CARDIFF UNIVERSITY

Cardiff School of Chemistry

Synthesis of active supported gold catalysts for CO oxidation and Light alkane activation

A thesis submitted to the Cardiff School of Chemistry, Cardiff University
in fulfilment of the requirement for the degree of

Doctor of Philosophy

BY

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2006

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DEDICATION

This thesis is dedicated to:

My parents

My wife and beloved Children

Abdullrhman

Shaden

Layan

ACKNOWLEDGEMENTS

First of all, the greatest appreciation to the God, Allah, for he has giving me and my family the good health and spiritual supports, emotional and physical strength, to go through this journey of life.

Special thanks to the people who have help in guiding and gathering the thesis: my supervisors Prof. Graham Hutchings, Dr. Stuart Taylor and Dr. Albert Carley. This work could not have been completed without their great support and sincere help. Thanks for giving me the opportunity to study my PhD, advice and support during the study.

I also would like to thank my employer, SAUDI BASIC INDUSTRIES CORPORATION (SABIC) for sponsoring my study. Thanks to Mr.Khalid Al-Salem, Mr. Fahad Al-Semaih, Special thanks to my supervisor in SABIC, Dr.Khalid Karim, for his support since I joined his group in SABIC R&D. Many thanks to my brother in Allah, Dr. Flaiyh Al-Anazi. Thanks to my colleagues and friends in lab 1.96 and 1.88 who have helped me during my study in Cardiff.

The great thanks and my heartful gratitude goes to my parents, my wife and my children for their emotional support.

Abstract

The preparation of gold catalysts supported on different metal oxides such as ZnO and Fe_2O_3, using two coprecipitation methods is investigated to determine important factors, such as selection of support material and preparation method, and preparation parameters, such as preparation temperature, pH, and ageing process. These factors control the synthesis of high activity catalysts for the oxidation of carbon monoxide at ambient temperature. The two preparation methods differ in the manner in which the pH is controlled during coprecipitation, either constant pH throughout or variable pH in which the pH is raised from an initial low value to a defined end point. Non-calcined Au/ZnO catalysts prepared using both methods are very sensitive to pH and ageing time. Catalysts prepared at higher pH give lower activity. However, all catalysts require a short indication period during which the oxidation activity increases. In contrast, the calcined catalysts are not sensitive to preparation conditions. Non-calcined Au/Fe_2O_3 catalysts exhibit high activity when prepared at pH $\geq$ 5. Active calcined Au/Fe_2O_3 catalysts can be prepared when the pH is controlled at pH 6-7, 8, whereas calcined catalysts prepared using the variable pH method are inactive. The study demonstrates the immense sensitivity of catalyst preparation methods on the performance. Catalysts exhibited excellent catalytic activity and stability compared with the pure supports, ZnO and Fe_2O_3, and the best preparation temperature was 80 °C. Use of temperatures $\geq$ 80 °C led to inactive catalysts. The deposition-precipitation (DP) method was also employed using four different supports in this study (ZnO, Fe_2O_3, MgO, and MnO_2). A comparison between these catalysts was taken rather than an investigation of the effect of the preparation parameters on catalysts prepared by DP method because they have been well studied previously. Several characterization techniques including AAS, BET surface area, XRD, TPR, and XPS, were utilised to investigate the physical and chemical properties of the prepared supported gold catalysts. Characterization results were combined with catalytic results for the low temperature CO oxidation reaction of catalysts in order to study the aforementioned factors that can affect either the properties of catalysts or their activities. Subsequently, several experiments at high GHSV were conducted to study the catalytic activities of these catalysts in-depth and to correlate data with alkane activation reactions. CH_4 activation reaction using supported gold catalysts at light temperatures and the effect of the preparation parameters, types of supports on catalysts activities were investigated. The Au/Fe_2O_3 catalyst prepared by coprecipitation method B at pH 8 showed the highest catalytic activity for CO oxidation and CH_4 activation reactions. The most active catalysts were also evaluated for C_2H_6 and C_3H_8 activation at low temperature. After this, a comparison between CO oxidation and alkane activation over supported gold catalysts was undertaken to investigate the relationship between the behaviour of supported gold catalysts for these two types of reactions. Activation energies and pre-exponential factors of many catalysts were calculated based on the Arrhenius equation either for CO oxidation or for alkane activation.

Micro Abstract

The preparation of gold catalysts supported on different metal oxides such as ZnO and Fe_2O_3, using two coprecipitation methods is investigated to determine the important factors that control the synthesis of high activity catalysts for the oxidation of carbon monoxide at ambient temperature. The effect of preparation methods, type of support, preparation parameters, such as temperature, pH, and ageing time on the catalytic activity of supported gold catalysts towards CO oxidation and light alkane (C_1-C_3) activation reactions was examined. Several characterization techniques such as; AAS, BET surface area, XRD, TPR, and XPS, were employed to investigate the physical and chemical properties of the prepared supported gold catalysts. comparative study of CO oxidation and alkane activation over supported gold catalysts was conducted to investigate the relationship between the behaviour of supported gold catalysts and these two types of reactions using activation energies and pre-exponential factors based on the Arrhenius equation, either for CO oxidation or for alkane activation.

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Chapter 1

Introduction

1.1. Background

1.1.1. Definition of catalysis

The world 'catalysis' was used for first time by J.J. Berzelius in 1836 when he explained some enhanced chemical reactions [1]. G. C. Bond defined the catalyst, as '' *a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process* '' [2].

1.1.2. Importance of catalysis

Catalysis is important in both academic and industrial research. It plays an essential role in the production of a wide range of products. Between 85-90% of chemical industry products are made through catalytic processes. In the presence of a catalyst, reactions can be conducted at lower temperatures or lower pressures. Also, some reactions such as ammonia synthesis are industrially only possible with the assistance of a catalyst. Catalysis is an essential part of the manufacturing process, catalysis has other important applications; for example, its successful use in the control of pollution, called green chemistry.

1.2. Types of catalysis

In general, there are three types of catalysis. Bio catalysis where reactions are catalysed by enzymes. This type of catalysis is very fast, selective, sensitive, and usually occurs at mild conditions. Homogeneous catalysis, where the catalyst is of the same phase as the reactants and no phase boundary appears. This type of catalysis usually occurs in the gas phase or in the liquid phase. However, it is not within the scope of this thesis to discuss these two types of catalysis.

1.3. Heterogeneous catalysis

Hetero implies different. Heterogeneous catalysis occurs when the catalyst is in a different state from the reactants. An example of this would be using a metal oxide to catalyse gas phase reactions. The essential principles of heterogeneous catalysis for gas-phase reactions are indicated involve;

1. The product of the catalysed reaction can be obtained from uncatalysed reaction. However, the uncatalysed reactions can be slow and non-selective to the desired products.
2. The presence of the catalyst changes the rate at which equilibrium is achieved.
3. The useful catalyst must have a high turn over number, which means the reaction steps must occur several times on the surface of the catalyst before the catalyst loses its activity.
4. Usually, the reaction takes place on the surface of the catalyst. The reaction may occur between gas molecules adsorbed on the catalyst's surface, or the topmost atomic layers of the catalysts can be involved in the reaction. However, the influence of the catalytic effect is restricted to the range of an atomic diameter into the gas phase.

The process of heterogeneous catalysis includes the adsorption of one or more of the reactants on to the surface of the catalyst at active sites, where one or more of the reactants adsorb to the catalyst's surface. The active site is a part of the surface which is particularly good at adsorbing reactants molecules and helping them to react. The adsorption process involves some kind of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This interaction might be an actual reaction with the catalyst's surface, or some weakening of the bonds in the attached molecules. After the adsorption, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one producing product and moving freely in the gas or liquid. This process is called desorption of the product molecules. Desorption simply means that the product molecules leave the catalyst's surface to the gas or liquid phase. This leaves the active site available for a new set of molecules to attach to and react. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react. Heterogeneous catalysis has many advantages, such as: easy separation of product and catalyst, high catalyst life time, production of chemicals, cleaning of waste and exhaust gas streams (environmental catalysis), and energy conversion- fuel cell.

1.4. Oxidation catalysis

This introduction is not intended to present a complete survey of all published works on oxidation catalysis, but rather to provide background details of this process and summarise commercial reactions in the petrochemical industry using this process. Challenges facing industrial/academic researchers and recent important developments in catalytic oxidation reactions, including oxidation by gold catalysis, will also be detailed.

There are many types of catalysed reaction used in the petrochemical industry such as dehydrogenation, hydrogenation, isomerization, and oxidation. However, oxidation catalysis processes include the production of chemicals, intermediate via selective oxidation catalysis, and environmental removal of pollutants process via total oxidation catalysis. The scientific design of the catalysts used in partial oxidation processes is a topic of interest for many industrial and academic researchers due to its important role in the industrial petrochemical production. Selective oxidation catalysts should activate the oxidant, the reactant, but not catalyse the oxidation of the required product [3].

Main challenges for the researchers aiming to optimise catalysts for oxidation processes are developing an understanding of the catalyst structure, the active site of the catalyst, employing useful preparation techniques and characterization of the catalyst as well as understanding the reaction mechanism and catalyst activity by studying the reaction kinetic [4]. The main aim of recent development in the heterogeneous oxidation catalysis is to look for the alternative, less expensive reagents and to reduce the environmental impact of chemical production process. A recent goal is also the selective oxidation of alkanes. Some of these reactions exist in the commercial process, such as production of acetic acid and maleic anhydride from ethane [5] and n-butane [6] respectively, using mixed oxide catalysts. Another recent interesting development in heterogeneous oxidation catalysis is oxidation by supported gold catalysts.

1.5. Oxidation by gold

1.5.1. Physical and chemical properties of gold

Gold's atomic number is 79; it is located in the third row of transition metals in the periodic table, in group IB. Its electronic configuration is $[Xe]4f^{14}5d^{10}6s^{1}$, and the common oxidation states are +1 and +3 . Gold is the least reactive of the noble metals and due to its electronegativity it does not react directly with electronegative elements such as oxygen [7].

1.5.2. History of catalysis by gold

Due to the unreactivity of gold, it was neglected as a catalyst for a long time. The first hint of gold catalysis was when Bond and Sermon prepared dispersed Au on SiO_2 as small nanoparticles [8]. The interest in gold catalysis was revitalised when Hutchings predicted in 1985, and then confirmed, that Au would be the most active catalyst for the hydrogenation of acetylene to produce vinyl chloride [9]. After that, Haruta [10] demonstrated that gold could catalyse CO oxidation at sub ambient temperature. This was a particularly exciting development in gold catalysis. In the last decade, there has been a rapid growth of interest in the catalysis by gold. Fig. 1.1 and 1.2 show the rapid increase in patents and publications in this subject.

