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SO_2 ABATEMENT USING GOLD CATALYSTS

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Degree of Master of Science in Engineering

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Master of Science in Engineering.

Johannesburg, 2009

DECLARATION

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

_____

(L A Chalom)

_____ Day of _____ 2009

ABSTRACT

Common species that are found in the flue gas of many coal burning industries are sulphur dioxide (SO_2) and carbon monoxide (CO). The current flue gas desulphurisation techniques used in practice are undesirable as they are uneconomical (they have high capital and operating costs) and they generate waste.

Many results in the literature show that if gold (Au) is finely divided and supported on metal oxide, it is effective as a catalyst for oxidising CO. However, there have not been many studies involving the reduction of SO_2 by CO over a gold catalyst. The main objective of this research project was to determine whether a gold catalyst supported on titania would be suitable for the reduction of SO_2 by CO.

Titania (TiO_2) was used as the metal oxide support and the gold catalysts were prepared by the deposition-precipitation method. Other gold catalysts were prepared by impregnating promoter ions (K^+, Na^+, SO_4^{2-}, PO_4^{3-}) onto the TiO_2 before the gold was added. The effect of TiO_2 calcined at 400°C without the addition of gold was also investigated for this reaction.

Since this work is novel, as the reduction of SO_2 by CO has hardly been performed over this type of catalyst before, the experimental method required screening several catalysts over a range of temperatures. The method used for screening the catalysts was the temperature "stepping method" where the reaction temperature was stepped in equal intervals of 25°C from a minimum temperature of 50°C to a maximum of 200°C. The results were analysed by integrating the SO_2 adsorption peaks.

It was found that a gold catalyst is in fact suitable for this application. TiO_2 without gold was effective at adsorbing SO_2, although it was not as effective as the gold catalysts supported on titania.

A catalyst time on stream experiment using the 0.8wt% Au/TiO_2 catalyst was used to understand the chemistry of the full reaction. It was observed that initially

the SO_2 blocks the active sites at the interface between the gold and the titania. The SO_2 gets adsorbed onto the surface of the catalyst and after some time the SO_2 molecule dissociates. After the S-O bond has been broken the active sites at the Au – TiO_2 perimeter are no longer blocked and SO_2 reduction occurs and CO oxidation decreases with time which suggests irreversible desorption of SO_2 reduction products on CO oxidation sites.

To my parents for teaching me the value of education

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It has been a long and challenging journey and at times during this project it seemed as though I would never finish. Just two weeks before completion I could hardly believe that this project was nearing the end. As strange as it may seem it was difficult to let go of this work that I have devoted so many painstaking hours to complete.

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LIST OF SYMBOLS

μg	=	micro grams
kWh	=	kilowatt hour
m^3	=	cubic metres
°C	=	degrees Celsius
ΔG^o_{rxn}	=	Standard state Gibbs Free Energy of Reaction
ΔH^o_{rxn}	=	Standard Enthalpy of Reaction
K_{eq}	=	Chemical Equilibrium Constant
T	=	Temperature
$_i$	=	species
α	=	alpha
γ	=	gamma
ν	=	stoichiometric coefficient
ΔG^o_f	=	Standard state Gibbs free energy of formation
ΔH^o_f	=	Standard Enthalpy of formation
H	=	Enthalpy
C_p	=	Constant pressure heat capacity
a, b, c, d, e	=	molecule specific constants for heat capacity equation
R	=	Universal Gas constant
cm^3	=	cubic centimetres
g	=	gram
h	=	hour
wt. %	=	weight percent
nm	=	nanometre
V	=	Valve
s	=	second
MPa	=	Mega Pascal
μg	=	microgram
ml	=	millilitre
mm	=	millimetre
mV	=	millivolts
M	=	Metal, Molar, gradient
ppm	=	parts per million
ppmv	=	parts per million by volume
P	=	Pressure of the system which was approximated as air Pressure in Johannesburg (84600 Pa)
Q	=	Volumetric flow rate (m^3/min)
Δt	=	change in time between measurements (min)

NOMENCLATURE

BET	=	Brunauer Emmet and Teller
CVD	=	Chemical Vapour Deposition
DP	=	Deposition-Precipitation
DRS	=	Diffuse Reflectance UV-visible Spectroscopy
ESP	=	Electrostatic Precipitator
FGD	=	Flue Gas Desulphurisation
GC	=	Gas Chromatography
GHSV	=	Gas Hourly Space Velocity
HDP	=	Homogenous Deposition-Precipitation
HF	=	Hydrogen Fluoride
HRTEM	=	High Resolution Transmission Electron Microscopy
HTR	=	High Temperature Reduction
ID	=	Internal Diameter
IGCC	=	Integrated Gasification Combined Cycle
IR	=	Infrared Spectroscopy
LTR	=	Low Temperature Reduction
PID	=	Proportional-integral-derivative Controller
SIMS	=	Secondary Ion Mass Spectrometry
SSBH	=	Single Step Borohydride Method
TEM	=	Transmission Electron Microscopy
TOF	=	Turnover Frequency
TPEC	=	Temperature Programmed Electronic Conductivity
XRD	=	X-Ray Diffraction
XPS	=	X-Ray Photoelectron Spectroscopy

1 LITERATURE REVIEW

1.1 Background

All fuels contain some amount of sulphur. The amount of sulphur depends on the composition of fuel. De Nevers (2000) lists the following examples: wood has a sulphur content of 0.1 % or less, whereas most coals have between 0.5 to 3 % sulphur. The sulphur content in oils is between that of wood and coal.

When any fuel that contains sulphur is burned under oxidising conditions, sulphur dioxide (SO_2) will be formed. Sulphur dioxide is a harmful gas that attacks the throat and lungs and can cause respiratory illness. Stern, Boubel, Turner and Fox (1984) note that for concentrations of 2000 $\mu g/m^3$ and above of SO_2 in the air, healthy people will have symptoms that affect them in their normal daily lives. In ill and elderly people, such high concentrations can cause untimely death. At SO_2 concentrations of 800 – 1599 $\mu g/m^3$, people with heart or lung disease will not be able to endure much exercise. The particulates, SO_2 and nitrogen oxides contained within the airborne emissions are responsible for respiratory disorders. Sulphur dioxide is not only harmful to people but to the atmosphere too; being one of the major contributors to acid rain.

Spalding-Fecher and Matibe (2003) highlight the fact that in 1999 there were 49 power stations in South Africa and 20 of these power stations were coal-fired. The paper by Spalding-Fecher and Matibe (2003) states that while SO_2 emissions have increased by 29 per cent, relative emissions (emissions/kWh) have declined. Eskom has made progress in reducing emissions by having high smoke stacks to disperse emissions more widely, and all power stations now have electrostatic precipitators to reduce particulate emissions.

Furthermore, Spalding-Fecher and Matibe (2003) note that a concern with SO_2 emissions are acid deposition which "affects human health, corrodes materials,

reduces crop yields and causes eutrophication in fresh water bodies". However, they argue that the extent to which acid deposition is a problem depends on the "levels and concentrations, dispersion patterns, and sensitivity to acid deposition". They therefore conclude that acid deposition will be a problem in the long-term but mainly from low-stack-height industrial applications where the dispersion is much lower.

There are a number of methods that are used at present that can deal with removing SO_2 from the atmosphere but which generate waste. The type of method used depends upon how much sulphur dioxide is produced in the gas stream and also whether the process is economically viable. Some of the major issues to consider when deciding on a suitable SO_2 removal process is the cost of the process, the capital cost of setting up the plant and the operating cost and whether it is therefore feasible to set up the plant. Other considerations include the efficiency of the process, how much SO_2 will actually be removed in the process and lastly whether there will be a large amount of waste left from the process. Some methods are briefly explained in the next section. After evaluating these methods it will be clear why new technology is required. This study proposes the use of gold catalysis for SO_2 abatement as an alternative to existing desulphurisation technologies.

Before the late 1980's, there was little research into the area of gold catalysis. This is because bulk metallic gold is a non-reactive metal. In a pioneering paper by Haruta, Kobayashi, Sano and Yamada (1987) it was shown that when gold nanoparticles are finely divided on a metal support, these particles act as a good catalyst especially for CO oxidation at temperatures below 0°C. There has been an extensive amount of research into the field of gold catalysis since then. Some researchers have focussed on the chemistry of gold catalysis (Meyer, Lemire, Shikhutdinov and Freund, 2004) whilst others have studied different preparation techniques (Bond and Thompson, 1999; Haruta, 2004; and Moreau and Bond, 2007) the effect of pre-treatment on gold catalysts (Tanielyan and Augustine, 1992; Tsubota, Nakamura, Tanaka and Haruta, 1998), different metal oxide supports (Okumura, Nakamura, Tsubota, Nakamura, Azuma and Haruta, 1998;

Schubert, Plzak, Garche and Behm, 2001a) and more recently enhanced supports for gold catalysts (Ma, Brown, Overbury and Dai, 2007; Moma, Scurrell and Jordaan, 2007).

1.1.1 Problem identification

SO_2 abatement technologies include: absorption, wet scrubbing (such as limestone scrubbing) and dry scrubbing. There are also other alternatives that can be used prior to combustion or gasification of the coal. Some alternatives include: changing the amount of sulphur in the coal or using low sulphur coal.

Most of the existing methods of flue gas desulphurisation (FGD) have proven to be uneconomical. Not only do these processes generate waste, they also require a chemical feedstock, the cost of which contributes to operating expenses. For example, limestone scrubbing produces gypsum. If this waste is not a saleable product then there will be a further cost involved in disposal of this waste. Another reason that FGD is not usually viable is because the capital cost of building and operating a treatment facility would result in the plant no longer being economically competitive.

In addition, using coal with a lower percentage of sulphur is not desirable for certain processes such as in aluminium smelting where the anodes (that are produced from the coal) will be consumed more rapidly in the process and will increase the frequency with which they have to be replaced. In other words the SO_2 released to the atmosphere per unit production of aluminium would increase and this is also an added cost to the plant. Also, as McMullan, Williams and Sloan (1997) mention, it is not always possible to use low sulphur coal as some of the existing coal resources have high sulphur content and it would be inefficient not to use these existing resources. There are a number of problems with the existing technology for removing sulphur from coal and for removing SO_2 from burned coal. Therefore, new research into this problem is required.

A process which may overcome the disadvantages mentioned above is the catalytic reduction of SO_2 to sulphur. Gold is thought to be one of the few catalysts resistant to sulphur poisoning and would be suitable for this application. Therefore, this project aims to investigate the use of a supported gold catalyst and carbon monoxide (CO) to reduce the SO_2 into elemental sulphur.

1.2 Current SO_2 Abatement Technologies

De Nevers (2000) states that all organic fuels contain some sulphur. Sulphur can be contained in the fuel in different forms. For example, De Nevers (2000) notes how in natural gas the sulphur is in the form of hydrogen sulphide and is easily separated from the other components in the gas, while in oil sulphur is chemically combined with hydrocarbons and therefore the chemical bonds have to be broken before the sulphur can be separated. In coal the sulphur is chemically bound but some can also be in the form of iron pyrite. Therefore, some sulphur in the coal may be easy to separate while the chemically bound sulphur may be more difficult to remove. The fuel always forms sulphur dioxide when burned in an oxidic environment, irrespective of the form of the sulphur in the fuel. Equation 1.1 shows the reaction that takes place when fuel is burned.

$$S + O_2 \rightarrow SO_2 \quad \text{.....(1.1)}$$

There are three places in a fossil fuel combustion gasification process where SO_2 can be removed. The first place is where the sulphur is removed from the coal (in other words before the coal is burned). Since SO_2 emissions are usually proportional to the amount of sulphur in the fuel (except for the case where some of the sulphur is retained in the ash) this method would seem the simplest for reducing emissions. This can be achieved by coal beneficiation, i.e. chemical and biological methods.

Secondly, SO_2 can be removed during the combustion stage which is seldom used as it is difficult to incorporate such a method into an existing process and is also

not energy efficient. There are two main methods used for this purpose: fluidized bed combustion and integrated gasification combined cycle system.

Thirdly, the SO_2 can be treated after combustion of the fuel. Three main processes that Armor (1992) explains for removal of sulphur dioxide after combustion of the fuel are limestone scrubbing, the Wellman-Lord Process and catalytic oxidation. Probably the most common process used in industry is limestone scrubbing; although it has disadvantages there appears to be no process that has been able to replace it as a suitable means for removing SO_2 from the atmosphere. These processes will be explained in more detail together with some of the advantages and disadvantages of the processes and why there is a need for a new improved process for abatement of SO_2 emissions.

This project concentrates on abatement, which is treating the SO_2 after combustion of the fuel. However, treatment in the first two process stages will be described briefly.

1.2.1 Reduction of sulphur in coal prior to combustion

For certain processes, such as, aluminium smelting it is not always possible to remove the sulphur prior to combustion. However, for processes where it is possible, reduction of sulphur in coal prior to combustion offers certain advantages. The main advantage being that the sulphur is treated before burning and so very little treatment is required after burning. The biggest disadvantage of chemical pre-treatment is the energy intensive processes and the chemical reagents that are required both of which are expensive therefore rendering the process unfeasible. Biological pre-treatment also has disadvantages: it is not entirely efficient and it requires large residence time. Therefore, both chemical and biological processes have little to no practical application.

Chemical processes

Karaca, Akyürek and Bayrakçeken (2003) name the three most common chemical processes for pyritic sulphur removal from coal. These are sulphur oxidation in the coal where the product is soluble sulphates, sulphur reduction where the elemental sulphur that is produced is then vaporised or the sulphur is removed by organic solvents. The last process is the reaction of the coal with hydrogen where H_2S is formed in the gaseous state. Karaca *et al*. (2003) list the following reagents that have been used in these chemical processes. These include nitric acid, hydrogen peroxide, ozone, oxygen, chlorine, potassium dichromate and ferric salts.

For their research, Karaca *et al*. (2003) used nitric acid as a reagent for the removal of sulphur in the coal. Karaca *et al*. (2003) found that due to varying process conditions, there are various chemical reactions that can occur between the nitric acid (HNO_3) and the pyrite. Two of these chemical reactions are shown by Equation 1.2 and 1.3.

$$FeS_2 + 4HNO_3 \rightarrow Fe(NO_3)_2 + 2S + NO + 2H_2O \quad \text{(1.2)}$$

$$2HNO_3 + S \rightarrow H_2SO_4 + 2NO \quad \text{(1.3)}$$

From their investigations it was found that an increase in process temperature and an increase in concentration of nitric acid increased the amount of pyritic sulphur that was removed. The coal had to be crushed to a finer particle size to achieve improved sulphur removal. The speed at which the coal – nitric acid solution were stirred had little effect on the amount of sulphur that was removed from the coal.

In his thesis, Koper (2004) notes that chemical processes have mostly been investigated on a lab scale because the technology is interesting, however it is not practical. He gives two reasons why it is not practical, the first being that it is an energy intensive process, the second being that chemical reagents will be required to treat the coal. In both cases, the cost outweighs the benefit of the process.

Section 2.3 of The National Environmental Management Act (1998) states that "development must be socially, environmentally and economically sustainable", from this statement, chemical processes would not be feasible because the process is not environmentally sustainable due to the large amount of energy required to drive the process and secondly, it is not economically sustainable because the energy input required and the cost of the raw materials would outweigh the benefit of the process. Furthermore, Section 4.4 (a)(vi) of the Act (1998) states "that the development, use and exploitation of renewable resources and the ecosystems of which they are part do not exceed the level beyond which their integrity is jeopardised". Again this emphasises that chemical processes would not be feasible due to the energy requirements.

Biological processes

Malik, Dastidar and Roychoudhury (2001) used a bio-desulphurisation process that required three stages. During the first stage the bacteria gets attached to the pyrite and the pyrite undergoes direct oxidation. Then, during the second stage, direct bacterial oxidation and indirect chemical oxidation takes place. Near the end of this stage, the attached bacteria became coated with a layer of sulphur and the direct oxidation slowed down. The desulphurisation rate slowed down during the final stage of the process. Finally, precipitation of jarosites and hydrated ferric sulphate occurs. This results in a decrease of ferric iron, which stops the indirect chemical oxidation. The process takes a total of 50 days to complete. Since the process is slow, it would not be practical for industrial application.

Malik *et al*. (2001) found that the rate limiting factors of the bio-desulphurisation process are availability of fresh pyrite, ferric/ferrous ratio and level of toxic minerals in the leachate. These three factors have to be controlled simultaneously to increase the rate of the reaction.

Malik, Dastidar and Roychoudhury (2004) mention that bio-desulphurisation is a low energy process and therefore should be suitable for reducing the harmful effect of combustion of high sulphur coal. However, it is not a feasible process

due to the slow rate of reaction. Malik *et al*. (2004) identified some rate limiting factors of some materials but in a commercial process there may be other substances that have not been studied that slow the reaction down and it is impossible to identify each and every substance that would limit the rate of the reaction.

According to Juszczak, Domka, Kozlowski and Wachowska (1995), since the biological process can operate at atmospheric temperature and pressure it has an advantage over other technologies such as chemical processes that require a large amount of energy and are therefore expensive. Furthermore, Juszczak *et al*. (1995) state that biological processes can remove both the organic and inorganic sulphur in the coal whereas, physical methods remove only the inorganic sulphur and chemical methods remove only the organic sulphur.

Juszczak *et al*. (1995) list a number of factors that determine the success of the biological processes. Some of these factors include the type of microorganism, the type of coal, surface area that is available, temperature, the pH value and the number of bacteria per unit mass of coal. Juszczak *et al*. (1995) suggest that before this method can be used on an industrial scale, further studies need to be conducted to establish which of these parameters are dependent on each other and also studies on the growth of microorganisms.

Coal beneficiation

The purpose of coal beneficiation is to reduce the size of the particles – in order for the coal to be processed further, to remove impurities (such as sulphur) and improve the quality of the coal. This will result in a reduction of harmful emissions after burning the coal.

Coal beneficiation employs physical methods to remove impurities from the coal. It is based on differences between coal and mineral matter. These differences can be with respect to density, surface activity (froth flotation, oil agglomeration),

magnetic and optical properties. There are many methods that have been proven to work and that are also operational in industry.

There are two broad categories that coal beneficiation can be classified into, that is wet or dry processes. Lockhart (1984) mentions that the main problem with the wet process is the large amount of water that is consumed. Much of this water is not recovered or gets evaporated while the water that remains is polluted and cannot be recycled. Also, the products from the process pollute the water further.

Lockhart (1984) established that the benefits of dry coal beneficiation are that the tailings are easier to dispose of because they do not require treatment before disposal like the products from the wet process require. If the climate is very dry, the feed materials may require little or no pre-treatment and if the feedstock did require pre-treatment it would be easier than treating the wet feed materials. Dry beneficiation does not require expensive resources such as thickeners, flotation reagents, flocculants, cyclones, centrifuges and filtering equipment that may be required for the wet process. Lastly, the dry coal cleaned by air is able to flow freely and does not absorb water while it is being transported or stored.

Lockhart (1984) lists some of the drawbacks of dry beneficiation being inferior separation, non-routine operation, lack of adjustability, high sensitivity to changes in the feed (rate, size, moisture), need for drying, greater attention to dust control and safety and the need for pre-screening into narrow size fractions and low capacities.

1.2.2 Removal of sulphur during combustion

McMullan *et al*. (1997), state that to minimise the environmental impact of coal-fired power stations, the overall plant efficiency should be maximised while the emissions of SO_2 and NO_x should be minimised.

Fluidised bed combustion

In fluidised bed combustion the coal and limestone are first crushed before being fed at the top of the bed (McMullan *et al.*, 1997). The bed is made up of unburned coal and ash and an inert bed material. Air is injected into the bottom of the bed, fluidising the bed. The air also acts as an oxidising agent for the combustion of the coal. The particles are in continuous motion and this allows for the reaction to happen at relatively low temperature of between 800 – 900°C. At this temperature, the limestone is calcined and therefore captures the sulphur from the coal. In this temperature range NO_x is also less likely to form. Steam is generated during the process from combustion and this steam is used to generate power via a steam cycle.

There are two types of fluidised bed combustion processes. The first is the bubbling process. In this process, low air velocities are used so that when the bed expands it remains steady and the reaction takes place in or just above the bed.

The second process, circulating fluidised bed combustion uses higher air velocities. Most of the particles are carried out of the bed and then re-circulated back into the bed via a high-temperature cyclone. The advantage of this process is that there is good mixing which allows for better contact between the gas and the solid. This improves efficiency and the amount of sulphur that is captured.

The process is usually operated at atmospheric pressure but can also take place at higher pressures. The advantage being that the hot gases from combustion are at high pressures and can therefore convert the energy from these gases into electricity. Only the bubbling fluidised bed combustion process is used in practice at high pressures but theoretically, the circulating process should work too.

Integrated gasification combined cycle system

McMullan *et al.* (1997) describe the integrated gasification combined cycle (IGCC) as a process whereby the coal is burned in a limited air supply chamber

and the fuel gas that ensues is then burned with air in the combustion chamber of a gas turbine. The impurities that are formed throughout the gasification process are in a reduced form and therefore the impurity from the sulphur is in the form of hydrogen sulphide (H_2S). The H_2S can then be removed by any common process such as the Claus process or any other scrubbing process. Again, a problem with this technology is that it cannot be used on its own; a further technology is required to remove the H_2S.

There are three types of gasifier namely, fluidized bed, entrained flow and fixed bed gasifiers. These three types of gasifier differ in the way in which the fuel supply and oxidant are brought into contact with each other.

In the fluidized bed gasifier, the dry fuel enters the column where it comes into contact with an absorbing material such as limestone. The limestone allows some of the sulphurous compounds to remain in the bed while the fuel becomes fluidized by the oxygen and is in a more pure state. The column operates at very high temperatures and pressures. McMullan *et al.* (1997) note that the temperature can be up to 1050°C and the pressure can be near 25 bar. McMullan *et al.* (1997) argue that this is feasible because the limestone can remove 90 – 95 per cent of the sulphur in the coal. However, this process is energy intensive while also requiring the sorbent material (limestone) to be purchased. This will prove to be a costly process.

The entrained flow gasifier is similar to the fluidized bed gasifier in that the solid fuel particles are also suspended in high-velocity jets. McMullan *et al.* (1997) state that the oxygen-blown operation is preferable to the air-blown operation as the oxygen ensures that the reaction occurs quickly and is complete in as short a residence time as possible. An advantage to the reactor is the short residence time. The short residence time leads to a high throughput rate and McMullan *et al.* (1997) comment that it probably has the highest throughput rate of any of the available systems.

A fixed bed gasifier is a reactor that has a metal grate on the bottom which supports the coal (McMullan *et al*., 1997). Oxygen is fed in the bottom of the reactor. The oxygen rises up through the grate and passes in between the coal particles. A reaction takes place between the coal and the oxygen and the product is a "residual char". This char contains ash and unburned carbon which needs to be removed to ensure steady operation. As the oxygen rises and the reaction takes place, the coal slowly moves downwards and the ash is removed. The reactor operates in a relative counter-current operation. It is relative since the coal moves down slower than the oxygen rises. McMullan *et al*., 1997 define efficiency as "the level of pollutants per unit of electricity generated". Efficiency was measured as grams of pollutant per kWh of electricity generated. Since the product is a gas at a relatively low temperature (between 450 – 600°C) the thermodynamic efficiency of the gas is high and this promotes a higher overall efficiency. A fixed bed gasification process is shown in Figure 1.1.

McMullan *et al*. (1997) compared the efficiency of various flue gas desulphurisation processes. The highest efficiency was less than 50 percent. The process has high capital and operating costs but there is no real benefit to this cost since the efficiencies are low. This just proves that this technology is not the most economical and an improved technology is required to lower the sulphur dioxide emissions.

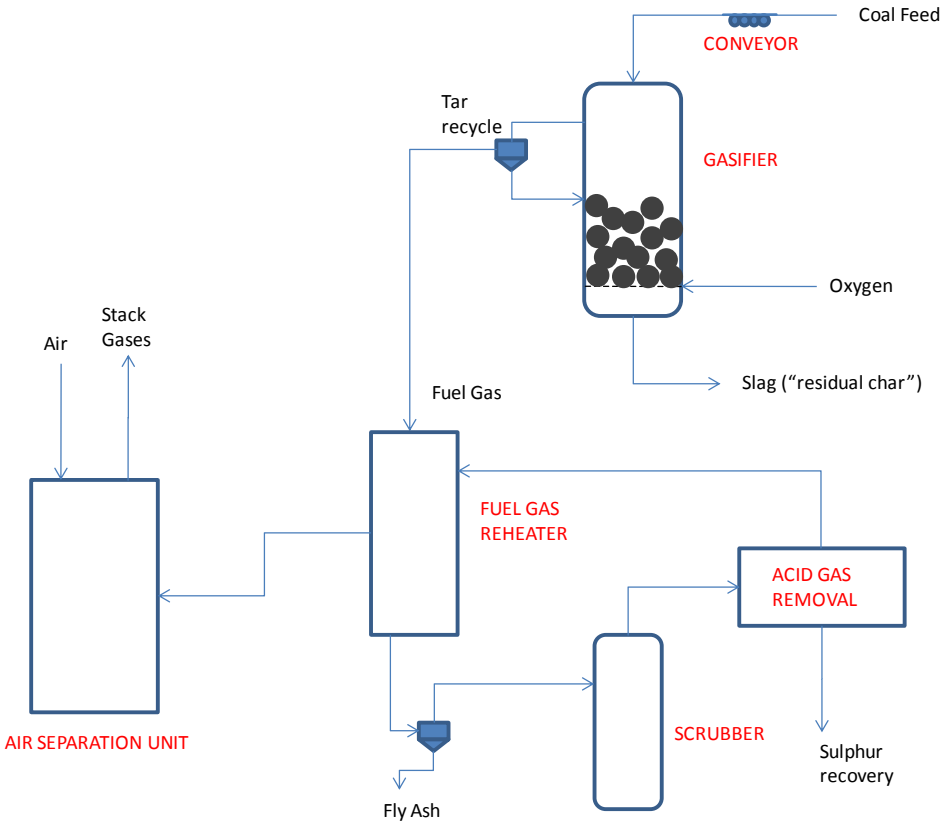

Figure 1.1 Schematic Representation of a Fixed Bed Gasification Process (Adapted from McMullan *et al.*, 1997)

1.2.3 Removal of sulphur after combustion

Scrubbing processes

Scrubbing is usually a single unit counter-current operation. A common scrubbing agent that is used is limestone. The limestone then converts the SO_2 into calcium sulphate ($CaSO_4$). The $CaSO_4$ is less harmful than the SO_2.

Armor (1992) describes the two stages in limestone scrubbing. In the first stage, fly ash is removed by passing the flue gas through an electrostatic precipitator (ESP). Then, the SO_2 is absorbed by a slurry of wet limestone. A reaction takes place between the SO_2 and limestone and $CaSO_3.5H_2O$ is formed. This product is then oxidized and gypsum ($CaSO_4.2H_2O$) is formed. The gypsum can be recovered in two forms, either as a wet sludge or as a dry product. The greatest disadvantage of this process is the large quantities of gypsum that are formed and

then have to be disposed of. Armor (1992) lists two options for the gypsum problem; either the product can be sold and used to make wallboard or it can be buried at a landfill site. The most difficult aspect in selling gypsum is that it is available in abundance and finding a market for it will be difficult and therefore it will not be profitable. Disposing of the gypsum at a landfill will also be costly.

Armor (1992) goes on to list two other alternative methods to this process. The first process is lime (CaO) spray-drying. A slurry containing CaO that has been finely atomized is brought into contact with the flue gas. The mixture of slurry and flue gas is then completely evaporated and a dry powder is formed. This powder and the fly ash are then separated as solids and then disposed of or reused in the process. The two disadvantages with this process are that the process is not as efficient as limestone scrubbing and it is an expensive process that is used mainly by small operations or where low sulphur coal is used.

The second method that Armor (1992) describes is the Claus Process. This process can be represented by Equation 1.4:

$$H_2S + SO_2 \rightarrow 2H_2O + 3S_{(s)} \quad \text{..... (1.4)}$$

Armor (1992) argues that the difficulty is finding a use for the sulphur produced from this process. Armor (1992) states that most refineries in the US supply sulphur for other processes so they no longer require the sulphur as a feed from other sources. Some of the sulphur can be used to produce sulphuric acid which is then used to produce fertilizer and some of the sulphur is buried.

For certain processes such as aluminium smelting, a certain percentage of sulphur in the zero oxidation state is required in the coal so that the cathode is not used up rapidly during the process. The sulphuric acid market has been saturated in the last few decades by the petrochemical industry and so it could be argued that elemental sulphur would not be useful for this application any longer.

Meikap, Kunda and Biswas (2002) developed a model to represent a "modified multi-stage bubble column scrubber". The work that they conducted showed that a high efficiency of SO_2 removal could be achieved due to the many stages in the scrubber. Furthermore, Meikap *et al*. (2002) showed that the air-SO_2 mixture required no additives or pre-treatment.

