounds.

2.2.4 Selective oxidation of hydrocarbons

The selective oxidation of hydrocarbons, comprising alkanes, alkenes and aromatics is an important chemical technology for conversion of oil- and natural gas- based feedstock to value added products such as oxygenates which are key intermediates for polymer and organic chemicals synthesis. H₂O₂ and hydroperoxides catalyze these reactions selectively in combination with titanosilicates and an organic solvent like methanol but H₂O₂ is very costly. The selective vapor-phase oxidations of saturated as well as

unsaturated hydrocarbons, propylene to propylene oxide, propane to acetone and isobutane to tert-butanol have been achieved over nanometer size gold particles prepared by deposition-precipitation method on TiO₂-containing supports, using H₂ and O₂ as co-feed. However, gold deposited by impregnation and gas-phase grafting methods result in poorly selective catalysts which produce CO₂ as the main product.⁵⁴

2.2.5 Carbon monoxide oxidation

One reaction that has attracted a lot of research interest has been the oxidation of carbon monoxide to carbon dioxide at ambient or lower temperatures.³³ Haruta⁴⁹ was the first to show that gold supported on metal oxides is very active for CO oxidation at and below ambient temperatures. In general, the oxides of 3d transition metals, especially Group 8-10, and hydroxides of alkaline earth metals lead to high activities even at temperatures as low as 203 K^{18,55}. CO oxidation is the reaction that has received the most attention amongst the reactions catalyzed by gold catalysts. The best gold catalysts have been reported to be even more active than conventionally prepared palladium and platinum catalysts.²⁸ Apart from metal oxide supports, other materials that have been used as supports for gold catalysts include zeolites⁵⁶ and carbon.⁵⁷

2.2.6 Hydrochlorination

The heterogeneously catalyzed addition of HCl to ethyne (acetylene) is important industrially because it is used for the manufacture of chloroethene (vinyl chloride) which is used as the monomer for the production of polyvinyl chloride (PVC). Supported metal chlorides have been used as catalyst for this reaction.⁵⁸ Mercuric chloride supported on carbon has also been used industrially.⁵⁹ Mercuric chloride catalysts deactivate quite rapidly under reaction conditions and these catalysts are quite toxic. Hutchings²⁶ was the first to use a gold-on-carbon catalyst for this reaction and this catalyst was found to be about three times more active than the commercial mercuric chloride catalysts. Although it still deactivated, it was more stable than supported mercuric chloride catalysts.

2.2.7 Epoxidation of propylene

Propene oxide (PO) is used extensively in the production of polyurethanes. Its current commercial production is based on the chlorohydrin process. However, the direct gas-phase synthesis of PO from propene, using molecular oxygen in the presence of hydrogen, offers the opportunity to eliminate chlorine from the production process, as well as reduce water consumption and salt byproducts. Patents for direct propene oxide production have been appearing in the literature in recent years,^{60,61} indicating the significant industrial interest in this application, and pilot plants are understood to be operating within the industry. Haruta,⁴⁹ obtained > 99% selectivities at low conversions in the oxidation of propene to propene oxide using a 1wt% Au/TiO₂ catalyst system at 323 K, when both oxygen and hydrogen are present in the feed gas. One of his more recently published works has improved these results further, such that yields are at a commercially acceptable level.⁶² The remaining technical challenge is the need to increase catalyst durability further, with deactivation currently occurring after a few hours on stream.⁶³

2.2.8 Direct production of hydrogen peroxide

Global sales of hydrogen peroxide are rising annually, due in part to it being an environmentally friendly alternative to chlorine. At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of alkyl anthraquinone.⁶⁴ This process is currently only economic on a large scale, whereas, it is often required practically on a much smaller scale.⁶⁵ Hydrogen peroxide is a hazardous material and transportation from point of manufacture to point of use is expensive.⁶³ In view of these facts, there is considerable interest in the direct manufacture of hydrogen peroxide from the catalyzed reaction of hydrogen and oxygen. Presently, some success has been achieved in using Pd as a catalyst, especially when halides are used as promoters.⁶⁶ It has been found that supported gold catalysts can be very effective for the synthesis of hydrogen peroxide, and furthermore, it can be enhanced by the use of a supported Au/Pd alloy.⁶⁵

2.2.9 Combustion of hydrocarbons

Gold supported catalysts have also been shown to be active for the complete oxidation (combustion) of hydrocarbon fuels.^{67,68} For example, amongst several metal oxides supported gold catalysts studied, Waters et al.⁶⁷ found Co_3O_4 to exhibit highest activity towards methane oxidation. It is inferior to Pd and Pt catalysts in the combustion of unsaturated hydrocarbons like propylene; however, it is as active or more active for saturated hydrocarbons like CH_4 and C_3H_8 .⁴⁹

2.3 METHODS OF PREPARATION OF GOLD CATALYSTS

The activity of gold catalysts for various reactions depends to a large extent on the degree of dispersion of the gold nanoparticles on the support material. This depends also on the method employed in the preparation. Several methods have been employed in different works to prepare active gold catalysts. However, amongst these, the most predominant are:

2.3.1 Impregnation

This involves impregnating a preformed support with a solution of gold salt, followed by drying and reduction. This may be done either by just filling the pores of the support with the solution or by suspending the support in a larger volume of solution, from which the solvent is then removed. Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sometimes referred to as auric chloride (AuCl_3 or Au_2Cl_6) or as hydrogen tetrachloroaurate is the salt commonly used. Some complex salts also used in this regard include potassium aurocyanide ($\text{KAu}(\text{CN})_2$) and the ethylenediamine complex, $[\text{Au}(\text{en})_2]\text{Cl}_3$. Common supports are silica, alumina, magnesia, titania, ferric oxide and magnesium hydroxide. Aqueous solutions have invariably been used, but chloroauric acid in solution is a strong acid quite capable of dissolving alumina and magnesia; and magnesia is also very rapidly hydrolyzed in water

at room temperature to brucite ($\text{Mg}(\text{OH})_2$), so there is little point in calcining it before immersing it in water.²⁷

Haruta and coworkers have reported that this method of preparation generally results in poorly active catalysts compared to other traditional methods of preparation.^{49,69} However, Bollinger and Vannice⁷⁰ have reported highly active catalysts prepared by impregnation using titania as support when a three stage pretreatment consisting of high temperature reduction at 773 K, calcination at 673 K and low temperature reduction at 473 K, was used. This preparation method has been widely used in the literature though, for the preparation of gold catalysts. For example, Debeila et al⁷¹, Li et al⁷² and Soares et al²⁹ have used impregnation to prepare Au/TiO₂ catalysts for different studies.

Impregnation usually leads to the formation of somewhat large gold particles, due to the need to apply calcination or reduction in order to achieve the metallic state and to the low melting point of gold (1337 K) which allows atomic mobility at quite low temperatures. According to Haruta⁷³, the formation of large particles results from the fact that the interaction of the gold precursor and the support is weak, and that the chloride ions present in the samples promote the sintering of the Au particles during heat treatment. Kung et al⁷⁴ suggested that the sintering is due to the high mobility of Au on the support in the presence of chlorides. Table 2.1 shows a selection of the particle size estimates reported for catalysts made by the impregnation method.

Table 2.1 Gold particle sizes in catalysts prepared by impregnation.

<i>Support</i>	<i>[Au] (wt%)</i>	<i>Au source</i>	<i>Size range (nm)</i>	<i>Method used to estimate particle sizes</i>	<i>Reference</i>
SiO ₂	5	HAuCl ₄	24; 26.5 (2-100)	XRD, TEM	75, 76
SiO ₂	0.19	KAu(en) ₂	<3	WAXS	77
SiO ₂	1.46	HAuCl ₄	<100	WAXS	77
SiO ₂	1.8	AuCl ₃	30	XRD	78
η-Al ₂ O ₃	10	HAuCl ₄	(5-100) ^a	TEM	79
η-Al ₂ O ₃	10	KAu(CN) ₂	(10-200) ^b	TEM	79
γ-Al ₂ O ₃	1.25	HAuCl ₄	20; 26	XRD, TEM	75, 76
γ-Al ₂ O ₃	0.06	[Au(en) ₂]Cl ₃	<3	WAXS	77
γ-Al ₂ O ₃	1.62	HAuCl ₄	>100	WAXS	77
MgO	0.67	KAu(CN) ₂	<3 ^b	WAXS	77
MgO	10	KAu(CN) ₂	500	TEM	79
MgO	4.39	HAuCl ₄	63	WAXS	79
MgO	10	HAuCl ₄	(10-120) ^a	TEM	79
MgO	1.5-15	HAuCl ₄	5-10	TEM	80
Mg(OH) ₂	5	HAuCl ₄ ^c	(0.6-4)	XRD, EXAFS	81
TiO ₂ (A) ^d	2.3	HAuCl ₄	3.5	TEM	82
TiO ₂ (D) ^e	2.3	AuCl ₃	25	XRD	78
α-Fe ₂ O ₃	1	HAuCl ₄	20-30	TEM	69

^aHeated to 413 K

^bHeated to 643 K

^cReduced with magnesium citrate

^dAnatase

^eDegussa P-25

Source: Based on reference 12.

Many values are in the range 2-30 nm, which is large by the standards of the noble metals of Groups 8-10, but some are even larger. In addition, when HAuCl_4 is used as the gold precursor in this method, the final catalyst is always associated with a large amount of chloride ions which are catalyst poisons for most reactions.

2.3.2 Ion exchange

In this method, protons or other cations associated with the support are exchanged with gold cations followed by washing, drying and reduction. The exchange process leads to atomically dispersed species and after calcination and reduction with hydrogen to extremely small gold particles. The procedure is particularly effective with zeolites and the Y form is being most often used. However a limitation to this method being widely used is the fact that there is a limited number of cationic gold complexes available, an example being the ethylenediamine complex.²⁷ Guillemot et al⁸³ introduced gold onto HY zeolite by cation exchange using the $[\text{Au}(\text{en})_2]^{3+}$ ion followed by thermal decomposition at 423 K. It was shown that 80% of the gold particles were between 1 and 4 nm in size, the smaller of which were in the cavities of the zeolite and a few larger particles (> 5 nm) were also seen on the outside. Grinding a mixture of Au_2Cl_6 and NaY zeolite and heating in vacuo causes the transport of the volatile salt into the pores; the presence of water causing a reduction to the Au(I) state.⁸⁴ Kang et al⁸⁵ also reported a procedure whereby NaY zeolite was stewed with dilute chloroauric acid solution at 353 K for 16 h and characterization of the product by TEM showed large hexagonal gold particles on the surface which were only 8% of the total; the rest were thought to be within the cavities of the zeolite.

2.3.3 Coprecipitation

This procedure devised by Haruta and his coworkers^{19,49,69} has been widely imitated, with the experimental procedures being all quite similar. An aqueous solution of the HAuCl_4 and a water soluble salt of the corresponding metal oxide support most preferably the nitrate is poured into an aqueous solution of Na_2CO_3 or NaOH under vigorous stirring and

the coprecipitate aged for a few hours and washed thoroughly with water to remove any sodium ions or chloride ions that may act as catalyst poison.²⁷ The metal salts form carbonates or hydroxides respectively under such basic conditions. The coprecipitates are oven dried after washing and may be calcined at a variety of temperatures in the range 473-1073 K. Wagner et al⁸⁶ reported that the sequence of mixing of precursor and the alkaline solutions can affect the performance of the final catalyst. An inverse coprecipitation involves adding the alkaline solution to the precursor and generally leads to less active catalysts. One of the drawbacks of coprecipitation is that, in this method, the pH is generally always very high (9.5-12) that a considerable amount of gold is solubilized in the form of $[\text{Au}(\text{OH})_4]$ leading to much of the gold remaining in solution. Even when inverse coprecipitation (adding the alkaline solution to the catalyst precursor) is used where the pH is less than with coprecipitation, about 50% of the gold can remain in solution.⁸⁷ Table 2.2 below shows a comparison of gold recovery from solution by deposition-precipitation and coprecipitation methods.

Table 2.2 Recovery of gold from solution by deposition-precipitation and coprecipitation methods.

<i>Au in the solution (mg)</i>	<i>Au in the product (mg)</i>
Deposition-precipitation	
25	24.8 (99.2%)
50	49.9 (99.8%)
Coprecipitation	
125	14.7 (11.8%)
250	32.3 (12.9%)
375	47.6 (12.7%)

Source: Based on reference 87.

Bond and Thompson²⁸ reported that coprecipitation leads to supports that are non-crystalline, which may in fact be hydroxides or hydrated oxides, and even after drying or calcination, they may be highly disordered or of complex structure. There is effective dispersion of the gold precursor amongst the support particles, although there is the risk of most of the active particles being buried within the support matrix and therefore not

being available for catalysis. They suggested that calcination is necessary to create porosity by loss of water, and hence create access to the gold particles. Tanielyan and Augustine⁸⁸ have however showed that active Au/Fe₂O₃ catalysts could be prepared without heat treatment and that calcination at 653 K led to a decrease in activity by more than an order of magnitude. Luengnaruemitchai et al⁹ compared the gold crystallite sizes of Au/CeO₂ catalysts prepared by coprecipitation with those prepared by impregnation and sol-gel methods and found those by coprecipitation to be < 5 nm whilst the other methods gave gold crystallites of about 30 nm. This coupled with the fact that catalysts prepared by impregnation are always associated with Cl⁻ ions, which are catalyst poisons, could be suggested to be the reason why coprecipitation yields more active catalysts than impregnation.

2.3.4 Deposition-precipitation

In the deposition-precipitation method, the precursor of the gold species e.g. HAuCl₄.3H₂O is brought out of solution in the presence of the support by raising the pH in order to precipitate the hydroxide; the surface of the support acts as a nucleating agent attracting the gold precursor. Deposition-precipitation has a great potential over coprecipitation in that all of the active component remains on the surface of the support and none is buried within it. It is important to avoid precipitation away from the support surface by avoiding local high concentrations of alkali. Geuss⁸⁹ showed that this can be achieved by slow decomposition of urea in solution at about 353 K, and hydroxyl ions are generated slowly and uniformly throughout the liquid phase and their concentration is always low because they are consumed almost as soon as they are formed. NaOH^{69,90} and Na₂CO₃⁹¹ have also been used as precipitating agents in preparation of a number of gold supported catalysts using this method. As in coprecipitation, it is also important to wash the precipitate formed, free from chloride ions. Washing could then be followed by heat treatment. The gold precursor can either be added to the support after its pH has been adjusted to the desired level or an inverse route can be followed in which the support is added to the gold precursor of appropriate pH value. The pH of the gold precursor is always adjusted at a fixed point in the range 6-10, which is primarily dependent on the

isoelectric points (IEP) of the metal oxide supports. Careful control of the concentration (around 10^{-3}M), pH (6-10), and temperature (323-363 K) of the aqueous HAuCl_4 solution enables selective deposition of $\text{Au}(\text{OH})_3$ on the surfaces of the support metal oxide without precipitation in the liquid phase.⁹² Kung et al⁷⁴ reported the preferable pH to lie in the range 7 to 8. At pH's lower than the isoelectric point of the support, the surface is positively charged and is capable of adsorbing more of the negatively charged gold species. This results in not only a larger gold loading, but also high concentration of chloride on the surface, the presence of which increases the mobility of Au on the support, leading to large Au particles and some vaporization of Au from the solid upon calcination. At a pH above the isoelectric point of the oxide, adsorption of the negatively charged $\text{Au}(\text{OH})_x\text{Cl}_{4-x}^-$ complex decreases rapidly resulting in a lower gold loading. However, there will also be less chloride at the catalyst surface, so small gold particles can be formed. Therefore, there is a narrow range of pH where sufficient Au can be deposited on the support with minimal chloride in the Au complex. Figure 2.1 below shows how the mean diameter of gold particles varies as a function of the pH of HAuCl_4 solution for Au/TiO_2 catalysts prepared by deposition-precipitation method.

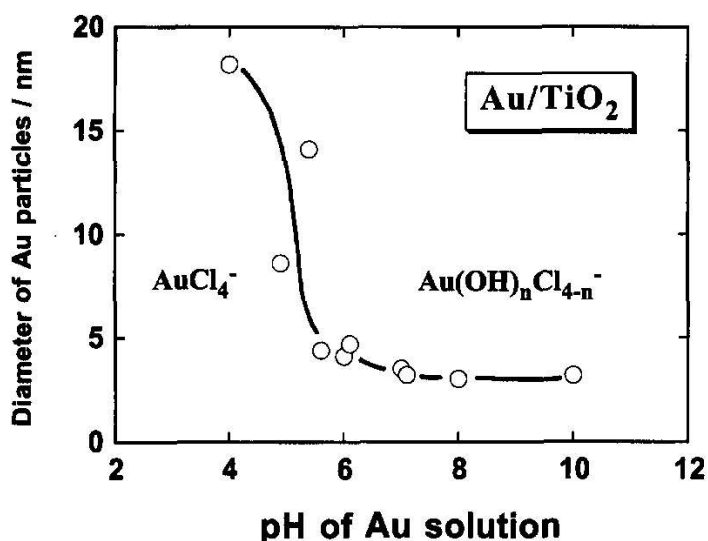


Figure 2.1. The mean particle diameter of Au as a function of the pH of HAuCl_4 solution for Au/TiO_2 catalysts prepared by deposition-precipitation method. (Source: Based on reference 49).

Deposition-precipitation is advantageous with respect to coprecipitation in that it gives a narrower particle size distribution.²⁷ Another potential advantage is that it is easily scalable and can work with many types of support.⁸⁷ The only constraint of deposition-precipitation is that it is not applicable to metal oxides whose isoelectric points are below 5, and to activated carbon. Gold hydroxide cannot be deposited on SiO₂ (IEP = 2), SiO₂-Al₂O₃ (IEP = 1), or WO₃ (IEP = 1).⁹²

2.3.5 Vapor-phase deposition and grafting

These two methods are similar and differ only in whether a solvent is used or not. In vapor-phase deposition (sometimes referred to as chemical vapor deposition, CVD), a stream of a volatile compound of gold is transported to a high area support by an inert gas, and it reacts chemically with the surface of the support to form a precursor on the active species. This method is suitable for acidic supports e.g. alumina-silica and non-metal oxide supports such as activated carbon for which deposition-precipitation would be inoperative. Chemical vapor deposition has been used to deposit gold nanoparticles on alumina in a vacuum system⁹³ and MCM-41⁹⁴ using dimethyl gold acetylacetonate and found to exhibit high activities for low temperature CO oxidation. Dimethylgold(III) β -diketone has also been used as gold precursor for a number of supports including alumina and titania and to silica and MCM-41.^{94,95} Parish⁹⁶ lists some common organometallic compounds of gold that are suitable for CVD.

Grafting involves reacting a gold complex in solution with the surface of a support forming species that are converted to a catalytically active form. The solution can be in the gas-phase (gas phase grafting) or in the liquid phase (liquid phase grafting). Liquid phase grafting and gas phase grafting using dimethyl gold acetylacetonate dissolved in acetone have been employed by Okumura and Haruta⁹⁷ to deposit gold on titania, alumina and silica and these catalysts show good activities for low temperature oxidation of CO and H₂.

2.3.6 Impregnation on as-precipitated supports

In 1996, Iwasawa's group⁹⁸ demonstrated a new method for the synthesis of highly active catalysts by impregnating a separately precipitated wet metal hydroxide support with an organometallic gold precursor. Co^{2+} , Fe^{3+} , Ni^{2+} , Zn^{2+} , Mg^{2+} and Cu^{2+} hydroxides were hydrolyzed from aqueous solutions of the metal nitrates using sodium carbonate solution in a similar manner to the coprecipitation method. Titanium hydroxide and vanadium hydroxide were similarly prepared from titanium-tetra-iso-propoxide and vanadium trichloride. The precipitates were repeatedly washed with deionized water to neutral pH. Phosphine stabilized gold was introduced by impregnation, as the gold phosphine complex $[\text{Au}(\text{PPh}_3)]\text{NO}_3$ dissolved in acetone and the gold phosphine cluster $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$ dissolved in methanol. They were vacuum-dried to remove the solvent at room temperature and then calcined at 673 K in a flow of air. During the calcination, the nitrate dissociates and leaves gold phosphine cations. The hydroxyl groups on the metal hydroxides bond to the phosphine groups,⁹⁹ and this interaction before calcination was suggested to be very important for the creation of highly active catalysts.¹⁰⁰ It is proposed that the high affinity of the ligand for gold prevents agglomeration and sintering, as it inhibits interaction between the gold atoms. However, the presence of triphenylphosphine in the calcination step has also been shown to affect the morphology of the support.¹⁰¹ This is also proposed as a factor as the catalysts are more effective when the support is amorphous.¹⁰⁰ Calcination decomposes the hydroxides to the oxides and the phosphine complexes are oxidized and lost. When the organic complex is supported on the wet hydroxide, it is more stable thermally than on Fe_2O_3 .⁹⁹ This effect causes the transformation of the support and the loss of the metal ligand to occur at similar temperatures (473-573 K) and it therefore follows that there is greater influence of the organic compound over the support.

2.3.7 Spray techniques

These involve a solution spray reaction method and a suspension spray reaction method and have been applied by Fan's group¹⁰² for the preparation of supported gold catalysts. They prepared Au/TiO₂ and Au/Al₂O₃ by the solution spray method using mixed aqueous solutions of HAuCl₄-TiCl₄ and HAuCl₄-Al(NO₃)₃ respectively, and found that the interaction between gold and the support was more intensified compared with those for analogous catalysts prepared by impregnation. However, agglomeration and sintering of gold particles tended to occur when a high spray reaction temperature was applied. Moreover, as one of the disadvantages of the solution spray method, some of the metal particles were partially buried or entrapped in the support particles, which led to a decrease in the number of exposed active sites. To solve this problem, the suspension spray method was developed to prepare Au/TiO₂, in which a suspension of TiO₂ powder was used instead of an aqueous solution of TiCl₄ (as in solution spray method). In this preparation, the support powder was suspended in distilled water by ultrasonic treatment; then an aqueous solution of HAuCl₄ added to obtain a spray suspension at the desired concentration. The suspension was atomized by an ultrasonic device to produce a mist without separation of components. This process was followed by calcination in an air flow under suction of an aspirator. The product fine particles were collected on a glass filter at the outlet. The quick decomposition of HAuCl₄, followed by a quick deposition of Au on TiO₂, prevented the coagulation of gold particles, leading to a higher dispersion of gold on the outer surface of support particles. Three different spray reaction temperatures of 673, 873 and 1073 K were used in the preparation and it was found that the activity of the catalysts for CO oxidation increased with increasing spray temperature. The surface structure of the catalysts is affected by the spray temperature. For samples prepared at relatively high spray temperatures, the gold particles were highly dispersed on the support, because the coagulation and sintering of gold particles were prevented by the strong interaction between gold and the support in the preparation process. The surface composition of gold was also shown to increase with increase in spray temperature.

2.3.8 Colloidal mixing

The use of “size-controlled” gold particles offers a route to synthesizing gold catalysts where the size of the gold particles is established before deposition on the metal oxide support and offers an insight into the role of the gold/metal oxide interface in catalysis. One possible strategy to prepare size-controlled gold particles is by use of monodisperse gold sols. Frens¹⁰³ reported the preparation of gold colloids in the range of 15-150 nm by reduction of chloroauric acid with sodium citrate and the tenfold difference in size could be produced by varying the amount of sodium citrate. The reduction of chloroauric acid with tetrakis(hydroxymethyl)phosphonium chloride results in gold particles in the range of 2 nm. Grunwaldt et al.¹⁰⁴ have extended the use of gold colloids to prepare Au/TiO₂, Au/Al₂O₃ and Au/ZrO₂ catalysts for the oxidation of carbon monoxide. This preparation procedure is composed of the following steps: the preparation of the gold sol, its purification if necessary, immobilization on metal oxides in acidic medium analogous to immobilization of metal complex anions, and finally, appropriate activation of the catalysts. In the preparation of the gold sol, successive charging of a vessel with continuously stirred water, sodium hydroxide solution, tetrakis(hydroxymethyl)phosphonium chloride (THPC) and chloroauric acid in the desired concentrations results in the rapid formation of a clear dark orange-brown solution. Five minutes are allowed between addition of THPC and HAuCl₄ and rigorous experimental cleanliness is required.¹⁰⁵ Extensive dialysis is performed to remove dissolved chemical species, e.g. Na⁺, OH⁻, Cl⁻, THPC and reaction products. To immobilize the colloid on the supports, the supports are suspended in water at pH 2 with ultrasonic treatment for about 15 mins. While stirring, an H₂SO₄-treated solution (pH = 2) with gold nanoparticles is added. After 10 mins, the suspension is then filtered by vacuum filtration, washed several times with water and dried at 323 K in *vacuo* for 15 h.

2.3.9 Other less widely employed methods in the synthesis of gold catalysts

Mallick et al.¹⁰⁶ have recently reported a novel approach for synthesizing supported gold catalysts referred to as the single step borohydride (SSBH) method. It is a simple single stage method, without pH control (the borohydride solution has a high pH) during the contact of the support with the gold source (an aqueous solution of HAuCl_4). The preparation is followed by washing with water and is reported to produce highly active and stable catalysts for CO oxidation with high gold dispersion. In a typical experiment, the support is suspended in distilled water with vigorous stirring and the required amount of the gold precursor added slowly with stirring. After complete addition, the mixture is aged for 30 mins. A solution of NaBH_4 is then added by use of an injection procedure under vigorous stirring condition and the suspension aged for a further 20 mins after which it is filtered, washed and oven-dried at 393 K for 30 mins.

Thin films of gold catalysts supported on Co_3O_4 were prepared by Kobayashi et al.¹⁰⁷ by magnetron r.f. sputtering deposition in an attempt to develop an optical fibre catalytic gas sensor. They reported that only co-sputtering of Au and Co_3O_4 produced catalytic films having CO oxidation activities higher than that of an Au-free Co_3O_4 film and that was much more active than Pt film catalysts. A proto-type model device of the gas sensor, fabricated from active Au/ Co_3O_4 film in combination with a temperature sensing device, gave an output temperature increase of about 7 K for 1vol% of CO in air at a device temperature of 423 K.

Pulsed laser deposition (PLD), with appropriate control of the amount of deposited material, has been used by Guzzi et al.¹⁰⁸ to produce a model Au/ FeO_x / SiO_2 / $\text{Si}(100)$ catalyst for CO oxidation. The catalysts were prepared by using the fundamental wavelength output (1064 nm) of a pulsed Q-switched Nd:glass laser with 35 ns pulse width and 1 Hz repetition rate. The laser beam was focused into a specific area on the target surface. The deposition process was carried out in a small ion-pumped vacuum system. The film thickness was monitored during deposition by a quartz crystal oscillator microbalance.

Venezia and coworkers¹⁰⁹ recently prepared gold catalyst supported on cerium oxide by a solvated metal atom dispersion (SMAD) technique, producing in one step zerovalent gold atoms on the support without metal precursor byproducts. The technique involves the following steps: deposition of solvent (acetone) on the walls of the metal vapor reactor cooled at 77 K (liquid nitrogen temperature); vaporization of the metal under vacuum followed by the rapid deposition of the atoms on the frozen solvent of the walls; and warming up of the condensate of solvated gold atoms, melting and collection of the products at the bottom of the reactor. The solution was then used to impregnate a weighed amount of ceria powder added into the reactor. The excess solvent was removed in a vacuum at room temperature. The catalyst was found to be more active for CO oxidation than Au/CeO₂ prepared by a coprecipitation method.

Gold nanoparticles supported on carbon nanotubes (CNTs) have been obtained using an electroless plating technique by Ma and coworkers.¹¹⁰ Multiwalled carbon nanotubes produced by using a catalytic decomposition of acetylene method were initially chemically modified with an H₂SO₄-HNO₃ treatment, and subsequently activated via a one-step activation approach. When the activated nanotubes were immersed in a gold-containing electroless plating bath, gold deposition occurred homogeneously on the outer surface of the nanotubes and displayed a spherical shape. The deposited clusters then catalyze further gold deposition on the tube surface (autocatalysis). Nanoparticles (around 3-4 nm in diameter) supported on the nanotubes resulted. These have potential applications as gold nanocatalysts.

Amorphous alloys of gold produced by arc-melting of the pure constituents have also been employed in gold catalysis. Shibata et al used a gold-zirconium alloy which afforded a Au/ZrO₂ catalyst⁵³ and the compositions Au₅FeZr₁₄ and Au₅AgZr₁₄ yielded the corresponding zirconia supported gold catalysts, promoted by the second element.¹¹¹ These catalysts have been used for CO oxidation.

2.4 FACTORS THAT AFFECT THE ACTIVITY OF SUPPORTED GOLD CATALYSTS

Catalytic properties of supported gold have been shown to depend very sensitively on a number of factors which can either be fine-tuned before catalyst preparation, e.g. choice of support and gold precursor, or during the preparation process variables such as temperature, pH of deposition, method of preparation or even after the preparation procedure. Conditions such as pretreatment prior to use in reactions and conditions of storage also affect the catalyst. Some of these factors are dependent on others and they vary from one reaction to another and also from one catalyst to another. There are however many discrepancies in the literature on the effects of these factors. Some of these factors and how they affect the activities of gold supported catalysts for various reactions are reviewed below.

2.4.1 Nature of support

A wide range of metal oxides and other materials have been studied as supports for various reactions over supported gold catalysts. By varying the support for gold, a wide control range over the reactions is available. Table 2.3 below gives effective support materials for gold for various reactions.

Table 2.3 Effective support materials for gold and reactions catalyzed by the gold.

<i>Reactions</i>	<i>Supports</i>	<i>Notes</i>
<i>Complete oxidation</i>		
CO	TiO ₂ , Fe ₂ O ₃ , Co ₃ O ₄ , NiO Be(OH) ₂ , Mg(OH) ₂	active even at -70°C active even at -70°C
CH ₄ (CH ₃) ₃ N	Mn ₂ O ₃ Co ₃ O ₄ NiFe ₂ O ₄	selective in H ₂ at 80°C as active as Pd selective to N ₂
<i>Partial oxidation</i>		
CH ₃ CH=CH ₂ → CHOCH=CH ₂	Bi ₂ Mo ₃ O ₁₂	enhanced catalytic activity with selectivity unchanged
C ₃ H ₈ → (CH ₃) ₂ CO	TiO ₂	selective in the presence of H ₂
C ₄ H ₁₀ → (CH ₃) ₃ COH	TiO ₂	selective in the presence of H ₂
C ₅ H ₁₁ OH → C ₄ H ₉ CHO	borosilicate glass	NO ₂ → NO
<i>Hydrogenation</i>		
CO ₂ , CO → CH ₃ OH	ZnO, Fe ₂ O ₃ , ZrO ₂	as active as Cu
H ₂ C=CH-CH+CH ₂ → H ₃ C-CH ₂ -CH=CH ₂	Al ₂ O ₃	highly selective
<i>Environmental</i>		
NO + C ₃ H ₆ + O ₂ → N ₂	ZnO, TiO ₂ , Al ₂ O ₃	less selective to N ₂ O
Decomposition of halogenated compounds	Al ₂ O ₃ , Co ₃ O ₄	longer life than Pt
HCN synthesis from chlorofluorocarbons	LaF ₃	more stable than Pt
Photocatalytic H ₂ production	TiO ₂	less active by 70% than Pt
<i>Others</i>		
CH≡CH + HCl → CH ₂ =CHCl	HAuCl ₄ /C	highest catalytic activity

Based on data contained in reference 49

In a study to investigate the role of the support in supplying oxygen during the CO oxidation reaction, Schubert and his co-workers¹¹² grouped the supports into two categories, the active and the inert metal oxides. They reported that gold catalysts with inert support materials such as SiO₂, Al₂O₃, or MgO are intrinsically less active and that improved activities with them could only be achieved with very small gold particles. For these materials, they expect oxygen adsorption to occur directly on the gold particles, either on defect sites or facilitated by variations in the electronic structure of small metal particles. On the other hand, active supports which are reducible transition metal oxides such as Fe₂O₃ exhibit significantly enhanced activities for CO oxidation, which is attributed to their ability to provide reactive oxygen. The existence of an oxygen reservoir on the support reduces the dependence of the turnover frequency on the gold particle diameter, since oxygen dissociation is no longer rate-limiting.

The diffuse reflectance Fourier transform infrared study of Grundwaldt and co-workers¹¹³ on Au/TiO₂ and Au/ZrO₂ catalysts demonstrated that the nature of gold sites in CO oxidation depends upon the support employed. Thus, while the number of low-coordinated gold sites was much higher on TiO₂, positively polarized gold atoms existed on ZrO₂. The better CO oxidation activity of Au/TiO₂ compared to that of Au/ZrO₂ in their study is attributed to the gold sites of low coordination, where the weakly bound CO molecules react with oxygen through an Eley-Rideal type reaction mechanism. The shape of the gold crystallites as influenced by the support, rather than their size, was thus shown to play a more important role in the catalytic activity.

The isoelectric points of the support materials also influence the pH needed to precipitate Au(OH)₃ during synthesis and hence the activities of the catalysts. Wolf and Schüth¹¹⁴ in a comparison of the isoelectric points of various supports showed that materials with an IEP between 6 and 9 e.g. TiO₂, ZrO₂ and Al₂O₃ result in active gold catalysts while SiO₂ with an IEP below 2 is an unsuitable support material for catalysts prepared by a deposition-precipitation method. SiO₂ does not allow the adsorption of [Au(OH)_nCl_{4-n}]⁻ species onto the support in the pH range needed to precipitate Au(OH)₃.

Haruta⁹² also reported that semiconductive metal oxides such as TiO₂, Fe₂O₃ and NiO provide more stable Au catalysts than do insulating metal oxides such as Al₂O₃ and SiO₂. Okumura and his co-workers¹¹⁵ however reported the turnover frequencies of Au supported on Al₂O₃, SiO₂ and TiO₂ at room temperature not to be very different, indicating that the contributions of the metal oxide supports are more or less similar in intensity. The difference is reported to appear in the moisture effect: Al₂O₃ and SiO₂ require a concentration of H₂O 10 ppm greater than for TiO₂ for CO oxidation to proceed at room temperature.¹¹⁶ Alkaline earth metal hydroxides such as Be(OH)₂ and Mg(OH)₂ are excellent choices for demonstrating high activity at a temperature as low as 196 K.⁸¹ In contrast, when an acidic material such as Al₂O₃-SiO₂, WO₃, or activated carbon is used as support, gold exhibits poor activity; even at temperatures above 473 K the conversions are below 100%.¹¹⁵

The use of mixed oxide systems as supports for gold catalysts has not been widely exploited. Grisel's group¹¹⁷⁻¹¹⁹ has used mixed oxide systems as supports for Au in a number of reactions. In one study, they compared Au/Al₂O₃ with Au/MO_xAl₂O₃ (M = Cr, Mn, Fe, Co, Ni, Cu and Zn) for low temperature CO oxidation and the oxidation of CH₄ and reported that in general, the addition of MO_x to Au/Al₂O₃ stabilized small gold particles present on the support in heat treatments up to 973 K. All the multi-component catalysts showed a remarkable enhancement in low temperature CO oxidation compared to the mono-component catalysts. The observed activities were reported to be directly related to the average Au particle size, whereas the identity of MO_x was less important. For CH₄ oxidation, the activity of Au/Al₂O₃ was also improved upon addition MO_x. The high activity observed for CuO_x and CrO_x containing catalysts was assigned to the intrinsically high CH₄ oxidation capability of these oxides themselves. In the other two studies,^{118,119} they investigated the role of a second oxide support on Au/Al₂O₃ on the selective oxidation of CO in the presence of H₂ and found that the addition of MO_x to Al₂O₃ improved the CO oxidation activity and selectivity towards CO₂. They ascribed the beneficial effect of MgO to the stabilization of small Au particles and that MnO_x and FeO_x implemented new routes for the supply of active oxygen needed for CO oxidation. Au/MnO_x/MgO/Al₂O₃ also showed higher selectivity towards CO₂ than Au/Al₂O₃. Wang et al¹²⁰, also studied composite oxide [MO_x/Al₂O₃ (M = Fe, Co, Mn, Cu)] supported gold catalysts for low temperature CO oxidation and found that the presence of a transition metal oxide proved to be beneficial to the improvement of catalytic performance of Au/Al₂O₃. They however attributed the enhancement in activity to the fact that the transition metal oxides are amorphous and lead to synergistic effects between gold and the supports. According to them, the nature of the transition metal oxide is important. In contrast to the above results, Mallick and Scurrill¹²¹ reported lower activities for CO oxidation over Au/TiO₂-ZnO catalyst compared with Au/TiO₂. Propene epoxidation has been studied on Au/TiO₂ and Au/TiO₂/SiO₂ by Mul and co-workers,¹²² and whilst Au/TiO₂ shows deactivation, the latter shows no deactivation.

2.4.2 Gold particle size effect

As early as 1970, Cha and Parravano¹²³ showed that the activity of gold catalysts for CO oxidation depended on the gold particle size and that this activity increased as the particle size decreased. This has been generally accepted as reported by more recent studies but there is contradiction in the literature on what the optimum size of the particles is, for various reactions. Bond²³ showed that as the size of metal particles decreases, the following happen: (i) the fraction of surface atoms increases, and because these vibrate more freely, the melting temperature falls and surface atom mobility increases; (ii) because the overlap of electron orbitals decreases as the average number of bonds between atoms becomes less, the band structure is weakened, and surface atoms in particular start to behave more as individuals than as a group; and, (iii) at the same time, a greater fraction of the atoms comes in contact with the support and the length of the periphery per unit mass of metal rises. These three factors could serve to explain the role of small gold particles in catalytic activity. Park and Lee⁹⁰ suggested that for CO oxidation the small gold particles are necessary as they provide sites for the reversible adsorption of CO and also increase the amount of oxygen adsorbed on the support oxides. Mavrikakis et al.¹²⁴ using DFT calculations showed that strong adsorption of CO and oxygen occurs in Au at step sites in agreement with experiments by Ruff et al.¹²⁵ where it is found that Au steps give rise to CO adsorption with a thermal desorption temperature close to that of CO on Cu surfaces. They indicated that the step density, defined as the fraction of atoms in the particle having seven or less neighbors, increases continuously as the particle size decreases. If the number of step-edge atoms of the particles in direct contact with the support is subtracted from the total number of step-edge atoms of the particles, a maximum emerges, characteristic of two-layer thick Au particles. This maximum gives the optimum particle size for CO and oxygen adsorption. Very large particles have much smaller relative concentration of step-edge sites thus providing low activity. Heiz and Schneider¹²⁶ prepared model catalysts by depositing size-selected Au anion clusters onto a single crystal of MgO and reported that the highest reactivity to CO was observed for the anion clusters consisting of 11 atoms. It was reported that 8 and 11 atoms are the smallest and second smallest number of atoms to exhibit catalytic activity for CO oxidation over MgO support. For the epoxidation of propylene over Au/TiO₂

catalysts in the presence of oxygen and hydrogen, Hayashi et al.¹²⁷ reported that when the gold particles are larger than 2 nm, the main product is propylene oxide which is the desired product, whereas smaller particles catalyze the formation of propane. The particle size however, depended on the metal loading, with loadings of 0.1 wt% and 0.4 wt% resulting in the larger gold particles and low metal loadings smaller than 0.1 wt% resulting in smaller gold particles. They attributed the product formation to be due to the shape of the particles. From TEM results, they found that the higher loadings gave particles having hemispherical shape, while the smaller loadings gave thinner and flatter particles. The critical diameter of 2 nm corresponds to a layer that is 3 or 4 atoms thick if the Au clusters are hemispherical in shape. The band gap measured with scanning tunneling spectroscopy shows that the electronic state of the Au clusters changes for layers that are 2 or 3 atoms thick.¹²⁸ Zanella et al.¹²⁹ reported the turnover frequencies of Au/TiO₂ catalysts for CO oxidation to increase with an increase in Au particle size up to a maximum of 2 nm, then decrease with a further increase in particle size. Haruta⁴⁹ and Valden et al.¹²⁸ however reported the optimum size of Au catalysts for CO oxidation to be 3-4 nm. Figure 2.2 below shows the dependence of activities of a number of gold supported catalysts with Au particle size for CO oxidation as reported by Haruta.