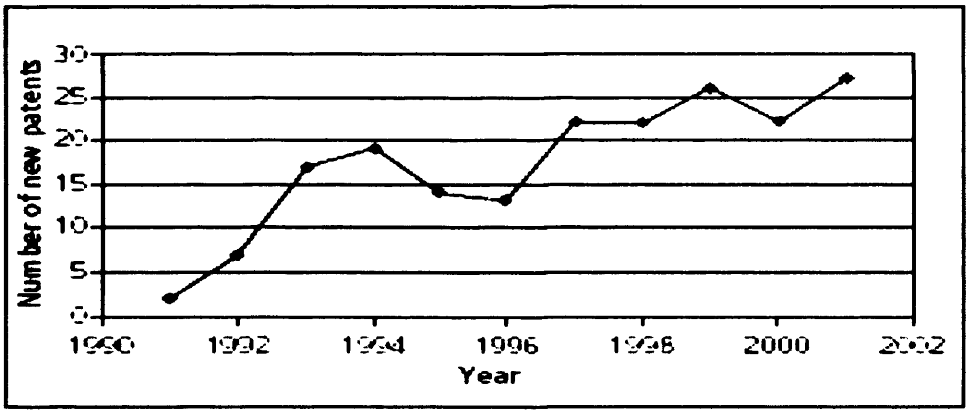

Figure 1.1 Number of patents based on catalysis by gold [11]

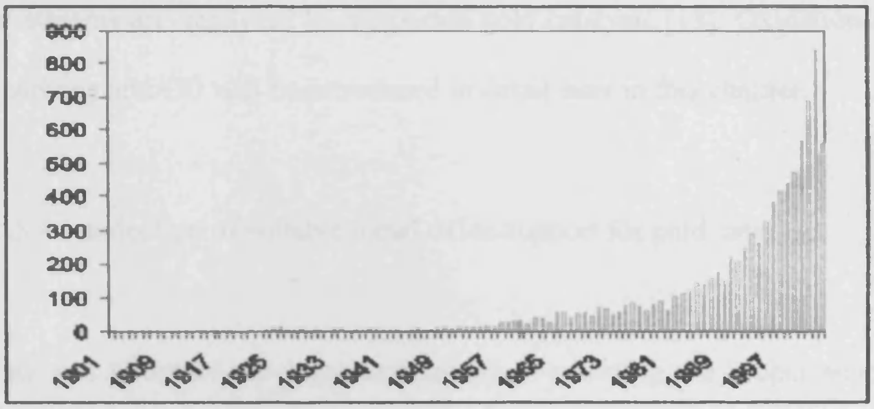

Figure 1.2. Number of publications based on catalysis by gold [11]

1.5.3. Importance and applications of gold catalysis

Many senior researchers envisage a good future overview for gold catalysis. Hutchings said " *Recent research shows that for a number of reactions gold can provide the highest catalytic activity when compared with other metals* " and Bond said " *We may confidently expect further developments, and early in the new millennium gold should take its place alongside its neighbours as a vital member of the armoury of transition metal catalysts* " [11] and Haruta said " *This type of element is ideal for use in the 21st century! What other element can meet all these objectives as well as gold does?*" [12]. Supported gold catalysts can be used for a wide range of reactions that have potential for applications in chemical processing, pollution control, and fuel cells. Hydrogenation of acetylene, oxidation of CO and hydrocarbons, selective oxidation of hydrocarbons, selective hydrogenations, water gas shift reaction, reduction of NO, hydrogen and oxygen reaction and removal of CO from hydrogen streams are catalysed by supported gold catalysts [13]. Oxidation reactions of hydrocarbons and CO will be introduced in detail later in this chapter.

1.5.4. Selection of suitable metal oxide support for gold catalysis

Type, state and structure are important factors in selecting the proper support. The support should be thermostable with a high surface area and suitable mechanical strength to be able to disperse the active component, in this case gold, and to increase its thermal stability and therefore increase the catalyst's life. The excellent catalytic performance by gold can be brought about by the proper selection of support materials. Gold becomes active as a catalyst when it is highly dispersed and deposited on reducible semiconductor metal oxide or hydroxides of alkaline earth metals [14]. Many examples of supports will be presented in the introduction to preparation methods for supported gold catalysts later in this chapter.

1.6. CO oxidation

CO oxidation is an important reaction for the removal of CO from air to produce high purity nitrogen and oxygen [15]. It is also an important reaction for breathing equipments. The industrial catalyst used for CO oxidation is called hopcalite, which is a mixed oxide of copper and manganese ($CuMn_2O_3$) [16]. However, this catalyst is deactivated by the presence of water and unstable for long-term use. Haruta was the first to show that supported Au catalysts are highly effective for the oxidation of carbon monoxide at sub ambient temperature [10]. However, it has been known since 1925 that gold surfaces are able to catalyse the oxidation of carbon monoxide [17]. In the last decade, there has been a rapid increase in research on CO oxidation using supported gold catalysts, and high activity of CO oxidation reaction has been reported for a range of supported gold catalysts at ambient temperature [18, 16]. While gold as a metal is known to be non active as a catalyst, any enhancement in the activity in Au-metal oxide catalytic systems may be exclusively attributed to the electronic interaction and / or the active sites on the interfacial boundary obtained from the deposition of gold on a support. The shape of the small gold particles is hemispherical and they are stabilised by contact with an amorphous layer. Supported gold catalysts with small gold particle size show high catalytic activities for low temperature CO oxidation, possibly because the small gold particles not only provide the sites for the reversible adsorption of CO but also significantly increase the amount of oxygen adsorbed on the support oxides [14].

Gold in the form of sponge, wire, powder and large supported gold particles is non-active for CO oxidation reaction. Much higher activity is shown by oxide supported small gold particles (<5 nm), choice of support is very important, the method of preparation is critical, and the pre-treatment mode is important. All these points are agreed by researchers. However, there are still some controversies concerning how gold catalyses oxidation of CO, the stability of the catalyst with time, the best conditions for calcination, and which is the catalytically active gold species, Au° or in oxidised species [19]. The figure below presents a suggested mechanism for CO oxidation reaction.

$$Au^{0} + CO \rightarrow Au^{0}...CO \tag{1}$$

$$Au^{III} + OH_{s}^{-} \rightarrow Au^{II}...OH \tag{2}$$

$$Au^{0}...CO + Au^{II}...OH \rightarrow Au^{II}...COOH + Au^{0} \tag{3}$$

$$O_2 + \Box_{s}^{-} \rightarrow O_2^{-}...\Box_{s} \tag{4}$$

$$Au^{II}...COOH + O_2^{-}...\Box_{s} \rightarrow Au^{II} + CO_2 + HO_2^{-}...\Box_{s} \tag{5}$$

$$Au^{II}...COOH + HO_2^{-}...\Box_{s} \rightarrow Au^{II} + CO_2 + 2\,OH_{s}^{-} + \Box_{s} \tag{6}$$

$$Au^{II} + \Box_{s} \rightarrow Au^{III} + \Box_{s}^{-} \tag{7}$$

Figure1.3. Proposed mechanism steps for CO oxidation [19]

In the above mechanism, the authors suggested that that both Au^0 and Au^+ present on the surface of the support and both are responsible for the activity of the supported gold catalyst. However, the authors noted that this mechanism might not be the same for all catalysts.

1.7. Hydrocarbon Oxidation catalyzed by supported gold catalysts

1.7.1. Low-temperature catalytic combustion

To-date, only methanol can be catalytically oxidised by gold at room temperature [20]. The complete oxidation of methanol, formaldehyde, and formic acid can be brought abut by gold supported on TiO_2, α-Fe_2O_3, or Co_3O_4, which is almost as active as Pd or Pt supported on Al_2O_3. The oxides of transition metals of group VIII and the hydroxides of alkaline earth metals are suitable supports for this reaction [15].

Haruta et al. [21] prepared Au, Pd and Pt catalysts on α-Fe_2O_3 and Al_2O_3 supports. They concluded that an Au/α-Fe_2O_3 catalyst is as active as Pt, Pd/Al_2O_3 catalysts for the oxidation of methanol, formaldehyde, and formic acid. They reported also that the pH of a starting solution, metal loading, and the calcination atmosphere are very important factors for preparing highly active supported gold catalysts.

1.7.2. Catalytic combustion of hydrocarbons

Hutchings at el. [22] prepared several Au/MgO catalysts ranging between 0.04 and 15 wt % of Au loading and investigated them for methane oxidation. $Mg(OH)_2$ was pelleted and sieved to a particle size of 600-1000 μm and then calcined in air at 450 °C for 24 h and 24 h at 800 °C to obtain MgO. The calcined support was impregnated with an aqueous solution of $HAuCl_4$, the catalysts were dried at 110 °C for 16 h and then calcined for 800 °C for 3 h. The prepared catalysts were tested for methane oxidation (CH_4 46%, O_2 8%, He 46%) at GHSV 750 h^{-1} and the reaction temperature was 750 °C. The addition of gold to MgO using the impregnation procedure had a significant effect on the MgO structure; the most significant effect of the addition of gold on the structure of MgO was that the crystallite size of MgO increased by increasing Au loading. This effect depended on the level of loading of gold on MgO. Also, two morphologies were indicated in the Au/MgO catalyst, two dimensional Au rafts, observed at low gold loading, and three dimensional Au particles between 5-10 nm in diameter. Catalyst activity data showed a significant effect with respect to Au loading. Three clear types of activity were observed using Au/MgO catalysts. The first type was observed at very low Au loadings (0.04 wt %); in this type of activity, methane coupling activity was observed. However, there was a decrease in CH_4 conversion, although the surface area increased when comparing the results of MgO only. This decrease was because of the decrease in the formation of the coupling products, due to blocking or poisoning of the surface sites by gold. However, higher gold loading showed a decrease in both surface area and methane conversion. The second type of activity was observed at intermediate loading of gold (up to 2 wt %); in this type of activity, by increasing the loading of gold, CO formation was increased. The third type of activity was observed at a high concentration of gold (≥ 5 wt %) and led to an increase in the formation of CO_2, which appeared to be due to the oxidation of CO obtained.

Smith et al. [23] studied the activities of coprecipitated gold on transition metal oxides for methane oxidation. The observed trend in activities was $Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3 >> Au/CeO_x$. XPS analysis showed the presence of reduced and oxidised gold and also that all gold supported catalysts had Na with a concentration higher than 5wt%, indicating that Na was in the form of carbonate (from the precipitant Na_2CO_3). The authors concluded that methane oxidation activities increased by increasing the oxidation state of gold. Haruta confirmed that the Au/Co_3O_4 catalyst showed the highest activity for combustion of hydrocarbons [15].

Su et al. [24] prepared a new generation of gold-vanadia catalysts supported on mesoporous zirconia and titania supports. The mesoporous supports were prepared using the surfactant templating method. Gold and vanadia were deposited on these supports. The authors reported that the vanadia loading stabilised the structure of both supports and this effect was stronger for zirconia than titania. They reported also that the presence of gold reduced the oxidation state of vanadia from V^{5+} to V^{3+}. The catalytic activity of the prepared catalysts was strongly dependent on the preparation procedure. On both supports, when vanadia was loaded on the supports first, the catalytic activity for complete benzene oxidation was lower than when gold was deposited initially. Also, when the gold-vanadia catalyst was deposited on mesoporous titania, a strong synergistic effect between gold and vanadia was observed and, therefore, gold-vanadia on mesoporous titania showed higher activity than gold-vanadia deposited on mesoporous zirconia.

1.7.3. Selective partial oxidation

Hutchings et al. [25] studied the direct formation of hydrogen peroxide from H_2/O_2 using supported gold catalysts. They prepared several gold catalysts supported on different oxides. Au/ZnO was prepared by coprecipitation procedure while was Au/Al_2O_3 prepared by the impregnation procedure. The catalysts were tested for hydrogen peroxide formation at 2 °C using methanol as a solvent. The results showed that the supported gold catalyst produced more H_2O_2 than the supported Pd catalyst. The authors also reported that when gold was alloyed with Pd as Au:Pd (1:1 by wt), more H_2O_2 was produced than with the supported gold catalyst, indicating that Pd was a promoter for the gold catalyst. They concluded that the effect of Pd on the hydrogen peroxide yield was either due to a decrease in the rate of H_2O_2 decomposition or an enhancement in the rate of H_2O_2 formation.

