

Gold Catalysts for Oxidation and Hydrogenation

Reactions

Thesis submitted in accordance with the requirements of the

University of Cardiff for the degree of Doctor of Philosophy by

Matthew Scott Hall

September 2004

UMI Number: U584673

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U584673 Published by ProQuest LLC 2013. Copyright in the Dissertation held by the Author. Microform Edition © ProQuest LLC. All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code.



ProQuest LLC 789 East Eisenhower Parkway P.O. Box 1346 Ann Arbor, MI 48106-1346

Acknowledgements

First and foremost thanks should go to my parents. Without their continued support and motivation none of this would have ever been possible.

A great many thanks also need to go to Dr Albert Carley, Dr Phil Landon and Professor Graham Hutchings, not only for the opportunity to pursue this PhD but also for all their help and guidance throughout the course of these past four years. Special thanks must also go to Dr David Morgan for stopping me dropping the ball at the last minute.

I want to thank all the people I've worked with since starting in the lab, especially Dave, Paul, Simon and Bob for all the banter and good times that made the time seem to go so much faster that it really did.

I also want to thank all of my other friends. If I listed all of your names I think the acknowledgements would be longer than the actual thesis. Special mention however should be made of Erin, Kalyn, and Young. You three were always around to lift my sprits when I needed it the most.

Thank you.

<u>Index</u>

Declaration	i
Acknowledgments	ii
Index	iii
Abstract	viii

<u>Chapter 1</u>

1.1 Background	1
<u>1.2 What is catalysis</u>	1
1.2.1 Factors affecting activity	2
1.2.2 Adsorption	2
1.2.3 Temperature	4
1.2.4 Reactant Factors	4
1.2.5 Surface Area	5
1.3 A Brief History of Catalysis	6
1.4 Background to Gold Catalysis for Carbon Monoxide Oxidation	8
1.4.1 The Activity of Gold	8
1.4.2 Gold Catalysis	10
1.4.2.1 Early Work	10
1.4.2.2 Recent work	11
1.5 Effect of preparation on catalyst activity	11
<u>1.6 – Effect of support</u>	12
<u>1.7 – The effect of particle size</u>	15
<u>1.8 – The Affect of Calcination</u>	15
<u>1.9 – Kinetics and mechanism</u>	16
1.9.1 – The Bond and Thompson model	18
1.9.2 - The Kung Model	21
1.10 Conclusions	22
1.11 References	23
1.12 Bibliography	26

<u>Chapter 2</u>

2.1 Introduction	27
2.2 The Photoelectric Effect	27
2.3 Koopmans' theory	28
2.4 The Fate of Core Holes	29
2.5 Final State Effects	31
2.5.1 Relaxation Shift	31
2.5.2 Shake Up and Shake Off	31
2.5.3 Spin Orbit Splitting	32
2.5.4 Multiplet Splitting	33
2.5.5 Asymmetric Core Level Peaks	34
2.6 The Chemical shift	34
2.7 Surface Sensitivity	36
2.8 The Photoionisation Cross-section	39
2.9 The Reference Level	40
2.10 Line Broadening Effects	41
2.10.1 The Natural Width of the Core Level	41
2.10.2 Instrumental Factors	42
2.11 Spectrum Processing	43
2.11.1 Spike Removal	43
2.11.2 Background Removal	43
2.11.3 Difference Spectra	44
2.11.3.1 Alignment	44
2.11.3.2 Normalisation	45
2.11.4 Curve fitting	46
2.11.5 Peak Area Measurement	47
2.12 Equipment	48
2.12.1 Features Common to all XPS Spectrometers	48
2.12.2 UHV Conditions	49
2.12.3 X-Rays	51
2.12.4 Electron Energy Analyser	53
2.12.5 Electron Detection	56
<u>2.13 ESCA 5</u>	55

2.13.1 Sample Handling	55
2.13.2 High Pressure Cell	57
2.13.3 Gas Handling Line	59
2.14 ESCALab 220	60
2.14.1 Fast Entry Lock	60
<u>2.15 ESCA 300</u>	61
2.15.1 Rotating Anode	61
2.15.2 Monochromator	61
2.16 References	62
2.17 Bibliography	63

Chapter 3

3.1 Introduction	64
3.2 Preparation Methods	64
3.2.1 Impregnation	64
3.2.2 Ion Exchange	65
3.2.3 Co-precipitation	66
3.2.4 Deposition-Precipitation	67
3.2.5 Vapor-Phase Deposition and Grafting	68
3.2.6 Catalyst Aging	69
3.3 Catalyst preparation	69
3.3.1 Au/Fe ₂ O ₃	69
3.3.1.1 Method 1- Precipitation at increasing pH	70
3.3.1.2 Method 2- Precipitation at constant pH	71
3.3.1.3 Heat Treatment of Catalysts	71
3.3.1.4 Method 1- Fan Assisted	72
3.3.1.5 Method 2 – Static Atmosphere	72
3.3.2 - Au/ZnO	72
<u>3.4 Experimental</u>	72
3.4.1 CO Oxidation	72
3.4.2 Hydrogenation Reaction Conditions	73
3.5 Characterisation	75
3.5.1 XPS	75

3.5.2 XANES	75
3.5.3 BET	76
3.5.4 TEM	77
3.6 References	78
3.7 Bibliography	79

<u>Chapter 4</u>

4.1 Background	80
4.2 Experimental	81
4.2.1 Spectroscopy	81
4.2.1.1 XPS	81
4.2.1.2 XANES	81
4.2.1.3 TEM	82
4.2.1.4 BET	82
4.3 Results	82
4.4 Discussion	98
4.4.1 Effect of pH	98
4.4.2 The Model of the Active Site	99
4.4.3 Effect of Heat Treatment	101
4.4.4 Origin of Binding Energy Shifts	102
4.4.5 Effect of Support	104
4.5 Conclusions	105
4.6 References	106

<u>Chapter 5</u>

5.1 Introduction	108
5.2 Experimental	111
5.2.1 Spectroscopy	111
5.2.1.1 XPS	111
5.3 Results	111
5.3.1 Activity of Iron oxide supported gold catalysts	111
5.3.2 Effect of Heat Treatment	113
5.3.3 Effect of pre-reduction on catalyst selectivity and	

conversion	120
7.2.4 XPS Characterization	123
5.5 Discussion	125
5.5 Conclusion	127
5.5 References	128

<u>Chapter 6</u>

6.1 Introduction	129
<u>6.2 Experimental</u>	131
6.2.1 Polycrystalline Gold Foil – Active Site Modelling	131
6.2.2 Model iron oxide support	132
6.2.3 Oxygen adsorption on bulk gold	133
6.3 Results	134
6.3.1 Polycrystalline Gold Foil – Active Site Modelling	134
6.3.2 Model Iron oxide films	136
6.2.3 Oxygen adsorption on bulk gold	139
6.3 Discussion	140
6.3.1 Polycrystalline Gold Foil – Au Particle Modelling	140
6.3.2 Model Iron Oxide films	143
6.3.2 Oxygen adsorption on bulk gold	144
6.5 Conclusions	144
6.6 References	145

<u>Chapter 7</u>

7.1 Conclusions	147
7.1.1 General Conclusions	147
7.1.2 CO Oxidation Conclusions	147
7.1.3 Crotonaldehyde Hydrogenation Conclusions	148
7.1.4 Model Catalyst Conclusions	149
7.2 Future Work	149
7.2.1 CO Oxidation	149
7.2.2 Crotonaldehyde Hydrogenation	150
7.3.1 Model Catalyst Studies	150

Abstract

Iron oxide supported gold catalysts were tested for the room temperature oxidation of carbon monoxide. The effect of heat treatment on the activity of the catalysts was investigated; the catalysts being heated to 75, 120, 200, 300 and 400°C. The most active catalysts were obtained by using a calcination temperature of 120°C.

Gold catalysts supported on zinc oxide were also tested for activity in the oxidation of carbon monoxide at room temperature. These catalysts were found to be less active than the Au/Fe_2O_3 catalysts. The effect of heat treatment was also investigated, and the uncalcined catalysts were found to be the most active.

Characterisation of both types of catalyst by XPS revealed a clear difference between catalysts of high and low conversion. Further investigation of the catalysts by XANES, TEM, and the XPS of gold colloids revealed that this difference was due to a change in the ratio of metallic and ionic gold, with the former being more abundant in catalysts with lower activities. The XANES analysis revealed the ionic gold to be in the form of Au¹. XPS analysis of the samples also revealed the presence of a surface hydroxyl species in the catalysts with high activity; conistant with the Bond-Thompson mechanistic model for CO oxidation

The iron oxide supported gold catalysts were also used in the hydrogenation of crotonaldehyde. The catalysts were tested for selectivity towards crotyl alcohol and total conversion at a variety of different heat treatments and reaction temperatures, and the highest conversions were obtained at a reaction temperature of 150°C. The best overall conversions were obtained with catalysts that had been heated at 75°C. The highest selectivity towards crotyl alcohol was obtained with catalysts which were calcined at 300°C.

The affect of reduction on the activity of the catalysts for crotonaldehyde hydrogenation was also explored. It was found that catalysts that were not reduced prior to reaction had a

higher activity and were less prone to deactivation during the reaction. The correlation between the oxidation state of the gold and the activity of the catalyst for the hydrogenation reaction was very similar to that found in the carbon monoxide oxidation catalysts.

"High pressure" XPS studies were carried out on polycrystalline gold foil, an iron oxide film, and a thick gold film to test the contributions that part makes to the activity iron oxide supported gold catalysts. Both the gold foil and the iron oxide and thick gold films proved to be unreactive towards carbon monoxide and oxygen.

Chapter 1: Catalysis

1.1 Background

90% of chemical manufacturing uses catalysis, making the field of central importance to both research and industry. Until recently, the majority of commercially viable catalysts were discovered and developed by empirical methods, and much more remains to be learned about the principles of catalysis and the forms which catalysts can take. Recent advances in the field of catalyst research have made possible the rational design of certain types of catalysts.

1.2 What is catalysis?

Catalysis can be broadly and simply defined as a process during which a reaction occurs more readily than the non-catalysed reaction, the reaction being accelerated by the presence of a catalyst, although the equilibrium of the reaction remains the same. There are two main types of catalytic reaction, heterogeneous and homogeneous. In homogeneous catalysis, both the catalyst and the reactants are in the same phase, they are either both solids, liquids or gases. Heterogeneous catalytic reactions are those in which the catalyst is in a different phase to the reactants. Commonly the catalyst occupies the solid phase and the reactants are either gases, as in the case of the work presented here, or liquids.

Regardless of the reaction being considered, the process of catalysis can be split up into several common stages. The first step in the action of a catalyst is the transport of the reactant molecules to the surface of the catalyst. During this step factors that play a part in determining the activity of a catalyst are limited to mass transport factors. The flow rate of the gases used in the reaction determines the length of time that the reactant gases are in contact with the catalyst. If the catalyst in question is porous, and the reaction capable of taking place on the interior surface of the catalyst then the size of the reactants and the size of the pores plays a part as well. If the reactants are much bigger than the pores then the catalyst might have a poor activity since very few reactants have access to the active sites.

The next stage in the action of a catalyst is adsorption, where the reactants are brought into contact with the surface of the catalyst. The adsorption of the reactants on the catalyst surface is a necessary part of the cycle because it is being bonded to the catalyst surface that allows for an alternative reaction pathway to become available. For diatomic molecules, there are two types of adsorption, associative and dissociative. During associative adsorption the molecule is adsorbed on the surface as a complete unit. In dissociative adsorption the molecule adsorbs as its component atoms. The strength of the diatomic bond determines whether the molecule dissociates on adsorption to the catalyst surface.

Depending on whether the reaction requires all the reactants to be adsorbed or not, and whether the reactants adsorb in a position to react, a phase of surface migration may take place as the reactants move across the surface into a position where they can react. This step is dependent on the energy available to the adsorbed species. The more energy it has the further it can move.

The reaction at the surface of the catalyst is the next stage in the process, and is often the rate determining step in the reaction. Depending on the complexity of the reaction there may be more than one intermediate involved in the reaction. The final stage is the desorption of the product and its transport away from the surface.

1.2.1 Factors Affecting Catalytic Activity

The overall activity of a catalyst is governed by a number of factors. It is by variation of these factors that a catalyst can be fine-tuned to give the greatest activity. Many of these factors interact with one another causing a great deal of complexity in the optimisation process.

1.2.2 Adsorption

At least one of the reactants in all heterogeneously catalysed processes must be attached for a significant period of time to the exterior surface of the solid catalyst. This gives rise to two distinct mechanistic possibilities for the surface catalysed transformation of gas phase species. Although the first mechanism is more frequently considered to be the most reliable, the distinction between the two can often be blurred. The first mechanism is widely known as the Langmuir-Hinshelwood mechanism. In this both reacting species are adsorbed on the surface and after surface migration come together and react with the final product being desorbed. (figure 1.1). The alternative is known as the Eley-Rideal mechanism. In this case there is only one of the reactants adsorbed onto the surface, and the reaction takes place when the second impinges on the first from the gas phase.



Figure 1.1: Reaction schematics showing the different methods of adsorption and reaction I) Langmuir-Hinshelwood and II) Eley-Rideal for the formation of the diatomic molecule c from its constituent elements a and b

The two main ways that adsorption affects the activity of a catalyst are, the rate of adsorption/desorption and the type of adsorption involved. The rate at which the reactants are adsorbed and the products desorbed plays an important role in govering the speed with which the reaction proceeds. The faster the rate the quicker and, therefore, more efficient the catalyst. The second facter also plays a role in this, because, if the reaction requires the reactant to be only physisorbed onto the surface then the number of reactants being adsorbed in this manner will be greater than the number if the reactants were required to be chemisorbed. The lower energy required for physisorbtion means

that for a given range of energies a greater number of molecules could be adsorbed on the surface over a set period of time.

1.2.3 Temperature

Temperature is probably the most widely studied variable affecting the activity of a catalyst. It is also one of the widest reaching. The effect of temperature can be broadly split into two areas, reaction temperature and pre-treatment temperature. Pre-treatment temperature covers the various methods of heating that a catalyst may be subjected to before it undergoes a reaction (refer to 1.8 for greater details). The reaction temperature can also have an affect on the activity and selectivity of a catalyst. By raising or lowering the temperature at which a reaction takes place it is possible to alter the rate at which the reaction takes place. This behaviour is more commonly know as Arrhenius behaviour and is detailed in this equation:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

where k is the rate constant for the reaction, A is the pre exponential factor, E_a is the activation energy of the reaction and is measured in kilojoules per mole. T is the absolute temperature and R is the gas constant.

In most cases raising the temperature increases the rate of reaction, which in turn has a similar affect on the activity of a catalyst. There is a point where this becomes ineffective however. At elevated temperatures supported metal catalysts undergo a process known as sintering; during this process the highly dispersed nanoparticles begin to former larger particles. These large particles are less active and as a result the effectiveness of the catalyst is diminished. The temperature at which the thermal deactivation of catalysts occurs varies from reaction to reaction and from catalyst to catalyst.

1.2.4 Reactant factors

The concentration and flow rate of the reactants in heterogeneous catalysis can also play a role in governing the activity of a catalyst. When comparing the activity of a catalyst sitting idle, in the case of low concentrations. As a result it is desirable to cor conversions and selectivitys of catalysts using the same reactant flow rates.

1.2.5 Surface area

When a gas phase reaction is catalysed by a solid material, the reaction takes the surface of the catalyst, both interior and exterior. The rate at which the p formed is a function of the available surface area, so it stands to reason that the the surface area accessible, the larger the amount of reactant is converted to The only exceptions to this are reactions where the rate of conversion is limited transport of reactants from the gas phase to the solid catalyst material. If the o porous, and the pores are of sufficient size, so that the passage of reactar hindered, and the internal surface is also energetically homogeneous, then the conversion is directly proportional to the surface are of the catalyst. A nar structure limits the reaction rate, because under these circumstances some of th surface area of the catalyst material may be inaccessible to the reacta furthermore, may restrict the rate of conversion to products by impeding the difference of the second secon reactants and products throughout the porous medium. In this case the reacti either proportional to the square root of the surface area, or, entirely independent The exact case is determined by the method of diffusion within the pore struct morphology of the catalyst surface is also important in determining the acti catalyst. The reactants for any given reaction will only be able to adsorb o areas of the surface with an appropriate construction. These formations are known as active sites. The number and distribution of these sites play a governing the activity of a catalyst. When packed close together the active inhibit each other energetically causing a loss of activity, but when spread out

5

with a higher number of active sites will be more active than a catalyst with a low number of active sites with an identical pattern of distribution.

1.3 A Brief History Of Catalysis

The phenomenon of catalysis has been extensively studied since the beginning of the nineteenth century [1]. In 1814 the catalysed hydrolysis of starch by acids, was discovered by Kirchoff. A few years later it was shown by Humphry Davis that the introduction of hot platinum into a mixture of air and coal gas resulted in the metal becoming white-hot. Catalytic poisoning was discovered in 1824 when Henry observed that the reaction between hydrogen and oxygen was inhibited by the presence of ethylene [2]. He also noted selective oxidation in the reaction between oxygen and a mixture of hydrogen, carbon monoxide and methane.

The discoveries continued throughout the eighteen hundreds with examples of catalysis being shown by Faraday, Grove and Henry, with countless examples of 'new' catalytic processes being observed, as well as the discovery of several poisons for existing processes [3]. In 1877 one of the first industrial catalytic processes was developed. The Deacon process used a clay brick impregnated with copper(II) salts as a catalyst for the oxidation of hydrochloric acid to chlorine [2]. The next major discovery in the field was made by Berthalet in 1879. He was researching the acid catalysed esterification of acids and hydrolysis of esters, confirmed that the catalyst did not influence the position of equilibrium [3].

At the start of the 20^{th} century the focus of research shifted more towards hydrogenation, whereas before it had been more centred around oxidation. There was also an increase in the number of industrial processes conceived [4]. On the 2^{nd} July 1909 Karlsruhe Fritz Haber was successfully able to prepare copious amounts of ammonia from nitrogen and hydrogen in the presence of a reduced Fe₃O₄ catalyst using high pressure apparatus [2].

Catalytic cracking first came into prominence In the late 1930s. Initially the most popular catalyst was acid treated montmorillanite type clay, although many years earlier Friedel-Crafts catalysts, such as AlCl₃ had been used for this purpose [1]. Significant

Battle of Britain. Also in the early 1940s, thanks to the work of Lewis and the fluid bed, or fluid catalysed cracking, became a commercial reality.

Following the Second World War the use of acid treated clays for catalytic became unpopular because of their lack of stability over extended periods of ti were replaced by amorphous synthetic silica-alumina catalysts. These gave a distribution of products and were more stable under the conditions used to a the catalysts [1]. Outside of industry the mid 1940s saw the rise in prominen electronic band structure based arguments regarding catalyst activity. The ide bulk electronic properties of the catalyst could be directly related to catalytic first looked promising, especially in relation to the interpretation of behaviou within the compositional variations in a fixed alloy system [4]. However this was later on dismissed as being overly simplified, when it was realised th compositions could be very different from bulk ones.

In the mid-1950s two significant achievements were made. The first was the of sterogenic polymerisation by Ziegler and Natta [2]. The second was the in of spectroscopic methods for probing adsorbed species attached to supported by Eischens, Terenin and Sheppard [2].

The 1960s saw a great deal of development in the industrial application of The catalytic applications of zeolites were first explored after Milton and B showed that zeolites could be readily synthesised [1]. Developments were m catalytic reforming of hydrocarbons with the introduction of bi-metallic cataly greatly improved the activity and life span of the previous platinum catal decade saw a growth in the number of catalysts designed to remove the organ and nitrogen containing components from crude oil.

7

From the mid 1980s onwards a major trend in the industrial application of cata tended towards the removal of harmful products from the environment in order up with the growing legislation on the concentrations of chemical species that emitted by industrial processes. There has also been a drive towards creat synthetic routes based on readily available starting materials. Catalyst reserve been geared towards the development of new techniques that are able to be us in-situ studies of real life catalysts, which can give rise to a more targeted p catalyst design [2].

1.4 Background to Gold Catalysis for Carbon Monoxide Oxidation

1.4.1 The Activity of Gold

Towards the end of the seventies, and the beginning of the eighties, the disagreement with regard to the interaction of gold surfaces with oxygen. [6-9 the studies that had been undertaken agreed that there was no adsorption on gold surface at room temperature, but there was some disagreement as to its b at higher temperatures. Studies of the Au(111) surface by Schrader [6], and Chesters and Somoraji [7] showed that at temperature between 373 and 873 K adsorption occurred which gave rise to a disordered chemisorbed layer. In both studies the investigators found that the surface oxide was remarkably stable. It removed from the surface by heating the sample to temperatures greater than The behaviour of the this oxide was different from that of the bulk gold oxide which has an endothermic heat of formation and cannot be formed by direct re oxygen and gold, and which also decomposes at around 410 K. The greater displayed by the surface oxide in comparison to the bulk oxide was attribut

exposed to 3 X 10^{-5} Torr of oxygen for an hour at temperatures between 300-10 not adsorb any oxygen.

It was suggested that the difference in results was due to impurities, which n altered the activity of the surface towards oxygen. Several studies showed that at the surface of gold could lead to greatly increased rates of adsorption [8-10 studies disagreed on the maximum oxygen coverage obtained in the pres calcium. One study [9] suggested that all the oxygen was associated with forming CaO at the surface. Another [10] suggested that spill over of oxyg calcium to gold could occur leading to a much higher O/Ca ratio than expected formation. Madix [11] suggested that this was not the case since spillover imp oxygen bound to calcium should have a similar stability to oxygen bound to g reasoned that this would be unlikely given the vast difference in the heats of fe of the two oxides. He also thought that calcium was not responsible, due to the it was not detected in the studies carried out, when, if it were present it would to detect than oxygen. By using a heated platinum filament to deposit atomic onto a clean gold surface, Madix was able to show that the strongly bound surfa that had been previously reported was due to the formation of silicon oxide from that had diffused out of the bulk gold on heating. He was also able to show that does not dissociatively adsorb onto gold at pressures up to 1400 Torr and temp up to 500 K.

1.4.2 Gold Catalysis

1.4.2.1 Early work

Research into gold as a catalyst has only really started in earnest over the past twenty years. Before that time, gold had a reputation as an unreactive metal. Experiments with gold in the form of wire, sponge, powder and large supported gold particles [12-14] gave poor results. The first reference to gold as a catalyst came in 1906 [16], with the observation that gold gauze was able to catalyse the oxidation of hydrogen. The earliest reference to gold as a catalyst for the oxidation of carbon monoxide comes from 1925 [14]. It has been shown that unsupported bulk gold can obtain only low levels conversion of carbon monoxide to carbon dioxide, although between -24 and 23°C fine gold powders, with a mean particle size of 7.6 nm have shown some activity [15]. Very little work was carried out between the 1950's and 1960's [17]. However during the 1970's there were two areas of work, which laid the foundations for a lot of the modern work to come.

It was shown that gold supported on either alumina or silica was active for alkene hydrogenation at 100°C [18-19]. When silica was used as the support good activities were shown by catalysts with very low gold loadings (0.01-0.05%), these catalysts were observed to have turnover frequencies 7000 times greater than catalyst with higher loadings. This type of catalyst also failed to show the double bond isomerism, which was common in catalysts made from other metals.

The second advancement took place in the area of matrix isolation chemistry [20-21]. The work that took place in this field is relevant to catalysis because the unstable complexes that are generated by this technique may resemble intermediate species formed in catalysed reactions at higher temperatures. By examining the reactions of gold and silver atoms with oxygen and carbon monoxide Ozin and McIntosh [21] suggested that the reactions that occurred on gold might serve as a model for the mechanism of the heterogeneously catalysed oxidation.

although the best results are gathered from clusters that range in size from 2-3 a 26]. This is true regardless of the method of preparation employed. The partic originate as a colloidal desertion with uniform sized gold particles [27-28], be by vapour deposition [29-32], or even by controlled aggregation of atoms or simple gold compounds [33-36]. Three major factors have been identified a important in gold catalyst; these are the type of metal oxide support, size of t particles, and the strength of the interaction between the gold particles and the su

1.5 Effect of preparation on catalyst activity

It has also been argued [24, 25, 37, 38] that both the method of preparation (det chapter 3) and pre-treatment play a role in shaping the properties of support catalysts. When they are prepared using conventional impregnation methods, get thought to be the most effective method for metals of Groups 8-10, the considerable less active than the platinum group metals prepared in a similar re For example, 1% Au/TiO₂ prepared by impregnation gives a rate of CO oxidation x 10⁻¹⁰ mol $g_{cat}^{-1}s^{-1}$ at 300 K, considerably lower than 1% Pt/ TiO₂ which gives 1 ⁷ mol $g_{cat}^{-1}s^{-1}$. However when a similar gold catalyst is prepared by dep precipitation it gives a rate of 5.5 x 10⁻⁶ mol $g_{cat}^{-1}s^{-1}$ under the same conditions [39]

High activity catalysts are obtained when deposition-precipitation or co-precipit employed. Even at temperatures as low as -76° C, 5% Au/ α -Fe₂O₃ is active. Exa few reports of activity at these low temperatures [40] recent research activitie focused more on the use of a range of temperatures from ambient up to 80°C.