Wei and Davis (2000) comment that new smelters do not use wet scrubbers to control emissions as there are many disadvantages. Some of the disadvantages include corrosion, scaling and the fact that the sulphide or fluoride would have to be recovered before it could be recycled into the process. The only advantage is that some of the sulphur dioxide in the off-gases can be removed.

An additional problem with scrubbing is that if the process is a "throwaway" process as described by De Nevers (2000), the reagent is used once and then thrown away. Therefore, this means that the reagent constantly needs to be purchased and disposed of. In other words an emission is turned into a solid waste after adding a chemical feedstock.

The other type of scrubbing process is dry scrubbing. De Nevers (2000) explains that in this process, a dry alkaline reagent is introduced into the gas stream. The SO_2 molecules attach onto the scrubbing agent and are removed by filtering or using some other "particle collection device". Again, a reagent has to be supplied constantly. This process is used at aluminium smelters but usually to scrub hydrogen fluoride (HF) from the waste gases emitted from the potlines. A scrubbing agent would have to be found that could simultaneously scrub HF and SO_2.

Wellman-Lord process

This process is explained in detail by Smith (2005). The process takes place in two stages. During the first stage, a dilute gas stream of SO_2 is sent to a scrubber where a solution of sodium sulphite Na_2SO_3 is sprayed into the scrubber, the SO_2 and Na_2SO_3 react according to Equation 1.5:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \quad (1.5)$$

The product, sodium bisulphite ($NaHSO_3$) is then heated either by an evaporator or a crystallizer to form a more concentrated stream of SO_2 as shown by Equation 1.6,

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O \quad (1.6)$$

Then, the concentrated SO_2 is catalytically reduced to sulphur either by methane as shown by Equations 1.7 and 1.8 (Armor, 1992) or with H_2S in the Claus Process shown by Equation 1.4.

$$CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + 2S \quad (1.7)$$
$$4CH_4 + 6SO_2 \rightarrow 4CO_2 + 4H_2O + 4H_2S + 2S \quad (1.8)$$

The Na_2SO_3 crystals can be regenerated in the process by dissolving them in water and returning them to the scrubber in the first stage. Smith (2005) summarises this process well by saying that a dilute gaseous stream of SO_2 produces a concentrated stream of SO_2. This concentrated stream then has to be treated further to remove the SO_2.

Catalytic oxidation processes

The most popular catalyst that has been used for this purpose is a vanadium pentoxide catalyst (V_2O_5). Dust and other particles are removed from the flue gas using an electrostatic precipitator. The gas is then oxidized over the catalyst where SO_3 is produced. The SO_3 is then treated with water to form H_2SO_4. Armor (1992) names a number of companies that all use technology similar to this. Monsanto which is one of these companies had to eventually stop this operation as the operating costs became too high.

1.3 The Reaction

1.3.1 Favourable reactions based on thermodynamics

If the SO_2 could be captured from the stack and then converted into elemental sulphur, in the reverse of Equation 1.1 it would be a very simple process. However, on further investigation of the thermodynamics, it was noted that sulphur oxidation (Equation 1.1) is very thermodynamically favourable and that the reverse reaction is not favourable at practicable conditions. Intuitively, this should be apparent but for illustrative purposes this is represented by Figure 1.2.

In Figure 1.2, the straight line representing the oxidation of elemental sulphur shows that at the temperature range of 50 - 250°C, the natural logarithm of the equilibrium constant is negative, indicating that the reaction is likely to take place at low temperatures. This is reinforced by the fact that the slope of the line is positive. A positive slope shows that the enthalpy of reaction is negative and that the reaction is exothermic. Exothermic reactions favour low reaction temperatures. The converse is true for the reverse reaction. The temperature of reaction would therefore have to be high for the reverse reaction. Since the reaction is highly endothermic, this temperature may be so high that the reaction no longer becomes practical.

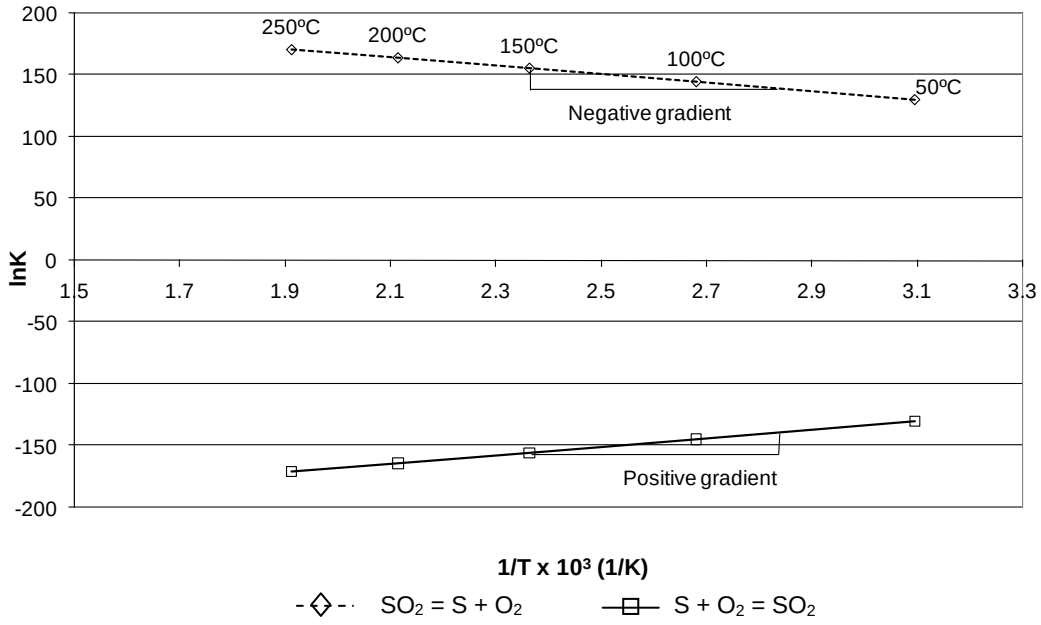

Figure 1.2 Illustration of a thermodynamically favourable reaction and an unfavourable reaction

There are three thermodynamic properties that characterise a reaction as either favourable or unfavourable. These three properties are the standard state Gibbs free energy of reaction (ΔG^{o}_{rxn}), the standard enthalpy of reaction (ΔH^{o}_{rxn}) and the chemical equilibrium constant (K_{eq}). The general form of the equation for calculation of ΔH^{o}_{rxn} is shown in Sandler (1999) as:

$$\Delta H^{o}_{rxn}(T = 25°C, 1bar) = \sum_i \nu_i \Delta \bar{H}^{o}_{f,i}(T = 25°C, 1bar) \quad \text{.....(1.9)}$$

Similarly, ΔG^{o}_{rxn} is:

$$\Delta G^{o}_{rxn}(T = 25°C, 1bar) = \sum_i \nu_i \Delta \bar{G}^{o}_{f,i}(T = 25°C, 1bar) \quad \text{.....(1.10)}$$

When the reaction occurs at temperatures other than 25°C then, the enthalpy for each species is given by (Sandler, 1999):

$$\bar{H}_i(T) = \bar{H}_i(T = 25°C) + \int_{T=25°C}^{T} C_{p,i}(T')dT' \quad \text{.....(1.11)}$$

Where, the general form of the constant pressure heat capacity equation is:

$$C_{P,i} = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^{-2} \quad \text{.....(1.12)}$$

The definition of the equilibrium constant is (Sandler, 1999):

$$K_{eq}(T) = exp\left(\frac{-\Delta G^o_{rxn}}{RT}\right) \quad \text{.....(1.13)}$$

The variation of K_{eq} with temperature can be derived using the definition of K_{eq}. The final equation is known as the van't Hoff equation (Sandler, 1999).

$$\left(\frac{d \ln K_{eq}}{dT}\right)_P = -\frac{1}{R}\frac{d}{dT}\left[\frac{\sum_i \nu_i \Delta \bar{G}^o_{f,i}}{T}\right] = \frac{1}{RT^2}\sum_i \nu_i \Delta \bar{H}^o_{f,i} = \frac{\Delta H^o_{rxn}(T)}{RT^2} \quad \text{.....(1.14)}$$

After integration of the van't Hoff equation, a simplified equation can be obtained for the variation of K_{eq} with constant temperature (Sandler, 1999).

$$ln\frac{K_{eq}(T_2)}{K_{eq}(T_1)} = -\frac{\Delta H^o_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{.....(1.15)}$$

Figure 1.3 shows two thermodynamically favourable reactions, the reduction of SO_2 by H_2S (Equation 1.4) and the reduction of SO_2 by CO (Equation 1.16).

$$SO_2 + 2CO \rightarrow 2CO_2 + S_{(s)} \quad \text{.....(1.16)}$$

Figure 1.3 shows that both reactions are exothermic, therefore both are favourable at low reaction temperatures. Equation 1.4 is favoured at temperatures below approximately 75°C, while Equation 1.16 is favoured at temperatures below approximately 100°C. Equation 1.16 has a steeper slope than Equation 1.4 in the

low temperature range (temperatures below 150°C). This indicates that Equation 1.16 is more favourable than Equation 1.4 at these temperatures. At higher temperatures Equation 1.4 should be more favourable than Equation 1.16 however, at these temperatures the value of the equilibrium constant is less than 1 indicating that the enthalpy of reaction and the Gibbs free energy are both positive and so both reactions are not favoured at these temperatures.

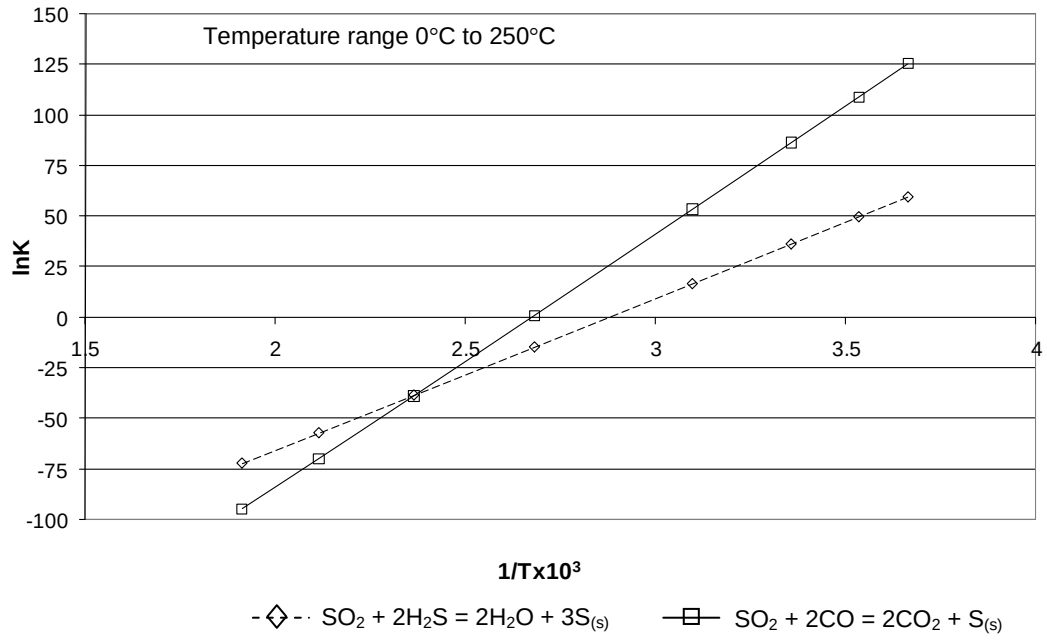

Figure 1.3 The van't Hoff Plot

The reaction that will be studied for this research project will be Equation 1.16. The first reason is that SO_2 reduction by CO is more favourable than SO_2 reduction by H_2S at lower temperatures as shown by Figure 1.3. The second reason is that both SO_2 and CO are present when coal is burned and so this would be practical in coal burning industries.

1.3.2 Reducing agents for SO_2

Flytzani-Stephanopoulos, Zhu and Li (2000) found that when methane was used to reduce SO_2 to elemental sulphur, the conversion of SO_2 could be increased by increasing the ratio of CH_4:SO_2 in the feed. However, this decreased the catalyst

selectivity to elemental sulphur. Above 650°C no decrease in selectivity was observed. The reaction temperature could be decreased while the SO_2 conversion and the selectivity were at an optimal level if excess methane was used.

The use of CO as a reducing agent for SO_2 is a good choice when considering burning coal as some CO is present in the gas emissions and therefore can be used as a reducing agent (Lee and Han, 2002). In other words, no further reagent will have to be added. Furthermore, Flytzani-Stephanopoulos *et al*. (2000) found that the reaction light-off temperature was 200°C lower than when CH_4 was used as a reducing agent.

In addition, Lee and Han (2002) found that the ratio of CO to SO_2 in the feed determined not only the conversion but also the amount of carbonyl sulphide (COS), the reaction intermediate that is formed. They found that when the molar ratio of CO to SO_2 was 2 a conversion of 97% was achieved and when the ratio was 3 a conversion of 99.8% was achieved. However, with molar ratios larger than the stoichiometric ratio, the concentration of COS increased by a large amount. The reduction of SO_2 by CO has practical applications and it is possible to achieve high conversions at low reaction temperatures. Therefore many researchers have studied this reaction and tried to optimise it.

1.3.3 Possible catalysts for the reaction

Khalafalla, Foerster and Haas (1971) investigated the use of a mixed alumina-iron catalyst. In their investigation they found that the reaction is extremely slow even at temperatures as high as 950°C. When iron and alumina were tested separately, the reaction did not proceed to a great extent. However, when the bi-functional iron-alumina catalyst was used with 41% iron in the mixture and 4.7% SO_2 in the feed, a conversion of 78% could be achieved at 500°C. This conversion is not optimal but at the time it was a large improvement on the conversions that were achievable and it made the reaction more attractive for use in industrial applications, as the reaction had not been used in practice before.

Alumina has also been combined with other transition metals such as Cu/Al_2O_3 (Querido and Short, 1973) where SO_2 was used to convert to elemental sulphur with CO as a reducing agent. They found that temperatures of about 380°C were needed to reduce 90% of the SO_2 in the feed. Furthermore, Querido and Short (1973) realized that for high rates (short contact times) temperatures greater than about 425°C were required. The maximum SO_2 removal efficiency was 97% when the CO ratio was 1.03. However, as the CO ratio and temperature were increased, COS production also increased.

It is evident that if alumina is used as a catalyst it is not effective for converting the SO_2 into elemental sulphur. However, if the alumina is combined with transition metal elements and used as the support for the catalyst, the reaction proceeds with much larger amounts of SO_2 converted into elemental sulphur.

Lee and Han (2002) investigated γ-Al_2O_3 supported catalysts of Ni and LaNi sulphide with different metal loadings. They had a number of important findings. First, they found that SO_2 conversion increased with increasing temperature. When the $2La_8Ni/Al_2O_3$ catalyst was used, 97% of the SO_2 was converted at temperatures above 400°C. Another important finding by Lee and Han (2002) is that when a small amount of La was added to the catalyst the SO_2 conversion increased at 350°C. Lee and Han (2002) propose that the effectiveness of their NiS_2/Al_2O_3 catalyst may be due to the bi-functional effect of each individual active component.

Ma, Fang and Lau (1997) report that when using a La_2O_2S catalyst, in the above reaction, over 98% conversion and selectivity of SO_2 could be achieved when the temperature was above 500°C, the ratio of CO to SO_2 in the feed was 2:1 (i.e., in stoichiometric proportions) and when the space velocity was 21,600 $cm^3g^{-1}h^{-1}$.

The results that Baglio (1982) presents demonstrates that the perovskite $LaCoO_3$ decomposes when used as a catalyst for the reduction of SO_2 by CO. The decomposition products are La_2O_2S and CoS_2. Also, Baglio (1982) found that any

un-reacted COS formed during the reaction can be removed by using either a rare earth oxide or oxysulphide only as the catalyst.

Ma *et al*. (1997) found that lanthanum oxysulphide alone was capable of reducing SO_2 to elemental sulphur with CO as a reducing agent. The work of Ma *et al*. (1997) disputes the work by Baglio (1982) because Baglio (1982) proposed that the lanthanum oxisulphide was incapable of reducing the SO_2 when CO was used as the reducing agent. However, the lanthanum oxysulphide could reduce the SO_2 when the reaction intermediate, COS was used as a reducing agent.

Bazes, Caretto and Nobe (1975) investigated three catalysts for the reduction of SO_2 with CO as a reducing agent. The three catalysts are $LaCoO_3$ (the perovskite-type catalyst), $CuCo_2O_4$ (the mixed oxide) and the oxide mixture CeO_2-Co_2O_4. They showed that when the stoichiometric ratio of SO_2 to CO in the feed was doubled, the CeO_2-Co_2O_4 catalyst was the most active out of all three catalysts tested and the mixed oxide $CuCo_2O_4$ was the least active catalyst. Furthermore, Bazes *et al.* (1975) found that for complete reduction of SO_2 the selectivity of all the catalysts was similar.

In a more recent study, Kim, Park, Woo, and Chung, (1998) considered the catalyst Co_3O_4-TiO_2 which is also a mixture of oxides. Kim *et al.* (1998) had two important findings. The first was that complete conversion of SO_2 was achieved above temperatures of 400°C. This temperature was between 50 and 150°C less than the temperature that Ma, Fang and Lau (1996a) achieved with their CoS_2-La_2O_2S catalyst. The second important finding is that a synergistic effect exists between the components of the catalyst and this allows for a much higher conversion of SO_2 at 350°C with less COS being produced during the reaction of SO_2 and CO. As temperature increases the synergistic effect decreases.

Wang, Wang, Li, Wang, Liu and Zhang (2006) considered four different supports for an iron oxide (Fe_2O_3) catalyst used to reduce SO_2 to elemental sulphur with CO as a reducing agent. In the study by Wang *et al*. (2006) the four supports used were γ-alumina (γ-Al_2O_3), HZSM-5 (a zeolite), silica (SiO_2) and magnesia (MgO).

They found that the $Fe_2O_3/\gamma\text{-}Al_2O_3$ was the most active of the catalysts, followed by Fe_2O_3/HZSM-5, Fe_2O_3/SiO_2 and Fe_2O_3/MgO. The most favourable result obtained by Wang *et al*. (2006) was 99.31% SO_2 conversion and a 99.17% sulphur yield. This was achieved with an iron content of 20 wt%, presulfidation at 500°C for 2 hours, a CO/SO_2 ratio of 2:1 at 380°C with a $Fe_2O_3/\gamma\text{-}Al_2O_3$ catalyst.

Flytzani-Stephanopoulos *et al*. (2000) tested the activity/selectivity of the following catalysts: 10at. % La-doped ceria, $Ce(La)O_x$ and Cu- or Ni-containing $Ce(La)O_x$ for the reduction of SO_2 by CO to elemental sulphur. They had some important findings for these catalysts.

The first was that by adding 5 at. % (~2.5 wt %) Cu or Ni to the $Ce(La)O_x$ catalyst, the low-temperature activity of the catalyst in the presence of 10 mol% water improved.

Secondly, the Ni-CeO_x catalyst gives a higher sulphur yield than the other catalysts which can be interpreted as a higher SO_2 conversion. They propose that this happens since the available CO adsorption sites on the metal are not poisoned by the water vapour.

Flytzani-Stephanopoulos *et al*. (2000) conclude that the CO-SO_2 reaction is favoured over the Ni- or Cu containing ceria due to enhanced redox activity of the ceria in the presence of nickel.

1.3.4 Carbonyl sulphide as a reaction intermediate

In the review by Bartholomaeus and Haritos (2005), they report that carbonyl sulphide (COS), is a colourless, odourless (when pure) gas. They also report that while COS is poorly soluble in water at 0 – 20°C (3.56-1.49 g/L); it is very soluble in toluene at 22°C (37 g/L). It has a boiling point of -50°C and Bartholomaeus and Haritos (2005) rank it as a relatively stable gas. Furthermore, Bartholomaeus and Haritos (2005) report that COS is "highly toxic at high atmospheric concentrations". Flytzani-Stephanopoulos *et al*. (2000) notes that

COS is more toxic than SO_2. Therefore, since COS forms part of the reaction mechanism of reducing SO_2 to CO, it is necessary to minimise its concentration by optimising the selectivity.

Bazes *et al.* (1975) found that the amount of COS formed during the reduction of SO_2 by CO could be reduced by ensuring that the ratio of CO to SO_2 in the feed is kept at 2 (the stoichiometric value). Lee and Han (2002) established that with a molar ratio of CO to SO_2 of 2 the concentration of COS was 3% but when the molar ratio was 3 the concentration of COS increased to 23%. Therefore, this shows that the reaction is sensitive to small changes in the molar ratio. Lee and Han (2002) also support the earlier findings of Bazes *et al.* (1975). Furthermore, Lee and Han (2002) found that when small amounts of La were added to their Ni alumina catalyst, the COS yield decreased at 350°C.

Wang *et al.* (2006) support the theory that the optimal feed ratio of CO to SO_2 is 2:1 and they went on to test how different feed concentrations in this ratio affect the SO_2 conversion and sulphur yield. They found that at low feed concentrations, there is a higher reduction rate and yield. A conversion of 94.5% could be achieved with a CO and SO_2 concentrations of 5000 and 2500 ppm respectively at 340°C. Furthermore, at 380°C a high SO_2 conversion and sulphur yield were obtained at any feed concentrations that they used.

Ma *et al*. (1996a) found that there is synergism between La_2O_2S and CoS_2 for the reduction of SO_2 by CO to form elemental sulphur. Furthermore, Ma *et al*. (1996a) established that the synergism was a result of the co-operation between the individual active components and is based on the COS intermediate mechanism. The COS intermediate mechanism as presented by Ma *et al*. (1996a) is as follows:

$$MS_x + CO \rightarrow MS_{x-1} + COS \quad (1.17)$$

$$2COS + SO_2 \rightarrow \frac{3}{2}S_2 + 2CO_2 \quad (1.18)$$

$$MS_{x-1} + S \rightarrow MS_x \quad (1.19)$$

The experimental results of Ma *et al*. (1996a) show that when the catalyst is a mixture of La_2O_2S and CoS_2 the activity and selectivity increases.

Flytzani-Stephanopoulos *et al*. (2000) propose a similar mechanism for the reduction of SO_2 using CO (as a reducing agent) over a cerium-oxide catalyst (enhanced with approximately 2.5 wt% copper or nickel). Although they propose that the Reaction 1.20 occurs before Reaction 1.17.

$$SO_2 + 2CO \rightarrow 2CO_2 + {}^{1}/_{X}\,S_x \quad \text{.....(1.20)}$$

In other words, Ma *et al*. (1996a) propose that the CO is converted to COS on the surface of the metal sulphide catalyst, whereas Flytzani-Stephanopoulos *et al*. (2000) propose that the sulphur is first formed by the reduction of SO_2 by CO, the CO then reacts with the sulphur to form COS and lastly, the COS reacts with the SO_2 to form sulphur gas and CO_2.

Furthermore, Ma *et al*. (1996a) found that 450°C was the critical temperature and below this temperature, COS was produced more rapidly but above this temperature, COS levels became depleted. The reaction rate between COS and SO_2 increased above 450°C.

In a further study, Ma *et al*. (1996b) found that lanthanum oxide can be activated to act as a catalyst in the reduction reaction where SO_2 is reduced to elemental sulphur by CO. The lanthanum oxide is pre-treated and then activated by a gas/solid sulphidization reaction between the gas-mixture of SO_2 and CO. The active phase of the catalyst after sulphidization was found to be lanthanum oxysulphide, La_2O_2S.

The catalyst support is also important for determining the amount of COS that is formed during the reaction. Flytzani-Stephanopoulos *et al*. (2000) comment that certain metal oxide catalysts (Cu, Fe, Mn, Cr, Ni, Pd, Ag, etc.) supported on alumina showed large concentrations of COS being formed relative to La_2O_2S (Ma *et al*., 1996a) perovskite mixed oxides at temperatures above 380°C and CO

to SO_2 feed ratio of 2.5 times the stoichiometric value (Bazes *et al*., 1975), and decomposed perovskite, $LaCoO_3$ which forms the active catalysts, La_2O_2S and CoS_2 (Baglio, 1982), Co_3O_4-TiO_2 (Kim *et al*. 1998) and cerium oxide catalysts with 1 – 5 wt.% Cu, Ni or Co (Flytzani-Stephanopoulos *et al*., 2000).

1.4 Gold as a Catalyst

In 1987, Haruta *et al*. identified that the need for a low temperature CO oxidation catalyst. Other catalysts that were in use at the time were either intolerant towards water, required water vapour for the reaction to take place, or only worked at high temperatures or for dilute CO concentrations. Haruta *et al*. (1987) documented that a new gold catalyst that they developed was more active and stable than the catalysts available at the time. Also, complete oxidation of CO was achieved at a temperature of -70°C. Haruta, Yamada, Kobayashi and Iijima (1989) improved the activity of their catalysts by adding α-Fe_2O_3, Co_3O_4, or NiO.

Also, Haruta *et al*. (1987) established that the gold particles were more finely divided when co-precipitation was used to prepare the catalysts instead of impregnation and, most importantly, "the high dispersion of gold brought about the extremely high activity for CO oxidation at temperatures below 0°C."

At the time, no researcher could have predicted how much the field of gold catalysis was going to grow, or how many new applications for gold catalysts would be developed. Today, Haruta and his co-workers are seen as the pioneers in the field, along with other researchers such as Bond, Thompson, Hutchings, and Scurrell to name a few.

Bond and Thompson (2000) reported that in 1999 there were about 60 published works on the topic of gold catalysis and at least half of the papers published involved the oxidation of carbon monoxide.

Bond and Thompson (2000) cite a number of aspects of gold catalysis that researchers are in agreement about. One aspect is that unsupported gold and large

supported gold particles show poor activity for CO oxidation whereas small gold particles that are dispersed on a metal oxide support show much higher activities. The support that is used, the method used to prepare the catalyst and the manner in which the catalyst is pre-treated are important in obtaining an efficient and active catalyst.

There are however, a number of aspects to gold catalysis that researchers have not yet been able to agree on. This has been made more difficult by the fact that the proof given is not always conclusive due to the varying characterization techniques that have been used. Therefore, there are a number of aspects that cannot yet be generalised for all gold catalysts. So, although the method of preparation is important, and it seems that deposition-precipitation is a robust method, a number of authors have used other methods of preparation that have yielded similar results. Also, there is not yet agreement as to what pre-treatment conditions are optimal. There have also been various views on the role of the support.

Armor (2005) warns scientists and engineers not to claim to have an industrially viable catalyst without testing conditions that would occur in an industrial plant. Armor (2005) provides insight into the criteria which are necessary for determining if a catalyst is "better" in industrial applications. These criteria can be broken down into three broad categories namely, process conditions, the catalyst and cost. Process conditions such as temperature, pressure and feed composition are necessary to know and understand the process and to make an informed decision about whether a particular catalyst is correct for the reaction. Once the catalyst is determined, certain criteria need to be optimised for the highest activity. These include: kinetics, the use of promoters, catalyst life, and shape or form of the catalyst as well as stability of the catalyst. In industrial processes, the deciding factor can sometimes be economic and so therefore cost is also important.

The message that Armor (2005) wanted to convey to researchers is that sometimes it is easy to conclude that the catalyst that has been developed in a particular lab is

the best that is available. However, that catalyst was only the best at those particular process conditions and it is therefore not always possible to draw a general conclusion for all the conditions for a specific catalyst but the catalyst is specific for a specific application. Perhaps this could explain why there are so many differing opinions when it comes to the field of gold catalysis.

By using Armor's (2005) perspective and the results obtained by various researchers, this literature survey aims to outline the various arguments and perhaps decide which is more probable for the work completed for this dissertation.

1.4.1 Preparation methods and particle size

Before the study was completed by Haruta *et al*. (1987), gold was considered to be a poor catalyst. This can be attributed to the fact that the size of the gold particles used for catalysis had diameters greater than 10 nm. Haruta *et al*. (1987) discovered that by depositing ultra-fine gold particles onto a metal oxide support, the chemistry was changed to a large extent.

Haruta (1997) notes that it is important to take care with respect to the following when preparing gold catalysts: the size of the gold particles, the support used and the method used in preparing the catalyst.

According to Haruta (1997), the method used to prepare a gold catalyst influences the size of the metal particles and therefore, influences the activity of the catalyst. Haruta (1997) mentions that the performance of a supported platinum catalyst was almost unaffected by the method in which it was prepared.

Haruta (2004) names up to eight different methods that can be used to prepare highly dispersed gold catalysts. The type of method used depends on the support material that is used and also what type of gold catalyst is needed for the specific application. For this dissertation, however, only three of the most commonly used

methods will be explored. The three methods are co-precipitation, impregnation, and deposition-precipitation.

Haruta *et al*. (1989) describe the process for co-precipitation. In the first step an aqueous solution of $HAuCl_4$ and a transition metal nitrate are added to an aqueous solution of sodium carbonate. During this step the solution is continuously stirred. The precipitate that is formed is then washed and vacuum dried before being calcined at 400°C for 4 hours.