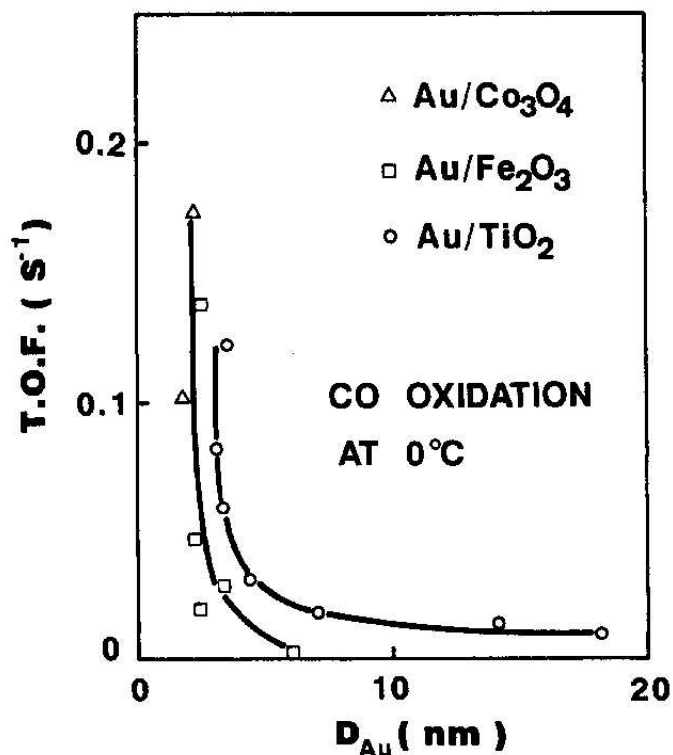


Figure 2.2. Turnover frequencies based on surface exposed gold atoms as a function of the mean particle diameters of gold in CO oxidation at 273 K, for various gold supported catalysts. (Source: Based on reference 49).

2.4.3 Method of preparation and variables involved

Reported activities of supported gold catalysts vary for different research groups because not only are the activities dependent on the different methods used in preparing the catalysts but also on variables involved in their preparation. Such variables include pH of deposition of the gold precursor, temperature of preparation, choice of precipitating agent, washing procedures employed, order of addition of the compounds involved etc.

Haruta and co-workers^{49,69} showed that the incipient wetness impregnation is unsuitable to produce highly dispersed gold catalysts and that because it requires the catalysts to be calcined at low temperatures (typically below 873 K), chlorine which is a catalyst poison still remains in the support and also that it results in relatively large gold particles. Other methods such as co-sputtering¹⁰⁷, chemical vapor deposition⁹³, adsorption of gold colloids on metal oxides¹⁰⁴ or supporting gold phosphine complexes on as-precipitated

wet metal hydroxides¹⁰¹ are suitable techniques. Coprecipitation is also reported to be an unsuitable method because in the preparation, much of the gold from the precursor remains in solution compared to that deposited on the support⁸⁴ and/or most of the active metal particles are buried within the support matrix and are therefore not available for catalysis²⁸. In addition, catalysts prepared by this method are always associated with chloride ions which are known to be a catalyst poison. The preparation which can be applied to the widest range of different support materials is the deposition-precipitation method. However, in deposition precipitation, careful control of the pH during synthesis is important. The suitable pH depends on the isoelectric point of the support material. The optimum pH of precipitation as reported by Kung and co-workers⁷⁴ lies in the range 7-8. Deposition-precipitation is not suitable for support materials with isoelectric points below 5 and also to carbon.⁹² At low pH values, there is a high concentration of chloride on the surface of the catalyst, which increases the mobility of gold on the support, leading to large gold particles during calcination. High pH values lead to little adsorption of gold precursor onto the support, leading to low gold loadings. Catalytic activity of gold supported catalysts therefore depends on the pH value of precipitation. Wang et al¹²⁰ reported that the dissolution of HAuCl_4 (gold precursor) in water can yield three different kind of gold species depending on the pH. At pH 5.5-7.0, most of the Au precursor is present as $\text{AuCl}_n(\text{OH})_{4-n}^-$, which can dissolve in water. At pH value around 7-8, most of the Cl^- will be displaced by OH^- leading to a neutral $\text{Au}(\text{OH})_3$ species, which precipitate from the solution. Under basic conditions, the $\text{Au}(\text{OH})_3$ can dissolve again as $\text{Au}(\text{OH})_4^-$. The pH of the precipitation solution is important because it determines the speciation of $\text{AuCl}_n(\text{OH})_{4-n}^-$ and influences the amount of chloride adsorbed on the support. They also reported that different metal oxides have different optimum pH values for synthesis of active gold catalysts. For example, the optimum pH of Au/ Al_2O_3 (the isoelectric points of Al_2O_3 is ~9) is 5.5-8.5; that of Au/ TiO_2 (the isoelectric points of TiO_2 is ~6-7) 7.0; and that of Au/ MgO (the isoelectric points of MgO is ~12) 9.6. These results are consistent with those of Lin and Wan¹³⁰ where they showed that the optimum pH for the preparation of Au/Y zeolite is in the range 5-6 and that at pH 7, there is an abrupt decrease in gold loading and in gold recovery from solution which is due to an increase in the concentration of neutral $\text{Au}(\text{OH})_3$ in solution. Li et al.¹³¹ however, prepared a series of

Au/TiO₂ catalysts by deposition-precipitation at different pH values from 7 to 11 and found that an increase in pH from 7 to 10 during precipitation led to more active catalysts and at pH 11, there was a decrease in activity. They reported the optimum pH value for the best catalysts to be 10 as earlier reported by Wolf and Schüth.¹¹⁴

The choice of precipitating agent used in the precipitation of the gold precursor has also been reported to affect the activity of the resulting catalysts. For example, Wang and co-workers¹²⁰ in preparing Au/MO_x/Al₂O₃ catalysts found that whilst there was no difference in the activity of catalysts prepared using NaOH, KOH, NH₄OH and Na₂CO₃ as precipitation agents, the use of urea resulted in more highly active catalysts. They attributed the higher activity catalysts using urea to be due to its slow and uniform decomposition to produce hydroxide ions in the preparation process. Zanella et al.¹²⁹ also recorded similar observations of more active Au/TiO₂ catalysts prepared by deposition-precipitation using urea as precipitating agent over NaOH and reported this to be as a result of being able to attain higher gold loadings with urea. For the epoxidation of propene over Au/Ti-MCM-48 catalysts, Uphade et al.¹³² obtained best catalytic results when NaOH was used as precipitating agent in the catalyst preparation compared with LiOH, KOH, RbOH and CsOH. They suggested that this could be as a result of the uniform and high dispersion of Au nanoparticles coupled with traces of alkali that could serve as a promoter. They also reported an increase in Au loading when the precipitating agent was changed from LiOH to CsOH and yet the worst catalytic performance was observed when CsOH was used to deposit gold. Hoflund and co-workers¹³³ prepared Au/MnO_x catalysts for low temperature CO oxidation by coprecipitation using the carbonates of Li, K and Na as precipitating agents and found that the use of Li₂CO₃ gave the most active catalyst followed by the catalyst prepared with K₂CO₃ and lastly that with Na₂CO₃.

When gold supported catalysts are prepared using HAuCl₄ as gold precursor, washing of the catalysts has to be carefully done to remove chloride, which is known to be a poison in oxidation catalysis. The procedure in which the washing is done has been reported to affect the properties of the catalysts. Wolf and Schüth¹¹⁴ observed that because freshly

precipitated catalysts prepared by coprecipitation are sticky and therefore difficult to wash, a second washing step after calcination improved the activities of the resulting catalysts. They found the temperature of 50% conversion for CO oxidation for coprecipitated catalysts to typically be reduced by more than 100 K after the catalysts were washed again after calcination compared to those that were not rewashed after calcination. For materials that were prepared by deposition-precipitation, the second washing after calcination did not lead to significant changes in the catalytic activity. Yang et al.¹³⁴ also explored different washing procedures to determine the most successful mean of removing chloride from Au/Al₂O₃ catalysts without removing gold in the process. They prepared various catalysts by the deposition-precipitation method, washed each of them with different wash solutions and calcined them at 873 K. They found that washing with formic acid at pH 6.5 retained the most Au as well as chloride and the resulting catalyst was inactive at 373 K for CO oxidation. Washing with acetic acid/tetramethyl ammonium hydroxide at pH 7 resulted in the highest degree of gold leaching. On the other hand, washing with ammonium hydroxide was the most effective way in removing chloride. There was some leaching of gold using this procedure, but the differences in the amount of Au and chloride removed could be minimized by increasing the stirring time in the wash solution, and this catalyst was the most active for CO oxidation. A recent study by Ivanova et al.¹³⁵ demonstrates that washing of Au/Al₂O₃ catalysts with water is not enough to remove chloride from the catalysts and that additional washing with ammonia solution replaced the chloride ligands of the gold complexes over alumina with OH⁻ groups thus reducing the chloride levels to undetectable limits.

The gold content of supported gold catalysts has also been reported to have an influence on their catalytic performance. The influence of the gold loading on catalytic activity was investigated by Wolf and Schüth¹¹⁴ for catalysts prepared by deposition-precipitation as well as for coprecipitated catalysts. They prepared Au/TiO₂ catalysts with gold contents of 0.9-10.7 wt% and calcined them at two different temperatures. After calcination at 473 K, the catalytic activity did not significantly depend on the loading with gold. In contrast, for the catalysts calcined at 573 K, a decreasing catalytic activity with increasing gold

loading was observed. While the 0.9 wt% Au/TiO₂ showed 100% CO oxidation activity at room temperature, the temperature of 50% conversion for the 10.7 wt% Au/TiO₂ was 432K. They attributed this to an increase in the ease of particle growth with upon calcination with the higher gold loading. Wang et al.¹²⁰ on the contrary reported an increase in activity with increase in gold loading for Au/FeO_x/Al₂O₃ catalysts in the range of 0.05-0.5 wt%, for CO oxidation. The catalyst with a gold loading of 0.5 wt% showed the highest catalytic activity and good catalytic durability. Similarly, Hodge et al.¹³⁶ prepared Au/Fe oxide catalysts with Au contents in the range of 1.15 to 2.10 at.% and found their activities for CO oxidation to increase significantly with gold loading. Whilst 1.15 at.% Au/Fe oxide gave conversions of about 3%, 2.10at.% Au/Fe oxide gave 100% conversions under similar conditions. For Au/TiO₂ (P25) having 0.5-3.1 wt% gold content, specific activities at 300K were reported by Bamwenda et al.¹³⁷ to be significantly lower at low loadings; the value of $6.5 \times 10^{-4} \text{ mol}_{\text{CO}}\text{s}^{-1}\text{g}_{\text{Au}}^{-1}$ for 3.1 wt% loadings falling by a factor of eight for 0.5 wt% catalyst, even though the average observable gold particle size (~ 3 nm) was similar for each loading. Other contradictory results reported by Moreau et al.¹³⁸ show the activities for CO oxidation of Au/TiO₂ catalysts with gold loadings in the range 0.06-1.9 wt% to depend linearly on gold loading indicating that the specific activity (per gram of gold) is the same for all the catalysts.

The length of time that the support and the gold precursor are allowed to mix is also reported to affect catalytic performance presumably because a finite time may be required in order to achieve speciation of the gold. Lin and Wan¹³⁰ prepared Au/Y-type zeolite catalysts for CO oxidation by an ion exchange method and varied the solution mixing time (1, 8 and 16 h). They found that the gold loading in each sample increased with the increase of solution mixing time due to more gold being deposited on the exterior surface of the zeolites, which is not active for CO oxidation. The activities of the catalysts therefore decreased with an increase in mixing time. Raphulu²² contrarily showed an increase in activity of Au/TiO₂-ZrO₂ catalysts prepared by a deposition-precipitation method for CO oxidation with an increase in aging time from 0 to 12 h. However, there was a significant decrease in activity for catalysts aged for 24 h. He suggested that an increase in the aging time led to an increase in the size of gold particles deposited on the

support for up to 12 h. However, after this optimum aging time, the gold particles tend to increase in size thereby leading to the decrease in activity observed.

Most of the syntheses of supported gold catalysts reported in literature have been carried out at room temperature. However, a few reporters have shown that the temperature of the solution during preparation could affect the activities of the resultant catalysts. Lin and Wan¹³⁰ prepared gold/Y-type zeolite catalysts at 298 K and 353 K and found that the solution temperature affected the metal loading, the percentage of Au recovery from solution, the average gold metal particle size and the maximum CO conversion on the catalysts. The catalyst prepared at 298 K had a metal loading of 1.8 wt%, an Au recovery of 50%, average gold particle diameter of 7.7 nm and the maximum CO conversion that was achieved was 9.3%. On the other hand, the catalyst that was prepared at 353 K gave a metal loading of 2.7 wt%, with 76% Au recovery from solution, average gold particle diameter of 4.1 nm and maximum CO conversion of 50%. Wolf and Schüth¹¹⁴ also reported a slight improvement in catalytic activity of several gold supported catalysts when the temperature of precipitation was increased from room temperature to 343 K. Haruta¹³⁹ reported that in the preparation of catalysts by the coprecipitation method, it is important to raise the solution temperature to 320-360 K to promote the exchange of chloride from the AuCl_4^- ion with OH^- .

2.4.4 Effect of calcination and temperature of calcination

Calcination has been employed in gold catalysis by various researchers for various reasons. For example, Bond and Thompson²⁸ reported that in the coprecipitation method of preparing gold catalysts, most of the active gold particles are buried within the support matrix and calcination is therefore necessary to create porosity by loss of water and hence create access to the gold particles. Haruta et al.⁶⁹ on the other hand, thought that calcination is necessary in order to decompose oxidic gold species present in the catalysts after the synthesis to metallic gold and form small particles, which they postulated to be the active catalytic sites. In some cases, calcination has also been used to convert the support metal oxide from an inactive oxidation state to an active one. For example for

Au/Co oxide and Au/Fe oxide catalysts prepared by coprecipitation method, calcining the freshly prepared catalysts at the appropriate temperature converts the metal oxide to Co_3O_4 and Fe_3O_4 respectively which are the most active forms for CO oxidation. Calcination has also been used to remove chloride poison.⁹³ Despite the fact that most researchers agree that calcination is necessary to yield more active catalysts, there have been discrepancies in what the optimum temperature of calcination is. Generally, very high temperatures of calcination results in sintering of gold particles thereby creating in poorly active catalysts. Haruta et al.¹⁹ and Wang et al.¹²⁰ suggested that the optimum calcination temperature for Au/TiO₂ and Au/MO_x/Al₂O₃ catalysts, that produce highly reduced gold particles without sintering, is 573 K. This is also consistent with the results of Daté et al.¹⁴⁰ who reported the optimum calcination temperature for Au/TiO₂ to be 573 K. Wolf and Schüth however found for many different supported gold catalysts that an increase in temperature of calcination from 473 K led to a significant decrease in catalytic performance and that the uncalcined materials had almost the same activities as those that were calcined at 473 K. Park and Lee⁹⁰ also found a decrease in CO oxidation activity for Au/Fe₂O₃ and Au/Al₂O₃ catalysts with an increase in calcination temperature from 373 K to 773 K. They reported an increase in Au particle size and an increase in metallic gold compared to ionic gold species with increase in calcination temperature. Bollinger et al.^{70,78} reported that impregnated Au/TiO₂ could become active catalysts after sequential pretreatments consisting of high-temperature reduction at 773 K, calcination at 673 K, and low-temperature reduction at 473 K but that deactivation was observed over a long period of time under reaction conditions. Haruta et al.^{69,141} also prepared a mechanical mixture of colloidal Au with TiO₂ powder and calcined them at different temperatures. Calcination at 473 K resulted in a sample composed of spherical Au particles which exhibited poor CO oxidation activity. The sample calcined at 873 K showed high CO oxidation activity which was comparable to that of an Au/TiO₂ catalyst prepared by the deposition-precipitation method.

Despite the controversies as to what the optimum temperature should be for the calcination of gold supported catalysts, there is another group of authors who believe that calcination is not a necessary step to obtain highly active catalysts. Tanielyan and

Augustine⁸⁸ showed that active Au/Fe₂O₃ catalysts could be prepared without heat treatment. According to their results, calcination at 653 K led to a significant decrease in activity (more than one order of magnitude). Khoudiakov et al.⁸⁷ also showed that for Au/Fe₂O₃ catalysts prepared by both deposition-precipitation and coprecipitation methods for CO oxidation, the as-prepared catalysts were more active than those calcined at 623 K.

2.4.5 Pretreatment conditions

Important also amongst the factors that affect the activity of supported gold catalysts is the conditions under which the catalysts are pretreated before the reaction. Pretreatment has commonly been used to activate these catalysts before use. Such pretreatments are carried out either in an oxidizing environment (e.g. using air or oxygen), in a reducing environment (e.g. in the presence of hydrogen gas) or in an inert environment (e.g. using Ar, N₂ or He gas) and are always done at temperatures above ambient. According to Haruta⁴⁹, for the CO oxidation reaction, supported gold catalysts should be pretreated in air normally at temperatures above 473 K and after this oxidizing pretreatment, CO and oxygen can coadsorb on the gold surface at room temperature.

Park and Lee⁹⁰ pretreated Au/TiO₂ catalysts for CO oxidation in air, N₂ and H₂ all at 373 K, and showed that the rates of CO oxidation were lower upon pretreatment in the reducing condition than in the inert condition, and the oxidizing pretreatment of the catalyst gave the highest activity. Gardner et al.¹⁴² examined Au/MnO_x before and after pretreatment in He at 328 K and reported that the pretreatment enriched the Au part of the surface of the catalyst and decreased the surface oxygen concentration on MnO_x which could be correlated with low temperature CO oxidation activity. Hoflund et al.¹³³ also investigated the effect of pretreatment of Au/MnO_x catalysts in He at 398 K, and found that whilst for one set of catalysts pretreatment did not have a significant effect on activity for CO oxidation, on another, pretreatment improved the activity. They attributed this effect to the possibility that this kind of reductive treatment could cause a change in the chemical state of the surface species and that species such as water and carbon

dioxide would desorb under the pretreatment conditions. In an earlier study¹⁴³, they showed that a 323 K pretreatment in 5vol% CO in He resulted in a significant improvement in activity. A similar pretreatment at higher temperatures did not result in a further improvement, and a mild pretreatment in an oxidizing environment resulted in poorer performance. Tanielyan and Augustine⁸⁸ also showed that oxidative pretreatment of a number of supported Au catalysts at 473 K gave the best results for CO oxidation compared to catalysts that were either similarly pretreated at different temperatures or in an inert environment. Cant and Ossipoff¹⁴⁴ on the contrary found that for Au/TiO₂ catalysts prepared by the incipient wetness method, only catalysts initially pretreated in hydrogen showed low temperature catalytic activity for the reaction of CO with oxygen and nitrogen oxides. Samples initially pretreated in O₂ showed no activity even after subsequent H₂ reduction.

2.4.6 Reaction conditions

Large variations are observed in the literature in the catalytic activities over catalysts of similar composition. Such discrepancies between reported activities also arise from differences in the conditions under which the reaction is performed.

It has been reported that the addition of water vapor to a CO oxidation feed had a positive effect in catalytic performance. Park and Lee⁹⁰ found enhancement in activity of Au/Fe₂O₃, Au/TiO₂ and Au/Al₂O₃ when the reaction gases were passed through a stream of water vapor compared with the corresponding catalysts studied under dry conditions. The presence of moisture was however found to have no effect on Au/Fe(OH)₃ prepared by impregnation of as-precipitated hydroxides¹⁴⁵ whilst a negative effect of moisture was reported by Bollinger and Vannice⁷⁰ for Au/TiO₂ catalysts for CO oxidation. Careful study of the effect of water on CO oxidation over Au/TiO₂ by Date and Haruta¹¹⁶ showed that depending on the partial pressure of water, its effect could be to suppress or enhance activity. The catalytic activity increased with increasing water partial pressure up to 200 ppm, then remained steady as the amount of water was increased to 6000 ppm. Further increase in the water partial pressure resulted in suppression of activity. In a separate

study, it was found that a H₂O partial pressure as low as 80 ppb could affect the activity of Au/Mg(OH)₂ for CO oxidation.¹⁴⁶ This extreme sensitivity of the CO oxidation activity of supported Au catalysts to moisture may contribute to the differences in reported catalytic activities. While it is clear that H₂O plays an important role in generating active supported Au catalysts, the exact nature of this role is not yet understood. It is possible that water has a direct effect on the catalytic active site. A model of the active site involving an ensemble of metallic Au atoms and Au⁺-OH has been suggested.^{28,147,148} It has also been suggested that water can remove chloride poison by hydrolyzing the Au-Cl bond.⁷⁴ Kung's group reported that the activity of an Au/Al₂O₃ catalyst lost by thermal treatment in a dry gas stream at 373 K, can be fully regenerated by exposure to water vapor at room temperature.^{147,148}

The partial pressures of the reactant gases also contribute to discrepancies between reported activities for gold supported catalysts. The work of Choudhary et al¹⁴⁹ showed the partial pressure dependence of the CO oxidation reaction on CO and O₂ at 293 K for Au/TiO₂ catalysts prepared by grafting an [Au₆(PPh₃)₆](BF₄)₂ complex onto TiO₂. In the study, the partial pressure of either CO or O₂ was maintained at 27.5 Torr while the other was varied (see Figure 2.3).

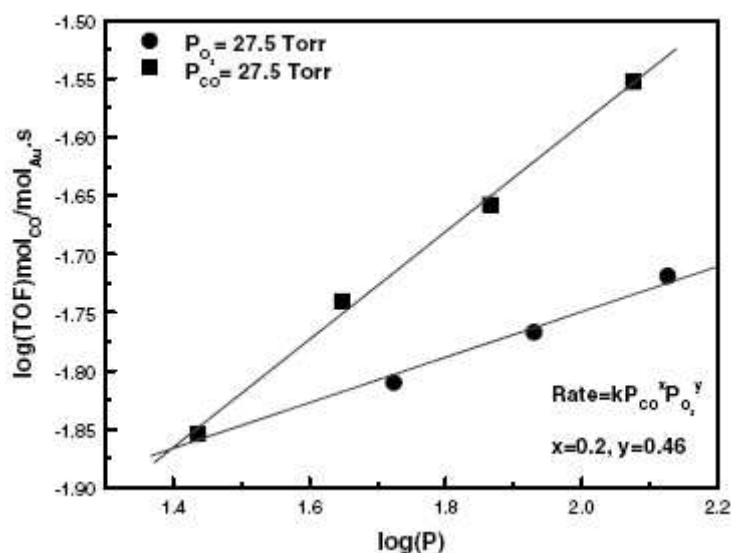


Figure 2.3. Partial pressure dependence of CO (at constant P_{O₂} = 27.5 Torr) and O₂ (at constant P_{CO} = 3.67 kPa) on the CO oxidation activity at 293 K (GHSV = 20,000 cm³/g/h). (Based on reference 149).

From the study, they found the order of the CO oxidation reaction to be 0.2 with respect to CO and 0.46 with respect to O₂. The results are in agreement with a recent study on similar systems, where the reaction orders were found to be 0.25 and 0.41 for CO and O₂ respectively.¹⁵⁰ On Au/TiO₂ catalysts prepared by the wet-impregnation method, Lin et al.⁷⁸ observed reaction orders of 0.24 (P: 17-187 Torr) and 0.4 for CO and O₂ respectively, at 313 K. Their studies indicate that the CO oxidation reaction orders are dependent on temperature and pressure.

The presence of hydrogen in the reaction medium has also been reported to affect the characteristics and the interaction of CO with gold supported catalysts for CO oxidation. The interest in the effect of H₂ arises from the potential application of these catalysts from the removal of CO from CO-contaminated H₂-rich feed gases for low temperature polymer electrolyte fuel cells (PEFCs) generated by steam reforming and/or partial oxidation of hydrocarbons or methanol. Schumacher et al.¹⁵¹ found that in the presence of hydrogen, the CO oxidation activity of Au/TiO₂ is reduced compared to a hydrogen-free atmosphere due to the parallel adsorption and reaction of hydrogen, which competes for the reactive oxygen species. The results correlate with those of Grisel et al.¹¹⁹ in which they reported that CO and H₂ compete for adsorption sites on metallic Au or at the Au/MO_x perimeter, and oxygen originates from the lattice of the metal oxide support in the vicinity of small Au particles or from activated oxygen at the Au/MO_x perimeter. They found that at low temperatures (< 373 K), there is high adsorption of CO leading to high CO₂ formation. However, higher temperatures decrease CO₂ selectivity due to higher H₂ oxidation rates.

2.5 NATURE OF ACTIVE GOLD SPECIES FOR CO OXIDATION

Although the catalytic activity of gold catalysts in low temperature CO oxidation has been intensively studied, the nature of the active species is still controversial. It has been suggested that the role of the metal oxide involves the stabilization of the gold

nanoparticles and that the reaction takes place on the gold surface.^{19,49,152,153} Other authors proposed that the reaction takes place at the gold/metal oxide interface and that the metal oxide could act as a source of oxygen.^{70,101,112} Also the electronic structure of gold in the active catalysts is unclear. Park and Lee⁹⁰ concluded from XPS investigations that oxidic gold is the active species. Minicò et al.¹⁵⁴ found a correlation between the occurrence of an IR band at 2159 cm^{-1} which can be assigned to the adsorption of CO on Au^+ , and the catalytic activity of coprecipitated $\text{Au}/\text{Fe}_2\text{O}_3$ catalysts. Boccuzzi et al.¹⁵⁵ carried out an FTIR and quadrupole mass spectral study of CO adsorption and oxidation with $^{16}\text{O}_2$ and $^{18}\text{O}_2$ on Au/ZnO catalysts and found that CO is activated by gold in two molecular forms a linear carbonyl species bonded at terrace Au sites and a carbonyl species bonded to Au peripheral sites. They also indicated a band related to CO adsorbed on Au oxidized sites and a scrambling reaction between CO and $^{18}\text{O}_2$ indicating that oxygen is also activated on gold sites. Through temperature-programmed reduction studies, Chang et al.¹⁵⁶ found ionic gold to provide active sites for CO oxidation.

In contrast, other authors have suggested low-coordination sites in the form of specific ensembles of gold atoms (metallic gold), to be the active species. Dekkers et al.¹⁵⁷ found through IR studies that during CO oxidation on Au/TiO_2 , the band responsible for CO adsorbed on ionic gold species was unstable whilst that of CO adsorbed on metallic gold at 2112 cm^{-1} was stable. They thus suggested that the reaction proceeded on metallic gold. A Mössbauer spectroscopic analyses of some supported gold catalysts by Tsubota¹⁵⁸ revealed that catalytic activity for CO oxidation on Au/TiO_2 occurred only in samples that had been calcined at 573 K and above and that in such active Au/TiO_2 samples no Au^+ species were present. He also concluded that for these samples, Au^+ species are inactive and that metallic gold species are required for the catalytic activity. However, in the same study, over $\text{Au}/\text{Mg}(\text{OH})_2$ he found that Au^+ species are important for the genesis of high catalytic activity and assumed that Au^+ species which were found at the interface between Au particles and the $\text{Mg}(\text{OH})_2$ support were the active species.

A mechanism for CO oxidation was proposed by Bond and Thompson²⁸ and they suggested that both Au^0 , Au^{x+} and the oxide support all have a role to play in the catalysis

of CO oxidation. They indicated that the interaction between gold and the support is particularly important since it dictates the nature of the interface at which the reaction takes place. Costello et al.¹⁴⁷ in studying the deactivation and regeneration phenomenon during room temperature CO oxidation over Au/ γ -Al₂O₃, considered the fact that thermal treatment at 373 K deactivated the catalyst. They also proposed that the active site is an ensemble consisting of a cationic Au⁺ with a hydroxyl ligand and neighboring metallic Au atoms as shown in figure 2.4 below.

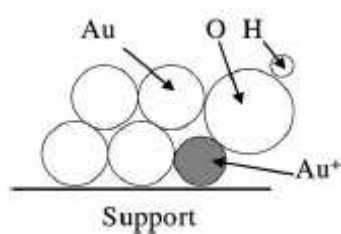


Figure 2.4: Schematic drawing of an active site for CO oxidation. (Based on reference 147)

They proposed that the OH group is associated with Au⁺ because alumina hydroxyls are stable to above 373 K. The CO oxidation reaction was proposed to proceed via the insertion of CO into the Au⁺-OH bond to form a hydroxycarbonyl, which is oxidized to a bicarbonate and the decarboxylation of the bicarbonate completes the reaction cycle.

2.6 INFLUENCE OF ADDITIVES IN SUPPORTED GOLD CATALYSTS

There are a few reports where supported gold catalysts have been modified with different elements or compounds and the additives have been shown to influence their catalytic behavior. Cant and Ossipoff¹⁴⁴ doped Au/TiO₂ catalysts for CO oxidation with 3d transition metals and found that cobalt had a promoting effect on activity, nickel had no effect whilst iron, chromium and especially manganese had detrimental effects on catalyst activity. They varied the cobalt loading from 0.5 to 5 wt% and found that the

catalysts with the optimum activity was that which contained 2 wt% of cobalt. Pestryakov et al.¹⁵⁹ modified γ -Al₂O₃ by addition of 5 wt% of Zr, Ce, La, and Cs oxides before gold impregnation and found that the modifying additions of rare and rare-earth metal oxides notoriously changed the electronic state of gold. These effects were reported to be caused not only by differences in the gold particle dispersivity, but also by interaction of gold atoms and ions with Lewis acid sites on the modified support. Addition of Ce and Zr oxides exerted an electron-seeking effect on supported gold, stabilized the oxidized state of the metal and increased the effective charge of gold ions. In contrast, La and Cs oxides lowered the effective charge of Au⁺ and Au_n^{δ+} and favored their fast reduction during redox treatments. In a follow up of the report by Haruta and co-workers that SO₂ treatment had a great negative impact on CO oxidation activity of supported Au catalysts,¹⁶⁰ Kim and Woo¹⁶¹ found a similar decrease in catalytic activity of Au/TiO₂ after SO₂ treatment.

The results obtained by Moreau and Bond¹⁶² in which they found that addition of iron in the preparation of Au/TiO₂, Au/SnO₂ and Au/CeO₂ catalysts for CO oxidation lowered the rate of deactivation of the catalysts contradict those obtained by Cant and Ossipoff.¹⁴⁴ Cant and Ossipoff attributed the improved stability of the inclusion of iron to the gold particles as due to the contact of an iron phase such as FeO(OH) with the Au. However, calcination removed the stabilization. Margitfalvi et al.¹⁶³ also found that Au/MgO catalysts modified with different amounts of iron and manganese showed improved and selective CO oxidation activities compared with the unmodified catalysts. Their results indicated that the addition of modifiers, such as iron and manganese, changed the type of “metal ion-metal nanocluster” active site involved in CO activation and that the new type of sites were more active. In another study, Margitfalvi and co-workers¹⁶⁴ modified Au/MgO catalysts for low temperature CO oxidation with ascorbic acid and found that the addition of ascorbic acid to the catalyst had a definite positive effect on the activity of Au/MgO. The effect strongly depended on the amount of ascorbic acid introduced which had a distinct optimum. Based on diffuse reflection UV-VIS and in situ FTIR spectroscopic data, they suggested that the addition of ascorbic acid slightly increased the

ionic gold/metallic gold ratio in the Au/MgO catalyst and suppressed the carbonate formation responsible for deactivation of the catalyst.

Hutchings' group¹⁶⁵ added nitrate ions to Au/TiO₂ catalysts, at different levels, using sodium nitrate and potassium nitrate and found that the addition of low concentrations of sodium nitrate (0.00625 and 0.0125 wt% of NaNO₃) led to a significant improvement in catalytic activity towards CO oxidation when compared with catalysts treated with water. However, higher concentrations of sodium nitrate led to much lower CO conversion and for the catalyst containing 0.0375 wt% NaNO₃, the conversion was very close to zero under their test conditions. Zhang et al.¹⁶⁶ found an enhancement of the CO adsorption energy and a remarkable blueshift of the CO stretch frequency in the presence of NO₂, when Ir was added to clean Au{111} surfaces. Gluhoi et al.¹⁶⁷ have also reported the promotional effect of doping of Au/Al₂O₃ catalysts for the total oxidation of propene with alkali (earth) metals. They found the doped catalysts to have very small gold particles and hence were much more active compared to the unpromoted catalyst. However, they found from the apparent activation energies of Au/Al₂O₃ and Au/MO_x/Al₂O₃ catalysts that the additives (Li₂O, Rb₂O, MgO and BaO) were not directly responsible for the higher catalytic activity, but that their role was to increase the concentration of the Au active sites.

In a similar study, Mallick and Scurrall¹²¹ introduced zinc oxide to titanium oxide in a 1:5 molar ratio before deposition of gold on the supports for CO oxidation. The addition of ZnO onto TiO₂ caused surface modification of TiO₂ that was associated with a negative charge effect on the catalytic activity of the resulting catalyst. For the two types of catalysts, prepared by supporting gold on TiO₂ and TiO₂-ZnO, a superior catalytic activity was achieved when only TiO₂ alone acted as the support.

2.7 CATALYTIC DURABILITY OF SUPPORTED GOLD CATALYSTS

The catalytic activity of a catalyst may decrease during its operational life for a number of different reasons: adsorption of impurities in the feed stream may poison the active sites; fouling of the surface and blockages of pores by carbonaceous residues formed during the reaction; loss of vital surface area by sintering which occurs by crystal growth and agglomeration; actual loss of catalytic species may also contribute to the decrease in activity of a catalyst if chemical transformations of the catalyst occur during the reaction. Gold supported catalysts are no exception to catalyst deactivation although in some cases, their activities have been shown to be quite constant with time.

Costello et al.¹⁴⁷ have studied the problem of deactivation and regeneration on Au/ γ -Al₂O₃ catalysts for CO oxidation. They found the activity of the catalyst to decline rapidly with time-on-stream. After 30 min time-on-stream, the conversion was about 6% from an initial 44%. The rate of deactivation depended on the operating conditions; increasing the O₂ content in the feed increased the initial conversion and also the deactivation rate. However, for selective CO oxidation in the presence of hydrogen, in addition to showing little deactivation, the presence of hydrogen could be used to regenerate the catalyst. It was also shown that water vapor could regenerate the activity of the CO oxidation-deactivated catalyst. Thermal treatment of an active catalyst at 373 K or higher in a dry gas stream also deactivated the catalyst and the activity of such a thermally treated catalyst could be restored by exposure to water vapor. With these results, they concluded that thermal deactivation was due to dehydroxylation of Au⁺-OH which can be reversed by exposure to moisture and that deactivation during CO oxidation is probably due to deprotonation of bicarbonate to a carbonate, such as by dehydroxylation. Regeneration by hydrogen is due to hydrogenation of the carbonate to a bicarbonate or to a hydroxycarbonyl and a hydroxyl.

Schumacher and co-workers¹⁶⁸ prepared Au/TiO₂ catalysts by a modified deposition precipitation method and followed their stabilities during CO oxidation reaction in both hydrogen-rich and hydrogen-free conditions for over 1200 min. There was a strong

decrease in activity at the beginning of the reaction, followed by a stabilization in the latter stages (1000 min). A similar behavior was also observed for other Au/metal oxide systems in their laboratory.¹⁶⁹ On characterizing the fresh and spent catalysts using electron microscopy and infra-red spectroscopy, they concluded that deactivation was caused by the accumulation and deposition of by-products on the catalyst surface and not by sintering of the gold particles. In the hydrogen-free atmosphere, the by-products were reported to be carbonate and formate species which were seen to increasingly cover the surface of the catalyst and act as catalyst poison. These species were also seen to outgrow the Au particle surface from the fact that CO adsorption on the Au particles was strongly affected. In the hydrogen-rich atmosphere, no significant contributions from carbonate and formate species were detected. Instead, there was evidence of the formation of water and surprisingly, intensity of the water band together with the CO and CO₂ signals decreased with time during the reaction. They concluded that water is a poison for the catalysts. It was also found that storing the catalysts in dark conditions reduced deactivation resulting from storage due to natural ageing.

Deactivation of Au/CeO_x catalysts has been reported by Kim and Thompson¹⁷⁰. Using X-ray photoelectron and infrared spectroscopic characterization methods, they reported the deactivation to be caused primarily by blockage of the active sites by carbonates and/or formate. These species were found to be formed by CO and H₂, and their formation was facilitated by oxygen deficient sites on ceria. The catalytic activity of the deactivated materials could be fully recovered by calcination in flowing air at elevated temperature.

Konova et al.¹⁷¹ found deactivation of Au/TiO₂ with time for CO oxidation and attributed it to the readiness of the catalyst to adsorb CO as surface carbonates and to stabilize them as a carbonate layer. Heating the catalyst resulted in the catalyst surface giving off CO₂ thereby reversing the deactivation. A second reason for the observed deactivation is the disturbance of the finely dispersed structure of the nanosized gold on the surface caused by the catalyst itself, by treatment with oxygen and by heat treatment. The resulting agglomeration causes slight irreversible deactivation.

The catalytic stability of Au/CeO₂ co-precipitated catalysts in the CO oxidation reaction in the presence of H₂ (preferential oxidation of CO) was tested by Luengnaruemitchai et al. over a two day period. The CO conversion and selectivity were maintained for the entire period with very slight loss of activity. The results showed the good stability of the Au/CeO₂ co-precipitation catalyst as compared with Au/Fe₂O₃ and Au/TiO₂ catalysts reported by Kahlich et al.³¹ and Lin et al.⁷⁸ respectively.

Hutchings et al.^{26,172} have studied deactivation using their knowledge of the effect of ageing of catalyst precipitation precursor in solution on the eventual catalyst performance for Au/CuO/ZnO, Au/ZnO and Au/CuO. These catalysts were prepared using a co-precipitation method in which the initial precipitate was stirred (i.e. aged) in the solution for 180 min before recovery and washing, and they were found to give sustained activity without deactivation during the 800 min experimental test. Similarly, Mallick and Scurrell¹²¹ also reported sustained activity of Au/TiO₂ catalysts for CO oxidation over a period of 180 min of time-on-stream.

Storage of gold supported catalysts has also been reported to lead to deactivation. Daté et al.¹⁴⁰ prepared standard samples of Au/TiO₂ catalysts and stored them in glass tubes for a month using three different conditions, i.e. office room, rest room and smoking area, while the unexposed reference sample was kept in a glass bottle with a screw cap. The catalysts stored under the three conditions showed deactivation towards CO oxidation after the storage period compared to the reference sample. In order to recover the initial catalytic activity, they carried out photo-cleaning of the samples using irradiation by light at 280 K after the introduction of oxygen into the reactor. During the photo-cleaning procedure it was found that oxygen was gradually consumed over a 10 h period. They assumed the deactivation to be caused by the presence of organic components such as house dust, amines, alkaloids, etc which must have been decomposed on the catalyst surface by photo-cleaning.

2.8 KINETICS AND MECHANISM OF CO OXIDATION OVER SUPPORTED GOLD CATALYSTS

There is no precise quantitative analysis of the reaction mechanism for the oxidation of CO over supported gold catalysts yet because there are few available kinetic results firm enough on which it might be based, and because of the large variety of types of supported gold catalysts that are active for CO oxidation. It is therefore not surprising that there is a possibility that the mechanism may differ from one catalyst to another. Table 2.4 shows how the orders of reaction and apparent activation energies for different supported gold catalysts vary from one to the other which confirms the possibility of different mechanisms.

Table 2.4: Kinetics of CO oxidation on supported gold catalysts; $r \propto P_{\text{CO}}^x P_{\text{O}_2}^y$ (Based on reference 27 and 28).

Support	[Au] (wt%)	d_{Au} (nm)	T (K)	x	y	E_A (kJ mol^{-1})	Reference
TiO ₂	3.3	2	273	0.05	0.24	34.3	69
TiO ₂	2.3	~30	313	0.24-0.6 ^a	0.4	~38 ^b -10 ^c	78
TiO ₂	1.0	33	293	0.43	0.03	~29	70
TiO ₂	1.0	33	313	0.56	0.13	-	70
α -Fe ₂ O ₃	0.66	4	304	0	0.05	35.1	69
Co ₃ O ₄	1.2	6-7	273	0.05	0.27	16.3	69
Ce(Ca)O _x	5	8	283-327	0.30	0.18	53.7 ^d	173
FeO _x	3.15	6.5	353	0.55	0.27	31	19
FeO _x	3	2.9	217	0.03	0.35	28	99,145
TiO ₂	3	-	263	0.25	0.41	24	150

^aThe order depends on the temperature and the carbon monoxide pressure range used.