Studies by Gardner and his group [43-44] have demonstrated the high acti Au/MnO_x catalysts prepared by co-precipitation; they were five time more active immediately after precipitation rather than being allowed to remain in contact solution for an extended time and aged. Earlier studies [45] with CuO/ZnO pr had shown that their aging could be a crucial with respect to the formation of catalyst for the hydrogenation of carbon monoxide. The effect of aging investigated for carbon monoxide oxidation. It was found that gold catalysts without an aging step can give initial carbon monoxide conversions that are however at 120°C it can rapidly deactivate and half lives of only 100-200 min been observed [46].

An alternative approach to supported gold catalyst preparation has been emp Baiker and co-workers [47]; amorphous metal alloys were prepared by melt and had the compositions Au_5FeZr_{14} and Au_5AgZr_{14} . When these glassy me were oxidized in situ at 280°C, $Au/ZrO_2/Fe_2O_3$ and $Au/Ag_2O/ZrO_2$, cataly produced, and, these were then used in the low-temperature oxidation o monoxide. Kinetic tests performed in a continuous tubular microreactor in the from -20 to 50°C showed that both catalysts were highly active for carbon r oxidation at low temperatures, the best activity, 95% conversion, being between 39 and 50°C.

Among new sources of gold for supported catalyst manufacture are isonit nitrates like Au(NO₃)(CNBu^t) [48] and dimethylgold(III) β -diketone [49]. Initrate complex has been used to deposit gold onto iron hydroxide, which freshly precipitated. The result is a 3% Au/Fe₂O₃ which after calcination at 40 complete conversion of carbon monoxide at -5°C. Gold particles with diame than 2nm were obtained using vapor-phase deposition of the diketone of followed by calcinations. The resulting catalyst proved to be active at -40°C.

12

In addition to the method of precipitation, the calcination temperature has been shown to have significant influence on the performance of the catalyst [50]. Haruta's method involved washing the co-precipitated catalyst in order to remove chloride ions, (that can act as a catalyst poison), followed by vacuum drying and calcinations in air at 400°C. However calcination in oxygen failed to reproduce Haruta's low temperature results [61].

1.6 Effect of support

Early work demonstrated that the nature of the support had a decisive role in the activity of gold catalysts: alumina- and magnesia-supported catalysts were found to be significantly more active than silica-supported gold [52]. There is now evidence that the interaction between the support and the gold particles has an important effect on the performance of a catalyst. Gold itself and pure titania are inactive for carbon monoxide oxidation below 227°C, whereas both 1% Au/TiO₂ and gold powder with titania deposited on its surface are active at 25°C [13, 52-53]. A rate of 2.3 x 10⁻⁶ mol g_{cat}^{-1} s⁻¹ at 100°C was recorded for a 1% Au/TiO₂ catalyst [25], which is a significant improvement on an earlier reported rate, 6.9 x 10⁻⁸ mol g_{cat}^{-1} s⁻¹, for 1.8% Au/SiO₂ at the same temperature.

Support effects have been studied in catalysts that have been derived from both a phosphine-stabalized mononuclear gold complex, Au(PPh₃)(NO₃), and a phosphine-stabalized gold cluster, [Au₉(PPh₃)₈](NO₃)₈ [54-55]. When supported on oxides such as α -Fe₂O₃ and TiO₂, by impregnation, the catalysts derived from both of these materials have low activity for carbon monoxide oxidation. When applied to fresh, asprecipitated metal hydroxides, M(OH_x), and followed by temperature programmed calcinations they had high activities. The rates obtained for 3% Au/Fe(OH)₃, which had a reported conversion of 39%, and co precipitated 4.1% Au/Fe₂O₃ were 9.7 x 10⁻⁷ mol g_{cat}^{-1} s⁻¹ at -70°C and 4.1 x 10⁻⁸ mol g_{cat}^{-1} s⁻¹ at -39°C respectively [54-55]. The dispersion of the gold particles during the precipitation was assisted by interaction between the many surface hydroxyl groups and the gold complexes. These catalysts showed high activity in low-temperature carbon monoxide oxidation, the most active

catalyst consisting of small gold particles, 2.9 nm, dispersed on poorly crystallized iron oxide containing a mixture of α - and γ -Fe₂O₃. The activity was promoted by the presence of sodium ions but lowered by the presence of chloride. Catalytic activity depends not only on the history of thermal treatment but also on the kind of precursor and the supports used. Au(PPh₃)(NO₃) supported on freshly precipitated Fe(OH)₃, Mn(OH)₂, or Co(OH)₂, followed by temperature programmed calcinations in a flow of dry air, was active for carbon monoxide oxidation at -70° C, and for the corresponding Ti(OH)₄, and Al(OH)₄ systems at -20° C and 0°C respectively. The gold particles on the freshly precipitated Fe(OH)₃ support were determined by EXAFS, XRD and TEM, and shown to be approximately 2.9 nm in size. The catalysts derived from the mononuclear gold complex showed higher activity than those from the cluster compound.

Conversely, catalysts not aged in the preparative reaction medium suffer a rapid deactivation (see 1.6). The original precipitate is amorphous and the recrystallization that occurs during aging might also occur during use. This recrystalization might be the cause of the rapid deactivation that has been observed in these catalysts [56].

For co-precipitated samples of Au/Fe₂O₃, the maximum activity was obtained with a gold content of approximately 5%, and activity was inversely dependant on the calcination temperature [50, 57-58]. The uncalcined catalyst was most active of all, suggesting that a hydrated gold species such as $Au_2O_3.nH_2O$ may be more active than the gold metal, which is obtained by calcinations. No direct correlation has been found between catalytic activity toward carbon monoxide oxidation and the gold species identified by Mössbauer spectroscopy, but catalytic activity did increase with the proportion of ferrihydrate in the support. It was suggested that ferrihydrate is important for the activation of molecular oxygen [57].

Au^{III} supported on Y-type zeolite has high activity for carbon monoxide oxidation, but it gradually and irreversibly deactivates during use. Initially the conversion is 100% but after 44 h of use the conversion has dropped to only 58% [59-60]. This was attributed to Au³⁺ ions being transformed into gold metal. Gold/iron/Y catalysts also deactivate during use, but in this case the deactivation can be reversed, and even completely recovered by thermal treatment, due to the ability to react suitably with oxygen.

1.7 The effect of particle size

It was recognized in the early work on the oxidation of carbon monoxide using gold that activity increased as the particle size decreased [61]. This has been confirmed by the more recent work that has been carried out on a range of oxide-supported catalyst [61]. The optimum size for gold particles supported on both metal oxides and molecular sieves is less than 5 nm. By careful control of the conditions used during coprecipitation, gold particles of this size can be formed. It has also been demonstrated that high activities are obtained with crystallites of approximately 4-5 nm [62-63]. There is a sharp rise in activity beginning at ~5 nm, as the gold particle size is decreased from 20 nm: for Au/CO₃O₄, Au/Fe₂O₃ and Au/TiO₂, the turnover frequency (TOF) rises rapidly from ~0.01 s⁻¹ to more than 0.1 s⁻¹ at 0°C Early evidence pointed to increasing activity as the size is further reduced [41, 64], but more recent investigations indicate that there is an optimum size for gold particles of 2 or 3 nm [49, 65].

The durability of a series of CuO- and ZnO-supported gold catalysts was investigated by Hutchings in comparison with CuO/ZnO containing no gold and prepared using the same co precipitation method as employed for the supported gold catalysts [42]. Examination by electron microscopy showed no morphological differences between any used catalyst and its unused counterpart. A common characteristic of all the catalysts was the presence of discrete gold particles, which frequently showed multiple twinning. There was, however, a distinct difference in the sizes and dispersion of the gold particles. The largest gold particles were observed with the Au/CuO catalyst, and these were in the range 20-50 nm. The best catalytic performance was obtained with the Au/ZnO catalyst in which much smaller particles, with a mean size of 2-3 nm, are supported on feathery zinc containing crystallites.

1.8 The Affect of Calcination

The dependence of catalytic activity of supported gold catalysts on the calcination temperature is complex and the results produced by different groups sometimes contradict one another.

at 200, 300, 400 and 600 °C, they found that the most active catalyst was the had been calcined at 300 °C. Again it was observed that the particle size incre calcination temperature. The higher activity of the sample calcined at 300 attributed to its small Au particle size, which offers the largest number of ste and corners, where the reaction can occur. The particle size of the sample c 200 °C was nearly identical to that of the 300°C sample; although its activity v [38].

<u>1.9 – Kinetics and mechanism</u>

No very precise or quantitative analysis of the reaction mechanism has presented. This is because there is not a large amount of firm kinetic results such conclusions might be based, and because of the variety of types of cat have been reported as being active for carbon monoxide oxidation. It has a suggested that there is a possibility that the reaction mechanism differs from c catalyst. This theory is supported by the activation energies and orders of rea have been reported so far [13, 20] (table 1.1).

The discussion of possible reaction mechanisms is complicated by the adsorbed states of the reactants and uncertainty with respect to the location reaction centers [19, 53, 68]. Oxygen is not extensively chemisorbed on met at reaction temperatures, even at small temperatures. The fractional positive (table 1), show that it cannot be gaseous oxygen molecules that enter determining step: the oxygen has to be adsorbed somewhere and the evided points to the support. Carbon monoxide is significantly chemisorbed on support catalysts, but much of it is on the support [13, 22, 41, 58, 64]. It is therefore whether the species identified by FTIR as being carbon monoxide reaction.

	(wt%)	(nm	temperature			
)	(°C)			
TiO ₂	3.3	2	0	0.05	0.24	34.3
TiO ₂	1.0	33	20	0.43	0.03	~29
TiO ₂	1.0	33	40	0.56	0.13	-
α -Fe ₂ O ₃	0.66	4	31	0	0.05	35.1
C0 ₃ O ₄	1.2	6-7	0	0.05	0.27	16.3
Ce(La)O _x	5	8	10-54	0.30	0.18	53.7

A number of possibilities for the reaction centers exist [13, 22, 41, 58, 64]]

- The reaction might take place entirely on the support, involving adsorbet monoxide molecules, which may have migrated from the gold particle spill over, and oxygen species, which may be peroxide or oxide ions [13]
- 2. The reaction might take place solely on the gold particles between cher carbon monoxide and oxygen atoms, which may have come from the su reverse spill over. There has been some spectroscopic evidence present shows these reacted species being adsorbed on the same gold atom [41,
- 3. The reaction may happen preferentially at the edges of gold particles, i either sites on the support adjacent to and influenced by the metal, or sit metal influenced by the support. FTIR results have been interpreted as carbon monoxide molecules on peripheral gold sites, but this of demonstrate that these are the locus of the reaction [64].

The orders of reaction (table 1.1) have been used [41] to support the final a presented, with the rate being governed by the number of support sites adjacent particles capable of adsorbing and being substantially covered by molecular ox

has been suggested that following reaction with carbon monoxide on the metal, a carbonate-like species is formed. It was claimed that such a mechanism could explain the approximate dependence of activity on the inverse of the square of the gold particle diameter [13]. When applied to the reaction on Au/TiO₂ [25] the use of a Langmuir-Hinshelwood rate expression has enabled the elimination of a potential mechanism involving oxygen atoms, on the grounds that derived thermodynamic adsorption parameters had inadmissible values. A later article [57] was able to resolve some of the earlier doubts that had arisen in relation to whether the reactants' adsorptions were competitive or non competitive. These doubts were resolved in favor of the latter method, but it was proposed that carbon monoxide adsorbed on the gold and oxygen molecules on the titania sites at the interface. This observation was based on DRIFTS studies that showed that oxygen had no effect on carbon monoxide coverage.

Of course, there is no reason why two or more mechanisms should not proceed side by side. It has been suggested [43] that a slow process, similar to the first method outlined above, accompanies a faster process akin to the third method detailed. The kinetic implications of this have yet to be pursued.

Activation energies for Pt/TiO₂ catalysts lie between 49 and 60 kJ mol⁻¹, as do those for Au/TiO₂ made by impregnation or photodecomposition, where the particle size is relatively large. However, the deposition-precipitation route leads to much lower values, (18-27 kJ mol⁻¹), and this lends support to the theory that electronic structure plays and important part in determining the activity of a catalyst. In other studies [13, 25], somewhat lower activation energies (<38 kJ mol⁻¹ [13], 18-31 kJ mol⁻¹ [25]), were reported. Very low values tend to suggest mass-transport limitations, but it has been suggested [38] that kinetic rates are much slower than mass transport rates. Very low values have also been found for gold wire and sponge [70].

1.9.1 - The Bond and Thompson model

The most widely accepted model for the reaction mechanism is one that was proposed by Bond and Thompson [71]. In this model they attempt to reconcile the conflicting opinions on the necessity of gold atoms and ions, (which they take to be Au^{III}), in the reaction mechanism [27, 72]. They state that the best way to understand these differing observations is in terms of a model in which the active catalyst consists of both gold atoms and ions, the latter forming a chemical glue which binds the particle to the support. The structure of the particles is not fixed however, and it is possible to change the ratio of the atoms and particles by a variety of process, including reduction in hydrogen, calcinations (depending on the temperature a certain portion of the gold ions will auto-reduce as oxygen is lost [36]) and during reaction. Therefore it can be seen that complete reduction is harmful because the glue to the support is lost and sintering can occur much more easily. By the same token the opposite situation, (the total loss of gold atoms), is also undesirable. Au⁰ is required because it acts as the locus around which the carbon monoxide is adsorbed. A partially reduced support surface may contain anion vacancies that assist in the adsorptions of oxygen (Figure 1.2).



Figure 1.2: The Bond and Thompson model of the active site for carbon monoxide oxidation on transition metal supported gold catalysts

This model can be refined to assign various tendencies for carbon monoxide to chemisorb on Au⁰ atoms of different co-ordination number, (CN), [73]. Large particles may possess only relatively small interfacial areas and few atoms having low CN and therefore diminished activity.

The mechanism for the model purposed by Bond and Thompson begins by a hydroxyl group, bonded to either a support cation or a peripheral Au^{III} ion, attacking a carbon monoxide on a gold atom, (Au⁰...CO), to form a carboxylate group attached to the Au^{III}. In turn, this is attacked by a super oxide ion, which is responsible for oxidizing two

$$O_{2} + \Box_{s}^{-} \rightarrow O_{2}^{-} ... \Box_{s}$$

$$Au^{II} ... COOH + O_{2}^{-} ... \Box_{s} \rightarrow Au^{II} + CO_{2} + HO_{2}^{-} ... \Box_{s}$$

$$(1.$$

$$Au^{II} ... COOH + HO_{2}^{-} ... \Box_{s} \rightarrow Au^{II} + CO_{2} + 2 OH_{s}^{-} + \Box_{s}$$

$$(1.$$

$$Au^{II} + \Box_{s} \rightarrow Au^{III} + \Box_{s}^{-}$$

$$(1.$$

The net reaction i.e. $2CO + O_2 \rightarrow 2CO_2$ is achieved by repeating the process reby equations 1.1-1.3 and then combining all the processes in the set. The anion used in equation 1.4 is created in equation 1.2 and, since the hydroxyl grad catalytically, is removed when it is restored to the surface in the process represented by equation 1.6.

There is infrared evidence for the presence of both $Au^0...CO$ and $Au^{x+}...C$ with the absorptions falling at 2112 and 2151 cm⁻¹ respectively [72]. In pr ferrihydrate supported catalysts Mössbauer spectroscopy has detected AuO Au⁺ has been shown to exist at the interface between gold and magnesium support [36]. XPS results are also consistent with the presence of gold hydrox on Fe₂O₃, TiO₂ and Al₂O₃ [25].

As previously mentioned in 1.9 the mechanism may not be the same on ever For example in catalysts where the support does not have any anion vacancies conditions where none are formed, the oxygen molecule might simply be bonded to a support cation, in place of equation 4. As another example in where mobile surface hydroxyl groups do not exist, equations 2 and 3 won't t In its stead the mechanism might involve direct reaction of a chemisorb monoxide with an oxygen molecule or a super oxide ion. Much of the detail information currently available [74-75] is confined to specific catal generalizations are difficult to make.

1.9.2 - The Kung Model

Aside from the model proposed by Bond and Thompson, another accepted model for the room temperature oxidation of carbon monoxide is that proposed by the Kung group, figure 1.3 [76].



The Kung model is similar to the one proposed by Bond and Thompson. The active site of the model consists of a particle composed of both metallic and cationic gold with hydroxyl ligands. Unlike the Bond and Thompson model, Kung speculates that the Au cation needs to be stable in the prescence of metallic gold as well as in a reducing environment. It is speculated that Au(I) would be more able to meet these requirements than Au(III). As a result Au(I)-OH is proposed as the cationic component of this model. Au/Mg(OH)₂ catalysts, when studied by Au¹⁹⁷ Mössbauer spectroscopy have shown that the most active catalyst was the one which contained the highest concentration of Au(I) [72]. XANES data obtained by Gates shows the presence of both metallic and ionic gold species in Au/MgO catalysts. Furthermore the XANES data suggests that the active species is Au(I) rather than Au(III) [77].

In this mechanism the reaction proceeds by the insertion of and adsorbed carbon monoxide species into an Au-OH bond to form a hydroxycarbonyl. Stable hydroxycarbonyls have been prepared on many group VIII metals [79] and their formation from the CO and OH ligands is enhanced by lower electron density at the metal [80]. The hydroxycarbonyl is oxidized to a bicarbonate, which is then

decarboxylated to Au-OH and CO₂. Kung suggests that the decarboxylation step is similar to a step in the water gas shift reaction.



Figure 1.4: The proposed mechanism for carbon monoxide oxidation by go catalysts by Kung

This mechanism does not involve participation of OH radical-like species, superoxides or the direct participation of the support, as has been suggested in models proposed by other groups [81-83].

1.10 Conclusions

The field of gold catalysis has seen a large increase in the amount of research conducted within it over the past 20 years. This research has led to a number of discoveries that have led to greater understanding of the way that gold catalysts function. In-depth research into the part played by factors like the choice of support, and pre-treatment has resulted in the beginnings of the development of programmed design for gold catalysts for carbon monoxide oxidation. However as it has been mentioned in several places in

this chapter, there are areas of research in this field where the results are contradictory, and these contradictions need to be explained or removed before any great advances can be made in the filed of carbon monoxide oxidation.

<u>1.11 – References</u>

- 1. M.W. Roberts, Catal. Letters. 2000, 67, 1.
- 2. J.M. Thomas, J.W. Thomas, Principles and Practice of Heterogeneous Catalysis, 1997, VCH
- 3. E.K. Rideal, H.S. Taylor, Catalysis in Theory and Practice, 1926, Macmillan & Co.
- 4. J.M. Thomas, J.W. Thomas, Introduction to the Principles of Heterogeneous Catalysis, 1967, Academic Press
- M.W. Roberts, C.S. McKee, Chemistry of the Metal-gas Interface, 1978, Oxford University Press.
- 6. M.E. Schrader, J. Colloid Interface Sci. 1977, 59, 456
- 7. M.A. Chesters, and G.A Somoraji, Surface Sci. 1975, 52, 21
- 8. D.D. Eley, and P.B Moore, Surface Sci 1978, 76, L599
- 9. P. P. Légaré, L. Hilaire, M. Sotto, and G. Maire, Surface Sci, 1980, 91, 175
- 10. N.B. Bazhutin, G.K Boreskov and V.I. Savchenko, Reaction Kinetics Catalysis Letters, 1979, 104, 337
- 11. N.D.S Canning, D. Outka, and R.J. Madix, Surface Sci, 1984, 141, 240
- 12. N.W. Cant, W.K. Hall, J. Phys. Chem., 1971, 75, 2914.
- 13. S.D. Lin, M. Bollinger and M.A Vannice, Catal. Lett., 1993, 17, 245.
- 14. W.A. Bone and G.W. Andrew, Proc. Roy. Soc. (London), 1925, 109A, 459.
- 15. Y. Lizuka, T. Tode, T. Takoa, K. Yatsu, T. Takeuchi, S. Tsubota and M. Huruta, J. Catal., 1999, 187, 50.
- 16. W.A. Bone, R.V. Wheeler, Philos. Trans. 1906, 206A, 1.
- 17. G.C. Bond, Gold Bull. 1971, 5, 11.
- 18. G.C. Bond, P.A. Sermon, Gold Bull. 1973, 6, 102.
- 19. P.A. Sermon, G.C. Bond, P.B. Wells, J. Chem. Soc., Faraday Trans. 1979, I 75 385.
- 20. G.A. Ozin, Acc. Chem. Res. 1977, 21, 10
- 21. D. McIntosh, G.A. Ozin, Inorg. Chem. 1977, 16, 51.
- 22. M. Haruta, Catal. Surv. Jpn. 1997, 1, 61
- 23. D. Outka and R.J. Madix, J. Phys. Chem. A, 1999, 103, 9573.