When Au, Pd, and Pt are supported on $Bi_2Mo_3O_{12}$, which is an active phase for the partial oxidation of propylene to acrolein, only gold increases the yield of acrolein maintaining selectivity unchanged while Pd and Pt enhance complete oxidation of propylene to CO_2 [15].

Hutchings et al. [26] studied the effect of doping lithium and gold on the structure morphology of MgO and the catalytic performance of methane oxidative coupling on this catalyst. MgO was prepared by thermal decomposition of $Mg(OH)_2$. Li^+ was doped on MgO by the incipient wetness impregnation method while Au was doped using the multiple impregnation method. The authors found that the addition of Li^+ decreased the surface area of the support and increased the grain size of the crystallites, while gold did not increase the crystallite size to the extent observed with lithium. They reported that doping lithium increased the activity and selectivity to C_2 hydrocarbons while gold decreased the selectivity of hydrocarbon and led to increased selectivity of CO_2. They reported also that Li^+ pinning could result in the formation of an active site for methane activation such as $[Li^+O^-]$ centres at the catalyst's surface. These centres are considered to be responsible for the methane coupling reaction. Gold is less selective for methane coupling.

Recently, Grzybowska et al. [27] prepared a range of gold catalysts supported on different supports using the deposition-precipitation method. The catalytic behaviour of Au/oxide support catalysts in the oxidation of CO, propane and propene was found to depend mainly on the nature of the support. They reported that the activity in CO oxidation was higher for Au-based catalysts with transition metal oxides as the supports than for those supported on oxides of main group elements (Mg, Si, Sn). Oxidation of propane gives carbon oxides as the only reaction products. Propene oxidation (in the presence of H_2) gives at temperatures higher than ~150 °C oxygenated products (mainly propanal and ethanal) on Au supported on oxides of main group elements, whereas catalysts with transition metal oxides perform in these conditions mainly total combustion. Propene oxide, as the main reaction product, was observed only at low temperatures (<150 °C) for catalysts containing Ti in the support, with a yield of ~1%.

1.8. Supported gold catalysts preparation methods

The common methods for preparing supported gold catalysts require a combination of several operational steps which can be described as: (i) introduction of the metal source on the support by impregnation, ion-exchange, coprecipitation and deposition-precipitation, and (ii) drying and calcination [28]. The impregnation method is not an ideal route for the preparation of supported gold catalysts, as it can leave impurities in the catalyst, the gold particles formed are very large (10-30 nm), and it does not give a high dispersion of gold species on the surface of the support.

The ion exchange method is especially effective with zeolites. In this preparation method, cations of the active metal replace the cations on the support surface or within its structure. Gold particles should be dispersed on the zeolite first and then calcined to form very small particles. This method has a disadvantage, which is the limited numbers of cationic gold complexes that can be formed [28]. Coprecipitation and deposition-precipitation methods obtain highly active supported gold catalysts because they provide the desired intimacy of contact between the metal and the support, and small (<5 nm) Au particles can be obtained by these methods. In order to produce active catalysts via coprecipitation and/or deposition-precipitation procedures, many variables have to be controlled, these variables will be described later. The coprecipitation procedure produces catalysts with uniform distribution of the active component on the support. It is the preferred procedure to prepare supported catalysts with a metal loading higher than 10-15%. Metallic gold with a narrow size distribution can be produced by the deposition–precipitation method. This method also prevents the formation of rafts of gold clusters, which are often observed in coprecipitated samples. My research study was based on coprecipitation and deposition methods; therefore, these two methods will be discussed in more details in the next subsections.

1.8.1. Coprecipitation

In the coprecipitation procedure, the solutions of the active metal salt and a salt of the compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxides and/or carbonate. The precipitation step is followed by filtration, washing, and then hydroxides and/or carbonate will be converted to oxides by heating. This technique can be applied to salts of metals in the first row of the transition series in groups 4-12 and also to Al and Mg, which can be precipitated as hydroxides or hydrated oxides [7].

The choice of salts and/or alkali depends on their solubility in the solvent (water), and on avoiding the introduction of compounds that can have negative effects on the final catalyst, such as chlorine, which is a well known poisoner of the catalyst. Therefore, nitrate salts or organic compounds, such as oxalate, are preferred to be used as sources of the precipitated solutions. Alkali carbonates, bicarbonates, and hydroxides can be used as precipitant agents.

In order to produce active catalysts via coprecipitation, many variables have to be controlled, such as; (1) temperature; (2) pH (for the multicomponents system, the pH (value and variations) has to be carefully controlled in order to avoid the precipitation of components at a different sequence that may affect the final structure of the catalyst. In coprecipitation method, the final pH is an important variable since the components present in the reaction mixture precipitate at different pH values [29]; (3) mixing rate; (4) ageing time, which often allows the precipitate to become a more crystalline structure; and (5) finally, filtering and washing [28].

1.8.1.1.Advantages and disadvantages

The coprecipitation procedure tends to produce catalysts with a uniform distribution of active components on the support and is the preferred procedure to prepare supported catalysts with a metal loading higher than 10-15%. Gold particles, hemispherical in shape; are firmly attached to the support by epitaxial contact, dislocations, or contact with an amorphous layer. However, in the coprecipitation method, the copresence of rafts of gold clusters, which inhibit the catalytic activity in some cases, is observed [14].

1.8.1.2.Precipitation agent

By the addition of base as precipitant, the metals are precipitated as hydroxides form and, can be transformed to oxides by calcination. It is known that in the recent literatures Na_2CO_3 is still very widely used as precipitant in the coprecipitation process, and that sodium ions can be difficult to remove by washing. Bond and Thompson suggested ammonium carbonate or bicarbonate as precipitation agents because the ion introduced by this reagent ions (NH_4^+ and CO_3^{2-}) decompose by calcination [7].

In 1989, Haruta et al. [10] prepared supported gold catalysts by coprecipitation from an aqueous solution of $HAuCl_4$ and the nitrates of various transition metals. Calcination of the coprecipitates in air at 400 °C produced ultrafine gold particles smaller than 10 nm which were uniformly dispersed on the transition metal oxides. Among them, Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO were highly active for H_2 and CO oxidation, showing markedly enhanced catalytic activities due to the combined effect of gold and the transition metal oxides. For the oxidation of CO, they were active, even at a temperature as low as −70 °C.

Hutchings et al. [18, 30] have used an inverse coprecipitation method to prepare gold catalysts supported on iron oxide and tested them for CO oxidation. Several gold supported on iron oxide rich in ferrihydrite ($Fe_5HO_8.4H_2O$) catalysts were prepared based on the initial concentration of gold source, by the slow addition of an aqueous solution of Na_2CO_3 to a mixture of $HAuCl_4$ and $Fe_2(NO_3)_3.9H_2O$. The precipitate product was cooled, filtered and washed with water several times to remove Cl^- and Na^+ ions. Afterwards, these gels were kept in the air for 4-6 weeks and then some were then dried in the oven at 120 °C for 18h, while other samples were calcined at 400 °C for 3 h. The inverse coprecipitation method has been previously described by Wagner et al. [31]. The difference between Hutchings's synthesis and that of Wagner is that in Hutchings's synthesis no digestion step was done so that little or none goethite or hematite would be present in the dried samples. The authors concluded that the highest activity for CO oxidation was observed in a dried sample that contained ferrihydrite and a non-crystalline and possibly hydrated gold oxyhydroxide phase; $AuOOH._xH_2O$.The calcination step changed the ferrihydrite to hematite and the gold transformed to metal particles with particle size of 3-5 nm. However, the calcined catalysts showed poor catalytic activities for CO oxidation.

Guczi et al. [32] prepared a 1 wt% Au/Fe_2O_3 catalyst by the coprecipitation method. The structure of the sample in the as prepared, oxidised and reduced states was investigated by means of X-ray photoelectron spectroscopy (XPS), transition electron microscopy (TEM), electron diffraction (ED), and X-ray diffraction (XRD). The structures of the samples after various treatments and their activity in CO oxidation were compared. The results showed the stability of gold particle sizes during these treatments. However, after oxidation, a slight shift in the Au *4f* binding energy towards lower values points to the formation of an electron-rich state of the metallic gold particles compared to that revealed in the as-prepared sample. The authors suggested that a structural transformation had occurred along the gold/support perimeter during the treatments and they proposed a possible mechanism for the effect of the oxidation treatment. They concluded that in order to enhance the catalytic activities for the prepared catalysts for CO oxidation reaction, an electronic interaction between gold particles and the support was required. Also, the most active samples contained gold in the metallic state and the support, Fe_2O_3, in hematite phase. Kahlich et al. [33] prepared 3.15 wt% Au/α-Fe_2O_3 by the coprecipitation method and studied the selective low temperature oxidation of CO in H_2 rich gas conditions. Two aqueous solutions, $HAuCl_4.3H_2O$, $Fe(NO_3)_3.H_2O$, and another containing Na_2CO_3 , were added together and gradually added into a glass beaker with distilled water which was stirred. The reaction mixture was kept at 80 °C and the pH was controlled within 8-8.5 while the two solutions were being added (coprecipitation at constant pH). After coprecipitation, the mixture was filtered and the precipitate was washed with hot water until it was chloride free (indicated by reaction with silver nitrate) and dried at 80 °C in air for 12 h, followed by calcination in flowing air at 400 °C for 2 h. Finally, the catalyst was ground. The average particle size of the ground catalysts was 20 μm and the BET surface area decreased from 250 m^2/g, for the dried catalyst, to 55 m^2/g for the calcined catalyst. The catalytic activity of this catalyst was compared with the catalytic activity of Pt/γ-Al_2O_3. The results showed that Au/α-Fe_2O_3 had the same activity and selectivity at a much lower temperature (80 °C compared to 200 °C).

Gupta et al. [34, 35] reported several studies on the adsorption of Au supported on iron oxide obtained by coprecipitation and on the effect of the reduction pretreatment. The effect of the pre-treatment of gold supported on iron oxide catalysts prepared by coprecipitation was also investigated by Horvath et al. [32]; the difference between their study and Gupta's study was Horvath used a different order of addition of the reactants. They prepared 1 wt% Au/Fe_2O_3 catalysts by a coprecipitation method using an aqueous solution of $HAuCl_4$ and $Fe_2(NO_3)_3.9H_2O$ and added in a 1M aqueous solution of Na_2CO_3 at 75 °C under stirring. The coprecipitate was kept in the solution at 77 °C for 18 h, and then washed several times with hot water and dried at 80 °C for 3 days. The results showed stable gold particle size during treatments. In CO oxidation, the oxidised sample displayed the highest activity and it was suggested that this could be the result of the cooperative effect of goethite, FeO and the electron rich metallic gold nanoparticles. They suggested that a structural transformation occurred along the gold/support perimeter during treatments.

Lee et al. [36] prepared Au-Mn- coprecipitates and dried them at several temperatures and in different atmospheres; the coprecipitates were tested for low temperature CO oxidation without any additional thermal treatment. The authors reported that samples dried at 120 °C in air exhibited the highest activity for CO oxidation.