Li, Comotti and Schüth (2006) describe the procedure used to prepare Au/TiO_2 catalysts using impregnation. The first stage is the suspension of the TiO_2 support in the hydrogen tetrachloroaurate ($HAuCl_4$) aqueous solution. This is done by adding the $HAuCl_4$ solution drop wise to the TiO_2 support whilst stirring. Then the sample is treated with ammonia to achieve stable $Au(OH)_3$. The solution is then heated in an oven at 50°C for 4 hours before filtering it with deionized water to remove the residual chloride ions. The final step involves drying the catalyst at 50°C for 16 hours.

Haruta (2004) presents two arguments for why impregnation should not be used to prepare gold catalysts. The first being that gold nanoparticles have a lower melting point and lower affinity for metal oxides than platinum group metals and are therefore more difficult to deposit on the support. The second reason is that during calcination, the chloride ion (that results from the $HAuCl_4$) increases agglomeration of the gold particles.

The method for deposition-precipitation is described by both Haruta (1997) and Bond and Thompson (1999). The method described below is a summary of the method that they have described. The active species (gold) is taken out of an aqueous solution of $HAuCl_4$. This is achieved by modifying the pH of the solution with NaOH to between 6 and 10 at room temperature. The metal oxide support is then added to the solution. According to Moreau and Bond (2007), the addition of the metal support decreases the pH further and so more NaOH is added to the solution to solve this problem. According to Haruta (1997), if the above

mentioned step is performed at the correct temperature and concentration then, ageing the solution for approximately 1 hour will result in the deposition of $Au(OH)_3$ onto the surface of the metal oxide support. This is a basic outline of the deposition-precipitation method but there are many variations.

Li *et al*. (2006) support deposition-precipitation for preparation of gold catalysts because the catalysts are reproducible. However, three factors are necessary to achieve reproducibility. These factors are precise control of pH, precise control of the drying conditions and ensuring that during the deposition stage of catalyst preparation, the suspension of the TiO_2 support must remain at a fixed volume. Furthermore, they were able to prepare active catalysts without the calcination step.

Wolf and Schüth (2002) aimed to determine the effect of pH, calcination temperature, gold content and washing procedures on the activity of gold catalysts. The catalysts were prepared by deposition-precipitation. They also wanted to establish how to produce catalysts that were reproducible. Wolf and Schüth (2002) found that to reproduce a catalyst, it should be prepared on the same day under the same synthesis conditions. Reproducibility was not enhanced by pH adjustment, variation of the precipitation agent, temperature during precipitation or by changing the aging period.

From X-Ray diffraction (XRD), Wolf and Schüth (2002) deduced that the particle size of the gold is reduced when the pH values during precipitation are increased, resulting in higher activity of the gold catalysts. The highest activity according to Wolf and Schüth (2002) was recorded when the pH was in the range of 7.8 – 8.8 during precipitation. Their explanation for this increase in activity is that the percentage of gold deposited on the support is reduced at pH values higher than 8.8. Therefore, the probability of agglomeration of gold particles is reduced. Agglomeration of the gold particles would reduce the activity of the catalyst. Wolf and Schüth (2002) observed the same trend with pH for various catalysts that they tested. These catalysts included Au/TiO_2, Au/Co_3O_4, Au/Al_2O_3 and Au/ZrO_2.

Moreau and Bond (2007) explain the chemistry involved in increasing the pH of the $HAuCl_4$ solution during deposition-precipitation. Firstly, $AuCl_4^-$ is hydrolysed as the pH of the solution increases. The higher the pH, the more the $AuCl_4^-$ is hydrolysed. Above pH of 8, all the $AuCl_4^-$ is converted to $Au(OH)_4^-$. Similarly, the charge on the TiO_2 surface is also reliant on pH. Therefore, when the TiO_2 is added to the $HAuCl_4$ solution, the pH is decreased because the hydrolysed $AuCl_4^-$ ions are neutralised.

So, according to Moreau and Bond (2007), precise control of pH throughout catalyst preparation ensures that the gold loading remains between 0.06 and 2.4wt%. At these low gold concentrations the particle size of the gold remains sufficiently small that Moreau and Bond (2007) could not detect a visible XRD peak. At temperatures -20°C, Moreau and Bond (2007) could achieve 100 percent conversion of CO when the gold loading was 1.9wt%.

Wolf and Schüth (2002) prepared Au/TiO_2 catalysts by deposition-precipitation and Au/Co_3O_4 catalysts by co-precipitation. Their results showed that by increasing the gold loading in the Au/TiO_2 catalysts, the activity was reduced. Again, they attribute this to the size of the gold particles. However, Wolf and Schüth (2002) found that the opposite occurred in the Au/Co_3O_4 catalysts suggesting that the percentage of small particles increased with the increased gold loading in these catalysts.

It is known that after depositing the gold onto the support and precipitating the catalyst, the catalyst is filtered, washed and then dried. The washing stage of the catalyst preparation is necessary to remove chloride ions which are known to poison catalysts. Wolf and Schüth (2002) tried to improve the catalysts by washing the catalyst a second time after calcination. Their results showed that there was no major difference in the activity of the catalyst in the case where deposition-precipitation was used. However, for the co-precipitated Au/Co_3O_4 catalyst, there was a great improvement in the catalyst activity.

Research has shown that the deposition-precipitation method consistently remains the most suitable method to prepare gold catalysts. With strict control of pH during the deposition-precipitation method the gold particles will remain small enough to yield high catalyst activity. Also, careful washing of the catalyst guarantees that the chloride ions which are a catalyst poison are removed. Another topic that will be explored is calcination temperature and the effect of pre-treatment on the gold catalyst as researchers have differing opinions about the effect that this has on catalyst activity. Also, co-precipitation has also produced comparable results to deposition-precipitation. However, there is evidence to suggest that impregnation is usually not suitable to prepare gold catalysts as it is more difficult to impregnate the gold onto the metal oxide support and the catalyst is easily poisoned by chloride ions.

1.4.2 Effect of pre-treatment on gold catalysts

As mentioned before, impregnation is not usually the preferred method to produce gold catalysts. However, Bollinger and Vannice (1996) prepared catalysts by impregnation but pre-treated the samples with high temperature reduction (HTR), followed by calcination and finally low temperature reduction (LTR). The HTR took place at 500°C in H_2 for 1 hour, the calcination took place at 400°C in a mixture of 20% O_2 in Helium for 1 hour and the LTR took place at 200°C in H_2 for 2 hours. From their results, Bollinger and Vannice (1996) concluded that the impregnated catalysts required pre-treatment for them to be most active. The impregnated catalysts with an Au particle size of 25 nm had a similar activity to the co-precipitated catalysts with an Au particle size of 4.5 nm.

Another important aspect of preparing the catalyst is the temperature at which the catalyst is calcined. Again, many diverse opinions have been put forward. Wolf and Schüth (2002) found that at a calcination temperature of 200°C the results of the catalysts were consistently improved. However, it is worth mentioning that they did pre-treat all their catalysts in air at 150°C for 1 hour so the pre-treatment temperature was not that different to that used for the 200°C calcined catalysts. The TEM images obtained by Wolf and Schüth (2002) are evidence that for the

catalysts calcined at 200°C most of the gold particles are less than 2 nm. However, for the catalysts calcined at 300°C, the average particle size was between 4 and 8 nm. The catalysts calcined at 400 and 500°C had particle sizes higher that 10 and 15 nm. Wolf and Schüth (2002) attribute the reduced activity of catalysts that have been calcined at higher temperatures to the increased particle size, caused by the agglomeration of the gold particles at higher calcination temperatures.

Tsubota *et al*. (1998) prepared Au/TiO_2 catalysts by deposition-precipitation and then calcined the catalysts at temperatures between 200 and 600°C. Their aim was to establish what the effect of calcination temperature is on catalyst activity. Their results showed that there is a direct relationship between catalyst activity and calcination temperature in other words, as the calcination temperature increases, so the catalyst activity increases. This result contradicts the findings of Wolf and Schüth (2002). The next finding was that when the mixture of gold on titania was calcined at 200°C the gold particles had a smaller spherical shape but when the calcination temperature was 600°C, the particles were much larger and had an irregular shape. Tsubota *et al*. (1998) found that the uncalcined mixture of Au/TiO_2 is not catalytically active for CO oxidation but by calcination of the mixture of Au/TiO_2, the activity is increased and the results are similar to those of catalyst prepared by deposition-precipitation.

The results of Tsubota *et al*. (1998) show that the gold titania interface is unique and that the size of the gold particles is not the only explanation for the high activity of the gold particles. Furthermore, it is speculated that calcination temperature modifies the interface between the gold and titania, to enhance the activity at this interface.

Tanielyan and Augustine (1992) applied various heat pre-treatments to the gold catalysts such as heating in oxygen before cooling in helium or, calcination of the catalyst for 4 hours at 380°C. Their most active catalyst was prepared by drying the co-precipitated solution containing gold at 95°C and then heating it in oxygen at 200°C. They found that the activity of the catalysts differed with different

supports. Tanielyan and Augustine (1992) suggested that perhaps a different pre-treatment method would be required to improve the activity of gold catalysts with different supports. They also confirmed that oxygen on the surface of the catalyst improved carbon monoxide adsorption.

Visco, Donato, Milone and Galvagno (1997) prepared an Au/Fe_2O_3 catalyst by impregnation and co-precipitation. The reaction that they investigated was the oxidation of CO. They obtained high activity with the co-precipitated catalysts that were not pre-treated and therefore decided to calcine the catalysts to determine whether this would improve the activity. Visco *et al*. (1997) found that when they calcined the catalysts at 100°C the initial concentration of CO_2 was lower than that of the catalyst that had not been pre-treated. Also, as the reaction progressed, the concentration of CO_2 continued to decrease. At 200°C the initial concentration of CO_2 was higher than the uncalcined sample however, the concentration continued to decrease as the reaction proceeded but was higher than the sample that was calcined at 100°C. The lowest activity was shown by the catalysts that were calcined at 330 and 400°C respectively. Therefore, the two important findings were that catalyst activity and catalyst stability both decreased when the Au/Fe_2O_3 catalysts were calcined.

Visco *et al*. (1997) explain that the amount of gold present on the catalyst affects the stability of the catalyst and is dependent on the pre-treatment methods used. Furthermore, they propose that it is hydrated gold oxide that is the active species in the catalyst for CO oxidation and that if water is present in the feed to the reaction then the catalyst will be more stable.

Visco *et al*. (1997) observed that by washing the catalyst prepared by impregnation with a solution of NaOH at room temperature, the catalyst activity showed a noticeable improvement. This is in agreement with the findings of Bollinger and Vannice (1996). The explanation that Visco *et al*. (1997) provide for this is that washing with NaOH leads to "hydrolysis of the Au-Cl bonds with the formation of the active hydrated gold oxide."

Finch, Hodge, Hutchings, Meagher, Pankhurst, Siddiqui, Wagner and Whyman (1999) propose that gold nanoparticles are not the active species in a supported gold catalyst but it is the "synergistic interaction" between $AuOOH.xH_2O$ and the metal oxide support (in their case ferrihydrite) that provides the activity of the catalyst. Furthermore, they found that calcination of their catalysts resulted in reduced catalytic activity. Their findings support those of Visco *et al*. (1997).

Daté, Okumura, Tsubota and Haruta (2004) determined that even low concentrations of water vapour have a significant effect on the oxidation of CO. Three supports were investigated in their study namely, alumina, titania and silica. The results of Daté *et al*. (2004) showed that for the Au/Al_2O_3 catalyst only concentrations of moisture above 200 ppm showed an improvement in activity whereas for the Au/SiO_2 catalyst the activity decreased when the moisture content decreased. When the moisture content was increased to 3000 ppm, the Au/TiO_2 catalyst activity was high enough to convert 100 percent of the CO during the reaction. For the Au/TiO_2 catalyst, Daté *et al*. (2004) also changed the pH during preparation to optimise the catalyst.

Daté *et al*. (2004) found that these catalysts behaved differently to what previous researchers had reported; for example, catalysts with larger Au particle sizes or smaller Au loadings remained active in the presence of moisture. Furthermore, they found that when no gold was loaded onto the support material, the activity of the support material was not high enough for the reaction and therefore should not contribute significantly when the gold is loaded onto the support. This suggests that perhaps it is the combination of the gold and the support that accounts for the activity of the catalyst as well as the effect that moisture has at enhancing the properties of the catalyst that account for the high activity. Two important observations were that the presence of moisture during the reaction does not alter the reaction mechanism and the nature of the support has a large effect on the reaction mechanism. They conclude that there are two functions that moisture has during the oxidation of CO over a gold catalyst. The first is that it activates oxygen and the second is that it decomposes the carbonate.

Therefore, pre-treatment methods can be important to enhance the activity of a gold catalyst but they have also been important in providing an understanding of the separate roles of gold and the support during the reaction and the synergistic effect of the gold and the support. A further understanding of how the gold interacts with the support is provided in the next section.

1.4.3 Metal oxide support

Haruta (1997) comments, that the selection of the correct support can enhance the activity of the gold catalyst. An example given by Haruta (1997) is that in the oxidation of CO, the reaction can take place on an unsupported gold catalyst. However when the gold catalyst was supported on titania, the catalytic activity per unit surface area of gold increased by about 100 times.

Okumura *et al*. (1998) had the aim of comparing gold supported on three different metal oxides, silica (Au/SiO_2), alumina (Au/Al_2O_3) and titania (Au/TiO_2). They wanted to determine whether alumina and silica were really inferior supports to titania or whether it was merely the weak interaction of the gold with the metal oxide support that resulted in poor dispersion and in turn caused these oxides to be inferior to titania. The method of investigating this was by using chemical vapour deposition (CVD) to deposit gold onto silica and alumina. This was because titania had already proven to be effective using this method of preparation. Okumura *et al*. (1998) also used liquid phase methods such as impregnation, co-precipitation, and deposition-precipitation to prepare the catalysts. The results of Okumura *et al*. (1998) showed that all three catalysts were highly active for CO oxidation when the CVD method was used. The activity of the catalysts when the co-precipitation method was used depended on the Au loadings. With Au loadings above 10 wt% the catalysts were active but when the Au loading was below 5 wt% the catalysts had a lower activity than when the other methods were used. Therefore, Okumura *et al*. (1998) showed that for the three catalysts, there was no major difference in catalytic activities when the CVD method was used.

Schubert *et al*. (2001a) performed a comparative study of various catalysts. The catalysts that they investigated were Au/α-Fe_2O_3, Au/TiO_2, Au/CoO_x, Au/NiO_x, Au/$Mg(OH)_2$, Au/CeO_2, AuSnO_2, Au/MnOx and they used Au/γ-Al_2O_3 as a reference catalyst with the reasoning that the alumina is inert at the low reaction temperature that they used (80°C). Schubert *et al*. (2001a) compared the catalytic activity, selectivity, deactivation and long-term stability of the catalysts for CO oxidation in H_2-rich gas.

Since Schubert *et al*. (2001a) used different methods to prepare the various catalysts, the metal dispersion or particle sizes of the catalysts differed. Therefore they wanted to eliminate any effects that this may have had on the catalysts and in so doing determined the turnover frequencies (TOF) of all the catalysts under investigation. Then, it emerged that three groups of catalysts could be defined based on their activity as highly active (TOF>1 s^{-1}), less active (initial TOF approximately = 1 s^{-1}) and least active (TOF < 1 s^{-1}). The catalysts that were included in the most active group included: Au/α-Fe_2O_3, Au/CeO_2, Au/SnO_2, Au/TiO_2 and Au/Ni_2O_3. The most active in the group was Au/α-Fe_2O_3 and the least active in the group was Au/Ni_2O_3. The second group included Au/$Mg(OH)_2$ and Au/MgO. The explanation given by Schubert *et al*. (2001a) for these catalysts being less active was that the average particle size of these catalysts (Au/MgO 5.8 nm average particle size) was much larger than the other catalysts (3 nm particle size on average). The last group with the least active catalysts included the reference catalyst, Au/γ-Al_2O_3 and Au/MnO_2. The activity of the Au/MnO_2 catalyst was unexpected since manganese is a reducible transition metal and should therefore have shown an activity close that of the catalysts that formed part of the first group of highly active catalysts.

Schubert *et al*. (2001a) postulated that the difference in activity of the metal oxide supports was as a result of the support's ability to adsorb oxygen and then the ease with which the support material could supply the oxygen for the reaction.

In the work completed by Schubert *et al*. (2001a), the catalyst that showed the highest selectivity was obtained with Au/Co_3O_4 (75 – 80%), followed by Au/MgO and $Mg(OH)_2$ (65 – 70%), $Au/\alpha\text{-}Fe_2O_3$ (60 – 65%). The other less selective catalysts in descending order are: Au/NiO_3, $Au/\gamma\text{-}Al_2O_3$ and Au/CeO_2 (approximately 55 – 60%), Au/TiO_2 (45 – 50%) and Au/SnO_2 (30 – 35%). Schubert *et al*. (2001a) did not have a concrete explanation for the different selectivities but hypothesized that there could be a competing redox reaction that was causing the difference. Schubert *et al*. (2001a) concluded that the $Au/\alpha\text{-}Fe_2O_3$ catalyst showed the best compromise because it showed high activity and high selectivity and that the deactivation of the catalyst was reversible.

On the contrary, Costello, Kung, Oh, Wang and Kung (2002), established during their research that the activity of the $Au/\gamma\text{-}Al_2O_3$ catalyst for CO oxidation has an activity that is similar to the activity reported for TiO_2 and Fe_2O_3. The turnover frequency that Costello *et al*. (2002) report for the Au/Al_2O_3 catalyst is between 0.17 to 0.46 s^{-1} using the deposition-precipitation method and the particle size of the gold is between 3 – 5 nm. Okumura *et al*. (1998) reported a turnover frequency of 1.3 s^{-1} for the Au/TiO_2 catalyst that was also prepared using the deposition-precipitation method with the average size of the gold particles at 1.7 nm. Okumura *et al*. (1998) suggested that a reducible transition metal oxide support was essential for a high activity gold catalyst while Costello *et al*. (2002) dispute this argument with the reasoning that the activity of the alumina supported gold catalyst is comparable to the activity of the titania supported gold catalyst. This seems surprising as the size of the gold particles in the study by Costello *et al*. (2002) were between 3 and 5 nm which was larger than the particle size observed by Okumura *et al*. (1998). Costello *et al*. (2002) suggest that the presence of chloride ions can poison the catalyst and so perhaps by preparing the catalyst by deposition-precipitation Costello *et al*. (2002) were able to remove the chloride ions whereas Okumura *et al*. (1998) were not able to remove the chloride ions by using the chemical vapour deposition method.

Wolf and Schüth (2002) tested five different supported gold catalysts. The five catalysts were Au/TiO_2, Au/Co_3O_4, Au/Al_2O_3, Au/ZrO_2 and Au/SiO_2. The catalysts were prepared using the deposition-precipitation method. Immediately, it was found that the SiO_2 support was unsuitable using this method of preparation. The Au/Co_3O_4 catalyst showed better results when the deposition-precipitation method was used than when using co-precipitation. An important result was that when the Au/TiO_2 catalyst was compared with the Au/Al_2O_3 catalyst, the Au/TiO_2 catalyst was more active. They also ensured that the particle sizes of the gold on each catalyst were of a comparable size. Therefore, they concluded that the activity of the catalyst is not merely as a result of the size of the particles. Also, Wolf and Schüth (2002) found that when the isoelectric point of the catalyst was between 6 and 9, and the synthesis conditions were optimized, the gold catalysts were highly active suggesting that the type of support is not the only influencing factor for the activity of the catalyst.

There are therefore two schools of thought when it comes to the activity of alumina as a support for gold catalysts. Some research has shown that alumina is as active or more active than titania and there is other research that has shown that alumina is less active than titania as a metal oxide support for gold catalysts. Okumura *et al*. (1998) showed that there was no major difference in activity when they compared three supports namely silica, alumina and titania. This result was confirmed by Costello *et al*. (2002). They established that the activity of the Au/Al_2O_3 catalyst was similar to both the Au/TiO_2 and Au/Fe_2O_3 catalysts. Schubert *et al*. (2001a) used the alumina supported gold catalyst as a reference catalyst for their experiments; the reasoning was that the catalyst was not active at the low reaction temperatures. Wolf and Schüth (2002) showed that when titania was used as a support for gold catalysts it was in fact more active than the gold supported on alumina.

Yan, Mahurin, Pan, Overbury and Dai (2005) conducted an experiment whereby they deposited gold onto titania via a deposition-precipitation method. The nanocrystalline titania was then modified by alumina using a surface sol – gel process. According to Yan *et al*. (2005), a problem encountered with gold

catalysts is stability during reaction conditions as the gold catalyst tends to sinter. Their major finding was that surface modified supports were less susceptible to sintering than gold catalysts with supports that had not been modified.

Tai, Murakami, Tajiri, Ohashi, Daté and Tsubota (2004) prepared gold catalysts supported on titania and titania-coated silica aerogels to oxidize CO. Tai *et al*. (2004) describe an aerogel as a porous material with a large surface area. The large pore size enables the reactant molecules to interact with the particles inside the pores and the large surface area allows the gel to keep the catalytic nanoparticles at a high number density. Their results show that the titania-coated composite aerogels had a higher activity (than the non-coated titania aerogel) for CO conversion.

Tai *et al*. (2004) explain that in the non-coated titania aerogels, the titania gel undergoes a structural change after heat treatment and therefore the Au nano-particles had a larger diameter and were supported on a smaller surface area. In the case of the titania coated composites, Tai *et al*. (2004) explain that the amorphous structure of the titania is maintained therefore preventing the gold particles from coagulating with each other. With these composite aerogels, the size and loading of the gold nanoparticles can be independently controlled which is not true for the non-composite gels.

Schubert, Hackenberg, van Veen, Muhler, Plzak and Behm. (2001b) divide metal oxides into two categories namely: "inert" and "active". The "inert" group are made up of irreducible metal oxides such as Al_2O_3 and MgO. In this group, Schubert *et al*. (2001b) proposes that adsorption and dissociation of oxygen occurs directly on the gold. The size of the gold particles has a profound effect on the activity of these "inert" catalysts. The "active" group includes Fe_2O_3, NiOx, CoOx and TiO_2 and are reducible. Schubert *et al*. (2001b) assume that these "active" supports have a role in the CO reaction.

Venezia, Liotta, Pantaleo, Beck, Horváth, Geszti, Kocsonya and Guczi (2006), also divide metal oxides into "active" and "inert" groups. Their "active" group

also includes Fe_2O_3 and TiO_2 in addition to CeO_2. Their "inert" group also includes Al_2O_3 in addition to SiO_2. The gold nanoparticles are stabilized by the stronger metal-support interaction with the active metal oxides. Venezia *et al*. (2006) note that silica does not allow the gold to disperse (therefore gold particles are too large) when prepared using traditional methods, rendering the gold catalyst inactive. However, they further state that there are properties of silica that would aid the activity of the gold catalyst that the titania cannot provide. These properties include: large surface area, high thermal stability, mechanical strength and simple structure. Although the titania on its own is a better support than the silica, the catalyst can be susceptible to sintering during reaction conditions. Therefore, Venezia *et al*. (2006) developed a catalyst by doping silica with increasing amounts of titania (between 2.5 and 20 wt% TiO_2). The sol gel method was then used to deposit the gold onto the modified support. The catalyst only proved to be more active when low concentrations of TiO_2 were used.

Although Tai *et al*. (2004) and Venezia *et al*. (2006) both found that when coating titania with silica, a synergy can exist where the different properties of each support can be utilized, it is important to mention that the catalyst would have to be optimized before generalizing that gels are proven to give a higher activity for CO oxidation. This can be seen from the finding of Venezia *et al*. (2006) that the catalyst was only more active at low TiO_2 concentrations.

Table 1.1 presents a summary of metal supports used for gold catalysis that have been mentioned in this section. From the table it is clear that CO oxidation was the most studied reaction but the support used and the method to prepare the catalysts varied widely.

Table 1.1 Summary of metal supports for gold catalysts

Reference	**Metal Support**	**Catalyst Preparation Method**	**Test Reaction**
Haruta, Kobayashi, Sano, and Yamada, (1987)	MnO_2, α-Fe_2O_3, Co_3O_4, NiO, CuO, Co-Mn composite oxides.	Co-precipitation	CO oxidation
Haruta, Yamada, Kobayashi, and Iijima, (1989)	α-Fe_2O_3, Co_3O_4, NiO, α-Fe_2O_3, γ-Al_2O_3 SiO_2	Co-precipitation Impregnation Reduction of $HAuCl_4$ with dimmonium citrate	H_2 oxidation CO oxidation
Li, Comotti, and Schüth, (2006)	TiO_2	Deposition-precipitation Impregnation	CO oxidation
Wolf, Schüth, (2002)	TiO_2, Co_3O_4, Al_2O_3, ZrO_2 SiO_2 (was unsuitable)	Deposition-precipitation Co-precipitation	CO oxidation
Moreau, and Bond, (2007)	TiO_2	Deposition-precipitation	CO oxidation
Bollinger, and Vannice, (1996)	TiO_2	Impregnation Deposition-precipitation Co-precipitation	CO oxidation
Tsubota, Nakamura, Tanaka and Haruta, (1998)	TiO_2	Mixture of colloidial solution of Au diluted with isopropyl ether and TiO_2 powder and deposition-precipitation	CO oxidation

Reference	**Metal Support**	**Catalyst Preparation Method**	**Test Reaction**
Tanielyan and Augustine, (1992)	Co_3O_4, Fe_2O_3,CuO	Co-precipitation	CO oxidation
Visco, Donato, Milone and Galvagno, (1997)	Fe_2O_3	Impregnation Co-precipitation	CO oxidation
Finch, Hodge, Hutchings, Meagher, Pankhurst, Siddiqui, Wagner and Whyman, (1999)	$Fe(NO_3)_3.9H_2O$	Co-precipitation	CO oxidation
Daté, Okumura, Tsubota, Haruta, (2004)	TiO_2, Al_2O_3, SiO_2	Deposition-precipitation	CO oxidation
Okumura, Nakamura, Tsubota, Nakamura, Azuma, and Haruta, (1998)	SiO_2, Al_2O_3, TiO_2	Chemical Vapour Deposition (CVD), co-precipitation, impregnation, deposition - precipitation	CO oxidation H_2 oxidation
Schubert, Plzak, Garche, and Behm, (2001a)	α-Fe_2O_3, Ni_2O_3, $Mg(OH)_2$, MgO	Co-precipitation	CO oxidation in H_2-rich gas
	α-Fe_2O_3, CeO_2, MnO_2	Deposition-precipitation	
	Co_3O_4, TiO_2, γ-Al_2O_3, SnO_2	Impregnation	

Reference	Metal Support	Catalyst Preparation Method	Test Reaction
Schubert, Hackenberg, van Veen, Muhler, Plzak, and Behm, (2001b)	α-Fe_2O_3	Deposition-precipitation	CO oxidation
	α-Fe_2O_3, NiO_x, $Mg(OH)_2$, MgO, Fe_2O_3.MgO	Co-precipitation	
	Al_2O_3, TiO_2, CoO_x	Impregnation	
Costello, Kung, Oh, Wang, and Kung, (2002)	Al_2O_3	Deposition-Precipitation	CO oxidation
Yan, Mahurin, Pan, Overbury, Dai, (2005)	TiO_2 modified by Al_2O_3 using surface sol-gel process	Deposition-precipitation	CO oxidation
Tai, Murakami, Tajiri, Ohashi, Daté, Tsubota, (2004)	TiO_2 aerogel and TiO_2-coated SiO_2 aerogel	Prepared aerogel support and incorporated Au into aerogel	CO oxidation
Venezia, Liotta, Pantaleo, Beck, Horváth, Geszti, Kocsonya, Guczi, (2006)	SiO_2 support containing 2.5 to 20 wt% TiO_2	"controlled sol formation technique"	CO oxidation
Valden, Pak, Lai, and Goodman (1998)	TiO_2 supported on Mo(100)	Vapour deposition	CO oxidation under ultra high vacuum (UHV) conditions

1.4.4 Enhancement of Au/TiO_2 catalysts

Solsona, Conte, Cong, Carley and Hutchings (2005) claimed to be the first researchers to notice that supported gold catalysts could be augmented by the addition of promoters. In their work, Au/TiO_2 catalysts were prepared by deposition-precipitation and then, various aqueous solutions (sodium nitrate, potassium nitrate, sodium acetate or sodium citrate) were added to the catalyst by impregnation. Solsona *et al*. (2005) experiments revealed two major findings, the first that promoters do in fact increase the activity of the supported gold catalyst and that the catalyst that was treated with nitrate was twice as active as the catalyst treated with citrate but containing the same concentration of Na^+. The second major result that Solsona *et al*. (2005) observed was that the results could

only be reproduced if the residual nitrate was removed thoroughly or if nitrate was removed in the same way each time so that the activity was the same for each experiment.