- 24. M. Valden, X. Lai and D.W. Goodman, Science, 1998, 281, 1647.
- 25. M.A. Bollinger and M.A Vannice, Appl. Catal. B: Enviromental, 1996, 8, 417.
- 26. M. Valden, S. Pak, X. Lai and D.W. Goodman, Catal. Letters, 1998, 56, 7.
- 27. J.D. Grunwealdt, M. Maciejewski, O.S. Becker, P. Fabrizioli and A. Baiker. J. Catal., 1999, 186, 458
- 28. J.D. Grunwealdt and A. Baiker J. Phys. Chem. B 1999, 102, 1002
- 29. K. Sayo, S. Deki, and S. Hayashi, J. Colloid and Interface Science, 1999, 212, 597
- 30. K. Sayo, S. Deki and S. Hayashi, J. Mater. Chem., 1999, 9, 937
- 31. V.A. Bondzie, S.C. Parker and C.T. Campbell, Catal. Letters, 1999, 63, 143
- 32. M. Arai, M. Mitsui, J.-I. Ozaki and Y. Nishiyama, J. Colloid and Interface Science, 1994, 118, 473
- 33. M.J. Kahlich, H.A. Gasteiger and R.J. Behm, J. Catal., 1999, 182, 430
- 34. A.M. Visco, F. Neri, G. Neri, A. Donato, C. Milone and S. Galvagno, *Phys. Chem. Chem. Phys.*, 1999, 1, 2869
- 21 R.M. Finch, N.A. Hodge, G.J. Hutchings, A. Meagher, Q.A. Pankhurst, M.R.H.
 Siddiqui, F.E. Wagner and R. Whyman, *Phys. Chem. Chem. Phys.*, 1999, 1, 485
- 36. E.D. Park and J.S. Lee, J. Catal., 1999, 186, 1
- 37. A.I. Kozlov, A.P Kozlova, H. Liu and Y. Iwasawa, Appl. Catal. A, Gen. 1999, 182,
 9.
- 38. G.C. Bond and D.T. Thompson, Cat. Rev. Sci. Eng., 1999, 41, 319
- 39. G.R. Bamwenda, S. Tsubota, T. Nakamura, and M. Haruta, *Catal. Lettera*, 1997, 44, 83
- 40. M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, J. Catal., 1998, 176, 426
- 41. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, and B. Delmon, J. Catal., 1993, 144, 175
- 42. G.J. Hutchings, Gold Bull., 1996, 29, 123
- 43. S.D. Gardner, G.B. Hoflund, M.R. Davidson, H.A. Laitinen, D.R. Schryer and B.T. Upchurch, *Langmuir*, 1991, 7, 2140
- 44. S.D. Gardner, G.B. Hoflund, B.T. Upchurch, D.R. Schryer, E.J. Kielen, and J, Schryer, J. Catal., 1991, 129, 114
- 45. R.W. Joyner, F. King, M.A. Thomas, and G. Roberts, Catal. Today, 1991, 10, 417
- 46. G.J Hutchings, M.R.H. Siddiqui, A. Burrows, C.J. Kiely, R. Whyman, J. Chem. Soc., Faraday Trans., 1997, 93, 187
- 47. A.Baiker, M. Maciejewski, S. Tagliaferri, and P. Hug, J. Catal., 1995, 151, 407

- 48. T.J. Mathieson, A.G. Langdon, N.B. Milestone, and B.K. Nicholson, *Chem. Commun.* 1998, 371
- 49. M. Okumura, K. Tanaka, A. Uda, and M. Haruta, Solid State Ionics, 1997, 95, 143
- 50. S.K Tanielyan and R.L Augustine, Appl. Catal. A: Gen., 1992, 85, 73
- 51. S. Galvangno, G. Parravano, Ber. Bunsenges, Phys. Chem. 1979, 83, 894
- 52. S.D. Lin, and M.A Vannice, Catal. Letters, 1991, 10, 47
- 53. Z.M. Liu and M.A Vannice, Catal. Letters, 1997, 43, 51
- 54. Y. Yuan, A.P. Kozolva, K. Asakura, H. Wan, K. Tsai, and Y. Iwasawa, J. Catal., 1997, 170, 191
- 55. A.P. Kozolva, S. Sugiyama, A.I. Kozlov, K. Asakura, Y. Iwasawa, J. Catal., 1998, 176, 426
- 56. G.J. Hutchings, Gold Bull., 1996, 29, 123
- 57. F.E Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano and S.D. Calogero, J. Chem. Soc. Faraday Trans., 1997, 93, 3403
- S. Mimico, S. Scire, C. Crisafulli, A.M. Visco and S. Galvagno, Catal. Letters, 1997, 47, 273
- 59. T.M. Kang and B.Z. Wan, Appl. Catal. A: Gen., 1995, 128, 53
- 60. T.M. Kang and B.Z. Wan, Catal Today, 1997, 35, 379
- G.R. Bamwenda, S. Tsubota, T. Nakamura, and M. Haruta, Catal. Letters, 1997, 44, 83
- 62. M. Okumura, S. Tsubota, M. Iwamoto and M. Haruta, Chem. Letters, 1998, 315
- 63. M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Letters*, 1998, **51**,53
- 64. S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schyer B.T. Upchurch and E.J. Kielin, Langmuir, 1991, 7, 2135
- 65. M. Valden, X. Lai and D.W. Goodman, Science, 1998, 281, 1647
- 66. A. Wolf, F Schuth, Appl. Catal. A, 2002, 226, 1
- 67. F. Boccuzzi, A Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa and M. Haruta, J. (Catal., 2001, 202, 256
- 68. Y. Iizuka, H. Fujiki. N. Yamanchi, T. Chijiiwa, S. Arai, S Tsubota, and M Haruta, J. Catal., 1997, 36, 155
- 69. F. Boccuzzi, A Chiorino, S. Tsubota and M. Haruta, J. Phys. Chem, 1996, 100, 3625
- 70. N. W. Cant and P.W. Fredrickson J. Catal, 1975, 37, 531
- 71. G.C Bond and D.T. Thompson, Gold Bull, 2000, 33, 41

- 72. M.A.P. Dekkers, M.J. Lippits and B.E. Nieuwenhuys, Catal. Today, 1999, 54, 381
- 73. M. Mavrikakis, P. Stolze and J.K. Norskov, Catal. Lett., 2000, 64, 101
- 74. A.P Kozlova, A.I. Kozlov, S. Sugiyama, Y. Matsui, K. Asakura and Y. Iwasawa, J. Catal., 1999, 181, 37
- 75. H. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, K. Asakura and Y. Iwasawa, J. Catal., 1999,185, 252
- 76. H.H. Kung, M.C. Kung, C.K. Costello J. Catal., 2003, 213, 425
- 77. Y. Kobayashi, S. Nasu, S. Tsubota, M. Haruta, Hyperfine Interact. 2000, 126, 95
- 78. J. Guzman, B.C. Gates, J. Phys. Chem. B, 2002, 106, 7659
- 79. P.C. Ford, A. Rokicki, Adv. Organomet. Chem. 1988, 28, 139
- 80. D.F. Gross, P.C. Ford, J. Amer. Chem. Soc. 1985, 107, 585
- M. Haruta, S. Tsubota, Y. Kobayashi, H. Kageyama, M. Genet, B. Delmon, J. Catal, 1993, 144, 173
- 82. D.A.H Cummingham, W. Vogel, M. Haruta, Catal. Letters, 1999, 63, 43
- 83. F. Boccuzzi, A Chioino, S. Tsubota, M. Haruta, J. Phys. Chem. 1996, 100, 3625

1.12 Bibliography

- 1. J.M. Thomas, J.W. Thomas, Principles and Practice of Heterogeneous Catalysis, 1997, VCH
- 2. E.K. Rideal, H.S. Taylor, Catalysis in Theory and Practice, 1926, Macmillan & Co.
- 3. J.M. Thomas, J.W. Thomas, Introduction to the Principles of Heterogeneous Catalysis, 1967, Academic Press
- 4. M.W. Roberts, C.S. McKee, Chemistry of the Metal-gas Interface, 1978, Oxford University Press.
Chapter 2: X-ray Photoelectron Spectroscopy

2.1 Introduction

This chapter details the theory behind X-ray Photoelectron Spectroscopy (XPS) and goes onto describe some of the features that arise in spectra, covering their origins and the information that can be gleaned from them. Also covered in this chapter are some of the methods used in the interpretation of spectra generated by XPS, and the equipment and conditions necessary for the generation of XP spectra.

2.2 The Photoelectric Effect

When a material is exposed to electromagnetic radiation of a particular wavelength the emission of electrons is observed. This process is known as the photoelectric effect. If an atom is irradiated with photons of a well-defined energy, hv, there is a chance that the atom will absorb the photon and then eject an electron in order to liberate the energy that was gained from the photon. That electron, which is termed a photoelectron, is ejected with a kinetic energy that can be defined by the Einstein Relationship [1].

$$\mathbf{E}_{\mathbf{k}} = \mathbf{h}\mathbf{v} - \mathbf{E}_{\mathbf{b}} \tag{2.1}$$

where E_k is the kinetic energy of the photoelectron, hv is the energy of the original photon, and E_b is the energy required to remove the electron from the atom completely. This is usually referred to as the binding energy.

Depending on the photon energy used, and the atom that is undergoing photoemission, X-ray radiation can interact with all of the core orbitals within an atom. Numerous electrons can be ejected and each of these will have a characteristic kinetic energy, which is entirely dependant on the orbital from which the electron originated. Each of these energies will be discrete because of the quantisation of atomic orbitals. This results in spectra composed of discrete bands, which each correspond to a different atomic orbital. There are other techniques that use photoemission to study different atomic energy levels. Such as ultra-violet photoelectron spectroscopy, (UPS), which used ionsing radiation lower than 50 eV to study the valence levels of an atom.

2.3 Koopmans' theory

In the Einstein relationship (eq1), E_b is often equated with the orbital energy of the electron in its initial neutral ground state, with the assumption that E_b of an electron is equal to the negative of its self-consistent field orbital energy, ε_b^{SCF} .

$$\mathbf{E}_{\mathbf{b}} = -\mathbf{\varepsilon}_{\mathbf{b}}^{\mathbf{SCF}} \tag{2.2}$$

This simple equation is usually attributed to Koopmans [2], and is at best only an approximation. This is because it is based on an assumption known as the frozenorbital approximation, which suggests that following ionization, brought about by the emission of a photoelectron there is no rescaling or relaxation of electron distribution.

Koopmans theorem also fails to take into account several other factors like electron correlation. The theorem assumes that the correlation energy is the same for both the neutral atom (M) and the excited ion (M^+), rather than allowing for the fact that local distortions of an orbital by an adjacent electron will affect the motion of other electrons in that orbital. SCF calculations also fail to take into account relativistic effects, and instead assume that the electrons move independently of each other. It is more realistic to say that the value of E_b is the difference between the energy of the initial state of the neutral atom (E_i) and the final state of the excited ion (E_f). The kinetic energy of the photoelectron is therefore best described as:

$$\mathbf{E}_{\mathbf{k}} = \mathbf{h}\mathbf{v} - (\mathbf{E}_{\mathbf{f}} - \mathbf{E}_{\mathbf{i}}) \tag{2.3}$$

The different final states of the singly ionised atom will alter the observed value of E_k , and hence cause the derived values of E_b to be slightly different to those predicted by Koopmans' Theorem.

2.4 The Fate of Core Holes

The ejection of an electron by photoemission leaves the ion in an excited state. Typically the ion will rid itself of this excess energy by one of two processes, either xray fluorescence or the emission of an Auger electron (figure 2.1).



FIGURE 2.1: ENERGY LEVEL DIAGRAMS ILLUSTRATING THE PROCESSES OF AUGER EMISSION AND X-RAY FLUORESCENCE.

Both of these processes involve the dropping of an electron from a higher orbital into the hole created by the ejected electron. The energy liberated by this transition is either given off as an X-ray photon in the case of x-ray fluorescence, or causes the ejection of a second electron from a higher orbital in the case of Auger emission.

Both of these processes play a role in core hole decay; however the process that predominates is dependent on the atomic number of the element involved. For elements with a low atomic number Auger emission is the more probable method of core hole decay. As the atomic number rises this probability decreases, and the probability of x-ray fluorescence occurring rises (figure 2.2).



There are spectroscopic techniques that utilize both Auger emission and X-ray fluorescence (XRF), because the energy of the emitted particle from either decay process is characteristic of some combination of atomic energy levels and therefore characteristic of the atomic species itself. It is possible to study Auger electron spectroscopy (AES) at the same time as XPS, since the XPS spectra will contain not only photoelectron signals but Auger signals as well. AES produces electrons with a short mean free path (see 2.7). This makes AES a surface probe, much like XPS and similarly to XPS if involving valence electrons can be particularly sensitive to the chemical environment of the emitting atom.

The technique that employs x-ray fluorescence is also known as XRF spectroscopy. Unfortunately it gives little information about the surface of a material due to the long mean free path of x-rays within the solid. However this property of x-rays does make XRF a very useful tool for the bulk analysis of solids.

2.5 Final State Effects

2.5.1 Relaxation Shift

The sudden appearance of a core hole causes the outer electron orbitals of the atom to contract towards the core. This makes it easier for the emitted electron to be removed from the atom, since the energy required for complete ionization is reduced. The result is that the photoelectron has a greater kinetic energy than would normally be expected.

$$\mathbf{E}_{\mathbf{k}} = \mathbf{h}\mathbf{v} - \mathbf{E}_{\mathbf{b}} + \mathbf{E}_{\mathbf{r}} \tag{2.4}$$

Where E_r is the energy contribution of the relaxation shift. There are two contributions to this factor, one due to the relaxation of the electrons in the atom, by the intra-atomic contribution, and one due to the screening of the valance electrons in the neighbouring atoms. This contribution is referred to as the extra-atomic relaxation, and is more important in large molecules and solids where the effect of screening by the valence electrons of neighbouring atoms is at its greatest.

2.5.2 Shake Up and Shake Off

Shake up and shake off are two related phenomena in which the ejection of a core electron is coupled to the simultaneous promotion of another electron to either a higher orbital in the case of shake up or off the atom entirely, to give rise to a doubly ionised state in the case of shake off. The shake up process give rise to features in photoelectron spectra known as satellites. In the process of Shake Up a discrete amount of energy from the exiting photoelectron excites another electron into a higher valence level. The photoelectron spectrum will show shake-up satellites at higher binding energy than the main peak. During shake off a minimum amount of energy from the exiting photoelectron is needed to eject a second electron into vacuum. Unlike shake-up, the photoelectron spectrum will not show discrete structure as the energy required for this process is not discrete. The shake-off electron is ejected and only contributes to spectral background intensity.



2.5.3 Spin Orbit Splitting

Spin orbit splitting is brought about by the magnetic interactions between the spin of an electron and its orbital angular momentum. It can only occur after photoionisation since the process requires an unpaired electron within an atomic sub-level. The process of spin orbit splitting gives rise to additional peaks in the photoelectron spectrum. All electrons orbiting a nucleus possess both orbital, and spin angular momentums, termed l and s respectively. In a neutral atom, there is a net magnetic moment of zero, since all the electrons exist in pairs of equal and opposite spins. After photoionisation there is an unpaired electron whose spin angular momentum vector \underline{s} and orbital angular momentum vector \underline{l} can interact to either reinforce or counteract one another.

The spin vector of the unpaired electron can have two orientations, $\pm \frac{1}{2}$, aligned either parallel or anti-parallel to the orbital angular momentum. This gives rise to two non-degenerate states, separated by an energy ΔE , with the parallel state usually being the

lowest in energy. The splitting brought about by the ionic state results in more than one final state for the atom, which is observed as a splitting of the photoelectron peaks into two peaks with different intensities. The splitting of the photoelectron peaks is proportional to the resultant value *j*, which is the coupling of the spin and angular momentum vectors and defined as the sum of these two factors.

For example: For an Au 4d electron, l = 2The unpaired electron resulting from photoemission can have a spin of either +½ or ½. When $s = +\frac{1}{2}$, j = s + l, =5/2

When $s = -\frac{1}{2}, j = 3/2$

The ratio of the intensities of the two peaks = 2j + 1. Therefore, the spectrum of the gold 4d electron would be a doublet with an intensity ratio of 3:2. The most intense peak is the one with the greatest value of j.

2.5.4 Multiplet Splitting

In the case of open shell systems, electrostatic coupling of one or more of the unpaired electrons in the valence sub-shell with the core hole will result in a splitting of the core energy level into one or more components, or mulitplets. For s core shells the observed feature takes the form of simple doublet splitting. For non s-levels the case in much more complicated, not least because these levels are also affected by spin orbit coupling.

For example, in the case of a core 1s electron interacting with one unpaired valence electron, (such as Li), either of the core electrons spin states can couple with either of the spin states of the valence electron. This gives rise to two final states, separated by energy ΔE . $\Delta E \propto (2S+1)$, where S is the sum of the individual s components of the unpaired electron, (in the case of Li these are 0 and 1). The intensity of the two resulting peaks are proportional to the multiplicity of the states and is given by 2(S+1). For one

unpaired core and valence electron (S=0 or 1) an intensity ratio of 2:1 would be observed.

2.5.5 Asymmetric Core Level Peaks

In the case of a metal, or semi-conductor like graphite, the electrons move in from the conduction band to screen the positive core hole, producing a distribution of electronhole pairs (or excitons). These one-electron states are available for shake up type events, giving rise to a low kinetic energy tail to the observed photoelectron peak.

2.6 The Chemical shift

The core level binding energies of an atom vary measurably with a change in the surrounding chemical environment. This effect can be explained by the redistribution of electric charge that occurs in valence orbitals when a chemical bond is formed. A good example is provided by the sulphur (2p) spectrum of sodium thiosulphate, (figure 2.4) which exhibits two well-resolved signals, with a separation of 5.9 eV. The thiosulphate anion $S_2O_3^{2-}$, contains two non-equivalent sulphur atoms, which will have unequal shares of the valence electron density of the system. Electronegativity considerations lead us to expect that the central sulphur atom, which is attached to three oxygen atoms, will have a less negative charge within a certain atomic distance around its nucleus, than within the same distance around the terminal sulphur atom nucleus. Electrostatic shielding of the 2p electron is therefore smaller for the central sulphur than for the terminal sulphur, leading to a distinctly greater binding energy in the case of the former, and hence the appearance of two well separated photoelectron signals in the thiosulphate spectrum. The equal intensity of the two peaks reflects the stoichiometry of the anion; both sulphur atoms are present in equal amounts. The shoulders present on each of the sulphur peaks is a result of spin orbit splitting, which is covered in more detail in 2.5.3

At the simplest level of approximation, embodying Koopmans theorem and an elementary description of the charge distribution in the system, the physical basis of the chemical shift is illustrated as an ionic model. The atomic valence oribitals define a spherical "valence shell" of electric charge, inside which the inner electrons reside.



The addition or removal of an electron to or from this shell, such as when the atom is bonded to another in a molecule or crystal alters the electrostatic potential inside the field. For example if q electronic charges are removed from the valence shell and brought to infinite distance, then the potential of the inner electrons decreases by the amount:

$$\Delta E = \frac{1}{r}q \tag{2.5}$$

where r is the mean atomic radius. The binding energy of the inner electron is then increased by a corresponding amount.

When chemical bonds are formed however, electrons are not taken to infinite distance, and the model can be improved by taking this into account. For an ionic compound $A^{+}B^{-}$, they are transferred from the valence shell of atom A to the valence shell of atom B. Therefore if the atomic distance between the two atoms is R the transfer in energy becomes:

$$\Delta E = \left(\frac{1}{r} - \frac{1}{R}\right)q \tag{2.6}$$

When the A^+ and B^- ions are arranged in a lattice to form a crystal, the Coulomb interaction of a core electron in one atom with all the ions in the lattice must be considered. Therefore equation 2.6 is modified by the Madelung constant α and becomes

$$\Delta E = \left(\frac{1}{r} - \frac{\alpha}{R}\right)q \tag{2.7}$$

As mentioned in 2.9 when exposed to ionizing radiation insulating materials can become charged. This has the effect of causing the photoelectron peaks of the spectrum to shift to higher binding energies. In order to correct for the shift a photo electron peak whose value can be explicitly defined is chosen, and its value fixed. All the other peaks in the spectrum are then calibrated according to the value of the difference between the experimental value of the calibration peak and its defined value. Typically calibration peaks include the $C_{(1s)}$ and, if applicable, bulk metal peaks.



2.7 Surface Sensitivity

After photoionisation the ejected electrons have to travel through the solid before they escape the surface. During this time there is a high probability that the electrons will lose energy through inelastic scattering events. This gives rise to an attenuation of the

main photoelectron peak as well as a background of inelastically scattered electrons. The scattering of electrons traveling through a solid is described by λ , and is referred to as the mean free path. It may be described as the thickness of matter that attenuates an incident electron flux by a factor e^{-1} .

If I_0 is the photoelectron flux at a particular kinetic energy E, originating at depth x below the surface of a solid, the ratio of the flux I_x emerging from the surface to the incident flux I_0 is given by equation 2.8 and represented graphically in figure 2.5.

$$\frac{I_x}{I_0} = \exp^{\left(\frac{-x}{\lambda}\right)}$$
(2.8)

The fraction of electron flux r, which is detected from within a depth x, of the solid is defined as:

$$r = 1 - \exp^{\left(\frac{-x}{\lambda}\right)}$$
(2.9)

Substituting $x=\lambda$ into equation 2.9 shows that when detected at normal emission, 63% of the emitted electrons come from a depth λ from the surface. While a typical X-ray photon might penetrate a solid to the depth of 10^4-10^5 Å only those electrons emitted from a very short distance below the surface can escape the surface and avoid being inelastically scattered.

In solids it has been shown experimentally [3,4] that the mean free path of an electron before being idealistically scattered is dependant on the kinetic energy of the emitting electron. When the mean free path is plotted against the energy of the emitting electron it produces a curve with a broad energy minimum from 10 -1000 eV. This corresponds to a mean free path of 4-20Å (figure 2.6). It is possible to enhance the surface sensitivity still further by variation of the angle at which the emitted electrons are detected ϕ (the "take off" angle). In practice only electrons which emerge at the take off angle are measured.



Figure 2.6: Graphical representation of the variation of kinetic energy with mean free path

If an electron is ejected from an atom at vertical depth d, the distance it will have to travel to escape the surface L is given by:

$$L = \frac{d}{\cos\phi} \tag{2.10}$$

As ϕ increases so does the value of L and hence the probability of inelastic scattering. By increasing the value of ϕ we can increase the surface sensitivity of the spectra. Sine the value of ϕ can affect the surface sensitivity equation 2.8 becomes:

$$\frac{I_x}{I_0} = \exp^{\left(\frac{-x}{\lambda\cos\phi}\right)}$$
(2.11)



Figure 2.7: The relationship between electron flux (I) and take off angle ϕ

This technique of angle profiling is most useful in determining the concentrations of surface materials in non-homogeneous materials. This technique involves taking XP spectra at a variety of different take off angles. The variation leads to a change in the intensity of the peaks of elements on the surface of the sample. These changes in intensity can be used to calculate the intensity of materials on the surface of non-homogeneous solids.

2.8 The Photoionisation Cross-section

The intensity of a photoelectron peak is dependant on a number of fundamental parameters, including the escape depth and the photoionisation cross-section (μ). The photoionisation cross-section is the probability that an electron will be ejected from a single orbital in a given atom. This parameter will vary with factors such as the element involved, shape, size and number of nodes of the orbital involved, and the energy of the ionizing radiation used. Generally it has been shown that for a given orbital the photoionisation cross-section is greatest when the incident photon energy is equal to the ionization potential. For photon energies much higher than this value the photoionisation cross-section falls of rapidly. Scofield has calculated values of μ for all elements up to Z = 96, for both AlK α and MgK α X-ray sources.

The photoelectron intensity is also a function of the angle θ between the direction of the incoming photons and the analyzer/detector. This angular variation of the photoemission from a sample can be defined as:

$$I(\theta)\alpha \left[1 + \frac{1}{2}\beta \left(\frac{3}{2}\sin^2\theta - 1\right)\right]$$
(2.12)

 β is called the asymmetry factor. It ranges from -1 to +2, and is a function of the incident photon energy and the nature of the photoemitting orbital [5].

$$\mu' = \mu \left[1 + \frac{1}{2} \beta \left(\frac{3}{2} \sin^2 \theta - 1 \right) \right]$$
(2.13)

The function detailed in equation 13, where μ is Scofield's tabulated photoionisation cross-section, is referred to as the modified photoionisation cross-section μ .

2.9 The Reference Level

In XPS the experimental binding energies are measured relevant to a suitable reference level, which serves as a zero binding energy.

For a conducting sample in contact with the spectrometer there will be a sharing of electrons to equalize their Fermi Levels. For this type of sample it is natural to use the fermi level as a reference point, and a simple relationship can be derived.

$$E_{bf} = h\nu - E_k - \phi_{sp} \tag{2.14}$$

 E_{bf} represents the binding energy relative to the fermi level, hv the energy of the incident photon, E_k the kinetic energy and ϕ_{sp} the work function of the spectrometer. Alternately the binding energy can be referenced to the sample vacuum level with the inclusion of the sample work function ϕ_{sa} to the binding energy data. However this choice of reference level posses several problems for solid samples, not least that the value of ϕ_{sa} must be known. This quantity is characteristic of the surface and varies,

often by quite a large amount, with the crystallographic orientation and preparation procedure used on the sample. In order to be a useful reference the sample work function must be known for each experimental condition used. To obtain precise and reliable values of ϕ_{sa} experimentally is no easy task, which is why the fermi level remains the only real choice of reference level for all solid samples.

For insulating materials and semi conductors it is generally assumed that the fermi level lies at the center of the band gap but the actual position will change depending on the concentration of donor and acceptor impurity atoms in the sample. Fixing of the energy scale with insulating materials is complicated further by the possibility of the sample becoming charged due to poor electronic conduction. This feature is caused by an inability of the sample to effectively screen core holes, and results in a positive charge on the surface, which acts as an attractive force on the outgoing photoelectron, causing it to lose kinetic energy, hence changing the measured binding energy value. This is usually what happens with real catalyst samples, and as mentioned in 2.6 the reference is most conveniently made to the C(1s) level of carbon, or another element on the surface that can be assigned an unambiguous value.

2.10 Line Broadening Effects

Since the basic process of photoemission is highly quantum mechanical, the spectra produced by the analysis of the photoelectrons kinetic energy should consist of a series of discrete lines. However the photoelectrons generated by the process of photoemission all fall within discrete bands, and the peaks generated in photoelectron spectra have finite widths as a result. The observed peak width, defined as the full width at half maximum height, or FWHM for short, is a convolution of several contributions.

2.10.1 The Natural Width of the Core Level

Heisenberg's Uncertainty Principle relates the natural width of the core hole, ΔE_0 , to the lifetime of the core hole, τ .

$$\Delta E_0 = \frac{\hbar}{\tau} \tag{2.15}$$

It can be seen that the narrower levels are derived from the longer-lived core hole states. For materials with a low atomic number, the neutralization of core holes takes place predominantly by the process of Auger emission, the efficiency of which governs the value of τ and hence the size of ΔE_0 . As a rule, an increase in the valence electron density enhances the probability of the relevant Auger transition, and thus decreases the lifetime of the core hole. As a result the line widths of the light elements, those whose main photoelectron peaks are a result of the emission of 1s or 2pelectrons, increase with increasing atomic number. It can also be noted that for a given atom the natural line width of a core level peak is inversely proportional to the orbital angular momentum quantum number $l_{.}$ For example, an Al_(2s) spectrum has a broader XP profile than that of the corresponding $Al_{(2p)}$ level. This is because the 2s core hole can be neutralized by either a transition from the valance band, or the 2p level, both of which would be accompanied by the simultaneous ejection of a valence electron via Auger emission. The 2p level can only be filled from the valence band, hence there is a greater probability of neutralizing the deeper 2s core hole, which means it will have a shorter lifetime and therefore a correspondingly broader peak.