^bBelow 300 K.

^cAbove 360 K.

^dTrue activation energy obtained from rate constants.

The subject of possible reaction mechanisms is complicated by the fact that there are several adsorbed states of the reactants and the location of the active sites is uncertain.^{70,78,157} It is known that oxygen does not extensively chemisorb on metallic gold

at reaction temperatures, even on small particles, but the fractional positive orders (Table 2.4) show that it cannot be gaseous oxygen molecules that enter the rate determining step: the oxygen has to be adsorbed somewhere and the evidence⁶⁹ points to the support. Carbon monoxide is significantly chemisorbed on supported gold catalysts, but much of it is on the support.⁷⁰ It is therefore unclear whether the species identified by FTIR as being carbon monoxide molecules chemisorbed at various locations on gold particles^{155,174} are, in fact, true reaction intermediates or not.

There are hence a number of possible scenarios to consider: Firstly, the reaction may occur exclusively on the support, involving adsorbed carbon monoxide molecules (which may have migrated from gold particles by spillover) and oxygen species which may be oxide or peroxide ions.⁶⁹ The second possibility is that the reaction may occur exclusively on metallic gold particles (or on some atoms acquiring some positive charge in consequence of accommodating some adsorbed species) between chemisorbed carbon monoxide molecules and oxygen atoms (which may have come from the support by reverse spillover). There is spectroscopic evidence^{49,174} for these reacting species being adsorbed on the same gold atom. Thirdly, the reaction may take place preferentially at the edges of gold particles, involving either sites on the support adjacent to the metal or sites on the metal influenced by the support.⁷⁸

A reaction mechanism proposed by Costello et al.¹⁴⁷ suggests that the CO oxidation reaction proceeds by insertion of an adsorbed CO into $\text{Au}^+\text{-OH}^-$ bond to form a hydroxycarbonyl. There then could be two possible reaction pathways for the hydroxycarbonyl. In one pathway, the hydroxycarbonyl is oxidized to a bicarbonate, which is then decarboxylated to $\text{Au}^+\text{-OH}^-$ and CO_2 . The other pathway is decarboxylation of the hydroxycarbonyl to CO_2 and Au-H , and the latter is oxidized to $\text{Au}^+\text{-OH}^-$ (Figure 2.5).

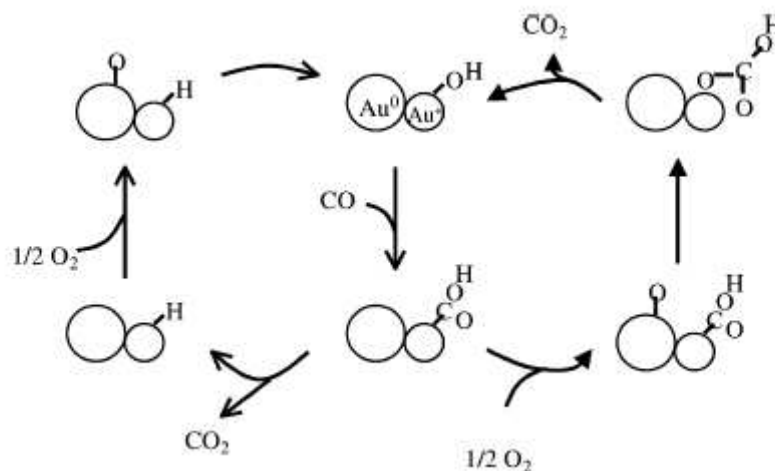


Figure 2.5: Proposed mechanism of CO oxidation on supported Au catalyst. (Based on reference 147).

This proposed cycle does not involve participation of OH radical-like species¹⁴⁶, or superoxide⁶⁹, or direct participation of the support¹⁷⁴ as suggested by others.

According to the mechanism proposed by Bocuzzi et al.¹⁷⁴, two independent pathways are probable for CO oxidation on supported gold catalysts. Firstly, molecular or atomic oxygen reacts directly with CO at the surface of the metallic particles, leading to the formation of molecular CO₂; and secondly, oxygen coming from the gas phase activates or enhances the reactivity of adsorbed CO species with the surface lattice oxygen to form carbonate-like species on the oxide support at the perimeter of the metallic particles. Moreover, CO molecules easily exchange oxygen atoms with the oxygen present in the gas phase. Their mechanism is represented in the following scheme (Figure 2.6).

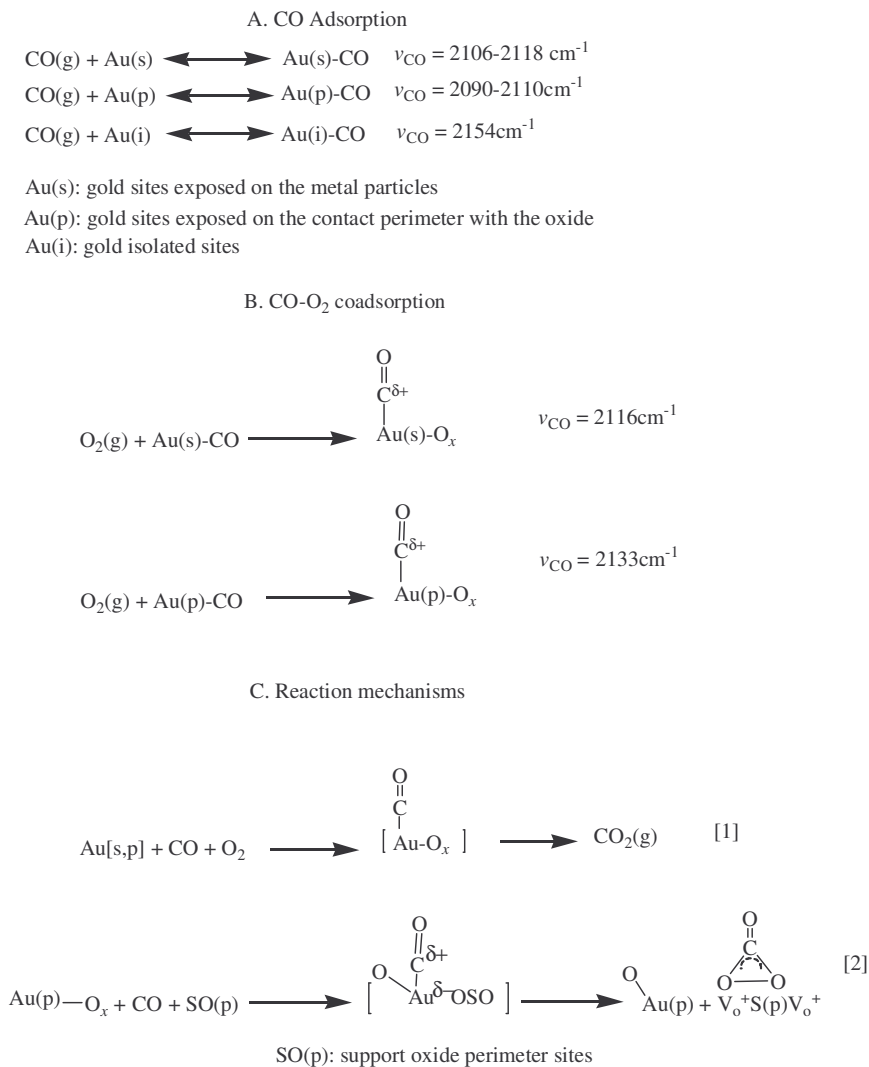
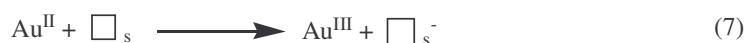
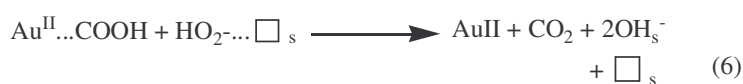


Figure 2.6: CO-O₂ reaction mechanism over Au supported on ZnO and TiO₂. (Based on reference 174)

A general mechanism involving reaction at the edge of a particle containing both gold atoms and ions Au^{III}, and involving the support was proposed by Bond and Thompson²⁸. According to this mechanism, a support hydroxyl ion attacks a carbon monoxide molecule on the gold (Au⁰...CO). The Au⁰...CO is attacked by a hydroxyl group either on a support cation or on a peripheral Au^{III} ion, forming a carboxylate group attached to the latter. This is in turn attacked by a superoxide ion, which is responsible for oxidizing two carboxylate ions: the hydroxyl group returns whence it came and is ready to re-engage in the catalytic oxidation. As a consequence, steps in the mechanism could include:



$\square_s^- = \text{anion vacancy.}$

The nett reaction, i.e. $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$, is obtained by doubling the processes represented by equations (1) – (3) and then adding all the processes in the set. A graphic representation of the initial stages of this mechanism is given in Fig. 2.7. From the figure, at the left, a carbon monoxide molecule is chemisorbed on a low coordination number gold atom, and a hydroxyl ion then moves from the support to an Au^{III} ion, creating an anion vacancy. At the right, the CO molecule and the hydroxyl ion react to form a carboxylate group, and an oxygen molecule occupies the anion vacancy as O_2^- . This carboxylate group is then oxidized by abstracting a hydrogen atom, forming carbon dioxide, and the resulting hydroperoxide ion HO_2^- then oxidizes a further carboxylate species forming another carbon dioxide and restoring two hydroxyl ions to the support surface.

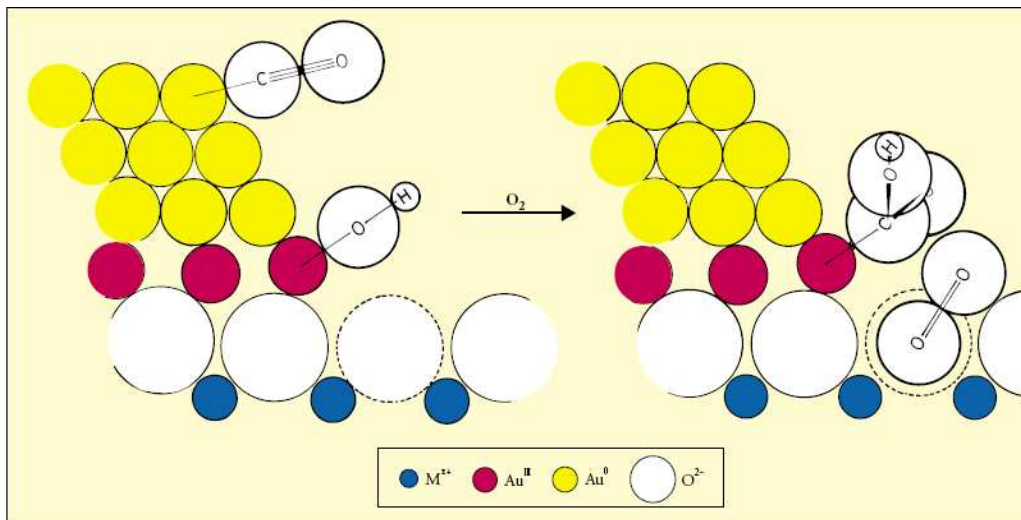


Figure 2.7: A representation of the early stages of the oxidation of carbon monoxide at the periphery of an active gold particle. (Based on reference 28).

They however suggested that the mechanism might not be the same on all supported gold catalysts. For example, one possible variant of the above scheme might apply for those oxides or under those conditions where anion vacancies are not formed: the oxygen molecule might simply be weakly bonded to a support cation instead of as shown in equation (4). Similarly, where mobile support hydroxyls do not exist, reactions (2) and (3) will not take place, and the mechanism may entail direct reaction of a chemisorbed carbon monoxide with an oxygen molecule or a superoxide ion.

2.9 SURFACE ANALYSIS AND CHARACTERIZATION OF SUPPORTED GOLD CATALYSTS

In order to gain an understanding into the origin of the catalytic activity of supported gold catalysts, several characterization techniques have been used and reported in the literature. Some of these techniques are uniquely suited for probing the catalysts under in-situ conditions whilst others can be adapted for the study of real-life systems. In this section some of the methods reported in literature are reviewed.

2.9.1 Transmission Electron Microscopy (TEM)

In catalysis, transmission electron microscopy is used to observe the size, shape and surface structure of the active sites that define the catalytic performance. In this characterization method, a beam of radiation is made to travel through vacuum in the column of the microscope which is then focused into a very thin beam using electromagnetic lenses. The electron beam passes through the sample and depending on the density of the sample, some of the electrons are scattered or disappear from the beam. The unscattered electrons hit a fluorescent screen, which gives rise to a “shadow image” of the specimen with its different parts displayed in varied darkness according to density. Because of the small size of gold particles, TEM observation is the most suitable method to analyze these items, especially when the gold loading is very small. Moreover, analytical TEM equipped with electron energy loss spectroscopy (EELS) capabilities yields information about chemical composition and electronic structure from a small area.^{175,176}

The major drawbacks of this method are firstly that there is always the risk that particles are not uniformly distributed over the support; it is thus desirable to inspect a number of different areas of the sample in order to obtain a representative impression. Secondly, reduction of the oxidized species to metal can occur during ultrahigh vacuum under the influence of the electron beam, and this can change the composition of the material being analyzed.²⁷

TEM and EELS investigations were carried out on Au/TiO₂ catalysts by Tanaka and Akita¹⁷⁶ who found that an epitaxial orientation, near (111)[011]_{Au}//(112)[021]_{TiO₂}, was preferred for gold and anatase titanium oxide while for rutile a TiO₂ support, the Au{111} plane was parallel to TiO₂{110}. The gold particle sizes were also found to be in the range 10-100 nm. Haruta et al.⁶⁹ studied some supported gold/metal oxide catalysts prepared by co-precipitation and found by TEM that for Au/ α -Fe₂O₃, small gold particles were homogeneously dispersed on the support particles with mean particle diameters of 3.6±1.3 nm. High magnification TEM showed that the gold particles were not spherical

but hemispherical in shape and that they were attached to the support with specific orientations.

References to other works where TEM has been used to determine gold particle size distribution and/or morphology include those by Mallick and Scurrall¹²¹, Gluhoi et al.¹⁶⁷, Moreau and Bond¹⁶², Kim and Thompson¹⁷⁰, Wolf and Schüth¹¹⁴, Lin and Wan¹³⁰, Grundwaldt et al.¹⁰⁴ etc.

2.9.2 Nitrogen physisorption (BET surface area)

Generally, for gas reactions catalyzed by solid materials, the formation of the product depends amongst other factors on the available surface area and so the greater the amount of surface area accessible to the reactants, the larger is the amount of reactants converted to products per unit time per unit mass of catalyst. Surface area measurement is therefore important in predicting catalyst performance and determining the role which the catalyst surface plays in any heterogeneous gas reaction although practically only a small fraction of the measured surface area is chemically active.¹ Volumetric physisorption of an inert gas such as nitrogen (nitrogen physisorption) is the method that has been commonly employed for surface area determination of supported gold catalysts. This method was developed by Brunauer, Emmet and Teller and the surface area derived is usually called the BET surface area, denoted S_{BET} and is expressed in m^2/g .

Many publications have reported the BET surface areas of gold supported catalysts, but their activities have not been directly correlated to their surface areas. In a recent paper, Kim and Thompson³⁶ showed that the BET surface areas of Au/CeO_x decreased with increasing calcination temperature and that the surface areas for the supported catalysts were similar to those of the support. For the low surface area catalysts, the gold loadings were much lower than the target loading of 5wt%. Gluhoi et al.¹⁶⁷ also compared the BET surface areas of several supported gold catalysts with the corresponding supports and found that although there is a slight decrease in surface area with gold deposition, the decrease is not very drastic. Solsona et al.¹⁶⁵ reported that although the modification of

Au/TiO₂ catalysts by addition of nitrate promoted its activity for CO oxidation, there was no significant change in the surface area of the catalysts following modification.

Similar to the report by Kim and Thompson³⁶, Hodge et al.¹³⁶ and Khoudiakov et al.¹⁷⁷ also found the BET surface areas of freshly prepared and dried Au/iron oxide catalysts to decrease quite drastically with calcination at 673 and 623 K respectively, and the activity of the calcined catalysts for CO oxidation also decreased significantly. The surface areas of Au(OH)₃ and Au₂O₃ could not be determined by nitrogen adsorption by Soares and Bowker, showing that the surface areas were less than 0.5 m²g⁻¹. Those of a physical mixture of the gold compounds and P25 titania were essentially the same as the P25 titania. Qiao and Deng¹⁷⁸ suggested a relationship between the high BET surface area of uncalcined Au/ferric hydroxide for selective CO oxidation in the presence of hydrogen with the high activity compared to the calcined samples.

2.9.3 X-ray diffraction (XRD)

X-ray diffraction information yields several important properties about supported gold catalysts. Firstly, it gives information as to whether the catalyst or a component of it is crystalline, non-crystalline or quasi-crystalline. Secondly, it can be used to estimate the size of the gold crystallites present in the catalyst. This is done by employing the Scherrer equation, $t = 0.9\lambda/\beta\cos\theta$, where t is the thickness of the crystal in a direction perpendicular to the diffracting planes, β is the full width at half maximum (FWHM) of the broadened gold peak in the diffraction pattern, λ is the X-ray wavelength and θ is the Bragg angle. Third, because XRD patterns yield d -spacings and unit cell dimensions, it gives an insight into the atomic constituents of the unit cell; and lastly, in favorable circumstances, from in-situ experiments, it can tell what influence reactant gas mixtures exert upon the internal structure as well as the crystalline order of the exterior surface of the catalyst.¹

Moreau and co-workers^{138,162} used XRD to show that Au/TiO₂ catalysts prepared at pH 8.5 contained small gold particles by the presence of a single weak peak at $2\theta = 77.4^\circ$,

which is characteristic of small gold particles. When the pH of the preparation solution was reduced to 6.4 and 2.5, the peaks became sharper, a characteristic of bigger gold particles. They confirmed the dependence of particle size on pH with TEM. For Au/TiO₂ catalysts prepared with different gold loadings, they found the intensity of the gold peak in the 2θ region from 75-85° to increase in intensity with Au loading. Margitfalvi et al.¹⁶³ showed from the XRD diffractograms of Au/MgO catalysts prepared by deposition-precipitation, that in the freshly prepared unreduced catalyst dried at 333 K, the support was fully hydrated [Mg(OH)₂] and no detectable gold could be seen. Reduction of the catalyst at 623 K resulted in full conversion of Mg(OH)₂ to MgO and the appearance of highly dispersed metallic gold. The mean gold particle size as calculated using the Scherrer equation was 3.8 nm. Using in-situ XRD, they were also able to show that the Au/MgO catalyst was stable in a CO atmosphere and that up to 523 K, no measurable changes in the gold particle size took place. Heating to 623 K resulted in an increase in the mean particle size up to 7.5 nm.

Pestryakov et al.¹⁵⁹ using the XRD patterns of unmodified Au/Al₂O₃ and Au/Al₂O₃ in which the supports were modified with 5 wt% of Zr, Ce, La, and Cs oxides, showed the gold dispersion in the modified catalysts to be higher than in the pure sample. Maciejewski et al. reported that the major Au peaks in the XRD pattern are due to the Au(111) and Au(200) reflections at 2θ = 38.2° and 44.4° respectively. Only weak gold reflections could be resolved around 2θ = 40° after subtraction of the support reflections for Au/TiO₂ and Au/ZrO₂. Chen and Yeh⁹³ prepared TiO₂ from Ti(i-OC₃H₇)₄ as a support for Au and found from XRD profiles that the freshly precipitated Ti(OH)₄ was dehydrated into amorphous TiO₂ after calcination at 473 K. The amorphous TiO₂ gradually converted to the anatase phase at higher calcination temperatures and finally transformed into the rutile phase at 973 K. The width of the diffraction peaks narrowed with increasing calcination temperature suggesting sintering into large particles on raising calcination temperature. This was confirmed by BET surface areas and TEM images.

The average Au particle size and crystalline phases present in Au supported on Al₂O₃, MgO, MnO_x and their composites was determined using XRD by Grisel and

Nieuwenhuys. They found that for all the catalysts, a maximum in reflection was detected at $d = 2.355 \text{ \AA}$, which is characteristic of metallic gold. A comparison of mean Au particles sizes determined by XRD and TEM agreed closely, except in the case of Au/MnO_x/MgO/Al₂O₃ where average the particle size obtained by XRD was 17.4 nm and that by TEM was $2.7 \pm 1.0 \text{ nm}$.

2.9.4 Inductively coupled plasma atomic emission/absorption spectroscopy

Inductively coupled plasma atomic emission/absorption spectroscopy (ICP) is used for determining the composition of a material that can be homogeneously dissolved (in a strong acid, for example) prior to being atomized on entry into a plasma for subsequent ionization and ion selection.¹ This technique has been widely used to determine the gold content of supported gold catalysts since in most cases, the actual gold loading is always lower than the intended gold loading.^{36,120,129,135,136,178,179}

2.9.5 X-ray photoelectron spectroscopy (XPS) and UV-induced photoelectron spectroscopy (UPS)

When a metal is exposed to a monochromatic X-ray source, electrons are emitted from the various defined core levels and from the broader valence bands. The difference between the energy of the radiation and kinetic energy of the emitted electrons and the work function is characteristic of every metal. The broad principles of UPS and XPS are the same but there are some important differences between the two. In UPS, the diminution in the energy of the stimulating source brings with it a better degree of resolution than in XPS and this stems in part from the greater monochromaticity of far-UV compared with X-ray light sources. However, UPS is restricted to electrons from valence shells. XPS and UPS can give information about the local chemical environment and bonding of the metal.¹

XPS and UPS analysis carried out by Guzzi et al.¹⁰⁸ over a Au/FeO_x/SiO₂/Si(100) model catalyst prepared by pulsed laser deposition showed that higher activity for CO oxidation

was associated with the amorphous iron oxide with Fe 2p binding energy of 711.3 eV. It was established that in developing the catalytic activity the gold should be metallic and the support should be amorphous with high binding energy and the reaction occurs at the perimeter of gold particles. In a similar study on Au/SiO₂/Si(100),¹⁸⁰ they used XPS and UPS to show that after implantation of Au on the support, the valence bands both at 2-3 eV B.E. and 6-7 eV B.E. (UPS) decreased. These peaks are characteristic of gold. They also found the formation of gold nanoparticles as evidenced by an approximately 1 eV shift of the Au 4f core level binding energy toward higher values (from 83.8 to 84.7 eV, Si 2p 99.2 eV). They also used XPS to show an agglomeration of the gold particles after CO oxidation catalytic measurements.

Characterization of Au/Al₂O₃, Au/MgO/Al₂O₃ and Au/MnO_x/MgO/Al₂O₃ prepared by homogeneous deposition-precipitation for CO oxidation in a hydrogen-rich environment by Grisel et al.¹¹⁹ using XPS all showed peak maxima at 87.3 and 83.7 eV binding energy, which are characteristic of 4f_{5/2} and 4f_{7/2} states of metallic Au. No ionic gold was detected although the apparatus they used had a low response and was probably insensitive to the presence of small amounts of oxidic Au. According to these results, they postulated a model in which CO is adsorbed onto metallic Au or at the Au/MO_x perimeter interface and reacted with oxygen, also present at the Au/MO_x perimeter interface.

Schumacher et al.¹⁸¹ prepared Au/TiO₂ catalysts by deposition-precipitation and applied three different conditioning procedures to them: (i) conventional conditioning by calcination in 10% O₂/N₂ at 673 K for 30 min, (ii) a reductive conditioning procedure including 45 min annealing in 10% H₂/N₂ at 473 K and (iii) a redox conditioning procedure including 45 min annealing in 10% H₂/N₂ at 473 K followed by 30 min calcination in 10% O₂/N₂ at 573 K. Characterization by XPS showed that the calcined samples consisted only of metallic Au with Au 4f binding energies between 83.9 eV and 84 eV. The redox conditioned and reductively conditioned samples showed metallic Au as the main component and small contributions of Au³⁺ species, which appeared at 1.9 eV higher B.E., at values of 85.7-86.0 eV. In contrast to these findings, Soares et al.²⁹ found

Au³⁺ contributions upon calcination up to temperatures of 723 K for a catalyst prepared via an incipient wetness method, while a similar conditioning procedure resulted in purely metallic Au particles for deposition-precipitation prepared catalysts upon calcination at temperatures of 393 K and higher.

2.9.6 Infrared (IR) spectroscopy

The analysis of IR spectra provides information on the physicochemical properties of surface complexes, the forms of adsorption on the substrate and molecular changes occurring during adsorption. Most of this information is important for elucidating mechanisms for adsorption and catalysis. The combination of IR spectroscopy and thermal desorption with mass spectrometric analyses of the desorption products can be used to prove that surface complexes participate as intermediates in the reaction, which makes it possible to establish that a reaction product can be formed from a certain surface compound, and the direct comparison of the rate constants or activation energies of the reaction of surface complexes with the corresponding reaction characteristics.

Infrared spectroscopic studies were carried out by Konova et al.¹⁷¹ to show that deactivation of Au/TiO₂ catalyst during CO oxidation was due to its readiness to adsorb CO as surface carbonates and to stabilize them as a carbonate layer. For CO oxidation over Au/FeO_x/Al₂O₃ catalyst Wang et al.¹²⁰ attributed an IR band at 2116-2131 cm⁻¹ to CO adsorbed on oxidized gold sites; a band at 2170-2190 cm⁻¹ to CO adsorbed on the support and two bands at 2361 and 2341 cm⁻¹ to CO₂ adsorbed on the catalyst. During the CO oxidation reaction, the band intensity of the CO₂ adsorption decreased, indicating that the desorption of CO₂ was relatively easy and could not be the rate-determining step of the reaction. Bands were observed in the 1700-1000 cm⁻¹ range which were assigned to carbonate-like species adsorbed on the support. The study of Boccuzz et al.¹⁸² showed that the carbonate-like species might be produced without the participation of molecular oxygen as no molecular oxygen was fed into the IR analysis system.

Co-precipitated Au/Fe₂O₃ catalysts for low-temperature CO oxidation were studied by Fourier Transform IR spectroscopy of adsorbed CO by Minicò et al.¹⁵⁴ They found that after preparation and exposure to a CO/O₂ mixture, gold was present on the surface mainly as Au¹⁺ and Au⁰ species. In the CO oxidation reaction, they found Au¹⁺ to be more active but less stable than Au⁰.

CO adsorption on metallic gold species has generally been reported to occur in the region of 2100-2110 cm⁻¹ whilst CO adsorption on ionic gold species is reported to take place at higher wavenumbers typically in the range 2110-2140cm⁻¹.^{69,70,164,174} Surface carbonates/carbonate-like peaks have been reported to be found at 1300, 1500, 2800 and 2900 cm⁻¹,¹⁷⁰ and 1700-1200 cm⁻¹.^{120,171}

2.9.7 X-ray absorption spectroscopy (XAS)

This spectroscopic technique has two variations that have been widely used for characterization in gold catalysis – extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). In an XAS measurement, a deep core electron is excited into a state above the Fermi energy. The photoelectron propagates as a spherical wave and scatters off surrounding atoms. The dipole mediated transition of an electron in a deep core state into an unoccupied state is then measured. XANES contains information about the valence and density of states of the absorber, as well as qualitative structural information and is often interpreted by simulation. EXAFS contains detailed information about the local atomic structure and is analyzed by curve fitting.

EXAFS has been used in supported gold catalysts to evaluate quantitatively the ratio between oxidized and reduced states of gold on the support surface.¹⁵⁹ These authors found most of the gold in Au/Al₂O₃ to be in the metallic state due to high-intensity signals of Au-Au bonds. The contribution of ionic states of gold (Au-O bonds) was only 8-15%. Haruta et al.⁶⁹ used EXAFS analysis to show the coordination number of Au atoms on Au/ α -Fe₂O₃ to be 8-10, corresponding to hemispherical Au particles with a diameter of 1.5-3 nm. In EXAFS studies of impregnated Au/ γ -Al₂O₃ and Au/MgO

catalysts,^{183,184} two distinct phases of gold were found. A part of the gold was structurally similar to metallic Au; the rest was present in the form of either two-dimensional or atomically dispersed clusters carrying a formal charge of +1. A study of Au L_{III} XAFS was made on ultrafine gold particles supported on $\text{Be}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$.¹⁸⁵ It was proposed that the catalytic activity for CO oxidation arose from the presence of Au-Au coordination in $\text{Au}/\text{Be}(\text{OH})_2$ and $\text{Au}/\text{Mg}(\text{OH})_2$, although in the latter Au-Au and Au-O coordination coexisted in the most active catalysts.

Pantelouris et al.¹⁸⁶ conducted X-ray adsorption spectroscopy for various Au compounds and reported that the absorption edge shift was not directly observable in the Au L_{III} XANES spectra for the Au^0 , Au^+ and Au^{3+} compounds. Guzman and Gates¹⁸⁷ used XANES to characterize gold complexes and clusters prepared from $\text{Au}^{III}(\text{CH}_3)_2(\text{acac})$ on MgO powder by adsorption of the precursor and subsequent treatment in flowing He and H_2 respectively. Their results indicate the existence of Au(III) in supported gold complexes prepared by adsorption of $\text{Au}^{III}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$. Treatment of these in H_2 at approximately 480 K caused reduction of the gold to zerovalent clusters. XANES also demonstrated the presence of zerovalent gold in the samples containing supported clusters that had been formed by treatment of the initial supported Au(III) complexes in He or H_2 at 573 K. Treatment of the samples containing mononuclear Au(III) complexes in CO led to partial reduction and formation of a mixture of Au(I) and Au(0).

2.9.8 Mössbauer spectroscopy

Mössbauer spectroscopy is used primarily to study the electron structure of materials. The resonant absorption is observed best in isotopes having long-lived, low-lying excited nuclear energy states. The resonant energies are extremely narrow and this extreme resolution allows the observation of the hyperfine interactions between the nucleus and the surrounding electrons. ^{197}Au is a valuable microscopic tool to characterize the electronic structure of gold supported catalysts. It is element-selective and sensitive to the local surroundings of the atoms. This makes it possible to resolve different metal sites

within the catalyst particles and thereby differentiate between metal atoms at the surface and atoms in the inner-core of the particles.¹⁸⁸

Wagner et al.⁸⁶ characterized gold/iron oxide catalysts obtained by different preparation methods with different gold loadings by Mössbauer spectroscopy in order to acquire information on the chemical nature of the two elements in the catalytic system and on the relationship between the physico-chemical characteristics and catalytic activity towards CO oxidation. They found the presence of metallic and oxidic gold species; the latter being more abundant in coprecipitated samples. Inverse precipitation resulted mainly in then formation of metallic gold. Catalytic activity tests revealed no correlation between activity and the gold species detected by Mössbauer spectroscopy.

A series of calcined and uncalcined gold/iron oxide catalysts were characterized by Hodge et al.¹³⁶ using Mössbauer spectroscopy. In the obtained spectra, they found one main absorption peak with an isomer shift of around -1.23 mms^{-1} typical of metallic gold for all the samples that were calcined. The spectra for the dried samples all showed two peaks, but with varying proportions. The first symmetric peak at a velocity of -1.23 mms^{-1} ascribed to metallic gold and a second asymmetric peak in the range $1-1.3 \text{ mms}^{-1}$ attributed to Au(III) oxyhydroxide.

Other methods that have been use in the literature to a lesser extent to characterize supported gold catalysts include: Diffuse reflectance ultraviolet visible (DR-UV/Vis) spectroscopy to examine the electronic state of Au in various catalysts;^{121,129,164,167} temperature programmed techniques such as temperature programmed desorption (TPD) to monitor the adsorption of reactant gases on different Au species,^{69,190} temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) to quantitatively determine amounts of different gold species present in an operating catalyst,^{163,164,187} to determine suitable conditions for the removal of carbonaceous deposits,³⁶ to determine the temperature at which the support changes state;¹⁷⁷ atomic absorption spectroscopy (AAS) for exact gold loading on a support;^{162,167,177} atomic

emission spectroscopy (AES) for surface composition of catalysts;¹⁵³ scanning tunneling microscopy and spectroscopy (STM/STS) for determination of the size and morphology of gold particles;^{153,191}

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 MATERIALS

The gold precursor $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ was obtained from Next Chimica and contained $50.0 \pm 0.5\%$ by weight of Au. Deionized water was used to prepare a 10^{-2} M solution of the HAuCl_4 . Titanium dioxide was obtained from Degussa as P-25 with a reported surface area of $50 \text{ m}^2/\text{g}$ and containing 80% of anatase and 20% of rutile phases. Nickel (II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ with 99% assay and manganese (II) tetrahydrate $[\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ of 98.5% purity were obtained from MERCK while zinc nitrate tetrahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, cobaltous nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ with minimum assay of 98% were obtained from SAARCHEM (Pty) Ltd and magnesium nitrate hexahydrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, copper (II) nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ and chromium (III) nitrate nonahydrate $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ with purity of $\geq 97.0\%$ were obtained from Fluka Chemie. Sodium borohydride (NaBH_4) was obtained from Fluka Chemie. Concentrated ammonium hydroxide (NH_4OH) was obtained from SAARCHEM and diluted to 15% using distilled water. Fine granular quartz (washed and calcined) was obtained from MERCK. Titanium (IV) isopropoxide (Acros Organics, 98+ %), propan-2-ol (ACE, 99.5%) and nitric acid (UniLab, 55%) and deionized water were used to synthesize TiO_2 . For the incorporation of ions into the catalysts, concentrated sulphuric acid (98% assay) was obtained from Glassworld, orthophosphoric acid of 85% purity from Aldrich, sodium hydroxide (98+ %) and potassium hydroxide (85%) from SAARCHEM. Lithium hydroxide (99+ %) was obtained from BDH Chemicals Ltd whilst hydrofluoric and hydrochloric (32%) acids were obtained from MERCK. The reactant gases 10% oxygen in helium and 20% carbon monoxide in helium were obtained from AFROX.

3.2 PREPARATION OF SUPPORTS

3.2.1 Preparation of metal oxide supports (M_xO_y)

The metal oxide supports (M_xO_y , where M = Zn, Mg, Ni, Fe, Cr, Cu, Mn and Co) were prepared from the respective metal nitrates by precipitation using ammonium hydroxide solution. Each of the metal nitrates was dissolved in distilled water with stirring. NH_4OH (15% solution) was then added to the solution dropwise under the same conditions until all the metal oxide was precipitated. The precipitate was then filtered, washed several times with distilled water, oven dried at 393 K and finally calcined at 723 K for 3 hours.

3.2.2 Preparation of metal oxide modified titanium oxide supports ($TiO_2-M_xO_y$)

The metal oxide modified titanium oxide supports ($TiO_2-M_xO_y$; where M = Zn, Mg, Ni, Fe, Cr, Cu, Mn and Co) were prepared by coprecipitation of each of the various metal nitrates with titanium dioxide using ammonium hydroxide solution as the precipitating agent. Each of the metal nitrates was dissolved in distilled water with stirring and the required amount of titania (Degussa P25) to give a $TiO_2:M_xO_y$ mole ratio of 5:1 added to the solution. NH_4OH (15% solution) was then added to the suspension dropwise under stirring conditions until all the metal oxide was precipitated from the nitrate. The suspension was then filtered, washed several times with distilled water, oven-dried at 393 K and finally calcined at 723 K for 3 hours.

3.2.3 Preparation and sulphation of titania from titanium (IV) isopropoxide

A measured amount of titanium (IV) isopropoxide was placed in a beaker and 8 times its volume of propan-2-ol added to it. This was placed in an ice bath with vigorous stirring and deionized water (pre-adjusted to pH 3 using dilute nitric acid) added to it dropwise until complete precipitation occurred. The resulting gel was refluxed at 353 K for 2 hours, allowed to cool, filtered and then dried at 393 K for 4 hours. This sample is

symbolized as TI373 hereafter. Aqueous impregnation using 0.01 M H₂SO₄ was used to incorporate SO₄²⁻ ions into the support at levels of 0.05, 0.1, 0.2, 0.4 and 2.5 mol% with respect to the support. The freshly prepared supports together with the ion modified supports were calcined at 673 K for 3 hours. These samples are symbolized as TI673, 0.05TI, 0.1TI, 0.2TI, 0.4TI and 2.5TI hereafter.

3.2.4 Preparation and sulphation of titania from titanium tetrachloride

Hydrated titania was prepared at pH 3 by adding aqueous ammonia to a stirred solution of titanium tetrachloride. The gel obtained was filtered and washed repeatedly to remove chloride ions (negative AgNO₃ test). This was then dried at 373 K for 10 hours. This sample is henceforth denoted as TT373. Aqueous impregnation using 0.01 M H₂SO₄ was used to incorporate SO₄²⁻ ion into the support at 2.5 mol% loading with respect to the support. The freshly prepared support and the ion modified support were calcined at 673 K for 3 hours. These samples are symbolized as TT673 and 2.5TT hereafter.

3.2.5 Preparation of potassium titanate

An amount (40 g) of TiO₂ (Degussa P25) was added to 500 ml of 6.25 M KOH solution in a 1 L stainless steel autoclave. The mixture was heated for 24 hours at 393 K with stirring at a rate of 500 rpm and a pressure of 2 bar. The autoclave was allowed to cool and the resulting material allowed to age for 48 hours in the base solution. It was then repeatedly centrifuged with deionized water until the conductivity of the wash water was below 30 μScm⁻¹. The material was dried in air at 393 K for 24 hours. This sample will be referred to as potassium titanate hereafter.

3.2.6 Incorporation of ions into TiO₂

PO₄³⁻, SO₄²⁻, NO₃⁻, F⁻ and Cl⁻ ions were incorporated into TiO₂ (Degussa P25) by aqueous impregnation using their respective dilute mineral acids (0.01 M) whilst Li⁺, Na⁺ and K⁺ were incorporated using 0.01 M solutions of their respective hydroxides. The

incorporation was done at ion levels of 0.05, 0.1, 0.2, 0.4 and 2.5 mol% with respect to the support. After the impregnation, the samples were dried in air at 393 K for 4 hours and then calcined in air at 673 K for another 4 hours. For the reference catalyst, titania was immersed in distilled water, dried in air at 393 K for 4 hours and calcined in air at 673 K for 4 hours.

3.3 PREPARATION OF CATALYSTS

3.3.1 Deposition-precipitation method

Gold supported on titania (Degussa P25) was prepared by the deposition-precipitation method with intended gold loadings of between 0.2 and 1 wt% with respect to the support. About 5 g of the supported was suspended in 100 ml of deionized water with stirring and the required amount of 0.01 M H₂AuCl₄ solution slowly added to it dropwise with continuous stirring. After complete addition, the slurry was allowed to stir for a further 2 hours after which a solution of 15% NH₄OH was added to it dropwise still under stirring conditions until the pH rose to between 8 and 8.5. This was then aged for 2 hours, filtered, the filtrate washed five times with 200 ml portions of warm (353 K) deionized water and dried in air at 393 K for 2 hours.

3.3.2 Single step borohydride method

This method was used to support gold on the metal oxide supports, the metal oxide modified titanium oxide supports, potassium titanate, the ion-modified titania supports and the reference support, with a intended gold loading of 1 wt% with respect to the support. In order to study the influence of gold loading on activity of the catalyst, Au/TiO₂ (TiO₂: Degussa P25) catalysts were also prepared by this method, varying the gold loading between 0.2 and 1 wt% with respect to the support. In a typical preparation, 3 g of the support is suspended in 500 ml of distilled water and vigorous stirring applied. The required amount of 0.01 M H₂AuCl₄ solution to give the desired gold loading was

then added dropwise with continuous stirring. After addition of HAuCl_4 , the suspension was aged for 30 min. A freshly prepared solution of NaBH_4 in ice cold distilled water was then rapidly added to the suspension by use of an injection procedure under vigorous stirring conditions. Upon addition of the NaBH_4 solution, the pH rose to 8.5. The suspension was again aged for a further 30 min after which it was filtered, the filtrate washed five times with 200ml portions of warm (353 K) distilled water and then oven-dried at 393 K for 2 hours.

3.3.3 Aqueous impregnation method

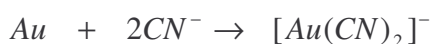
A slurry of titania (Degussa P25) was made by adding 3.0 g of the support in 20 ml of distilled water with stirring. 30.5 cm^3 of 0.01 M HAuCl_4 solution was then added to the slurry dropwise with continuous stirring. This gives an intended gold loading of 1 wt% with respect to the support. This was then aged for 3 hours, then filtered and washed five times with 100 ml portions of distilled water. The solid obtained was put back in about 10 ml of distilled water and ammonia solution added to it with stirring until the pH did not change (pH 12.5). This slurry was again filtered, washed five times with 100 ml portions of distilled water and dried in an oven at 373 K overnight.