Gluhoi, Tang, Marginean and Nieuwenhuys (2006) developed an Au/Al_2O_3 catalyst with various alkali (earth) metal oxides such as Li_2O, Rb_2O, MgO and BaO added to the catalyst. The catalyst with BaO showed the highest activity and there was 100 percent conversion of CO at room temperature. The presence of Rb_2O and Li_2O also improves the catalytic activity for CO oxidation of the Au/Al_2O_3 catalyst. However, the order in which the Li_2O is added to the catalyst is important. When the Li_2O was added after Au deposition onto the support, there was a decrease in catalytic activity when compared with all the other alkali (earth) promoted catalysts. A possible explanation of this phenomenon given by Gluhoi *et al*. (2006) is that the interaction between Au and the support is stronger if the Li_2O is first added to the alumina therefore resulting in a higher catalytic activity.

Ilieva, Pantaleo, Ivanov, Venezia and Andreeva (2006), studied the effect of gold catalysts supported on mixed metal oxides. They studied three catalysts namely, gold supported on ceria (Au/CeO_2), gold supported on ceria-alumina mixed support containing 10 wt% alumina in ceria (Au/CeO_2-Al_2O_3) and 20 wt% alumina in ceria (Au/CeO_2-Al_2O_3). The ceria-alumina mixed oxide support was prepared by co-precipitation and the gold was loaded by deposition-precipitation (while parameters such as pH, temperature and stirring speed were controlled). Ilieva *et al.* (2006) found that adding 10 wt% alumina to the catalyst decreased the catalyst activity. While, when 20 wt% alumina was added the catalyst activity improved. Their explanation is that when 10 % alumina was added, it caused an increase in the average particle size of the gold but with the higher concentration of alumina, the ceria was more dispersed while the average particle size of the gold was almost unchanged.

Ilieva *et al.* (2006) studies agree with the literature reports that the more finely divided the gold particles are of a supported gold catalyst, the higher the catalyst activity. Another important result obtained by Ilieva *et al.* (2006), is that the

activity of the catalyst for NO_x reduction by CO increased as more hydrogen was added to the feed. They conclude that hydrogen is active in surface catalyst reduction as well as participating in NO reduction.

Zhang, Zheng, Wei, Lin, Zhang, Li and Cao (2006) also studied the effect of mixed metal oxide supports on a gold catalyst (for the water gas shift reaction under hydrogen-rich conditions). The catalysts studied by Zhang *et al.* (2006) were gold/iron oxide catalysts promoted with ZrO_2 and Nb_2O_5. Their catalysts were prepared by parallel co-precipitation using varying amounts of Nb_2O_5 and fixed amounts of Au and ZrO_2. Then, an Au, iron and zirconium solution was co-precipitated with the Nb_2O_5 solution. Zhang and co-workers found that the catalyst activity was enhanced over a wide temperature range and the difference in activity between the mixed metal oxide supported gold catalyst and the Au catalysts without promoters was more pronounced at higher temperatures. Zhang *et al.* (2006), ascertained that the increased catalyst activity was due to three main reasons: 1) increase in gold dispersion (smaller gold particles), 2) increase in specific surface area of the catalyst and 3) smaller magnetite particles.

Therefore, Ilieva *et al.* (2006) and Zhang *et al.* (2006) concur that when metal oxides are used as promoters for gold catalysts, they are effective when the gold particles are more highly dispersed. Ilieva *et al.* (2006) found that higher concentrations of the promoter (alumina) were needed for the catalyst to be more active. This suggests that not all metal oxide promoters enhance the catalytic activity of gold catalysts and that the correct concentration of the promoter has to be determined to optimise the catalyst.

Recent studies by Ma *et al*. (2007) and Moma *et al*. (2007) have been done to determine the effect of integrating ions into Au/TiO_2 catalysts.

The purpose of the work carried out by Ma *et al*. (2007) was to produce a catalyst that remains active at high temperatures as Au/TiO_2 catalysts lose activity at higher temperatures (above 400°C) due to sintering. The study by Ma *et al*. (2007) investigated the effect of adding phosphate into the gold catalyst. This was done

via two methods. The first being to add the phosphate (diluted H_3PO_4) before the gold was loaded onto the titania and the second method was to load the gold onto the titania and then incorporate the phosphate (diluted H_3PO_4) into the prepared Au/TiO_2 catalyst.

Ma *et al*. (2007) found that washing the PO_4^{3-}/TiO_2 before the gold was loaded, increased the activity of the catalyst to a level comparable to an Au/TiO_2 catalyst that has not been modified. Then, using this result Ma *et al*. (2007) changed the temperature at which phosphate was added to the TiO_2 and the temperature at which the catalyst was calcined. Their results showed that calcination of the catalyst at 500°C improved the activity of the catalyst so that the catalyst was slightly more active than an Au/TiO_2 catalyst calcined at 200°C. Furthermore, Ma *et al*. (2007) found that if higher concentrations of phosphate were added to the catalyst, a blocking effect of the active sites was noticed. Therefore, it seems that for this catalyst, an extremely controlled procedure is necessary to synthesize this catalyst and the activity of the catalyst is then only slightly higher for the oxidation of CO than an Au/TiO_2 catalyst that has not been modified.

In the second method of preparation, Ma *et al*. (2007) again showed that when the temperature used to add the phosphate was high, it led to a higher concentration of phosphate on the catalyst and therefore, reduced activity. Also, the phosphorus content was high if the catalyst was not washed.

The aim of the work by Mohapatra, Moma, Parida, Jordaan and Scurrell (2007), was firstly to establish if preparing the support in different ways affects the activity of the catalyst and secondly to determine the effect that the sulphate ion has on gold-promoted titania. The first result was that the lower the sulphate loading on the catalyst, the higher the activity (compared to the activity of un-promoted Au/TiO_2 catalysts), regardless of the method of preparation that was used.

Mohapatra *et al*. (2007) observed that over a 10 hour period, the activity of all the catalysts that were tested did not show much change (i.e. the sulphate ion did not

hinder or improve the stability of the catalyst). In trying to understand the first observation, they measured the gold particle size distribution and found that there were no major differences again indicating that the sulphate ion was in no way involved in the distribution of the gold particles on the surface. However, Mohapatra *et al*. (2007) found that for high sulphate contents, there was some increase in surface area of the catalyst and lastly, the gold content in all catalysts was similar and close to the target of 1 wt%.

The conclusion that Mohapatra *et al*. (2007) reached from their study was that the sulphate ion does not cause any physical change to the catalyst and that the change must be chemical and so they used two characterization methods, namely X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) to try to collect more evidence about the interaction of the gold with the sulphate ion at the surface of the catalyst.

From the XPS study, Mohapatra *et al*. (2007) learnt that there was no major change in the binding energy of the gold and hypothesized that perhaps the sulphate ions and a small fraction of gold ions have direct interaction or that the sulphate ions interact with perimeter sites on the catalyst. Their SIMS study showed that there was both Au and S on the surface.

The suggestion is that the exact interaction between the gold and the sulphate anion are unknown due to the small quantities that are interacting (and can therefore not be detected by the current characterization techniques) but that there is definitely some interaction between the two species causing the catalysts with low concentrations of sulphate ions to be more active than the un-promoted Au/TiO_2 catalysts.

Moma *et al*. (2007) tested phosphate, sulphate, chloride, fluoride, lithium, sodium and potassium ions added to Au catalysts supported on TiO_2. Two methods were used to prepare the catalysts. In the first method, the promoter was added to the TiO_2 before the gold was loaded. While in the second method the anion or cation was impregnated into the Au/TiO_2 catalyst.

Moma, *et al*. (2007) found that the lower the ion loading, (for all ions that were tested and regardless of the method used to add the promoter), the higher the activity of the catalyst. There was only evidence in the case of the support that was modified with sulphate that there was both gold and sulphur on the surface. Moma *et al*. (2007) conclude that the promotional effect of the sulphate is due to the direct interaction between the gold centres and the sulphate. Furthermore, for the other modified supports, they found that there was an interaction between the support and the ion rather than direct interaction between the ion and the gold centres as was the case for the sulphate ion.

The studies that have been mentioned above have all showed that by modifying the support, there is some improvement in the catalytic activity of the gold catalyst. The work by Mallick and Scurrell (2003) is therefore interesting because when they modified the TiO_2 support with ZnO, it was found that not only was the modified support less active for CO oxidation, it was also less stable then the unmodified Au/TiO_2 support. The Au/TiO_2 catalyst was prepared by deposition-precipitation and then filtered to ensure that all the gold particles were supported on the TiO_2. For the ZnO modified support, the catalyst was prepared by depositing the ZnO on the TiO_2 before precipitating out the solution. The precipitated solution was then filtered. The gold was added in a similar manner as for the unmodified Au/TiO_2 catalyst. From the diffuse reflectance UV-visible spectroscopy (DRS), it was shown that there was no evident chemical interaction between the TiO_2 and ZnO with the gold particles. The TEM study showed that for the modified and unmodified supported gold catalyst, the particle size was less than 3 nm for both samples. This ruled out the possibility therefore that the less active $Au\text{-}TiO_2\text{-}ZnO$ catalyst was caused by a large difference in the size of the particles. As mentioned before, this study showed that when the TiO_2 support was modified with ZnO the modified catalyst was less active and less stable. However, Mallick and Scurrell (2003) have no definite or conclusive reason as to why this is so. Their only speculative reason being that "only a fraction of the total amount of CO adsorbed is able to participate in the catalytic oxidation process".

Lai, Zhang and Ng (2004) modified the titania support by using zirconium dioxide (ZrO_2). They prepared various combinations of mixed oxide support, some sulphated while others were non-sulphated. Two reagents were used to prepare the mixed oxide supports – ammonia and sodium hydroxide (NaOH). The gold was added by the deposition-precipitation method after the mixed oxide support was prepared in each case. The results obtained by Lai *et al*. (2004) showed that when the ammonia was used to prepare the catalysts, it caused the gold particles to be larger and therefore have a lower activity for CO oxidation. When NaOH was used as a reagent to prepare the catalysts, the catalyst was found to be active but only when the CO oxidation reaction was conducted at room temperature and with moisture present in the air.

A possible explanation for some researchers finding that modifying the metal oxide support (before adding the gold to the catalyst) improves the activity of the catalyst could be due to the method used to prepare the metal oxide support or due to the particular process conditions that the reaction was performed under. However, more work may need to be conducted to investigate whether these so-called "enhanced" catalysts always prove to be more effective for catalyst activity or whether the catalyst is only enhanced under certain conditions. Also, the stability of these catalysts will have to be investigated to ensure that small changes in either the method of preparation or process conditions will not have a large effect on the activity of the catalyst.

Table 1.2 presents a summary of the enhanced metal supports that have been studied in the literature. Again, CO oxidation was the most researched reaction while various methods of preparation were used.

Table 1.2 Summary of metals used to promote metal oxide supports used for gold catalysts

Reference	**Metal Support**	**Catalyst Preparation Method**	**Test Reaction**	**Promoter**	**Notes**
Gluhoi, Tang, Marginean and Nieuwenhuys, (2006)	Al_2O_3	Homogenous deposition-precipitation (HDP)	CO oxidation	Not promoted	BaO had the best promoting effect, acted as structural promoters
	MO_x/Al_2O_3	Impregnation	CO oxidation	M: Rb, Li, Ba	
Ilieva, Pantaleo, Ivanov, Venezia, Andreeva, (2006)	CeO_2, CeO_2-Al_2O_3	Co-precipitation	NO_x reduction by CO	CeO_2	Higher concentration of Al_2O_3 caused CeO_2 to be more dispersed increasing catalyst activity
Zhang, Zheng, Wei, Lin, Zhang, Li and Cao, (2006)	Fe_2O_3	Parallel co-precipitation	Water gas shift reaction under hydrogen rich conditions	ZrO_2 and Nb_2O_5	Enhanced activity and stability. Structural promoters delayed sintering of gold catalyst. The main reasons for the enhanced performance are that the promoter created more active gold sites, a larger surface area and smaller magnetite particles
Solsona, Conte, Cong, Carley and Hutchings, (2005)	TiO_2	Deposition-precipitation	CO oxidation	Sodium nitrate, potassium nitrate, sodium acetate or sodium citrate added by impregnation	Catalyst activity was enhanced by the addition of promoters

Reference	Metal Support	Catalyst Preparation Method	Test Reaction	Promoter	Notes
Ma, Brown, Overbury and Dai, (2007)	TiO_2	Deposition-precipitation	CO oxidation	PO_4^{3-}	Calcination temperature = 500°C improved activity and washing support increased activity
Mohapatra, Moma, Parida, Jordaan and Scurrell, (2007)	TiO_2	Sulphate introduced into the titania by impregnation with dilute H_2SO_4, then the Au was added using the single step borohydride method	CO oxidation	H_2SO_4	Higher activity was recorded with the addition of the promoter
Moma, Scurrell and Jordaan, (2007)	TiO_2	Au nanoparticles loaded onto promoted support by single step borohydride (SSBH) method	CO oxidation	PO_4^{3-}, SO_4^{3-}, F^-, Cl^- impregnated into titania and Li^+, Na^+, K^+ hydroxides used to impregnate into TiO_2	Addition of ions to support before gold was added resulted in higher activity (in most cases) whilst addition to Au/TiO_2 resulted in lower activity
Mallick and Scurrell, (2003)	TiO_2	Deposition-precipitation	CO oxidation	ZnO	Surface modification of TiO_2 leads to reduced activity
Lai, Zhang and Ng, (2004)	TiO_2-ZrO_2	Deposition-precipitation	CO-oxidation	H_2SO_4 incorporated by impregnation	Catalyst active when NaOH used as reagent to prepare catalyst but only when reaction was conducted at room temperature with moisture in the air.

1.4.5 Reaction mechanisms

There is a question in the literature about the role of the metal oxide support during the reaction. According to Schubert *et al*. (2001b), there is consensus among researchers in catalysis that in the CO oxidation reaction over gold catalysts, the CO is adsorbed on the gold particles. However, Schubert *et al*. (2001b) mention that what researchers are in disagreement about is the

"mechanism for oxygen adsorption and activation". The reason why this is an important issue is that oxygen (at the atomic level) is required for the CO oxidation to readily occur. Schubert *et al*. (2001b) describe the three main proposed mechanisms for oxygen adsorption.

The first mechanism proposes that the oxygen adsorption takes place "directly on the gold particles". This mechanism then assumes that the metal oxide support merely stabilizes the gold particles and the gold particles are the reactive species in the catalyst.

The second mechanism assumes that the adsorption of oxygen takes place on the support or at the interface between the gold and metal oxide support. This mechanism places far more importance on the role of the support within the catalyst.

The last mechanism suggests that the oxygen adsorbs on the support and then dissociates immediately. The molecular oxygen can then react either at the interface between the support and the gold or react directly on the gold particles. In this mechanism the function of the support can change depending on how the oxygen is dissociated and whether it came into contact with the interface or the gold particle.

The results published by Haruta *et al*. (1989) revealed that the catalysts that they used had different activities for H_2 oxidation and CO oxidation. From their results, Haruta *et al*. (1989) postulated that perhaps the gold particles and the metal oxide support react at different stages of the reaction i.e., that there is some "bifunctional mechanism". Furthermore, they proposed that it is likely that the gold nanoparticles interact with the metal oxide support in such a way that the surface properties of the gold are changed. This changed surface may then be good for one reaction while in another reaction the activity of the catalyst may be low.

Haruta (1997) suggested that the gold particles and the metal oxide support need to be in contact in a certain orientation so that the length of the perimeter interface is maximised, yielding a high catalyst activity at a low temperature. A reaction pathway was proposed by Haruta (1997) where first the CO adsorbs on the surface and boundary interface of the gold, then dissociative adsorption of O_2 occurs at the boundary interface between the Au and the TiO_2. The CO then reacts on the surface of the Au before reacting on the surface of the metal oxide support. Here Haruta (1997) shows that the reaction occurs in two stages but is always on the Au surface.

Valden, Pak, Lai and Goodman (1998) agree with Haruta's (1997) proposed reaction pathway and that the "larger perimeter interface" allows for the Au particles to be more dispersed and therefore exhibit a higher activity. Okumura *et al*. (1998) are also in agreement with the conclusion reached by Haruta (1997).

Bollinger and Vannice (1996) found that depositing TiO_x overlayers onto Au powder produced high activity. Therefore, they concluded that the size of the gold particles is not the main reason for high catalyst activity. Based on their research, Bollinger and Vannice (1996) support the theory that the boundary between the Au and the TiO_2 is unique to this system and this is the reason for the high activity these catalysts.

There is no concrete evidence that proves without a doubt that any one of these proposed mechanisms is the correct one. Again, the experiments performed by the researchers have been performed at different process conditions and the reaction has been examined using various characterization techniques. However, the fact that researchers are having the debate about what the role of the metal oxide support is means that perhaps these researchers are one step closer to solving this question.

1.4.6 Interaction of SO_2 with TiO_2 and Au/TiO_2

Rodriguez, Liu, Jirsak, Hrbek, Chang, Dvorak and Maiti (2002), corroborate the findings of Haruta (1997) in their work in that when gold particles are supported on titania, the system is more active than either pure gold or pure titania.

The research conducted by Rodriguez *et al*. (2002) focussed on how the gold-titania system breaks the S-O bond in sulphur dioxide. They found that this system was effective for adsorbing the SO_2 and breaking the S-O bond. Rodriguez *et al*. (2002) notes that titania is the most common catalyst support for the removal of SO_2 in the petrochemical industry. The reaction proceeds according to the Claus Reaction (Equation 1.4).

Rodriguez *et al*. (2002) compared the results obtained from using unsupported gold as a catalyst and found that bulk metallic gold does not interact with the SO_2. According to their research the complex interactions between gold and titania simultaneously enhance the desulphurisation activity of gold and titania.

Rodriguez *et al*. (2002) found that the SO_2 molecule is not able to dissociate in the presence of an unsupported gold catalyst. The reason is that the SO_2 molecule forms weak adsorption bonds with the gold as gold is not a reactive metal in the bulk form.

Rodriguez *et al*. (2002) note that for the reduction of SO_2 by H_2S in the Claus Process, TiO_2 is the catalyst that has been used most often. Through their research, Rodriguez *et al*. (2002) established that SO_2 does get adsorbed onto TiO_2 but the molecule only partially dissociated at a temperature of 327°C. Therefore they identified that another catalyst was required to completely dissociate the SO_2 molecule.

For a gold catalyst supported on titania, Rodriguez *et al*. (2002) found that SO_2 gets adsorbed and both SO_4 and elemental sulphur get deposited on the surface, indicating that the SO_2 molecule gets dissociated. To obtain a greater dissociation

of the SO_2 molecule, Rodriguez *et al*. (2002) state that a high Au surface coverage must be obtained on the TiO_2.

Rodriguez *et al*. (2002) argue that Au adatoms improve the reactivity of the system by altering "the rate of exchange of O vacancies between the bulk and surface of titania". Furthermore, that Au/TiO_2 is able to easily break the S-O bonds. Therefore, Rodriguez *et al*. (2002) conclude that Au/TiO_2 is more chemically active than either pure gold or pure titania.

Ruth, Hayes, Burch, Tsubota and Haruta (2000), mention that H_2 oxidation over a gold catalyst occurs at the Au surface and therefore the support that is used for the catalyst is not so important. However, for the CO oxidation reaction, the support that is used is important, indicating that the reaction occurs at the boundary between the Au and the support. Ruth *et al*. (2000) found that SO_2 had a significant effect on the CO oxidation reaction and they concluded that the interaction between the SO_2 molecule and the metal oxide surface is stronger than the interaction of SO_2 with metallic surfaces. Therefore, they concluded that SO_2 blocks the perimeter sites and acts as a poison for the CO oxidation reaction.

Chen, Jiang, Li, Jin, Tang and Hu (1999), studied the Claus reaction over a TiO_2 catalyst. Chen *et al*. (1999) found that SO_2 does not form strong adsorption states on the TiO_2 surface and therefore SO_2 can easily be transformed into other adsorption species that easily desorb from the surface of the TiO_2 below temperatures of 300°C. The TiO_2 surface is therefore more resistant to sulphur poisoning. Chen *et al*. (1999) deduced from their infrared (IR) spectroscopy and temperature programmed electronic conductivity (TPEC) experiments that the adsorption states of SO_2 on the TiO_2 surface were S, SO_2^- and SO_3. When Chen *et al*. (1999) pre-treated the TiO_2 catalyst with hydrogen gas, SO_2 was reduced to elemental sulphur.

1.5 Concluding Remarks

In conclusion, a new process is required to convert SO_2 to elemental sulphur after combustion of coal. The reason being that SO_2 is harmful to people and the environment. Existing technologies have some advantages but there are also disadvantages. The most important factors to consider are the capital and operating cost of a chemical plant, the efficiency of the process and how much waste will remain that will need to be disposed of.

Some of the most common problems with the existing SO_2 reduction catalysts are that:

- Some are not effective in increasing the rate of the reaction even at high temperatures,
- At CO: SO_2 ratios above 2:1, the harmful by-product COS is formed and therefore the feed composition needs to be carefully controlled,
- Some are unable to reduce the selectivity towards the formation of COS and
- Some are intolerant towards water or require water vapour for the reaction to occur.

A gold catalyst offers a possible solution to some of the problems that remain with existing technologies, especially since the allure of the gold catalyst is its ability to oxidise CO at very low reaction temperatures. Also, gold catalysts could possibly increase the selectivity towards CO oxidation and minimise the production of COS. Some researchers have also reported that water vapour increases the activity of gold catalysts.

TiO_2 has been used as a catalyst industrially in the Claus process. It has been shown that SO_2 forms weak adsorption states on TiO_2 and can therefore easily be desorbed and partially dissociated from the TiO_2.

The Au/TiO_2 catalyst is able to break the S-O bonds thereby possibly reducing the SO_2 to elemental sulphur.

This dissertation provides details of experiments conducted to investigate whether a gold catalyst is suitable for SO_2 reduction with CO used as a reducing agent.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of Catalysts

2.1.1 Method used for preparing gold catalyst

The proposed method for producing the gold catalyst is the deposition-precipitation (DP) method. The first stage of this method requires depositing the gold onto the support. In this project, titania (Degussa P25, with a surface area of approximately $50m^2/g$ and comprising of 80% anatase and 20% rutile phases) was used as a support. First, approximately 150 to 200 ml of deionised water was added to a beaker that had a magnetic stirrer placed at the bottom. Six grams (6 g) of titana was measured and added to the beaker. Added to the titania was 30 ml of 0.01 M $HAuCl_4$ solution. Next Chimica supplied the $HAuCl_4.xH_2O$ for this solution and it contained 50.0 ± 0.5% by wt. Au. It was important to add this solution drop by drop for uniform dispersion. The solution was then left stirring for 2 h.

The next stage of the procedure was to precipitate the gold. First, the pH of the solution was checked to ensure that it was low i.e., the solution was acidic. A few drops of 15% NH_4OH solution (obtained from SAARCHEM in a concentrated form) were added to raise the pH to between 8 and 8.5. It was important to stir the solution continuously throughout this stage. Then, the solution was left to stir for another 2 hours.

The last stage in producing the gold catalyst was to filter the catalyst to remove excess water. The catalyst was washed with approximately 2 litres of warm water to remove any remaining chloride ions as chloride is a poison for the gold catalyst. While the catalyst was filtered, care was taken to ensure that the catalyst surface was wet. This allowed the water to filter through the catalyst and not through the cracks. Then, the catalyst was calcined for two hours at 120°C.

After the catalyst was prepared, a purple powder with very fine Au particles was formed. The catalyst was then pelletized. The reason for pelletizing the catalyst was because the powdered catalyst causes a large pressure drop across the reactor and therefore only a small amount of catalyst would lower the pressure drop. However, a small amount of catalyst may result in a low conversion of the gas. Therefore, a pelletized catalyst has larger particles which reduce the pressure drop.

The catalyst was pelletized by placing 1 g of the powdered catalyst into a 1 cm dye. The dye was then positioned underneath a force balance. The catalyst was pressed at a force of 5 MPa and a single pellet was formed. The pellet was then crushed with a pestle and mortar. The reason for crushing the pellet is that the gas would not be able to pass through the single pellet. After crushing the pellet the remaining particles were screened. Three screens were used, a 500 μm screen, an 1180 μm screen and a 1400 μm screen. The particle sizes that were used for the reactor were between 500 and 1180 μm.

2.1.2 Addition of ions into titania support

The method used to modify the titania support is summarised from the work completed by Moma *et al*. (2007). The ions that were added to the TiO_2 were PO_4^{3-}, SO_4^{2-}, Na^+ and K^+. The negative ions were a 0.01M solution of their respective dilute acids (A 98% assay of H_2SO_4 obtained from Glassworld and 85% pure orthophosphoric acid obtained from Aldrich). The positive ions were a 0.01M solution of their respective hydroxides (98+ % sodium hydroxide and 85% potassium hydroxide both obtained from SAARCHEM). Two concentrations of ions were used, 0.1 and 0.4 mol% with respect to TiO_2. The method used to add the ions to the TiO_2 was aqueous impregnation using 0.01 M of each of the ions in solution. A mineral acid was used for the anions and a hydroxide was used for the cations. The supports were then dried at 120°C and calcined at 400°C for 3 hours.

2.1.3 Preparation of titania

The preparation of the titania was based on the method used by Jalama, Coville, Hildebrandt, Glasser, Jewell, Anderson, Taylor, Enache and Hutchings (2007). In the preparation of the titania, 1 g of TiO_2 (Degussa P25) was added to 50 ml of distilled water. The mixture was then stirred for 15 minutes using a magnetic stirrer before being filtered and then dried for 1 hour at 120°C. The dried TiO_2 was then calcined in air at 400°C for approximately 16 hours. The powder was then pressed using a force balance and then crushed (as explained in Section 2.1.1). The crushed TiO_2 was then sieved to sizes between 500 and 1180 μm.

2.2 Setup of Experimental Rig

A glass reactor, 30 cm in length and 12 mm internal diameter (ID) was used for the reaction. The reactor was orientated horizontally. This allowed for the design of the reactor to be simple i.e. a straight glass tube could be used. This avoided having to design something complicated that if broken would take a long time to replace i.e., reducing downtime. The reactor was enclosed by a mild steel casing with an ID of 15 mm. The casing enclosed a coil that was needed to heat the reactor. The glass tubing was too narrow and would also have been too brittle to wrap the coil around. A thin steel sheet was then bent around the coil and fibreglass was used to insulate the reactor. The metal casing, coil, steel sheet and fibreglass form the heating jacket for the reactor. A temperature probe was used between the steel casing and the glass reactor. This is used to measure the outside temperature of the reactor. The probe is connected to a proportional-integral-derivative (PID) controller which keeps the reactor set at a specific temperature (the reactor is isothermal). Figure 2.1 shows this probe in red. The reactant gases were a mixture of 268 ppm sulphur dioxide (SO_2) and 787.7 ppm of carbon monoxide (CO) with helium (He) used for the balance of the gas. The gas mixture was obtained from Air Liquide.