2.10.2 Instrumental Factors

These are the major causes of line broadening in XPS and arise from two sources. The first is the inherent width of the ionizing radiation, which for AlK α and MgK α is 0.85 and 0.7 eV respectively. This means that peaks observed under AlK α radiation will be fractionally broader than the corresponding peak observed under MgK α . The second is the imperfect response of the electron analyzer, which can have line-broadening effects of up to 2eV when the spectrometer is operating at high sensitivity.

2.11 Spectrum Processing

2.11.1 Spike Removal

A spike is an anomalous point in a spectrum that can be generated by power surges. One or two such points can have a serious effect on data analysis, and so the facility exists to replace these points with a more realistic one. There are two methods of spike removal, automatic and manual. The automatic method removes all the data points with intensity far in excess of the data points surrounding it. The manual removal process relies on the judgement of the user to remove the spikes in the spectrum one at a time. Overuse of this technique can lead to the distortion of the spectra being examined so it should only be applied to a limited number of points.

2.11.2 Background Removal

In XPS the background arises from inelastically scattered photoelectrons, as well as photoionisation by high energy Bremsstrahlung radiation. In general a varying background function, increasing in intensity towards lower kinetic energy results, on which the parent photoelectron peak is superimposed. The absolute intensity of the peak can only be measured accurately following the careful removal of the contribution to the spectra made by the background. A rather crude background removal may be achieved by subtracting a linear background drawn as a straight-line tangent between the high and low energy sides of the peak. This approach, whilst simple to use, is arbitrary and does not take into account the physics of the processes that give rise to background electrons. A much better method is suggested by Shirley [6]. It assumes that the inelastic background intensity at any point under a photoelectron peak arises solely from the scattering of electrons with a higher kinetic energy, and thus is proportional to the partially integrated photoelectron intensity to higher kinetic energy, (figure 2.7). The result is a spectrum constrained to zero at either end.



2.11.3 Difference Spectra

Often an experimental spectrum consists of a dominant feature and several less intense chemically shifted peaks. The aim of spectral subtraction is to remove the dominant feature from the raw data and leave only the less well-defined peaks to be analysed. In order to get meaningful results from this procedure, a number of different factors have to be taken into consideration.

2.11.3.1 Alignment

The first step in any subtraction spectra is to make sure that the two spectra are correctly aligned, so that their data points correspond directly in kinetic energy. This necessitates that both spectra have the same number of data points per electron volt (figure 2.8). If the spectra are not aligned correctly, it may lead to the appearance of artefact peaks in the resulting spectra.



2.11.3.2 Normalisation

Once the two spectra have been aligned, they must then be normalised before the difference can be calculated. This is achieved by multiplying the spectrum to be subtracted by the correct scaling factor. The value of the scaling factor is dependant on the region under study and the information that is trying to be retrieved by the spectrum. For example, when the peak to be removed is the one at lowest binding energy (leading edge) side of the spectrum. The two regions can be matched either manually or by using an automatic procedure, which involves minimising the sum of the squares of the differences between the co-ordinates of the two spectra with in a user defined region, (usually the leading edge). In order that the presence of artefacts in the resulting spectra be avoided, care must be take not to over or under subtract the spectrum by choosing too large or too small a scaling factor (figure 2.9).



2.11.4 Curve Fitting

Curve fitting is probably the most widely used tool in the interpretation of spectra. The analyst alters a series of parameters, (height, width and binding energy), defining a user chosen number of peaks, until the calculated spectra is a reasonable fit to the experimental data. The parameters of the component peaks are then refined according to an iterative least squares method in order to obtain the best correlation possible. In practice, parameter constraints are frequently required to ensure convergence to a physically realistic solution. The most commonly used procedure is to estimate as accurately as possible the parameters of the minor peaks, and then to fix the parameters for one or more of these during the first few iteration cycles.

Often it is possible to generate more than one "best fit" for a particular XP spectrum and as such curve fitting should be applied with great caution. Meaningful results can only be obtained if independent information about the expected constituents of the spectrum is available. This data will enable the analyst to define correctly the number of peaks present, and also allows a reasonable estimate of the number of component features present. A good fit can be measured by checking the residual spectrum, which should consist only of noise.



The most common mathematical curve fitting functions are the Gaussian and Lorentzian peaks. The analysis software used in this thesis makes use of the Gaussian peaks. This function is used as it provides a better fit for adsorbate peaks which often suffer from low intensity and line broadening effects.

2.11.5 Peak Area Measurement

In order to perform the operation the spectral background must first be removed. A straight line is then plotted between two user-chosen points either side of the peak, (A and B in figure 11) and the integrated area between the line and the peak computed. It is important that the user-chosen points be such that they are part of a flat baseline, rather than extending into the actual peak. This avoids under-estimation of the peak area, which could lead to misinterpretation of results. The integrated peak areas are used in the calculation of surface coverage.



Figure 2.11: Peak integration for an O_(1s) peak following the removal of the inelastically scattered background signal

2.12 Equipment

The experimental work presented in this thesis was carried out on three separate instruments. A customised VG spectrometer given the name ESCA 5, fitted with a "high pressure" cell, an ESCAlab 220 equipped with a fast entry lock and the NCESS (National Centre for Electron Spectroscopy and Surface analysis), Scienta ESCA 300 which is equipped with a rotating Cr/Al rotating anode and monochromator.

2.12.1 Features Common to all XPS Spectrometers

The majority of all XPS spectrometers are built around the same basic design. This consists of two connecting chambers, one which is used for the analysis of materials and one which is typically used for the cleaning and preparation of samples prior to analysis. These two chambers are typically named for their function, the preparation and analysis chambers. Spectrometers also all contain a hemispherical analyser, which is attached to the analysis chamber, and a pumping system. These will be covered in more detail in later sections.



Figure 2.12: Top down schematic of a generic spectrometer (a) paralleled with the ESCA 5 spectrometer (b) used in the thesis

2.12.2 UHV Conditions

There are 3 main considerations to be taken into account when determining the pressure at which a photoelectron spectrometer operates:

- The pressure must be sufficiently low to avoid discharges that might damage the x-ray source and the electron multiplier.
- 2. Emitted electrons should come into contact with as few gas molecules as possible between the sample and the analyser, in order to avoid being inelastically scattered and lost from the spectra.

monolayer of residual gas within approximately 0.1-1 seconds, (assuming a s probability of one). A typical XP spectrum takes in excess of 10 minutes, esp during experiments when several regions are being scanned. In these circumsta sample could be scanned for several hours. Operating pressures of 10⁻¹⁰ Torr or are required for experiments involving clean surfaces. Experiments involvi analysis of catalyst samples can be run at slightly higher pressures, but as a gener lower pressures are preferable.

Ultra high vacuum (UHV) conditions can only be maintained by "bakin spectrometer at regular intervals. This involves heating the spectrometer up t temperatures, around 470 K, for several hours in order to accelerate the rate at adsorbed layers are removed from the internal surfaces. Upon cooling, the outgassing or desorption drops by several orders of magnitude, and the pumps a capable of producing and maintaining UHV conditions once more.

The necessity of baking provides some limitations on the sort of materials that used in the construction of a spectrometer. It cannot contain any materials the disintegrate, outgas excessively or loose strength at elevated temperatures. F reason most of the UHV systems currently in use are constructed of stainless jointed together by flanges sealed with copper gaskets.

Pressures of 10⁻¹⁰ Torr were routinely achieved on all of the UHV systems used combined action of various types of pump. UHV pumps cannot be opera atmospheric pressure, and therefore a rotary oil pump was used initially to rough the system to a pressure of approximately 10⁻³ Torr. Pumping via a polypheny filled diffusion pump, backed by an oil rotary pump, was then used in conjunction liquid nitrogen traps to take the vacuum system into pressures associated with

50

limitations of vacuum pumps and the different types of pressure gauge documented in a variety of texts [7-8].

2.12.3 X-Rays

X-ray sources utilise the characteristic emission lines from a target (or bombarded by high-energy electrons. The suitability of a particular source work depends upon the width of the emission line, which should be sufficiently as to avoid limitation of the achievable resolution. Acceptable emission line w considered to be less than 1.0 eV. Another consideration is the x-ray energy, s determines the deepest core level from which an electron can be emitted unambiguous spectra the energy must be high enough to excite a wide photoelectron lines. The most commonly used X-ray lines in XPS are the emission lines of Al and Mg. These have line widths of 0.85 eV and 0.7 energies of 1486.6 eV and 1253.6 eV respectively. The K $\alpha_{1,2}$ line is an un doublet resulting from $2p_{3/2} \rightarrow 1s$ and $2p_{1/2} \rightarrow 1s$ transitions subsequent to the of a 1s or K hole by electron impact. "Satellite" lines can also arise from at transitions in multiply ionised atoms, (K α_3 , K α_4 , etc) and from valance ba transitions, (K β). There are other kinds of X-ray sources that use these transition as the rotating Cr anode which will be covered in more detail in 2.15.1

The discrete X-ray lines are superimposed on a continuous radiation spectrum Bremsstrahlung. This continuum is formed when the high-speed electrons loos as they are slowed down rapidly via multiple high-speed collisions within the material. Removal of satellite interference, and improvement of signal to elimination of the Bremsstrahlung continuum, can be achieved by monocromat x-rays. This comes at the cost of the reduction of the photon flux by a factor of 15-20, (see 4.5.2 for more details).



Both the ESCA 5 and ESCALab 220 spectrometers used a double anode x-ray source, (figure 2.13). This source consists of two filaments for electron bombardment and two water-cooled anode surfaces, one of aluminium and the other of magnesium. The main reason for employing a twin anode is that in any X-ray excited spectrum both photoelectron and Auger peaks appear, and interference can result. Since photoelectron energies are linked to the energy of the exciting photon and auger energies are fixed, by switching anodes any interference can be resolved. The photon source is separated from the sample by a thin Al window, typically 2µm thick. This screens the sample from any stray electrons and from any possible contamination originating in the source region. It also serves as a filter for Bremsstrahlung radiation and for impurity emission lines.

and secondary electrons in the window that can irradiate the sample. The prese AlK α is a disadvantage if an Mg anode is in use, whilst the additional sec electrons can give rise to degradation in certain samples. Separate pumping of th source region avoids contamination of the sample by degassing product conversely maintains a clean anode surface when gassy or volatile samples are stu

2.12.4 Electron Energy Analyser

The function of an electron energy analyser is to measure the energies of ele emitted from the sample. The layout of the concentric hemispherical analyser, (and the electron detection system commonly used in x-ray photoelectron spectron shown in figure 2.14.

Two hemispheric surfaces with an inner radius R_1 and an outer radius R_2 are posconcentrically in the CHA. A potential difference ΔV is applied to the surfaces the inner hemisphere is at a positive potential, and the outer hemisphere is at a nepotential. The entrance and exit slits are centred on the median equepotential with radius $R_0=0.5(R_1+R_2)$ between the hemispheres. The electrostatic field b the two hemispheres disperses the electrons in such a way that for any given fie those within a narrow energy range pass through the field and are picked up electron detection equipment.



The equation relating the potential across the hemispheres, ΔV , their radii R₁ and R₂, and the energy E_p of the electrons that successfully pass round the analyser, in an orbit of radius R₀, is given by equation 1.

$$\Delta V = E_p \left(\frac{R_2}{R_1} - \frac{R_1}{R_2} \right) \tag{2.16}$$

Since the values of R_1 and R_2 are known when the analyser is manufactured equation one tends to be rewritten.

$$\Delta E = E_{p}H \tag{2.17}$$

where H is the hemispherical constant.

Most spectrometers are operated at a fixed electron pass energy, E_p and hence a fixed value of ΔV , which can be preset to any number of values. Typically values of 50 and 100 eV are used. A spectrum is generated, by scanning a variable retarding potential V_r applied to the Hertzog plate and analyser hemispheres while the sample remains earthed, thereby successively decelerating electrons of initially different kinetic energy E_p necessary for transmissions around the analyser to the detector.

$$E_i = E_p + V_r \tag{2.17}$$

Typical XP spectra use a retarding scan range of either 1250 eV to determine the gross features of the electron energy distribution, or 25 eV in order to analyse particular features in detail.

The degree of resolution that a spectrum can achieve is limited by the resolving power of the analyser.

$$\frac{\Delta E_p}{E_p} = \frac{\omega}{2R_0}$$
(2.18)

Where ΔE_p is the signal width at half height, E_p is the pass energy, ω is the total (entrance and exit) slit width and R_0 is the median analyser radius. Thus by decreasing the pass energy and ω the resolution can be enhanced. It must be remembered that by decreasing the slit size fewer electrons will be admitted into the detector and as a result the strength of the signal will be reduced. Similarly as the pass energy is decreased the transmission efficiency of the analyser also decreases. High resolution can only be obtained by sacrificing sensitivity, and as a result a compromise between the two needs to be reached. In this study, the sizes of the slits were unchanged, but the pass energy varied in accordance with the study being undertaken. When determining what features were present on the surface of a catalyst a high pass energy was used in order to give the best picture of what elements were present. When the individual elements were studied in detail a lower pass energy was used so that the features of the peaks present could be better resolved.

2.12.5 Electron Detection

The low electron current $(10^{-16}-10^{-13} \text{ A})$ emerging from the analyser is amplified using a chaneltron electron multiplier. This consists of a coil of semi-conducting glass, the inner surface of which is covered with a high resistance material, of high secondary emission coefficient. If a potential is applied to the ends of the tube, the surface acts as a continuous dynode. An electron entering the low potential end of the tube will strike the inner wall and cause a shower of electrons. These electrons will be accelerated along the tube, and strike the inner surface, once again causing a shower of electrons. The avalanche effect can result in a large number of electrons emerging from the high potential end of the tube; gains are in the order of 10^8 being obtained.



Figure 15: Layout of a channeltron electron multiplier

2.13 ESCA 5

2.13.1 Sample Handling

In order to change the sample a simple procedure is followed. Firstly the sample probe is positioned in the preparation chamber. Next in order to preserve the vacuum in the analyser chamber the gate valve that connects the two is closed. Because the preparation chamber is going to be opened up to the air it is important that the diff. pump connected to it is isolated to avoid damaging it. The probe is now unfastened and removed from the spectrometer. When the probe has been removed from the spectrometer, the sample holder is unfastened. Figure 2.16 shows the method by which the sample holder is secured to the probe. The previous sample is removed and the holder cleaned with acetone.



Usually a sample is secured onto the sample holder by wire clips. However this method is not feasible when studying powders, so an alternative is needed. When dealing with small amounts of material the best method is to fix the sample to the holder via the use of non-conducting double sided adhesive tape. The tape is cut to the same size as the sample holder to ensure that during analysis only the photoelectron peaks pertaining to the sample are detected. To avoid contamination the sample is placed on a sterile glass plate, and then pressed onto the tape. The process is repeated until there is an even covering of the sample over the holder. The sample holder is then reattached to the probe, which is then reattached to the spectrometer.

2.13.2 High Pressure Cell

The ESCA 5 spectrometer can be fitted with a "high-pressure" gas cell, which allows the study of samples at ambient gas pressures of up to 1 mbar. Going someway to bridging the gap that exists between model and real catalytic studies. In general model catalysts when studied are done so under ultra high vacuum conditions but industrially catalysts always operate at high pressures and temperatures, and whilst the pressures achieved in the high pressure cell are far below those used in industry they are still a great deal higher than normal UHV conditions.

Before the high-pressure cell could be installed modifications needed to be made to the sample holder used in the spectrometer. The original holder was too large and too high up to be inserted into the cell at the angle required for analysis. The solution was to insert a dogleg into the holder to lower the sample in relation to the foil window of the high-pressure cell (figure 2.16).



The high-pressure cell itself, figure 2.17, consists of a metal tube with rubber gaskets at either end, which is placed in the analyser chamber. The gaskets form an airtight seal with the end of the chamber, (through which gases are dosed), and the gate valve. A rubber gasket is also fitted onto the sample probe, in such a position so that when wound into the analyser chamber the interior of the high-pressure cell is isolated from the rest of the spectrometer, and allows UHV conditions to be maintained inside the preparation chamber. An aluminium foil window is placed on the high-pressure cell at the point opposite that of the X-ray anode. The purpose of the window is to allow the passage of photons into the cell, but to keep the interior of the cell isolated from the rest of the spectrometer. The window is held onto the cell by means of a temperature resistant epoxy resin. This ensures that the seal around the interface of the window and the cell will not be damaged by any heating that takes place or by the bake out that is

necessary after installing the cell. Further care must be taken during installation to ensure that the window is not punctured in anyway, this includes when the machine is pumped down to UHV after installation of the cell is complete. If the pressure inside the cell becomes too high relative to the pressure outside it, the aluminium window on the high pressure cell will break as the pressure attempt to equalise. The same is true if the pressure outside the cell becomes much greater than the pressure inside the cell. To avoid this, the both the inside and outside of the cell are pumped down together.

In order for the photoelectrons generated by XPS to be detected while the high-pressure cell is in place, a small hole is drilled at the point of the cell which faces the electron input lens. A cone is also placed on the lens itself to minimise the amount of escaping gas that can come between the sample and the lens (figure 2.18).



Figure 2.18: Set up of "high pressure" gas cell inside spectrometer

2.13.3 Gas Handling Line

The gas handling system provides a way to store and admit ultra-pure gases from their containers into the preparation chamber, and thereby minimise contamination to both the sample and to the gases.

The system, shown schematically (figure 2.19), consists of a stainless steel mixing chamber, a vacuum pumping system, four gas cylinder inlet ports, two variable

admission leak valves, and an ion gauge. Numerous valves allow some degree of control over gas mixture composition.



2.14 ESCALab 220

2.14.1 Fast Entry Lock

Both the ESCAlab and the ESCA 300 were fitted with a fast entry lock, to allow for easy transfer of samples. The fast entry lock consists of an isolatable chamber with a hinged door fitted with a rubber gasket. When the chamber is sealed the fast entry lock can be opened quickly and samples changed over with a minimum of fuss.

The preparation chamber also contained a parking bay for samples, so that multiple sample plates could be stored under UHV even while the entry chamber itself was being let up to air.

2.15 ESCA 300

2.15.1 Rotating Anode

The ESCA 300 was fitted with a rotating anode X-ray source that made use of $CrK\beta$ and AlK α radiation. In principle the rotating anode generates x-rays in the same method as the fixed anode (2.13.1). It has been found that the power of the x-rays can be greatly enhanced by continually presenting a freshly cooled surface to the electron beam. A typical rotating anode utilizes this principle by continually cooling a rotating disc composed of the anode material, chromium and aluminium in the case of the ESCA 300 at NCESS, which is cooled by a continuous flow of water as it rotates. The anode is required to rotate at speeds of 4000 and 10000 rpm, depending on which type of radiation is being used, and needs excellent dynamic balancing to keep the electron beam focused on the disc. The disc itself is a 300 mm in diameter Ti alloy disc [9]. Radiation is generated by focusing the electron gun onto either an Al or Cr band on the rim of the anode.

2.15.2 Monochromator

Both the ESCAlab 220 and the ESCA 300 were fitted with monochromators, although only the monochrometer on the ESCA 300 was used in the work presented in this thesis. A monochromator is a device which is used to improve signal resolution by removing background caused by satellites and bremsstrahlung radiation. This is done be focusing the x-ray flux with a series of quartz crystal dispersers to focus only radiation of a specific energy onto the sample. On the ESCA 300 beryllium foil prevents electrons from the anode chamber reaching and damaging the quartz crystals. An Al foil window separates the monochromator chamber from the sample analysis chamber. This maintains good vacuum in the analysis chamber and prevents electrons generated in the monochormator chamber from entering and contributing to the background of the spectra. The two foils transmit approximately 60 % of the emitted AlK α radiation [10]. This allows useful signals from elements present at small concentrations, or from small analysis areas to be obtained, although it does also lead to a loss in signal strength and longer scanning times.





There are other benefits to using a monochromatic x-ray source. The lack of unwanted radiation and heat, which occurs due to the sample being separated from the x-ray source, means that any damage caused that could be caused to the sample by these factors, is minimized. The monochromator also provides a much better energy resolution than standard achromatic sources. This is beneficial because it allows for the separation of photoelectron peaks whose binding energies are very similar.

2.16 References

- 1. A. Einstein, Ann. Phys. 1905, 17, 132
- 2. T.A. Koopmans, Physica 1933, 104, 1
- 3. D. Penn, J. Elect. Spec. Rela. Phen. 1976, 29, 9
- 4. C.R. Brundel, J. Vac. Sci. Technol., 1974, 11, 212
- 5. R.F. Reilman, A. Msezane, S.T. Manson, J. Elec. Spec. Rela. Phen. 1976, 8, 389,
- 6. D.A. Shirley, Phys. Rev. B, 1972, 5, 4709
- 7. H.J.J Braddick, The Physics of Experimental Method, Science Paperbacks, 1963
2.17 Bibliography

D. Briggs, M.P. Seah, Practical Surface Analysis by Auger and X-ray Photos Spectroscopy. John Wiley and Sons Ltd, 1984.

D. Briggs, Handbook of X-ray and ultra-violet Photoelectron Spectroscopy, Ha Son, London, 1977

A.F. Carley, PhD thesis, University of Bradford, 1980

This chapter also describes the rigs used to test the activity of the catalysts, an brief details of the characterisation techniques used.

3.2 Preparation Methods

In the study of gold catalysis, a large number of different methods have been pr in the literature [1-3]; however of these methods three dominate the field:

- 1. Impregnation of a preformed support with a solution of a salt of the meta used, in this case gold, followed by drying and reduction; this my be don by filling the pores of the support with a solution of the metal, or by susp the support in a larger volume of the metal solution and removing the solu-
- Exchange of protons or other cations associated with the support for cather the desired element, followed by washing drying and reduction.
- Precipitation of hydroxides or similar precursors to both support and followed by drying, calcinations, or reduction.

3.2.1 Impregnation

This is the simplest method of catalyst preparation, and was employed widely early attempts to create supported gold catalysts. The process itself is fairly forward. A solution of the active component of the catalyst is made up and the material dipped into a tank containing the component solution.

The salt used most frequently in this process is chloroauric acid (HAuCl₄.3H₂O but some times auric chloride (AuCl₃ or Au₂Cl₆) is used instead [7]. Complementioned in connection with this method include potassium aurocyanic

not limited to, calcinations at temperatures as high as 800°C [11], and reduced hydrogen at 250°C [11]. Low concentrations of chloroauric acid on silica (< 0. and on γ -alumina (<5 wt%) are thermally unstable and the pristine yellow changes to a mauve that resembles the colour colloidal gold. This change occurs normal drying in air and has been followed as a function of time at 120°C by exponenced chloroaurate ion with water [12]. After such decomposition, require no further reduction to render them active, but when decomposition take place it requires reduction in hydrogen at 120-250°C.

A common form of impregnation is a technique called incipient wetness. In this of normal impregnation technique, rather than being submersed in a tank of the solution it is added to the support material drop wise until the saturation point is In both cases the uptake of the solution is determined by the porosity of the support the concentration of the active solution.

3.2.2 Ion exchange

The process of cation exchange by which protons or other cations within the structure on the surface of a support material are replaced by cations of the active metal g to atomically dispersed species, and then if calcination and reduction in hydre undertaken, small metal particles. This method has not been applied widely, or great effect, for preparing small particles of gold. The most likely explanation f the limited number of cationic gold complexes available. The ethylenediamine $[Au(en)_2]^{3+}$ is known and the ammine of Au^1 , $[Au(NH_3)_2]^+$ has only recent reported [10] but has yet to be applied to the preparation of supported gold catal

3.2.3 Co-precipitation

The first row transition elements in Groups 4-12, as well as some of the preceding spmetals like aluminum and magnesium, form hydroxides or hydrated oxides when a solution of a soluble salt is rendered basic. In some cases the structure of the dried precipitate can be easily identified as a hydroxide, but in others it may be poorly defined or amorphous until the material is dehydrated and a recognizable oxide formed [13]. It is dubious whether all of the substances formed by precipitation from nitrate solutions with sodium carbonate, or hydrolysis of the chlorides as in the case for vanadium and titanium supports, can be described as hydroxides. Co-precipitation of two hydroxides has frequently been used to prepare supported base metal catalysts, usually with alumina acting as the support. Mixed hydroxides of base metals have served as precursors to bimetallic or alloy catalysts [14]. Ammonium carbonate or bicarbonate has often been used to raise the pH, because its ions readily decompose during calcination. It is necessary to raise the pH of the solution to facilitate the precipitation of the support and active material. The sodium ion is renowned for being difficult to remove by washing, which makes it a strange choice for use in the preparation of gold catalysts. It seems probable that a great deal of gold catalysts made by this method contains significant concentrations of sodium ions, and if a metal chloride was used as a precursor, chloride ions. Both of these may act as a catalyst poison [15].