Hutchings et al. [37] prepared a range of ZnO supported gold catalysts by coprecipitation and studied the effect of Au loading, reduction temperature and thiophene-pretreatment on their catalytic performance for buten-2-enal hydrogenation. A mixed solution of $Zn(NO_3)_2.H_2O$ and $HAuCl_4.H_2O$ (in the appropriate ratio to give a gold loading of 0.25,0.5,1,2,5 and 10 wt%) was heated to 80 °C, and 1 M Na_2CO_3 solution added with continuous stirring until the pH reached 9. The precipitate was aged for 20 mins, filtered, washed with hot water, dried overnight at 110 °C and calcined at 400 °C for 4h. The catalysts were found to be selective for the formation of the unsaturated alcohol, but-2-en-1-ol rather than the saturated aldehyde, butanal, and thiophene to enhance the yield of the unsaturated alcohol. Thiophene modification did not affect the gold particle size or morphology, but it seemed to give a surface in which the Au sites were electronically promoted by sulphur. The highest but-2-en-1-ol selectivities were observed for the 5wt% Au/ZnO catalysts reduced at 400 C prior to reaction. They suggested that the origin of the high selectivity for this reaction was related to the presence of large Au particles (10-20nm) in diameter.

Au/ZnO catalysts prepared by the co-precipitation method with different Au:Zn atomic ratios were studied for room-temperature CO oxidation in the presence/absence of water in the feed stream by Zhang et al. [38]. They reported that the catalysts exhibited excellent catalytic activity and stability compared with pure ZnO. Further, it was found that the lifetime of Au/ZnO catalysts was improved significantly by increasing CO concentration but was decreased by the addition of H_2O in the feed stream. The deactivation may be related to the sintering of metallic gold and the accumulation of carbonate-like species in the catalyst. They have also investigated the calcination temperature and precipitant effect [39] on CO oxidation in the presence or absence of H_2O in the gas stream. They concluded that ZnO is a more effective support than the hydrozincate, and the small ZnO particles and wide surface areas are beneficial to the catalytic performance for CO oxidation over Au/ZnO catalysts. The stability is inversely proportional to the amount of hydrozincate in the Au/ZnO catalysts. Also, they concluded that the precipitant affects the particle size of gold and ZnO, and Na_2O_3 is the best precipitant to produce small gold and ZnO particles. The small particle size of gold is beneficial to the improvement of stability for CO oxidation. Sintering of Au and the formation of hydrozincate might decrease the activity of Au/ZnO catalysts. They reported that the Na^+ ion can suppress the accumulation of carbon-like species, and controversially suggested that this ion may have a positive effect on the CO oxidation performance for Au-based catalysts.

Galvagno et al. [40] reported an FT-IR study of CO adsorbed on coprecipitated Au/Fe_2O_3 samples in order to identify the active species responsible for CO oxidation. FT-IR results showed that after preparation and exposure to the CO/O_2 mixture gold was present on the surface mainly as Au^+ and Au^0 species. The authors reported also that Au^+ species were more active towards CO oxidation than Au^0. However, Au^+ was not stable and tended to be irreversibly reduced to Au^0 during the reaction, accounting for the irreversible deactivation observed. In order to prepare active and stable gold catalysts for CO oxidation, the stabilisation of Au^+ species on the support is required.

Demczyk et al. [41] prepared gold particles supported on Fe_2O_3 and treated them in air at 200 °C and above. Their study showed that the heat treatment temperature effected changes in the structural properties and performance of the catalyst. Two characterisations techniques were used, XRD and Mossbauer spectroscopy. They observed an increase in crystallinity in the iron oxide support as a result of increasing the calcination temperature. The gold particle size also increased and more uniform distribution of the gold particles was obtained by increasing the calcination temperature as well.

Manganese oxide-supported gold (Au/MnO_x) catalysts were prepared by a coprecipitation method and tested for low-temperature (< 100°C) carbon monoxide oxidation in stoichiometric mixtures of CO and O_2 containing no carbon dioxide in the feed gas. A very small decay in Au/MnO_x catalysts was observed, possibly due to carbon dioxide retention. The optimum gold content was determined to be 10 % of the manganese content [42].

Titania-supported gold catalysts were prepared by different preparation methods; impregnation, deposition-precipitation, and coprecipitation by Vannice et al. [43]. These catalysts were extremely active for room temperature CO oxidation; however, deactivation was observed after 2-3 h under their reaction conditions for the impregnated Au/TiO_2. The catalyst prepared by coprecipitation had much smaller Au particles size than the impregnated Au/TiO_2 and was active at 273 K after either low temperature reduction or calcination pretreatment.

1.8.2. Deposition-precipitation

In the deposition-precipitation procedure, a metal hydroxide, carbonate or basic carbonate precipitates on the particles of a powder support by addition of a precipitant. Due to the precipitation of the metal hydroxide, carbonate or basic carbonate particles inside the pores of the support, nucleation and growth on the support surface will result in the uniform distribution of small particles on the support. In contrast, rapid nucleation will lead to large particles and inhomogeneous distribution. Therefore, the large particles will be unable to enter into the pores and will deposit only on the external surface. To produce superior precipitation distributions of the metal on the support surface, an effective mixing and a very slow addition of the precipitant solution must be achieved. After the deposition-precipitation step, the catalyst is filtered, washed, and dried. The sole disadvantage of the deposition-precipitation procedure is the difficulty in obtaining a catalyst with a high concentration of the active metal [28].

In the deposition-precipitation method, the active species precipitate from the solution and interacts with the support due to the increase in the pH that precipitates the hydroxide or basic carbonate of the active component. This method, if well performed, leads to a very good interaction between the active component and the support.

1.8.2.1.Advantages & disadvantages of DP

The advantage of the deposition–precipitation method is the maintenance of the precipitation of the active component only on the surface of the support and avoiding its interaction with the bulk of the support. This achieved by avoiding local high concentrations of the precipitant [7]. Also, deposition-precipitation leads to narrower particle size distribution. It is also recommended that the support should have high surface area, larger than $50m^2/g$ [44]. This method also prevents the formation of rafts of gold clusters, which were often observed in coprecipitated samples [14].

1.8.2.2.What makes gold catalysts prepared by deposition-precipitation active?

The catalytic properties of gold nanoparticles prepared by the deposition-precipitation method on metal oxide supports have been reported in several papers [7, 14, 45]. The catalytic activity of gold supported catalysts is defined by three important factors: contact structure between gold particles and support, selection of a suitable support, and the gold particle size. The first factor is the most important because it was suggested from both characterisation and catalytic results that CO reaction may occur at the perimeter interfaces around gold particles.

1.8.2.3.Contact structure between gold particles and support

In the deposition-precipitation method, gold is deposited on the metal oxide support surface in the form of $Au(OH)_3$ or AuOOH. After calcination, the base gold oxide is decomposed to metallic gold and this interacts with the support surface. Gold particles stay as nanoparticles even after calcination at temperatures above 300 °C due to the strong contact of the gold nanoparticles with the metal oxide support if they are carefully distributed on the surface of the metal oxide support during preparation. Controlling the pH in the range 6-10, and the preparation temperature in the range 50-100 °C are important preparation parameters that permit a uniform distribution of gold particles on the surface of the support to form and to perform the selective deposition of $Au(OH)_3$ on the surface of support with no loss of gold in the solution. Disordered structures are usually obtained by the deposition-precipitation method especially in the metal-oxide interface. This may result from crystallisation of the surface hydroxide layer formed during deposition-precipitation in aqueous solution. Consequently, the crystalline surface is enclosed with an amorphous phase, in which small gold particles appear. This boundary structure may play a role in the stabilisation of small gold particles against agglomeration [14].

1.9. Selection of a suitable support

For CO oxidation using gold catalysts, many metal oxides have been used as supports. The semiconducting metal oxides (TiO_2, Fe_2O_3, Co_3O_4 and NiO) exhibit more stability as supports for gold catalysts than insulating metal oxides (Al_2O_3 and SiO_2) [14, 44]. $Mg(OH)_2$ was found to be the preferred support for gold catalysts with high activity, even at -77 °C. However, the results of CO oxidation using $Mg(OH)_2$ support show that this catalyst is strongly structurally dependent. The stability of the catalysts is limited to 3 to 4 months [10]. Co_3O_4 was found to be the optimal support for gold supported catalysts for the combustion of hydrocarbon [23, 46]. Only TiO_2 and TiO_2-silicate have been found to be effective supports for gold catalysts used for hydrocarbon selective oxidation, the anatase form of TiO_2 making gold selective as an oxidation catalyst. However, rutile or amorphous TiO_2 were not active as supports [47-50]. The reason for this is not clear yet. TEM analysis has shown that gold particles more contacted on anatase than on the other supports.

Park et al. [51] prepared gold supported on Fe_2O_3, TiO_2 and Al_2O_3 using the deposition-precipitation method to study the effect of treatment conditions in CO oxidation. The precipitant was NaOH; the catalyst was dried at 100 °C, and calcined at five temperatures 200, 300, 400, and 500 °C. Catalysts exhibited decreasing activity with increasing calcination temperatures. XPS analysis showed the change in Au phase from Au_2O_3 to metallic gold when the calcination temperature was increased. Therefore, the oxidation states of gold were important for CO oxidation, the oxidised gold species being more active than metallic gold. However, Au/Al_2O_3 catalysts showed lower activity than that of the other two catalysts supported on Fe_2O_3 and TiO_2.

Haruta et al. [14] prepared a number of catalysts (Au/Fe_2O_3, Au/Co_3O_4, and Au/TiO_2) using the deposition-precipitation method. Catalysts were calcined in the range 200-400 °C. They concluded that the deposition-precipitation method can lead to a high dispersion of gold on the surface of the metal oxide supports. These catalysts were active for CO oxidation using fixed bed reactor, 200mg of catalysts, and flow rate of 67ml/min of 1% CO in air. The authors also reported that the deposition-precipitation method leads to disordered structures in the metal-oxide interface. They reported that this disordering in the structure might occur due to the crystallisation of the surface hydroxide layer formed during deposition-precipitation in aqueous solution. This crystalline surface is covered with an amorphous phase, where small gold particles are located. This structure may enhance the small gold particles to be stable against coalescence. They reported that the small gold particles that are formed offer sites for reversible adsorption of CO and increase the amount of oxygen adsorbed on the support surface. In further research [21], they concluded that the catalytic performance of supported gold catalysts depends on the pH, the gold loading and the calcination temperature. These parameters are described in Fig. 1.4.

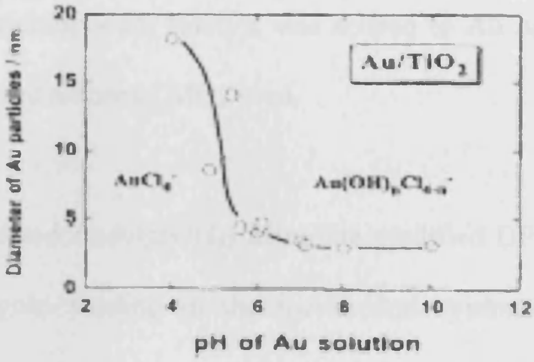

Figure 1.4. The mean particle diameter of Au as a function of the pH of HAuCl4 solution [21]

Andreeva et al. [52] prepared a number of gold catalysts supported on Fe_2O_3, ZnO, ZrO_2 as well as mixtures of these oxides by the deposition-precipitation method. All of these catalysts were tested for water gas shift reaction.

$$CO + H_2O \rightarrow H_2 + CO_2$$

The activity of the catalysts depended strongly not only on the high dispersion of gold particles on the surface of the support, but also on the nature and textural structure of the supports, with the highest activity reported for Au/Fe_2O_3 and Au/ZrO_2. They reported that there are some surface defects present in the amorphous support, which increases the interaction between gold particles and the support, which prevents gold agglomeration to bigger particles. These catalysts were, however, not evaluated for CO oxidation.