3.3.4 Incorporation of ions into gold supported titania catalysts

PO_4^{3-} , SO_4^{2-} , NO_3^- , F^- and Cl^- ions were incorporated into 1wt% Au/TiO_2 (TiO_2 : Degussa P25 and titanium isopropoxide derived TiO_2) by aqueous impregnation using their respective dilute mineral acids (0.01 M) whilst Li^+ , Na^+ and K^+ were incorporated using 0.01 M solutions of their respective hydroxides. The incorporation was carried out at ion levels of 0.4 and 2.5 mol% with respect to the support. After the impregnation, the samples were dried in air at 393 K for 4 hours. As reference sample, unmodified 1 wt% Au/TiO_2 was immersed in distilled water and dried in air at 393 K for 4 hours.

3.3.5 Leaching of Au/TiO₂ catalysts

In order to gain some insight into the possible role of metallic gold on the catalytic activity of Au/TiO₂ catalysts for CO oxidation, 1wt% Au/TiO₂ catalysts prepared by the deposition precipitation method was leached with potassium cyanide solution at different Au:CN⁻ ratios. In the leaching process, some metallic gold forms a complex with the cyanide ion and is therefore removed from the catalyst according to the following equation:



According to the equation, 2 moles of CN⁻ are required for every mole of gold. The leaching was carried out at Au:CN⁻ molar ratios of 1:1, 1:2 and 1:6.

The pH of the required amount of a 0.01 M KCN solution for the leaching process was adjusted to 12 using 25% NH₄OH solution. The required mass of catalyst was then added to the solution under stirring conditions and allowed to stir for 5 mins. The suspension was filtered, washed several times with distilled water and oven-dried at 393 K for 2 hrs.

3.4 CATALYTIC ACTIVITY MEASUREMENTS

The activities of the catalysts towards CO oxidation were measured using a fixed bed flow reactor with a thermocouple inserted into the catalyst bed for temperature measurements (figure 3.1). The masses of catalyst used in each case varied from 50 mg to 200 mg depending on how active the catalyst was. In the experiment, the mass of catalyst was diluted with an amount of quartz to make up 500 mg and placed in the reactor bed. This was then pretreated in-situ with 10% oxygen balance helium at a flow rate of 40 mlmin⁻¹ at 573 K for 2 hours. This was then allowed to cool to room temperature still under a flow of oxygen. The reactant gas mixture consisting of 10%CO, 5%O₂ and

85%He at a total flow rate of 40 mlmin^{-1} was admitted through the catalyst in the reactor and the effluent gases analyzed by means of gas chromatography.

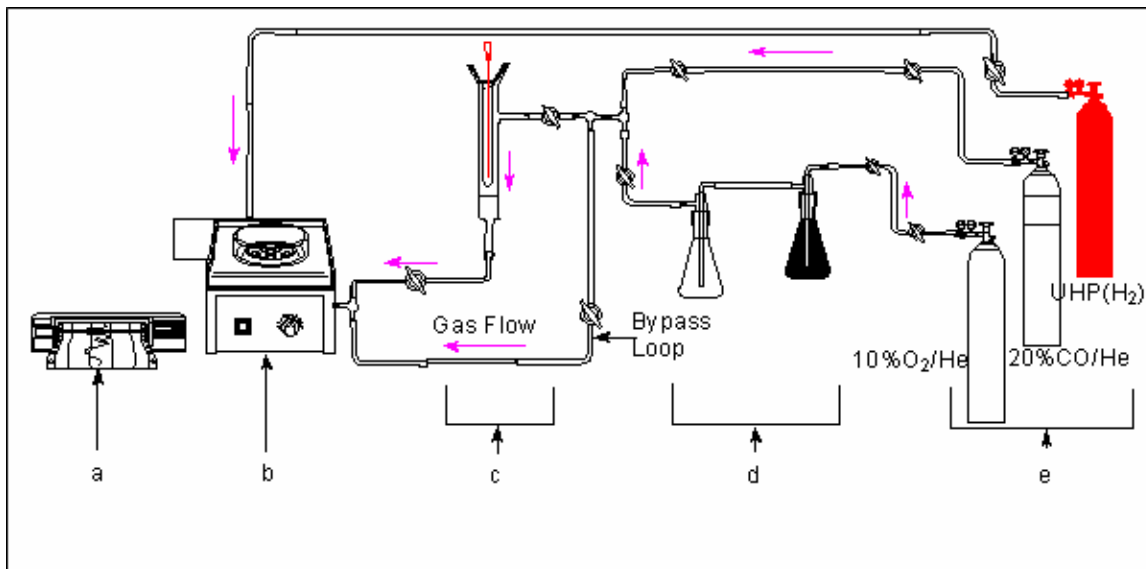


Figure 3.1: Schematic diagram of CO oxidation flow chart: (a) integrator, (b) gas chromatograph equipped with thermal conductivity detector, (c) fixed bed flow reactor equipped with thermocouple, (d) drying agents (activated carbon & anhydrous NaOH pellets), (e) gas cylinders.

3.5 CALCULATIONS

$$(a) \% \text{ Conversion} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100\%$$

$$(b) \% \text{ wt Au} = \frac{M_{Au}}{M_{Au} + M_{sup}} \times 100\%$$

Where:

CO_{in} = peak area of carbon monoxide for the reactor inlet gas stream obtained from chromatogram.

CO_{out} = peak area of carbon monoxide for the reactor outlet gas stream obtained from the chromatogram.

M = molecular weight.

sup = support.

3.6 CATALYST CHARACTERIZATION

3.6.1 Surface area determination

The surface areas of some of the supports and catalysts were determined by BET surface area measurements using a Micromeritics ASAP 2010 porosimeter. In a typical experiment, about 250 mg of sample was placed in the sample holder and degassed by passing nitrogen over it whilst heating it at 393 K for 6 hours in order to remove any adsorbed water or other volatile materials from the surface of the sample. After cooling down to room temperature, the sample was then removed from the degassing pot to the analysis pot where it was made to adsorb nitrogen at liquid nitrogen temperature. The amount of nitrogen adsorbed was then used to determine the surface area of the sample.

3.6.2 X-ray diffraction (XRD)

Information on the structure and composition of the supports and catalysts were obtained by measuring their XRD patterns. This was performed on a Siemens D5000 powder x-ray diffractometer using Ni-filtered Cu K_{α} radiation at 45kV and 35mA.

3.6.3 High resolution transmission electron microscopy (HRTEM)

In order to determine the gold particle sizes of some of the catalysts, high resolution TEM images were obtained using a JEOL 2010 electron microscope with a LaB₆-cathode operated at a voltage of 200 kV. Powdered samples were suspended in ethanol with sonication treatment for a few minutes, after which an amount 2 μ l of the suspended solution was dropped onto a carbon coated grid using a micropipette. The copper grid was then left for 2 minutes to allow for the evaporation of ethanol before the grid was inserted into the instrument. Micrographs of the samples were then obtained at high resolutions.

3.6.4 X-ray photoelectron spectrometry (XPS)

Scanning X-ray photoelectron spectroscopic measurements were carried out at the National Metrology Laboratory of the Council for Scientific and Industrial Research in Pretoria. A PHI Quantum 2000 spectrometer was used. The samples were lightly pressed into stainless steel cups of approximately 4 mm diameter and 3 mm depth. The X-rays generated were monochromatic Al K_{α} with an energy of 1486.6 eV and power of ~20W. For the wide scans a pass energy of 117.4 eV was used whilst for the narrow scans, 29.35 eV was used, and, in order to minimise as far as possible any X-ray beam induced changes in the state of the samples, particularly with respect to gold, spectra were collected over a relatively short (*ca.* 0.5h) period. Charge neutralization was applied and the base vacuum was less than 1E-8 Torr. In addition, a binding energy reference value of 284.8eV was applied to the C(1s) peak due to the presence of adventitious hydrocarbon species on the surface. There was no evidence that the carbon signals were in any way different for the various samples and, in any event deconvolution of the C(1s) signals was always carried out prior to the assignment of the reference value to the most prominent sub-component for each sample. The beam diameter was 100 microns and the scanning area was 500 x 500 microns.

3.6.5 Secondary ion mass spectrometry (SIMS)

A Time of Flight Secondary Ion Mass Spectrometer (ION TOF 5) at the National Metrology Laboratory of the Council for Scientific and Industrial Research, Pretoria was used for SIMS data collection. The sample powders were pressed onto indium foil and analyzed as is. A 25 kV Bi⁺ ion beam with a pulsed current of 1 pA and a pulse rate of 10 kHz was used. The extractor was operated at 2 kV and charge neutralization was applied. The beam diameter was 1 μ m and the analysis area was 100 x 100 microns and 128 x 128 pixels.

3.6.6 Fire assay and gravimetric finish

The actual gold content of the catalysts were measured using fire assay for total gold followed by gravimetric finish at Performance Laboratories in Randfontein.

CHAPTER 4

THE EFFECT OF ADDITION OF Mn_xO_y TO TiO_2 AS SUPPORT FOR Au ON CO OXIDATION ACTIVITY

4.1 INTRODUCTION

Relatively recently, there have been many reports on the preparation of highly dispersed gold and its catalytic applications. Gold has been found to be remarkably active for low temperature CO oxidation when it is well dispersed and deposited on various metal oxides or hydroxides of alkaline-earth metals. This surprising activity is now being studied by various groups, because the low temperature CO oxidation is an attractive way of purifying air in houses and offices, of reducing CO in industrial and automobile emissions and also finds applications in CO detection devices etc.⁴⁹

The choice of support material has been reported to have a significant effect on the activity of the resulting catalysts. Au supported on TiO_2 has been most widely studied for CO oxidation because it yields some of the most active catalysts. However, there could be possibilities of enhancing the activity of Au/ TiO_2 catalysts by modifying the surface of TiO_2 through addition of a second metal oxide support.

There are reports where mixed oxide support systems have been shown to have a beneficial effect on the activity of the resulting catalysts over each of the single oxide systems. Pestryakov et al.¹⁵⁹ have shown that modifying additions of rare and rare-earth metal oxides notoriously change the electronic state of supported gold. They found that these additives modify the metal particle dispersivity and also change the nature of the interaction of gold atoms and ions with Lewis acid sites of the modified support. Addition

of Ce and Zr oxides to γ - Al_2O_3 before gold addition exerted an electron-seeking effect on supported gold, stabilized the oxidation state of the metal and increased the effective nuclear charge of gold ions whereas addition of La and Cs oxides as modifiers lowered the effective charge of Au^+ and $Au_n^{\delta+}$ and favoured their fast reduction during redox treatments. Grisel and Nieuwenhuys¹¹⁸ also found that addition of MO_x ($M = Mg, Mn$) to Al_2O_3 before gold addition improved the activity and selectivity of the catalysts towards CO_2 for selective oxidation of CO in the presence of H_2 . They ascribed the beneficial effect of MgO to stabilization of small Au particles which are more active for the reaction. The MnO_x is thought to supply the active oxygen needed for the reaction. In a similar study carried out by Wang et al.¹²⁰, several composite oxide MO_x/Al_2O_3 supported gold catalysts were prepared for low temperature CO oxidation and it was found that the presence of transition metal oxides was beneficial to the improvement of catalytic performance of Au/Al_2O_3 .

With these background considerations and the fact that no reported attempts have been previously made to improve the activity of Au/TiO_2 catalysts for CO oxidation by the addition of a second metal oxide to TiO_2 , the objectives of this section were to make mixed oxide based TiO_2 supports for gold catalysts, and compare the activities of these catalysts with each of the mono-component supported gold systems.

4.2 RESULTS AND DISCUSSION

4.2.1 Catalyst characterization

4.2.1.1 X-ray diffraction (XRD)

Figures 4.1 to 4.8 show the X-ray diffractograms of TiO_2 and $TiO_2-M_xO_y$, Au/M_xO_y and $Au/TiO_2-M_xO_y$ for all the metal oxides studied, measured from 2θ values from 20° to 60° . The assignment of the various crystalline phases are based on the JCPDS powder diffraction file cards.¹⁹²

The XRD profile for TiO_2 fits with the JCPDS data, with the major peaks being the anatase phase (101), (103), (004), (112), (200), (105) and (211) peaks at $2\theta = 25.35$, 37.01 , 37.84 , 38.64 , 48.14 , 53.97 and 55.18° respectively and the rutile phase (110), (101), (200), (111), (210), (211) and (220) peaks at $2\theta = 27.49$, 36.15 , 39.27 , 41.32 , 44.14 , 54.44 and 56.76° respectively.

Modifying the surface of TiO_2 with M_xO_y leads to a decrease in the intensity of the TiO_2 peaks as expected. In figure 4.1, the obtained profile for cobalt oxide fits with the JCPDS data for Co_3O_4 with the peaks corresponding to the (220), (311), (222), (400) and (511) planes at 2θ angles of 31.34 , 36.93 , 38.64 , 44.92 and 59.51° respectively. This suggests that the oxide obtained for cobalt is Co_3O_4 . The Au(111) and (200) peaks expected at 38.14 and 44.39° respectively are not seen probably because they overlap with the Co_3O_4 (222) and (400) peaks respectively.

In the profile of Au/ Cr_2O_3 in figure 4.2, the main Cr_2O_3 peaks are (012), (104), (110), (006), (113), (202), (024), (116), (211) and (122) peaks at $2\theta = 24.50$, 33.61 , 36.20 , 39.77 , 41.49 , 44.20 , 50.23 , 54.86 , 57.11 and 58.41° respectively. The Au(111) peak is seen with very low intensity at 38.14° while the Au(200) peak overlaps with the Cr_2O_3 (202) peak. The pattern also fits with the JCPDS data for Cr_2O_3 .

The profile of Au/ CuO in figure 4.3 also fits reasonably with the JCPDS data. The major CuO peaks are the (110) at 32.49° , (002) at 35.50° , (111) at 37.83° overlapping with the (200) peak at 38.93° , the (202) peak at 48.66° , the (020) peak at 53.43° and the (202) peak at 58.37° . The Au peaks are not seen probably due to their low intensities.

The major peaks for Fe_2O_3 in Fig. 4.4 are assigned as (012) at 24.29° , (104) at 33.38° , (110) at 35.83° , (113) at 41.11° , (024) at 49.78° , (116) at 54.45° and (018) at 58.05° . The Au peaks are of very low intensities and cannot be seen. The Fe_2O_3 XRD profile obtained also correlates with the JCPDS data.

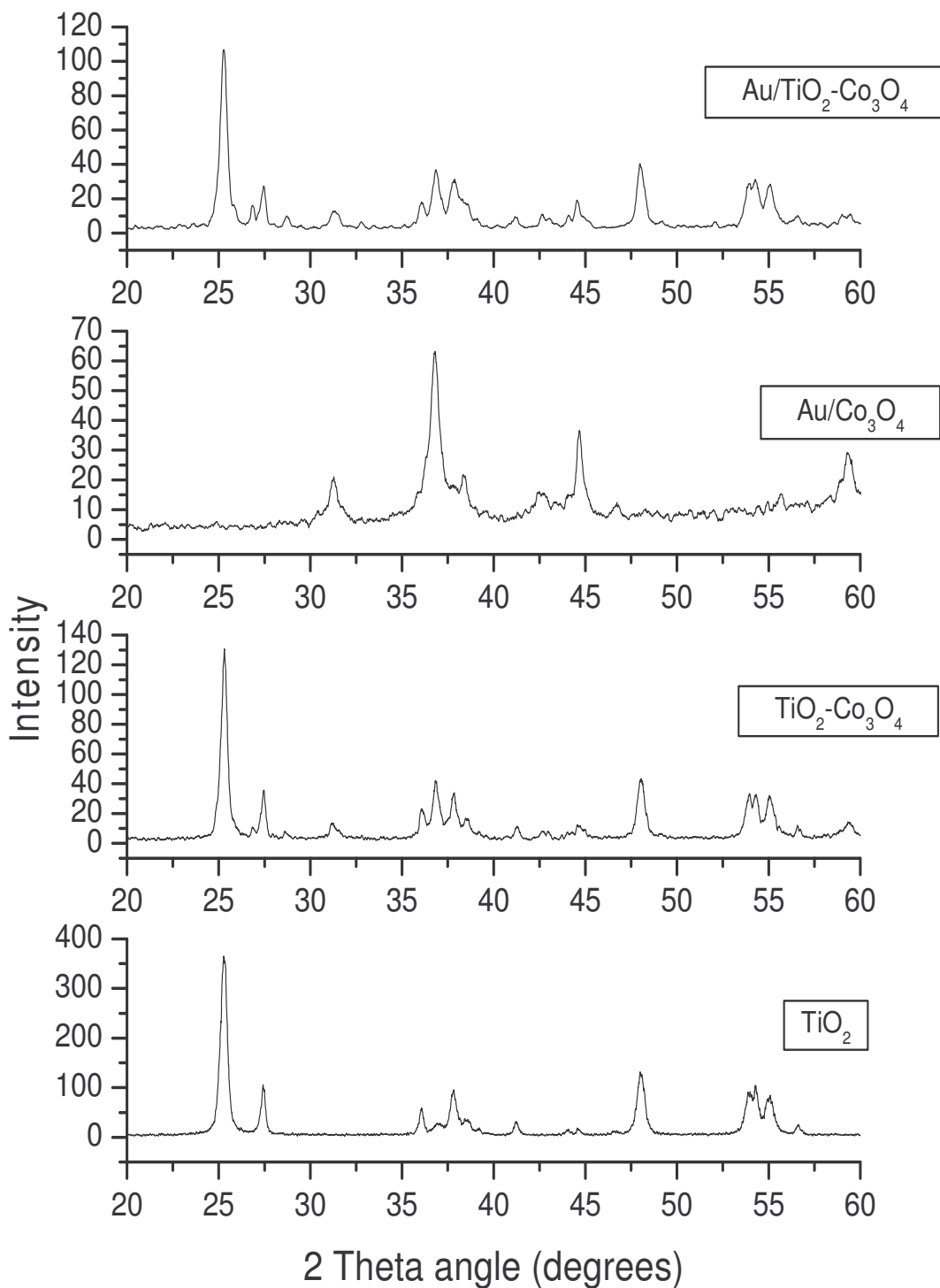


Figure 4.1: X-ray diffractograms of TiO_2 , $TiO_2-Co_3O_4$, Au/Co_3O_4 and $Au/TiO_2-Co_3O_4$

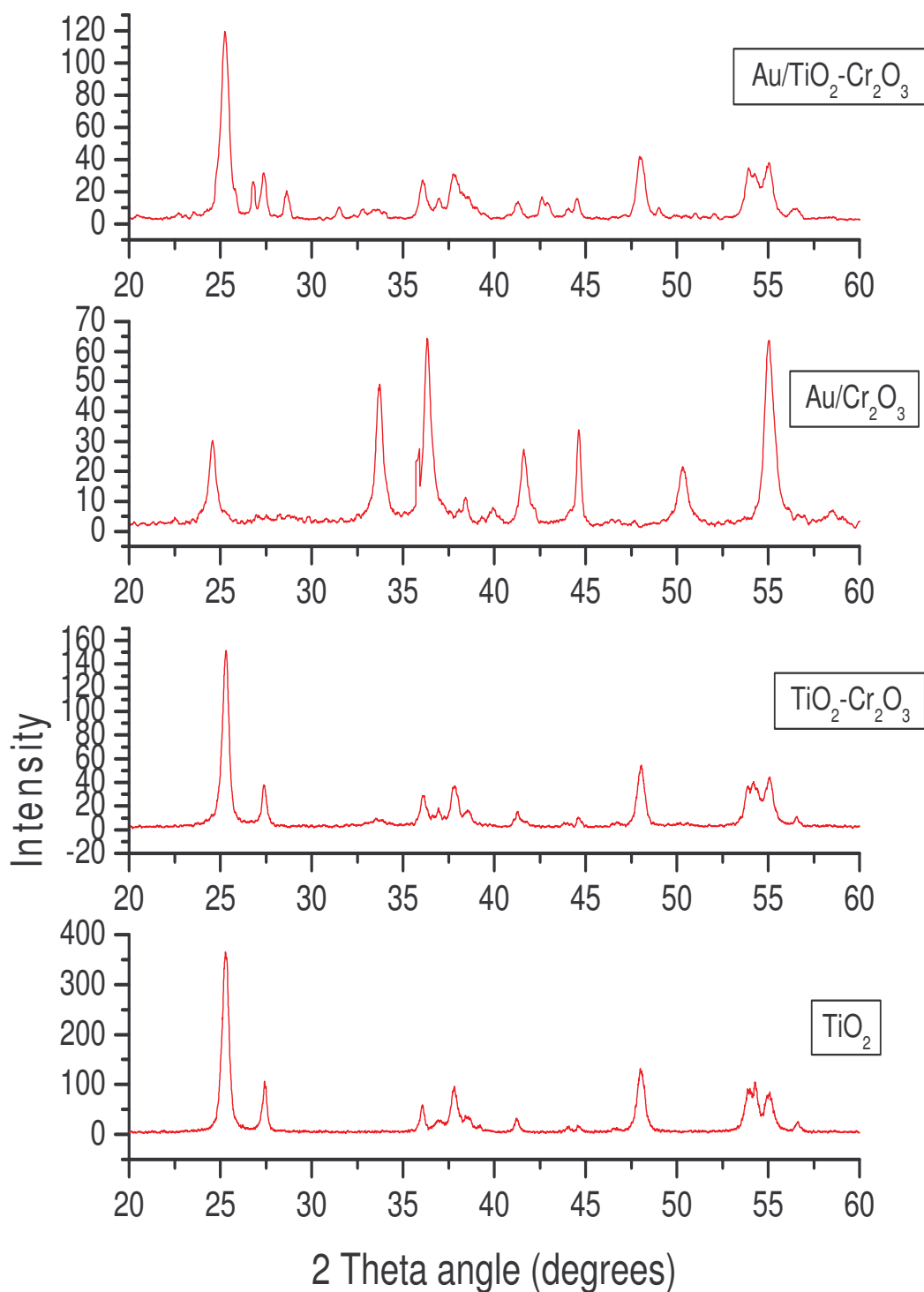


Figure 4.2: X-ray diffractograms of TiO_2 , $TiO_2-Cr_2O_3$, Au/Cr_2O_3 and $Au/TiO_2-Cr_2O_3$.

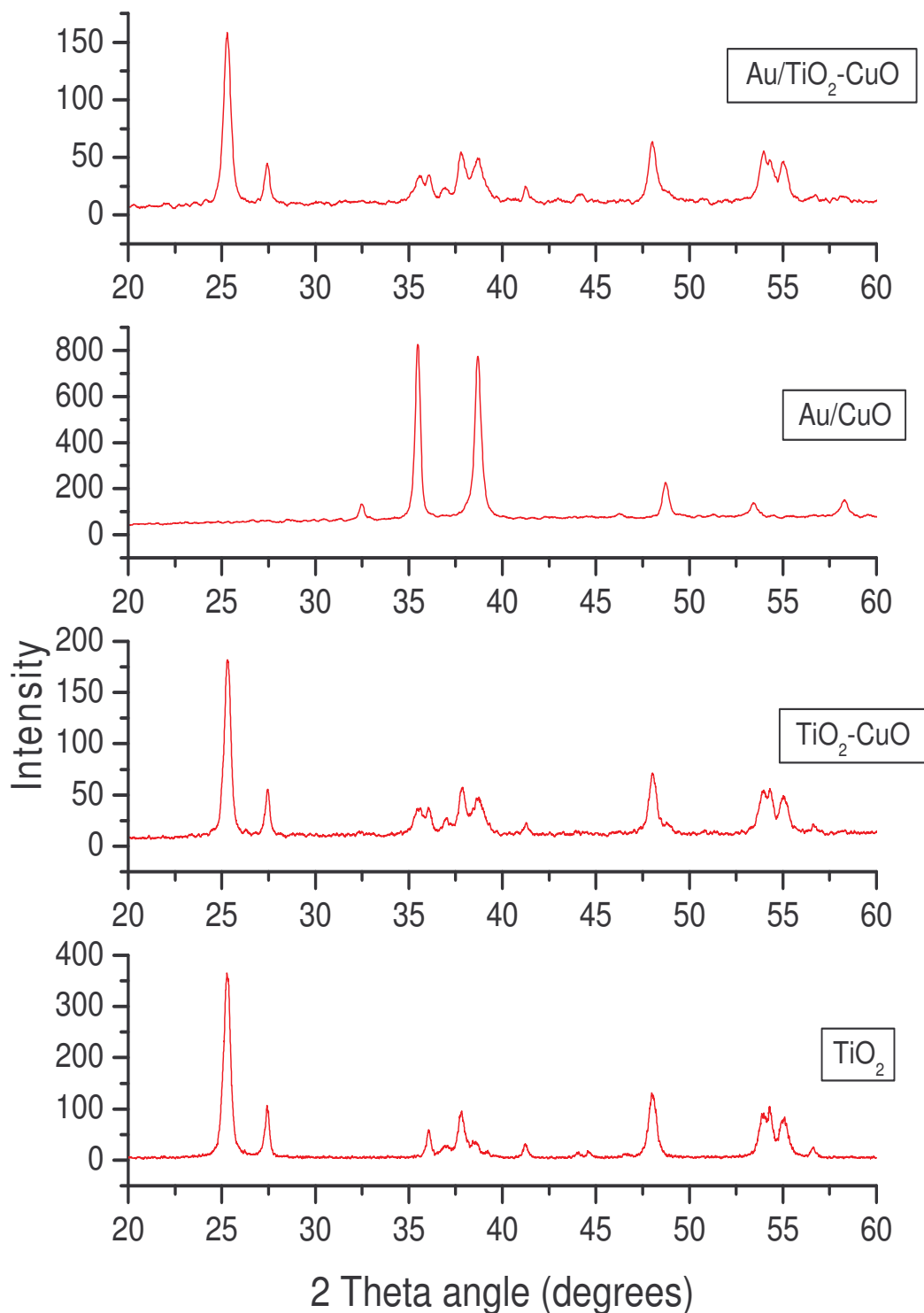


Figure 4.3: X-ray diffractograms of TiO_2 , TiO_2 -CuO, Au/CuO and Au/ TiO_2 -CuO.

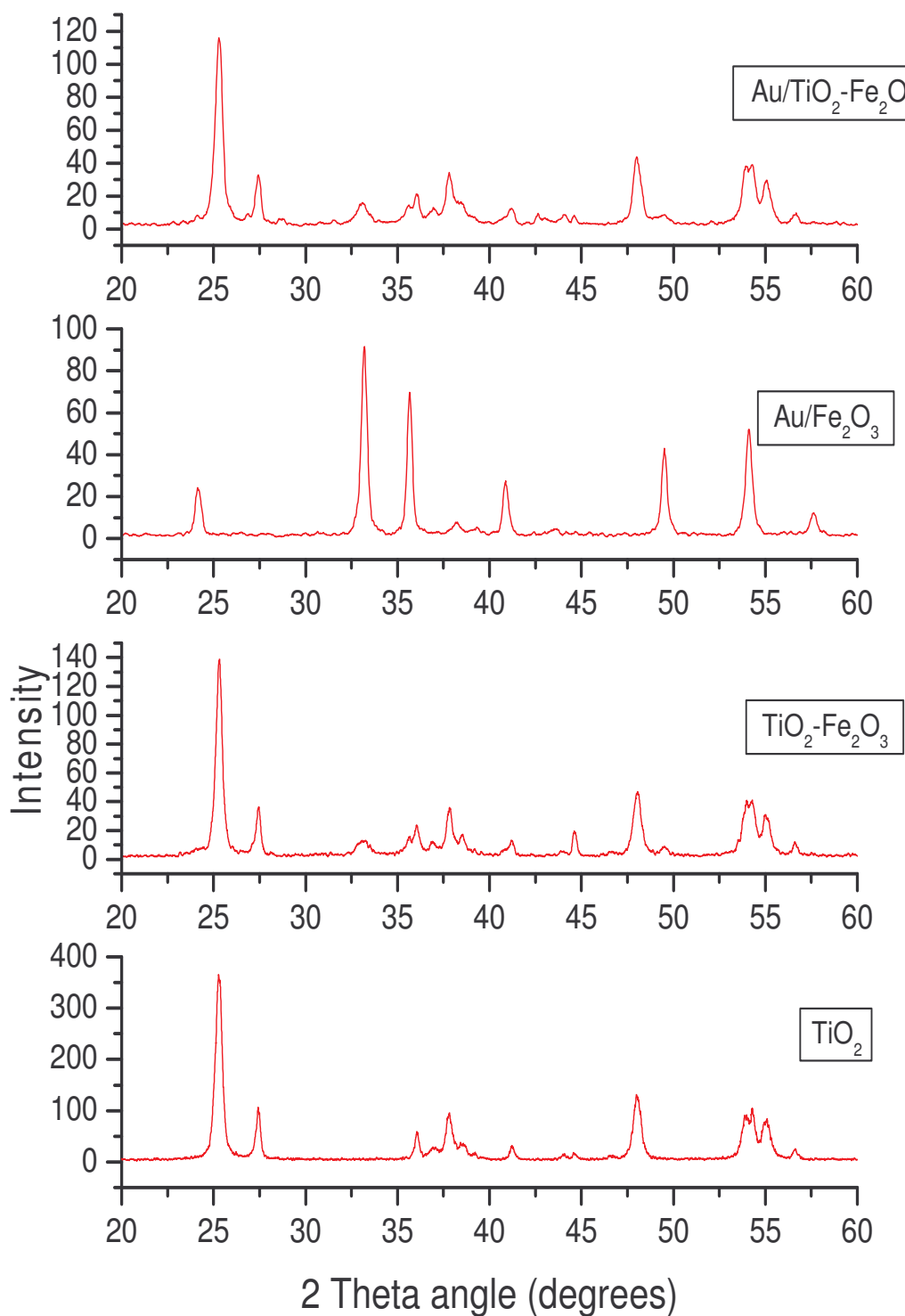


Figure 4.4: X-ray diffractograms of TiO_2 , $TiO_2-Fe_2O_3$, Au/Fe_2O_3 and $Au/TiO_2-Fe_2O_3$.

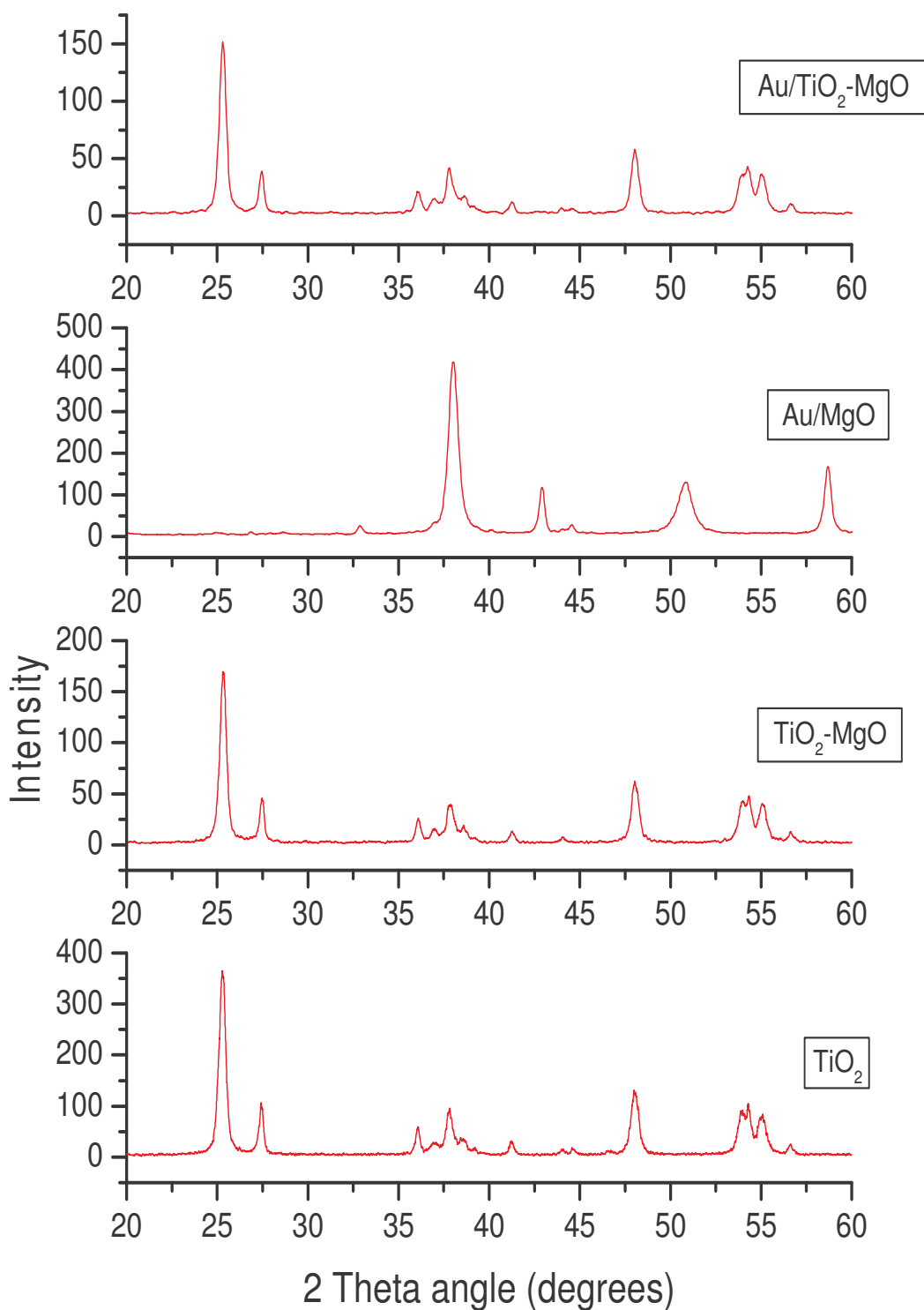


Figure 4.5: X-ray diffractograms of TiO_2 , TiO_2 -MgO, Au/MgO and Au/ TiO_2 -MgO.

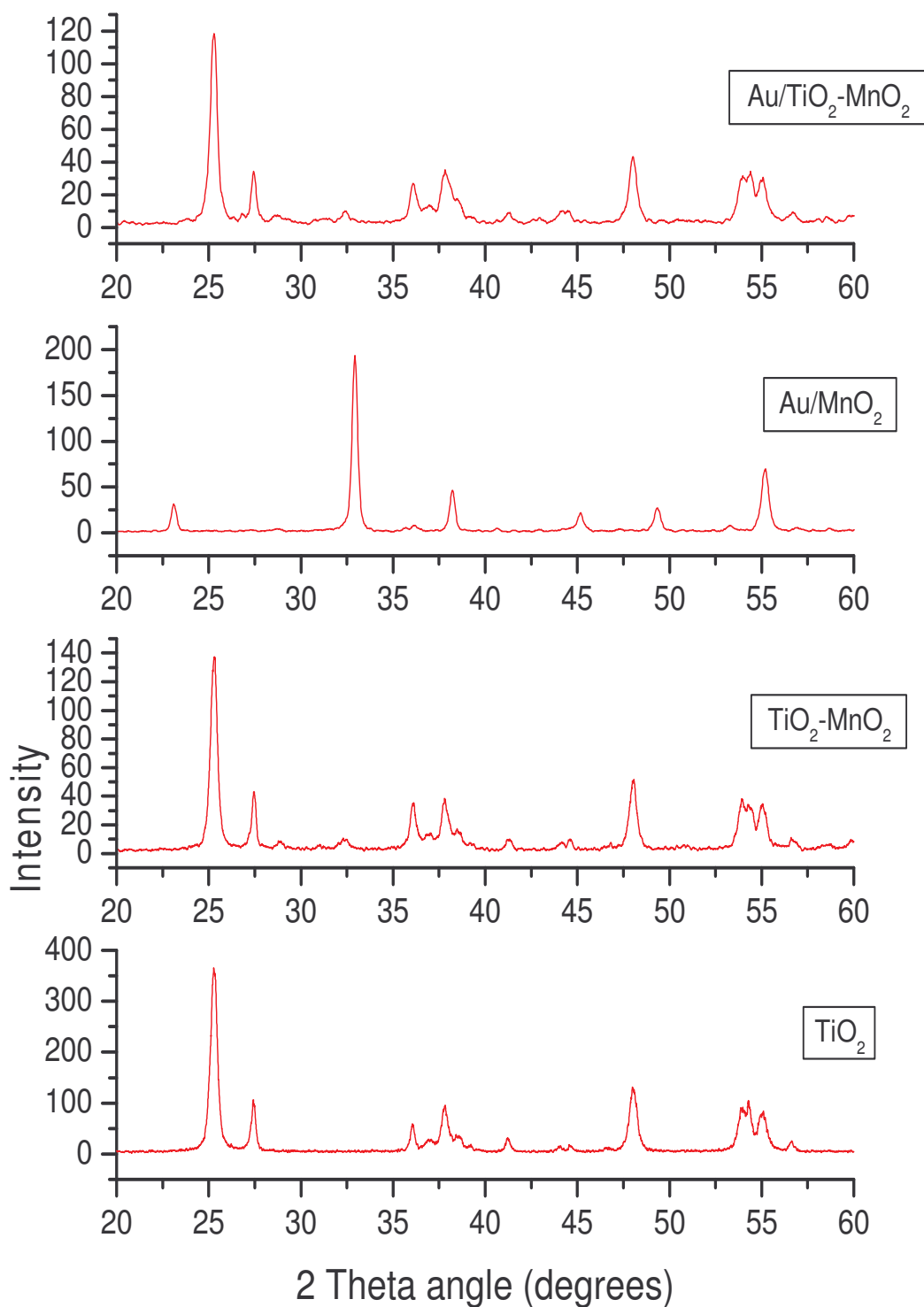


Figure 4.6: X-ray diffractograms of TiO_2 , TiO_2 -MnO, Au/MnO and Au/ TiO_2 -MnO.

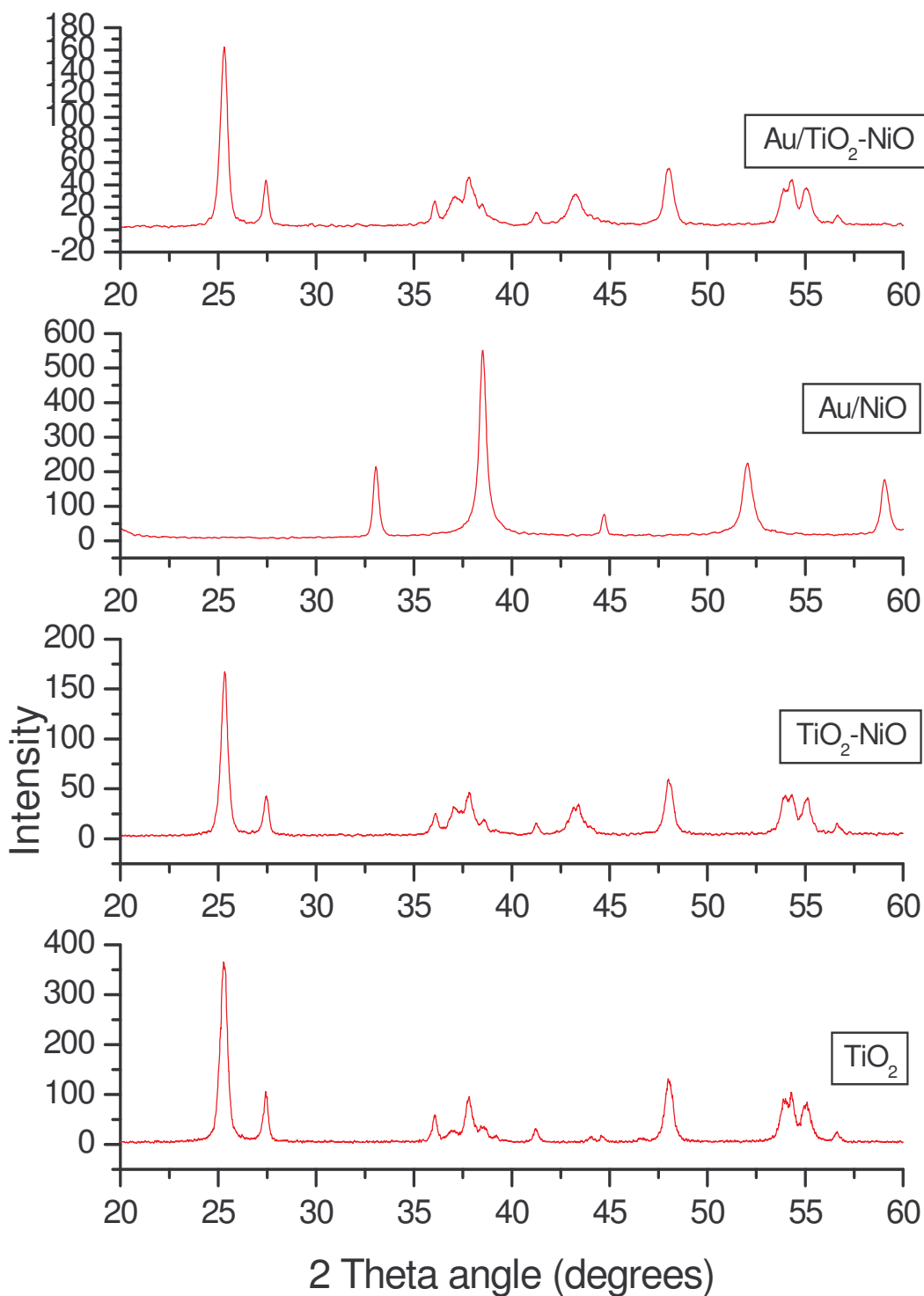


Figure 4.7: X-ray diffractograms of TiO_2 , TiO_2-NiO , Au/NiO and Au/TiO_2-NiO .