The co-precipitation route devised by Haruta and his co-workers [15] has been widely copied, giving rise to a variety of similar experimental procedures, including one semi-automated method [16-17]. After drying the precipitated catalysts are sometimes calcined, at a variety of temperatures ranging from 200-800°C [6, 18, 19]. There has been no systematic study of the process that occurs during calcination.

3.2.4 Deposition-precipitation

This method involves bringing the precursor of the active species out of solution in the presence of a suspension of the support in a manner similar to that of co-precipitation, (i.e. by raising the pH). The surface of the support acts as a nucleating agent and if this method is preformed properly, leads to the greater part of the active precursor being attached to the surface. The key to this technique lies in preventing precipitation away

from the support surface by avoiding local high concentrations of alkali. The most successful method used to achieve this was developed by Geus [27]. This method involved the slow decomposition of urea in solution at about 353 K; hydroxyl ions are generated uniformly throughout the liquid phase and the concentration is always low because they are consumed almost as soon as they are formed.

Deposition-precipitation has the advantage over co-precipitation in that the entire active component remains on the surface of the support, and none is buried within it. The procedure has been used to prepare a number of supported gold catalysts [18, 20, 21-22] and is preferred to co-precipitation on the grounds that it gives narrower particle size distribution. The urea precipitation method has yet to applied to the construction of supported gold catalysts, instead the pH of a solution of gold chloride is raised to a value between 6 and 10, and the partially hydrolyzed species [Au(OH)_nCl_{4-n}]⁻ (n=1-3) then react with the surface of the support to form Au(OH)₃. The rate and particle size after calcination is dependent on the temperature and the value of n, which increases with pH. Particles smaller than 4 nm are formed when the pH is in excess of 6.

It has been found that, for both co-precipitation and deposition-precipitation, precipitation at a pH ranging from around 7 to 8 is preferable depending on the oxide support [23]. At this pH the value of n of the partially hydrolyzed species $[Au(OH)_nCl_4]$ [Au(OH) is close to 3. At lower pH there is less hydrolysis of the Au-Cl bond. Also, at pHs below the isoelectric point of the support, the surface is positively charged and is capable of adsorbing more of the negatively charged gold species. This gives rise to not only a larger gold loading, but also a higher concentration of chloride on the surface. When present, chloride increases the mobility of gold on the support, which leads to larger gold particles [24]. At pHs above the isoelectric point of the support oxide, adsorption of the negatively charged $[Au(OH)_nCl_{4-n}]^-$ complex decreases rapidly, resulting in a lower gold loading. On the other hand the particles that are formed will be much smaller, since there will be less chloride on the surface.

Another effect of the pH used for precipitation concerns the adsorption of Cl ions in addition to the gold complex, $[Au(OH)_nCl_{4-n}]^T$. The amount of chloride adsorbed decreases as the isoelectric point is approached, when the oxide is no longer positively charged. The adsorbed Cl ions cause agglomeration of the gold particles during

involves a stream of a volatile compound of gold transported to a high area su an inert gas. Here the gold compound reacts chemically with the surface of the to form a precursor to the active species. Dimethylgold(III) β -diketone has been to a number of supports, including alumina and titania [13], as well as som supports that deposition-precipitation would not be appropriate for.

In the grafting method, a gold complex in solution reacts with the surface of a forming species convertible to a catalytically active form. The con $[Au(PPh_3)]NO_3$ and $[Au_9(PPH_3)_8](NO_3)_3$ have been grafted onto the surface o precipitated hydroxides to give catalysts active for carbon monoxide or Manganese and cobalt hydroxides have been shown to be particularly effect supports [24-25].

Standard vacuum evaporation from a heated source has been used to make ve gold particles [38], but they are not "supported" in the sense that they are po useful catalysts. However the co-sputtering of gold on a metal oxide in oxyg annealing, leads to films that are quite useful as sensors. [26]

3.2.6 Catalyst Aging

Although not an actual method of preparation, aging is an important process play a big role in determining the activity and stability of a catalyst. The behind aging is twofold; to simulate the process of spending long periods of catalytic reactor and to alter the support, simply to see the effect it will have activity of the catalyst. This is done for two reasons; the first is to see how n activity of the catalyst will change over time, and to see how this change is about. Obtaining catalysts that have been used for several years is not really level of 1 part in 10⁹, then 1 year of poisoning by the plant could be simulated by 50ppm of poison to the gas stream for 10 minutes [29]. The drawback to this ap is that the adsorption and subsequent reaction of the poison might be different to a catalyst that had been in a reactor for a year as the conditions under which the built up are different.

3.3 Catalyst preparation

3.3.1 Au/Fe₂O₃

Catalysts were prepared with various loadings; 5.7, 2.9 or 1.5 atom% Au. correspond to approximate loadings of 11, 5.5 and 2.75 wt% Au. The notation 'Au' is used to refer to the percentage of metal atoms that are Au atoms. For example, Au means that in that particular catalyst there is 5 Au atoms for every atoms.

The catalysts were prepared using one of two different co-precipitation method precipitation was chosen over other methods such as impregnation for several referstly, catalysts produced by co-precipitation have proven to be some of the active for carbon monoxide oxidation [27]. Secondly previous studies by Hu group [6] have focused on catalysts produced by the method described in 3 following a similar preparation method and similar reaction conditions a more a comparison is possible.

Two methods of preparation were used to investigate the effect of pH on the acti the catalyst. When catalysts are created by co-precipitation, such as in the r described below in 3.3.1.1, the pH is raised from an acidic solution to around 7 of is unknown whether or not the change in pH affects the activity of the catalyst, or whether only the final pH plays a role. By comparing the activities of catalysts prepared by a method where the pH is changed (3.3.1.1) and a method where the pH remains the same (3.3.1.2) the effect of pH could be investigated.





Figure 3.1: Experimental set up for the production of iron oxide supported gold catalysts by co-precipitation

This method involved the dropwise addition of an aqueous solution of sodium carbonate, Na₂CO₃, to a mixture of chloroauric acid, HAuCl₄, and iron nitrate, Fe(NO₃)₃.9H₂O, in order to obtain a precipitated product [14]. The equipment used in the preparation of the catalysts is shown in figure 3.1. For example in the preparation of the 5.7 atom% Au samples, 50 ml of Fe(NO₃)₃.9H₂O solution (10.1 g, 25 mmol in 250 ml deionised water) was mixed with 5 ml of HAuCl₄ solution (5 g, 15 mmol in 250 ml deionised water). The mixture was stirred constantly and precipitated at 80°C using a 0.25 M Na₂CO₃ solution until a pH of 8.2 was reached. The precipitate was filtered and

washed with deionised water (1 l) heated to 80°C. Following washing, the catalyst was dried in air for a period of 12 hours.

3.3.1.2 Method 2- Co-Precipitation at constant pH

The second method of preparation was similar to the first, except instead of Na_2CO_3 being added to the Fe(NO_3)₃/HAuCl₄ solution until a pH of 8.2 was reached, the Fe(NO_3)₃/HAuCl₄ solution was added to a solution of Na_2CO_3 at a pH of 8.2. The pH was maintained by the addition of extra Na_2CO_3 when it fell below 8.2, and the addition of an acid, HCl or acetic acid, when the pH rose above 8.2. With the exception of the iron/gold and sodium carbonate solutions, the experimental setup was the same as depicted in figure 3.1.

3.3.1.3 Heat Treatment of Catalysts

Subsequent to the drying process, samples (typically between 0.5 - 1g depending on the mass of the catalyst produced) were taken and heated at various temperatures for varying lengths of time. The temperatures selected and the times that the samples were heated are as follows; 75°C/8 h, 120 °C/8 h, 200 °C/8 h, 300 °C/3 h, 400°C/3 h.

There were two methods of heat treatments used, and it became apparent during testing that the different methods employed led to differing catalyst activities.

3.3.1.4 Heating Method 1 – Fan Assisted

In this method the sample was placed in a GC oven and raised to the required temperature quickly, with a ramp rate of 10°C/min. The fan oven provided rapid air circulation during the heating process.

3.3.1.5 Heating Method 2 – Static Atmosphere

In this method, the sample was placed inside a glass vessel, with an internal diameter of 30 mm, in a furnace and heated to the required temperature at a rate of 5 °C/min. Here

detailed in 3.3.1.1, and had a gold loading of 5 wt%. Solutions of HAuCl₄ (15 250 ml deionised water) and zinc nitrate, $[(Zn(NO_3)_2.H_2O), 25 \text{ mmol} in deionised water]$ were mixed together and heated to 80 °C. 0.25M Na₂CO₃ solutionadded dropwise with continual stirring until a pH of 8.2 was reached. The precipitate was then filtered immediately, and washed with warm water (1 being allowed to dry at room temperature overnight.

The zinc supported catalysts were heat treated in the same manner as the in supported catalysts, at temperature of 120°C and 400°C.

3.4 Experimental.

3.4.1 CO Oxidation Reactor

The catalyst samples produced underwent online testing for CO oxidation temperature (figure 3.2). The flow rates of the oxygen, pure, and CO, 1 balanced in He, were fixed at 50 ml/min and 5 ml/min respectively, giving a g space velocity of 3300 ml h^{-1} . The samples were tested in amounts of 0.02 period of 8 h.

The flow rates of the gases were controlled by two Brooks 5058 series m controllers positioned in front of the sample. The catalyst was placed in a glas and maintained at a temperature of 23°C by a water bath. This was done to fluctuations in conversion caused by variations in ambient temperature. Afte over the catalyst, the composition of the exit mixture was determined by a Var gas chromatograph equipped for online analysis. The gas chromatograph v with a thermal conductivity detector and a carbosensitive column. The percentage of the CO converted to CO_2 was calculated by dividing the area of the CO peak detected by the gas chromatograph by the summation of the areas of both the CO and CO_2 peak areas and multiplying by 100. As both CO and CO_2 have almost identical thermal conductivities there was no need to correct for different response times.



3.4.2 Hydrogenation Reaction Conditions

Several samples of Au/Fe₂O₃ catalysts were tested online for the hydrogenation of crotonaldehyde. The reactor (figure 3.3) consisted of a glass reaction vessel (i.d. = 9 mm), into which the catalyst sample was placed, which was connected at both ends to two stainless steel tubes. The outlet was connected directly to the gas chromatograph, and the other allowed reactant feed into the reactor. The reactor was fitted with a thermocouple in order to allow for monitoring of the temperature inside the reactor. Catalysts were tested in 0.2 g amounts for a period of 3 h. The weight hourly space velocity for each experiment was 0.7 (g crotonaldehyde) (g of catalyst)⁻¹ h⁻¹, the H₂: crotonaldehyde ratio was 14:1. In some cases, before experiments were carried out, the catalyst samples were reduced in hydrogen for a period of 1 h, at a temperature of 250°C. The reaction was carried out over a range of temperatures from 250 °C to 100°C.

Crotonaldehyde was fed into the reactor via a syringe pump set to deliver a constant amount of crotonaldehyde over a 3 h period. The syringe was located down stream of the glass reaction vessel to allow the crotonaldehyde to vaporise and mix with the hydrogen before reaching the catalyst. The reactor was tested without any catalyst sample present to ensure that no reaction occurred due to materials used in its construction.





A Varian 3400 gas chromatograph, equipped for on-line analysis and fitted with a flame ionisation detector, was connected to the reactor upstream from the glass reaction vessel to analyse the products of the reaction. A 30 m DB wax capillary coloumn (i.d = 0.53mm) was used.

Products were identified by comparing reaction times with authentic samples of the expected products. The selectivity of each products was calculated by dividing the peak area of the product by the summation of the peak areas of all the products and multiplying the result by 100. No correction was made for the differing response times of the molecules in the FID. However since all of the products have the same carbon

information that can be derived from them.

3.5.1 XPS

In XPS the sample is bombarded with photons from an x-ray source, usually All the emitted electrons analyzed. The advantages of XPS are that it is chemic: elementally sensitive, since the energies of the emitted electrons vary with elem that elements immediate environment. Due to the nature of the emitted elect technique is also surface sensitive, detecting only the first couple of layers of a the surface. XPS was a primary method of characterization used in this projec explained in greater detail in Chapter 2

3.5.2 XANES

XANES (X-ray Absorption Near-Edge Structure) is an x-ray adsorption te similar to EXAFS (extended x-ray adsorption fine structure). It involves dim monochromatic x-ray beam at a sample. The energy of the beam is increased s traverses the adsorption edge of the elements contained in the sample. Th adsorption edge region is defined as energy up to ~1000 eV past the energy at w photon emitted by the x-ray beam is completely absorbed, and a photoelectro core hole produced (see 2.1 for more information).

The post-adsorption edge is typically divided into two areas, the near edge extended fine structures. The near edge region typically runs to 30-40 eV absorption edge, while extended region covers the 40-1000 eV photon energy. The intensity of the emitted photoelectron flux is modified by scattering

photoelectron wave by near by atoms, and in the near edge region multiple scattering events dominate the spectra. These are less common in the extended fine structure. Theoretical multiple scattering calculations are compared with experimental XANES spectra in order to determine the geometrical arrangement of the atoms surrounding the absorbing atom. In XANES the absolute position of the adsorption edge contains information about the oxidation state of the adsorbing atom. XANES can also provide information on the vacant orbitals and electronic configuration of the absorbing atom.



3.5.3 BET

This technique is used to measure the surface area of a material. It takes its name from the Brunauer-Emmett-Teller isotherm, which is used to obtain the values necessary for the calculation. The technique works by measuring the volume of gas, generally nitrogen, adsorbed by the catalyst at 77K over a series of pressures, and using the BET isotherm calculate the volume of adsorbed monolayer.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c - 1)}{V_m c} \frac{P}{P_0}$$
(3.1)

$$c = e\left(\frac{H_1 - H_L}{RT}\right) \tag{3.2}$$

Where V is the volume of gas adsorbed, V_m is the volume of an adsorbed monolayer of gas, P the pressure of gas and P₀ the saturated vapour pressure of the liquid; H₁ is a fixed heat of adsorption and H_L the latent heat of evaporation, R is the gas constant and T is the temperature. Once V_m has been obtained it is used to calculate the surface area. If V_m is recorded in m³/g, and expressed at standard temperature and pressure, then the number of moles adsorbed in one monolayer can be calculated by dividing V_m by 0.0224 (the amount of space occupied by one mole of gas at standard temperature and pressure expressed in m³). The number of molecules in that monolayer can then be derived by multiplying the result by Avagadros number. If A is the area occupied by a single adsorbate molecule, then the surface area S_g of the catalyst must be given by :

$$S_g = \frac{V_m}{0.0224} \times 6.023 \times 10^{23} \times A \tag{3.3}$$

3.5.4 TEM

Using electron microscopy, it is possible to form structural images from electrons transmitted through a sample or from those that rebound from the sample. Transmission Electron Microscopy (TEM) is used to give high-resolution images of internal structures and relies on the incident electrons that pass through the sample when it is subjected to a beam of monoenergetic electrons.

The electron beam is formed in a similar manner to the one used in Scanning Electron Microscopy (SEM). Incident electrons are formed on a tungsten filament by passing through an electric current. A voltage is then applied to accelerate the electrons which are then focused by electromagnetic lenses whilst progressing towards the sample. The

- Amsterdam,
- J.R Anderson, The Structure of Metallic Catalysts, 1975, Academic Pro York,
- 3. F. Pinna, Catal. Today, 1998, 41, 129
- 4. J. Schwank, G Parravano, and H.L. Gruber, J. Catal., 1980, 61, 19
- P.A. Sherman, G.C. Bond and P.B. Wells, J. Chem. Soc., Faraday Tran 75, 385
- G.J. Hutchings, K. Blick, T.D. Mitrelias, S.J. Hargreaves, R.W. Joy Kiely, and F.E. Wagner, Catal. Lett., 1993, 50, 211
- 7. S.D. Lin, M. Bollinger and M.A Vannice, Catal. Lett., 1993, 17, 245.
- 8. S. Galvagno and G. Parravano, J. Catal, 1978, 55, 178
- 9. J.Y. Lee and J. Schwank, J. Catal., 1986, 102, 207
- 10. Y. Yuan, A.P. Kozolva, K. Asakura, H. Wan, K. Tsai, and Y. Iwasawa, 1997, 170, 191
- 11. E.D. Park and J.S. Lee, J. Catal., 1999, 186, 1
- 12. D.M.P. Mingos, J. Chem. Soc. Dalton Trans., 1996, 561
- 13. V. Ponec and G.C. Bond, Catalysis by Metals and Alloys, 1999, Amsterdam,
- S.D. Gardner, G.B. Hoflund, M.R. Davidson, H.A. Laitinen, D.R. Sch B.T. Upchurch, *Langmuir*, 1991, 7, 2140
- 15. M. Haruta, Catal. Today, 1997, 36,153
- 16. S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schyer B.T. Upchurch Kielin, *Langmuir*, 1991, 7, 2135
- 17. R.D. Waters, J.J. Weimer, and J.E. Smith, Catal. Lett., 1995, 30, 181
- 18. A.I. Kozlov, A.P Kozlova, H. Liu and Y. Iwasawa, Appl. Catal. A, Ge 182, 9.
- 19. W. Vogel, D.A.H. Cunningham, K. Tanaka, and Haruta, Catal. Lett., 1 175

- J. Catal. 2002, 210, 375
- 25. M. Valden, X. Lai and D.W. Goodman, Science, 1998, 281, 1647.
- 26. K. Heinemann, H.K. Kim, and H. Poppa, J. Vacuum Sci. Technol., 1979
- 27. G.C. Bond, Catal. Rev. Sci. Eng. 1999, 41, 319
- 28. C.B. Faust, Modern Chemical Techniques, 1992, RSC
- 29. M.V. Twigg, Catalyst Handbook 2nd Edition, 1989, Wolfe

3.7 Bibliography

- J.M. Thomas, J.W. Thomas, Principles and Practice of Heterogeneous C 1997, VCH
- E.K. Rideal, H.S. Taylor, Catalysis in Theory and Practice, 1926, Mac. Co.
- 7. J.M. Thomas, J.W. Thomas, Introduction to the Principles of Hetero Catalysis, 1967, Academic Press
- M.W. Roberts, C.S. McKee, Chemistry of the Metal-gas Interface, 1978 University Press.
- 9. M.V. Twigg, Catalyst Handbook 2nd Edition, 1989, Wolfe

<u>Chapter 4: Room Temperature Oxidation of Carbon</u> <u>Monoxide by Supported Gold Catalysts</u>

4.1 Background

Until about 25 years ago [1], it was thought that when oxygen was adsorbed onto a gold surface a very stable oxide was formed. It was also noted that the presence of calcium on the surface led to an increase in the ability of gold to adsorb oxygen [2, 3]. However none of the studies in that particular area could agree on the extent of the oxygen coverage. In the end it was found that the strongly bonded oxygen state was due to impurities in the gold samples studied; in this case calcium

Research has shown [4-6] that in general unsupported gold (powder, wire etc) is at best only weakly active towards processes such as carbon monoxide adsorption. It is worth noting, however, that gold powder with a mean particle size of 76 nm has shown activity between -24 and 21°C for carbon monoxide adsorption [7]. The smallest catalytically active cluster was found to be $Au_8[8]$.

Much higher activity for CO oxidation has been shown by gold particles with a size below 5 nm supported on an oxide. Regardless of the method of preparation of the catalyst, the particle sizes that showed the highest levels of activity were those with a size between 2 and 3 nm [9-11]. The choice of support for the catalyst is also important. Current research indicates that the most successful types of support are those that utilise an oxide of the first row of the transition elements, generally from Groups 4 – 12 [12]. Recently iron and titanium oxides have generated a lot of interest, though the oxides of nickel, manganese, and cobalt are also effective [13]. Good catalytic activity is very often associated with disorder in the support, either generally or just in the neighbourhood of the gold particle [13].

It has also been argued [10,13] that both the methods of preparation and pre-treatment play a rule in shaping the activity of gold catalysts. It is not readily apparent, however, under what circumstances some of these processes, calcination being a prime example, have a beneficial effect on the activity of the gold catalyst. It is also unclear as to which oxidation state the active gold particles are in.

It has been suggested that the active site was to be found at the junction between a small gold particle and a transition metal oxide support [12,14]. In support of that idea is the observation that under comparable conditions large unsupported gold particles are at best only poorly active [5], although large unsupported particles also have less surface area, which could also contribute to the effect. However it is also possible that the active site may be related to the periphery of the gold clusters. If this is the case then clearly, as far as the peripheral gold atoms are concerned, the rate will increase as the particle size decreases. Electrocatalytic oxidation studies [13] suggest that gold atoms having low coordination number (CN) are more easily oxidisable than those with a high CN due to the fact that they are more electropositive. Therefore the simultaneous presence of both atoms and ions cannot be ruled out. Recent research has also shown that there are differences in the low CN sites, and that only those around the periphery of the gold particles play a role in the oxidation of carbon monoxide [33].

4.2 Experimental

4.2.1 Spectroscopy

4.2.1.1 XPS

All of the XPS analysis carried out in this chapter was performed using the ESCA 5, ESCALab 220, and ESCA 300 spectrometers that have been previously detailed in Chapter 2.

4.2.1.2 XANES

The XANES experiments were performed at beamline X-18B at the national Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY, USA. The storage ring electron energy was 2.5 GeV, and the ring current varied within the range of 110-250 mA. The XANES spectra were collected at room temperature in

fluorescence mode, which was chosen rather than the transmission mode, because of the high absorbance by Fe at the Au L_{III} edge (11919 eV). The Si (111) channel cut crystal monochromator was detuned by 20-25% at the Au L_{III} edge to suppress the higher harmonics in the X-ray beam.

4.2.1.3 TEM

TEM was performed in a JOEL 2000EX high-resolution electron microscope operating at 200 kV. A low light level TV camera and video recorder were used to capture images at low illumination level in order to minimize the possibility of electron beam induced sample modification.

4.2.1.4 BET

The BET surface area of selected samples was obtained from N_2 adsorption data which were measured at liquid nitrogen temperature with a Micromatic Gemini. Prior to analysis, the sample was degassed under helium at 105°C for a period of 30 minutes.

4.3 Results

Several iron oxide supported gold catalysts were tested for room temperature oxidation of carbon monoxide by using the method described in chapter 3. These catalysts had a loading of 5.66 atm%Au and were dried in air for a period of 12 hours. These catalysts displayed an initial activity of 99% but suffered from a small decrease in activity over the course of the experiment. The final activity of the samples was 95%.

In order to clarify if the observed activity of iron oxide supported gold catalysts was an effect of either the gold or iron oxide alone each material was tested individually. This was achieved by precipitating both the gold and iron oxide species separately, using the same method as detailed in Chapter 3 for the preparation of the catalysts by coprecipitation with increasing pH. After precipitation the samples were washed with 1 l of hot water before being allowed to dry in air for a period of 12 hours. The supported catalysts proved to be far more active than either material alone (figure 4.1).



conversion of CO to CO₂ over the course of the experiment (figure 4.2). When compared to the activity of the 5.7 atom % Au/Fe₂O₃ catalyst a clear difference between the individual gold and iron oxide powders and the iron oxide support gold can be seen. This seems to indicate that the activity of the catalyst is not a result of the activity of either of the unsupported gold or the pure iron oxide

When heated to 120°C for 8 hours in a furnace oven the activity of the 5.7 atom% catalyst changes very little in relation to that of the uncalcined material (figure 4.3). The initial activity of the uncalcined catalyst is slightly higher than that of the catalyst dried at 120°C, and this activity is maintained for a longer period of time before the catalyst starts to deactivate. When calcined at 400°C for three hours the activity of the catalyst drops to 30% of the value of the uncalcined material. This conversion drops over time to 20%.



The 1.5 atom% catalysts also show a very high activity (figure 4.4). The uncalcined 1.5 atom% catalyst has an initial activity of 96%, which drops steadily over a period of 400 minutes to reach a seemingly steady conversion of 85%. The activity of the 1.5 atom% catalyst improves slightly when the material is heated at 120°C for 8 hours. The catalyst has a higher initial activity, achieving complete conversion of carbon monoxide

to carbon dioxide. The 1.5 atom% catalyst calcined at 120°C is also more stable than the uncalcined material. While it still deactivates over the time online its activity only drops to 95%.

All of the supported catalysts show a small drop off in activity, typically around 10% over a period of 500 minutes. As previously mentioned (1.6), it has been shown that deactivation due to recrystalisation of the support occurs in both CuO and ZnO supported catalysts that do not undergo aging after being precipitated [26]. Since the Au/Fe₂O₃ catalysts are not aged either, it seems possible that the deactivation is due to a similar cause; the recrystalisation of the amorphous precipitate with the passage of time [26].