Grisel et al. [53-55] prepared a number of gold catalysts (Au/Al_2O_3 and Au/MO_x/Al_2O_3 (M= Cr, Mn, Fe, Co, Ni, Cu and Zn) using DP method with urea as the precipitant. The multicomponent catalyst showed increased conversion to CO oxidation, while Au/MO_x catalysts were less active. They concluded that the increase in activity of the multicomponent catalyst was related to Au particle size, and there was little influence of the nature of MO_x used.

Haruta et al. [56] prepared Au/$Mg(OH)_2$ using the modified DP method to produce a catalyst with a 5% gold loading in the icosahedral symmetry by extending the deposition time to 3 days with slow addition of $HAuCl_4.3H_2O$ to a suspension of MgO. The catalyst was calcined at 250 °C for 100 min in air. CO oxidation studies showed 45% conversion of CO at 180 °C, in the presence of water. However, no details were to define the GHSV.

Jia et al. [57] prepared a 10% gold supported on Al_2O_3 via the deposition-precipitation procedure and then tested for hydrogenation of ethyne and ethene. Ethyne and hydrogen reacted readily to produce ethene in the temperature range between 40 and 250 °C, At these reaction temperatures no ethane was produced. The hydrogenation of ethene to ethane on this catalyst occurred only at temperatures higher than 300 °C. The author proposed that the activity of the selective hydrogenation of ethyne over the Au/Al_2O_3 catalyst depended on the size of the ultrafine gold particles deposited on Al_2O_3, which showed a maximum activity at a diameter around 3 nm.

Kung et al. [58] prepared several Au/γ-Al_2O_3 catalysts using the deposition-precipitation method. They found that in the presence of magnesium citrate, the Mg/Au ratio was 1.55 in the preparation solution, which had a considerable effect on the properties of the catalyst, especially on reducing Au particle size. Catalysts prepared without citrate contained larger Au particles, and were less active for CO oxidation. They suggested that there might be an optimal average Au particle size of about 5-10 nm for the best catalytic activity. They prepared the catalysts at sub-ambient temperature in order to minimise the presence of gold clusters in solution. Later, Kung et al [59] investigated the effect of Cl^- on supported catalysts. They concluded that Cl^- not only agglomerates gold particles during calcination but also deactivates the catalytic performance by poisoning the active site. They further concluded that the high attraction of Cl^- to the gold active site indicates that the active site is cationic in part.

Schuth et al. [60] studied the effect of the deposition-precipitation preparation parameters such as pH, ageing time, calcination temperature, the order of addition of precipitant or gold precursor to support suspensions, and the effect of the support on the catalytic activity for CO oxidation. They used two different deposition-precipitation methods. In method (A), a solution containing the gold precursor ($HAuCl_4$) was added to an aqueous suspension of the support, and the pH adjusted with Na_2CO_3 to the desired value (5-10). In method (B), the pH of the precursor solution was adjusted with Na_2CO_3 before addition of the support material. The Preparation temperature ranged from room temperature to 70 °C, and the ageing time was in the range 2-12 h. The material was then filtered, washed and dried at 90 °C, and calcined at four temperatures (200, 300, 400, and 500 °C). Four catalysts (Au/TiO_2, Au/Co_3O_4, Au/Al_2O_3 and Au/ZrO_2) were prepared in this way and optimised to achieve the high catalytic activity of these catalysts. SiO_2 was an unsuitable support for the deposition-precipitation procedure. Increasing catalytic activity was observed for CO oxidation by increasing the pH in the preparation and decreasing the temperature during calcination. The optimum pH was in the range 8-9 and optimum calcination temperature was 200 °C. XRD and TEM analyses showed that increasing catalytic activity was observed by decreasing the gold particle size. Also, the evaluation of two samples with similar gold particle sizes showed that Au/TiO_2 was more active than Au/Al_2O_3. This confirms that catalytic activity, in addition to the effect of particle size, is related to the support, which plays a very important role in the stabilisation of gold particles.

Boccuzzi et al. [61] carried out a FTIR study of CO adsorption at -183 °C on three Au/TiO_2 catalysts prepared using the deposition-precipitation procedure with a low gold loading (1%). Three calcination temperatures (180, 300, and 600 °C) produced catalysts of different gold particle mean sizes (2.4, 2.5, and 10.6 nm respectively). From these adsorption studies they conclude that: (i) carbon monoxide and oxygen are adsorbed on gold step sites competitively and in molecular form at -183 °C; (ii) reaction between CO and O_2 occurs only when CO is pre-adsorbed on the calcined gold particles; and (iii) the reaction does not occur on the catalyst with 10.6 nm of gold particles, at that temperature. The same study [62] used a pure anatase support calcined at 400 °C to assess the effect of temperature and pressure on the FTIR spectra of CO adsorbed on Au/TiO_2 mentioned in the above studies. In collaboration with Andreeva [63], they extended these studies to Au, Ag, and Cu catalysts supported on TiO_2 prepared by the deposition-precipitation procedure and tested these catalysts for hydrogen production by CO water gas shift reaction. The Ag/TiO_2

catalyst was not active, while Au/TiO_2 exhibited performance higher than that for Cu/TiO_2.

A 3% Au/CeO_x catalyst [64] was prepared by the same group using the deposition-precipitation procedure. Combining water gas shift reaction (WGS) catalytic data with FTIR studies, it was reported that the WGS reaction occurs at the boundary between metallic gold particles and ceria, where CO adsorption on gold and H_2O dissociation on ceria take place.

The adsorption and kinetics of CO oxidation on Au/TiO_2 prepared by deposition-precipitation and on unsupported gold powder were studied [65]. This study concluded that CO oxidation reaction occurs on the surface of the deposited gold and/or the perimeter interface between gold and TiO_2 However, the precipitant they utilized was not specified.

The effect of pH on the Au/γ-Al_2O_3 catalyst prepared by the deposition-precipitation method, using $AuCl_3$ as precursor, was studied by Lin et al. [66] using EXAFS, and the results correlated with catalytic activity results for CO oxidation reaction. EXAFS showed that for the catalysts prepared at pH in the range from 4.1 to 9.4, Au-(O)-Al bonding was observed, indicating the deposition of Au species occurs via the coordination of surface hydroxyl groups. However, Au-(O)-Au was found in the catalyst prepared at high pH of 10.5, suggesting the deposition of polymeric $Au(OH)_3$. Uncalcined catalysts were also evaluated for CO oxidation. The catalyst prepared at a pH 10.5 was active for CO oxidation reaction at 50 °C, while the catalyst prepared at pH 4.1 had no activity. Based on these results, it was suggested that a specific Au-O morphology, such as the polymeric $Au(OH)_3$, might be responsible for the high CO oxidation activity of supported Au catalysts.

A modified deposition-precipitation procedure was used by Schumacher *et al.* [67] to prepare Au/TiO_2 catalyst. Catalytic results showed that the catalyst with small metallic Au particles (<2 nm) had a very high activity for low temperature CO oxidation, and the activity performance decreased with the accumulation of undesired products.

1.10. Aim of the study

The aim of this research is to study the preparation of active supported gold catalysts and to investigate the parameters that affect the catalytic activity of these catalysts, such as; selection of a suitable support, and selection of the preparation procedure. Many variables during the preparation processes, such as preparation temperature, pH, and ageing times are also investigated. Several characterisation techniques are used to investigate the physical and chemical properties of the catalysts prepared in this research study, including BET surface area, X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), temperature programming reduction (TPR), and X-ray photoelectron spectroscopy (XPS). Catalytic activities of catalysts prepared in this research are determined by low temperature CO oxidation reaction and light alkane (C_1-C_3) activation reactions. Correlation between the catalytic activities of catalysts over both reactions is investigated and discussed.

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Chapter 2

Experimental

2.1. Catalyst preparation

A series of supported gold catalysts were prepared. Two coprecipitation procedures were used; at variable and constant pH and via deposition-precipitation procedure.

2.1.1. Coprecipitation

2.1.1.1. Coprecipitation at variable pH

Several Au/ZnO catalysts were prepared by coprecipitation using a variable pH method at constant temperature, in which the pH of the precipitating solution was gradually raised. An aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) was added to an aqueous solution of $Zn(NO_3)_2.6H_2O$ (100 ml, 0.1 mol/l, Aldrich) and was stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until the desired pH was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium and chloride ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h. Several Au/ZnO catalysts were prepared via this procedure based on the difference in pH (5 to 8) and ageing times (no ageing, 3 h, 5 h, 8h, and 12h).

Several Au/Fe_2O_3 catalysts were prepared in a similar manner. An aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) was added to an aqueous solution of $Fe(NO_3)_3.9H_2O$ (50 ml, 0.1 mol/l, Aldrich) and stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until a pH of 8.2 was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium and chloride ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h. The procedure is shown schematically in Figure 2.1

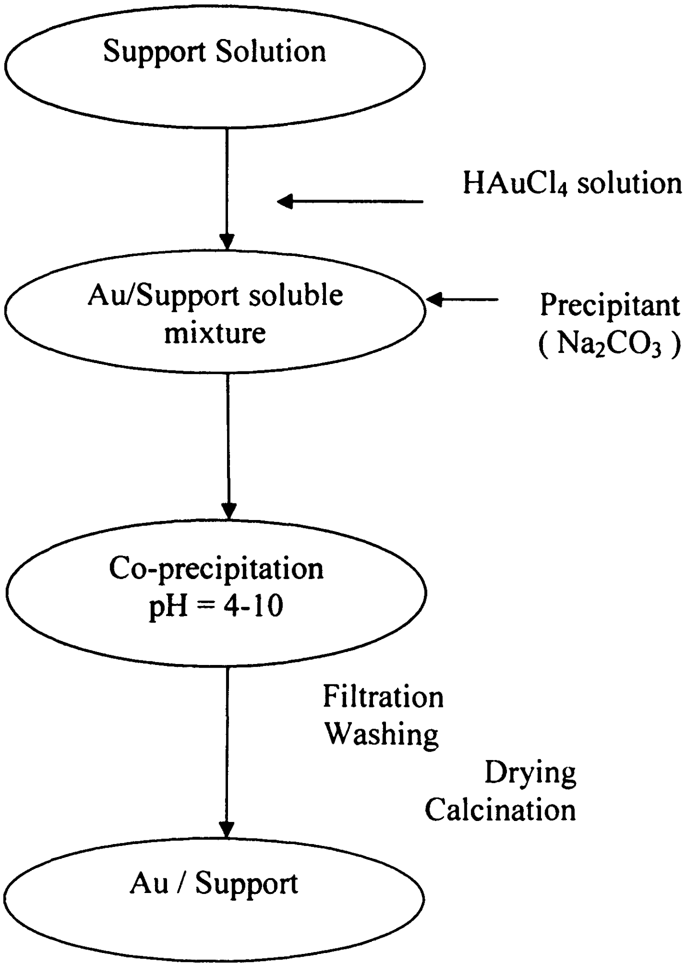

Figure 2.1 supported gold catalyst preparation via coprecipitation at variable pH

2.1.1.2. Coprecipitation at constant pH

Several Au/ZnO catalysts were prepared using the coprecipitation procedure at constant pH and constant temperature. An aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) was added to an aqueous solution of $Zn(NO_3)_2.6H_2O$ (100 ml, 0.1 mol/l, Aldrich) and stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was similarly preheated. The two solutions were then fed at a controlled feedrate to a thermostated precipitation vessel. The flowrates were adjusted dropwise so that the desired constant pH was maintained. Following the precipitation process the material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium and chloride ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16 h. Samples were also calcined in static air at 400°C for 3 h. Several Au/ZnO catalysts were prepared *via* this procedure based on the difference in pH (5 to 8) and ageing times (no ageing, 3 h, 5h, 8h, and 12h).