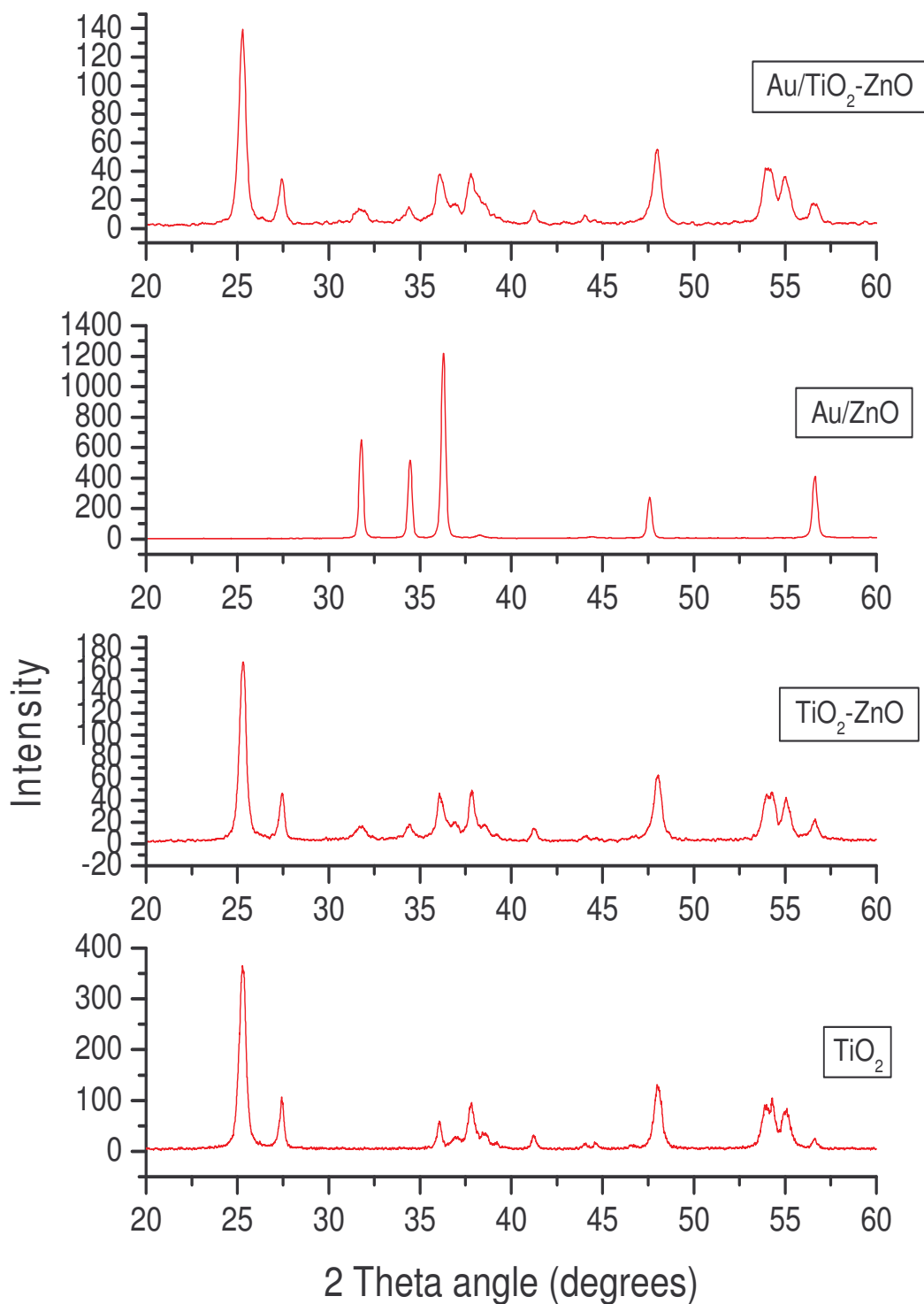


Figure 4.8: X-ray diffractograms of TiO_2 , TiO_2 -ZnO, Au/ZnO and Au/ TiO_2 -ZnO.

In figure 4.5, the XRD has peaks that can be assigned to $Mg(OH)_2$ as well as peaks for MgO . The low intensity peak at 32.85° can be assigned to the $Mg(OH)_2$ (100) plane, the peak at 38.07° assigned to $Mg(OH)_2$ (101) plane, 51.04° to $Mg(OH)_2$ (102) plane and 58.66° to $Mg(OH)_2$ (110) plane. However, the MgO (200) peak is seen at 42.90° and the MgO (111) peak at 36.93° overlapping with the $Mg(OH)_2$ (101) peak. It can thus be inferred that there was incomplete oxidation from $Mg(OH)_2$ to MgO and therefore the prepared sample contained a mixture of both $Mg(OH)_2$ and MgO .

The profile for Au/MnO_2 in figure 4.6 correlates with manganese oxide existing as Mn_2O_3 . The major peaks are therefore assigned to Mn_2O_3 as the (211), (222), (400), (332), (134) and (440) planes at 2θ angles of 23.08, 32.87, 38.14, 45.05, 49.23 and 55.04° respectively.

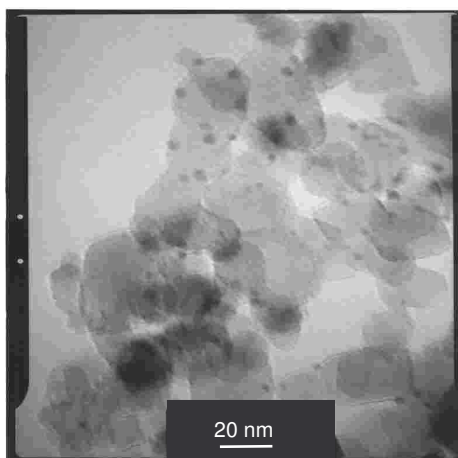
The profile obtained for NiO in figure 4.7 fits the JCPDS data for $Ni(OH)_2$ with the peaks assigned $Ni(OH)_2$ (100), (011), (012) and (110) planes at 33.01, 38.45, 51.89 and 58.97° respectively. The peak at 44.39° can be assigned to the $Au(200)$ plane while the $Au(111)$ peak possibly overlaps with the $Ni(OH)_2$ (011) peak. The support obtained was therefore likely $Ni(OH)_2$ and not NiO as expected.

The profile obtained for ZnO in the diffractogram of Au/ZnO in figure 4.8 fits with the JCPDS data. The ZnO peaks are assigned to the (100), (002), (101), (102) and (110) planes at 2θ angles of 31.76, 34.41, 36.25, 47.53 and 56.59° respectively. The Au peaks are of low intensities but can be seen at 38.14 and 44.39° as expected.

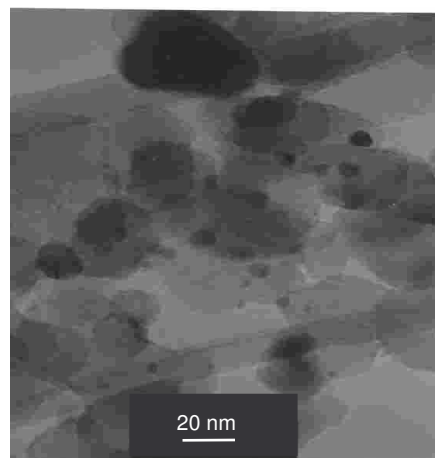
The XRD results obtained indicate that while Cr_2O_3 , CuO , Fe_2O_3 and ZnO were obtained as expected, cobalt oxide was obtained as Co_3O_4 instead of CoO , manganese oxide as Mn_2O_3 instead of MnO_2 , while in the case of magnesium oxide, a mixture of both MgO and $Mg(OH)_2$ was obtained and for NiO , only the hydroxide ($Ni(OH)_2$) was obtained.

4.2.1.2 High resolution transmission electron microscopy (HRTEM)

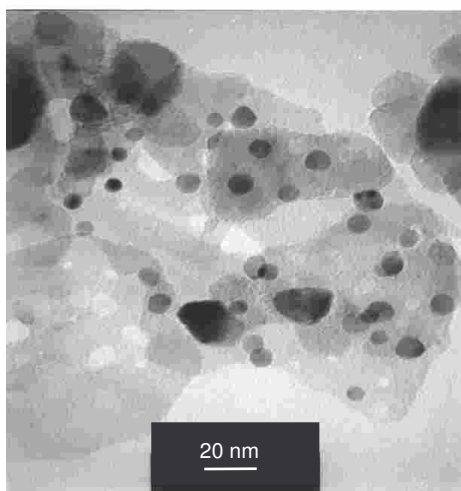
Figure 4.9 shows the HRTEM micrographs of Au/ TiO_2 , Au/ TiO_2 -Mg(OH) $_2$ /MgO, Au/ TiO_2 -Ni(OH) $_2$ and Au/ TiO_2 -ZnO.



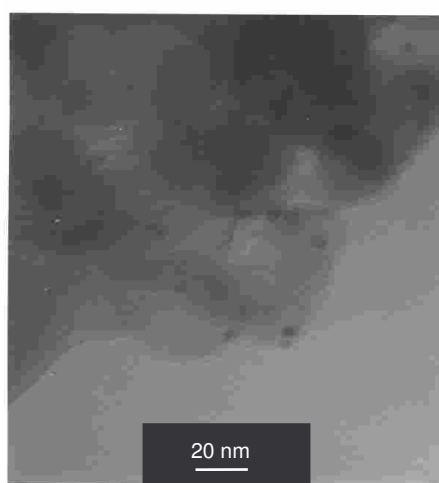
(a) Au/ TiO_2



(b) Au/ TiO_2 -Mg(OH) $_2$ /MgO



(c) Au/ TiO_2 -Ni(OH) $_2$



(d) Au/ TiO_2 -ZnO

Figure 4.9: HRTEM micrographs of (a) Au/ TiO_2 , (b) Au/ TiO_2 -Mg(OH) $_2$, (c) Au/ TiO_2 -Ni(OH) $_2$ and (d) Au/ TiO_2 -ZnO.

The gold particles on the Au/ TiO_2 and Au/ TiO_2 -ZnO catalysts can be seen to be highly dispersed with an average particle size of 3.0 ± 0.5 nm. For Au/ TiO_2 -Ni(OH) $_2$, the Au

particles are much larger with an average particle size distribution of 4.8 ± 1.0 nm while for $Au/TiO_2-Mg(OH)_2/MgO$ the particle size range is much broader averaging 3.5 ± 1.5 nm. However, the gold particle sizes for these catalysts are still within the range to give them reasonable activity for CO oxidation.

4.2.2 Catalytic activity measurements

The catalytic activities in terms of percentage conversion of CO to CO_2 of Au/TiO_2 and the Au/M_xO_y catalysts for CO oxidation at atmospheric pressure using 10%CO/5% O_2 /85%He at a total flow rate of 40 mlmin^{-1} (in stoichiometric ratio) are shown in Table 4.1 as a function of reaction temperature.

Au/TiO_2 catalyst with Au particle size of about 3.0 nm shows significantly higher activities than the Au/M_xO_y catalysts at all temperatures. At 303 K, the Au/TiO_2 catalyst gives a percentage conversion of about 40% with about 100% conversion being achieved at 373 K. $Au/Ni(OH)_2$ only shows an initial activity at about 343 K with a 2% conversion and full conversion at about 523 K while $Au/Mg(OH)_2/MgO$ shows an initial activity at 323 K of 2.5% conversion but only 32% conversion at 523 K.

Table 4.1: Percentage conversion of Au/ TiO_2 and the various Au/ M_xO_y catalysts for CO oxidation as a function of temperature (K).

Reaction temperature (K)	Catalyst								
	Au/ TiO_2	Au/ ZnO	Au/ $Mg(OH)_2/MgO$	Au/ $Ni(OH)_2$	Au/ Fe_2O_3	Au/ Cr_2O_3	Au/ CuO	Au/ MnO_2	Au/ Co_3O_4
303	38.8	2.7			5.4	4.6	13.0	8.8	10.5
313	60.0	6.3			9.4	4.9	13.2	11.7	3.4
323	73.1	8.3	2.5		12.4	7.2	13.5	15.0	6.3
333	80.8	11.1	4.4		18.8	12.2	14.0	20.0	8.2
343	88.8	12.7	5.9	2.0	23.8	17.6	14.6	24.7	12.0
353	92.6	13.2	8.1	3.5	28.1	21.2	15.2	31.9	18.3
363	96.4	15.1	9.8	4.5	31.9	25.9	15.9	37.2	30.2
373	97.6	16.8	10.8	5.2	37.0	28.1	16.6	43.4	44.5
383	98.8	18.3	12.0	6.3	45.1	31.9	18.2	48.9	56.4
393	99.4	19.9	13.0	7.3	53.5	35.7	21.3	54.0	70.9
403		20.8	14.2	10.0	60.2	38.1	25.1	59.6	88.8
413		22.0	16.8	12.6	66.2	43.1	30.8	63.6	95.6
423		23.5	18.1	20.8	71.0	47.7	35.8	69.5	99.5
433		24.2	18.5	27.0	76.8	51.9	40.6	73.4	
443		25.8	19.0	41.2	82.5	58.9	47.9	79.1	
453		26.3	20.2	55.1	86.4	63.4	55.1	83.5	
463		27.5	21.6	69.3	88.8	69.4	62.9	88.3	
473		28.6	23.3	76.1	91.7	74.0	70.6	91.6	
483		30.3	25.8	87.5	93.6	80.3	78.0	94.1	
493		33.5	27.3	93.4	95.5	83.9	84.1	96.7	
503		38.0	29.3	97.3		86.2	87.9		
513		42.3	31.6	99.1		90.5	91.8		
523		45.6	32.3	99.8		92.7	94.8		

Au/Co₃O₄ shows an initial high activity of about 10.5% conversion at 303 K but rapidly deactivates to about 1.5% conversion and gives full conversion at about 423 K. For Au/TiO₂ and Au/Co₃O₄, there was a rise in reaction temperature from ambient to about 323 K on passing the reactant gas mixture over the catalysts. The initial high activity observed for Au/Co₃O₄ can be assigned to the intrinsically high CO oxidation capability of cobalt oxide itself. None of the other M_xO_y systems have been reported to catalyze CO oxidation on their own. Jansson et al¹⁹³ found Co₃O₄ to have a high initial activity for CO oxidation but the catalyst deactivated with time. They explained the deactivation to be as a result of one or a combination of any of the following factors. Firstly, the deactivation could occur by irreversibly reducing the oxidation state of the surface cobalt ions so that they could not be re-oxidized at the low reaction temperature. Another possibility is that the active sites are blocked by carbonyl, carbonate, coke or H₂O/OH species while a third deactivation mechanism could be that the creation of oxygen vacancies when reacting with adsorbed CO leads to a reconstruction of the cobalt oxide surface making cobalt sites unavailable for CO adsorption. Thus several hypotheses can be put forward to explain the initial high activity and deactivation of Au/CoO catalyst during CO oxidation in this work.

Figure 4.10 shows a graphical comparison of the activities of Au/TiO₂ and the various Au/M_xO_y catalysts for CO oxidation.

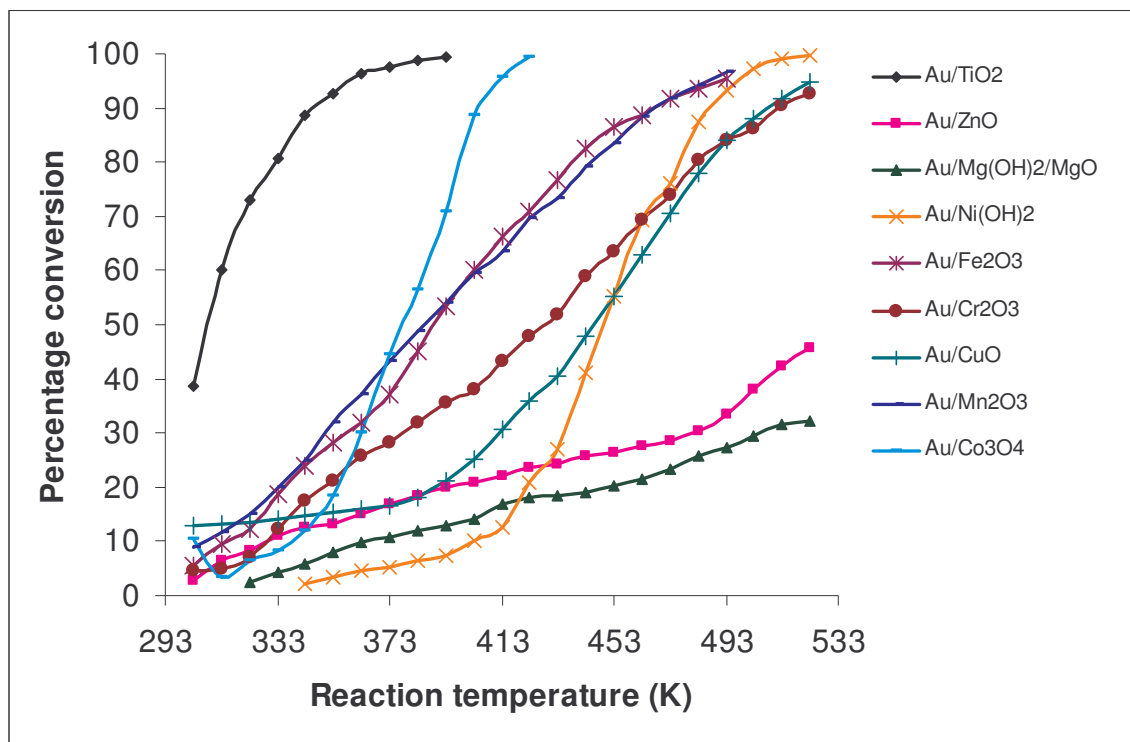


Figure 4.10: Activity for CO oxidation reaction (percentage conversion) on Au/TiO₂ and various Au/M_xO_y catalysts as a function of temperature (K).

The order of activities for CO oxidation over Au/M_xO_y catalysts decreases in the following order: Au/Mn₂O₃ > Au/Fe₂O₃ > Au/Co₃O₄ > AuCr₂O₃ > Au/CuO > Au/ZnO > Au/Mg(OH)₂/MgO > Au/Ni(OH)₂.

Table 4.2 shows the activity of the Au/TiO₂ and the various Au/TiO₂-M_xO_y catalysts for CO oxidation measured as a function of temperature. Again, it is seen that Au/TiO₂ has a higher activity than any of the Au/TiO₂-M_xO_y catalyst systems at all temperatures. Addition of M_xO_y to TiO₂ generally decreases the activity of Au/TiO₂ and increases the activity of M_xO_y for CO oxidation, except in the case of MnO₂ where Au/MnO₂ is seen to have a higher activity than Au/TiO₂-MnO₂ for temperatures above 323 K.

Table 4.2: Percentage conversion for Au/ TiO_2 and the various Au/ TiO_2 - M_xO_y catalysts for CO oxidation as a function of temperature (K).

Reaction temperature (K)	Catalyst								
	Au/ TiO_2	Au/ TiO_2 -ZnO	Au/ TiO_2 -MgO	Au/ TiO_2 -NiO	Au/ TiO_2 - Fe_2O_3	Au/ TiO_2 - Cr_2O_3	Au/ TiO_2 -CuO	Au/ TiO_2 - MnO_2	Au/ TiO_2 - Co_3O_4
303	38.8	12.6	19.6	8.9	9.5	2.3	8.5	12.3	55.9
313	60.0	16.4	35.8	17.0	14.2	3.3	17.1	13.6	29.4
323	73.1	27.3	48.8	28.9	29.9	9.6	24.7	14.5	29.5
333	80.8	35.8	60.4	37.3	56.4	21.3	29.0	16.0	41.7
343	88.8	40.6	69.2	45.9	69.2	44.0	35.7	20.0	53.9
353	92.6	45.6	77.2	55.1	78.2	63.7	39.9	23.0	71.9
363	96.4	49.2	83.0	62.7	86.6	74.7	42.9	25.0	87.8
373	97.6	54.7	88.3	71.7	92.9	85.9	47.8	28.0	95.0
383	98.8	58.3	92.3	75.5	96.3	92.2	54.4	37.1	98.2
393	99.4	62.4	94.6	79.9	98.5	95.8	65.4	44.2	
403		64.8	96.8	85.4		98.1	77.8	50.1	
413		66.4	97.6	86.5		99.1	89.3	55.4	
423		67.8	98.4	90.7			95.4	60.1	
433		71.0		93.8			97.9	65.5	
443		75.1		95.3			98.5	70.1	
453		78.8		97.3				75.5	
463		85.9						80.2	
473		87.8						84.2	

In the case of $Au/TiO_2-Co_3O_4$ as in Au/Co_3O_4 , there is an initial high activity of about 56% conversion which rapidly drops to about 30% and full conversion is achieved at about 383 K. Fig. 4.11 shows a graphical comparison of the activities of Au/TiO_2 , with those of the $Au/TiO_2-M_xO_y$ catalysts for CO oxidation.

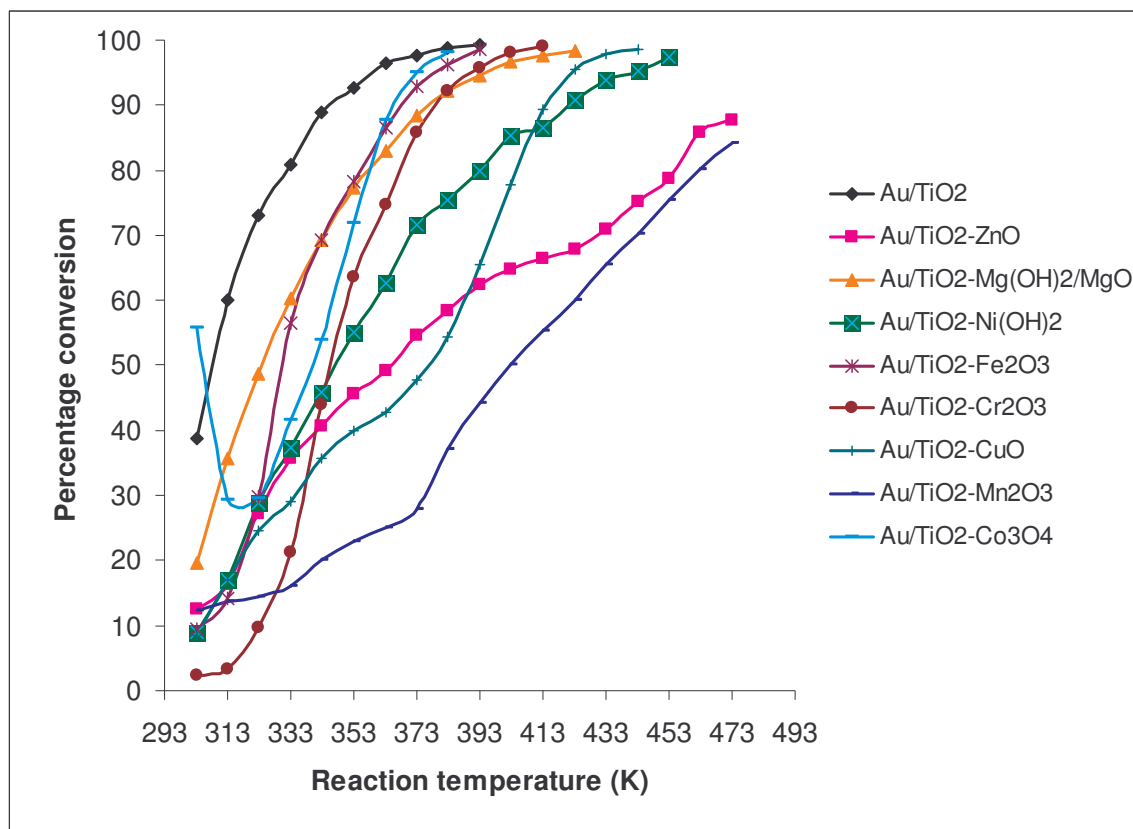


Figure 4.11: Activity for CO oxidation reaction (percentage conversion) on Au/TiO_2 and various $Au/TiO_2-M_xO_y$ catalysts as a function of temperature (K).

The order of activity of the $Au/TiO_2-M_xO_y$ catalysts increases thus: $Au/TiO_2-Mn_2O_3 > Au/TiO_2-CuO > Au/TiO_2-ZnO > Au/TiO_2-Ni(OH)_2 > Au/TiO_2-Cr_2O_3 > Au/TiO_2-Co_3O_4 > Au/TiO_2-Fe_2O_3 > Au/TiO_2-Mg(OH)_2/MgO$. This order is different from that of the Au/M_xO_y catalysts, suggesting that the influence of M_xO_y on TiO_2 varies from one metal oxide to the other. In a similar study by Grisel and Nieuwenhuys¹¹⁷ in which they compared the activity of Au/Al_2O_3 and $Au/MO_x/Al_2O_3$ (where $M = Cr, Mn, Fe, Co, Ni, Cu$ and Zn) in low temperature CO oxidation and the oxidation of CH_4 , they observed a remarkable enhancement in CO oxidation activity with all the multi-component catalysts

compared to the mono-component catalysts and the activity over $Au/MO_x/Al_2O_3$ increased in the order $CuO_x > CrO_x > CoO_x > FeO_x > ZnO_x > NiO_x > MnO_x$. They also observed that this order of activity is directly related to the average Au particle size whereas the identity of MO_x is less important and the enhancement of activity upon addition of MO_x to Al_2O_3 attributed to stabilization of small Au particles initially present on the support. Their observations are different from those of this work in that adding M_xO_y to TiO_2 rather leads to a decrease in the activity of Au/TiO_2 for CO oxidation, and the order of activities for the multi-component systems are quite different in both works. In all the catalysts, the $Au/TiO_2-M_xO_y$ systems show a better activity than the corresponding Au/M_xO_y systems with Au/TiO_2 having the best activity.

4.3 CONCLUSIONS

Upon precipitating $Ni(NO_3)_2 \cdot 6H_2O$ with ammonium hydroxide followed by drying and calcination at 673 K, we obtain $Ni(OH)_2$ instead of the oxide, while $Mg(NO_3)_2 \cdot 6H_2O$ gives a mixture of $Mg(OH)_2$ and MgO . The other nitrates give the corresponding oxides. The single step borohydride method of preparation of gold supported catalysts gives catalysts with high activity. The control of pH in this method using NH_4OH is not an essential requirement as upon reduction of the gold precursor with $NaBH_4$, the pH rises to about 8.5 which is the required pH range for preparation of active gold supported catalysts.

TiO_2 stands out to be the most active support for gold supported catalysts for CO oxidation and the beneficial effects seen for some mixed metal oxide support systems for some other reactions and for some other supports for CO oxidation are not universally applicable.

There is no apparent correlation of activity with gold crystallite size, suggesting that metallic gold itself may not be the sole seat of catalytic activity for CO oxidation in these systems.

**COMPARISON OF ACTIVITIES OF VARIOUS TITANIA
BASED SUPPORTS FOR GOLD FOR CO OXIDATION**

5.1 INTRODUCTION

Titania has been steadily gaining importance for use as catalyst or catalyst support because of its unique properties such as acidic, basic and redox sites, capacity of resist thermal shock, ionic conductivity, chemical inertness and metal support interaction.¹⁹⁴

Titania exists in three major crystalline forms: rutile, anatase and brookite. Rutile is the most stable phase; however, anatase and brookite are commonly formed in metastable nanocrystalline synthetic and natural samples. Anatase and brookite transform into rutile upon heating.¹⁹⁵ Pure titania does not occur in nature but is derived from ores. Several synthetic methods have been used to produce titania. Depending on the method used, the resulting material may vary in relative composition of the various crystalline phases. As a result, the properties of titania obtained by different preparation methods may be different.

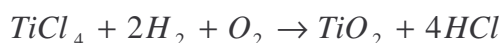
Ranade et al.¹⁹⁶ synthesized anatase titania from $(\text{NH}_4)_2\text{Ti}(\text{OH})_2(\text{C}_3\text{H}_5\text{O}_3)_2$ and cetyltrimethylammonium chloride. From this they derived anatase-rutile samples by heating at 623 K. They also synthesized amorphous titania using a mixture of titanium ethoxide and ethanol. Rutile samples were also synthesized by a sol-gel method using titanium trichloride and ammonium hydroxide.

Titania has also been prepared by adding a 1:1 mixture of ammonia and water to a stirred aqueous solution of titanium tetrachloride at pH values of 7 and 3. The obtained gels

were filtered and washed repeatedly to remove any residual chloride ions (negative AgNO₃ test), and dried at 373 K for 10 h.¹⁹⁴

Redispersible anatase titania nanoparticles have been produced by hydrolysis of titanium alkoxides complexed with acetyl acetone in acid medium. The “xerols” are readily redispersible in both organic and aqueous solvents with no signs of aggregation. By varying the ratio of the acetyl acetone to the alkoxides, the bulk nanoparticles size can be selectively fixed between 1.5 and 4 nm.¹⁹⁷ There is an advantage of synthesizing TiO₂ by gelling titanium alkoxides as in such preparation specific surface area, titania crystallite size and crystalline titanium phase can be controlled. Final properties of sol-gel catalysts can be controlled by varying the hydrolysis pH.¹⁹⁸

Titania has been most commonly used as support for gold catalysts for CO oxidation because it produces some of the most active catalysts. Of the various types of titania that have been used in the literature as support for gold catalysts for CO oxidation, the commercial Degussa P25 has been most widely used. It is a hydrophilic fumed titanium dioxide with a surface area (BET) of approximately 50 m²/g and an average primary particle size of 21 nm. It is synthesized by flame hydrolysis of titanium tetrachloride. In the synthesis, the titanium tetrachloride is evaporated and hydrolyzed in an oxyhydrogen flame according to the following equation.¹⁹⁹



This chapter therefore compares the activities of Au/TiO₂ catalysts prepared using the commercial form of titania (Degussa P25) with other synthesized forms of titania as support. The synthesized titania based supports studied include titania (TI673) and sulphated titania from titanium (IV) isopropoxide (0.05TI, 0.1TI, 0.2TI, 0.4TI and 2.5TI), titania (TT673) and sulphated titania (2.5TT) from titanium tetrachloride and potassium titanate (PT). The effect of addition of the sulphate ion to the supports prepared from titanium isopropoxide and tetrachloride are therefore reported. The corresponding gold

supported catalysts will henceforth be denoted with the prefix Au before each of the support symbols. Some characterization attempts have also been made to compare the properties of the various materials synthesized and relate these to the observed catalytic properties. A comparison is also made between the carbon monoxide oxidation activities of catalysts prepared by different routes. The preparation methods include the DP, SSBH and aqueous impregnation (IMP) methods.

5.2 CHARACTERIZATION

5.2.1 X-ray diffraction (XRD)

X-ray diffractograms were collected for the support samples derived from titanium isopropoxide and for PT and AuPT between two theta values of 20 to 90°. These diffractograms are shown in Figures 5.1 and 5.2 below.

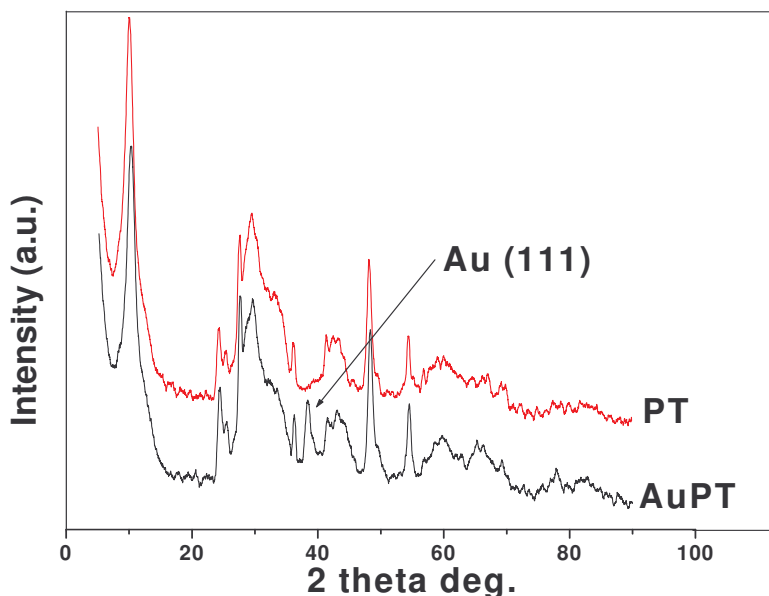


Figure 5.1: X-ray diffractograms of PT and AuPT.

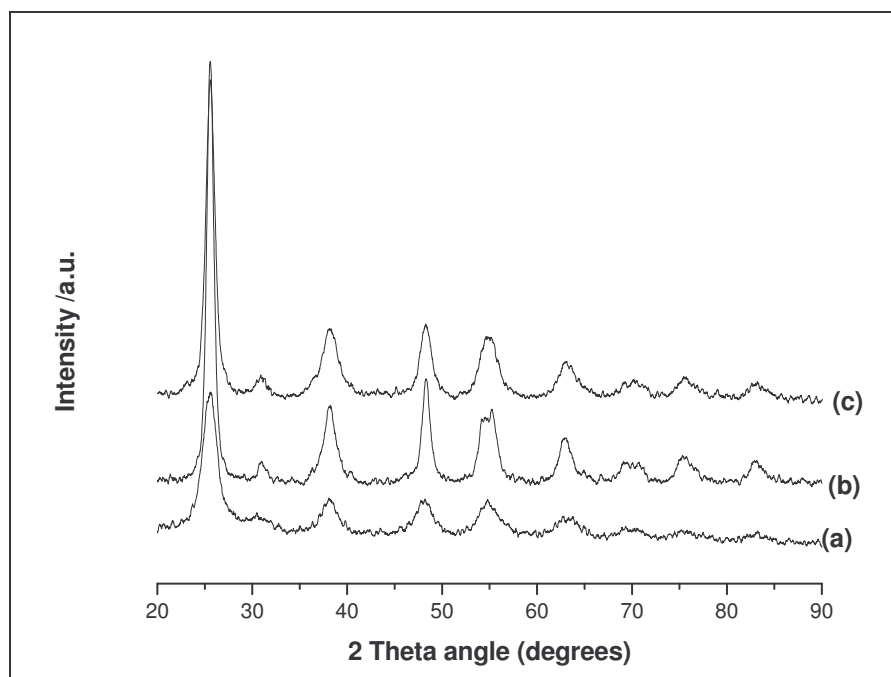


Figure 5.2: X-ray diffractograms of (a) TI373 (b) TI673 and (c) Au2.5TI

Few well defined peaks are seen in the diffractogram of the titanate samples. These peaks are much broader than for titania (Degussa P25) and cannot be attributed to any of the crystalline phases of titania. Upon deposition of gold on the titanate, a gold peak is observed at $2\theta = 38.4^\circ$ which is not seen in the case of Au/TiO₂. The x-ray diffractograms for TI373 (a), TI673 (b) and Au2.5TI (c) show that the anatase phase of TiO₂ dominated the rutile phase in the support. The intensities of the peaks and hence the crystallinity of the support increased with calcination. The expected peaks for metallic Au in the diffractogram of Au2.5TI are not seen probably due to the low metal loading on the support.

5.2.2 BET surface areas

According to Table 5.1, TI373 has a high surface area of 310 m²/g. However, upon calcination at 673 K, the surface area decreases to 87 m²/g. Sulphate levels of 0.05 to 0.4 mol% do not significantly affect the surface area of the support. However, 2.5 mol%

sulphate level increases the surface area to 117 m²/g. Gold deposition slightly decreases the surface area in the resulting catalysts.

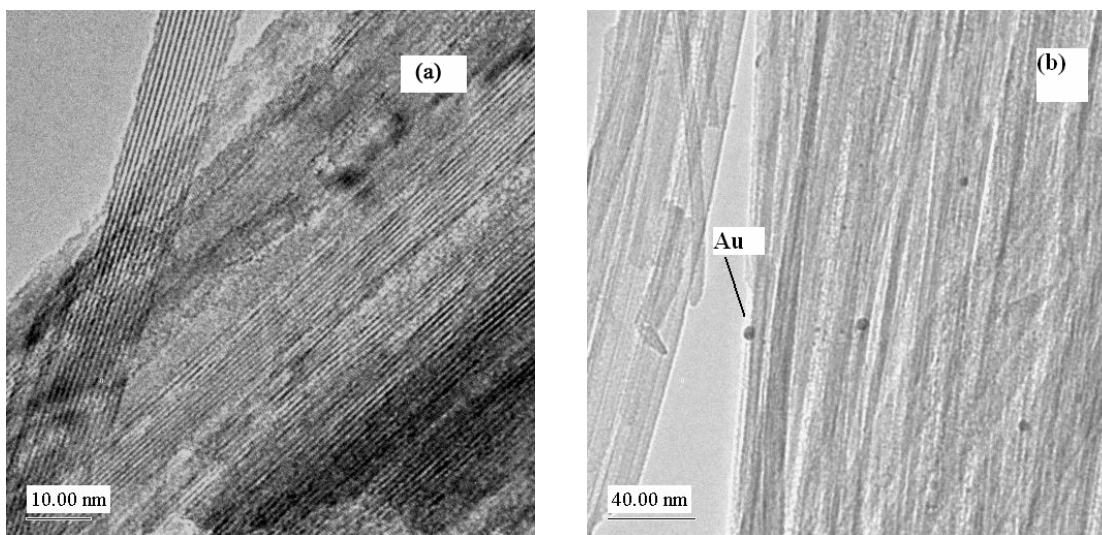
Table 5.1: BET surface areas of various support and catalyst samples.

Sample	Surface area (m ² /g)	Sample	Surface area (m ² /g)
TiO ₂	50	Au/TiO ₂	47
TI373	310		
TI673	87	AuTI	85
0.05TI	86	Au0.05TI	80
0.1TI	74	Au0.1TI	67
0.2TI	79	Au0.2TI	73
0.4TI	72	Au0.4TI	70
2.5TI	117	Au2.5TI	106
PT	182	AuPT	162

The synthesis of PT from TiO₂ leads to a more than three fold increase in surface area from 50 m²/g to 182 m²/g, both of which also slightly decrease upon gold deposition.

5.2.3 HRTEM

The morphology of PT can be seen in Figure 5.3 (a) and (b), and shows the derived material to be made up of very thin sheets which give it its high surface area.



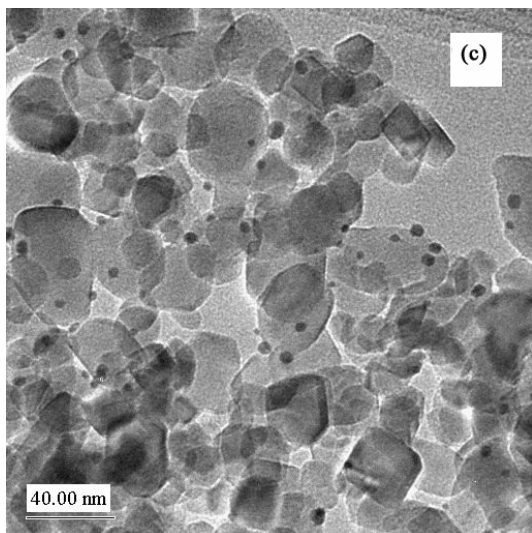


Figure 5.3: HRTEM images of (a) PT (b) AuPT and (c) Au/TiO₂

The gold particles can be seen to be highly dispersed on both AuPT and Au/TiO₂. Analyses of the micrographs in both cases give the gold particle size distribution shown in Figure 5.4.