The method of co-precipitation, either by increasing pH or static pH, used to prepare the catalysts has little effect on the activity of a catalyst. It can be clearly seen that all variations of the methods used gave similar activities (figure 4.1 and 4.5). The choice of acid used to stabilise the pH has a small effect on the activity of the catalyst. When

HCl is, used the catalyst deactivates slightly faster. The most prophable reason for this is that chlorine from the acid ends up on the surface of the catalyst and reduces its activity. Chlorine has been shown to be a poison on many different gold catalysts [17].



The uncalcined 2.91 atm%Au catalyst showed a lower initial activity for CO oxidation than either the 1.5 or 5.7 atm%Au catalysts. The uncalcined 2.91 atm%Au catalysts also deactivated further than the catalysts with other Au loadings. The calcination of the uncalcined 2.91 atm%Au at different temperatures was undertaken to see if it is possible to change the activity of a catalyst and thereby discover what series of treatments is necessary to produce the best possible catalyst for CO oxidation.

The uncalcined iron oxide supported catalyst (figure 4.6) shows an initial activity of around 90%. This tails off to 70% over a period of 420 minutes before flattening off and giving a steady state conversion of 65%. When the catalyst samples are heated to 75°C for 8 hours the initial activity is around 40%, which stays relatively constant throughout the reaction time, but does drop in activity to 35% towards the end. When heated at 120°C for 8 hours the activity of the iron oxide supported gold catalyst rises to

nearly 100%. This activity is reasonably constant for the entirety of the reaction, with the final activity being 96%. The activity of the catalysts heated to 200°C for 8 hours is constant throughout the reaction time, achieving a steady state conversion of 10%. Heating the catalyst for 3 hours at 300°C raises the initial activity of the catalyst to just below 60%. This is followed by a rapid loss of activity, with a final activity of between 25 and 30% being recorded. Calcining the catalyst at 400°C for three hours produces an initial activity of 35% but this drops off, until a steady state conversion of 20-25% is achieved.



While it has been shown that the temperature of calcination plays an important role in determining the activity of a catalyst, it may not be the only factor (figure 4.7). When the uncalcined 2.91 atm%Au catalyst is heated in a GC oven at 120°C with circulating air for 8 hours the activity, as previously noted is on average 98%. However when the same sample is heated to the same temperature in a furnace under static conditions the reactivity of the catalyst is much lower, never managing to rise above a conversion of 1%.



The uncalcined zinc oxide supported catalyst (figure 4.8) has an initial activity of 90%, although it shows a steady decrease in conversion with time on-line, with the final steady state activity being 80%. When heated to 120°C for 8 hours the initial activity of the zinc oxide supported catalysts drops to 30%. There is a slight drop off in activity of 5% over the course of the reaction, with the catalyst achieving a steady state conversion of 25%. When calcined at 400°C for three hours the catalyst shows very little activity at all. The initial activity is around 1% but this conversion drops off to zero after 100 minutes online. The possible causes for this deactivation are discussed in more detail in section 4.4.3.

The effect of calcinations on Au/ZnO catalysts shows a great deal of difference to that observed for Au/Fe₂O₃. In the case of the former support, the only effect achieved by the heat treatment of the catalyst is to cause it too lose activity. This effect is most noticeable when the zinc oxide supported samples are compared to the 2.91 atm% Au/Fe₂O₃ samples heated to 120 °C. When heated at 120 °C for 8 hours the activity of iron oxide supported gold catalysts is very high, higher than that of the uncalcined material. When the same heating method is used on an Au/ZnO catalyst the activity is

lowered significantly, to a little over 30% of the precursor material. It is possible to assume that the gold particles themselves are affected differently by the heating. When considered as an isolated unit, gold particles will subjected to the same transformations when heated. As the only variable differing between the two types of catalyst is the support, it is most likely the interaction between the support and the gold particles that causes the difference in the activity.



BET surface area analysis was carried out on the 5.7 and 2.9 atom% catalysts calcined at 120°C and 400°C. The uncalcined catalysts were not tested as prior to the actual analysis the samples have to be degassed for 30 minutes at 105°C. This heat treatment would have affected the surface area of the uncalcined catalysts. The 5.7 atom% catalysts were found to have a surface area of 139.2 m²/g for the catalyst calcined at 120°C and 37.0 m²/g for the catalyst calcined at 400°C. The surface areas for the 2.9 atom % catalysts were very similar, the catalyst calcined at 120°C having a surface area of 139.8 m²/g and the catalyst calcined at 400°C a surface area of 40.0 m²/g.

Having obtained a variety of different catalysts with a range of activities they were studied using XPS. By studying the surface of the catalyst it was hoped that it would be

possible to identify features in the support and the metal particles that lead to high activity (figure 4.9). As discussed in chapter 2, it is possible to gain an understanding of the surface composition of a catalyst from the XPS spectrum, and in combination with techniques such as XANES and TEM to gain an understanding into the particle sizes and oxidation states of the species on the surface of a catalyst.



binding energy

Figure 4.9: Survey spectra of a 2.9 atom% Au/Fe₂O₃ catalyst, highlighting the photoelectron peaks studied

A comparison of the $Au_{(4d)}$ - $C_{(1s)}$ values shows a marked difference between catalysts with a high activity and those with a low activity. The high activity catalysts all have a binding energy difference of around 51 eV, their less active counter parts displaying values of about 50 eV (figure 4.10).



This effect is reproduced when the difference between the Au(4d) and the O(1s) or Fe(2p) peaks are compared (fig 4.11-4.12).





This correlation can also be seen in the Au/ZnO catalysts (figure 4.13). This change in binding energy is brought about by either a change in the particle size of the gold or a change in the oxidation state of the gold particles. These two effects have similar effects on the XPS spectrum of a catalyst. This is because when the oxidation state of an atom changes the change in the charge of the atom will make it either easier or harder for the photoelectron to escape, depending on whether the atom is positively or negatively charged. If the atom is positively charged it makes it harder for the photoelectron to escape and this lowers the kinetic energy of the detected photoelectron, which in turn raises the binding energy. If the atom is negatively charged it is easier for the photoelectron to escape from the atom, and so when detected it will have a higher kinetic energy. This translates into a lower binding energy. When small metal particles undergo sintering and form larger particle, as is often used to explain a fall in catalytic activity, the binding energy of the relevant metal peaks shifts to lower values, which gives rise to a smaller energy difference when compared to peaks with a higher binding energy than the metal. The same situation is repeated with oxidation state.

The difference in magnitude of the $Au_{(4d)}$ - $C_{(1s)}$ values for catalysts with high and low activities, could therefore be down to either oxidation state of the gold, the gold particle size or a combination of the two. However there is no way to tell which is responsible from the XP spectra alone, and other characterization techniques are needed. The

difference between catalysts of high and low activities are of a similar magnitude, 1 eV for Au/Fe₂O₃ and 0.8 eV for Au/ZnO. In contrast to the Au/Fe₂O₃ results the binding energy values of the different activities are lower for Au/ZnO. The lower activity catalysts tending to have an Au_(4d)-C_(1s) binding energy difference of 49.5 eV and the higher activities clustering at around 50.5 eV. This may be due to a difference in the shape, or co-ordination of the gold clusters. As both cluster size and coordination number decrease so does the binding energy of the photoelectron peak of the atom involved. For example; as the size of the gold cluster decreases, the gold binding energy values will move away from that of bulk gold towards lower values. The same is also true of the coordination number. It has been shown that as this decreases the binding energy of the gold is also lowered [32]. A lowering of the binding energy of the gold results in a lowering of the binding energy difference between the Au_(4d) and C_(1s) photoelectron peaks.



To try and elucidate the cause of the difference of activity between catalysts with high and low carbon monoxide conversion, a variety of samples underwent examination by TEM (table 4.1). The results of the analysis showed that there was no correlation between the average size of the gold particles and their activity. This is unexpected as previous studies [34] have shown that an increase in particle size, usually a result of calcination, lowers the activity of a catalyst. It may be possible that the activity of the activities of the two catalysts could not be more different. If the shift in binding e could not be explained in terms of particle size effects, then the next likely would be that the oxidation state of the gold was responsible, since particle s oxidation state have been identified as the two main contributing factors in gold activity [15-17].

Table 4.1: Sample description, activity and particle sizes of samples studied b TEM.

Description	Average Particle size	Steady state CO
	nm	conversion / %
2.91 atom% Au	18	66
2.91 atom% Au 70°C/8 h (furnace)	17	32
2.91 atom% Au 200°C/8 h (furnace)	12	7
2.91 atom% Au 300°C/3 h (furnace)	23	26
2.91 atom% Au 120°C/8 h (furnace)	10	0
2.91 atom% Au 120°C/8 h (GC Oven)	10	100

The XANES spectra for a sample with low activity, 2.91 atom% Au/Fe₂O₃ or 400° C/3 h, and a high activity sample, 2.91 atom% Au/Fe₂O₃ uncalcined, a considerable difference (figure 4.15). The data pertaining to the uncalcined indicates the presence of both cationic gold and metallic gold, with the latter bein present in only a small fraction. The XANES data for the calcined sample ind mixture of both metallic gold and cationic gold. The latter is most likely Au⁺, w former occupies the greater percentage of the gold present in the sample



Figure 4.14: TEM microanalysis of 2.9 atom% Au/Fe₂O₃ catalysts, (a) TEM image of a sample with low activity, (b) an energy dispersive X-ray map of the same area using the Au signal, (c) TEM image of sample with high activity, (d) an energy dispersive X-ray map of the same area using the Au signal







Figure 4.16: In-situ XANES spectra for 2.9 atom% Au/Fe₂O₃ catalysts (a) calcined at 120°C for 8 hours and (b) 400°C for 3 hours.

Analyses of samples before and after reaction as well as by in-situ XANES have shown that there is no change in the chemical composition of the gold particles during reaction (figure 4.16).

The O1s spectra of the catalysts reveal an interesting feature. In the high activity catalysts the O1s peak contains a clear well defined shoulder. However this feature is missing in all of the spectra for the low activity catalysts (figure 4.17). The fact that this feature is only present in catalysts of high activity is suggestive of a surface oxygen species that plays an important role in the mechanism of oxidation. This observation lends a strong degree of credence to the widely championed mechanism presented by Bond and Thompson [17], which suggests that surface hydroxyl groups play a significant role in the reaction.





The deposition, and subsequent analysis of gold colloids on an amorphous graphite surface has shown a shift in the $Au_{4f7/2}$ photoelectron peak towards the value of bulk gold (84.0 eV) with increasing particle size (figure 4.18). The full width half maximum of the Au_{4f} peaks also show a change towards that of bulk gold with increasing particle size. The total difference in the binding energies of the smallest cluster examined (2 nm) and bulk gold is 0.33 eV. This shift in binding energy is far smaller than the one that is observed between Au/Fe_2O_3 catalysts of high and low activity. This is indicative that the binding energy difference observed in the catalyst is due to more than just a change in the size of the gold particles.



4.4 Discussion

4.4.1 Effect of pH

It has been suggested in the literature that the method of preparation of the catalyst has an effect on its reactivity. In the case of co-precipitation, the pH that the catalyst is precipitated at and the time the catalyst is aged in solution both play a role in governing the reactivity. It has been found for a variety of supports including titania and zinc
oxide, that the most active catalysts are prepared at a pH of between 7 and 8 [15]. The exact value is dependant upon the support that is being used. The value is determined by the pH at which the isoelectric point of the support is reached. At this point it is possible for sufficient gold to be deposited onto the support without adding too much chloride to the catalyst as well. By changing the method by which the catalyst was precipitated it was possible to show if the change in pH leading up to the final pH plays a role in determining the activity of a catalyst. It seems apparent from the data that the overall change in pH during the precipitation process has little influence on the final reactivity of the catalysts prepared in this work. It is also worth noting that the formation of an active catalyst by co-precipitation at constant pH contradicts the suggestion that such a method would not be successful [13] due to the support and active metal being precipitated at different times.

4.4.2 The Model of the Active Site



oxidation of carbon monoxide by gold supported catalysts.

One current model for CO oxidation is that proposed by Bond and Thompson (figure 4.19) [17]. In this model, the active catalyst contains both gold atoms and gold ions. The latter forming the chemical glue, which secures the particle to the support. It is believed that a change in the ratio of the ionic and metallic gold, via calcination, oxidation and reduction, which accounts for the wide range of activities that are reported [15 18 19]. Complete reduction harms the activity of the catalyst because the

loss of the "glue" that bonds particle and support makes sintering of the gold much easier. In contrast, the absence of Au^0 is also unwanted, since it is this that forms the locus for the chemisorption of the carbon monoxide. The evidence gathered in this thesis from the XANES and TEM experiments support this theory since they clearly show the presence of two gold species in differing ratios in active and inactive catalysts. and a lack of particle size effects respectively. There is some debate as to which species of gold is the active part of the catalyst. Work by Wolf and his research group [15] has suggested that the active portion of the catalyst is metallic gold, since after calcination at 400 °C all the gold should be metallic, and yet the catalysts still show some degree of activity. The idea that metallic gold is required for CO convcersion is repeated in the model of activity proposed by Bond and Thompson [17]. In their model they theorise that the gold particles are composed of metallic gold held in place by ionic gold particles that act as a kind of glue and provide a place for the hydroxyl groups, which are used in the catalytic reaction, to bond. Investigation by XPS has shown that the ratio of ionic to metallic gold generally decreased with increasing calcination temperature, suggesting that the active part of the catalyst is ionic gold, rather than metallic gold, although metallic gold might be necessary as an overall part of the mechanism. This theory has been ratified by the results of other research groups [20-22], which show that the most active catalysts were those with the largest ratio of ionic to metallic gold. The data generated in this thesis by XANES support the latter contention, since these too indicate that the catalysts with the greater amount of ionic gold are the more active.

Of the three different gold loadings tested the uncalcined 5.7 and 1.5 atom% had very similar activities. The uncalcined 2.9 atom% catalyst has a lower activity (90% compared to 100/96% initially and 70% compared with 95% and 86% after 400 minutes on-line). A possible explanation for this is that 2.9 atom% catalyst is less active that the others because it has less gold than the 5.7 atom% catalyst, and so less gold clusters with which to catalyse the oxidation of CO, but also its particles are bigger than the 1.5 atom% catalyst, and consequently less active sites.

BET surface area analysis of the 5.7 and 2.9 atom% catalysts fits with those done previously [32]. The similar value of the two different loading suggests that gold content plays a very small role in determining the overall surface area of the catalyst.

4.4.3 Effect of Heat Treatment

The effectiveness of heat treatment seems to vary depending on the support used. In the case of zinc-supported catalysts heat-treating the catalyst only serves to lower the catalyst activity. The iron oxide supported catalysts however exhibit their highest activity after heating at 120 °C. In terms of the Bond and Thompson model, it has been suggested that heating of the catalyst removes the hydroxyl groups bound to the interface of the gold particle and its support, as well as altering the ratio of ionic and metallic gold present. These hydroxyls are thought to play an integral role in the reaction mechanism for CO oxidation [23]. They bond with the carbon monoxide adsorbed on Au^o, and allow it to be converted to CO₂ via a carboxylate. The lack of a visible hydroxyl peak in the XPS spectrum of catalysts with poor activity suggests that this is part of the model is accurate. It has been shown in work by both Hutching's and Kung's group that the presence of water vapour can reactivate a deactivated catalyst [14 24]. The alteration of the ratio of metallic and ionic gold by different heat treatments is also supported by the XANES data. It shows a clear difference between amount of metallic and ionic gold in the 2.9 atom% catalyst calcined at 120°C and the 2.9 atom% catalyst calcined at 400°C.

The effects of heating on the 2.9 atom% Au/Fe₂O₃ catalysts are in agreement with those described by the Bond and Thompson model, in so far as there is a rearrangement of the ratio of ionic to metallic gold. However changes in activity are not just brought about by the temperature at which the catalyst is heated. The difference in activity between the 2.9 atom% Au/Fe₂O₃ catalysts calcined at 120°C/8 h shows that the method of heating also plays a role in determining activity. There are two substantial differences in the methods used. The first is the heating rate; the GC oven reaches temperature much faster than the furnace, the second is that the GC oven circulates air around the catalyst because of its fan. The origin of this effect could lie in the rate at which the oven gets up to temperature, the differing environments, or a combination of the two. It has already been shown that the presence of hydroxyl groups on the surface has an effect on the activity of the catalyst. It is possible that the circulation of air in the GC oven helps to replace these groups as they're removed by the process of heating. Another possibility is that the deactivation is the result of contamination from previous samples heated in the furnace. However, although the XPS analysis of catalyst samples

heated in this manner does not show any contamination further investigation is needed to rule this possibility out.

4.4.4 Origin of Binding Energy Shifts

It is somewhat harder to rationalise why the method of heat treatment should have such a drastic effect on the activity of the catalyst. This effect is unlikely to be caused by the longer period of time it takes the furnace to heat up to the required temperature leading to less sintering of the gold particles for two reasons. Firstly the lower heating rate has shown to give a lesser activity than the much faster rate used in the GC oven. Examination by XPS of catalysts that have been heated by the two methods shows that there is a difference in the make up of the gold particles, demonstrated by both the differing values of the $Au_{(4d)}$ - $C_{(1s)}$ binding energy differences and the presence of a shoulder in the $Au_{(4t)}$ spectra of the high activity catalyst which indicates the presence of ionic gold (figure 4.20).



120°C for 8 hours in (a) a GC oven and (b) a furnace

TEM analysis performed on the samples have shown that the different heating methods have no effect on the average size of the gold particles in the catalyst. Analysis of samples by XANES has shown that the less active of the catalysts, has a much lower ionic gold content than the catalysts that had been dried in a GC oven. Further corroboration is given by the analysis of gold clusters deposited on graphite. These studies have shown that the total difference in the value of the gold photoelectron peaks between clusters far smaller than the ones found in Au/Fe₂O₃ catalysts, and bulk gold is 0.33 eV. Based on this evidence the 1 eV difference between catalysts of high and low activity is far too large to be caused by a change in the size of the gold particles. As mentioned below it should be noted that because of the interaction between the support and the gold clusters the support material has an effect on the value of binding energy of clusters, so the exact contribution to the binding energy difference seen in the catalyst made by a change in the size of the gold nanoparticles cannot be properly quantified based on these experiments alone.

Core electron emission from a positively charged cluster will have a higher binding energy as a result of attraction of the negatively charged photoelectron to the positively charged cluster, a factor commonly know as the coulomb attraction barrier [25]. The ability of a support to affect the binding energy of core electrons in clusters comes from the supports ability to neutralise the charging of a cluster brought about by the process of photoemission, and this depends on the density of states at the Fermi energy in the support, as well as the shape of the cluster. This process increases the binding energy of the cluster relative to that of the bulk, however there are also two processes that lower the binding energy of core electrons as the size of a cluster decreases. Final state relaxation processes in the bulk will decrease the core electron binding energy compared to that of an isolated atom [26]. This is expected from the decrease of the conduction electron screening of the core hole produced by photoionization due to the discretization of the conduction band with decreasing particle size [27-28]. The other process that reduces the core electron binding energy is the decrease in screening of core holes by neighbouring atoms brought about by the reduction in coordination as the size of a cluster decreases.

The trends in binding energy shift observed during experimentation are similar to those reported in literature, 0.4 eV Cu/ZrO₂ [29], 0.5 eV Au/SiO₂ [30] and 1eV for Au/Graphite [31]. Preparation and cluster size vary for each of the results quoted and as such the differences in the results can be ascribed to differences in the effect of the final and initial state effects mentioned above.

4.4.5 Effect of Support

Both of the supports studied, have shown a correlation between their activity and the $Au_{(4d)}$ - $C_{(1s)}$ binding energy difference. However the actual values of the binding energy difference are different for each support. It has been shown [32] that the particular support that a particle is mounted upon has some influence upon the degree of rounding of the particles. It has also been suggested that the shape of the particle has an effect on the binding energy of photoelectrons emitted during XPS. Claus has suggested that with a decrease in coordination number there is a corresponding shift of binding energy to lower values [32]. In gold particles that have large facets, the number of atoms at edges, corners or steps is lower than for more rounded particles, so it has been suggested that these faceted particles will have a higher binding energy as the atoms making up the particle have a higher coordination number that their counterparts in more rounded particles. If the gold particles on the iron and zinc supported catalysts are different shapes this would explain the difference in the sizes of the Au_(4d)-C_(1s) values. Gold particles supported on zinc oxide have been shown to be largely faceted [32]. This gives rise to a higher gold binding energy, and thus a larger Au_(4d)-C_(1s) value. High activity iron oxide supported gold catalysts have larger Au_(4d)-C_(1s) binding differences, which could be seen as being indicative of rounder particles. The difference between the two sets of values is consistent with the difference reported by Claus [32] between catalysts with rounded particles and those with more faceted gold particles. The information indicating a greater number of low co-ordination interface sites, lends credence to the idea in Bond and Thompson's model that the reaction takes place on the interface of the support and the gold cluster.

It has been reported several times in the literature [10, 15, 16, 24] that different supports give different activities, even under the same conditions. We have also shown that the ratio of metallic gold to cationic gold is important to the activities, and that through

heating, this ratio can be modified and thus the activity of the catalyst affected. It has been shown that the same heat treatment will affect two differently supported catalysts in different manners. The reasons for this could be two fold, firstly in terms of surface hydroxyls, and secondly in terms of the supports interaction with the gold particles. It is probable that when heated the surface hydroxyl groups that are necessary for the reaction will be stripped from the surface at different rates. It is also possible to suggest that if the surface hydroxyls are stripped at the same rate from the surface, that the strength with which the gold particle is bonded to the support may affect the way in which the ratio of metallic to cationic gold changes during the coarse of heating. That is to say that different supports will have different ratios of metallic and cationic gold and hence different activities.

4.5 Conclusions

In the preparation of the Au/Fe_2O_3 catalysts only the final pH affects the activity. The pH change the catalyst undergoes to reach that point seemingly plays no role in shaping its activity.

There is a clear difference in the nature of catalysts of high and low activity. It can be shown, from the TEM and XANES data, which for iron oxide supported gold catalysts the active site consists of a gold particle made up of Au^0 and ionic gold (probably Au^+). The latter is in the majority in the more active catalysts. Also correlated with high activity is a surface hydroxyl species.

Heat treatment affects the activity of catalysts by altering the ratio of Au^0 and Au^+ and stripping the hydroxyl groups from the surface. The critical ratio for this effect has yet to be determined but XANES experiments have shown that it lies in favour of the cationic gold.

Differences in the support of a catalyst alter its activity and the effect that of treatment will have.

Binding energy shift can be used as a method of indicating or predicting the activity of a catalyst.