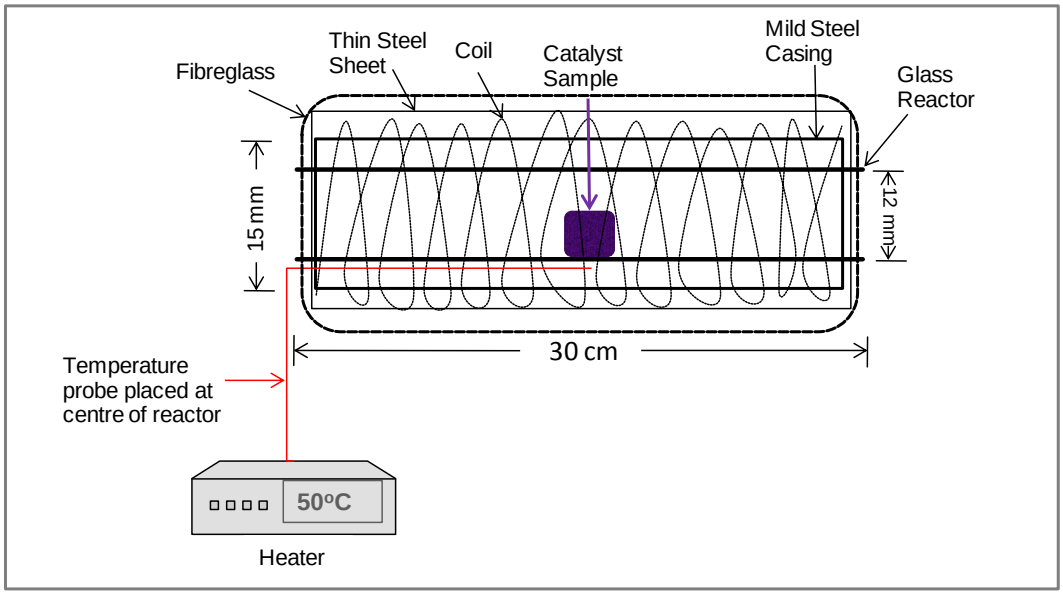

Figure 2.1 Schematic representation of Reactor

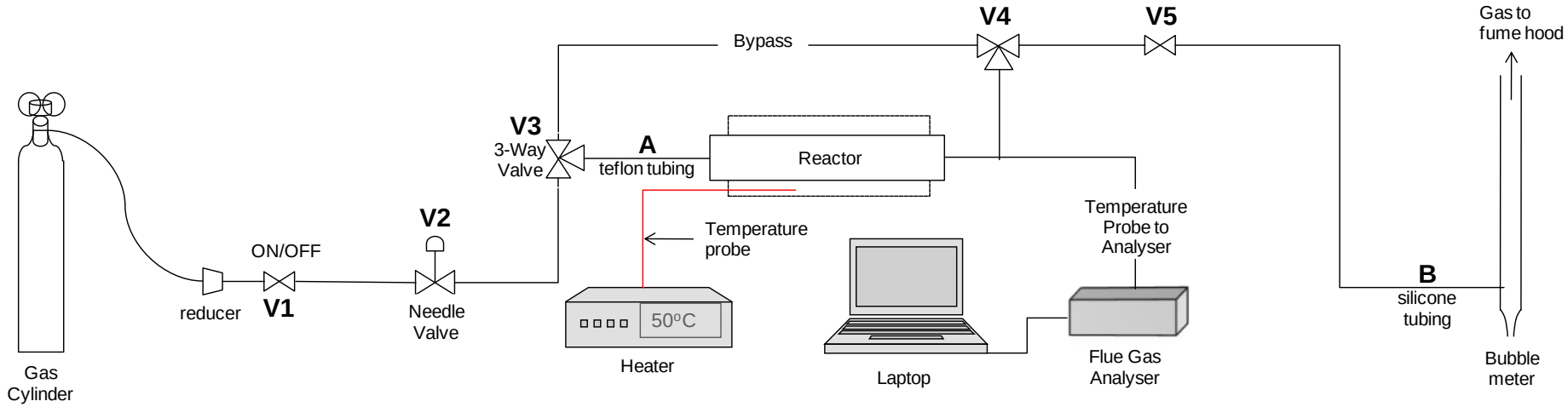

Figure 2.2 The setup of the experimental rig

The length of the rig from the gas cylinder to the outlet of the reactor was about 3 meters. Swagelok fittings were used at the inlet and outlet of the reactor to connect the glass reactor to the tubing that was 1/8th of an inch ID. The probe that measured the concentration at the outlet to the reactor fitted in the glass with 8 mm Swagelok fittings. This probe was connected to the flue gas analyser. The gas from the reactor passed through this probe and to the analyser.

There is also a bypass to the reactor. The bypass was used to measure the flow rate of the gas. First, the three-way shut-off valve (V3 on Figure 2.1) was opened so that gas could only pass through the bypass. The gas flowed to a bubble flow meter. The flow rate of the gas was adjusted by a needle valve (V2). The volumetric flow rate of the gas through the bypass was measured. This procedure was repeated with the V3 opened so that the gas only flowed through the reactor. The valve V4 also had to be opened so that all the gas would flow into the flue gas analyser and no gas would be able to flow back to the bypass.

Initially it was decided that stainless steel tubing, 1/8th of an inch ID would be used throughout the rig. The stainless steel tubing worked well throughout the rig except at 2 points. The first was at the inlet to the reactor (this is shown by point A on Figure 2.1). Stainless steel Swagelok fittings were used directly on the glass reactor with Teflon ferrules and only tightened finger tight. When the stainless steel tubing was connected to the fittings at the inlet to the reactor, it did not allow any flexibility which meant that replacing the catalyst would be difficult. When the small piece of stainless steel tubing was replaced by Teflon tubing it allowed the glass to be removed easily.

The second point where Stainless Steel tubing could not be used was at the flow meter (this is shown by point B in Figure 2.1). Here, silicone tubing was connected to the glass and a Swagelok union connected the rubber tubing to the stainless steel tubing.

Two methods were used to test for leaks. In the first method, the gas cylinder was opened to a certain pressure and the shut off valves at the inlet and outlet were

closed. Then, the cylinder valve was closed. The rig was left for 24 hours. A drop in pressure indicated that there was a leak in the system. If there was a drop in pressure it was shown by a pressure gauge located before the reactor. The gas cylinder was opened for the second method and while the gas flowed through the rig, a soap water solution was sprayed on all the joins. If the soapy solution started to bubble, it indicated that there was a leak at that join. The first method tested for leaks in the system but not the location of the leaks. The second method determined the location of leaks in the system but not how serious the leaks were. Once the rig had been leak tested and all the leaks eliminated, catalyst testing could begin.

2.3 Procedure for Analysis

2.3.1 Operation of flue gas analyser

The analyser that was used to measure the outlet gases was a Testo 350XL gas analyser. It is a portable device that is usually used for measuring flue gas on site at a chemical plant. The motivation for using the analyser was that it is simple to operate and it collects the data immediately when in use so there is no long initial waiting period like for a gas chromatograph (GC). Also, it measures the concentration of SO_2 directly using an electrochemical cell.

The analyser consists of two main parts, the control unit and the analyser box. The control unit attaches into the analyser box. The analyser box contains six gas sensors: O_2, H_2S, SO_2, CO, NO_2 and NO. The gas at the outlet from the reactor will pass through the probe and into the analyser box. Only the SO_2, CO and O_2 cells were necessary for measuring gases during the experiments conducted for this research. The SO_2 cell measures the concentration of SO_2 directly in the range of 0 to 5000 ppm with an accuracy of ±5 % mV in the range of +100 to +2000 ppm of SO_2 which is the range in which the SO_2 is measured for the purposes of this experiment. The reaction time is 30 s for the SO_2 cell. The CO cell measures CO in the range of 0 to 10000 ppm. The accuracy of this cell is ±5 % mV in the range of 200 to 2000 ppm CO. The CO cell has a reaction time of 40 s. The O_2

cell measures the volume percent of O_2 in the gas outlet stream. The instrument can measure O_2 volume percent in the range 0 to 25 Vol% O_2 with an accuracy of ±0.8%. The cell has a reaction time of 20 s (Testo 350M/XL User's Manual, 2005).

The sampling probe is 700 mm in length and has a diameter of 8 mm. The maximum temperature that it can measure is 1000°C. The sampling probe is able to measure the flue gas temperature with its integrated thermocouple. The accuracy of the probe is ±0.5°C for -40 to 99.9°C and ±0.5% mV for the 100 to 1000°C range (Testo 350M/XL User's Manual, 2005).

The gas from the reactor passes over the sampling probe. The measured gas pump then starts automatically and cools the measuring gas to between 4 and 8°C. The condensate is then pumped into a condensation tank at regular intervals. The dry gas passes through a particle filter which removes any particles from the gas. Water in the system will damage the pump and gas sensors. The filter also acts as a water trap. If there is any water present, the pores of the filter will close permanently. Then the gas passes through the pump to the gas sensors. Only a small amount of the gas diffuses through the membranes to the gas sensors, where a signal is given out and recorded using Comsoft (the computer software used with the instrument). The excess gas is removed through the exhaust of the analyser box (Testo 350M/XL User's Manual, 2005).

The analyser was calibrated by the company Unitemp and the cells were replaced before the experiments were started.

2.3.2 Catalyst screening

Two research topics have been studied extensively in the literature. The first is the reduction of SO_2 using CO as a reducing agent and the second is CO oxidation over a gold catalyst. In Section 1.3.3, the first topic was investigated and it was found that what all the researchers' experiments had in common was that high reaction temperatures were required. For instance, Querido and Short (1973)

required a temperature of 380°C to reduce 90% of the SO_2 in the feed and to increase the rate further, temperatures greater than 425°C were required (increasing the reaction intermediate COS). Ma *et al*. (1997) required temperatures greater than 500°C to achieve 98% conversion of SO_2 over their La_2O_2S catalyst, while Kim *et al*. (1998) required temperatures greater than 400°C to achieve complete conversion of SO_2 over the Co_3O_4-TiO_2 catalyst.

However, Haruta *et al*. (1987) discovered that a gold catalyst showed high activity for CO oxidation when the reaction was operated at low temperatures.

The aim of this research project was to use a gold catalyst for the reduction of SO_2 using CO as a reducing agent. This work is very novel as it combines these two research topics that have been studied previously. Therefore, there is little in terms of guidelines to suggest likely operating conditions. The principle of this method was to screen a number of different Au/TiO_2 catalysts at temperatures ranging from 20°C (Room Temperature) to 200°C. The temperature was stepped up in intervals of 25°C after a fixed period of time. The feed gas of SO_2, CO and He was used throughout the experiment. If the chosen temperature was too high, not enough SO_2 would be adsorbed because Au is a low temperature catalyst. However, if the temperature is too low, the reaction would be too slow and the reactants would not be able to overcome the activation energy required for a reaction to take place.

The flue gas analyser measures the disappearance of the reactants, to determine if a reaction is indeed occurring, but it cannot determine if COS is forming or whether SO_2 is reduced to solid sulphur or S_2 gas.

The gas hourly space velocity (GHSV) for all the catalysts that were screened and the TiO_2 are shown in Table 2.1. The bulk density of the catalyst was measured to be 0.84 g/ml and this was used to calculate the GHSV. The GHSV was between 14000 and 32000 h^{-1} for all the catalysts that were screened.

Table 2.1 Gas hourly space velocity of catalysts that were screened

Catalyst	Mass (g)	volumetric flow rate (ml/min)	GHSV (hr^{-1})
TiO_2	0.50	236.85	24160
0.6 wt% Au/TiO_2	0.51	246.31	24672
0.8 wt% Au/TiO_2	0.42	242.60	29547
1 wt% Au/0.1 mol%Na^+ TiO_2	0.60	228.43	19257
1 wt% Au/0.1 mol%K^+ TiO_2	0.39	247.98	32002
1 wt% Au/0.1 mol%SO_4^{2-} TiO_2	0.65	238.11	18615
1 wt% Au/0.1 mol%PO_4^{3-} TiO_2	0.39	240.66	30923
1 wt% Au/0.4 mol%SO_4^{2-} TiO_2	0.85	239.38	14321
1 wt% Au/0.4 mol%Na^+ TiO_2	0.61	247.62	20703

After the catalysts were screened, an experiment was performed whereby the temperature was kept constant at 50°C and the experiment was left for over 50 hours of run time. The initial adsorption peak indicates the amount that can adsorb; the subsequent smaller peaks indicate that a reaction is occurring.

2.3.3 Interpretation of data

The experiment was conducted by first allowing gas to flow through the reactor at room temperature. The baseline concentration of SO_2 was taken as 268 ppm; this is also the concentration of SO_2 in the cylinder. Thereafter, the temperature was increased to 50°C. A peak in the results was seen before the concentration of SO_2 decreased back to the baseline concentration (or within approximately 5% higher or lower than the baseline concentration). The temperature was then increased in increments of 25°C up to 200°C, the maximum temperature. The desorption peaks corresponded to a temperature rise at each fixed time interval.

Each peak that was formed due to the increase in temperature was integrated to establish the number of moles of SO_2 that were adsorbed onto the surface of the catalyst. First, the start and end of each peak had to be recorded. Therefore the starting time and concentration were known and the end time and concentration were also known. Since the baseline concentration was not always exactly equal where the temperature was "stepped", the relationship between the start and end

was a straight line so the gradient and y-intercept of this line could be established from these two points. Equation 2.1 shows how the baseline concentration could be calculated at each point:

$$[SO_2]_{baseline} = Mt + c \quad \text{.....(2.1)}$$

Where M is the gradient of the line, c is the y-intercept and t is the time (in seconds).

The number of moles at each point was then calculated by Equation 2.2 as follows:

$$n_{SO_2} = \left[\left[\frac{[SO_2]_{measured} - [SO_2]_{baseline}}{1 \times 10^6}\right]\left[\frac{PQ}{RT}\right]\right]\Delta t \quad \text{.....(2.2)}$$

Where the concentration of SO_2 was in ppm, P is the pressure of the system which was approximated as air pressure in Johannesburg (84600 Pa), Q is the volumetric flow rate (m^3/min), R is the Universal gas constant (8.314 J/molK), T is the temperature (K) and Δt is the change in time between measurements (min).

The total number of moles at each peak was therefore the sum of the number of moles at each point divided by the time difference between the start and end of the peak. A detailed example of how the peaks were integrated is shown in Appendix A.

The experiment where 0.8wt% Au/TiO_2 was used as a catalyst was repeated twice. The peaks were integrated to calculate the number of moles of SO_2 per gram second that was adsorbed onto the surface of the catalyst at each temperature (as described above). From that the mean value and standard deviation was calculated per temperature. The standard error was calculated by dividing the standard deviation by the square root of 2 (where 2 was the number of observations).

3 CATALYTIC RESULTS

3.1 Gold Catalyst Supported on Titania

Since this work is novel, as the reduction of SO_2 by CO has hardly been performed over this type of catalyst before, the experimental method required screening several catalysts over a range of temperatures.

The temperature was "stepped" in equal temperature intervals of 25 degrees and equal time intervals (which varied between experiments). Figure 3.1 is the result of conducting the reaction over titania whereas Figures 3.2 and 3.3 show the result of using 0.6 wt% Au/TiO_2 and 0.8 wt% Au/TiO_2 respectively. Figures 3.1 to 3.3 show SO_2 adsorption peaks at temperatures ranging from room temperature (20°C) to 200°C.

The valves on the rig were opened so that the feed gas flowed through the catalyst bed while results were recorded. The baseline concentration was taken as the concentration of SO_2 in the gas cylinder, 268 ppm. In the first experiment (Figure 3.1), it took approximately 45 minutes before the baseline concentration of 268 ppm was reached. The reaction chamber was open to air before the experiment was started each time. After the reactor was closed and the gas cylinder opened, it took some time for the air to be completely removed from the reactor.

The time taken for the first peak to form was recorded. In this experiment it took 25 minutes from the time the temperature was increased (from room temperature, 20°C to 25°C) to form the first peak and return back to the baseline concentration. Then each subsequent temperature step was recorded for 25 minutes. At 25°C, the level of SO_2 increased to 368 ppm, at the next three temperature steps, the concentration gradually increased up to 374 ppm, 399 ppm and 418 ppm. The largest peaks were observed at 125 and 150°C where the level of SO_2 reached 511 and 524 ppm respectively.

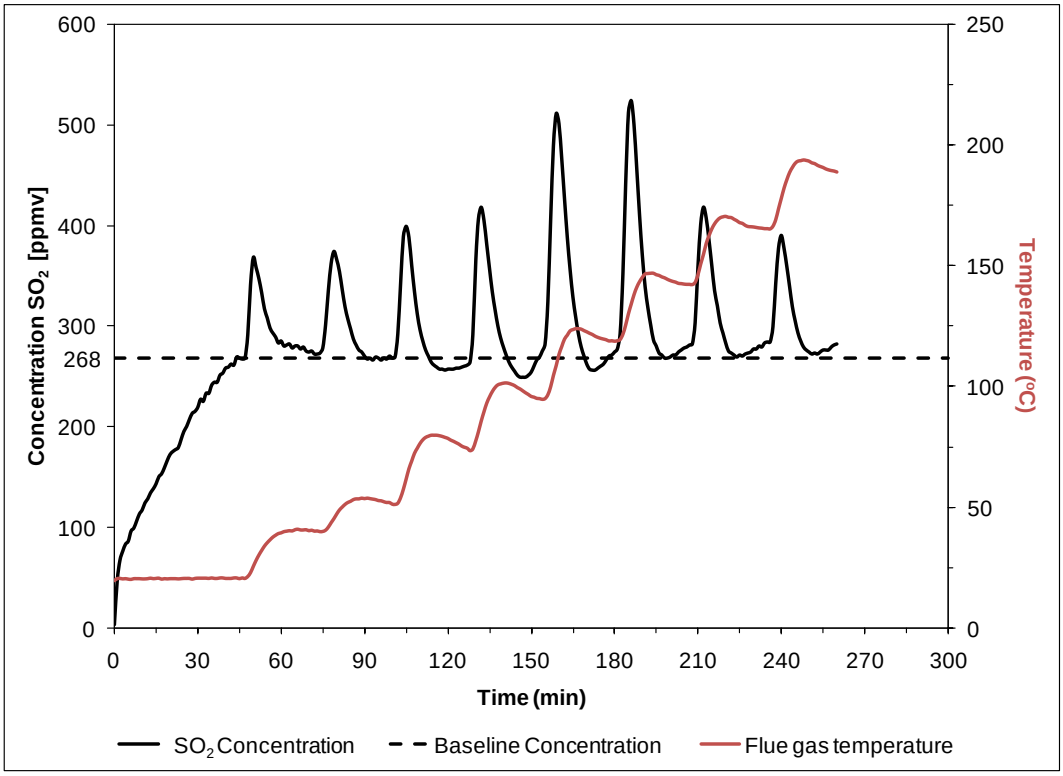

Figure 3.1 SO_2 adsorption peaks observed over titania

Figures 3.2 and 3.3 show that after about an hour and a half, the SO_2 concentration had not yet reached the baseline concentration. However, the concentration had remained stable for some time (20 minutes in Figure 3.2 and 30 minutes in Figure 3.3) and so the temperature was then "stepped" at this stage. The first temperature step was between room temperature and 50°C. This peak was the highest observed throughout this experiment. The duration of the adsorption peak was 15 minutes. In Figure 3.2, the peak that formed from 50 to 75°C was at the lowest level (297 ppm) and from there on the level of the peaks increased up until 150°C (324 ppm, 365 ppm, 445 ppm) after which the level of the peaks trailed off (355 ppm, 323 ppm). In Figure 3.3 the six peaks following the first peak were all at a similar level (304, 287, 299, 302, 304, 303 ppm).

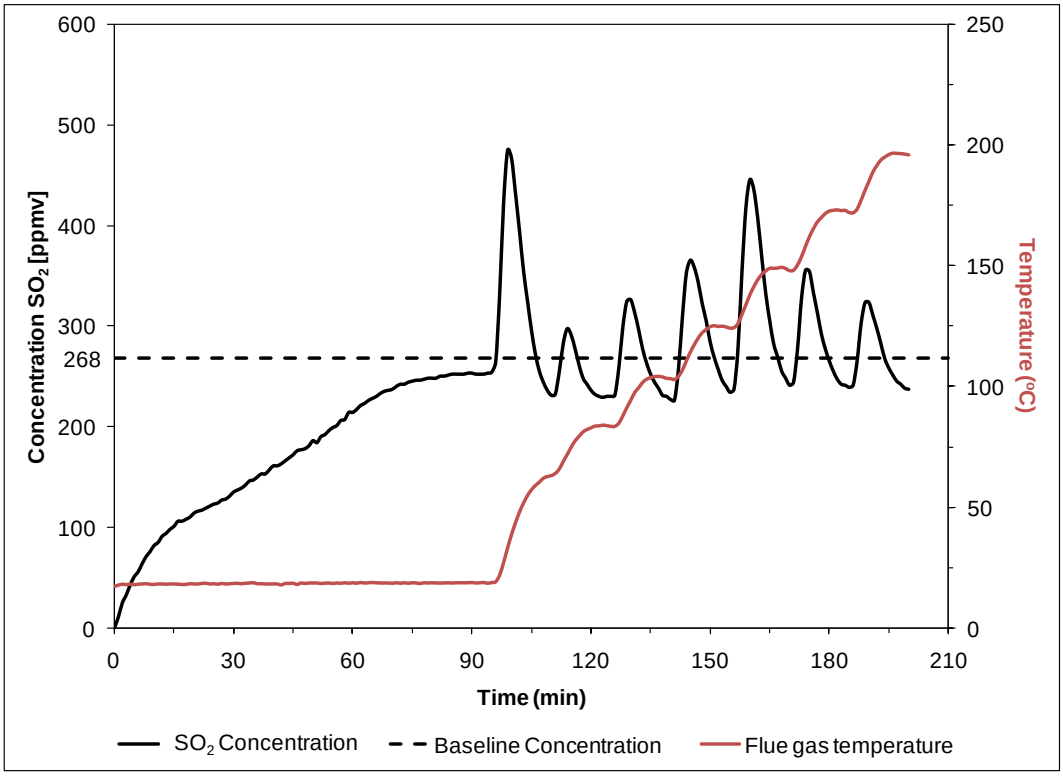

Figure 3.2 SO_2 adsorption peaks observed over a 0.6 wt% Au/TiO_2 catalyst

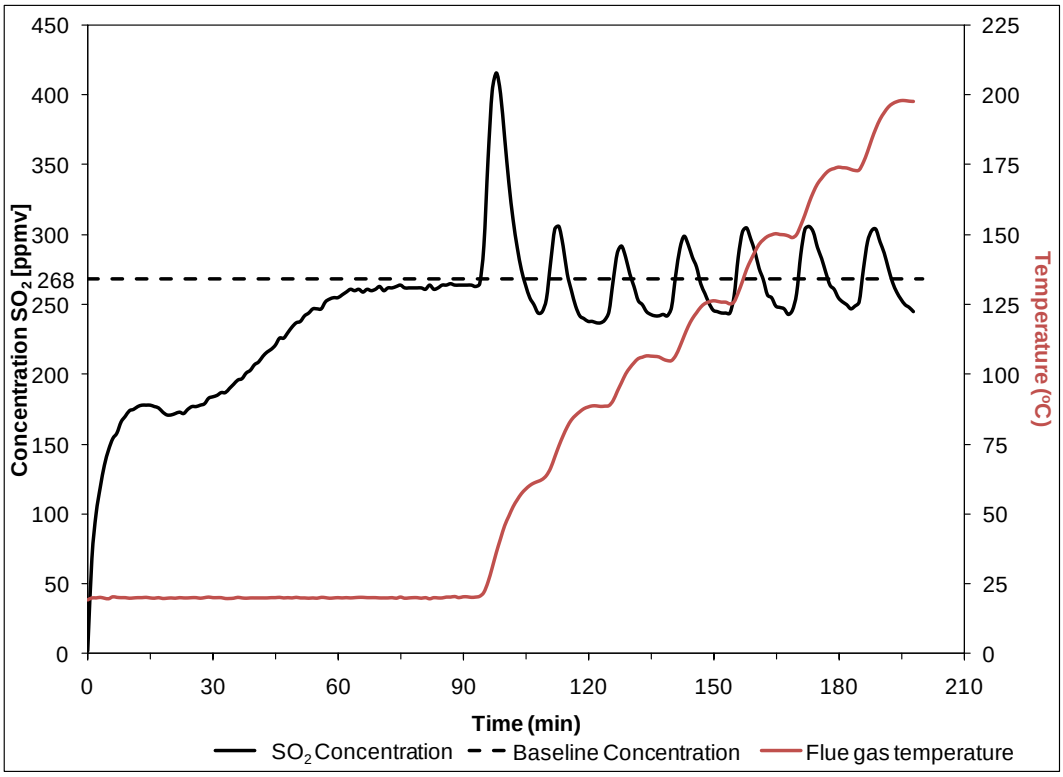

Figure 3.3 SO_2 adsorption peaks observed over a 0.8wt% Au/TiO_2 catalyst

Figures 3.4 to 3.6 illustrate the CO oxidation reaction over titania and the 0.6 and 0.8 wt% Au/TiO_2 catalysts. At the bottom of each graph is the temperature profile throughout the reaction. The most notable feature of all three of these graphs is that when the temperature was increased, there was little change in the CO concentration. In Figures 3.1 to 3.3 there were obvious peaks that were observed in the SO_2 concentration whereas in these graphs, in the case of titania the CO concentration increases at room temperature (20°C) and then from 25 to 75°C the CO decreases before showing a slight increase for the remaining temperature steps. For the case of the gold catalysts, the CO appears to show a slight upward trend.

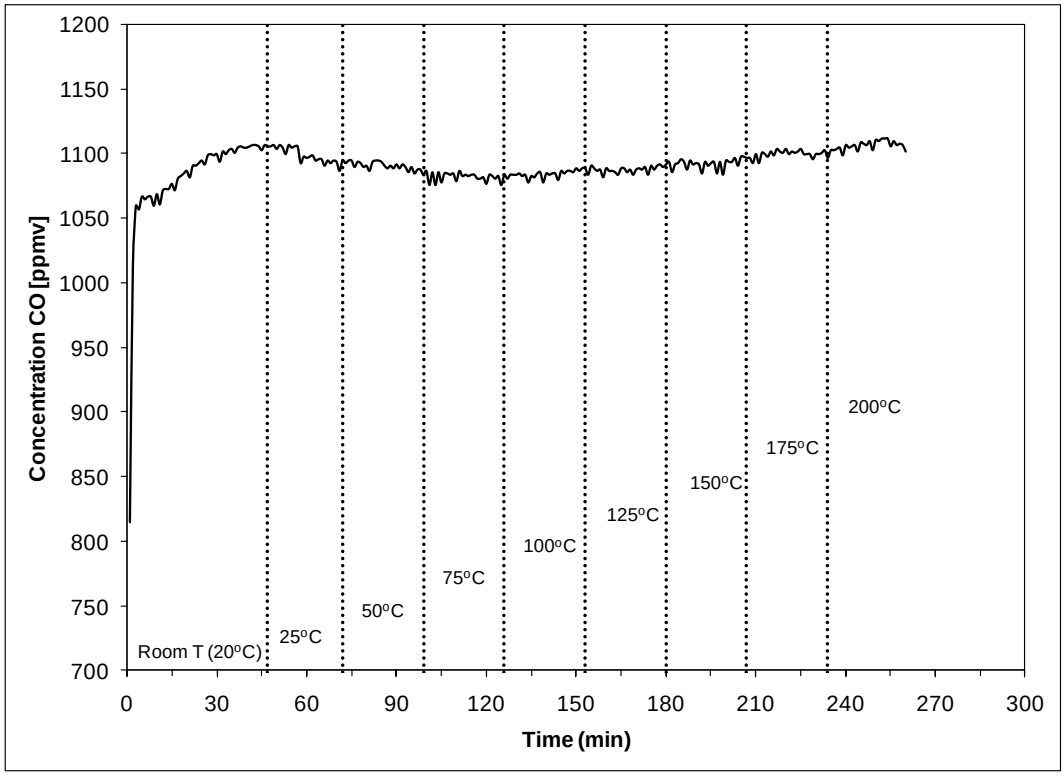

Figure 3.4 CO oxidation on titania

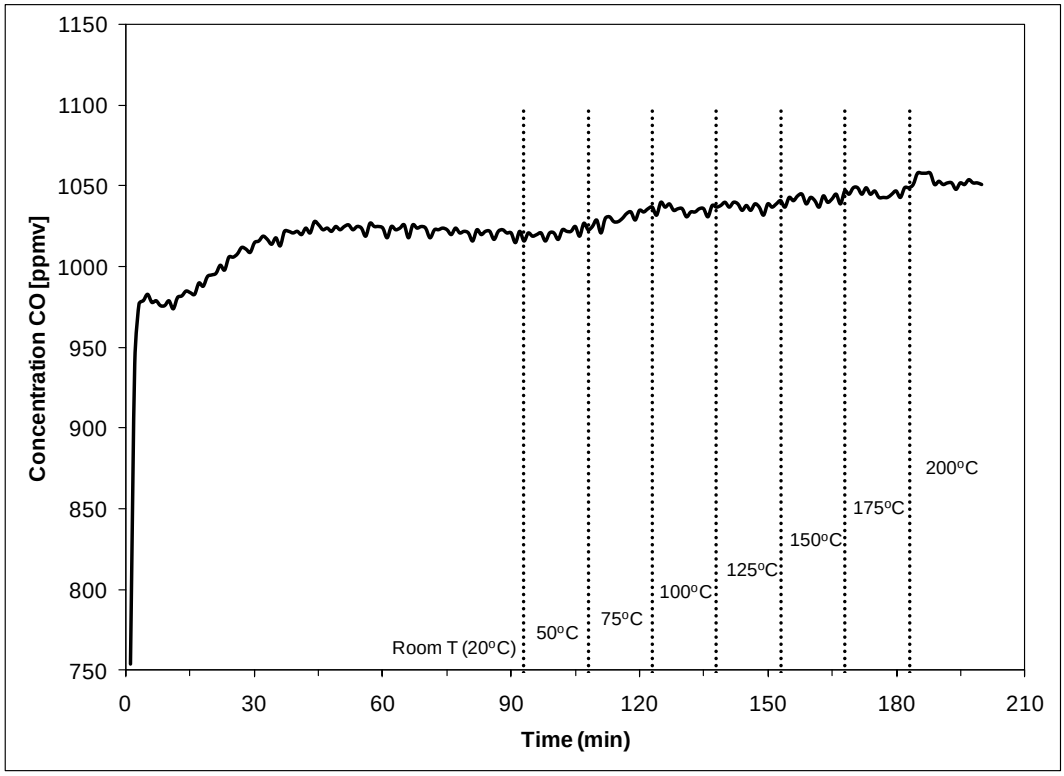

Figure 3.5 CO oxidation over 0.6 wt% Au/TiO_2

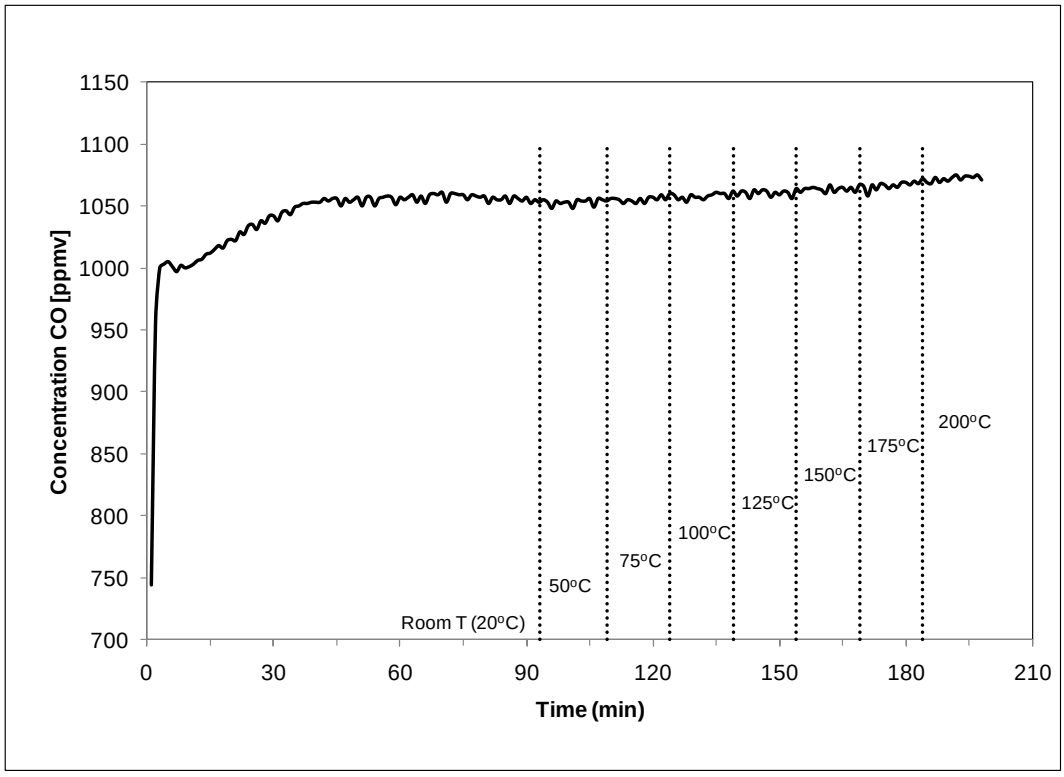

Figure 3.6 CO oxidation over 0.8 wt% Au/TiO_2

3.2 Addition of Promoter Ions onto Titania

3.2.1 Na^+ and K^+ ions

Figure 3.7 and 3.8 are the result of adding 0.1 mol% Na^+ and 0.4 mol% Na^+ to the TiO_2 support respectively. After more than one hour at room temperature, it appeared that the concentration of SO_2 did not seem likely to reach the baseline concentration and so the temperature was "stepped" at this point. After the formation of each peak the SO_2 concentration dropped below the baseline concentration and only increased again with the increase in temperature.