Several Au/Fe_2O_3 catalysts were prepared in a similar manner using an aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) and $Fe(NO_3)_3.9H_2O$ (50 ml, 0.1 mol/l, Aldrich) maintained at 80°C. Several Au/Fe_2O_3 catalysts were prepared via this procedure based differences in pH (4 to 8.2) and Au loadings (5%, 2.5%, 1%, and 0.5%). The procedure is shown schematically in Fig. 2.2

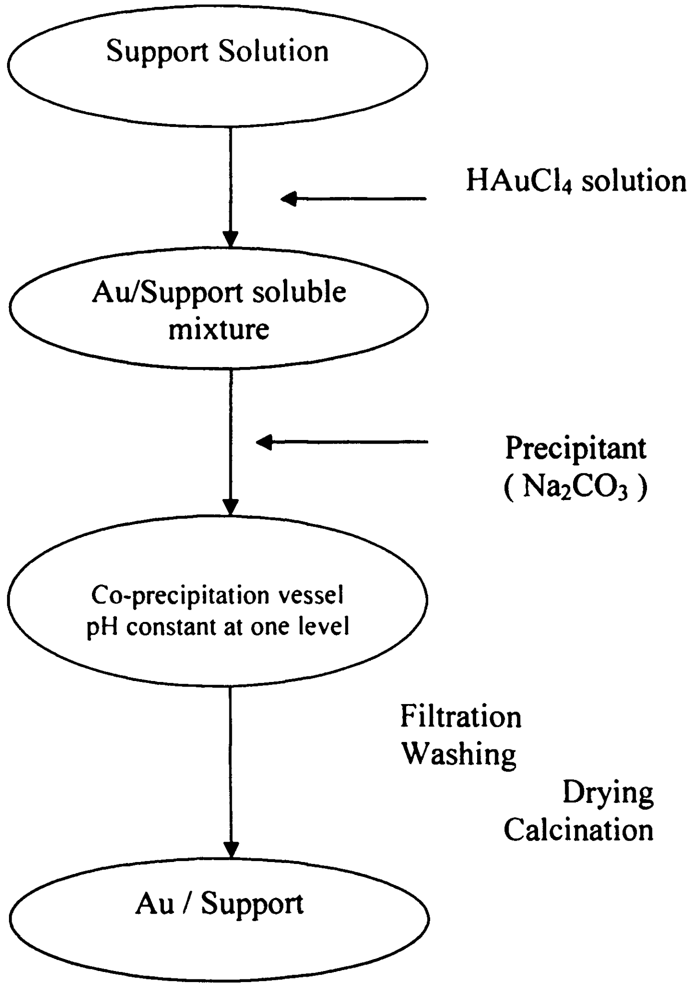

Figure 2.2 Supported gold catalyst preparation via coprecipitation at constant pH

2.1.2. Deposition-precipitation

The same two supports used in the coprecipitation procedure, ZnO and Fe_2O_3, were also used in this preparation method. However, both supports were prepared via two different procedures.

2.1.2.1. Support preparation methods

2.1.2.1.1. Preparation method A

The ZnO support was prepared by precipitation method using a variable pH method at constant temperature, in which the pH of the precipitating solution was gradually raised. An aqueous solution of $Zn(NO_3)_2.6H_2O$ (100 ml, 0.1 mol/l, Aldrich) was stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until a pH of 8.0 was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium ion. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16 h. Samples were also calcined in static air at 400°C for 3 h.

The Fe_2O_3 support was prepared in a similar manner. An aqueous solution of $Fe(NO_3)_3.9H_2O$ (50 ml, 0.1 mol/l, Aldrich) was stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until a pH of 8.2 was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h.

2.1.2.1.2. Preparation method B

The ZnO support was prepared using a precipitation procedure at constant pH and constant temperature. An aqueous solution of $Zn(NO_3)_2.6H_2O$ (100 ml, 0.1 mol/l, Aldrich) was stirred at 80°C. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was similarly preheated. The two solutions were then fed at a controlled feedrate to a thermostated precipitation vessel. The flowrates were adjusted dropwise so that the desired constant pH was maintained. Following the precipitation process the material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium ion. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h.

The Fe_2O_3 support was prepared in a similar manner using $Fe(NO_3)_3.9H_2O$ (50 ml, 0.1 mol/l, Aldrich) maintained at 80°C.

2.1.2.2. Supported gold catalysts prepared *via* deposition-precipitation

Au/ZnO catalysts were prepared using deposition-precipitation at variable pH and at constant temperature, in which the pH of the suspension was gradually raised. The prepared ZnO support (2g) was added to 100 ml water and then stirred at 80°C. An aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) was added to the suspension. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until a pH of 9.0 was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium and chloride ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h.

Au/Fe_2O_3 catalysts were prepared using deposition-precipitation at variable pH and at constant temperature, in which the pH of the suspension was gradually raised. The prepared Fe_2O_3 support (2g) was added to 100 ml water and then stirred at 80°C. An aqueous solution of $HAuCl_4.3H_2O$ (5 ml, 0.058 mol/l, Johnson Matthey) was added to the suspension. Aqueous sodium carbonate (0.25 mol/l, Aldrich) was added dropwise until a pH of 9.0 was obtained. The material was recovered by filtration and washed several times with cold and then hot water to ensure removal of the sodium and chloride ions. After drying initially at room temperature, the material was then dried in an oven at 90°C for 16h. Samples were also calcined in static air at 400°C for 3 h. The procedure is shown schematically in Fig. 1.3

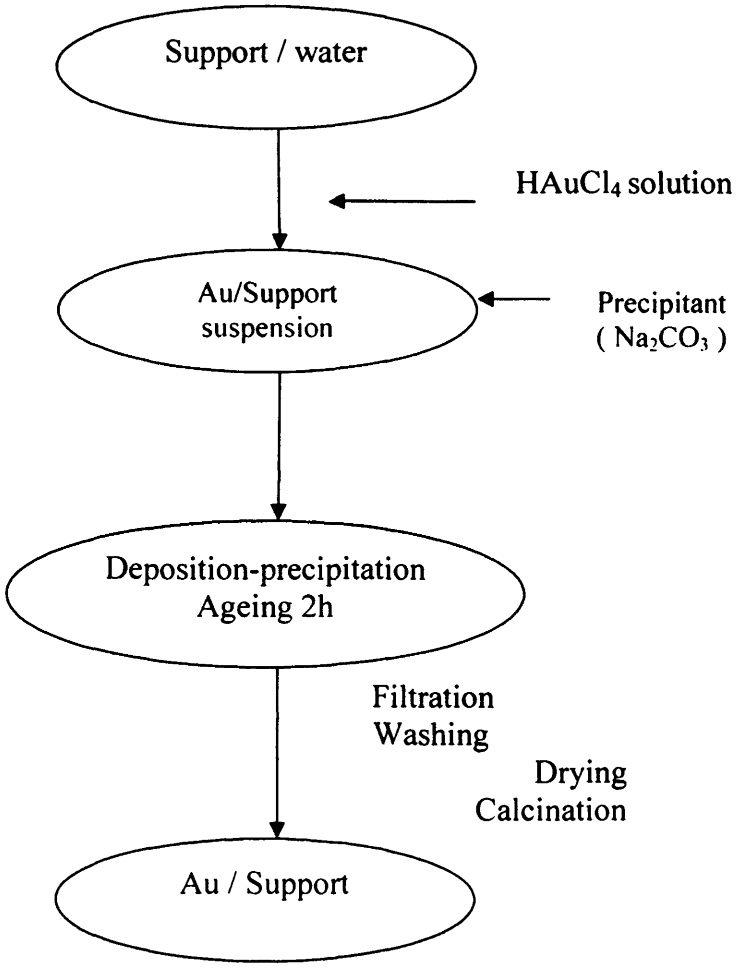

Figure 2.3 Supported gold catalyst preparation via deposition-precipitation procedure

2.2. Catalyst characterization

Several techniques were used to characterize the prepared supported gold catalysts. These techniques are BET surface area analysis, X-ray diffraction analysis (XRD), X-ray photo electron spectroscopy (XPS), and temperature programmed reduction (TPR).

2.2.1. BET surface area analysis

2.2.1.1. Introduction and theory

This method was discovered by Brunauer, Emmet and Teller (BET) [1]. The principle of this method is to use the physical adsorption of an inert gas, such as N_2, onto the catalyst surface to calculate the total surface area of the solid. This method is based on a theoretical model, with the adsorption isotherm measured, which is the nitrogen adsorbed volume (V_a) against its relative pressure, which is the actual pressure (P) divided by the vapour pressure (P_o) of the adsorbing gas at the experimental temperature. From this by a mathematical analysis the calculation of the monolayer capacity of the adsorbent can be determined. The BET equation has the form:-

$$P / V_a (P_o - P) = [(C-1) / (V_m C) . P / P_o] + 1 / V_m C$$

Where P / P_o = Pressure / Saturated Vapour Pressure at experimental temperature

V_a = Adsorbed Volume

V_m = monolayer Capacity

C = Constant related to Adsorption and Liquefaction

Once the monolayer volume has been calculated the surface area can be determined by the following equation

Surface area = $V_m \sigma N_a / M V_o$

Where σ = Area of adsorbate = 0.162 m^2 at 77 K

N_a = Avogadro Number

M = Mass of the sample

V_o = molar volume of gas

2.2.1.2. Experimental

BET surface area measurements were carried out using a computer controlled Micromeritics ASAP 200 and Micromeritics Gemini surface area analyser system. Prior to adsorption measurements, all samples were degassed at 100 °C. to ensure accurate measurements, approximately 0.3-0.5 gm of sample was used and surface areas were determined for the catalysts by measuring the extent of adsorption of nitrogen at the boiling temperature of nitrogen, 77 K. The duration of the process depends on the type of the materials, which is usually around 40 min for the samples.

2.2.2. Atomic Absorption

Atomic absorption (AA) is a quantitative spectroscopy technique based on the absorption of a monochromatic wave by an atomised element present in the sample. It provides an elemental analysis and in this work it has been used for the determination of the metal loading in the supported metal catalysts [2]. The analyses were carried out with a Varian SpectAA 55B atomic absorption spectrometer. The radiation was generated by hollow cathode lamps and the following wavelength, 242nm, was used for the analysis of gold. The samples were atomised using an 0.5/3.5 acetylene-air flame. The sample solutions were prepared by dissolving the catalyst using equal amounts of 5% HCl and conc HNO_3. After dissolution of the sample, the solutions were diluted with water prior to analysis. The calibration curves were constructed using a standard 1000ppm Au/HCl solution purchased from Aldrich.