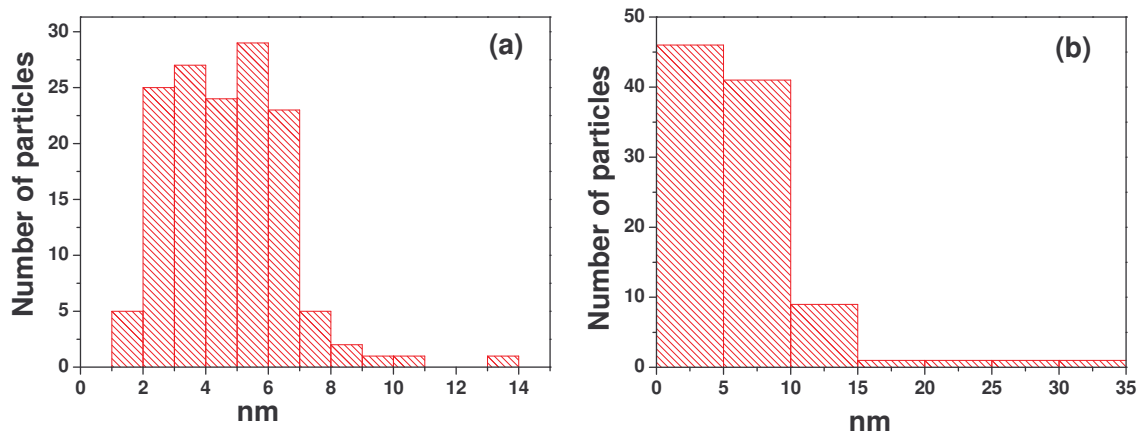


Figure 5.4: Particle size distributions of metallic gold particles in (a) Au/TiO₂ and (b) AuPT estimated from HRTEM images.

For Au/TiO₂, the gold particle size distribution is much narrower with most of the particles being in the range of 2 to 6 nm. For Au PT, the size distribution of gold particles

is much broader and particles can be seen with sizes up to 10 nm. A few particles are present with sizes up to 35 nm.

Figure 5.5 and 5.6 show the HRTEM images and the gold particle size distribution of the representative samples in the titanium isopropoxide derived samples.

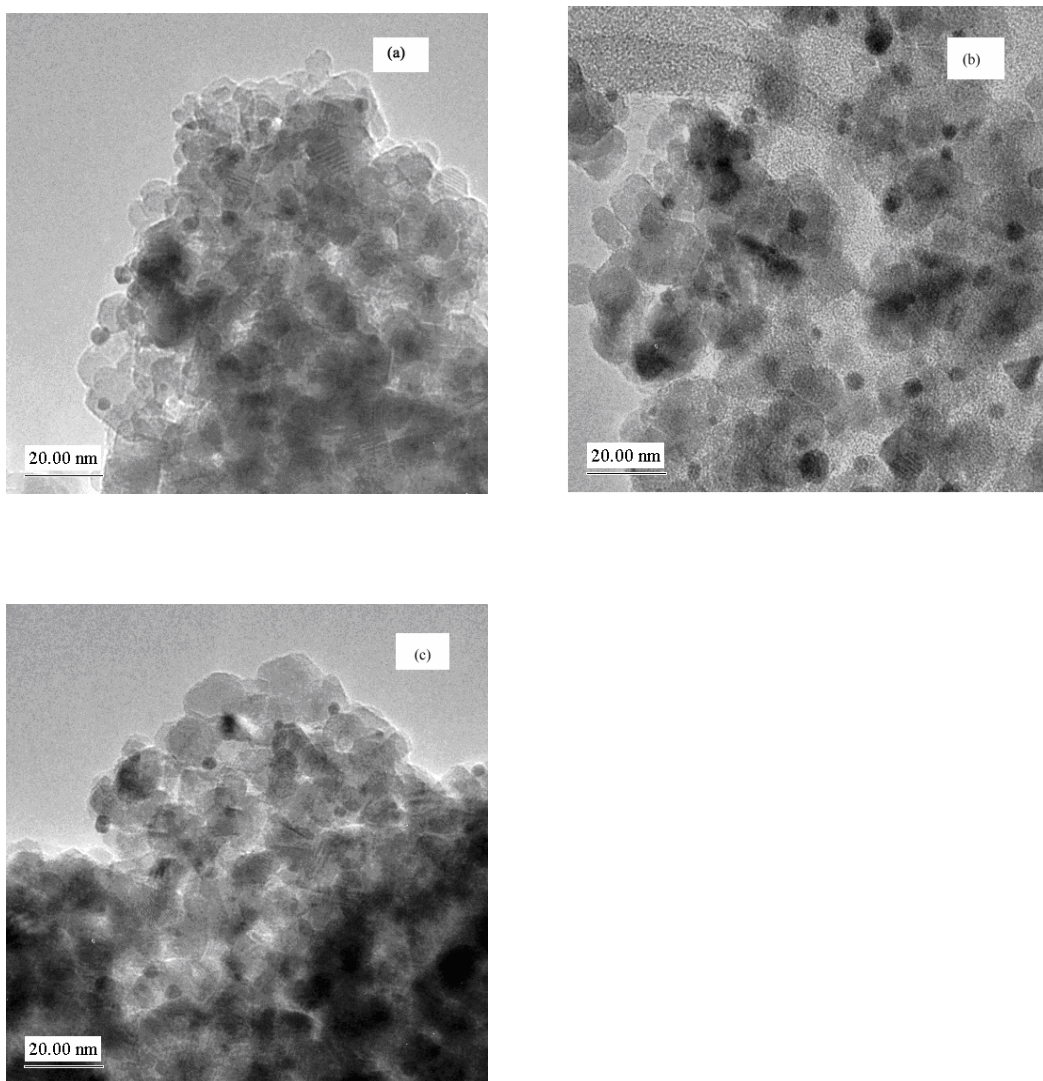


Figure 5.5: HRTEM images of (a) AuTi673, (b) Au0.4TI and (c) Au2.5TI

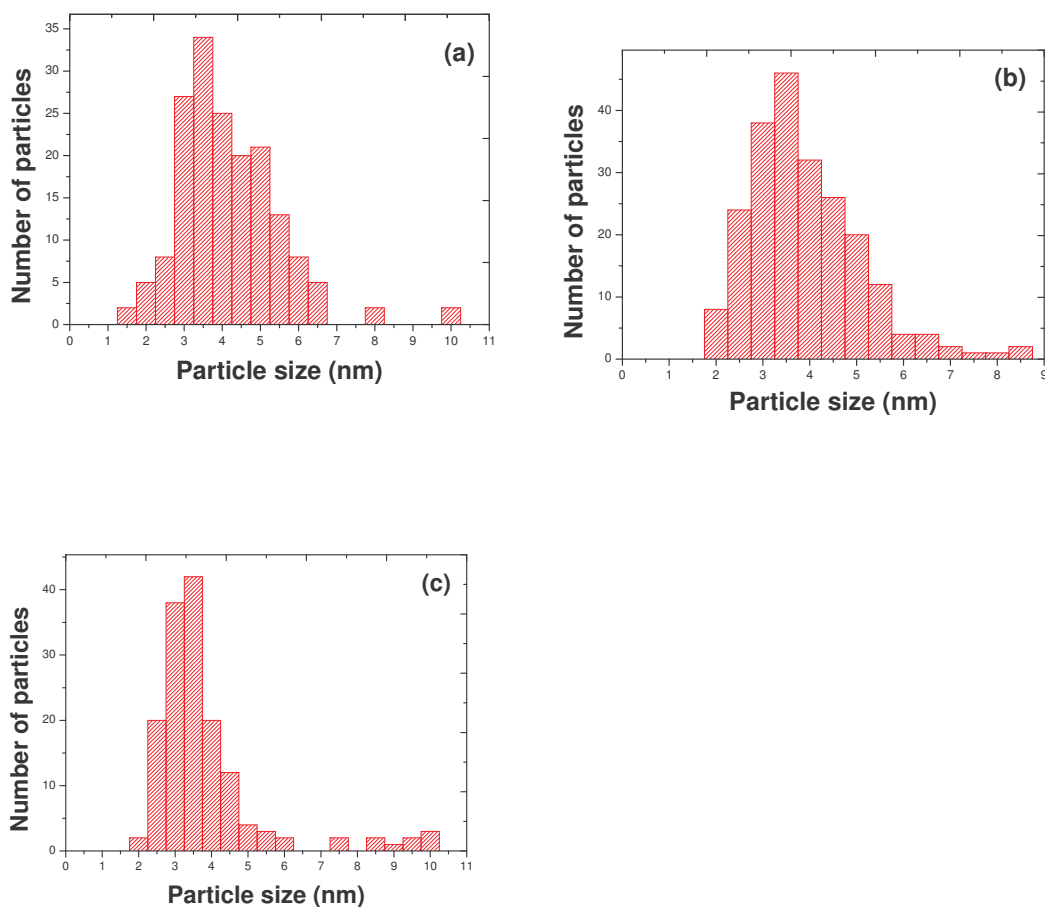


Figure 5.6: Particle size distributions of metallic gold particles in (a) AuTi673 and (b) Au0.4Ti and (c) Au2.5Ti estimated from HRTEM images.

The HRTEM images show a fairly uniform distribution of gold particles in the isopropoxide derived samples while the particle size distribution show that in these samples, the majority of the gold particles are in the range of 2 to 6 nm. The addition of sulphate ions to the support prior to gold deposition does not significantly affect the gold particle size distribution.

5.2.4 Gold content measurements

The gold contents in the catalysts were measured by the method of fire assay and gravimetric finish. According to Table 5.2 the gold contents measured in these catalysts are very similar and close to the target 1 mass% loading.

Table 5.2: Gold content of some of the catalysts as determined by fire assay and gravimetric finish method.

Sample	Gold content (wt%)
AuTI673	1.06
Au2.5ST	0.97
Au0.4ST	1.01
Au0.2ST	0.97
Au0.1ST	1.00
Au0.05ST	0.99

The incorporation of the ions into the support prior to loading of gold therefore does not affect the amount of gold that is subsequently deposited on the support.

5.2.5 XPS data

Table 5.3: XPS data showing elemental composition and Au 4f binding energies of some of the catalysts.

Catalyst	Elemental composition	Au 4f binding energy (eV)
Au/TiO ₂	Au, C, O, Ti	83.22
AuTI673	Au, C, O, Ti	83.52
Au0.05TI	Au, C, O, Ti	83.52
Au0.1TI	Au, C, O, Ti	83.50
Au0.2TI	Au, C, O, Ti	83.52
Au0.4TI	Au, C, O, Ti	83.19
Au2.5TI	Au, C, O, Ti	83.21

Table 5.3 shows the elemental composition and Au 4f binding energies of some of the catalysts studied. It is worth noting that sulphate ions are not detected in the catalysts once the supports are sulphated. The detection limit of the instrument used is 0.1 at%. There is therefore a likely indication that if the sulphate ion is present in the catalyst, it is present below the detection limit of the instrument. There are also some significant differences between the Au 4f binding energies in the catalysts. The values of these are in the range of 83.19 to 83.52 eV.

5.2.6 SIMS results

For this set of samples, SIMS data were collected for Au0.1Ti only. The SIMS data are presented in Table 5.4 below.

Table 5.4: SIMS data for Au0.1Ti

Catalyst	Atomic mass	Approximate peak height (counts)	Probable species present
Au0.1Ti	31.9719	4E2	S
	47.9481	3E5	Ti
	63.9420	1E3	TiO, S ₂
	63.9449	2E5	TiO, S ₂
	79.9430	1E4	TiO ₂ , S ₂ O
	79.9460	1E4	TiO ₂ , S ₂ O
	95.9344	8E4	TiO ₃ , S ₂ O ₂
	111.924	1E3	TiO ₄ , S ₂ O ₃
	127.894	1E4	Ti ₂ O ₂ , TiS ₂ O, S ₄ , TiSO ₃
	143.886	3E4	Ti ₂ O ₃ , TiS ₂ O ₂ , S ₄ O
	175.871	5E3	TiS ₃ O ₂ , S ₅ O, Ti ₂ O ₅ , TiS ₂ O ₄ , S ₄ O ₃
	196.967	7E2	Au
276.905	2E2	TiAuS, TiAuO ₂ , AuS ₂ O, AuSO ₃	

The peak at atomic mass value of 31.9719 indicates the presence of some sulphur related species in the sample. Using closest peak approximations, the peak at atomic mass value of 276.905 can be attributed to AuS₂O species which therefore indicate the possibility of direct interaction between S and Au centers.

5.3 CATALYTIC ACTIVITY MEASUREMENTS

5.3.1 Effect of source of titania

The catalysts were prepared with a nominal gold loading of 1 wt% using the SSBH method. For Au/TiO₂, 50 mg of catalysts was used while for AuTI673, AuTT673 and AuPT, 100 mg of catalysts were used in each reaction. The activities of the catalysts were measured under similar conditions using a reactant gas mixture consisting of 10%CO, 5%O₂ and 85%He at a total flow rate of 40 mlmin⁻¹. The activities were measured as a function of temperature.

Table 5.5 shows a comparison of the activities of the catalysts prepared using different sources of titania.

Table 5.5: Catalytic activity (percentage conversion) for CO oxidation over gold-titania catalysts prepared using different sources of titania.

Catalyst	Reaction temperature (K)					
	303	313	323	333	343	353
<i>Au/TiO₂</i>	33.3	43.4	54.7	77.3	86.1	98.0
<i>AuTI673</i>	43.0	55.2	77.6	84.4	91.1	95.2
<i>AuTT673</i>	0.0	0.0	0.0	0.0	0.0	0.0
<i>AuPT</i>	9.5	13.4	20.0	26.7	32.7	38.4

The results obtained show that the commercial form of titania (Degussa P25) yields the most active catalyst among the supports studied. Titania prepared from titanium

tetrachloride yields a catalyst that is inactive for CO oxidation at temperatures up to 393 K. Titania prepared from titanium isopropoxide shows superior activity as support compared to potassium titanate despite the fact that the latter has a much higher surface area than all the other supports. It is unlikely that the differences in activities could be as a result of differences in gold loading as the gold loading for the catalysts measure are very close to the nominal loading of 1 wt%.

5.3.2 Effect of sulphate addition to support

Sulphate ions were added to TI373 at levels ranging from 0.05 to 2.5 mol% and to TT373 at 2.5 mol% followed by calcination prior to gold deposition. As shown in Table 5.6, the effect of the incorporation of ions into the support depends on the choice of the support and also on the level of the ions added.

Table 5.6: Percentage CO conversion showing the effect of addition of sulphate ions to the support prior to gold deposition

Catalyst	Reaction temperature (K)					
	303	313	323	333	343	353
<i>AuTI673</i>	29.0	40.3	45.6	53.1	70.8	84.5
<i>Au0.05TI</i>	41.8	55.2	77.6	84.4	91.1	-
<i>Au0.1TI</i>	40.6	53.7	64.5	80.8	90.6	-
<i>Au0.2TI</i>	38.8	50.8	62.2	75.8	90.1	-
<i>Au0.4TI</i>	35.3	47.4	58.4	69.3	84.0	93.6
<i>Au2.5TI</i>	20.4	25.0	32.8	43.0	59.8	64.5
<i>AuTT673</i>	0.0	0.0	0.0	0.0	0.0	0.0
<i>Au2.5TT</i>	2.0	2.6	3.4	4.6	6.1	8.1

For TI373, the addition of relatively low amounts of sulphate ions increases the catalytic activity of the resulting catalysts. The increase in activity is observed with decrease in the sulphate levels from 0.4 to 0.05. However, the highest level of sulphate incorporation (2.5 mol%) leads to a decrease in the activity of the resulting catalyst.

On the other hand, addition of 2.5mol% of sulphate ions to TT373 results in activity enhancement of the resulting catalyst. The catalyst prepared with no sulphate incorporation into the support shows no activity at temperatures up to 373 K. However, with the incorporation of 2.5 mol% of sulphate ions into the support, the catalyst shows some activity for CO oxidation although the increase is not as significant as with the TI373 derived catalysts.

5.3.3 Effect of method of catalyst preparation

The activities of 1 wt% gold-titania (Degussa P25) catalysts prepared by aqueous impregnation (IMP), deposition-precipitation (DP) and single step borohydride methods are shown in Table 5.7.

Table 5.7: Comparison of activities of Au/TiO₂ catalysts prepared by different methods

Preparation method	Reaction Temperature (K)							
	303	313	323	333	343	353	363	373
IMP	8.5	10.0	11.3	14.4	17.6	20.8	22.6	28.5
DP	33.3	42.9	52.3	67.0	77.6	86.2	92.5	96.2
SSBH	33.3	43.4	54.7	77.3	86.1	98.0	-	-

The results indicate that the DP and SSBH methods of synthesis yield gold-titania catalysts that have comparable activities towards CO oxidation. At higher reaction temperatures the SSBH appears to show higher activities. With the IMP method, the activity of the catalyst is about a factor of four lower than for the catalysts prepared using the other two methods.

5.4 DISCUSSION

The commercial form of titania (Degussa P25) has been commonly used as support for gold as a catalyst for the oxidation of carbon monoxide because it yields some of the most active catalyst systems so far reported. The findings of this work are similar to such reports. Titania (Degussa P25) produces more active catalysts compared with titania synthesized from titanium isopropoxide and titanium tetrachloride and also potassium titanate as seen by their activities for CO oxidation in Table 5.5. This enhanced activity of Au/TiO₂ over AuTI, AuTT and AuPT could be attributed to TiO₂ being more crystalline than the other supports. Gold particle size distribution in all the catalysts are quite similar and so differences in activities are not likely to be due to large differences in gold particle sizes.

Surface area measurements show that TI673, and PT have much higher surface areas compared with TiO₂, yet catalysts derived from them show lower activities compared with Au/TiO₂. This implies that observed differences in activities are not due to surface areas of the supports.

The method of catalyst synthesis used for the preparation of these catalysts produce catalysts with very similar gold contents and so any differences in activity observed are unlikely due to differences in the gold contents of the catalysts.

This work also confirms that the DP method of catalyst synthesis produces more active gold-titania catalysts for CO oxidation compared with the aqueous impregnation method as widely reported in the literature. The SSBH method compares with the DP method and is more advantageous than the DP method because as reported by Mallick et al.¹⁰⁶, the number of preparation variables involved in this method is fewer than for DP and there is no need for rigorous pH control during catalyst preparation as with the DP method.

The incorporation of relatively low amounts (0.05 – 0.4 mol%) of sulphate ions into TiO₂ improves the activity of the resulting Au supported catalysts for CO oxidation. However, an addition of 2.5 mol% results in a lowering of the activity of the catalyst. These

observed effects are seen not to be as a result of any physical changes in the support upon sulphate incorporation as the physical properties of all the catalysts are quite similar. In the case of 2.5TI, there is a significant increase in surface area upon addition of 2.5 mol% of SO_4^{2-} ; however the resulting catalyst shows suppressed activity. For AuTT however, the non-sulphated catalyst shows no activity for CO oxidation, but the addition of 2.5 mol% of sulphate ion slightly improves its catalytic performance.

From XPS characterization data, the only peaks clearly detected for the Au-containing samples can be explained as arising from species containing only Au, Ti and O. The detection limit of the instrument used is reported as 0.1 at%. There is therefore a likely indication that the incorporated ions in all cases are present in the samples at levels below the detection limit of the instrument, yet they have a significant influence on the catalytic property of the samples. The relatively small shifts in the Au *4f* binding energies for the samples obtained from the XPS data suggest that the majority of the gold is present as zero-valent metal.

SIMS data on Au0.1T indicates that these ions are present in the catalysts as shown by the peak at atomic mass 31.97. Quantitative assessment of the SIMS data shows evidence of direct interaction between Au and S-containing entities. The intensity ratio ($m/e = 277 / m/e = 197$) for this sample is 0.28 and is fairly consistent with other samples studied and different from the ratios found for sulphur-free systems (see Chapter 7). This leads to the implication that the peak at $m/e = 277$ to be attributed to species containing both gold and sulphur (TiAuS and/or AuS_2O and/or AuSO_3).

5.5 CONCLUSIONS

The SSBH method of synthesis of Au-titania catalysts for CO oxidation is an effective preparation method as it results in catalysts equally as active as those produced by the DP method which is largely reported to yield the most active catalysts. The SSBH also results in most of the gold being deposited on the support and involves fewer steps than with DP.

The effect of sulphate ion addition on gold-titania catalysts for CO oxidation depends on the source of titania and also on the amount of sulphate ion added. Although no direct and concrete reasons have been given for the observed SO_4^{2-} effects on gold-titania catalysts, it is thought that there is direct interaction between Au and S-containing entities and so the effects have at least some chemical nature. It is not yet clear whether the very low surface concentration of the ions reflect a very subtle but significant direct modification of the support, prior to gold loading, which affects catalytic action by controlling the detail of how gold-containing species interact with the support surface during catalyst preparation. However, it is clear that the activity of gold supported catalysts can be extremely sensitive to the details of preparation, including the exposure to “foreign ions” and at the same time suggests that the specific activity of gold can be improved through the judicious use of such ions.

INFLUENCE OF METAL LOADING AND CYANIDE LEACHING OF Au/TiO₂ ON CATALYTIC ACTIVITY

6.1 INTRODUCTION

The oxidation of carbon monoxide on supported gold catalysts is receiving intense scrutiny. From a practical perspective, the comparative price of gold relative to platinum and the greater availability of gold could be attractive. However, in a wider sense, gold is still relatively expensive, implying that for economic reasons it is vital to secure high activities per unit of gold, at least for many of the applications envisaged, including carbon monoxide oxidation. However, many studies have involved catalysts with relatively high gold content. For example, catalysts with mass loadings of gold in the range 4-15% can readily be found.^{80,114,168}

It has been shown that the specific activity for CO oxidation on Au/TiO₂ is independent of gold loading in the mass loading range of 0.06 to 1.9%.¹³⁸ Overall, although an increasing number of publications involve catalysts with loadings of gold in the range 1-2 mass%, there are very few accounts of catalysis by systems with much lower loadings of about 0.1 to 0.2 mass%. For Au/TiO₂ having gold contents in the range 0.5 to 3.1 mass%, specific activities at 300 K were reported to be significantly lower at low loadings; the value of $6.5 \times 10^{-4} \text{ mol}_{\text{CO}}^{-1} \text{ g}_{\text{Au}}^{-1}$ for 3.1 mass% falling by about a factor of eight for 0.5 mass% even though the average observable gold particle size was similar for each loading.¹³⁷ Many other authors have reported high activities at these loadings, but have not discussed trends with loading.

Cyanide extraction of gold has been used to lower gold loadings on supported gold catalyst systems. It has also been used as a means of discriminating between different

gold species in oxide-supported gold catalysts and results have been interpreted in terms of a disproportionately high contribution to catalysis by ionic gold for the water gas shift reaction on gold-ceria.²⁰⁰

In this chapter, the effect of gold loading on the specific activity of Au/TiO₂ for CO oxidation is discussed. The catalysts were prepared by both the DP and SSBH methods with gold loadings in the range of 0.2 to 1.0 wt%. The gold loading of 1.0 wt% catalyst prepared by the DP method has been manipulated by leaching and the effect on the activity of the resulting catalysts reported. The leaching of metallic gold in a supported catalyst via the cyanoaurate anion takes place as indicated in the following equation:



The reaction only takes place under oxidative conditions since Au⁺ is present in the cyanoaurate complex. The leaching in this study has been carried out at Au:CN⁻ mole ratios of 1:1, 1:2 and 1:6.

6.2 RESULTS AND DISCUSSION

6.2.1 Catalyst characterization

6.2.1.1 Metal content of catalysts

The gold content of the catalyst samples were measured by fire assay and gravimetric finish at the Performance Laboratories in Randfontein. This was done to determine if the amount of gold precursor used in the catalyst synthesis affected the amount of gold deposited on the support and also to calculate the specific activity per unit of gold in the catalysts.

Table 6.1: Gold content (wt%) of 1wt% Au/TiO₂ catalyst samples prepared by the DP method and leached at different Au:CN⁻ ratios.

Extent of leaching			
<i>Unleached</i>	<i>Au:CN⁻ = 1:1</i>	<i>Au:CN⁻ = 1:2</i>	<i>Au:CN⁻ = 1:6</i>
0.745	0.534	0.503	0.374

Table 6.2: Gold content (wt%) of Au/TiO₂ catalysts prepared by deposition-precipitation and single step borohydride methods with nominal gold loadings in the range 0.2 to 1.0wt%

Preparation method	Nominal gold loading (wt%)						
	<i>0.2</i>	<i>0.4</i>	<i>0.5</i>	<i>0.6</i>	<i>0.7</i>	<i>0.8</i>	<i>1.0</i>
SSBH	0.154	0.345	0.443	0.578	0.693	0.734	0.883
DP	0.100	0.229	0.356	0.360	0.478	0.497	0.745

Table 6.1 shows the gold content of the catalysts prepared by the DP method before and after cyanide leaching of the sample. It is seen that as the Au:CN⁻ molar ratio is increased more gold is removed from the catalyst sample. Table 6.2 reveals that the SSBH method leads to more gold being deposited onto the support compared with the DP method at the same nominal gold loading.

6.2.2 Catalytic activity measurements

The activity of the catalysts towards the oxidation of CO at atmospheric pressure were measured using 10%CO/5%O₂/85%He at a total flow rate of 40 mlmin⁻¹. In all cases, the catalysts were pretreated oxidatively (10% oxygen in He at a flow rate of 40 mlmin⁻¹) at 573 K for 2 h and allowed to cool to room temperature before the reaction was carried out. In these experiments, 50 mg of catalyst was used in each case.

The following calculation is used to convert the activity of the catalysts from units of percentage conversion to molCO(molAu)⁻¹s⁻¹.

Gas in relative volume: CO = 20
 O₂ = 10
 He = 170
Total volume = 200

$$P_{\text{CO}} = \frac{20}{200} \times P_{\text{tot}}$$

40 mlmin⁻¹: 20%CO in He and 10%O₂ in He such that CO:O₂ = 2:1

P_{Tot} = 640 mmHg = 0.84 atm = 84 kPa

$$\text{➤ } P_{\text{CO}} = \frac{20}{200} \times 84 \text{ kPa} = 8.4 \text{ kPa}$$

$$\begin{aligned} \text{➤ } f_{\text{rateCO}} &= \frac{40 \times 0.10}{2240} \times 0.84 \times \frac{273}{293} \text{ mol min}^{-1} \\ &= 1.3976 \times 10^{-4} \text{ molmin}^{-1} \\ &= 2.329 \times 10^{-6} \text{ mols}^{-1} \end{aligned}$$

Assuming 100% conversion, then conversion = 2.329 x 10⁻⁶mols⁻¹

Mass of catalyst = 50 mg

Mass of gold = 0.5 mg (assuming 1wt% of Au on support)

$$\text{Moles of gold} = \frac{0.5 \text{ g}}{197 \text{ g/mol}} = 2.538 \times 10^{-3} \text{ mmol} = 2.538 \times 10^{-6} \text{ mol}$$

$$\begin{aligned} r_{\text{co}} &= \frac{2.329 \times 10^{-6}}{2.538 \times 10^{-6}} \text{ molCO(molAu)}^{-1} \text{ s}^{-1} \\ &= 0.9176 \text{ molCO(molAu)}^{-1} \text{ s}^{-1} \end{aligned}$$

6.2.2.1 Effect of metal loading

Table 6.3 and Table 6.4 below show the activities of the catalysts prepared by the DP method with different nominal gold loadings in terms of percentage conversions and specific activities respectively.

Table 6.3: % Conversion for CO oxidation as a function of gold loading for Au/TiO₂ catalysts prepared by the DP method.

Nominal gold loading(wt%)	Reaction temperature (K)							
	303	313	323	333	343	353	363	373
0.2	6.4	9.2	14.8	21.5	30.2	40.3	51.5	61.5
0.4	14.4	17.3	23.2	30.1	39.8	51.6	64.6	73.8
0.5	18.6	23.4	30.6	42.4	53.6	65.9	77.2	85.8
0.6	20.9	25.8	33.1	44.1	55.8	67.8	79.7	87.6
0.7	27.2	38.2	46.9	58.2	68.4	79.1	82.6	90.5
0.8	29.4	40.5	47.5	59.0	70.3	80.8	90.3	94.6
1.0	33.3	42.9	52.3	67.0	77.6	86.2	92.5	96.2

Table 6.4: Specific activity/molCO(molAu)⁻¹s⁻¹ for CO oxidation as a function of gold loading for Au/TiO₂ catalysts prepared by the DP method.

Nominal gold loading(wt%)	Reaction temperature (K)							
	303	313	323	333	343	353	363	373
0.2	0.59	0.84	1.36	1.97	2.77	3.70	4.73	5.64
0.4	0.58	0.69	0.93	1.21	1.60	2.07	2.59	2.96
0.5	0.48	0.60	0.79	1.09	1.38	1.70	1.99	2.21
0.6	0.53	0.66	0.84	1.12	1.42	1.73	2.03	2.23
0.7	0.53	0.73	0.90	1.12	1.31	1.52	1.59	1.74
0.8	0.54	0.75	0.88	1.09	1.30	1.49	1.67	1.75
1.0	0.41	0.53	0.64	0.83	0.96	1.06	1.14	1.19

As is expected, the activity of the catalysts in terms of percentage conversion increases with increasing gold content and reaction temperature. However, analysis of the activities in terms of specific activities per unit of gold per second as seen in Figure 6.1, shows that the catalysts with lower gold contents show higher activities per unit of Au. The specific activities are calculated based on the actual gold content of the catalysts as shown in Table 6.2.

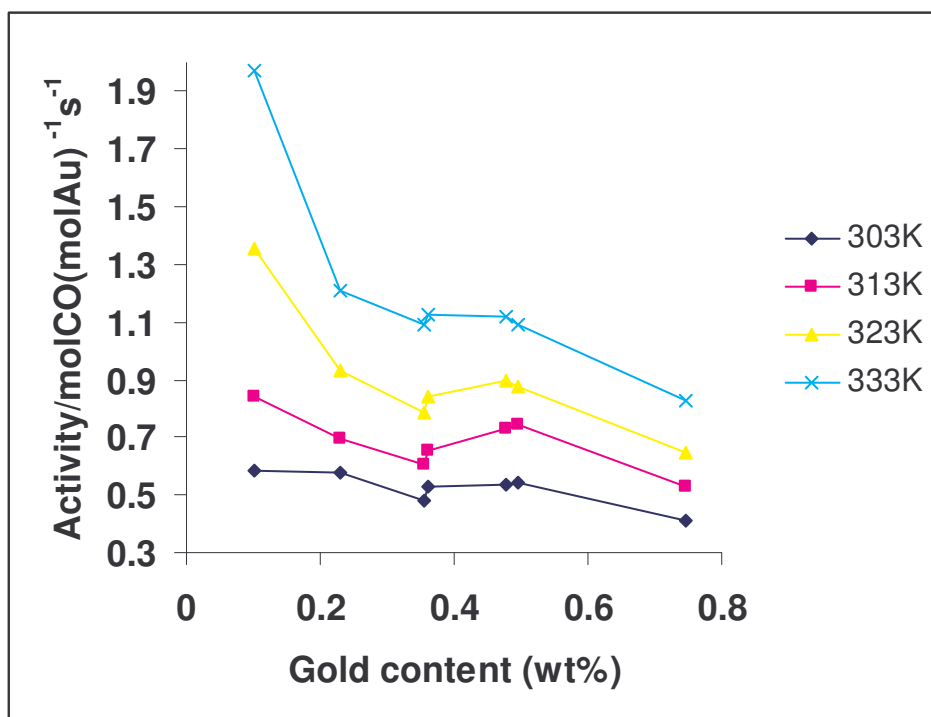


Figure 6.1: Activities of Au/TiO₂ catalysts prepared by DP as a function of gold content at different temperatures.

The SSBH method also shows a similar trend as shown by the DP method with an increase in metal loading leading to an increase in percentage conversion for CO oxidation (Table 6.5) but with the specific activities decreasing with an increase in gold content as shown in Table 6.6. However, a comparison of Figure 6.1 and Figure 6.2 shows that the decrease in specific activity is more pronounced in the case of catalysts prepared by the DP method compared with the SSBH method. The method of preparation

may therefore be a crucial factor in determining how the specific activity of the catalysts depends on the gold loading.

Table 6.5: % Conversion for CO oxidation as a function of gold loading for Au/TiO₂ catalysts prepared by the SSBH method.

Nominal gold loading(wt%)	Reaction temperature (K)							
	303	313	323	333	343	353	363	373
0.2	6.8	8.9	11.6	16.0	22.2	26.3	34.0	41.9
0.4	13.5	17.2	23.5	31.7	42.8	51.6	64.6	73.8
0.5	16.7	22.3	28.6	39.8	53.4	60.4	77.2	85.8
0.6	20.9	25.8	35.6	46.8	59.7	67.8	79.7	92.3
0.7	23.8	30.5	38.6	54.9	68.4	79.1	82.6	96.1
0.8	26.2	35.4	45.2	62.2	70.3	80.8	87.2	98.0
1.0	33.3	43.4	54.7	77.3	86.1	98.0	-	-

Table 6.6: Specific activity/molCO(molAu)⁻¹s⁻¹ for CO oxidation as a function of gold loading for Au/TiO₂ catalysts prepared by the SSBH method.

Nominal gold loading(wt%)	Reaction temperature (K)							
	303	313	323	333	343	353	363	373
0.2	0.41	0.53	0.69	0.95	1.32	1.57	2.03	2.50
0.4	0.36	0.46	0.63	0.84	1.14	1.37	1.72	1.96
0.5	0.35	0.46	0.59	0.82	1.11	1.25	1.60	1.78
0.6	0.33	0.41	0.57	0.74	0.95	1.08	1.27	1.47
0.7	0.32	0.40	0.51	0.73	0.91	1.05	1.09	1.27
0.8	0.33	0.44	0.57	0.78	0.88	1.01	1.09	1.23
1.0	0.35	0.45	0.57	0.80	0.89	1.02	-	-

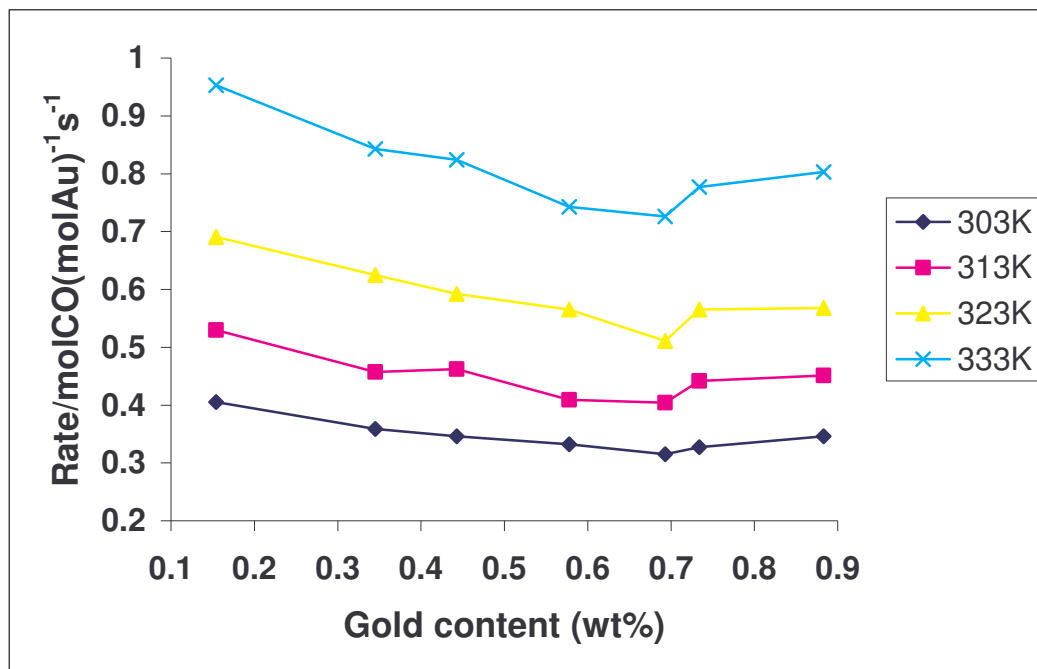


Figure 6.2: Activities of Au/TiO₂ catalysts prepared by SSBH method as a function of gold content at different temperatures.

The results of this work parallel those of some other reports. Wang et al¹²⁰ reported an increase in specific activity with an increase gold loading for Au/FeO_x/Al₂O₃ catalysts in the range 0.05 to 0.5 wt% for CO oxidation. The catalysts with a gold loading of 0.05 wt% showed highest activity and durability. A similar report on gold-iron oxide catalysts with Au content in the range of 1.15 to 2.10 at.% found the activities for CO oxidation to increase significantly with metal loading.¹³⁶ Bamwenda et al. found the specific activities of Au/TiO₂ catalysts having 0.5 to 3.1 wt% gold loading to be significantly lower for lower loadings. The activity of the 3.1 wt% catalyst dropped by a factor of about eight for the 0.05 wt% catalyst.¹³⁷

Moreau et al¹³⁸ showed that the activities of Au/TiO₂ catalysts prepared by deposition precipitation for CO oxidation with metal loadings in the range of 0.06 to 1.9 wt% depend linearly with the gold loading, indicating that the specific activity is the same for all the catalysts.

For Au/TiO₂ catalysts prepared by both deposition precipitation and coprecipitation methods with gold loadings in the range 0.9 to 10.7 wt% and calcined at two different temperatures of 473 and 573 K, Wolf and Schüth¹¹⁴ found that for catalysts calcined at 473 K, the activity did not significantly depend on gold loading. For catalysts calcined at 573 K, they observed that the catalytic activity decreased with an increase in gold loading. They however attributed this to an increase in gold particle sintering with the higher loading catalysts at the higher calcination temperature.

6.2.2.2 Effect of cyanide leaching

The CO oxidation activities of the cyanide leached catalyst samples at the different gold:cyanide levels are shown as percentage conversions and also in units of rate/molCO(molAu)⁻¹s⁻¹ in Table 6.7 and Table 6.8 respectively.

Table 6.7: Percentage conversion for CO oxidation over cyanide leached Au/TiO₂ catalysts with different Au:CN⁻ ratios as a function of reaction temperature.

Au:CN ⁻ ratio	Reaction temperature (K)					
	303	313	323	333	343	353
Unleached	44.5	58.2	73.5	80.2	88.5	95.6
1:1	40.2	56.2	72.3	82.5	90.6	93.4
1:2	35.0	47.5	68.8	80.0	86.9	95.4
1:6	26.8	37.0	49.3	59.2	70.7	77.7

Table 6.8: Rate/molCO(molAu)⁻¹s⁻¹ for CO oxidation over cyanide leached Au/TiO₂ catalysts with different Au:CN⁻ ratios as a function of reaction temperature.

Au:CN ⁻ ratio	Reaction temperature (K)					
	303	313	323	333	343	353
Unleached	0.548	0.717	0.905	0.987	1.090	1.177
1:1	0.691	0.966	1.242	1.418	1.557	1.605
1:2	0.638	0.866	1.255	1.459	1.585	1.740
1:6	0.657	0.908	1.209	1.452	1.735	1.906

The activity per unit mass of gold is seen to increase as more gold is removed from the catalyst. A c.a. 30% removal of gold by leaching with a Au:CN⁻¹ ratio of 1:1 results in about a 10% decrease in CO percentage conversion which corresponds to about 26% increase in the specific activity.

These results are essentially in line with previous suggestions that a significant fraction of the gold present in these systems do not contribute to catalytic activity.²⁰¹ The result also parallels that reported by Fu et al.²⁰⁰ for gold-ceria catalyst examined for water-gas-shift reaction, based essentially on examination of the extracted solids by XPS, that the gold in the residue is in an ionic state, the +1 oxidation state, and that this form of gold is exclusively responsible for catalytic activity.