In Figure 3.7, the maximum concentration was observed at 50°C where the level reached 622 ppm. The concentration dropped to 340 ppm at 75°C before increasing gradually up to 519 ppm at 150°C. The last peak was recorded at 175°C and the concentration fell to 452 ppm.

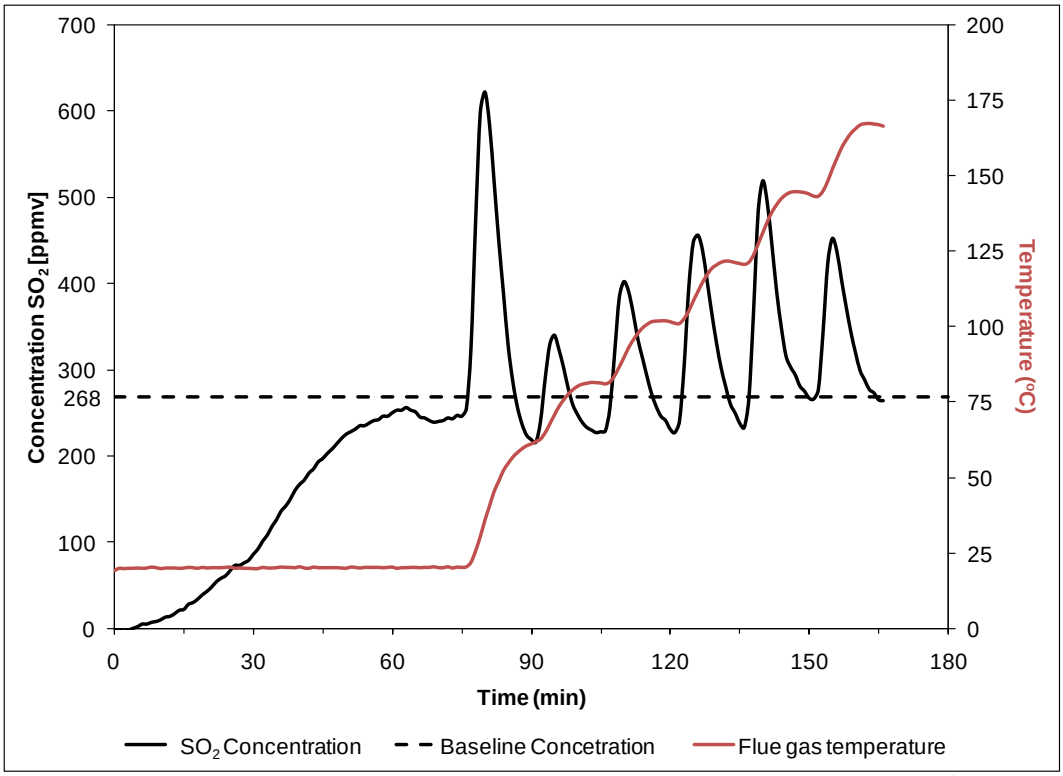

Figure 3.7 SO_2 adsorption peaks observed over a 1 wt% Au/0.1 mol% Na^+ - TiO_2 catalyst

In Figure 3.8 the maximum SO_2 level was also observed at 50°C but the level of SO_2 was at 519 ppm. The levels of the SO_2 peaks observed in Figure 3.8 were lower than the levels observed in Figure 3.7. There was also a large drop in concentration from 50 to 75°C (in Figure 3.8), where the SO_2 peak level dropped to 273 ppm. At 100°C and 125°C the SO_2 levels were at 359 ppm, increasing to 402 ppm at 150°C before decreasing to 357 ppm at 175°C and 350 ppm at 200°C.

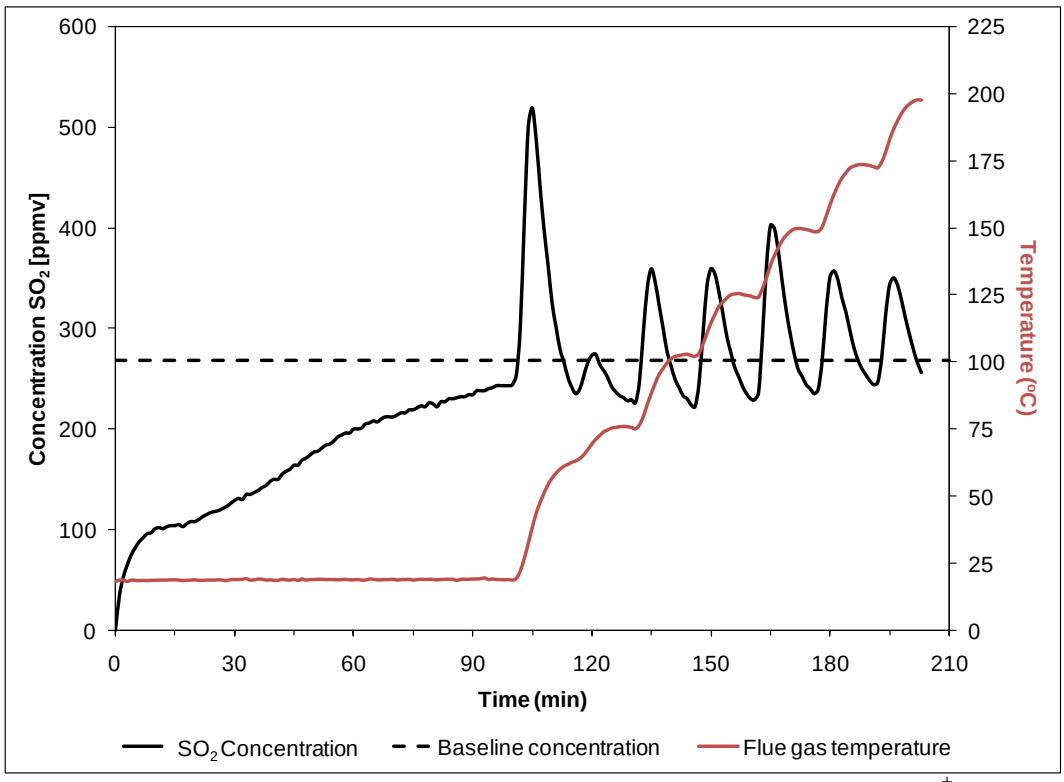

Figure 3.8 SO_2 adsorption peaks observed over a 1 wt%Au/0.4 mol% Na^+ - TiO_2 catalyst

The same experiment was conducted but instead of adding Na^+ to the TiO_2, 0.1 mol% K^+ was added. The results of this experiment are shown in Figure 3.9. It took just over an hour for the SO_2 concentration to reach the baseline concentration at room temperature. This graph shows that the concentration of SO_2 remains at or slightly below the baseline concentration at each temperature interval. The largest adsorption peak was observed at 50°C where the SO_2 concentration rose from 268 ppm to 484 ppm. This was followed by the lowest peak observed at 75°C where the SO_2 concentration rose to 308 ppm. The level of

the peaks then increased more gradually until 150°C and thereafter the level of the peaks reduced at 175 and 200°C.

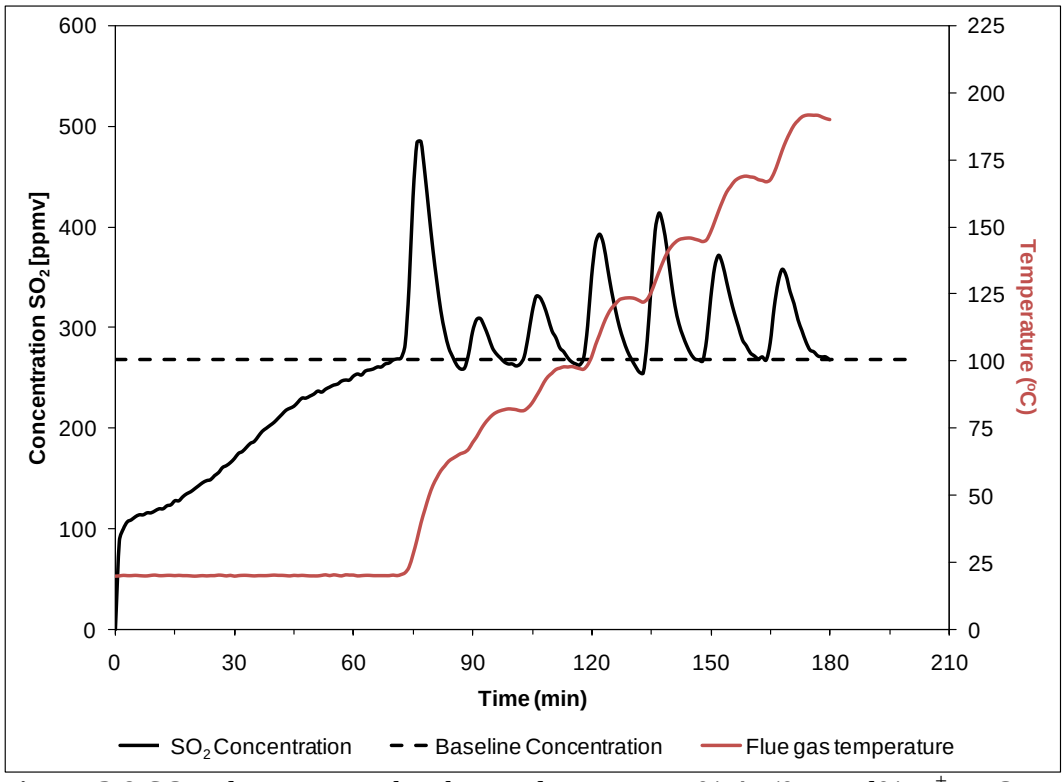

Figure 3.9 SO_2 adsorption peaks observed over a 1 wt% Au/0.1 mol% K^+ -TiO_2 catalyst

Figures 3.10 to 3.12 show that at each temperature interval, the concentration of CO diminishes. This is the most notable difference between these graphs and those shown in Figures 3.4 to 3.6. There is almost an inverted peak of CO disappearance at each temperature interval and it is most obvious in Figures 3.10 and 3.11 with the addition of Na^+ ions to the gold catalyst. As the temperature is increased, the level of CO decreases.

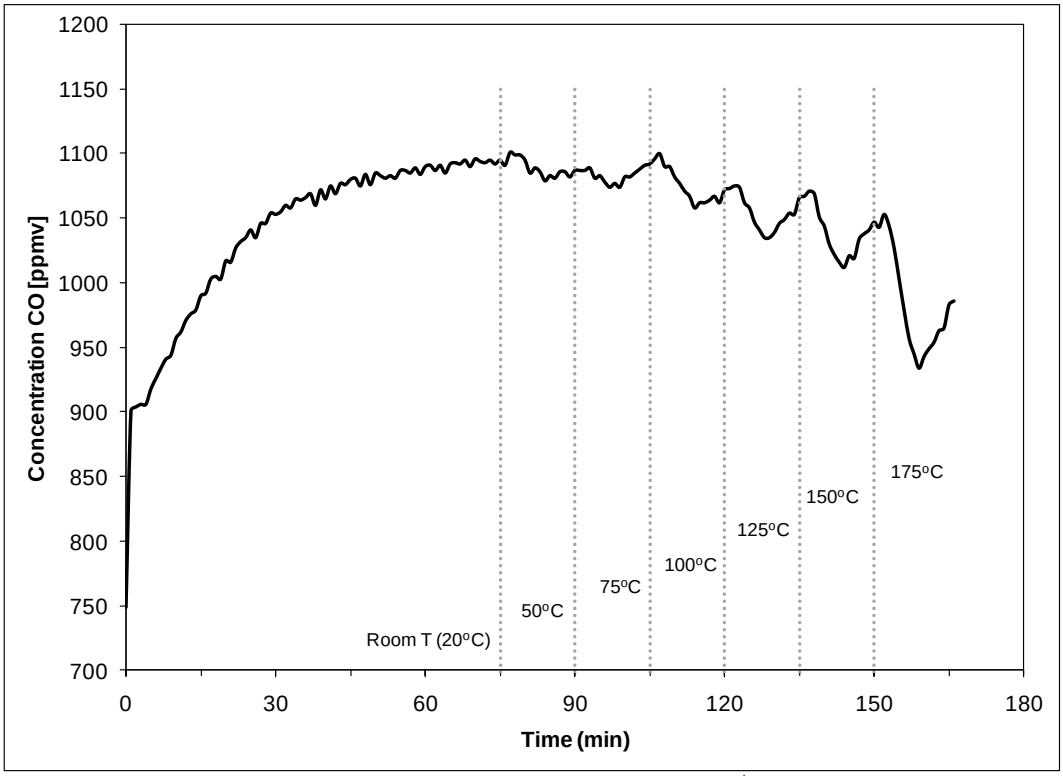

Figure 3.10 CO oxidation over a 1 wt% Au/0.1 mol% Na^{+} -TiO_2 catalyst

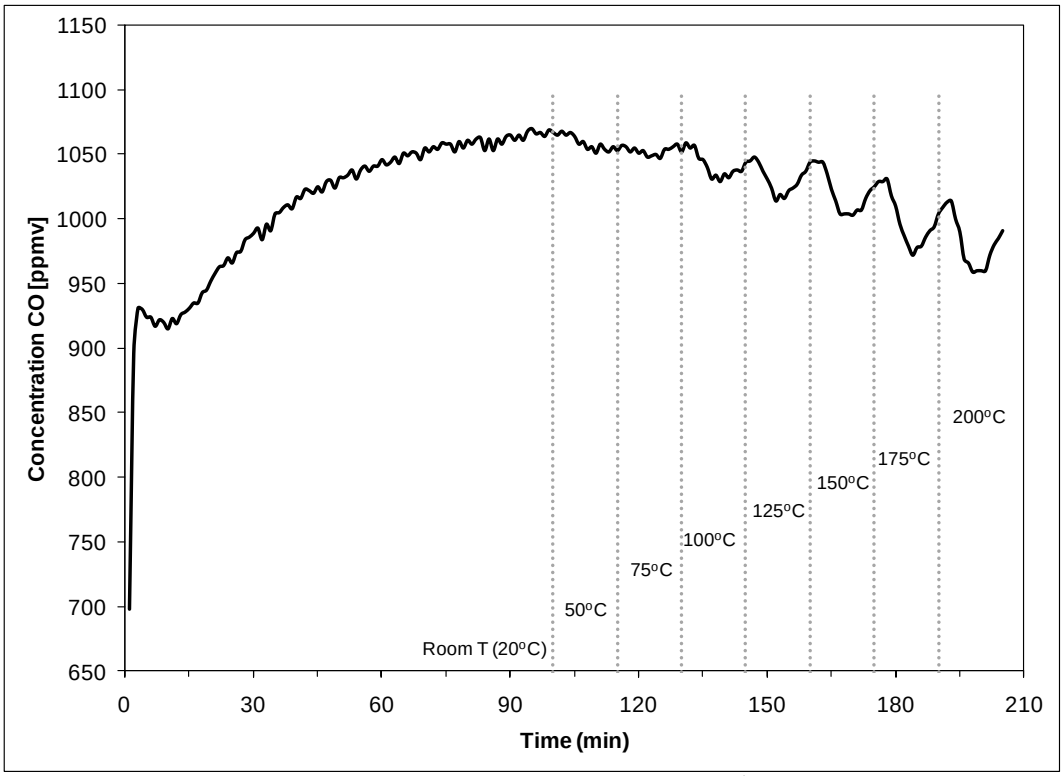

Figure 3.11 CO oxidation over a 1 wt% Au/0.4 mol% Na^{+} -TiO_2 catalyst

Figure 3.12 shows that the CO concentration appears to change more and reduces further with each step increase in temperature.

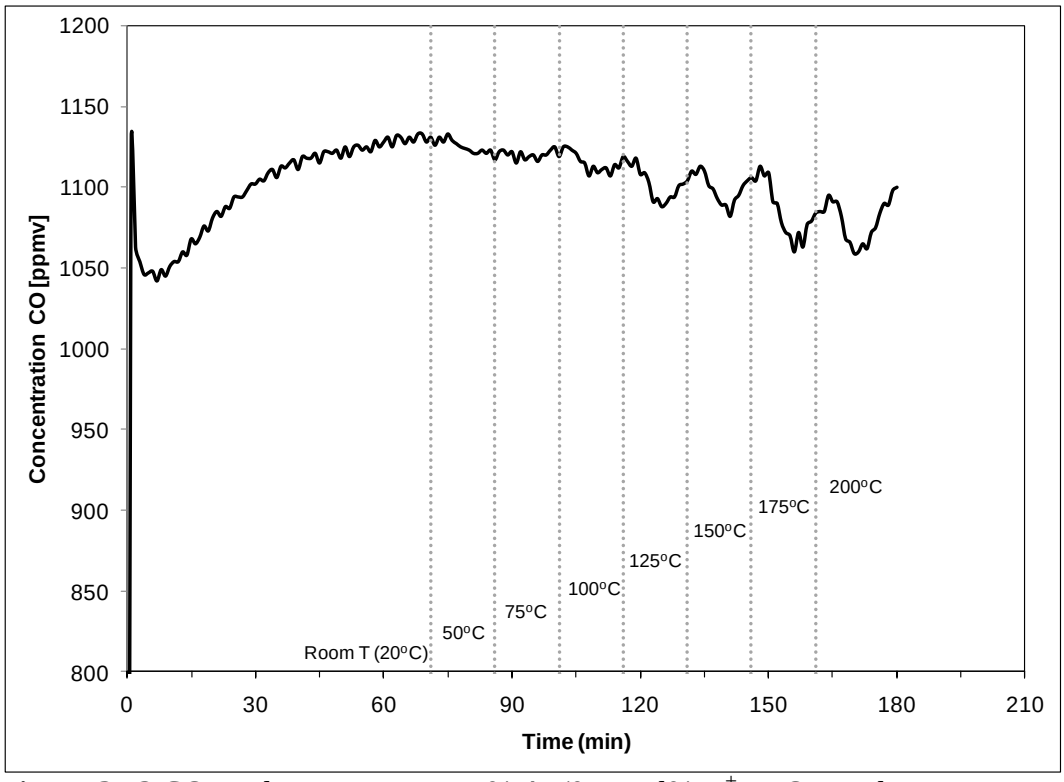

Figure 3.12 CO oxidation over a 1 wt% Au/0.1 mol% K^{+} -TiO_2 catalyst

3.2.2 SO_4^{2-} and PO_4^{3-} ions

Figure 3.13 shows the SO_2 desorption peaks observed when 0.1 mol% SO_4^{2-} was added to the TiO_2. After approximately 1.5 hours, the concentration of SO_2 was far from the baseline concentration (268 ppm). The temperature was "stepped" to 50°C at this stage. At the second peak (75°C) the concentration barely increased above the baseline concentration (275 ppm). Again, the largest peak was observed at 50°C where the SO_2 concentration was at 375 ppm. From 75 to 150°C the level of the peaks increased gradually from 275 ppm to 336 ppm. At 175°C the level of the SO_2 concentration fell to 324 ppm before returning to 336 ppm at 200°C.

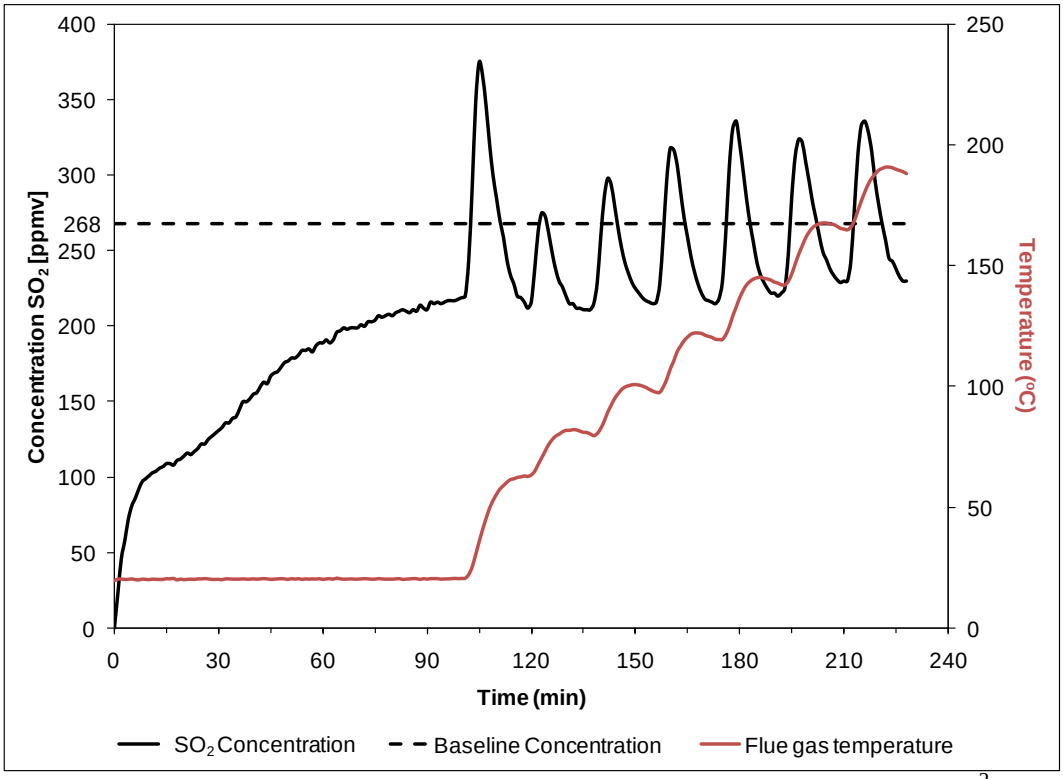

Figure 3.13 SO_2 adsorption peaks observed over a 1 wt% Au/0.1 mol% SO_4^{2-} - TiO_2 catalyst

The mol% of the SO_4^{2-} ions was then increased from 0.1 to 0.4. The results are presented in Figure 3.14. Large peaks were observed at 50°C (423 ppm), 125°C (397 ppm) and 150°C (414 ppm). Much lower levels were observed at 75°C (286 ppm) and 100°C (303 ppm). At the temperatures greater than 175°C and 200°C the level of the peaks reduced to 373 ppm and 368 ppm respectively.

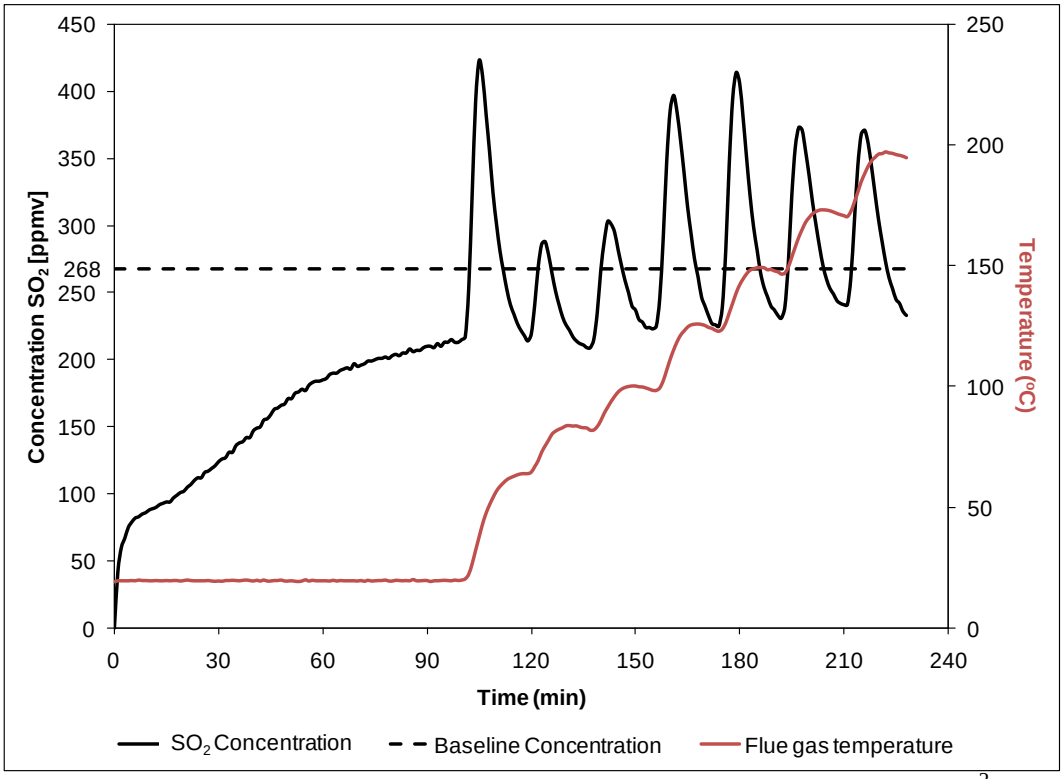

Figure 3.14 SO_2 adsorption peaks observed over a 1 wt% Au/0.4 mol% SO_4^{2-} - TiO_2 catalyst

Figure 3.15 shows the effect on the SO_2 adsorption peaks when 0.1 mol% PO_4^{3-} is added to the TiO_2. The peaks from 50°C to 150°C (481 ppm, 297 ppm, 317 ppm, 350 ppm, 397 ppm) show a similar trend to those in Figure 3.13 although the levels of the peaks in Figure 3.15 are higher. At 175°C the SO_2 level decreases to 327 ppm before decreasing to 313 ppm at 200°C.