4.6 References

- 1. M.E. Schrader, J Colloid Interface Sci. 1979, 59, 456.
- 2. P. Legare, L. Hilaire, M. Sotto and G. Maire Surf. Sci. 1980, 91, 175.
- 3. M. E. Schrader, Surface Sci., 1978, 78, L227.
- 4. N.W. Cant, W.K. Hall, J. Phys. Chem., 1971, 75, 2914.
- 5. S.D. Lin, M. Bollinger and M.A Vannice, Catal. Lett., 1993, 17, 245.
- 6. W.A. Bone and G.W. Andrew, Proc. Roy. Soc. (London), 1925, 109A, 459.
- Y. Lizuka, T. Tode, T. Takoa, K. Yatsu, T. Takeuchi, S. Tsubota and M. Huruta, J. Catal., 1999, 187, 50.
- 8. D. Outka and R.J. Madix, J. Phys. Chem. A, 1999, 103, 9573.
- 9. M. Valden, X. Lai and D.W. Goodman, Science, 1998, 281, 1647.
- 10. M.A. Bollinger, M.A Vannice, Appl. Catal. B: Enviromental, 1996, 8, 417.
- 11. M. Valden, S. Pak, X. Lai and D.W. Goodman, Catal. Lett., 1998, 56, 7.
- 12. A.I. Kozlov, A.P Kozlova, H. Liu Y. Iwasawa, Appl. Catal. A, Gen. 1999, 182, 9.
- 13. G.C. Bond and D.T. Thompson, Cat. Rev. -Sci. Eng., 1999, 41, 319.
- G.J. Hutchings, Q.A. Pankurst, R.M. Finch, N.A. Hodge, A. Meagher, F.E. Wagner, R. Whyman *et al. Phys. Chem. Chem. Phys.*, 1999, 1, 485
- 15. A. Wolf, F. Schuth, Appl. Catal. A, 2002, 226, 1
- 16. H.H. Kung, M.C. Kung, C.K. Costello. J. Catal., 2002, 375, 210
- 17. G.C. Bond, D.T. Thompson, Gold Bull., 2000, 33, 41
- M. Haruta, M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, Catal Lett., 1998, 51, 53
- A.M. Visco, A. Donato, C. Milone, S. Galvagno, React. Kinet. Catal. Lett., 1997, 61, 219
- 20. E.D. Park, J.S. Lee, J. Catal., 1999, 1, 186
- 21. S.Minico, S.Scire, C. Crisafulli, S. Gavagno, Appl. Catal. B, 2001, 34, 277
- 22. G.J. Hutchings, Q.A. Pankurst, R.M. Finch, N.A. Hodge, A. Meagher, M.R.H. Siddiqui, F.E. Wagner, R. Whyman. Catal. Today, 2002, 72, 133
- 23. H.H. Kung, M.C. Kung, C.K. Costello, J. Catal., 2003, 216, 425
- 24. H.H. Kung, M.C. Kung, C.K. Costello. Appl. Catal., A 2002, 232, 159
- 25. G.K Wethhiem, S.B. DiCenzo, S.E. Youngquist, Phys. Rev. Lett., 1983, 51, 2310
- 26. M.G. Mason, Phys. Rev. B., 1983, 27, 748

- 27. A. Kawabata, R. Kubo, J. Phys. Soc. Jpn., 1966, 21, 1765
- 28. M.E. Lin, R.P. Andres, R. Reifenberger, Phys. Rev. Lett., 1991, 67, 477
- 29. J.P. Espios, J. Morales, A. Barranco, A. Caballero, J.P. Holgado, A.R. Gonzalez-Elipe, J. Phys. Chem. B., 2002, 106, 6921
- 30. D. Dalacu, J.E. Klemberg-Sapieha, L. Marttinu, Surf. Sci., 2001, 472, 33
- 31. G.U. Kulkami, C.P. Vinod, C.N.R. Rao, Surface Chemistry and catalysis (edited by A.F Carley, P.R. Davis, G.J. Hutchings and M.S. Spencer), Kluwer Academic/Plenum Pulishers, 2001
- 32. J. Radnik, C. Mohr, P. Claus, Phys. Chem. Chem. Phys., 2003, 5, 172
- 33. H.J Freund, Sh.K. Shaikutdinov, R. Meyer, M. Naschizki, M. Baeumer, Catal. Lett., 2003, 86, 211
- 34. J. Hua, K. Wei, Q. Zheng, X. Lin., Appl. Catal. A, 2004, 259, 121

Chapter 5: Hydrogenation of Crotonaldehyde

5.1 Introduction

In the hydrogenation of crotonaldehyde there are three main products formed, the unsaturated alcohol, the saturated aldehyde and the saturated alcohol. A simplified reaction scheme is shown in (figure 5.1). Because of the stronger negative free reaction enthalpy, thermodynamics favours the hydrogenation of the C=C over the C=O group. However, in terms of industrial application, the most favourable product in the reaction is the unsaturated alcohol.



Figure 5.1: Reaction scheme for the hydrogenation of crotonaldehyde

This type of reaction is very important in the industrial synthesis of fine chemicals, particularly pharmaceuticals and cosmetics [10,11], and has consequently attracted a great deal of interest for research in catalysis.

Conventional hydrogenation catalysts [12] mainly provide the saturated aldehyde, but catalysts are required to control the selectivity of product formation. Steric and electronic effects, as well as the structure and morphology of metal particle surfaces are some of the most effective factors controlling intramolecular selectivity [12]

Catalysts based around other metals have shown activity for the hydrogenation of α , β -unsaturated aldehydes in general, and crotonaldehyde specifically [4-6]. Initial approaches towards catalysing this reaction focused on supported metal catalysts where the support was considered to play an important role in controlling metal cluster morphology. Ni/Cu/Al₂O₃ [3], Pt/TiO₂ [4], Pt/Fe/SiO₂ [5] and Cu/Cr₂O₃ [6] have all shown improved selectivity for the hydrogenation of the carbonyl bond in preference to the carbon-carbon double bond. In the hydrogenation of α , β -unsaturated aldehydes to allylic alcohols the control of the selectivity of the reaction has always been considered an important factor, rather than the overall activity of the catalyst. Pt catalysts have shown an improvement in product selectivity in this reaction when Ge, Ga or Sn additives are present in the catalyst [7]. Similarly both gold [8] and copper [9] have shown an enhancement in the selectivity of crotyl alcohol when partially poisoned, by either thiophene [8] or chlorine compounds [9].

For a long time there was very little research conducted into catalysis by gold, due to its low catalytic activity attributed to its completely filled d-band [1]. This situation was reversed when Haruta [2] reported that, by using very small gold nanoparticles on suitable supports, the oxidation of carbon monoxide could be achieved at room temperature. Despite some promising examples [1] of the capabilities and applications of gold as a hydrogenation catalyst, this area was largely ignored in favour of oxidation reactions.

There is some debate over the role metal particle size plays in the selectivity of catalysts used for crotonaldehyde hydrogenation and this also applies to gold. Hutching's group conducted experiments on Au/ZnO catalysts in which the particle size of the catalyst was raised by either increasing the loading of the gold or by raising the temperature at which the catalyst was reduced [8]. The particles sizes achieved by altering the gold loading were 2-4 nm with a loading of 2 wt%, 4-5 nm with a loading of 5 wt% and a bimodal distribution of 1-3 and 6-10 nm with a catalyst loading of 10 wt%. The effect of changing the particle size of 4-6 nm was achieved by reducing the catalyst at 250°C, 3-8 nm by reduction at 300°C, 10-15 nm at 350°C and up to 20 nm by reducing the catalyst at 400°C. It was reported that the selectivity of the catalyst towards crotyl alcohol

increased with both increasing gold loading and increasing reduction temperature. It was hypothesized that high selectivity for the hydrogenation of crotonaldehyde to crotyl alcohol was linked to the presence of large gold particles.

Hutchings observations contrast with those made by Claus and his group [17]. Studying the hydrogenation of both acrolein and crotonaldehyde over Au/TiO₂ catalysts with average particle sizes of 1.1, 2.0, and 5.3 nm they discovered a decrease in the turn over frequency of the catalyst by two to three orders of magnitude and a decrease in selectivity when the size of gold particles decreased from 2.0 to 1.1 nm. No change in either the turn over frequency or the selectivity of the catalysts was observed between the 2.0 and 5.3 nm catalysts. Claus suggested that the sensitivity of the selectivity of the reaction towards the small gold particles was due to an alteration of the metallic properties of the smallest gold particles brought about by quantum size effects.

Alternative studies on Au/TiO₂ catalysts reported different results to those observed by Claus [17] and gave an alternative explanation for the observed low activity [19]. It was suggested that the differences in activity were down to the methods of preparation of the catalysts, the former being made by the sol-gel method as opposed to co-precipitation. This study also concluded that better selectivity for the hydrogenation of crotonaldehyde to crotyl alcohol was obtained by using very small particles of gold (~ 1 nm).

Later work by Claus [18] on Au/ZrO₂ using co-precipitation at various pH's, to obtain catalysts with gold particle sizes of 4.0, 6.9, and 7.7 nm, found that the turn over frequency decreased by nearly one order of magnitude, and the selectivity to crotyl alcohol increased from 15 to 35% when the particle size increased. It was also noted that the activity of the Au/TiO₂ catlysts had a much higher activity than the Au/ZrO₂ catalysts despite both catalysts having the same average particle size of 5 nm. The difference was attributed to the fact that the gold particles were round shaped on TiO2 and facetted on ZrO2. It was suggested that the round-shaped gold particles would contain a higher proportion of low-coordinated surface sites.

5.2 Experimental

5.2.1 Spectroscopy

5.2.1.1 XPS

All of the XPS analysis carried out in this chapter was performed using the ESCALab 220, and ESCA 300 spectrometers that have been previously detailed in Chapter 2.

5.3 Results



5.3.1 Activity of iron oxide supported gold catalysts

When tested alone at 250°C neither gold nor iron oxide, formed by precipitation, has any ability to catalyse the hydrogenation of crotonaldehyde. When the two are combined by the same co-precipitation method used to make the catalysts tested for CO oxidation in Chapter 4 described in 3.3.1.1, with a loading of 2.9 atom%, the effect on the reactivity on the pre-reduced catalysts is clear (figure 5.2). The activity here starts off extremely high, but decreases to around 40-60% conversion. As previously noted however, the activity is secondary to the selectivity of the catalyst. When the reaction was first run the main product appeared at a retention time that did not correspond to any of the expected products. It was found through analysing the products of the reaction using Gas Chromatography Mass Spectrometry (GCMS) that this product was butene.



This raised the question of at what point in the suggested reaction scheme did the loss of the aldehyde or alcohol functional groups occur. In order to elucidate this, the hydrogenation reactions were run again using a different reactant in the place of crotonaldehyde. In order determine the stage of the reaction pathway in which butene was produced, it was decided to conduct the test by analysing the reaction scheme in reverse. This was done by taking each of the products formed in the reaction, starting with the fully saturated alcohol and testing it in place of crotonaldehyde in the reactor, thus eliminating each product step by step and allowing the stage at which butene is produced to come to light. It was found that the evolution of butene is brought about by the dehydration of the fully saturated alcohol, butan-1-ol. This means that for iron oxide supported gold catalysts the reaction scheme now looks like the one shown in figure 5.3. In order to eliminate the possibility that butene was being produced as a function of the support, the experiments were repeated using a freshly precipitated sample of iron oxide. The results showed that iron oxide alone was not active for the dehydration of the butan-1-ol. It is clear that dehydration of the fully saturated product is due to the Au/Fe₂O₃ catalyst.



0.2 g catalysts tested at 250°C. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ Reduced in H₂ @ 250°C/1 h. H₂: crotonaldehyde ratio = 14:1

The production of butene as the major product of the reaction was not limited to the 2.9 atom% catalysts. The uncalcined 1.5 atom% Au/Fe₂O₃ has a constant conversion of 100% over a period of 3 hours; see figure 5.4 The major product of the reaction is butene which makes up between 60 and 80% of the products. Butan-1-ol is the next most produced product followed by butanal and then crotyl alcohol.

5.2.2 Effect of heat treatment

Crotonaldehyde hydrogenation was then carried out using catalysts that had been given a range of different heat treatments, (figures 5.5-5.9). The uncalcined catalyst initially showed a high conversion, although this dropped over the course of the reaction from 100% conversion down to around 50%. The major product was butene, although the production of this too falls over time; this is also the case for butan-1-ol, which starts off as the second most abundant product, but by the end of the reaction is the one that is produced the least. The production of both butanal and crotyl alcohol remains fairly constant over the coarse of the reaction, with butanal being the slightly more favoured product of the two. After pre-treating the catalyst at 75°C for 8 h the catalyst shows a very different reactivity. The conversion is initially as before, but this time there is no catalyst deactivation over time. A similar situation was also observed with the distribution of the products; butene is once again the major products, although butan-1ol is produced in fairly large quantities as well. Butanal is produced in much less amounts and crotyl alcohol hardly at all. After pre-treatments at higher temeratures the activity of the catalyst starts to drop off dramatically, with initial activities below 5%. However with the drop off in activity, there is also a change in the selectivity of the catalyst. Crotyl alcohol becomes the major product, with butanal as the secondary product. Butan-1-ol and butene are not produced at all.



0.2 g catalysts tested at 250°C. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ Reduced in H₂ @ 250°C/1 h. H₂: crotonaldehyde ratio = 14:1



Figure 5.6: Product selectivity and activity of 2.9 atm% Au/Fe₂O₃ 75°C/8 h

0.2 g catalysts tested at 250°C. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ Reduced in H₂ @ 250°C/1 h. H₂: crotonaldehyde ratio = 14:1



Reduced in H₂ @ 250°C/1 h. H₂: crotonaldehyde ratio = 14:1



After investigating the effect of calcination temperature on the catalyst, the reaction temperature was also varied, to see if this would alter the activity and selectivity of the catalyst. The work detailed above demonstrated it was possible to achieve complete crotonaldehyde conversion at 250°C, and it seemed that lowering the reaction temperature would be likely to give more of the intermediate products at the cost of the overall conversion. The un-heat treated catalyst was chosen, so that any changes observed would be down to the effect of the reaction temperature alone, and not a result of any pre-treatment the catalyst had undergone (figures 5.10-5.14). At 100 °C and below no reaction was observed. Between 110 and 140 °C, the initial conversion is between 10 and 20 %. The catalysts tested at these temperatures deactivated over a period of time, with final conversions of ~ 3 %. In all cases crotyl alcohol was the major product, and butanal the secondary. As in the case of the calcined catalyst samples, both butene and butan-1-ol were not formed. When the reaction was run at 150 °C the initial conversion rises dramatically to 80 %, although it suffers from the same deactivation problems as the catalysts that were run at lower temperatures, with its final conversion being around 4 %. The selectivity follows a similar trend, initially butene is the major product for the reaction, but as the conversion drops off so does the percentage of butene produced. As has been the case for the other temperatures used, when the production of butene drops off the major product produced is crotyl alcohol.



H₂: crotonaldehyde ratio = 14:1



Figure 5.11: Product selectivity and activity of uncalcined 2.9 atm% Au/Fe₂O₃ reacted at 110°C,

0.2 g catalysts tested. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ H₂: crotonaldehyde ratio = 14:1



Figure 5.12: Product selectivity and activity of uncalcined 2.9 atm% Au/Fe₂O₃ reacted at 120°C,

0.2 g catalysts tested. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ H₂: crotonaldehyde ratio = 14:1



5.2.3 Effect of pre-reduction on catalyst selectivity and conversion

In order to explore the effects of the pre-reduction step on the activity of the catalyst, a series of catalysts was tested where the reduction step was not carried out (figures 5.15-5.19). It is clear to see that the reactivity of the catalysts tails off very rapidly at heat treatments higher than 200°C. The selectivity of the catalyst also changes as the calcination temperature rises above 200°C. In the cases of catalysts with heat treatments ranging from un-treated to 200°C, the major product is butene. When heat treated at 300°C the activity drops to around 1% conversion after 3 hours, with the major products being a mix of butanal and crotyl alcohol. Heat treatments of 400°C cause the activity to drop still further to 0.75% conversion. The major products remain the same, but whereas before it was crotyl alcohol that was being produced in slightly greater quantities, this time it is butanal that is produced in greater amounts, although it has also been shown that with catalysts that have been calcined at this temperature the difference is very small indeed



Figure 5.15: Product selectivity and activity of unreduced uncalcined 2.9 atm% Au/Fe₂O₃

0.2 g catalysts tested. GHSV = 66000 ml (gas) (g of catalyst)⁻¹ h⁻¹ H₂: crotonaldehyde ratio = 14:1



H₂: crotonaldehyde ratio = 14:1



H₂: crotonaldehyde ratio = 14:1

deactivation of the catalysts that had been heat treated at higher temperatures. It also indicate if there were any differences between catalysts with high activit catalysts with low activity. A comparison of the XP spectra of used and u catalysts showed very little difference between the two types of sample (table 5.1).

A comparison of the Au_{4d}-C_{1s} binding energy differences (figure 5.20) between catalysts of high and low activity revealed a clear difference between the two. catalysts with high activities towards crotonaldehyde had an average binding edifference of 50.4 eV, whilst those with low activities had an average binding edifference of 50.0 eV. This is suggestive of a difference in the composition of the nanoparticles, either in the size of the gold clusters or of the oxidation state of the itself.

Table 5.1 Comparison of the $Au_{(4d)}$ - $C_{(1s)}$ binding energy differences between used and unused crotonaldehyde hydrogenation catalysts

Unreduced Sample	Activity (%)	$Au_{(4d)}-C_{(1s)}$ (e
2.9 atom% Au/Fe ₂ O ₃ uncalcined	99	50.30
Used 2.9 atom% Au/Fe ₂ O ₃ uncalcined	95	50.35
2.9 atom% Au/Fe ₂ O ₃ 200°C/8 h	99.3	50.49
Used 2.9 atom% Au/Fe ₂ O ₃ 200°C/8 h	99.3	50.50
2.9 atom% Au/Fe ₂ O ₃ 400°C/3 h	5	50.05
Used 2.9 atom% Au/Fe ₂ O ₃ 400°C/3 h	2	49.95

When examined by high resolution XPS (Figure 5.21) the $Au_{(4f)}$ peaks of 2.9 at Au/Fe_2O_3 calcined at 120°C for 8 hours show a small shoulder at 83 eV, whi indicative of the presence of ionic gold. This is consistent with previous re-



obtained in Chapter 4. This shoulder is absent from 2.9 atom% Au/Fe₂O₃ catalysts that have been calcined at 400° C

samples and below 75°C for the reduced samples, all show the same selectivity butene as the main product of the reaction. The catalysts that have been heat tr high temperatures display a similar distribution of products, although the catalysts show a very slight increase in the selectivity crotyl alcohol. Sin reduction step is the only difference between the two sets of results it is clear t step is the source of the differences. Much like calcination the reduction of cataly been shown to alter the ratio of metallic and ionic gold [13]. It seems logical, the that the differences in activity and stability between the reduced and unreduced c are due to an alteration of the ratio of metallic and ionic gold, although it possible that the reduction step may have an effect on the support of the catal could lead to the observed differences. A similar effect on the ratio of metal ionic gold with heat treatment has been shown in this thesis (Chapter 4) and the of both sets of catalyst samples decreases as the calcination temperature rises theory is supported by the high resolution XPS spectra obtained (Figure 5.21). indicates the presence of ionic gold in unreduced catalysts with high activi effects of these two processes are more likely to cause catalyst samples to h lower activities than would be expected if either process was used alone. This explain the reason why the activity of the reduced catalysts would drop off a temperatures than their unreduced counter parts.

A drop in the activity of both types of catalyst is accompanied by an increase selectivity towards the formation of crotyl alcohol. It has been shown [14] increase in the average gold particle size can be responsible for both o observations and that the effect is not inconsistent with the heating of catalysts temperatures. This also fits with observations that the close packed structure of surfaces of gold particles preferentially activates the hydrogenation of the C=(15]. These faces are more common in larger gold particles than in smalle coordinated ones. This seems to contradict the other findings, which have stat

the sites for adsorption and then hydrogenation of the C=O group were located at the interfacial sites of the catalyst [8]. However the lower activities and selectivities reported would seem to suggest that these interfacial sites are not very common, even in catalysts that have not been heat-treated.

Compared to gold supported on other transition metal oxides, iron oxide supported gold catalysts have a much higher activity [8,14,16] for hydrogenation especially when heat treated at lower temperatures. Depending on the support used, conversions range form 41% for zinc oxide supported catalysts [8] to 30% for gold nanoclusers supported on titania [17], 13% for alumina supported gold catalysts [17] and 3 % for catalysts supported on silica [16]. This range of activities is a clear indication that interaction between the support and the gold particles plays a role in determining the activity of the catalyst. Au/Fe₂O₃ catalysts are not the only catalysts that produce butene as a product for the hydrogenation of crotonaldehyde [19]. However butene has not been reported as being a major product in this reaction, rather it is listed as a very minor product. Also it has been speculated [19] that on Au/TiO₂ catalysts that butene is formed by the conversion of crotyl alcohol first into butadiene, and then from that into butene. This is suggestive that the dehydration step that leads to the formation of butene is a result of the support used. However when tested iron oxide that had been prepared the same way as the catalysts showed no signs of being active for either hydrogenation of crotonaldehyde or the dehydration of butan-1-ol. As the effect could not come from the support alone, it is possible that the production of butene is the result of two separate catalytic processes acting in sequence with one another. Competition is unlikely, as the dehydration step requires the formation of butan-1-ol before it can proceed.

As mentioned before, activity alone is not sufficient to judge of how good a catalyst is for this type of reaction since the selectivity is also of importance in the reaction. At lower heat treatments the selectivity towards crotyl alcohol is very low, but as the calcination temperature rises so does the amount of crotyl alcohol produced. For the heat treatments where crotyl alcohol is observed the selectivity is usually around 40-60 % for the catalysts that underwent the reduction step and 30-50 % for those that did not. In terms of the selectivity of other reported catalysts, these results are consistent with other findings. Following modification with thiophene catalysts, supported by zinc either a dependence on the ratio of metallic to ionic gold, or that ionic gold a responsible for the activity of the catalyst for hydrogenation of crotonaldehyd provide a more accurate answer the amounts of metallic and ionic gold of more cat with a greater range of activities need to be examined.

The uncalcined 1.5 atom% catalyst is more both more active and more stable t 2.9 atom% equivalent (figure 5.4 and 5.5 respectivly). This higher activity ma result of the lower particle size of the 1.5 atom% catalyst, which is probably a re the lower gold loading. The idea that increasing gold loading causes an incre particle size is not a new one, and has been shown in previous publications [8, 19 observation that a decrease in particle size also lends credence to Claus's theory the active site for selective hydrogenation is connected to small gold particles [17].

5.4 Conclusion

Iron oxide supported gold catalysts have been shown to have high activity 1 hydrogenation of crotonaldehyde. At low heat treatments the major product is t but as the temperature of the pre-treatment is increased the major product of the re changes to crotyl alcohol, although with lower conversion of crotonaldehyde.

The hydrogenation of crotonaldehyde over supported gold catalyst has been sho be affected in a number of ways, by a variety of different factors such as: re temperature, interaction between the metal and the oxide support and pre treatme the case of iron oxide supported gold catalysts, it has also been shown that the further step in the reaction pathway, the formation of butene.

- 5. J. Sommik, P. Berannek, Coll. Czech. Chem. Comm. 1972, 37, 353
- 6. T.R. Bonnelle, R. Hubant, M. Daage, Appl. Catal. 1986, 22, 237
- T.B.L.W. Marinelli, J.H. Vleeming and V. Ponec, Proc. 10th Int. Co Catalysis, 1993, 1211
- J.E. Bailie, H.A. Abdullah, J.A. Anderson, C.H. Rochester, N.V. Richar Hodge, J. Zhang, A. Burrows, C.J. Kiely, G.J. Hutchings, *Phys. Chen Phys.*, 2001, 3, 4113
- 9. G.J. Hutchings, F. King, I.P Okoye, C.H. Rochester, Cat. Lett. 1994, 23,
- 10. R.L. Augustine, Heterogeneous Catalysis in Organic Synthesis, Dekk York, 1995
- 11. K. Bauer, D Garbe, in: Ullmann's Encyclopedia of Industrial Chem Edition, Electronic release 2000
- 12. P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 1998, 40, 8
- 13. J. Radnik, C. Mohr, P. Claus, Phys. Chem. Chem. Phys., 2003, 5, 172
- 14. S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Brückner, J. Ra Hofmeister, P. Claus, Catal. Today, 2002, 72, 63
- 15. F. Delbecq, P. Sautet, J. Catal., 1996, 164, 152
- 16. M. Okumura, T. Akita, M. Haruta, Catal. Today, 2002, 74, 265
- 17. P. Claus, A. Brückner, C. Mohr, H. Hofmeister, J. Am. Chem. Soc. 20 11430.
- 18. C. Mohr, H. Hofmeister, P. Claus, J. Catal. 2003, 213, 86
- 19. R. Zanella, C. Louis, S. Giorgio, R. Touroude, J. Catal., 2004, 223, 328

Some techniques, such as low energy electron diffraction (LEED) and high-reelectron energy loss spectroscopy (HREELS) use beams of electrons as direct p the surface, while others such as XPS use another form of excitation to electrons which are then examined [1-2]. Whatever the method employed mean free path of electrons through a gas has always required that the techn employed under ultra high vacuum conditions (see chapter 2 for more informati

Using these types of techniques catalysis on single crystals was first stucharacterising a single crystal surface before a reaction. This way information gathered about any adsorbate coverage already present on the surface and str the crystal before any reaction had taken place. The crystal would then be real a high pressure of whatever gases were being studied. By studying the composite gas and the rate at which this changed the kinetics of the reaction could be out. Following the completion on the reaction the surface could be re-characted. This approach to the study of catalysts brought to light information on the surface of the single crystal before and after reaction, and as a result any that might have occurred during the reaction. However it was not possible information on surface intermediates that may have formed during the reaction.

Other studies were carried out using gases at pressures that allowed for in situ spectroscopic measurements. These studies were able to produce data about that had previously been unstudied; however the vast gap between the pre which catalysts are operated in industry and the conditions necessary for the ap of UHV techniques is so vast that the information gathered was not always of u catalysis [5-6]

The various approaches all have the requirement that the substrate on which the is built needs to be electrically conductive. This is necessary because as explain section 2.9, if the model is built on an insulating material the photoionisation physical will lead to sample charging, which will effect the resulting spectra. Typically oxide films are used to model catalyst supports since these are usually insulator severe charging of the model can result if the support is too thick. The oxide laye typically either grown from a crystal of the corresponding metal [8] or by evaporate the metal on to a second metal substrate followed by oxidation [13]. The particles are also deposited on the surface in variety of different ways, ince evaporation of the metal [9], chemical vapour deposition [14] and wet impregispin coating [15].