This work does not permit such a definitive conclusion to be drawn in the case of the gold-titania catalysts for carbon monoxide oxidation because extensive characterization of the leached catalysts is required. Such characterization will probably require catalysts to be examined under *in situ* or even operando conditions.

Nevertheless, this result is consistent with the idea that gold exists in more than one state on gold-titania and that the different states probably contribute differently to catalysis. The cyanide treatment appears to result in near-selective removal of inactive gold, as evidenced by the relatively large increase in specific rate of the catalyst with gold removal.

It is also clear that changes in specific activity as a function of gold loading are not obtained by the more direct method of varying the gold loading in synthesizing catalysts with different gold loadings from the start. In the latter approach, as was shown earlier, although there is an increase in specific activity with lower gold contents, such an increase is not as pronounced as with the cyanide leached samples. The reasons why cyanide extracted samples exhibit a different behavior is not yet clear. The most simple explanation is that the distribution of gold in gold-titania is even more heterogeneous than the simple two state concept (i.e. metallic and ionic gold) suggests. The simple idea,

implicit in the work on gold-ceria²⁰⁰ is that cyanide ions selectively remove metallic gold, leaving ionic gold entities on the surface.

However, it is also quite possible that cyanide ions may also react, at least to some extent, with ionic gold, a process that would not necessarily require any change in the oxidation state of gold if Au⁺ is involved. Moreover, even if cyanide ions attack only metallic gold, it is also conceivable that by removing surface gold from metallic particles, the resulting particles may be corrosively reduced in diameter to a size which might be in the range associated with higher specific activities.^{23,90}

6.3 CONCLUSIONS

The implications of the results presented here are that for economic and practical reasons, it would be better to prepare gold supported catalysts with low gold loadings. Replacement of higher gold loaded catalysts with a larger amount of lower gold loaded catalysts would be preferable. The lower surface density of gold particles in the lower gold loaded catalysts will also allow more effective heat transfer and control of temperature hotspots resulting from the exothermicity of the reaction and will also minimize sintering of gold particles if the reaction is carried out at high temperatures.

The results obtained for the cyanide leaching of the catalysts suggest that gold thrifting is attainable in supported gold catalysts for carbon monoxide oxidation. However, more work with catalysts having a relatively low gold loading (c.a. 0.1 to 0.5 wt%) would be worthwhile. The results also show some promise of enabling a deeper understanding of the seat of catalytic activity in these catalysts to be obtained, but demands are that extensive characterization work be carried out on the extracted solids in order to pursue this aspect.

CHAPTER 7

EFFECTS OF INCORPORATION OF IONS INTO Au/TiO₂ CATALYSTS FOR CARBON MONOXIDE OXIDATION

7.1 INTRODUCTION

The study of catalyst promotion and poisoning by specific entities has always been a source of fruitful information on two levels. In a practical sense it has led to the development of improved catalysts and processes via the judicious use of promoters and/or by the elimination of poisons, or, in many cases, by the use of poisons to increase selectivity. On a scientific level much insight into the seat of catalytic activity has been revealed by poisoning experiments. Hence a deeper understanding of acid catalysis through the studies on the interaction of bases with catalysts, or appreciation of the effects of strongly coordinating entities such as sulphur-containing species on the selectivity of metal catalysts in hydrocarbons transformations has been achieved.

Some of the factors that influence the activity of supported gold catalysts include the nature of the support, the gold crystallite size and the method of preparation.²⁷ It has been suggested that the role of the support is to supply oxygen to form active oxidic gold sites.¹¹² The interface between gold and the support has also been considered to be crucially responsible for catalytic activity in CO oxidation.^{174,202} Charge transfer between the support, particularly involving negatively charged defect sites and the Au particles, has also been associated with catalytic performance.²⁰³ Despite the fact that there are numerous examples of the general promotion of heterogeneous catalysts by the addition of cations and anions,^{204,205} to date relatively little attention has been paid to the subject of the promotion of the catalytic activity of gold by the addition of cations and anions. Some conclusions of promotion/poisoning studies on gold can however be summarized. The poisoning effect of residual chloride ions in gold supported catalysts prepared using an aqueous HAuCl₄ solution is well documented.^{70,78,130,206,207} Residual chloride is found

to affect the activities in two different ways; it facilitates agglomeration of Au particles during heat treatment; and it poisons the catalytically active sites.²⁰⁷ It has recently been shown that the addition of low levels of nitrate ions to Au/TiO₂ catalyst enhances activity towards CO oxidation.¹⁶⁵ Addition of low levels of sodium nitrate (0.00625 and 0.0125 wt% of NaNO₃) led to a significant improvement in catalytic activity compared to non-promoted Au/TiO₂. However, higher concentrations of sodium nitrate led to a decrease in activity with catalyst containing 0.0375 wt% Na being almost inactive. Although little insight was gained into the origin of these effects, the authors suggested that other cations and anions could induce similar effects. Lin et al have also shown that modifying the surface acidity of Y-type and iron/Y-type zeolites by treating them with NaNO₃ solution resulted in an activity enhancement of the corresponding gold supported catalysts for CO oxidation,¹³⁰ though they did not attribute the higher activity to direct effects due to presence of nitrate ions. The enhancement of activity of Au/iron oxide catalyst in the water-gas shift reaction by the addition of ruthenium has also been reported.²⁰⁸

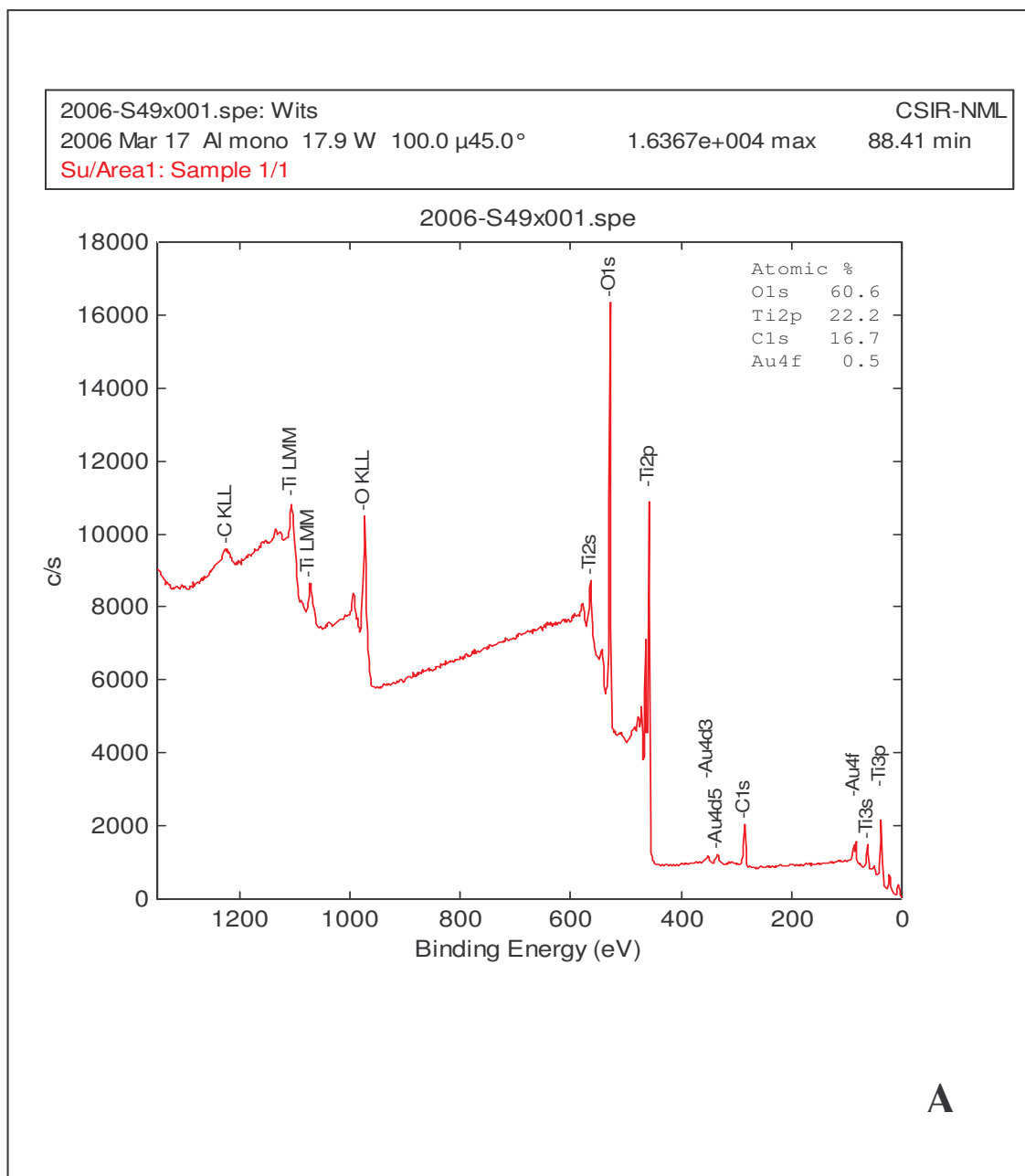
With these background considerations, this chapter reports the effects of addition of a number of anions and cations at different levels into Au/TiO₂ catalysts for CO oxidation. The anions studied include PO₄³⁻, SO₄²⁻, F⁻, NO₃⁻ and Cl⁻ while the cations include Li⁺, Na⁺ and K⁺. In some cases, with addition of the ions, the activity of the resulting catalyst is enhanced, while in others, the activity is depressed. The effect seen depends on the amounts of ions added and the manner of addition. In order to search for synergistic effects operating between the added ions and the support and/or gold, these ions have been incorporated into the support before catalyst preparation and into the catalyst after catalyst preparation. In cases where the ions are incorporated into the support before catalyst preparation, the incorporation has been done at ion/support ratios of 0.05, 0.1, 0.2, 0.4 and 2.5 mol% while where the ions are incorporated into the catalyst, the incorporation has been done at ion/support ratios of 0.4 and 2.5 mol%. Titania (TiO₂, 50 m²/g, Degussa type P25 powder) has been chosen as support because it is the most studied support for gold for CO oxidation and yields some of the most active catalysts so far reported. All the catalysts have been prepared under identical conditions and tested for CO oxidation reaction activity under similar conditions.

7.2 CHARACTERIZATION OF SAMPLES

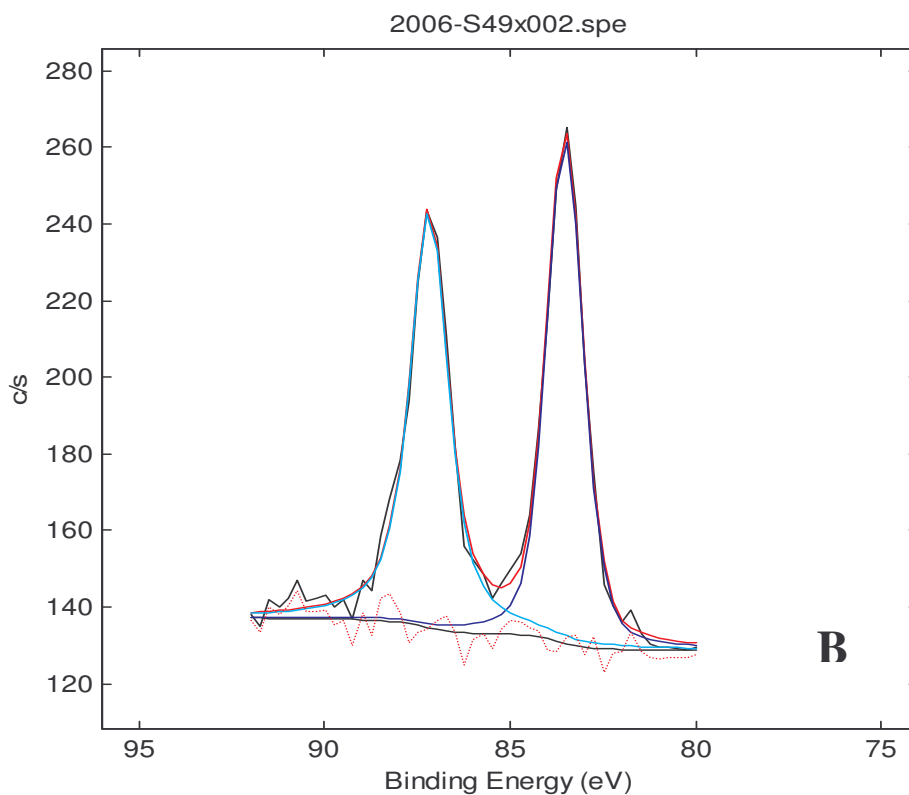
Some characterization techniques have been employed to the catalyst samples and support materials, in order to gain an understanding of the effects observed. These characterization techniques include the following:

7.2.1 X-ray photoelectron spectroscopy (XPS)

Elemental compositions and the 4*f* binding energies of Au for some of the catalysts in which the ions were incorporated into the support before catalyst preparation, were obtained by XPS measurements conducted with a PHI Quantum 2000 Scanning X-ray photoelectron spectrometer. The X-rays used were monochromatic Al K α with an energy of 1486.6 eV and power of ~20 W. In order to minimise as far as possible any X-ray induced changes in the state of the samples, particularly with respect to gold, spectra were collected over a relatively short (ca. 0.5 h) period. In addition, a binding energy reference value of 284.8 eV was applied to the C(1s) peak which was present as adventitious hydrocarbon species on the surface. There was no evidence that the carbon signals were in any way different for the various samples. In any event deconvolution of the C(1s) signals was always carried out prior to the assignment of the reference value. Figure 7.1 below shows a representative XPS spectrum obtained for one of the catalysts. The full spectrum and elemental compositions obtained are listed in Figure 7.1A. The portion of the spectrum showing the Au peaks and the Au 4*f* binding energy is shown in Figure 7.1B. The XPS data for the other catalysts measured in this study are presented in Appendix B. Table 7.1 gives a summary of the XPS data for some of the catalysts measured.



2006-S49x002.spe: Wits
 2006 Mar 17 Al mono 17.9 W 100.0 μ45.0° 2.6521e+002 max 24.83 min
 Au4f/Area1: Sample 1/1 (Shft)



Spec	Band	Pos	PosSep	B_FWHM	FWHM	Height	%Gauss	Area	%Area	ChiSquared
1	1	83.52	0.00	1.18	1.18	131	65	193	50.25	1.56
2	2	87.19	3.67	1.24	1.24	109	30	191	49.75	

Figure 7.1: XPS data for catalyst in which is impregnated with 0.05 mol% PO₄³⁻ prior to gold loading.

Table 7.1: Elemental composition and Au 4f binding energies (eV) for various catalyst samples in which support was impregnated with ions before gold deposition. Data for the catalyst prepared using the unmodified support are also given.

Catalyst	Ion loading with respect to TiO ₂			
	0.05	0.1	0.4	2.5
Au/PO ₄ ³⁻ -TiO ₂	O, Ti, C, Au 83.52	O, Ti, C, Au 83.53	O, Ti, C, Au, P 83.49	O, Ti, C, Au, P 83.38
Au/SO ₄ ²⁻ -TiO ₂	O, Ti, C, Au 83.49	O, Ti, C, Au 83.47	O, Ti, C, Au 83.46	O, Ti, C, Au 83.46
Au/Na ⁺ -TiO ₂	O, Ti, C, Au 83.48	O, Ti, C, Au 83.48	O, Ti, C, Au 83.49	O, Ti, C, Au 83.49
Au/K ⁺ -TiO ₂	O, Ti, C, Au 83.45	O, Ti, C, Au 83.47	O, Ti, C, Au 83.53	O, Ti, C, Au 83.54
Au/TiO ₂ (unmodified)	O, Ti, C, Au 83.22			

In comparison, the binding energy for the untreated system is 83.22 eV. Only in the cases of 0.4 and 2.5 mol% PO₄³⁻ is the instrument able to detect the presence of the incorporated ions. The detection limit of the instrument is 0.1 at%. The incorporated ions are present in the samples at levels below the detection limit of the instrument.

7.2.2 Secondary ion mass spectrometry (SIMS)

Secondary ion mass spectrometry using an ION TOF 5 spectrometer was used to identify the elemental composition of and the chemical status near the surface of the catalysts. This was performed on selected catalysts in cases where the ions were incorporated into the support before catalyst preparation. Figure 7.2 shows SIMS data obtained for the sample in which TiO₂ was impregnated with 0.1 mol% PO₄³⁻ while Table 7.2 shows a summary of the SIMS results for the catalysts measured. The full SIMS results for the other catalysts studied are shown in Appendix A.

Possible Combinations x

1 combinations Act. mass

Mass	Substance	Abundance	Deviation (ppm)
38.96370	K	93.258%	2.325

Possible Combinations x

1 combinations Act. mass

Mass	Substance	Abundance	Deviation (ppm)
47.94794	Ti	73.800%	23.911

Possible Combinations

1 combinations Act. mass 63.941799

Mass	Substance	Abundance	Deviation (ppm)
63.94286	TiO	73.624%	16.611

63.94286 TiO

Add selected to mass list Cancel OK

Possible Combinations

1 combinations Act. mass 70.959503

Mass	Substance	Abundance	Deviation (ppm)
70.95353	KO_2	92.814%	84.076

70.95353 KO_2

Add selected to mass list Cancel OK

Possible Combinations ✕

1 combinations Act. mass

Mass	Substance	Abundance	Deviation (ppm)
79.93777	TiO_2	73.449%	17.830

Possible Combinations ✕

1 combinations Act. mass

Mass	Substance	Abundance	Deviation (ppm)
196.96656	Au	100.000%	0.269

Mass	Substance	Abundance	Deviation (ppm)
276.90433	TiAuO_2	73.449%	5.259

Figure 7.2: Representative SIMS data for catalysts in which TiO₂ is impregnated with 0.1 mol% PO₄³⁻ before gold loading.

Table 7.2: SIMS data for some selected samples showing possible species present in the ion-modified catalysts (support modification before introduction of gold)

Catalyst	Atomic mass	Approximate peak height (counts)	Probable species
Au/PO ₄ ³⁻ -TiO ₂	47.9469	4E6	Ti
	62.9641	3E4	PO ₂
	63.9417	3E6	TiO
	79.9392	6E4	TiO ₂
	196.967	1E3	Au
	276.908	1.5E2	TiAuO ₂
Au/SO ₄ ²⁻ -TiO ₂	31.9722	4E2	S
	63.9422	4E3	TiO, S ₂
	79.9429	4E4	TiO ₂ , S ₂ O
	95.9344	6E4	TiO ₃ , S ₂ O ₂
	111.924	1E3	TiO ₄ , S ₂ O ₃
	175.871	5E3	TiS ₃ O ₂ , S ₅ O, Ti ₂ O ₅ , TiS ₂ O ₄ , S ₄ O ₃
	196.967	7E2	Au
	276.906	2E2	TiAuS, TiAuO ₂ , AuS ₂ O, AuSO ₃
	47.9465	4E5	Ti
	63.9430	4E5	TiO, S ₂
	79.9439	2E4	TiO ₂ , S ₂ O
	127.892	2E4	Ti ₂ O ₂ , TiS ₂ O, S ₄ , TiSO ₃
	143.885	5E4	Ti ₂ O ₃ , TiS ₂ O ₂ , S ₄ O
Au/K ⁺ -TiO ₂	38.9638	1,5E5	K
	47.9468	4E6	Ti
	63.9418	3E6	TiO
	70.9595	1E3	KO ₂
	79.9392	7E4	TiO ₂
	196.967	2,5E3	Au
	276.906	2E2	TiAuO ₂
Au/Na ⁺ -TiO ₂	22.9896	1,2E6	Na
	47.9468	3,5E6	Ti
	63.9417	3E6	TiO
	79.9393	6E4	TiO ₂
	196.967	3E3	Au
	276.909	2E2	TiAuO ₂ , Na ₃ O ₁₃

The SIMS results show the presence of the added ions in the catalyst samples. However, a qualitative examination of the SIMS data reveals that there is no evidence for any species on the surface which arise from the direct interaction between Au centres and the added anion or cation. The only peaks clearly detected for Au-containing entities can be explained as arising from species containing only Au, Ti and O.

7.2.3 BET surface areas

BET surface areas of the catalysts were measured on a Micromeritics Tristar 3000 using nitrogen adsorption-desorption isotherms at -196 °C. These are shown in Table 7.3 below.

Table 7.3: BET surface areas (m²g⁻¹) of various catalyst samples

(a) samples in which support is impregnated with ions before gold deposition

Catalyst	Ion loading with respect to TiO ₂ (mol %)	
	0.4	2.5
Au/PO ₄ ³⁻ -TiO ₂	49	51
Au/SO ₄ ²⁻ -TiO ₂	47	50
Au/Cl ⁻ -TiO ₂	45	49
Au/F ⁻ -TiO ₂	47	49
Au/Li ⁺ -TiO ₂	47	48
Au/Na ⁺ -TiO ₂	47	47
Au/K ⁺ -TiO ₂	53	47

(b) samples in which various ions are impregnated into Au/TiO₂

Catalyst	Ion loading with respect to TiO ₂ (mol %)	
	0.4	2.5
Au/PO ₄ ³⁻ -TiO ₂	46	48
Au/SO ₄ ²⁻ -TiO ₂	47	46
Au/Cl ⁻ -TiO ₂	46	45
Au/F ⁻ -TiO ₂	47	48
Au/Li ⁺ -TiO ₂	47	46
Au/Na ⁺ -TiO ₂	46	45
Au/K ⁺ -TiO ₂	47	47

In comparison, the reported surface area of the pure support is 50 m²/g. The results show that the surface areas of the catalysts are quite similar and do not change significantly with addition of the ions. The surface areas appear to decrease slightly upon gold deposition, probably as the result of a degree of pore narrowing or blocking.

7.2.4 Fire assay and gravimetric finish

The actual gold deposited from the solution onto the support during catalyst preparation was measured by fire assay and gravimetric finish at the Performance Laboratories in Randfontein. This was performed for selected catalysts where the supports were modified with ions before catalyst preparation and to the unmodified catalyst to determine if the presence of the incorporated ions affected the amount of gold deposited onto the support. The determination was not carried out for samples where the ions were added to the prepared catalyst because the ions were added by aqueous impregnation followed by drying and therefore the Au content is expected not to change. The gold content of the samples measured are shown in Table 7.4.

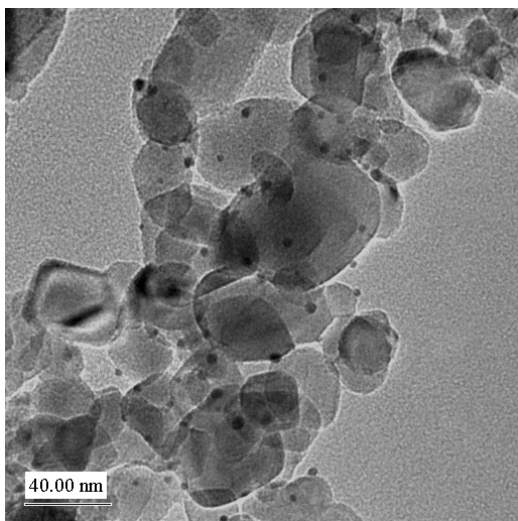
Table 7.4: Gold content of some selected catalyst samples in which the TiO₂ is impregnated with ions before gold deposition.

Catalyst	Ion loading with respect to TiO ₂ (mol%)	
	0.4	2.5
Au/PO ₄ ³⁻ -TiO ₂	0.57	0.58
Au/SO ₄ ²⁻ -TiO ₂	0.73	0.70
Au/Cl ⁻ -TiO ₂	0.72	-
Au/F ⁻ -TiO ₂	0.72	0.70
Au/NO ₃ ⁻ -TiO ₂	0.61	-
Au/Li ⁺ -TiO ₂	0.81	0.50
Au/Na ⁺ -TiO ₂	0.69	0.62
Au/K ⁺ -TiO ₂	0.70	0.71

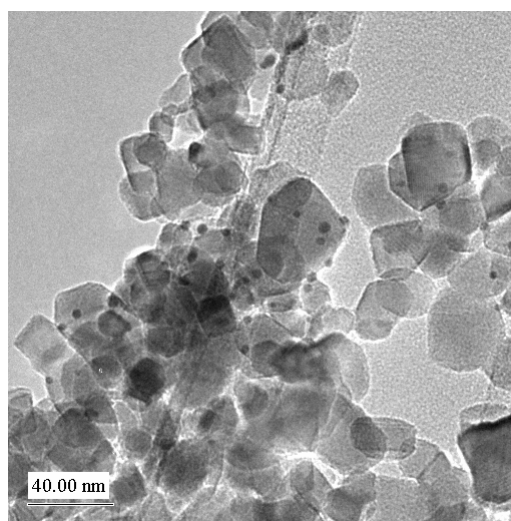
The gold contents are seen to vary between 0.5 and 0.8 wt% with most of the samples containing about 0.7 wt% of Au. The gold content for the unmodified Au/TiO₂ catalyst is 0.7 wt%. The intended gold loading in these catalyst is 1 wt%. It is clearly seen that the presence of the incorporated ions on the support does not influence the amount of gold deposited onto the support during catalyst preparation.

7.2.5 Au crystallite size and distribution

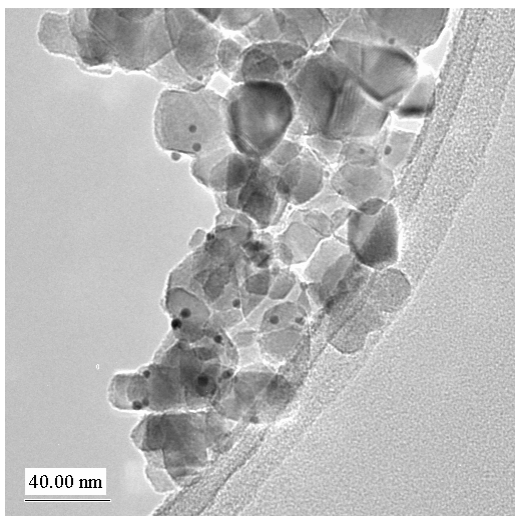
Micrographs obtained using high resolution transmission electron microscopy (HRTEM) were used to determine the gold particle sizes and particle size distribution in some selected catalyst samples. A minimum of 150 gold particles per sample were measured from the micrographs. The gold particle size distributions and average gold particle sizes were obtained from the measurement. All the samples showed similar particle size distributions with Au crystallite sizes ranging from 2 to 10 nm and the majority of particles being in the range 2 to 5 nm. Addition of ions to the support before gold deposition and addition of ions to the catalyst did not seem to significantly affect the gold particle size distributions. Figure 7.3 (a - h) shows the HRTEM micrographs of some selected samples.



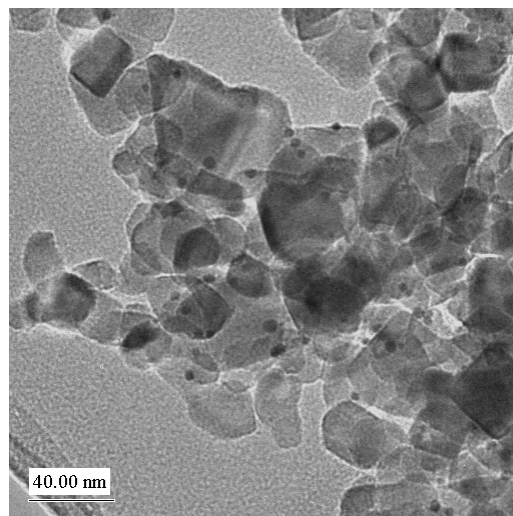
(a)



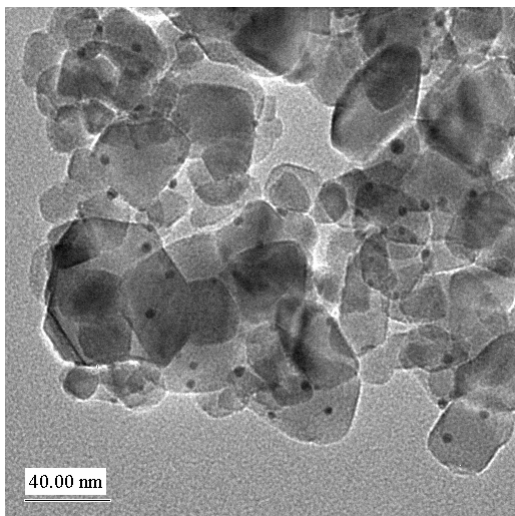
(b)



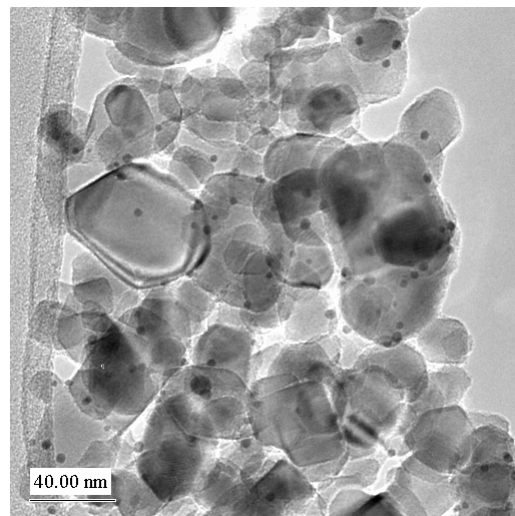
(c)



(d)



(e)



(g)

Figure 7.3: HRTEM of (a) $\text{Au}/\text{PO}_4^{3-}\text{-TiO}_2$ (b) $\text{Au}/\text{SO}_4^{2-}\text{-TiO}_2$; containing 0.4 and 2.5 mol% ions respectively with the ions incorporated onto the support before gold deposition; (c) $\text{Au}/\text{Cl}^-\text{-TiO}_2$ (d) $\text{Au}/\text{SO}_4^{2-}\text{-TiO}_2$ (e) $\text{Au}/\text{K}^+\text{-TiO}_2$; containing 0.1, 0.4, 2.5 mol% ions with ions respectively added to unmodified Au/TiO_2 and (e) unmodified Au/TiO_2 .

7.3 CATALYTIC ACTIVITIES FOR CO OXIDATION

The catalytic activities of all the catalysts were measured under identical conditions. In each case, 50 mg of catalyst diluted with about 450 mg of inert quartz was used. The catalysts were pretreated in an oxidizing environment (10% O₂ bal. He at a flow rate of 40 mlmin⁻¹) at 573 K for 2 hours and allowed to cool to room temperature, before activity measurements. The reactant gas mixture consisted of 10%CO, 5%O₂ and 85%He at a total flow rate of 40 mlmin⁻¹. The activities were measured as a function of temperature from 303 K.

Figure 7.4 shows a comparison of the activities of catalysts in which different levels of ions were incorporated into TiO₂ before gold addition with the unmodified Au/TiO₂ catalyst as reference and Table 7.5 shows the catalytic activities in terms of percentage conversion of CO to CO₂.

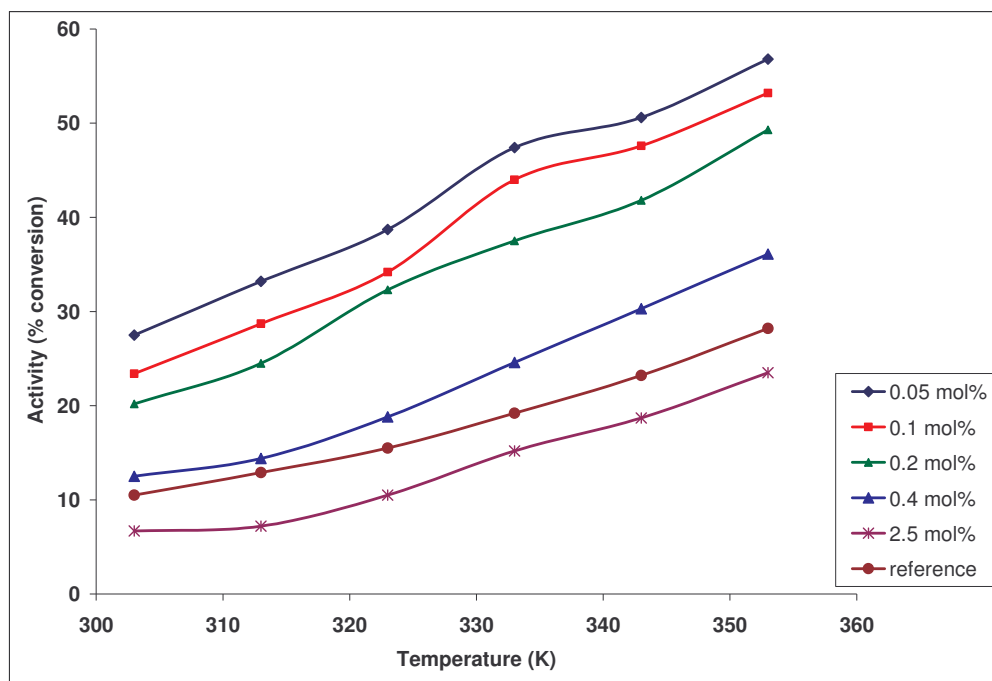


Figure 7.4: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of phosphate ion.

Table 7.5: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with phosphate ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	PO ₄ ³⁻ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	27.5	23.4	20.2	12.5	6.7
313	12.9	33.2	28.7	24.5	14.4	7.2
323	15.5	38.7	34.2	32.3	18.8	10.5
333	19.2	47.4	44.0	37.5	24.6	15.2
343	23.2	50.6	47.6	41.8	30.3	18.7
353	28.2	56.8	53.2	49.3	36.1	23.5

An enhancement in activity is observed with decreasing phosphate content in the support from 0.4 to 0.05 mol%. Support phosphate content of 0.05 mol% leads to about a three-fold increase in activity compared with the non-phosphate treated reference catalyst with c.a 28 % CO conversion compared to 10.5 % conversion for the reference catalyst at 303K. There is however a decrease in the activity of the resulting catalyst when the phosphate content of the support is increased to 2.5 mol%. Although the effect of incorporation of phosphate ions into supported gold catalysts has not previously been reported, phosphate content of up to 10 wt% has been shown to increase the total acidity and catalytic activity of TiO₂ towards alcohol and cumene conversion. The phosphate ion is reported to strongly bind bidentately to TiO₂.¹⁹⁴

For catalysts in which TiO₂ was impregnated with sulphate ions before gold deposition, a similar trend in activity is observed (Figure 7.5 and Table 7.6).

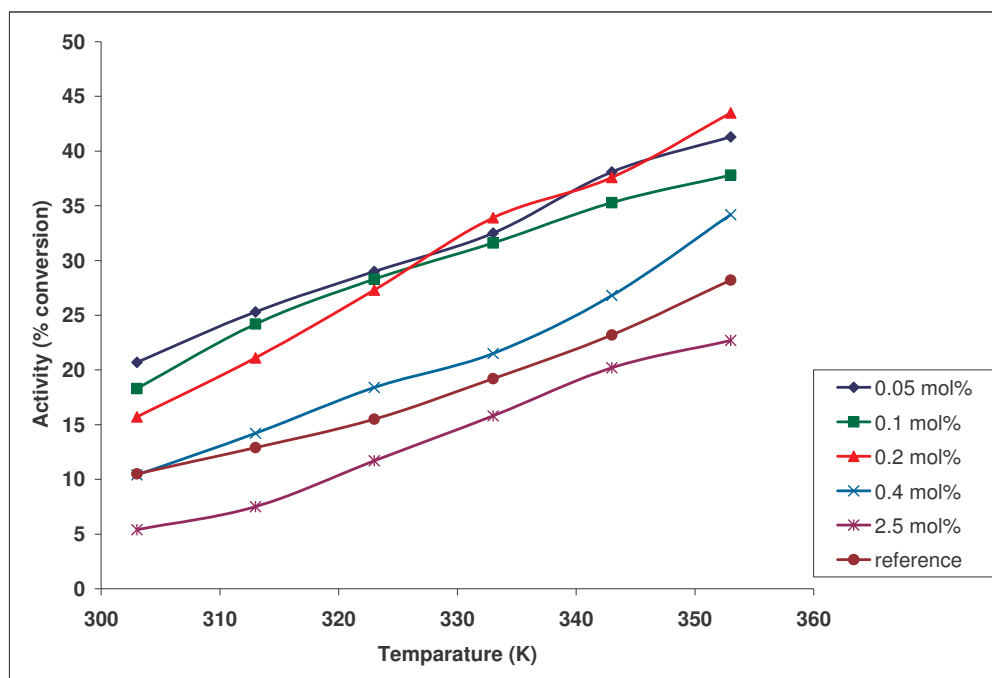


Figure 7.5: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of sulphate ion.

Table 7.6: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with sulphate ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	SO ₄ ²⁻ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	20.7	18.3	15.7	10.4	5.4
313	12.9	25.3	24.2	21.1	14.2	7.5
323	15.5	29.0	28.3	27.3	18.4	11.7
333	19.2	32.5	31.6	33.9	21.5	15.8
343	23.2	38.1	35.3	37.6	26.8	20.2
353	28.2	41.3	37.8	43.5	34.2	22.7

An increase in activities of the catalysts compared to the reference catalyst is observed with decreasing sulphate content from 0.4 mol% to 0.05 mol% with respect to TiO₂. Similarly, addition of 2.5 mol% SO₄²⁻ to the support leads to a drop in activity of the resulting catalyst as with the case of phosphate ion. However, the effect of sulphate

addition on the activity of the catalysts is not as pronounced as in the case of phosphate incorporation. In the case of SO₄²⁻ addition, 0.05 mol% incorporation leads to about a double increase in activity.

In a recent study, Kim and Woo reported the suppression of CO oxidation activity by SO₂ treatment of Au/TiO₂ catalysts. They found sulphate formed on the TiO₂ support after SO₂ treatment and attributed the decrease in activity upon SO₂ treatment to increase in adsorption strength between Au and CO which suppresses the migration of CO adsorbed on Au particles to the Au-TiO₂ perimeter sites to form CO₂. The sulphates also inhibit the formation of carbonate species by blocking migration of CO adsorbed on Au to the oxygen adsorbed on TiO₂.¹⁶¹

Similarly, Haruta et al¹⁶⁰ found a strong deactivation of the CO oxidation activity by SO₂ over Au/TiO₂ catalyst and reported that the SO₂ blocks the active sites for the reaction over the catalyst. Their results are consistent with a model in which the perimeter sites have a special role in the CO oxidation reaction over Au catalysts.

On the other hand, the addition of sulphate ions to TiO₂ has been reported to modify its surface and textural properties and also improve its catalytic performance in the reduction of NO by NH₃. The number of Lewis acid sites increase after doping TiO₂ with sulphate ions.²⁰⁹ Sulphate modification of ZrO₂ has also been reported to inhibit recrystallization of ZrO₂ leading to retention of high surface areas at high temperature and thereby improved catalytic activities towards several reactions.²¹⁰

The modification of TiO₂ with chloride ions before gold deposition results in catalysts with activities similar in trend and comparable to those of the sulphate modified titania catalysts as seen in Figure 7.6 and Table 7.7.

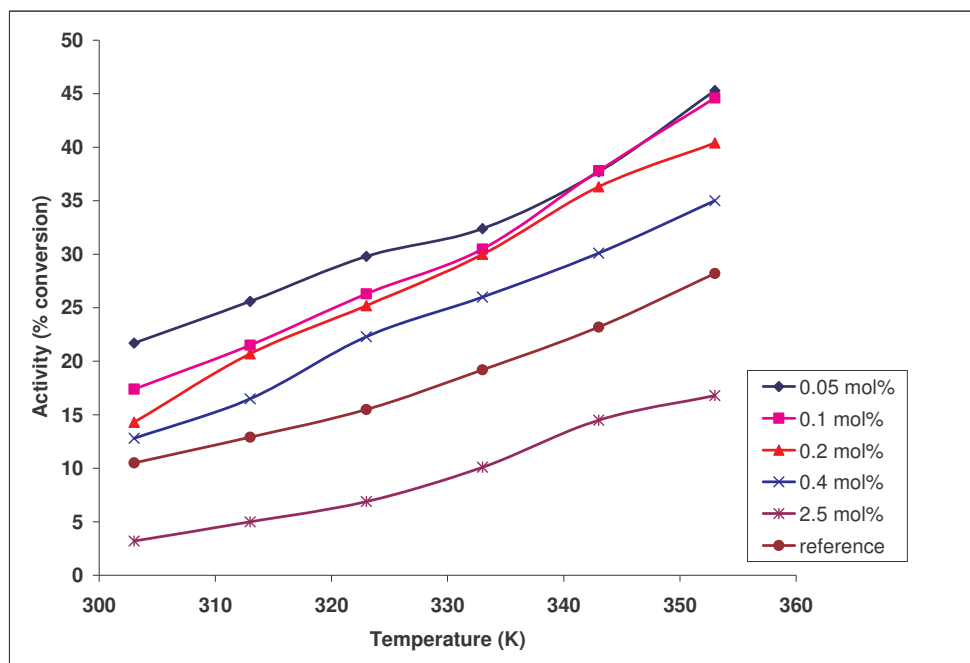


Figure 7.6: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of chloride ion.