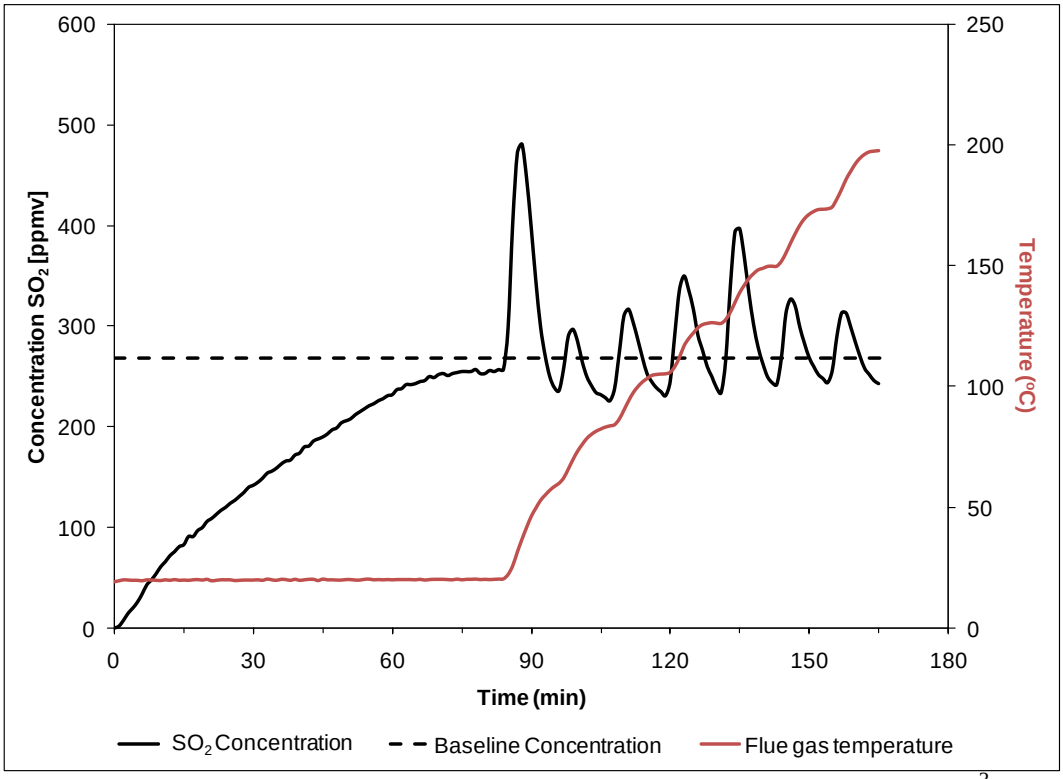

Figure 3.15 SO_2 adsorption peaks observed over a 1 wt% Au/0.1 mol% PO_4^{3-} - TiO_2 catalyst

Figures 3.16 and 3.17 show a reasonable amount of change in the CO concentration, while in Figure 3.18, the concentration of CO remains quite flat and only really shows some change at 175 and 200°C. In Figure 3.16 the concentration of CO rose to above 900 ppm at the beginning of the experiment but at 200°C the CO concentration drops to below 800 ppm. The CO concentration decreases gradually with each increase in temperature. In Figure 3.17, the level of the CO concentration is higher (between 900 to 1000 ppm) than the concentration that was recorded in Figure 3.16. The amount by which the CO concentration decreases is also steadier in Figure 3.17.

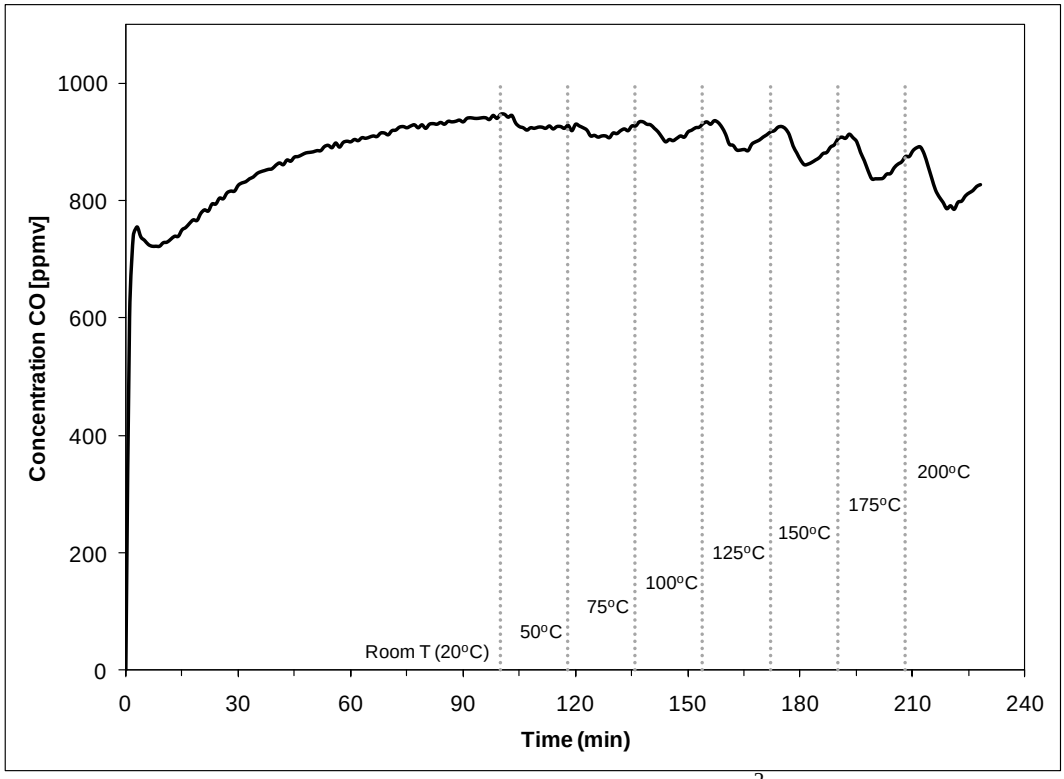

Figure 3.16 CO oxidation over a 1 wt% Au/0.1 mol% SO_4^{2-} -TiO_2 catalyst

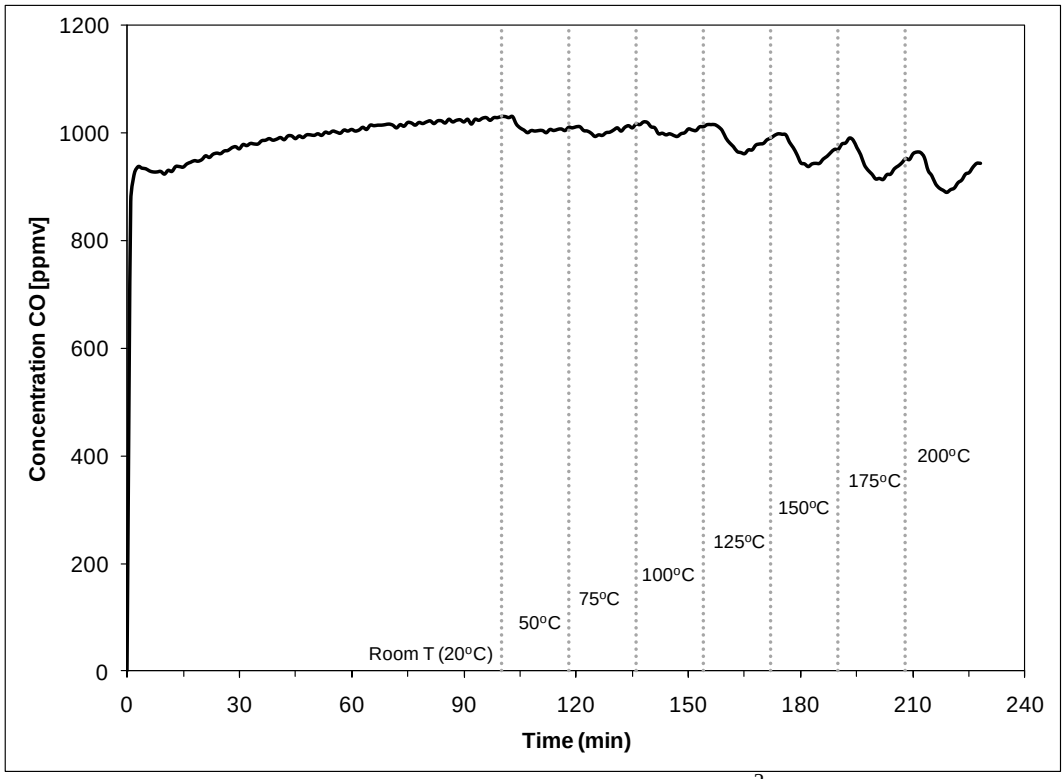

Figure 3.17 CO oxidation over a 1 wt% Au/0.4 mol% SO_4^{2-} -TiO_2 catalyst

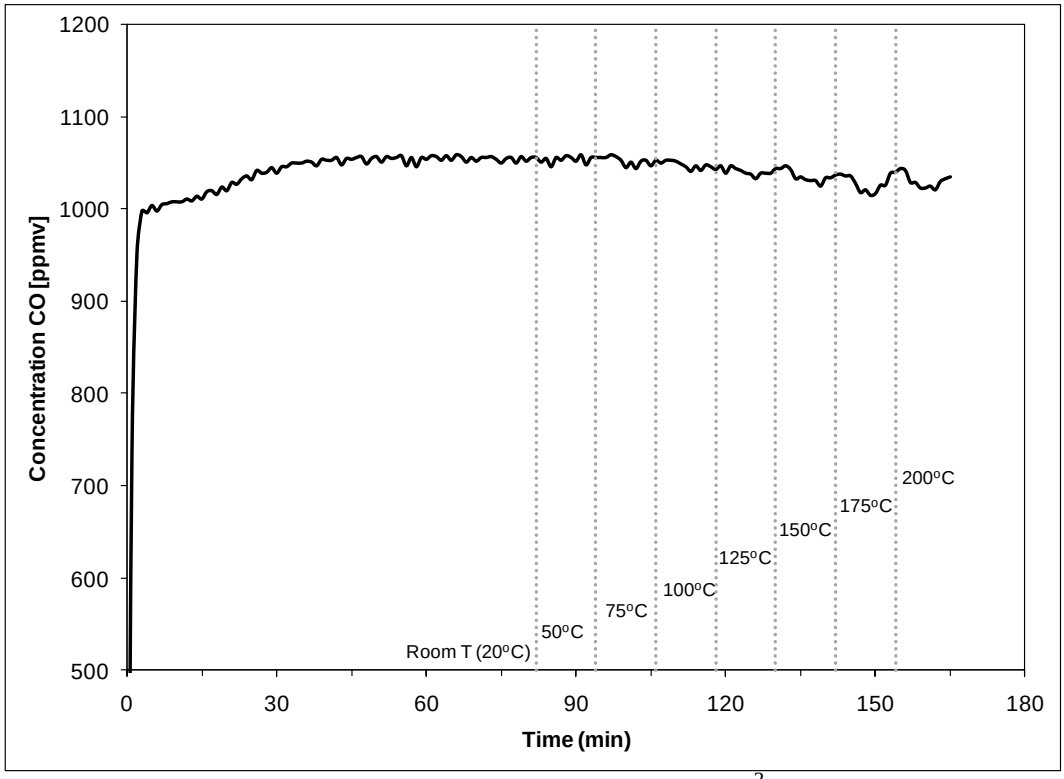

Figure 3.18 CO oxidation over a 1 wt% Au/0.1 mol% PO_4^{3-} -TiO_2 catalyst

3.3 Time on Stream Experiment

The experiment shown in Figures 3.19 and 3.20 was carried out at a constant temperature of 50°C over a period of 52 hours. A 0.8wt% Au/TiO_2 catalyst was used for the reaction. The gas flow rate for the experiment was 250 mL/min. The feed gas was a mixture of 268 ppm SO_2, 787.7 ppm CO and the balance of the gas He. Figure 3.19 shows that it took 1.13 hours to reach the maximum SO_2 concentration of 264 ppm during the experiment. This was also the time it took to reach steady state. Between point A and point B, the concentration of SO_2 decreases gradually and linearly. For the remainder of the experiment the SO_2 concentration decreases exponentially to almost 0 ppm.

Figure 3.20 shows that the CO concentration increases linearly throughout the experiment.

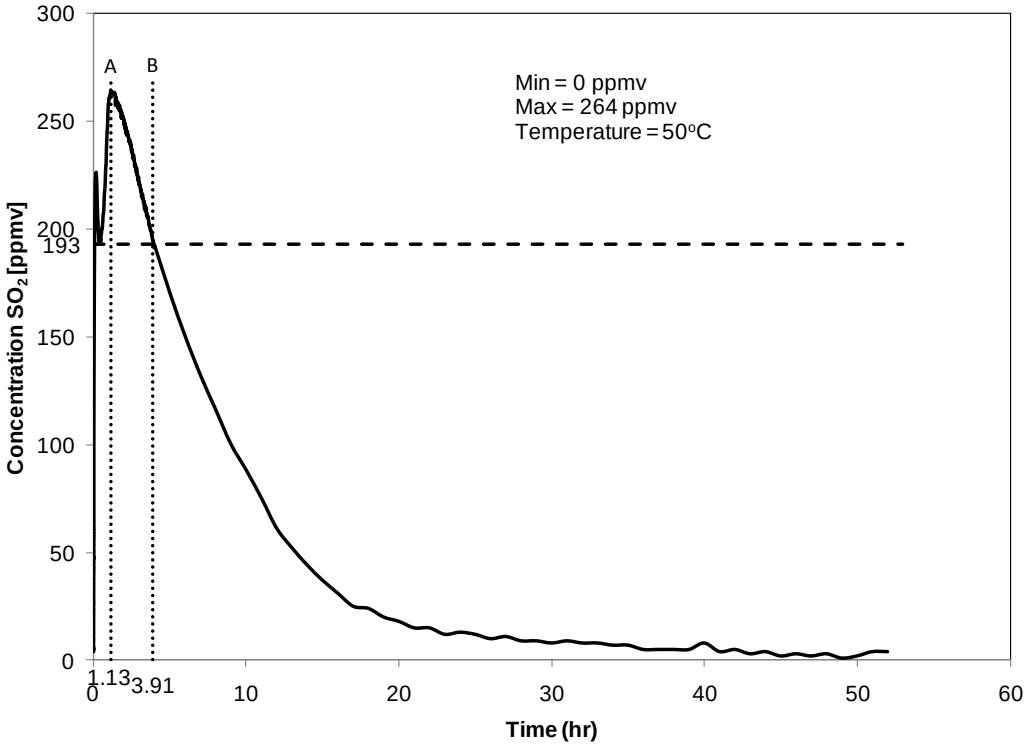

Figure 3.19 SO_2 Adsorption and reduction over a 0.8 wt% Au/TiO_2 catalyst at a constant temperature of 50°C

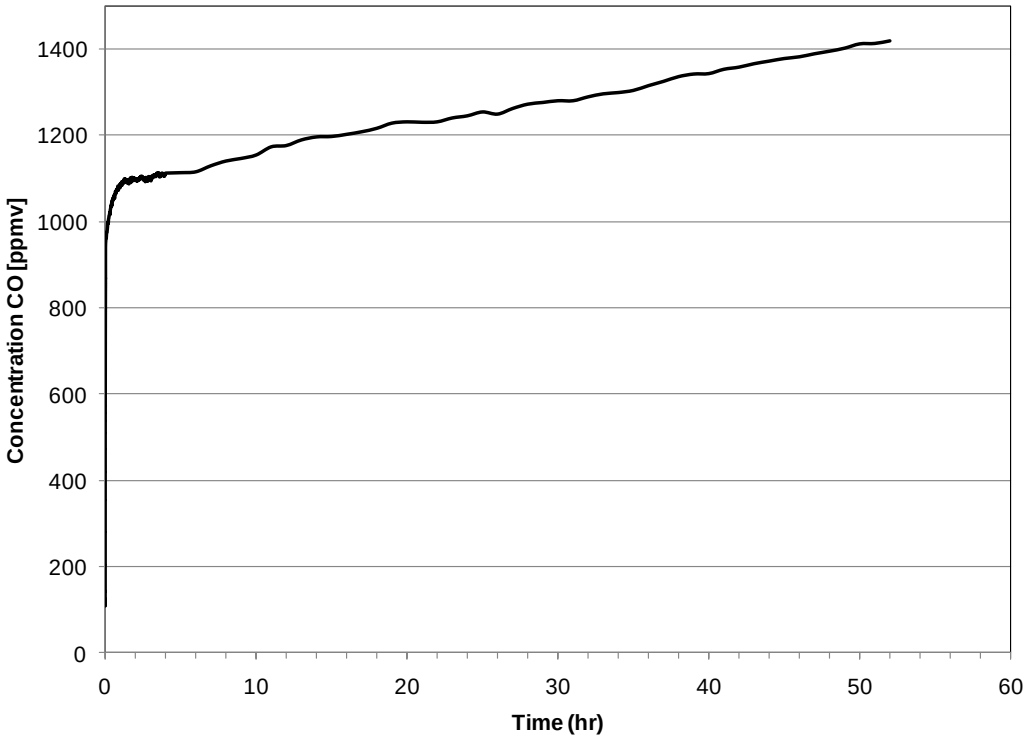

Figure 3.20 CO oxidation over a 0.8 wt% Au/TiO_2 catalyst at a constant temperature of 50°C

The next step was to determine how much SO_2 was adsorbed on each catalyst. This was done by integration of each of the peaks at each temperature. Various catalysts were then compared and in this way the most suitable catalyst and temperature for this application could be determined. A discussion of this analysis is presented in Chapter 4.

4 DISCUSSION: SO_2 ADSORPTION AND CO OXIDATION ON GOLD CATALYSTS

4.1 Background Information on the Catalysts

Brunauer Emmet and Teller (BET) surface area measurements on TiO_2 and the 0.4mol% PO_4^{3-}, SO_4^{2-}, Na^+, K^+ modified TiO_2 supports with 1wt% Au loading were done by Moma (2007). He found the BET surface area of TiO_2 to be 50 m^2/g. When the TiO_2 was modified with 0.4 mol% PO_4^{3-} (before gold loading), Moma (2007) found that the surface area of the catalyst did not change. Addition of 0.4 mol% SO_4^{2-} or Na^+ to the TiO_2 (before gold loading) decreased the surface area to 47 m^2/g, whilst addition of the K^+ to TiO_2 (before gold loading) increased the surface area to 53 m^2/g. In all cases, modifying the TiO_2 with different ions before gold deposition, did not increase or decrease the surface area significantly.

The TiO_2 prepared for this project to be used for comparison with the Au loaded catalysts (that is TiO_2 that was not modified by addition of ions and without gold loading) was calcined at 400°C. At this calcination temperature, Moma (2007) found that the BET surface area of TiO_2 was 87 m^2/g. This value is significantly higher than the surface area of the uncalcined TiO_2 that was used as a support for the gold catalysts.

The target gold loading for the gold catalysts with 0.4mol% modified TiO_2 supports was supposed to be 1wt%. However, Moma (2007) determined by fire assay gravimetry that the actual gold loadings were 0.57, 0.73, 0.69 and 0.70 wt% for the PO_4^{3-}, SO_4^{2-}, Na^+, K^+ modified TiO_2 supports respectively whereas the actual loading of the prepared 1% Au/TiO_2 with no promoter ions, calcined at 400°C was 1.06 wt%. Since the gold loading for each of the promoted catalysts was considerably less than 1 wt%, a gold catalyst with an unmodified TiO_2 support was prepared with a lower gold loading of 0.8 wt% for comparison. The time on stream analysis shown in Figures 3.19 and 3.20 were performed using this 0.8 wt%Au/TiO_2 catalyst.

The average size and size distribution of the catalyst particles was measured with high resolution transmission electron microscopy (HRTEM) by Moma (2007). The catalyst that he investigated was the Au catalyst with TiO_2 support with 0.4 mol% PO_4^{3-} incorporated into the TiO_2. He also investigated various other catalysts with different concentration of ions incorporated into the TiO_2 and catalysts where the Au/TiO_2 catalyst was first prepared and then modified by adding various ions at different concentrations. Those catalysts were not studied for this work. The results from the HRTEM showed that most of the Au particles had a size range of between 2 – 5 nm and that the size distributions in most cases were between 2 – 10 nm. Therefore, Moma (2007) concluded that the size of the gold particles was not influenced by the method in which different ions are incorporated into the catalyst, in other words whether the support was modified before gold was loaded or whether the gold catalyst was prepared and then ions were later incorporated into the catalyst.

4.2 Effect of Adding Gold to TiO_2

Figure 4.1 compares the number of moles of SO_2 per gram second adsorbed on the surface of titania (P25 Degussa) with the amount adsorbed on 0.6 and 0.8 weight percent gold catalysts supported on titania. The most obvious observation is the comparatively large amount of SO_2 adsorbed on the 0.6 wt% Au/TiO_2 at 50°C. This amount is almost 5 times and 1.6 times higher than the amount of SO_2 adsorbed on the TiO_2 and 0.8 wt% Au/TiO_2 respectively. Haruta *et al*. (1987) found that gold catalysts are low-temperature catalysts and that for the most favourable results for CO oxidation, low reaction temperatures were required.

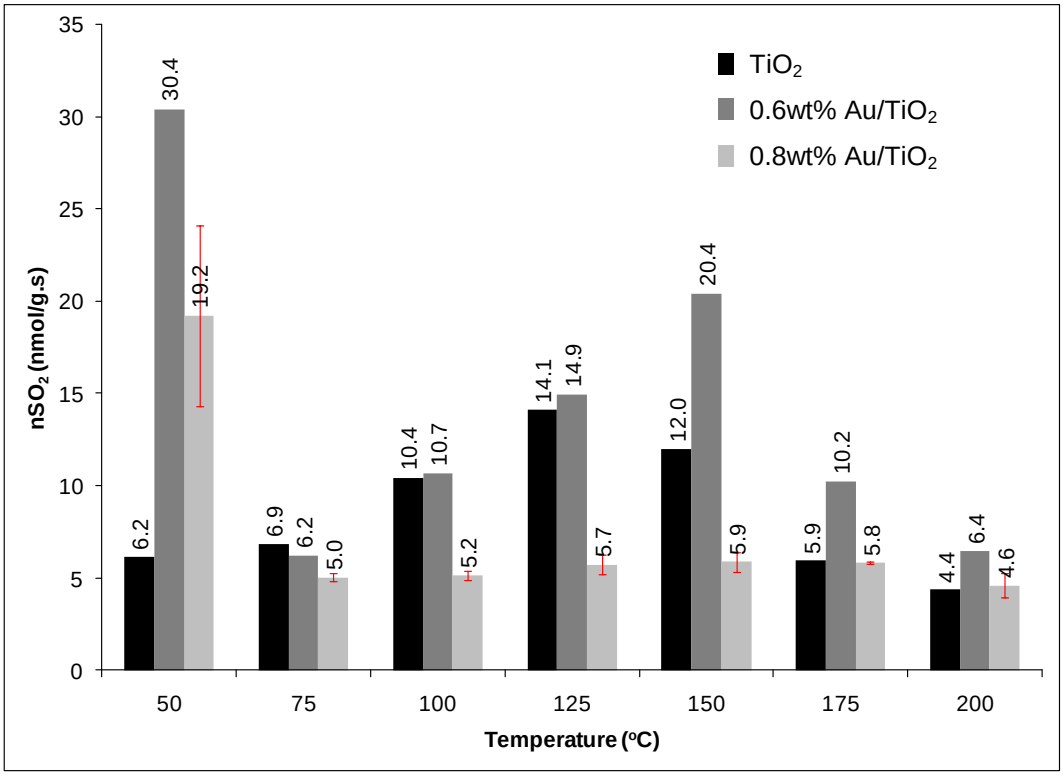

Figure 4.1 Amount of SO_2 desorbed from the surface of TiO_2 and gold-loaded catalysts

The only case where the titania showed a higher adsorption of SO_2 than the 0.6 wt% Au/TiO_2 was at 75°C and at this temperature the difference in amount adsorbed (per gram second) between the titania and the 0.6 wt% Au/TiO_2 was small. This confirms the conclusion of Rodriguez *et al*. (2002), namely that gold supported on titania is more active than either pure gold or pure titania. However, the concentration of gold loaded onto the catalyst is important for the catalyst activity too.

The 0.8 wt% Au/TiO_2 only showed one spike in number of moles of SO_2 adsorbed per gram second of catalyst and that was at 50°C. After that temperature, the amount of SO_2 adsorbed remained between 4.6 and 5.87 nmol/g.s at a temperature of 200°C and 150°C respectively. A possible explanation for this could be that the SO_2 is more likely to adsorb onto the catalyst at low temperatures when the gold loading is higher.

From 75°C to 125°C, the amount of SO_2 adsorbed on the titania and 0.6 wt% Au/TiO_2 was very similar. However, at 150°C, there was a spike in the amount of SO_2 adsorbed onto the 0.6 wt% Au/TiO_2 catalyst. The significance is that after 150°C less and less SO_2 adsorbs on the catalyst. At 175°C the amount of SO_2 adsorbed onto the 0.6 wt% Au/TiO_2 catalyst halved to 10.21 nmol/g.s and then decreased further at 200°C to 6.44 nmol/g.s. At low temperatures it is expected that more SO_2 will be adsorbed, and as the temperature increases, the amount adsorbed decreases. This explains the decrease in SO_2 adsorption peaks on the 0.6 wt% Au/TiO_2 catalyst from 150 to 200°C. This means that at temperatures above 150°C less SO_2 is desorbed from the catalyst surface suggesting that less SO_2 adsorbs on the catalyst surface at these temperatures.

The number of moles of SO_2 adsorbed onto the 0.6 wt% Au/TiO_2 was consistently higher than the SO_2 adsorbed onto the 0.8 wt% Au/TiO_2. This could be related to the size of the gold particles as Wolf and Schüth (2002) discovered that by increasing the gold loading in Au/TiO_2, the activity of the catalyst decreased and that was related to the size of the gold particles. It is known that for gold catalysts to be active for CO oxidation, the particle size of the gold must be sufficiently small. This result was confirmed by Moreau and Bond (2007) who found that when the gold loading was sufficiently low (1.9 wt %) and the temperature was low (-20°C), 100 percent conversion of CO could be achieved.

Another important result in comparing the TiO_2 with the two gold catalysts is that the amount of SO_2 desorbed from the surface of the TiO_2 remained comparatively high throughout the experiment. Chen *et al*. (1999) investigated the adsorption of SO_2 on titania. They found that total desorption of SO_2 occurred below 300°C. Another result from their work was that SO_2 "cannot form strongly adsorbed states" on TiO_2 and this is due to the SO_2 being converted into other species and those species readily desorb from the surface or that the adsorbed state of SO_2 simply desorbs from the surface. For this reason, TiO_2 is more resistant to sulphur poisoning than Al_2O_3. In other words not only is titania good for SO_2 adsorption it has also been shown that it is a suitable support for this application.

Rodriguez *et al.* (2002) found that only SO_4^{2-} was produced when SO_2 gas was passed over TiO_2 at a temperature of 300K. However, when gold was introduced into the catalyst, it was able to dissociate the SO_2 molecule and elemental sulphur was produced.

Therefore, the addition of gold to the catalyst could be important because it may be the gold that promotes the conversion of SO_2 to elemental sulphur while the TiO_2 allows for the adsorption of the SO_2 on the surface and for the reaction to take place without the catalyst being poisoned by the sulphur.

Error bars are shown in red on Figure 4.1 for the 0.8wt% Au/TiO_2 catalyst. This experiment was repeated twice. The error bar shows that at 50°C, where the number of moles of SO_2 that was adsorbed onto the surface of the catalyst was large the potential for error was large. At all the other temperatures, where the number of moles adsorbed was lower, the error was lower.

4.3 Effect of Integrating Ions into TiO_2 Support

4.3.1 Na^+ and K^+ ions

Figure 4.2 shows that by adding sodium and potassium ions into the TiO_2 before the addition of the Au, the amount of SO_2 adsorption is very similar to the gold catalyst supported on TiO_2. At 100 and 125°C slightly larger differences in SO_2 adsorption are seen where the modified supports outperform the gold catalyst prepared with unmodified TiO_2. At 150°C the 0.6 wt% Au/TiO_2 catalyst outperforms the 1 wt%Au/0.1 mol%K^+-TiO_2 and 1 wt%Au/0.1 mol%Na^+-TiO_2 catalysts. In all three catalysts, a similar trend in adsorption is seen at the various temperature steps.