2.2.3. X-Ray Diffraction (XRD)

2.2.3.1. Introduction and theory

X-ray diffraction is an important analytical technique for chemists. The data of X-ray diffraction is used to identify unknown materials: over 150,000 unique powder diffraction data sets have been collected from organic, organometallic, inorganic and mineral samples. It is also used to study and monitor the purity of products and structure refinement, and it determines the crystallite size. X-ray tubes generate X-rays by bombarding a metal target with high-energy electrons (10-100 keV). When the incident electrons have sufficient energy, a core electron from a metal atom is removed and the vacancy is subsequently filled by an electron from a higher energy level. The relaxation from a higher energy state is accompanied by the emission of an, X-ray photon. When a parallel, monochromatic and coherent beam of X-rays of wavelength (λ) are incident on a crystalline material, having inter-planar distances of d_{hkl} and an x-ray incidence angle (θ), then reflections will occur from each plane. The reflections will only be reinforced if the conditions of the Bragg equation are met [3], i.e.

$$n\lambda = 2\, d_{hkl}\sin\theta$$

Where n has an integer value correcponding to the first, second and third order reflections, ect.

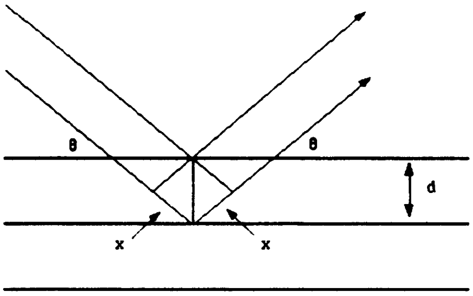

Figure 2.4 Diffraction from a set of lattice planes

2.2.3.2. Experimental

Diffraction studies on the catalysts were performed using an Enraf Nonius FR 590 instrument with a monochromatic $CuK_{\alpha 1}$ source with a wavelength of 1.54066 Å and operated at 40 keV and 30 mA. Patterns were obtained in the range $2\theta = 4.4°$ to 124.6°. The powdered samples were compressed into a metal sample holder. The diffraction pattern is reregistered by means of a position sensitive detector (PSD120), which is a curved wire counter which covers all 2θ in the range highlighted earlier, and can simultaneously register all Bragg reflections. All samples were tested over half hour periods. Data was analysed using Traces 4.0 software, which allowed the removal of the contribution of the background, and peak positions and relative intensities determined. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

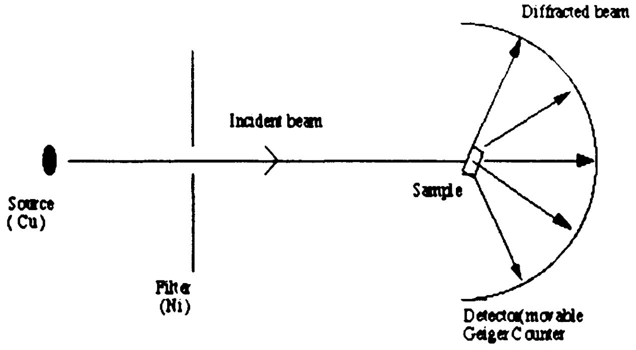

Figure 2.5 Schematic of an X-ray powder diffractometer

2.2.4. X-ray photoelectron spectroscopy (XPS)

2.2.4.1. Introduction and theory

For the development of new catalytic systems it is extremely important to investigate the changes of the surface electronic, chemical and structural properties during a particular process. X-ray photoelectron spectroscopy (XPS) is one of the most suitable methods for the analysis of surfaces because it probes a limited depth of the sample [4, 5]. XPS is one of a large number of instrumental surface analytical techniques that have been developed over the past 40 years since the pioneering work of Kai Siegbahn (Nobel prize winner, 1981) and his colleagues at Uppsala, Sweden. [6]. Due to the limited escape depth of the photoelectrons, and in consideration of the fact that the part of catalysts most involved in the catalytic reactions is limited to the topmost layers, the XPS technique is particularly suitable for the understanding of the electronic and morphological structure of heterogeneous catalysts. Moreover XPS is an important tool for studying the dispersion of supported catalysts.

XPS is based on the photoelectric effect, arising when high energy photons (usually in the keV range) hit a material with the consequent emission of electrons (photoelectrons). The photoelectron kinetic energy, E_k, which is the measured quantity in the experiment, is given by Einstein's law

$$E_k = h\nu - E_b$$

where $h\nu$ is the energy of the incident radiation and E_b the binding energy of the electron in a particular level.

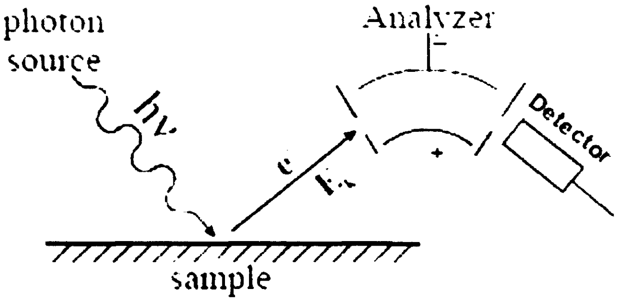

Figure 2.6. Analysis by XPS

XPS set up should have a source of fixed-energy radiation (an X-ray source), an electron energy analyser (which can disperse the emitted electrons according to their kinetic energy), and a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions). Such a system is exemplified schematically below:

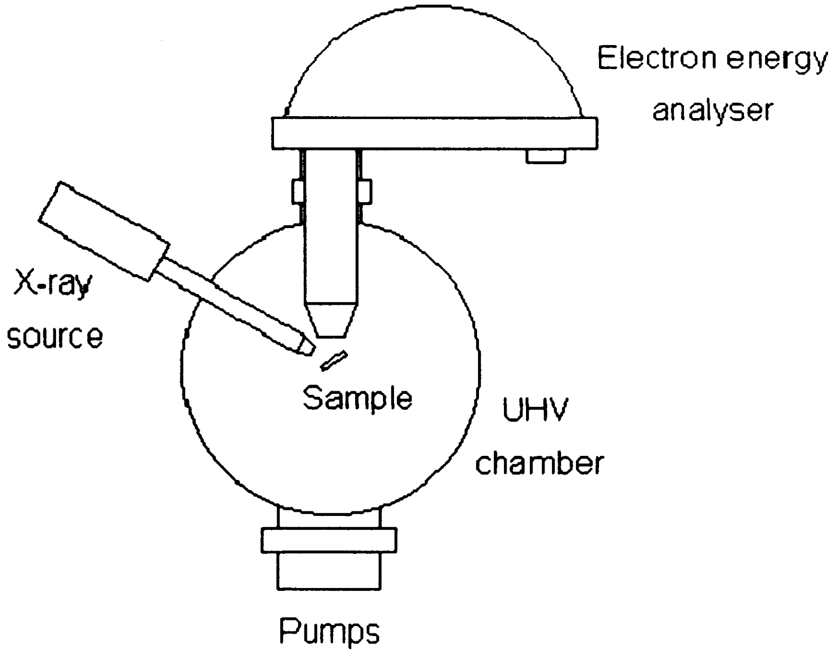

Figure 2.7. Schematic of XPS

There are many different designs of electron energy analyser but the preferred option for photoemission experiments is a concentric hemispherical analyser (CHA) which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy [7].

2.2.4.2. Experimental

X-ray photoelectron spectra were recorded on a VG EscaLab 220I spectrometer, using a standard AlKα X-ray source (300W) and an analyser pass energy of 20eV. Samples were mounted using double-sided adhesive tape and binding energies are referenced to the C(1s) binding energy of adventitious carbon contamination taken to be 284.7eV.

2.2.5. Temperature programmed reduction (TPR)

2.2.5.1. Introduction and theory

Temperature programmed reduction (TPR) is a technique that can measure the reducibility of a metal oxide species in supported or unsupported catalysts [8,9]. The main information that TPR gives is the number of reducible species in the metal oxide and ease with which these species can be reduced. This information is obtained by the number of defined peaks from the TPR profile and the temperature at which these peaks occur. By comparing different catalysts, in this study a range of loadings, it may be possible to compare their TPR profiles and try to explain difference in activity and selectivity. TPR experiments are carried out upon the catalyst using a reductive gas usually hydrogen while the temperature is uniformly increased over a period of time.

$$MO + H_2 \rightarrow M + H_2O$$

Where MO is the metal oxide

During a TPR changes in the gas stream concentration from where the reduction and consuming of hydrogen is taking place by reacting with oxygen present in the sample (forming water) are monitored using a thermal conductivity detector (TCD) and results are plotted against temperature. A cold trap is required to avoid the water reaching the TCD.

In the case of supported catalysts the shape and the position of the reduction signals are very sensitive to the interaction of the reducible species with support and other species present in the catalyst.

2.2.5.2. Experimental

The TPR experiments were performed with a Micromeritics Autochem 2910 equipped with TCD detector using a flow of 10% H_2 in Ar (50ml/min) with a ramp rate of 10 °C/min from room temperature to a maximum temperature of 1100 °C.

2.3. Catalytic Evaluation

2.3.1. CO Oxidation

2.3.1.1. Reactor design

A quartz micro reactor operated at atmospheric pressure was used for this reaction. The gas flow rate was controlled using mass flow controllers (Brooks Mass Flow 5850 Series) and flow rate was measured by a bubble flow meter. Reaction temperatures were controlled by water bath.

Analysis of the reaction product was carried out on-line using gas chromatography with a Porapak Q column and thermal conductivity detector. The reactor set up scheme is shown schematically in Fig. 2.8.