There are differences in the way that the model catalysts made by these metho perceived. Models constructed by wet impregnation techniques are seen as being to industrial catalysts, since the method of construction is similar. However this t model requires far more complex methods of characterisation, which may h understanding of the surface processes taking place. Alternatively model system are constructed by the step-wise construction of the catalyst, by the growth of pa by metal vapour deposition onto a pre-constructed metal oxide film for examp much easier to characterise. These models tend to be criticised by practical ca chemists, who question whether or not the model system is actually active f reaction it is supposed to be modelling [11].

This chapter covers the preliminary work carried out using the high pressure cell attempt to produce a better way of producing model catalysts by trying to bridge the between operational pressures and those used to study catalysts under ultra high vaconditions.

6.2 Experimental

6.2.1 Polycrystalline Gold Foil – Active Site Modelling

The experiments carried out were designed to examine the behaviour of model catalyst samples. The first tests carried out tested the activities of the individual parts of a real catalyst; the gold and the metal oxide support. To model the active sites on gold nanoparticles, before each experiment a gold foil was cleaned by argon sputtering for a period of 30 minutes. After sputtering the gold foil was not annealed, so that the rough surface would mimic aspects of the appearance of small gold clusters.

The role of the gold in the catalysis of carbon monoxide was tested by trying to adsorb 4 different gas mixtures onto the surface of the gold film; carbon monoxide only, a 50:50 mixture of carbon monoxide and oxygen $(3x10^{-6}: 4x10^{-6} \text{ mbar})$, an oxygen rich mixture $(2x10^{-6}: 7x10^{-6} \text{ mbar})$, and a carbon monoxide rich mixture, $(9x10^{-6}: 1.5x10^{-6} \text{ mbar})$. If it were possible to adsorb CO onto the model surface this would be a clear indication that the active component of the catalyst was the gold particles. Each time the gold foil was examined the following regions were scanned; $C_{(1s)}$, $O_{(1s)}$, $Au_{(4d)}$ at a pass energy of 50 eV, and a survey scan at a pass energy of 100 eV.

One of the problems associated with working with "high pressures" of gas is that it leads to a loss of signal intensity. This happens because the gas increases the change of elastic scattering of the emitted photoelectrons, and hence a rise in the background signal and a reduction in peak intensity (see Chapter 2 for more details). The best way to overcome this is to increase the length of time the sample is scanned for. This allows for the collection of more a greater number of inelastically scattered photoelectrons and hence a better signal. However this takes more time, and runs the risk of damaging the sample by prolonged exposure to ionising radiation. A compromise between the two must therefore be reached

6.2.2 Model iron oxide support

The role of the oxide support was tested in a similar fashion. The support was modelled by oxidizing an iron foil. First the iron crystal was clean using argon sputtering (5 kV beam energy, 4kV focus, 15-30 μ A filament current). The crystal was then annealed at 700K for one hour. Still at 700K the crystal was then exposed to 5 x10⁻⁵ mbar of oxygen for 5 minutes. The crystal was then moved under UHV, into the high-pressure cell where it was exposed to a further 10⁻² mbar of oxygen at 700K for a further 5 minutes. After this time the crystal was returned to the preparation chamber and allowed to cool in oxygen (5x10⁻⁵ mbar). Cooling was facilitated by passing air through an inlet on the sample probe. The cooling process typically took one hour to complete.

The activity of the iron oxide film was tested in a similar manner to that of the gold foil, by exposures to gases at "high" pressure, in this case carbon monoxide, and a mixture of oxygen and carbon monoxide. All exposure of gases was done at a pressure of 10^{-2} mbar. Each time the iron oxide film was tested the following regions were scanned; $C_{(1s)}$, $O_{(1s)}$, $Fe_{(2p)}$, $Ni_{(2p)}$ and at a pass energy of 50 eV, and a survey scan at a pass energy of 100 eV. The reactivity of the oxygen/carbon monoxide mixture is tested by the examination of the $C_{(1s)}$ photoelectron peak since any adsorption of oxygen on the iron is likely to be obscured by the large $O_{(1s)}$ peak that arises from the iron oxide. The Ni_(2p) region was scanned as prior experiments indicated that there was a possibility of nickel contamination effecting the results of the experiment.

The growth of the iron oxide film was characterised by the calculation of the stoichiometry of the iron and oxygen peaks, as well as the comparison of the XPS spectra of the model foil and the binding energy values associated with iron oxide.

By comparing the intensities of the peaks involved in a compound A_xB_y with the sensitivities, and mean free paths of the respective photoelectron peaks it is possible to derive the stoichiometry of the system [16].

$$\frac{I_A}{I_B} = \frac{\mu_A}{\mu_B} \times \frac{x}{y} \times \frac{\lambda_A}{\lambda_B}$$
(6.1)

where I is the intensity of the photo electron peaks for $A_x B_y$, μ are the sensitivities of the peaks, and λ the mean free path. It is possible to approximate the factor of the equation involving the mean free paths by using this equation [16]

$$\frac{\lambda_A}{\lambda_B} \approx \left[\frac{K.E_A}{K.E_B}\right]^{0.75}$$
(6.2)

where $K.E_A$ is the kinetic energy of the main photoelectron peak for element A and $K.E_B$ is the kinetic energy of the main photoelectron peak for element B. The ratio of

kinetic energies resulting from Fe₂O₃ is 0.75, giving $\frac{\lambda_A}{\lambda_B} \approx \left[\frac{K.E_A}{K.E_B}\right]^{0.75} \approx 0.8$

Using the approximation derived above, and substituting the values of the known variables equation 1 simplifies down to:

$$\frac{I_A}{I_B} = \frac{(5.60 + 10.82)}{2.93} \times 0.75 \times \frac{x}{y}$$
$$\Rightarrow \frac{I_A}{I_B} = 4.203 \times \frac{x}{y}$$
(6.3)

The stoichiometry is calculated by solving the following equation:

$$x+y=100$$
 (6.4)

A gold film was then built up on the iron oxide surface. This was done by depositing gold onto the surface for 20 minutes. This surface was then exposed to the same gases as the iron oxide film. As previously mentioned all gas exposures were carried out at a pressure of 10^{-2} mbar.

6.2.3 Oxygen adsorption on bulk gold

There are several methods commonly used for the deposition of oxygen onto metal surfaces [14]. These include the use of ozone and mixtures Several early studies

of temperatures between 1127°C and 1527°C and exposed to oxygen $(5x10^{-5} \text{ m})$ The gold foil was then examined by XPS to see if any oxygen had adsorbed surface. The C_(1s), O_(1s) and Au_(4f) regions were examined at a pass energy along with a survey spectra taken at a pass energy of 100 eV. The Au_(4f) re extended to allow for the scanning of the nearby Pt_(4f) peaks. This would allow detection of any Pt adsorbed along with the O₂.

6.3 Results

6.3.1 Polycrystalline Gold Foil – Au Particle Modelling

When exposed to the various gas mixtures at high pressure, the only one that any reaction with the gold foil was the oxygen rich mixture (figures 6.1-6. particular mixture showed a build up of both oxygen and carbon on the surfat gold. Although not visible in the survey scans, analysis of the $Ni_{(2p)}$ region highlights the presence of nickel on the surface of the gold foil (figures figures and the survey scans) are substantial of the $Ni_{(2p)}$ regions from the other experiments also showed the of nickel contamination. The most probable source of nickel is the stainless s which the spectrometer is constructed.

In order to reduce the possibility of nickel contamination in further work is carbon monoxide, modification to the way in which the high-pressure cell w was required. Since making a spectrometer out of something other than stainless prohibitively expensive, the best solution was to find a way of removing the carbonyl from the gas flow before it reaches the sample, and to minimize the a stainless steel between the trap and the sample, so as to prevent further nickel from forming. This was achieved by placing a liquid nitrogen trap in front of valve that connects the gas line to the high-pressure cell. This removed the
carbonyl form the gas stream and is situated in such a way that the only stainless steel feature between the trap and the gas line is the leek valve itself.





The effectiveness of the cold trap was tested by exposure of the gold foil to carbon monoxide at a pressure of 10^{-2} mbar for 2 hours. No change in the signal of the Ni_(2p) peak was detected either before, during or after the exposure.

6.3.2 Model Iron oxide films

It can be seen that there is a strong correlation between the expected binding energy values of the Fe_(2p) peak for Fe₂O₃ and the values obtained from the analysis of the XPS spectra of the iron oxide film (figures 4-5). This gives a good indication that the film is composed of iron oxide. Substitution of the intensities of the O_(1s) and Fe_(2p) peaks into equation 3, gives rise to a value of 0.7143 for $\frac{x}{y}$. This gives a value $\frac{y}{x}$ of 1.4, which can be used in equation 4 to generate a stoichiometry of Fe₄₁O₅₉. This value is very close to the ideal stoichiometry of Fe₂O₃, and when combined with the XPS data shows that the oxide film generated is Fe₂O₃.



Analysis of the XPS results obtained by the exposure of the iron oxide film to various gases shows that there is no reaction between the surface and the gases. Figure 6.6 shows the $C_{(1s)}$ spectra for the iron oxide film after exposure to CO. The $C_{(1s)}$ spectra derived from the exposure of the other gas mixtures to the iron oxide film also show the same lack of reaction Analysis of the Ni_(2p) regions of the spectra shows that no deposition of nickel took place during the exposure of the gases.

The survey spectrum of a deposited gold film (figure 6.7) shows that the gold peaks dominate the spectrum. Closer examination of the surface, particularly around the binding energies of the $Fe_{(2p)}$ and $O_{(1s)}$ peaks shows that there is a complete attenuation of the signal from the underlying iron oxide film.



Figure 6.6: $C_{(1s)}$ Spectra of iron oxide film a) before exposure, b) during exposure and c) after exposure to CO

XPS analysis of the deposited gold foil shows little difference in the spectra taken before, during and after exposure to CO, NH_3 and a CO/O₂ mixture. This is lack of adsorption is indicative of there being no reaction between the newly deposited gold film and the gases.



6.2.3 Oxygen adsorption on bulk gold



It can be seen from figure 6.8 that it is possible to adsorb oxygen on bulk gold using a hot platinum filament by the method suggested by Madix [24]. However examination of the $Au_{(4f)}$ peaks (figure 6.9) shows the clear presence of Pt, which must have been adsorbed along with the oxygen.



6.3 Discussion

6.3.1 Polycrystalline Gold Foil - Au Particle Modelling

The presence of nickel on the surface of the sample suggests that the build up of carbon and oxygen onto the surface of gold foil is a result of the formation of nickel carbonyl, which adsorbs onto the surface of the gold. As a consequence, the much broader than expected peaks for carbon and oxygen, suggest that after the initial formation of nickel carbonyl clusters on the surface, further carbon monoxide is adsorbed, which spills over onto the gold foil itself. From the position of the oxygen and carbon peaks, 530 eV and 284 eV respectively, it seems likely that the adsorption is dissociative. If the adsorption were molecular, then the photoelectron peak of the carbon would be expected to shift towards higher binding energies. As the electro-negativity of the oxygen will cause an increase in the positive character of the carbon, which will cause the remaining electrons on the carbon to require more energy to remove, thus lowering the kinetic energy of the electron and raising its binding energy.



Figure 6.10: Suggested mechanisms for the nickel assisted adsorption of CO on gold foil

Two possible reaction pathway are suggested in figure 6.10. Spectrum (c) in figure 6.1 also shows a shoulder to the main carbon peak at 287 eV. This is suggestive of the formation of a carbonate on the surface. The broad nature of the $O_{(1s)}$ peak in figure 6.2 means that the signal from the oxygen component of the adsorbed carbonate is not clearly visible. The suggested mechanism is shown in figure 6.10, and involves the

scavenging of CO by adsorbed oxygen species. It is also possible that the carbonate could be formed by reaction of molecularly adsorbed CO with oxygen.

The source of the nickel is the stainless steel that the spectrometer is made from, leached by the carbon monoxide. This poses a problem for any study that uses carbon monoxide, since if the CO is removing nickel from the stainless steel, a lot of the results reported could well be artefacts instead of genuine chemical properties. Extended scanning of the $Ni_{(2p)}$ region of both used and unused iron oxide supported gold catalysts shows no traces of nickel (figure 6.11). This indicates that the results of the reactor studies are reliable, despite the presence of stainless steel in the construction of many carbon monoxide oxidation reactors. It seems probable that there is some sort of electronic effect between the particles and the support, which cannot be replicated on a polycrystalline foil. Support phenomena are possible and have been noted in metal doped semiconductors [17]



The lack of change in the signal of the $Ni_{(2p)}$ peak on the foil after prolonged exposure to CO shows that the $N_{2(1)}$ cold trap is an effective means of removing contaminants from the gas stream.

6.3.2 Model Iron Oxide films

The method used to grow the iron oxide film differs from that used by other groups. An alternative method is that pioneered by Freund and co-workers. His method involves the growth of the oxide on a platinum single crystal [18-19]. This is done by the evaporation of 1ML of iron on the Pt(111) single crystal, followed by oxidation in 10^{-6} mbar of oxygen at 1000K for a period of 2 minutes. This gives rise to a surface layer of FeO(111), which is slightly rotated with respect to the underling Pt(111) surface. The surface gives rise to a characteristic LEED pattern and this is used to judge the quality of the films. Freund is also able to grow Fe₃O₄ films by a similar method. This time the film is grown by repeated cycles of iron deposition at 90 or 300K, followed by oxidation at 900K. The process was finished with a final oxidation of the film 10^{-6} mbar of oxygen at 1000K for 5 minutes. These samples were characterised by the same method as the FeO films [20].

When compared to the films used by Freund to model Fe_2O_3 , it can be seen that the method used in this thesis just as successful. Most importantly the method of film growth form an iron crystal results in the actual formation of Fe_2O_3 , rather than the formation of a different allotrope.

As with the gold foil experiments, the iron oxide films show a lack of reaction with any of the gases it was exposed to. It seems reasonable therefore to conclude that the iron oxide support alone is also not responsible for the reported activity of iron oxide supported gold catalysts, and that the combination of the two are required for any sort of activity. What is not clear from these experiments is in what way the combination of gold nanoparticles and Fe_2O_3 is responsible for the activity these catalysts have shown. It is also worth noting that the lack of activity of the iron oxide film shows that the surface of the film remains unaffected by prolonged exposure to ionising radiation.

It has been noted that under certain conditions the adsorption of various species can be stimulated by exposure to ionising radiation [21]. It is possible for the physisorption of NO₂ on sputtered gold to be induced by exposure to x-rays. A low energy electron flux from the metal substrate irradiates the gold adlayer. It is this electron attachment which leads to adsorption of the NO_2 [21].

The complete attenuation of the iron and oxygen peaks in the deposited gold films shows that the film is at least 40 Å in depth, since this is the maximum escape depth of inelastically scattered photoelectrons produced by Alk α radiation. If the gold film were thinner than the signal from the iron oxide film beneath it would be visible in the spectrum.

Any defects on the surface of the iron oxide film will not be replicated on the surface of the gold film as the difference in size between the gold atoms and the iron and oxygen atoms that make up the iron oxide film. Instead the surface of the gold film with have a different range of defects brought about by both the previously mentioned mismatch in sizes of the gold and iron oxide foils and the way in which the surface is built up during the deposition of the gold. The lack of reactivity of this thick film suggests that a smaller film is needed to produce a better model of the activity of gold nanoclusters deposited on iron oxide.

6.3.2 Oxygen adsorption on bulk gold

The presence of adsorbed platinum is constant with the results of Yates [25], which shows that it is impossible to adsorb atomic oxygen on gold by using a heated platinum filament between the temperatures of 27 and 1627°C without contamination of the sample by platinum. This result calls into question previous studies which have used a Pt filament as a thermal source of atomic oxygen.

6.4 Conclusions

When exposed to an oxygen rich mixture of carbon monoxide and oxygen, nickel is leached out of stainless steel and adsorbed onto polycrystalline gold in the form of nickel carbonyl. When the nickel contamination is removed from the gas stream the polycrystalline gold is shown to be entirely unreactive towards the adsorption of oxygen and carbon dioxide.

It has been shown that it is possible to grow an iron oxide film from an iron single crystal. These iron oxide films have shown to be unreactive when exposed to oxygen, and carbon monoxide. However, these films have shown that they are unaffected by exposure to ionising radiation for extended periods of time. As a model for catalytic metal oxides supports the iron oxide films have demonstrated that the support alone does not have the activity reported in literature. Instead a combination of both metal oxide support and small gold particles is necessary to achieve any kind of activity.

Thick gold films deposited on top of the iron oxide film have proved to be unreactive when exposed to high pressures of oxygen, and carbon monoxide.

6.5 References

- 1. G.A. Somorjai, Introduction to surface chemistry and catalysis, Wiley, New York, 1994
- 2. G.A. Somorjai, Surf. Sci. 1999, 299, 849
- D.W. Blakley, E. Kozak, B.A. Sexton, G.A. Somorjai, J. Vac. Sci. Technol. 1976, 13, 1091
- 4. A.L. Cabrera, N.D. Spencer, E. Kozak, P.W. Davis, G.A. Somorjai, Rev. Sci. Instrum. 1982, 53, 1888
- 5. R. Imbihl, M.P. Cox, G. Ertl, J. Chem. Phys. 1986, 84, 3519
- 6. K. McCrea, J. Parker, G.A. Somorjai, Surface Chemistry and catalysis (edited by A.F Carley, P.R. Davis, G.J. Hutchings and M.S. Spencer), Kluwer Academic/Plenum Pulishers, 2001
- 7. H.P. Bonzel, Surf. Sci. 1977, 68, 236
- 8. H.J. Freund Ber. Bunsenges. Phys. Chem. 1995, 99, 1261
- 9. M. Baumer, H.J. Freund Progr. Surf. Sci. 1999, 61, 127
- 10. D.W. Goodman Surf. Rev. Lett. 1995, 2, 9
- 11. P.L.J. Gunter, J.W.H. Niemantsverdriet, F.H. Ribero, G.A. Somorjai, Catal. Rev. Sci. Eng. 1997, 39, 77
- 12. D.A. Bonnel, Progr. Surf.Sci. 1998, 57, 187
- 13. H.J. Freund, H. Kuhlenbeck, V. Staemmler, Rep. Progr. Phys. 1996, 59, 283

- 14. B.C. Gates, L. Guczi, H. Knozinger, Metal Clusters in Catalysis, Elsevier, Amsterdam, 1986
- 15. H.J. Freund, M. Bäumer, H. Kuhlenbeck, Adv. in Cat. 2000, 45, 333
- 16. A.F. Carley, PhD thesis, University of Bradford, 1980
- 17. L.S. Wielunski, D.H. Hill, J. Quinn, R.A. Bartynski, P. Wu, Y. Lu, Nuc. Inst. & Meth. Phys. Res. B 2004, 219-220, 708
- 18. W. Weiss, M. Ritter, Phys. Rev. B, 1999, 59, 5201
- 19. Sh. Shaikhutdinov, M. Ritter, X.G. Wang, H. Over, W. Weiss, *Phys. Rev. B*, 1999, **60**, 11062
- 20. Sh. Shaikhutdinov, R. Meyer, M. Naschitzki, M. Bäumer, H.J. Freund, Cat. Lett. 2003, 86, 211
- 21. D.J. Morgan, personal communication, 2004
- 22. M.E. Schrader, J. Colloid Interface Sci. 1977, 59, 456
- 23. M.A. Chesters, and G.A Somoraji, Surface Sci. 1975, 52, 21
- 24. N.D.S Canning, D. Outka, and R.J. Madix, Surface Sci, 1984, 141, 240
- 25. V.S. Sementkowski, J.T. Yates, J. Vac. Sci. Technol. A, 1993, 12, 224

Chapter 7: Conclusions and Future Work

7.1 Conclusions

7.1.1 General conclusions

Small gold particles supported on iron oxide have shown to be highly active for a wide range of different catalytic reactions, including oxidation, hydrogenation, and dehydration. However it is difficult to directly compare these results with those obtained by other groups due to the wide variety of conditions reported in the literature.

Through examination by XPS a clear difference has been shown between catalysts of high and low activities both for crotonaldehyde hydrogenation and carbon monoxide oxidation.

Through the use of the correlations shown in this thesis it is possible to indicate or predict the activity of a catalyst based on characterization data obtained through XPS.

The presence of Au^+ in catalysts that display a high activity for both carbon monoxide oxidation and crotonaldehyde hydrogenation, combined with its absence in catalysts with a low activity for both reactions, suggests that ionic gold is required in the rate determining step of both reactions. It also hints that both reactions require a similar active site, although further work is required to prove this.

7.1.2 CO Oxidation conclusions

It has been clearly shown in this thesis that differing supports alter both the activity of a catalyst and the effect that heat treatment has on the activity of a catalyst.

In the preparation of the Au/Fe₂O₃ catalysts by co-precipitation only the final pH affects the activity. The pH change the catalyst undergoes to reach that point seemingly plays no role in shaping its activity.

Characterization of Au/Fe₂O₃ catalysts by XPS and XANES has suggested that heat treatment affects the activity of catalysts by altering the ratio of Au^0 and Au^+ and stripping the hydroxyl groups from the surface. The critical ratio for this effect has yet to be determined but XANES experiments have shown that it lies in favour of the cationic gold.

TEM and XANES analysis of Au/Fe₂O₃ catalysts supports the theory that the active site of the catalyst consists of a gold particle made up of Au⁰ and ionic gold (probably Au⁺). The latter gold species is in the majority in the more active catalysts.

XPS characterization of iron oxide supported gold catalysts indicated the presence of a surface hydroxyl species in catalysts with a high conversion of carbon monoxide. These findings are consistent with currently accepted models of the active site for this reaction.

7.1.3 Crotonaldehyde Hydrogenation Conclusions

The hydrogenation of crotonaldehyde over iron oxide supported gold catalyst has been shown to be affected in a number of ways, by a variety of different factors such as: reaction temperature, interaction between the metal and the oxide support and pre treatment

The highest conversions were obtained at a reaction temperature of 150°C.

At low heat treatments the major product of this reaction is butene, but as the temperature of the pre-treatment is increased the major product of the reaction changes to crotyl alcohol, although with lower conversion of crotonaldehyde.

It has been postulated that the production of butene is the result of a second reaction catalyzed by iron oxide supported gold catalysts; that of the dehydration of butnan-1-ol.

7.1.4 Model Catalyst Conclusions

When exposed to an oxygen rich mixture of carbon monoxide and oxygen, nickel is leached out of stainless steel and adsorbed onto polycrystalline gold in the form of nickel carbonyl. When the nickel contamination is removed from the gas stream the polycrystalline gold is shown to be entirely unreactive towards the adsorption of oxygen and carbon dioxide.

It has been shown that it is possible to grow an iron oxide film from an iron single crystal. These iron oxide films have shown to be unreactive when exposed to oxygen, and carbon monoxide. However, these films have shown that they are unaffected by exposure to ionising radiation for extended periods of time. As a model for catalytic metal oxides supports the iron oxide films have demonstrated that the support alone does not have the activity reported in literature. Instead a combination of both metal oxide support and small gold particles is necessary to achieve any kind of activity.

Thick gold films deposited on top of the iron oxide film have proved to be unreactive when exposed to high pressures of oxygen, and carbon monoxide. This unreactivity would seem to indicate that the model used is a poor one, since it does not resemble the activity produced under catalyst testing.

7.2 Future Work

7.2.1 CO Oxidation

The catalysts used in this thesis could undergo further characterization buy techniques such as XRD and Mossbauer spectroscopy to better clarify the active site for this reaction.

The effect of heat treatment between 100°C and 200°C requires more in depth analysis. The effect had by the method of heat treatment on the activity of catalysts needs further investigation, especially the possibility of contamination of samples by the equipment being used to calcine them. Further studies could be carried out on the effect of water vapour on the activity of used Au/Fe₂O₃ catalysts.

Binding energy correlations could be investigated in gold catalysts with different supports, as well as in bimetallic catalysts.

Further catalytic data needs to be generated on different supports using the reaction conditions used in this thesis, as there are very few catalytic studies that can be directly compared due to differing reaction conditions.

The effect of long term usage on the activity of iron oxide supported gold catalysts could also be investigated.

7.2.2 Crotonaldehyde Hydrogenation

The hydrogenation rig could be modified to provide a more constant flow of crotonaldehyde over the catalyst sample.

The use of Au/Fe₂O₃ as a catalyst for dehydration reactions could be investigated.

Further characterization of the catalysts similar to that reported in chapter 4 could be undertaken to give better insight into the active site for this reaction. This characterization could be undertaken for both reduced and unreduced catalysts.

The activity of the catalysts could be tested at lower reaction temperatures in order to eliminate the dehydration step of the reaction, and to test the selectivity of the catalysts that displayed a high conversion of crotonaldehyde to butene.

7.3 Model Catalyst Studies

Different methods of modelling small gold particles need to be investigated as the ones used in this thesis proved to be ineffective.