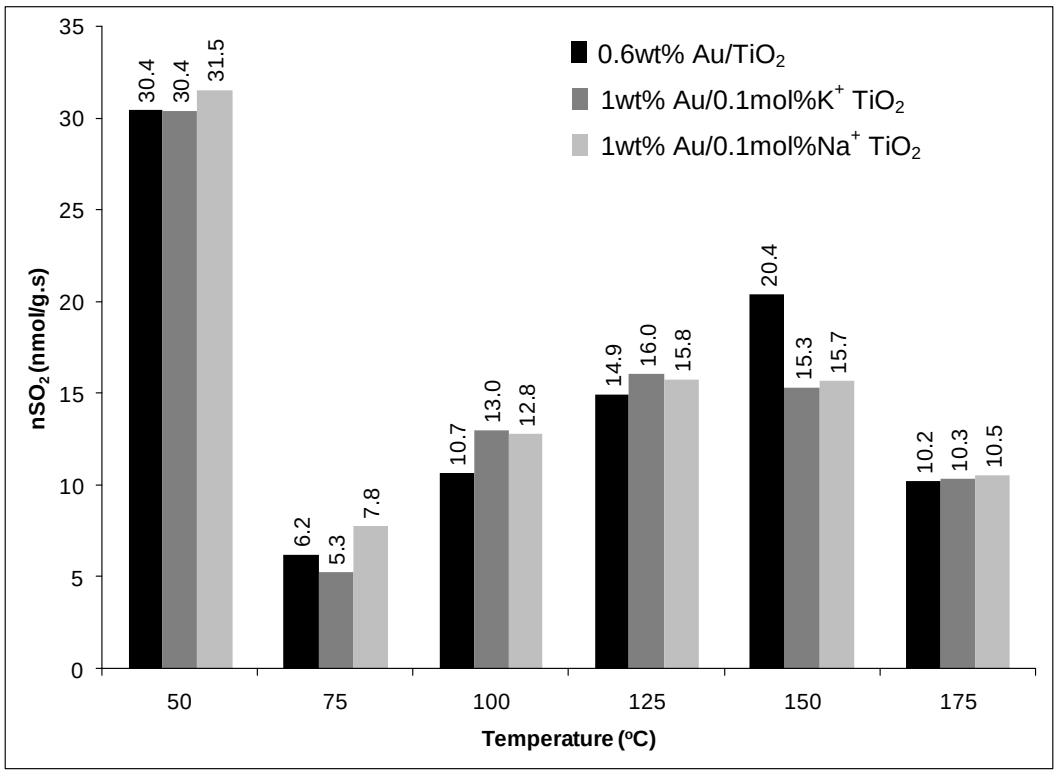

Figure 4.2 Addition of positive ions into 1 wt%Au/TiO_2 catalyst

Figure 4.3 shows that the modified titania with the lower concentration of Na^+ always has more SO_2 adsorbed onto the surface than the catalyst with 0.4 mol% Na^+ added to the TiO_2 support.

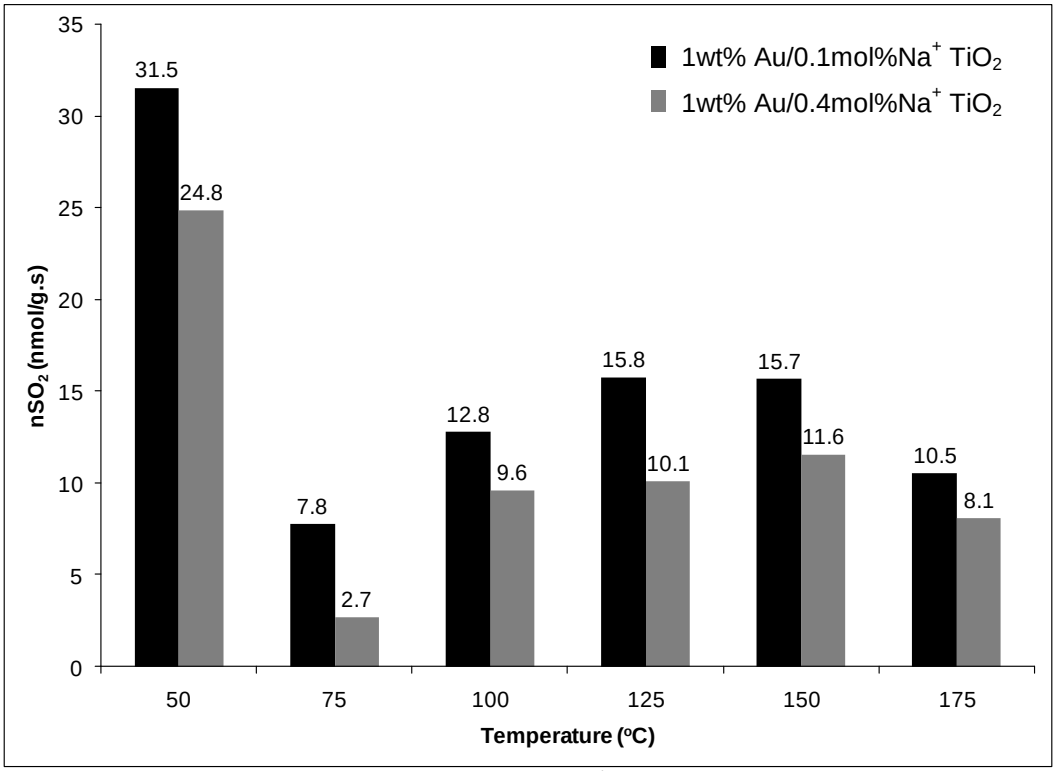

Figure 4.3 Two different concentrations of Na^+ ions added to Au/TiO_2 catalyst

4.3.2 SO_4^{2-} ions

The most noticeable feature about Figure 4.4 is that more SO_2 was adsorbed onto the 0.6 wt%Au/TiO_2 catalyst than either of the catalysts where sulphate ions were added to the titania.

An important observation in Figure 4.4 is that for all temperatures except 125 and 150°C, the amount of SO_2 that was adsorbed on the surface of the SO_4^{2-} modified titania was very similar. This could indicate that the concentration of sulphate ions introduced into the titania support is immaterial for this particular reaction. The sulphate ions appear to block the active sites on the titania where the SO_2 would usually be adsorbed.

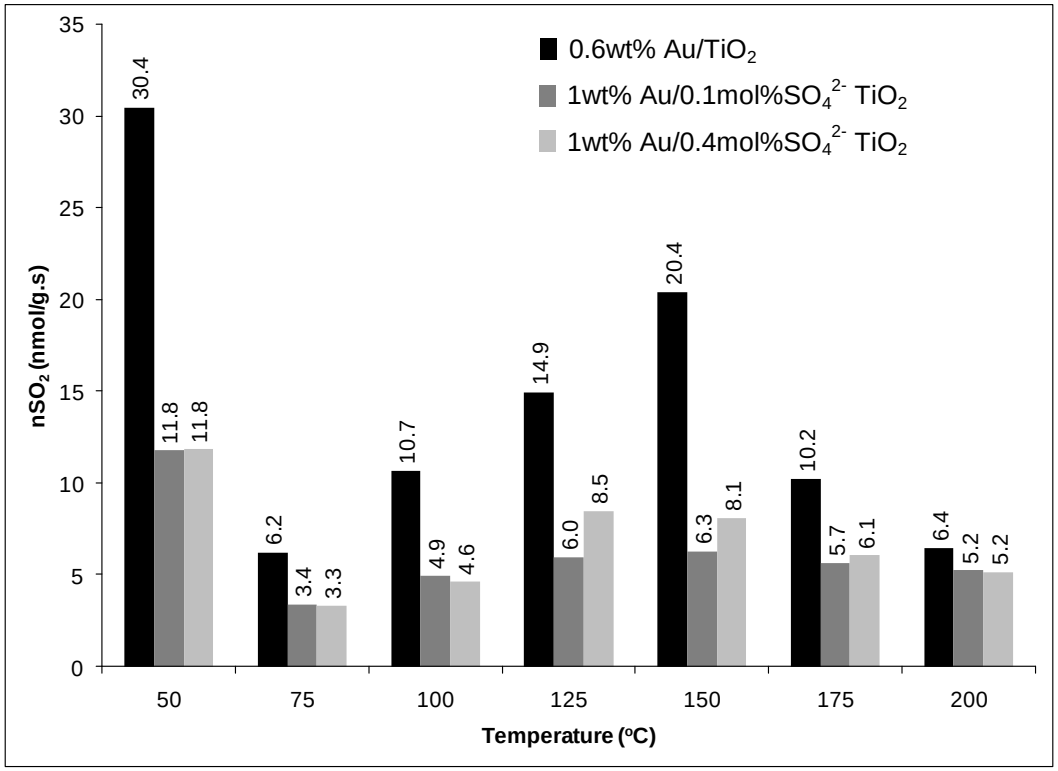

Figure 4.4 Comparison of gold catalyst with and without sulphate ions of varying concentrations

Although Moma *et al*. (2007) and Mohapatra *et al*. (2007) found that the addition of sulphate ions improved the activity of the gold catalyst for CO oxidation, the reaction that they studied was CO oxidation.

For the SO_2 reduction reaction by CO, it seems that adding sulphate into the Au/TiO_2 catalyst reduces the amount of SO_2 that can adsorb onto the surface of the catalyst. The other important discovery is that for this reaction the amount of SO_4^{2-} introduced into the catalyst has little effect on the amount of SO_2 adsorbed onto the surface.

4.3.3 PO_4^{3-} ions

Figure 4.5 compares the 0.6 wt%Au/TiO_2 catalyst and the 1 wt%Au/TiO_2 catalyst with 0.1 mol% of PO_4^{3-} added to the support. An interesting observation from this graph is that the two catalysts display a similar trend even though more SO_2 is

adsorbed on the 0.6 wt%Au/TiO_2 catalyst at each temperature step (except at 75°C where the adsorption of SO_2 is almost the same).

This result is not surprising as Ma *et al*. (2007) have reported that an Au/TiO_2 catalyst always outperforms an Au/PO_4^{3-} - TiO_2 catalyst when pre-treated at 200°C for the CO oxidation reaction. Ma *et al*. (2007) were able to enhance this modified support by pre-treatment at 500°C and also with washing procedures. The result for the gold catalyst and the gold catalyst with the enhanced phosphate support look similar. This is important because it indicates that the addition of phosphate, maintains activity, almost to levels of the unmodified gold catalyst. Ma *et al*. (2007) produced TEM images of Au/TiO_2 catalysts and Au/PO_4^{3-} - TiO_2 catalysts pre-treated at 500°C. From these images, they found that the catalysts with modified supports had gold particles that had sizes in the range of 3-10 nm. The unmodified Au/TiO_2 catalysts that were pre-treated at 500°C had most of the gold particle sizes in the range of 5-30 nm. They concluded that gold catalysts with modified titania supports, pre-treated at 500°C remained active at room temperature because the gold particles were stabilized from sintering.

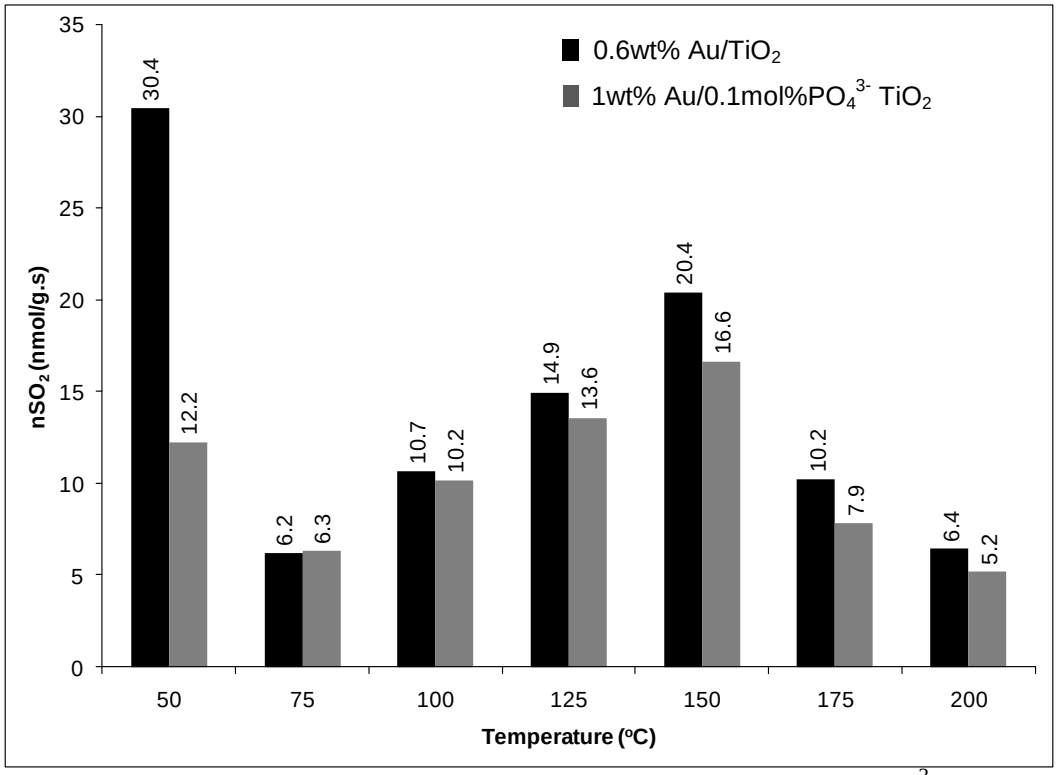

Figure 4.5 Comparison of 0.6wt%Au/TiO_2 with 1wt%Au/0.1mol%$PO_4^{3-}$$TiO_2$

4.4 Time on Stream Experiment and the "Temperature Stepping" Method

Figure 3.19 showed that after more than 1 hour of the experiment, the SO_2 concentration reached a maximum value of 264 ppmv (point A). After this point, the SO_2 concentration continued to decrease throughout the reaction. From the start of the reaction, it seems as though the SO_2 gets adsorbed onto the 0.8 wt% Au/TiO_2 catalyst. From point A to point B, desorption takes place where the concentration decreases back to the level that it was at the start. Then, the SO_2 concentration decreases to almost zero by the end of the reaction. From point B onwards, the SO_2 reduction reaction takes place and almost all the SO_2 reduces into either S_2 gas or elemental sulphur (that was not determined in this experiment).

Figure 4.6 shows that almost 100 percent conversion of SO_2 was achieved during the time on stream experiment after about 50 hours of reaction time.

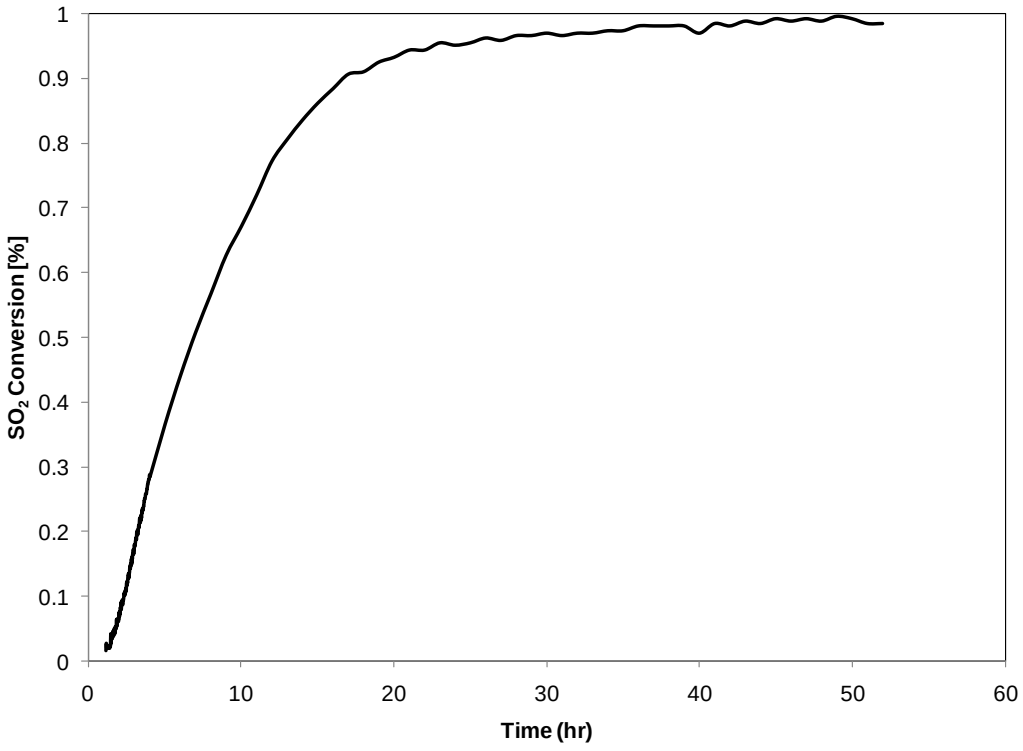

Figure 4.6 Conversion of SO_2 during Time on Stream Experiment

In Chapter 1, Section 1.4.5 various reaction mechanisms were discussed. Haruta (1997) suggested that for CO oxidation, the following reaction mechanism was followed:

- CO adsorbs on the surface and boundary interface of the Au,
- Dissociative adsorption of O_2 occurs at the boundary interface between the Au and TiO_2 and then,
- CO reacts on the surface of the Au before reacting on the surface of the metal oxide support.

Ruth *et al*. (2000) investigated the effect that SO_2 had on CO oxidation. They considered platinum (Pt) and gold catalysts. Their results showed that the Au/TiO_2 catalyst was deactivated more by the SO_2 than the Pt/TiO_2 catalyst. From this result they considered that the reaction mechanism for CO oxidation is different for each of the catalysts. For the Pt catalyst, Ruth *et al*. (2000) note that CO oxidation occurs on the PtO_x surface whereas in the case of the Au catalyst, the reaction takes place at the interface between that Au and the TiO_2 support. This is the reaction mechanism proposed by Haruta (1997). Furthermore, Ruth *et al*. (2000) state that SO_2 has a stronger interaction with oxide surfaces than with the surface of the metal. They propose that the SO_2 in fact blocks the perimeter sites by being adsorbed at the interface between the Au and TiO_2.

This explains the result seen in Figure 3.19. From the start of the reaction until point B, the SO_2 is adsorbed at the interface between the Au and TiO_2. The active sites for CO to be oxidised become blocked. However, this does not explain why the SO_2 appears to react after point B.

Rodriguez *et al*. (2002) found that Au/TiO_2 was effective for adsorbing the SO_2 and breaking the S-O bond. Perhaps this is what happens after point B. After the SO_2 has been adsorbed at the interface of the Au and TiO_2, the SO_2 molecule

dissociates and the perimeter sites between the Au and the TiO_2 are no longer blocked and this allows the reaction to take place.

From this reaction it would appear that this catalyst is suitable for complete reduction of SO_2 at 50°C. Perhaps, the time taken for the SO_2 to completely react could be reduced if a different catalyst was used. This is an important result because although there was no means to determine what was produced during the reaction it answered the question about whether gold catalysts could be used in the reduction of SO_2 by CO. Now that it is known that gold catalysts are suitable for this reaction, the next step would be to confirm what products are formed and then to optimise the catalyst (i.e., what gold loading should be used, should the gold catalyst be enhanced or modified with anions or cations, are any pre-treatment methods necessary) and the process (what temperature should be used, what is the maximum conversion that can be achieved, can the time taken for complete reaction be optimised) with the guidelines given from the work completed in this research project.

The "temperature stepping" method was a quick method to determine whether SO_2 would adsorb reversibly onto the surface of the catalyst. The experiments showed that SO_2 did in fact adsorb onto the surface at various temperatures. From those experiments, the amount of SO_2 that was adsorbed could be calculated. Comparisons could then be made between different catalysts, quantifying the amount of SO_2 that gets adsorbed onto the catalyst. By running the experiment over an extended period it confirmed that an adsorption peak would in fact form after some time and that there was only one adsorption peak and thereafter SO_2 reduction occurs and CO oxidation decreases suggesting irreversible adsorption of SO_2 reduction products on CO oxidation sites. The "temperature step" method did not show whether the reaction would occur but merely whether the SO_2 would be adsorbed onto the surface of the catalyst.

The results in Chapter 3 show that for the 0.6wt%Au/TiO_2, 0.8 wt%Au/TiO_2, 1 wt%Au/0.1 mol%SO_4^{2-}, 1 wt%Au/0.4 mol%Na^+-TiO_2, 1 wt%Au/0.1 mol%Na^+-TiO_2 and the 1 wt%Au/0.1 mol%K^+-TiO_2 catalysts, the baseline concentration of

SO_2 was not reached even after the gas had been passing over the catalyst for an extended period of time. Also, the peak at 75°C was always smaller than the peak at 50°C.

5 RECOMMENDATIONS AND CONCLUSIONS

The literature shows that gold catalysts prepared using methods that yield small gold particles at low gold loading can be effective for complete oxidation of CO to CO_2. This is dependent on what metal oxide support is used for the catalyst and also on the reaction temperature.

The reaction that was studied for this research was the reduction of SO_2 by CO. These are species commonly found in the flue gas of many coal burning industries such as power plants and aluminium smelters. The main objective of this research project was to determine whether a gold catalyst supported on titania would be suitable for the catalytic decomposition of SO_2.

The experimental procedure consisted of a number of screening tests at various temperatures with different gold catalysts (i.e., different gold loadings and the addition of promoter ions to the titania support) to find out firstly whether SO_2 would be adsorbed onto the catalyst and secondly, which gold catalyst would be optimal for this application.

An interesting finding of this work was that TiO_2 without gold was effective at adsorbing SO_2, although it was not as effective as the gold catalysts supported on titania. Therefore, it may be worth investigating the effect of incorporating Na^+, K^+ and PO_4^{3-} ions into the TiO_2 without gold and to compare the activity with the gold loaded catalysts.

From this work, it was found that a gold catalyst is in fact suitable for this application. The following catalysts all show significant SO_2 adsorption at 75°C:

- 0.6 wt% Au/TiO_2,
- 0.8 wt% Au/TiO_2
- 1 wt%Au/0.1 mol%SO_4^{2-}/TiO_2,

- 1 wt%Au/0.4 mol%Na^+/TiO_2,
- 1 wt%Au/0.1 mol%Na^+/TiO_2,and
- 1 wt%Au/0.1 mol%K^+/TiO_2

This is evident because none of these catalysts reached the baseline concentration before the first temperature step and the second peak is smaller than the first.

The results from the time on stream experiment show that the 0.8 wt% Au/TiO_2 is catalytically active at 50°C for SO_2 decomposition.

There was no change in the CO concentration during the screening tests where unmodified gold catalysts and titania were used. However when the titania supports were modified by adding different ions, CO adsorption peaks similar to the SO_2 adsorption peaks were observed. When the experiment was run using the 0.8wt% Au/TiO_2 catalyst for an extended period of time, the SO_2 was reduced and all the SO_2 was consumed during the reaction. The CO concentration increased during the reaction. From these results it can be deduced that SO_2 reduction occurs over this catalyst and CO oxidation decreases with time suggesting that irreversible adsorption of SO_2 reduction products occurs on CO oxidation sites.

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APPENDIX A: INTEGRATION OF SO_2 ADSORPTION PEAKS

Figure A1 is an enlarged portion of Figure 3.3. It shows only the adsorption peak of the SO_2 at 50°C for the 0.8 wt% Au/TiO_2 catalyst.

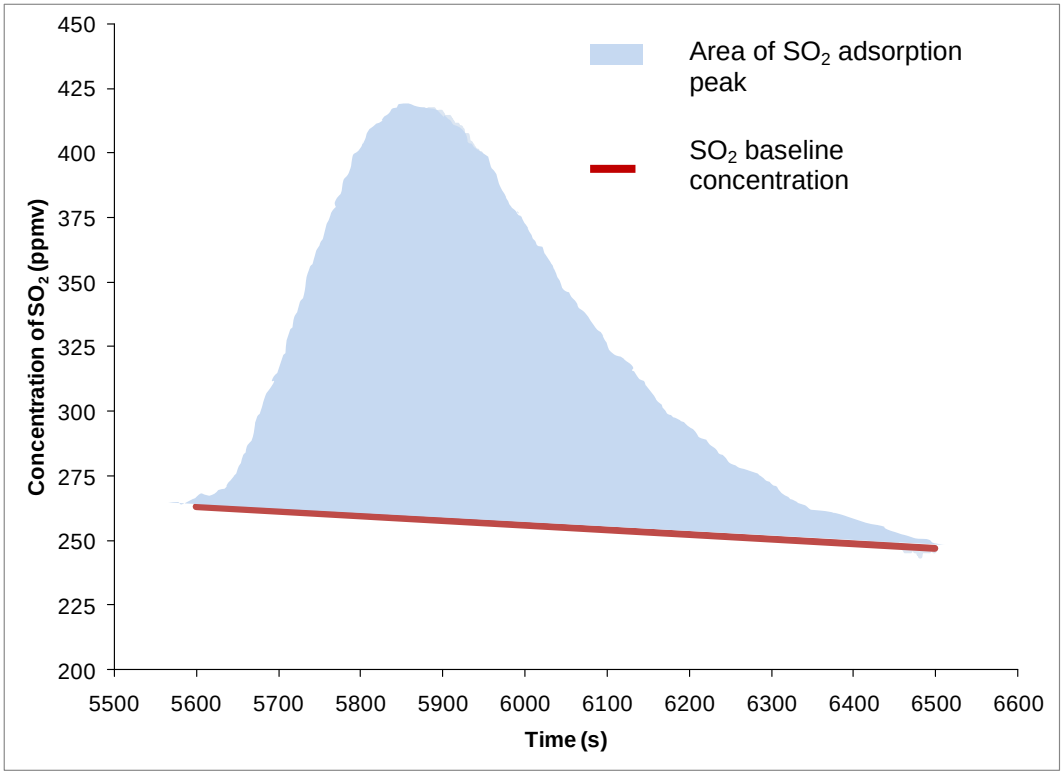

Figure A1 SO_2 adsorption peak on 0.8 wt% Au/TiO_2 at 50°C

The blue shaded area is the area that is integrated. The red line represents the baseline concentration of the SO_2. Each measurement that was recorded by the flue gas analyser is shown on the graph.

Table A1 is a selected portion of the data, the first 5 readings, the middle 5 readings and the last 5 readings from the flue gas analyser are shown. Since the analyser recorded the data each second, there was too much data to be shown in this report (900 lines of data for one peak). The analyser had been recording the SO_2 concentration for some time before the temperature was stepped to 50°C therefore the time does not start from 0s.

Table A1 Sample data from flue gas analyser

Time (s)	Concentration SO_2 (ppmv)	Temperature (°C)
5600	263	20.4
5601	263	20.3
5602	264	20.3
5603	264	20.3
5604	264	20.3
.	.	.
.	.	.
.	.	.
6050	344	48.8
6051	343	49.1
6052	343	49.1
6053	341	49.3
6054	341	49.3
.	.	.
.	.	.
.	.	.
6496	247	62.2
6497	247	62.2
6498	246	62.2
6499	246	62.1
6500	247	62.1

From the data in Table A1 the following values could be calculated: the baseline concentration of SO_2, the temperature in Kelvin and the number of moles of SO_2 in nmol. Equation 2.1 is the equation of the straight line. To calculate the gradient, the following equation was used:

$$\frac{\Delta y}{\Delta x} \quad \text{..... .....} \quad \text{(A1)}$$

Where Δy is the change in concentration of SO_2 between the last reading and the first and Δx is the corresponding time values in seconds. So for the SO_2 adsorption peak shown in Figure A1, the gradient is:

$$\frac{247 - 263}{6500 - 5600} = -0.0178 \text{ s}$$

The y-intercept is calculated by substituting one point on the graph back into Equation 2.1. The first point (5600, 263) was used to give a y-intercept of:

$$263 - (-0.0178 \times 5600) = 363 \text{ ppm}$$

Therefore, the equation of the straight line is:

$$\text{Baseline Concentration} = -0.0178t + 363 \quad \text{.....(A2)}$$

The time that is inputted into the equation must be in seconds.

To convert the temperature in °C into K, the following conversion formula was used:

$$T[K] = T[°C] + 273.15 \quad \text{.....(A3)}$$

Equation 2.2 was used to calculate the number of moles of SO_2. The pressure in Johannesburg was taken as 84600 Pa for all experiments. The value used for the universal gas constant was 8.314 J/molK. For this experiment, the volumetric flow rate was 0.000242599 m^3/min.

An example calculation is presented below for the reading where the time is equal to 6052s.The values given above were substituted into Equation 2.2.

$$nSO_2 = \left[\left(\frac{343 - (-0.0178 \times 6052 + 363)}{1 \times 10^6}\right) \times \left(\frac{84600 \times 0.000242599}{8.314 \times (49.1 + 273.15)}\right)\right] \times \frac{6052 - 6051}{60}$$

Therefore, the number of moles of SO_2 at time 6052 s is 1.12^{-8} mol and converting this into nmol gives 11.2 nmol.

This calculation was done for each reading. The number of moles of all the readings was summed up to give the total number of moles and this total was divided by the time taken to form the peak. For this peak, the total number of moles was 7.19 μmol. The time taken to form the peak was 900 seconds. Therefore the number of moles per second was 0.00799 μmol/s or 7.99 nmol/s. At the start and end of the peak, it is possible for the baseline concentration to be above the measured concentration. In that case, the calculated number of moles is a negative number. All those values that were negative were excluded from the calculation.

Then for comparative purposes the number of moles was divided by the mass of each catalyst that was used. The mass of the 0.8 wt%Au/TiO_2 catalyst was 0.416 g and so the number of moles per gram second of catalyst for this experiment was 19.2.