Table 7.7: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with chloride ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	Cl ⁻ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	21.7	17.4	14.3	12.8	3.2
313	12.9	25.6	21.5	20.7	16.5	5.0
323	15.5	29.8	26.3	25.2	22.3	6.9
333	19.2	32.4	30.5	30.0	26.0	10.1
343	23.2	37.7	37.8	36.3	30.1	14.5
353	28.2	45.3	44.6	40.4	35.0	16.8

There is an increase in catalytic activity with decrease in chloride content of the support from 0.4 to 0.05 mol% whilst 2.5 mol% chloride content leads to decrease in activity. About a two-fold increase in activity is observed with chloride content of 0.05 mol%. The observed enhancement of the catalyst activity with low chloride addition contradicts

popular reports about the poisoning effect of residual chloride ions in gold supported catalysts prepared using an aqueous solution of H₂AuCl₄ solution. Residual chloride ions have been reported to lead to the formation of somewhat large gold particles during catalyst calcination^{73,74} and also poison the active sites of the catalyst.²⁰⁷

A similar trend in activity is observed with the case of fluoride and nitrate ions as shown in Table 7.8 and Table 7.9 respectively. In both cases, there is an enhancement in catalytic performance with a decrease in the ion content of the support from 0.4 to 0.05 mol%, while 2.5 mol% ion content of the support results in a decrease in activity. In both cases, the increase in activities are quite comparable with the same ion content but are less significant compared with the activity enhancement with the phosphate and sulphate ions incorporation.

Table 7.8: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with fluoride ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	F ⁻ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	18.2	16.2	13.8	13.6	4.5
313	12.9	22.3	20.4	18.3	16.0	6.0
323	15.5	26.7	25.9	24.7	20.6	8.2
333	19.2	30.3	29.8	29.7	25.8	11.5
343	23.2	36.3	35.4	34.2	31.0	15.0
353	28.2	41.8	40.2	38.5	35.3	20.3

Table 7.9: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with nitrate ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	NO ₃ ⁻ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	18.0	17.5	15.3	12.3	5.5
313	12.9	22.5	20.4	19.7	15.5	6.7
323	15.5	27.8	25.1	22.3	19.8	9.0
333	19.2	31.3	28.7	26.5	23.7	12.6
343	23.2	35.7	34.3	33.3	28.2	16.3
353	28.2	40.4	39.3	38.2	33.6	20.6

The dramatic effect of anion treatment on CO oxidation activity recorded at room temperature is shown in Figure 7.7 where anion contents of 0.05 mol% results in catalysts with the highest activities. It is also noted that the absolute rate of CO oxidation on the unmodified catalyst compares favourably with the highest rates found for other Au/TiO₂ catalysts, including those based on the use of Degussa P25 titania. The promotional effect of the ions is clearly not due to the base catalyst being of unusually low activity.

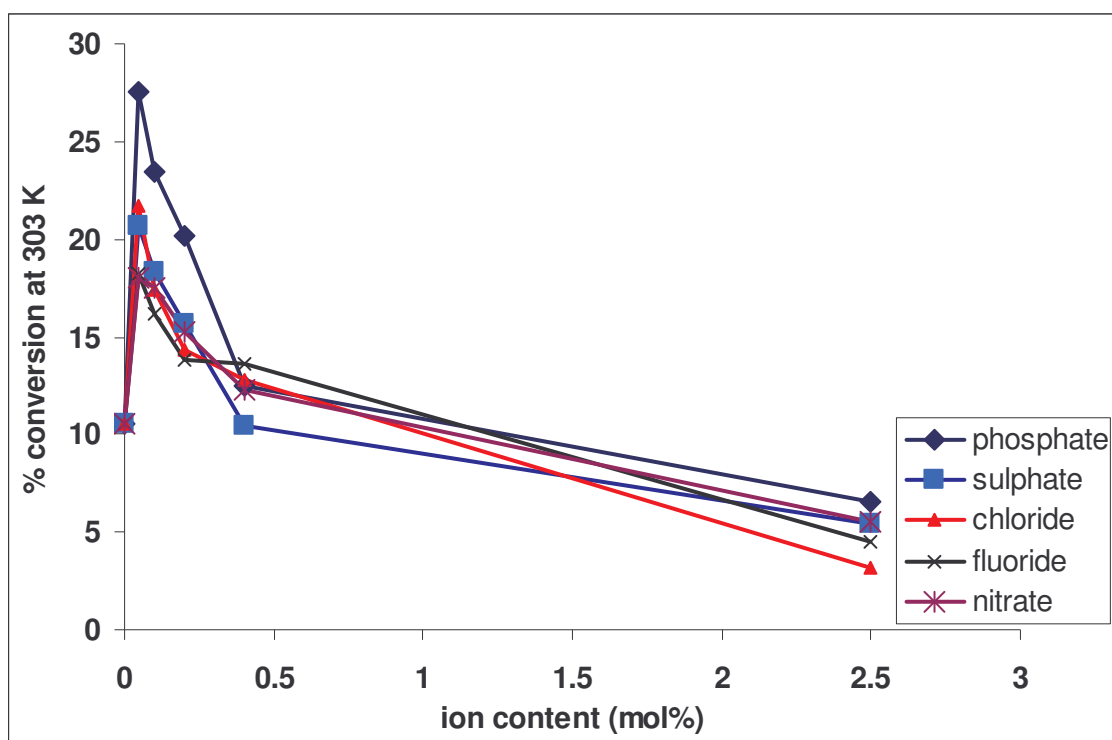


Figure 7.7: Activity at 303 K of various anion modified catalysts as a function of the anion content.

Modification of TiO_2 with cations prior to gold loading also leads to a similar but less significant trend in catalyst activity for CO oxidation as seen for the anions. In the case of Li^+ , there is a slight increase in activity from 10.5 to 12.0% CO conversion at 303K with the incorporation of 0.4 mol% Li^+ into the support. The activity enhancement gradually increases with a decrease in the Li^+ content to 16.3% conversion for 0.05 mol% Li^+ content at 303 K. As seen in Figure 7.8 and Table 7.10, the difference in activities for the catalysts for which there is activity enhancement with Li^+ incorporation is quite small. Again, it is seen that addition of 2.5 mol% Li^+ results in a decrease in activity.

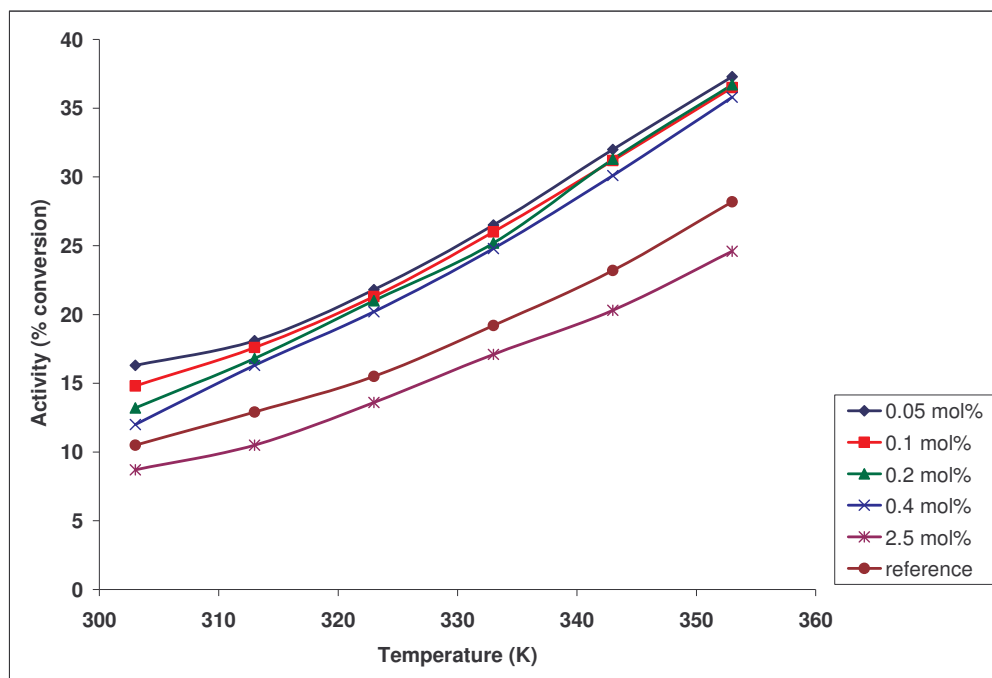


Figure 7.8: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of lithium ion.

Table 7.10: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with lithium ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	Li ⁺ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	16.3	14.8	13.2	12.0	8.7
313	12.9	18.1	17.6	16.8	16.3	10.5
323	15.5	21.8	21.3	21.0	20.2	13.6
333	19.2	26.5	26.0	25.2	24.8	17.1
343	23.2	32.0	31.2	31.3	30.1	20.3
353	28.2	37.3	36.5	36.7	35.8	24.6

As seen in Figure 7.9 and Table 7.11, there is also a slight improvement in catalytic activity of the resulting catalysts with addition of 0.05 – 0.4 mol% Na⁺ ions to TiO₂. However, the activities within this range do not change significantly with a change in the Na⁺ content.

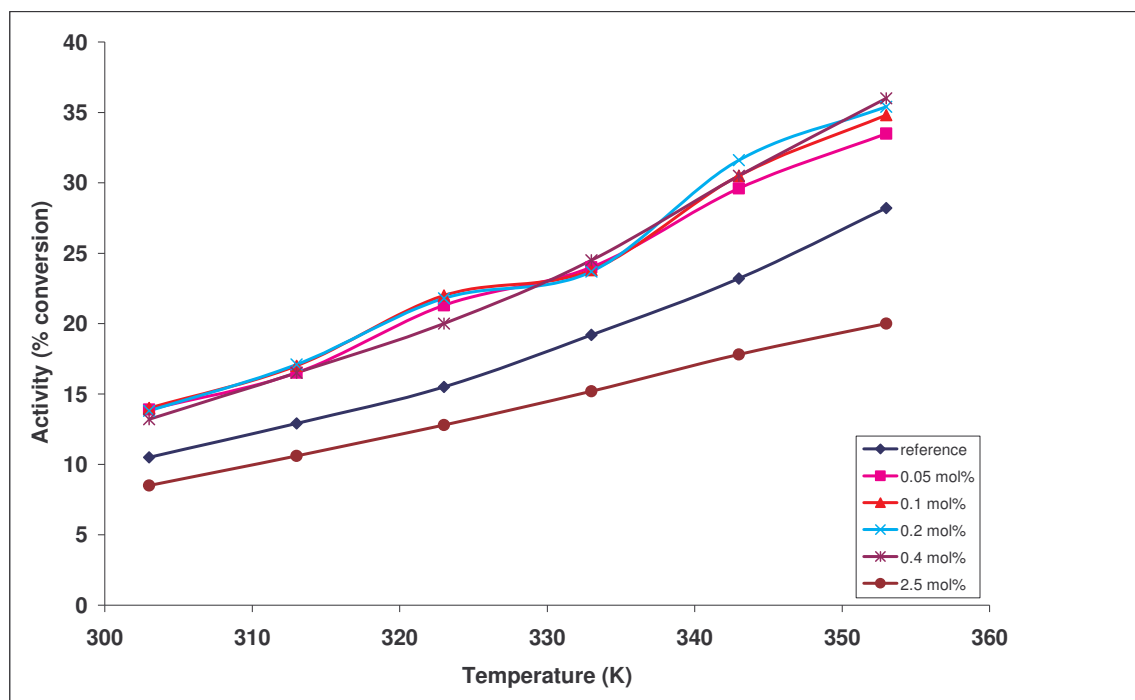


Figure 7.9: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of sodium ion.

Table 7.11: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with sodium ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	Na ⁺ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	13.9	14.0	13.8	13.2	8.5
313	12.9	16.5	17.0	17.1	16.5	10.6
323	15.5	21.3	22.0	21.8	20.0	12.8
333	19.2	24.0	23.8	23.7	24.5	15.2
343	23.2	29.6	30.5	31.6	30.5	17.8
353	28.2	33.5	34.8	35.4	36.0	20.0

In the case of K⁺, there is a decrease in activity at 2.5 mol% on the support, no significant change at 0.4 mol% and a slight increase with 0.2, 0.1 and 0.05 mol% K⁺ content (Figure 7.10 and Table 7.12).

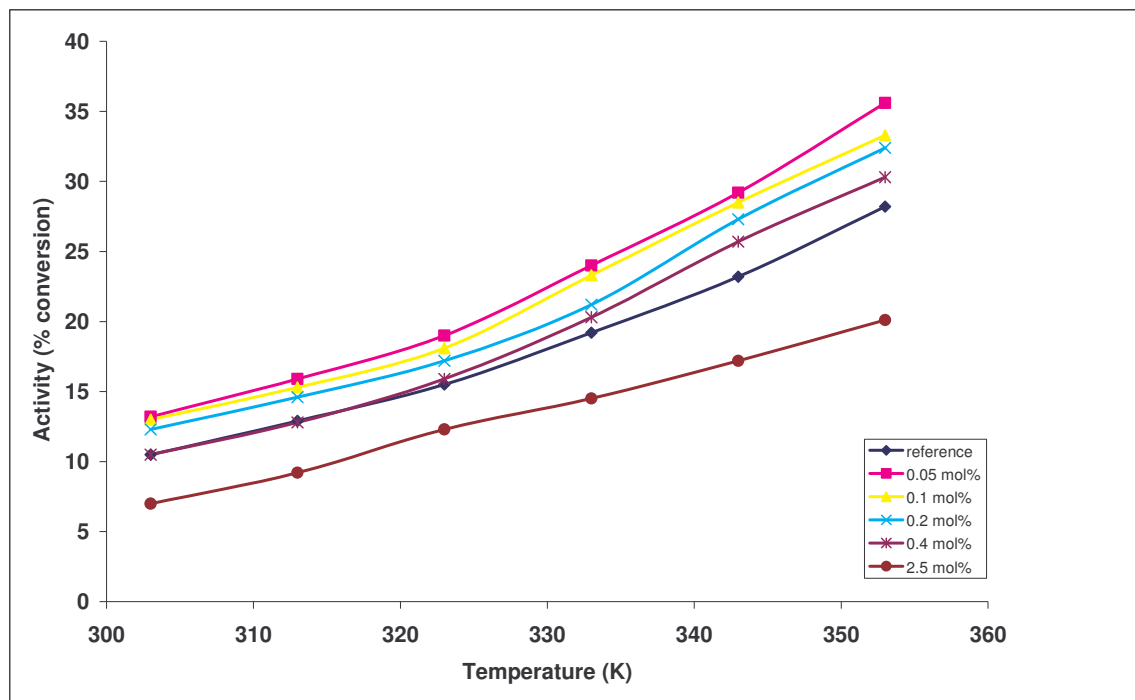


Figure 7.10: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with different levels of potassium ion.

Table 7.12: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts in which the support is impregnated with potassium ions at different levels before gold deposition with the untreated catalyst (ref).

Reaction temp (K)	K ⁺ content in support (mol%)					
	0.0 (ref)	0.05	0.1	0.2	0.4	2.5
303	10.5	13.2	13.0	12.3	10.5	7.0
313	12.9	15.9	15.3	14.6	12.8	9.2
323	15.5	19.0	18.1	17.2	15.9	12.3
333	19.2	24.0	23.3	21.2	20.3	14.5
343	23.2	29.2	28.5	27.3	25.7	17.2
353	28.2	35.6	33.3	32.4	30.3	20.1

Figure 7.11 shows the effect of cation treatment on the CO oxidation activity recorded at room temperature where again, as in the case of the anions, cation contents of 0.05 mol% yield catalysts with highest activities.

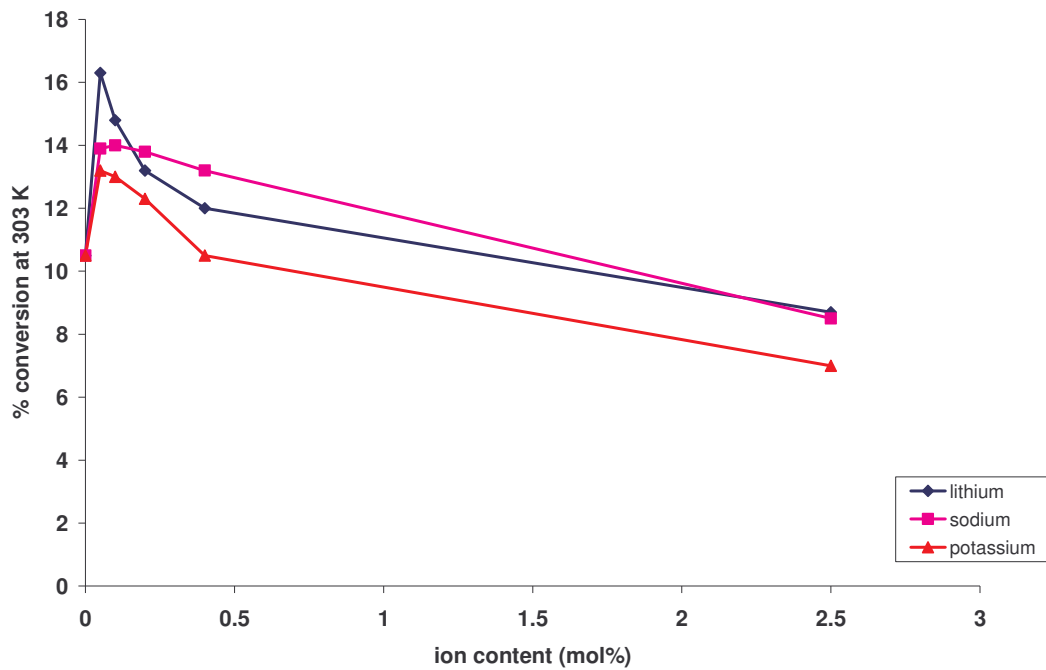


Figure 7.11: Activity at 303 K of various cation modified catalysts as a function of the cation content.

A comparison of the activities of the catalysts at 0.05 mol% ion incorporation to TiO₂, shows that impregnation of 0.05 mol% of phosphate ion into the support results in a more significant increase in activity when compared with the other anions (Figure 7.12). Although the other anions show an increase in activity compared with the non-treated sample, they show no significant difference in activity with each other. For the cations (Figure 7.13), the lithium ion shows a slightly higher activity compared to sodium and potassium ions, both of which are quite comparable in activity. The observed enhancement in activity with the incorporation of these ions may therefore not be directly related to the charge or the size of the ions.

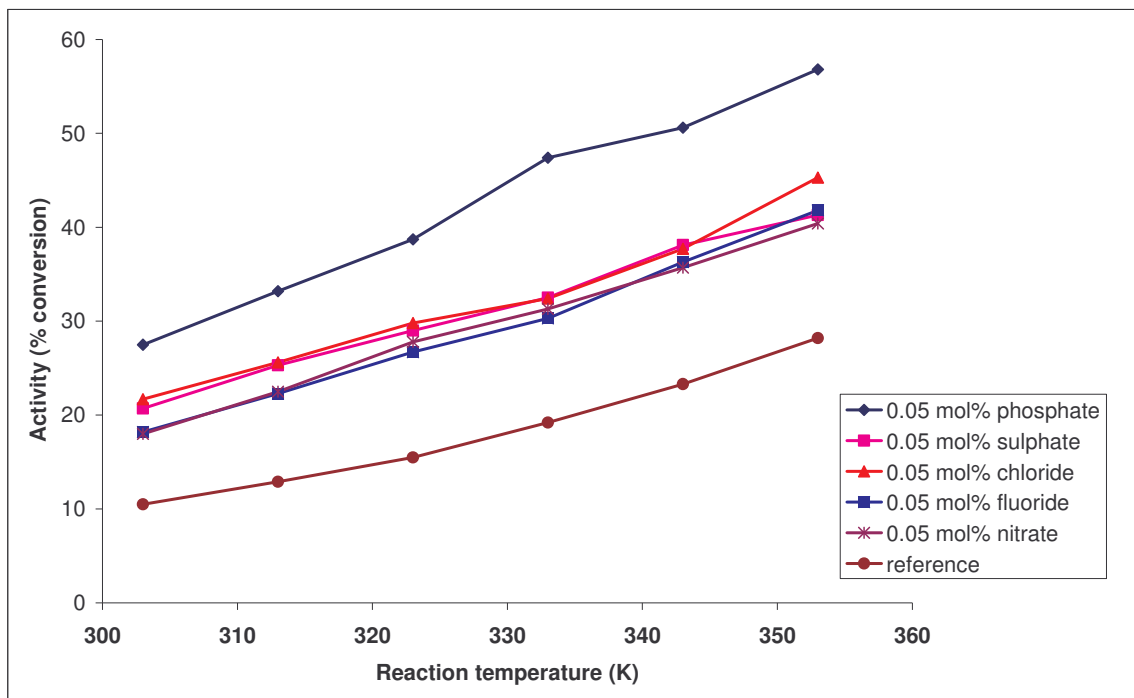


Figure 7.12: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with 0.05 mol% of different anions.

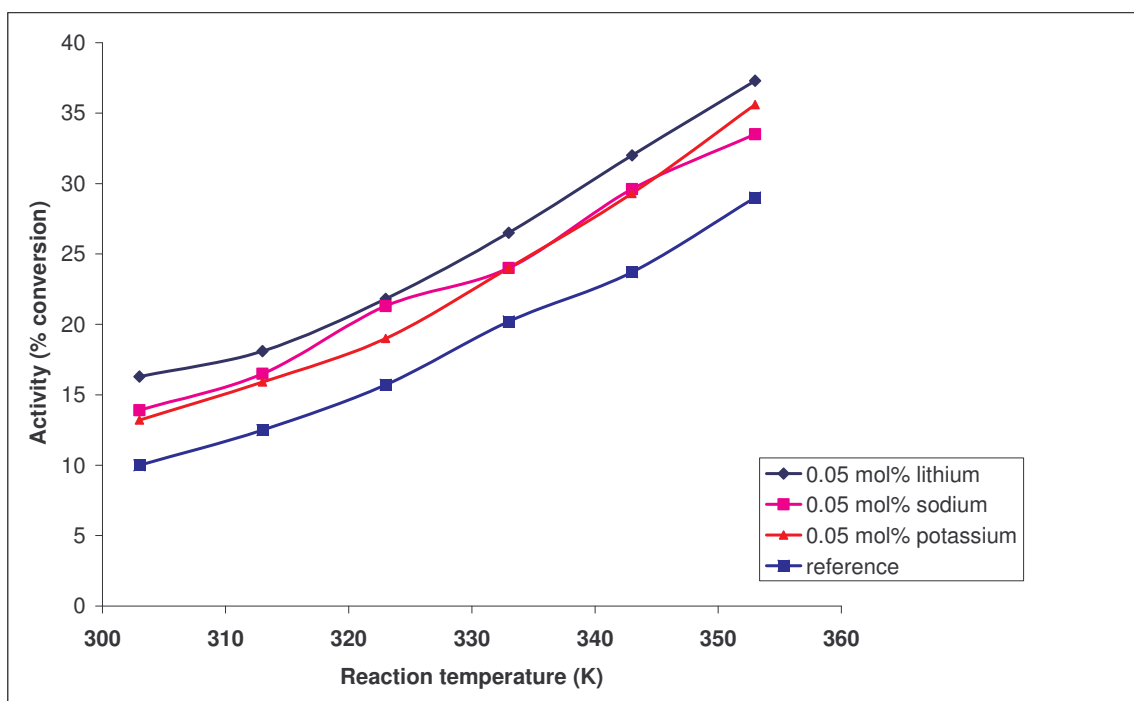


Figure 7.13: Graphical comparison of CO oxidation activity (% conversion) as a function of reaction temperature (K) of Au/TiO₂ catalysts for which TiO₂ is impregnated with 0.05 mol% of different cations.

The addition of the ions to Au/TiO₂ at levels of 0.4 and 2.5 mol% with respect to TiO₂ in all cases lead to a decrease in activities of the catalysts compared to the unmodified catalyst.

Table 7.13: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts impregnated with 2.5 mol% level of different anions with the unmodified catalyst (ref).

Reaction temp (K)	Unmodified catalyst (ref)	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	F ⁻	NO ₃ ⁻
303	10.0	1.2	1.0	0.0	1.5	1.8
313	12.5	1.8	1.5	0.0	3.5	2.6
323	15.7	2.6	2.4	0.0	5.8	4.5
333	20.2	4.0	3.8	0.0	8.6	7.0
343	23.7	6.8	5.9	0.0	11.4	9.6
353	29.0	9.0	7.8	0.0	13.8	12.3

Table 7.14: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts impregnated with 0.4 mol% level of different anions with the unmodified catalyst (ref).

Reaction temp (K)	Unmodified catalyst (ref)	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	F ⁻	NO ₃ ⁻
303	10.0	2.0	1.6	0.5	2.2	2.6
313	12.5	3.5	3.3	1.2	4.5	4.2
323	15.7	5.8	5.4	2.3	6.8	7.3
333	20.2	8.7	8.0	3.6	9.0	10.5
343	23.7	11.2	10.6	5.5	13.2	14.7
353	29.0	14.5	13.8	7.0	17.9	19.2

Table 7.13 and Table 7.14 show that for anion incorporation into Au/TiO₂, an increase in the ion content in all cases leads to an increase in the level of activity depression of the catalysts. With 2.5 mol% Cl⁻ ion level, the catalyst shows no activity. This is consistent with the earlier report that residual chloride ions in gold supported catalysts prepared using HAuCl₄ as gold precursor, poison the active sites of the catalysts.²⁰⁷

Incorporation of cations into Au/TiO₂ also shows a similar trend in catalytic activity (Table 7.15 and Table 7.16) as with the anions but the activity suppression is less significant compared with the anions.

Table 7.15: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts impregnated with 2.5 mol% level of different cations with the unmodified catalyst (ref).

Reaction temp (K)	Unmodified catalyst (ref)	Li ⁺	Na ⁺	K ⁺
303	10.0	2.0	2.0	1.8
313	12.5	3.8	4.0	3.5
323	15.7	6.7	7.8	5.9
333	20.2	10.2	10.8	8.3
343	23.7	13.9	14.2	10.9
353	29.0	18.0	18.7	14.7

Table 7.16: Comparison of catalytic activities (% conversion) for CO oxidation of catalysts impregnated with 0.4 mol% level of different cations with the unmodified catalyst (ref).

Reaction temp (K)	Unmodified catalyst (ref)	Li ⁺	Na ⁺	K ⁺
303	10.0	3.0	3.2	3.2
313	12.5	6.2	6.0	6.3
323	15.7	13.0	12.5	12.3
333	20.2	16.7	15.2	15.5
343	23.7	20.2	18.6	18.4
353	29.0	24.9	21.4	20.9

7.4 DISCUSSION

As seen from XPS characterization, even though the incorporated ions are present in the samples at levels below the detection limit of the instrument, they have a significant influence on the catalytic properties of the samples. The XPS data suggests that the majority of the gold tends to be present as zero-valent metal, but there is a tendency for

higher CO conversion levels to be associated with samples having slightly more electron deficient gold as evidenced by small shifts in the binding energy (Figure 7.14). The observed shifts are small, however and much more data is needed before reaching a firm conclusion.

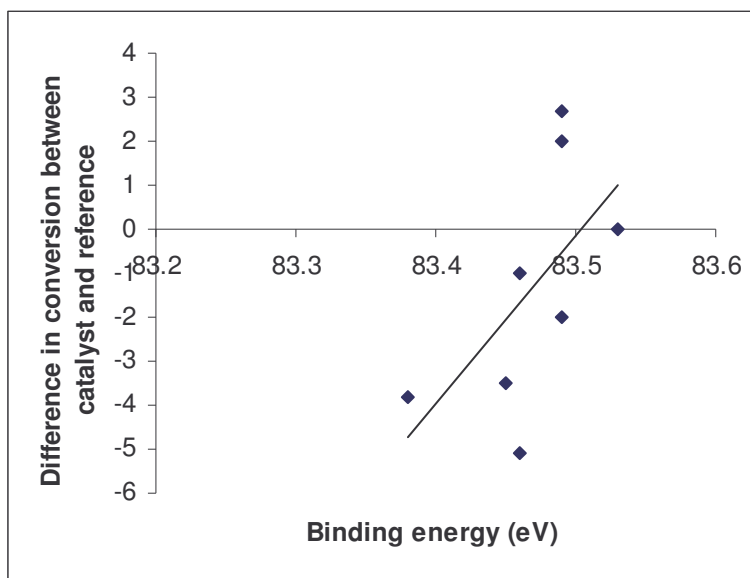


Figure 7.14: Plot of Au 4*f* binding energy versus difference in conversion between catalysts and reference catalysts.

The electron density on the gold might have been considered as being susceptible to modification by presence of either cations or anions. So far such effects cannot be convincingly demonstrated. Indeed, it is clear that the added ions cannot be readily detected by XPS at all, except in the case of phosphorus. SIMS measurements do reveal their presence.

From an analysis of the SIMS data, in general there is no evidence for any species on the surface which arise from direct interaction between Au centres and the added ions. This suggests that the catalytic modification arises via indirect interactions between the gold centres and the added anions or cations, or, alternatively the catalytic action of gold is modified by subtle changes in the support surface, brought about by exposure to anions and/or cations prior to gold deposition. Only in the case of sulphate modification of the titania support is there evidence from a qualitative assessment of the SIMS data that

direct interaction between Au and S-containing entities take place. Thus the intensity ratio ($m/e = 277 / m/e = 197$) are fairly constant at values of 0.07 (Na^+), 0.08 (K^+) and 0.15 (PO_4^{3-}) except for that where the titania support was modified by sulphate ions. For this specific sample the intensity ratio is much higher at about 0.3, implying that at least some contribution to the $m/e = 277$ peak for this specific sample arises from species containing both gold and sulphur (TiAuS and/or AuS_2O and/or AuSO_3). This view is strongly supported by the fact that for a Au/titania sample prepared without addition of sulphate to the titania support, no peak at 277 is seen in the SIMS spectrum. For a sulphate modified support therefore, there is direct evidence that entities containing both Au and S exist on the surface in the final catalyst and it may well be therefore that the promoting effect of sulphate is due, at least in part, to a direct interaction occurring between gold centres and sulphate or sulphate-derived entities. This conclusion, taken together with XPS evidence strongly suggests that such enhancement is associated with gold centres having a relatively high electron deficiency, which is, in turn, consistent with proposals that ionic gold contributes to catalytic activity. This does not rule out that zero-valent gold is also involved.^{27,28,208} The actual oxidation state of the gold remains somewhat unclear, and for this reason, the relative electron deficiencies are preferably discussed. The use of XPS does not help in clarifying the situation, given the appearance of Au(4f) peaks having binding energies below 84.0 eV normally associated with metallic gold. This is consistent with the XPS data recorded by others for Au-titania²¹¹⁻²¹⁴. Formal assignment of the low BE peak at *ca.* 83.2-83.3 eV to $\text{Au}^{\delta-}$ has been considered, with its formation arising from an intimate interaction between Au(0) and surface Ti^{3+} centres at defects in the titania^{213,214}. Finally, it is worth emphasizing that the Au(4f) peaks in this current study are relatively narrow and symmetrical. This is in contrast to those seen when zirconia-titania supports are used with gold. Then there is clear evidence²⁰¹ from the peak near 83-84 eV of a high binding energy component present at *ca.* 8-10% of the total peak area and assigned to an entity best regarded as $\text{Au}^{\delta+}$.

Returning to the other anions and cations, other than sulphate, it appears that these exert an influence on catalytic activity via their interaction with the support, rather than by direct interaction with gold centres. It is yet to be determined whether the very low

surface concentration of the ions reflect a very subtle but significant direct modification of the support in the final working catalyst, or whether the effect operates via a surface modification of the support, prior to gold loading. This would affect catalytic action by controlling the detail of how gold-containing species interact with the surface in the deposition-precipitation-reduction process of catalyst preparation.

7.5 CONCLUSION

This work provides further support for the idea that the activity of gold can be extremely sensitive to the details of catalyst preparation, including the exposure to “foreign” ions¹⁶⁵, and at the same time suggests that the specific activity of gold can be improved through the judicious use of such ions. The very low concentration levels of added ions at which enhanced activity is observed, coupled with the probability that only a fraction of the gold centres may contribute to catalytic activity pose a significant challenge in determining more precisely the origin of these effects. Direct anion-gold interaction appear to be taking place in the case of sulphate-modified titania.

CHAPTER 8

GENERAL CONCLUSIONS

In the literature review of this work, it was shown that highly dispersed gold nanoparticles on suitable supports have been reported to exhibit high catalytic activities for the low temperature oxidation of carbon monoxide to carbon dioxide. The choice of the catalyst support as well as the method of catalyst preparation are reported amongst several other factors to be important and to affect the activity of this group of catalysts. Amongst many supports that have been used for gold nanoparticles for this reaction, titanium dioxide, more often the commercial form, Degussa P25, has been most widely used because it is reported to yield some of the most active and stable catalysts. It is also known that the modification of catalyst supports and/or supported metal catalysts by the inclusion of additives during catalyst preparation, could affect their catalytic behavior. With this in mind, this study was aimed at modifying TiO₂ as support for gold for CO oxidation by the inclusion of several additives during catalyst preparation and evaluating the effects that such modification would have on the catalytic properties of the resulting catalysts.

In Chapter 4 of this work, the surface of TiO₂ was modified by preparing mixed oxide based TiO₂ supports using a number of transition series metal oxides. These were used in preparing the corresponding supported gold catalysts and tested for CO oxidation. In all cases it was found that the unmodified TiO₂ supported gold catalyst had superior catalytic performance when compared to the mixed oxide and other single metal oxide supported catalysts. The beneficial effects that are seen for some mixed oxide support systems do not apply universally to reactions. Characterization of the catalysts by transmission electron microscopy showed no correlation between catalytic activity and gold particle size, suggesting that metallic gold may not be the sole gold species that are responsible for catalytic activity for CO oxidation in these catalyst systems.

In Chapter 5, other forms of TiO_2 were prepared to support Au for CO oxidation reaction and their catalytic activities were compared with that of the commercial form of TiO_2 (Degussa P25). The supports prepared include titania and the corresponding sulphated titania prepared by aqueous hydrolysis of titanium (IV) isopropoxide, titania and the corresponding sulphated titania prepared from potassium tetrachloride, and potassium titanate. The CO oxidation catalytic activities of Au/ TiO_2 catalysts prepared using different synthesis methods was also evaluated and the preparation methods studied include the deposition-precipitation method, the single step borohydride method and the aqueous impregnation method. The results obtained showed that the commercial form of titania TiO_2 (Degussa P25) produced the most active catalysts compared to the synthesized forms. The enhanced superior activity of the TiO_2 (Degussa P25) derived catalyst could be attributed to its higher crystallinity relative to the other supports.

The incorporation of relatively low amounts (0.05 – 0.4 mol%) of sulphate ions into TiO_2 improved the activity of the resulting Au supported catalysts for CO oxidation. However, an addition of 2.5 mol% resulted in a lowering of the activity of the catalyst. These observed effects do not arise as a result of any physical changes in the support upon sulphate incorporation since the physical properties of all the catalysts are quite similar. For the catalyst where the supports was prepared from titanium tetrachloride however, the non-sulphated catalyst showed no activity for CO oxidation. However, the addition of 2.5 mol% of sulphate ion slightly improved its catalytic performance.

The DP method of catalyst synthesis was found to produce more active gold-titania catalysts for CO oxidation compared with the aqueous impregnation method. Catalysts produced by the SSBH method compared well in activity to those prepared by the DP method. The SSBH method is however more advantageous over DP as it involves fewer steps. It cannot be ruled out entirely that the SSBH method offers some its high activity to promotional effects of Na^+ from sodium borohydride. In Chapter 7 it was shown that addition of small amounts of Na^+ to TiO_2 improved the catalytic activity of Au/ TiO_2 for CO oxidation.

In Chapter 6, the effect of gold loading on the specific activity of Au/TiO₂ catalysts was studied by preparing catalysts using the DP and SSBH methods with gold loadings in the range of 0.2 to 1.0 wt%. Leaching of some of the gold from the 1wt% Au/TiO₂ prepared by the DP method was also studied. For catalysts prepared with varying gold contents, the specific activity per unit of gold for CO oxidation catalysis was found to increase with a decrease in the gold loading. This effect was more significant for catalysts prepared by the DP method when compared to catalysts prepared by the SSBH method. For catalysts where cyanide leaching using aqueous potassium cyanide solution was used to extract some of the gold in the catalysts, the activity per unit mass of the gold was found to increase as more gold was removed from the catalyst.

These results suggest that a significant fraction of the gold in these catalyst systems do not contribute to the CO oxidation catalytic activity. This is consistent with the idea that gold exists in more than one state in gold-titania for CO oxidation and that the different states contribute differently to catalysis. The cyanide treatment appears to result in near-selective removal of inactive gold, as evidenced by the relatively large increase in the specific rates of the catalyst upon gold removal.

It is also clear that changes in specific activity as a function of gold loading are not obtained by the more direct method of varying the gold loading in catalyst synthesis with different gold loadings. Although there is an increase in specific activity with lower gold contents, such an increase is not as pronounced as with the cyanide leached samples. The reasons why cyanide extracted samples exhibit a different behavior is not yet clear. The most simple explanation is that the distribution of gold occurs in many oxidation states in gold titania, and that the gold is found not only as metallic and ionic gold.

The implication of the results presented here is that for economic and practical reasons, it would be better to prepare gold supported catalysts with low gold loadings. Replacement of higher loaded catalysts with a larger amount of lower loaded catalysts would be preferable. The lower surface density of gold particles in the lower loaded catalysts will also allow more effective heat transfer and control of hotspots resulting from the

exothermicity of the reaction and will also minimize sintering of gold particles if the reaction is carried out at high temperatures.

The results obtained for the cyanide leaching of the catalysts suggest that gold leaching is attainable in supported gold catalysts for carbon monoxide oxidation. However, more work with catalysts having a relatively low gold loading (c.a. 0.1 to 0.5 wt%) would be worthwhile. The results also show some promise in enabling a deeper understanding of the seat of catalytic activity in these catalysts, but extensive characterization work needs to be carried out on the extracted solids in order to pursue this aspect.

It cannot be ruled out entirely that the enhanced activities of the cyanide leached catalysts are as a result of K^+ ions from the KCN solution being present as these ions have been seen to lead to enhanced catalytic activities at modest levels (Chapter 7).

Chapter 8 reports on the effects of the addition of a number of anions and cations at different loadings (0.05 to 2.5 mol% with respect to the support) into Au/TiO₂ catalysts for CO oxidation reaction. The anions studied include PO₄³⁻, SO₄²⁻, F⁻, NO₃⁻ and Cl⁻ while the cations include Li⁺, Na⁺ and K⁺. In order to search for synergistic effects operating between the added ions and the support and/or Au, the ions were incorporated into the support before catalyst preparation and into the catalyst after catalyst preparation. The catalytic results obtained for the CO oxidation reaction reveal that in all cases where the ions were added to the catalysts after catalyst preparation, there was a decrease in the activity of the resulting catalysts with the decrease being more significant as the ion level increased. However and more interestingly, addition of 0.05 to 0.4 mol% of the ions to the support, prior to gold addition, resulted in most cases in activity enhancement whilst similar addition of 2.5 mol% of the ions resulted in a decrease in activity. It is assumed here that the mol% of the ions added equals the final concentration of the ions in the catalysts and that no ions are lost in solution during catalyst preparation in the cases where the ions are added to the support prior to catalyst preparation. This assumption is based on the fact that if some of the ions were lost during catalyst preparation, the clear trends seen would not be expected. Although attempts have been made to understand the

origin of the observed effects, the enhanced activities observed at very low ion concentrations in cases where the ions are added to the support before gold addition requires the development of extensive analytical methods in order to fully understand the origins of these effects.