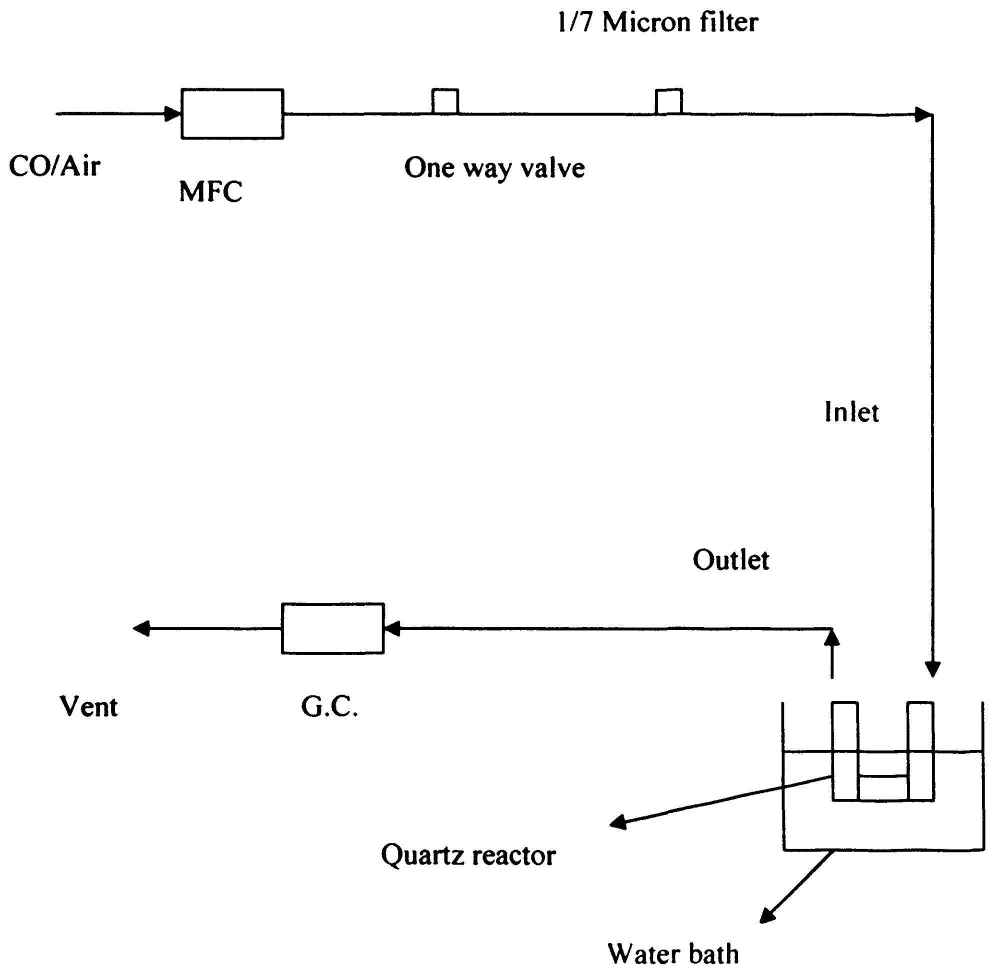

Figure 2.8 CO oxidation set-up

2.3.1.2. Experimental details

The catalytic activity for CO oxidation was determined in a fixed bed quartz micro reactor, operated at atmospheric pressure. The feed consisted of CO/synthetic air (CO_2 free) with a molar ratio of 0.5/99.5. The combined flow rate was maintained at 20 ml min^{-1} and different catalyst loading was employed. The reaction was maintained at different temperatures by immersing the quartz bed in a thermostatically controlled water bath. Analysis of the reaction product was carried out on-line using gas chromatography.

2.3.2. Hydrocarbon activation catalytic evaluations

2.3.2.1. Reactor design

A stainless steel micro reactor operated at atmospheric pressure was used for hydrocarbon activation reactions. Methane, ethane, and propane were used with oxygen and helium as feed stocks for this study. Hydrocarbon explosion limits with O_2 were taken in mind during the reactions. The gas flow rates were controlled using mass flow controllers (Brooks Mass Flow 5850 Series) after calibration using a bubble flow meter, Fig. 2.9 shows the calibration of methane, helium and oxygen MFC. Reaction temperatures were controlled by carbolite furnace which is capable of maintaining temperatures up to 1200 °C, and the reaction temperature was measured by movable thermocouple, which is located in the contact with the catalyst bed to measure the actual reaction temperatures.

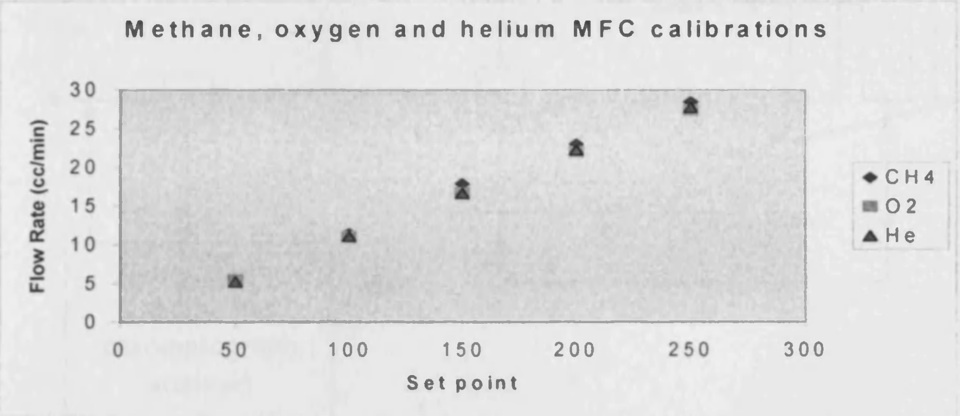

Figure 2.9 Calibration of MFC of CH4, He, and O2

Analysis of the reaction products was carried out using on-line gas chromatography with Porapak Q and Molsieve columns and thermal conductivity and flame ionisation detectors.

Hydrocarbon activation reactor set up is shown schematically below

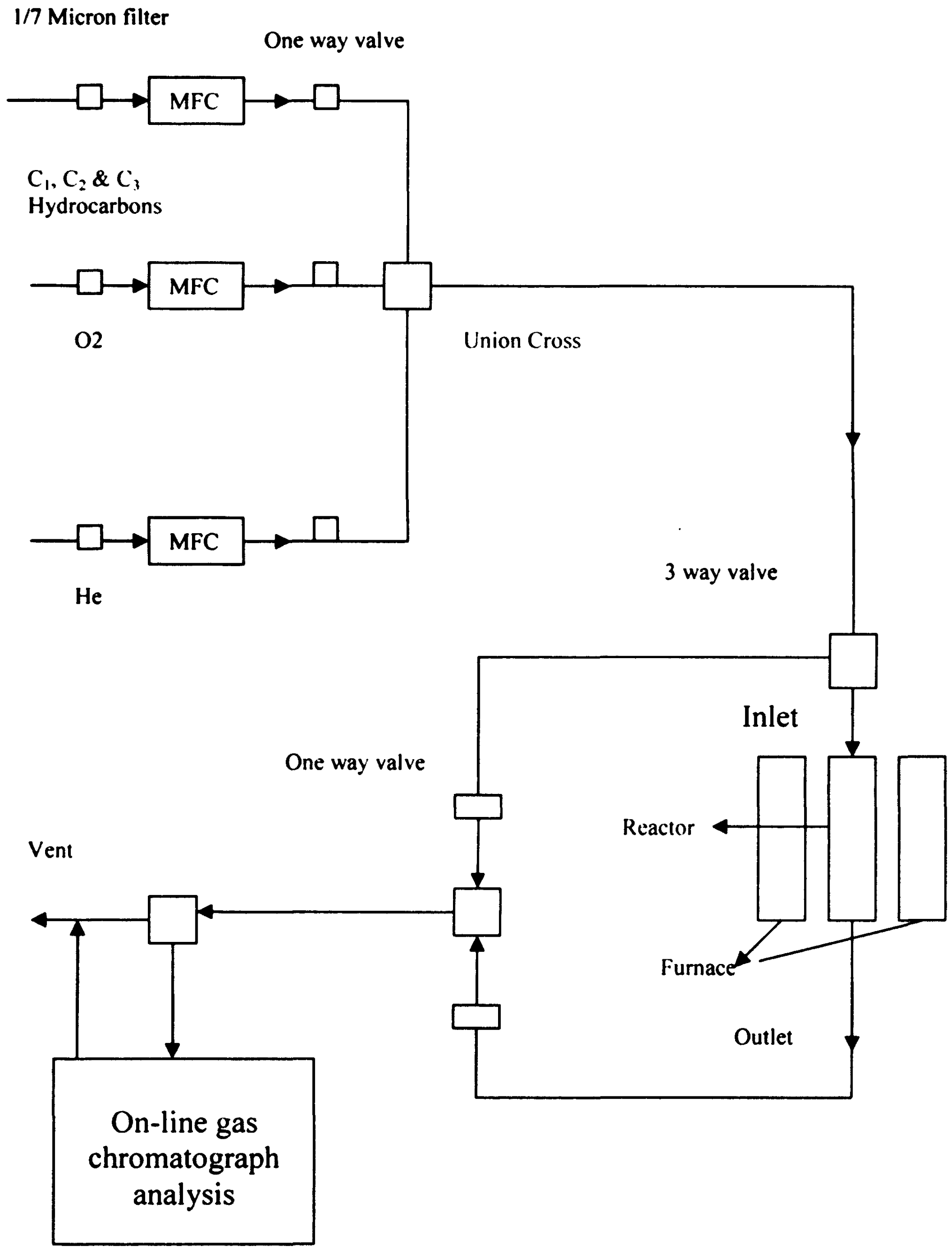

Figure 2.10 Hydrocarbon activation set-up

2.3.2.2. Experimental details

The combined flow rate was maintained at 30 ml min^{-1} and 0.25 cm^3 of catalyst loading was employed to produce a Gas Hourly space Velocity (GHSV) of 7200 h^{-1}. The composition of gases was adjusted based on the type of the hydrocarbon gas and its explosion limit. Once flow rate were set, the reactor temperature was set to 100 °C, where no catalytic activity was shown, and allowed to equilibrate for half an hour. After that, temperature was increased gradually by 50 °C up to 500 °C which was the maximum temperature reached.

Analyses of the reaction products were carried out using on-line gas chromatography. The calculation of the feed gases conversions and products selectivities were based on the detected products, in accordance with the following equations:-

$$\text{Feed gas conversion \%} \quad = \quad \frac{\text{amount of detected products}}{\text{amount of feed in gas analysis}} * 100$$

$$\text{Product selectivity \%} \quad = \quad \frac{\text{amount of detected product}}{\text{amount of converted feed gas}} * 100$$

2.4. Gas Chromatograph analysis system

The gas chromatograph used for CO oxidation experiments was a Varian 3400, while Varian 3800 was used for alkane activation expariments. The columns used were Porapak Q (2m * 2mm internal diameter) and Molecular Sieve (2m * 2mm internal diameter) which is known as Molsieve. The two columns were connected in series, and reactants and products were monitored by a TCD and FID. The two columns were respectively chosen to separate reactants and products. The use of two separate columns was necessary to prevent CO_2 entering the Molsieve, leading to irreversible absorption and resulting in column deactivation. A simplified summation is shown below:

Sample in → Valve → Porapak Q → Molsieve → Valve → TCD → FID → PC

For CO oxidation reaction, only CO_2 was detected. The column temperature used 200 °C, thus ensuring full separation of peaks, and each run took approximately 5 minutes. In the method used for alkane activation experiments, table 2.1, the sample loop was allowed to fill whilst the Porapak column was being cleaned using the back flush. Once the loop was filled it was injected into the Porapak via two valves in series. By using the valves in both bypass and series configurations, it was possible to fully separate all the gases that were detected. In order to obtain quantitative results from the GC analysis, it was essential to use correction factors, known as response factors. These response factors are independent of carrier gas, temperature, flow rate and concentration.

For alkane activation experiments, the initial column temperature used was 50 °C, beginning with switching valve 1 to injection after 0.02 minutes. Untill 1.27 minutes; valve 2 was in bypass, after that it was switched to series until 2.5 minutes. After that, the run continued in bypass until 4.5 minutes, and then it was switched to series, table 2.1. The temperatures of the oven and ramping rate are shown in table 2.2.

Table 2.1 Valves status

Time	Valve 1 - bypass, + injection	Valve 2 - series, + bypass
Initial	-	-
0.02	+	-
1.27	+	+
2.5	+	-
4.5	+	+

Table 2.2 Oven temperature ramping rate

Temperature °C	Rate °C/min	Hold min	Time min (total)
100	-	3	3
140	20	0	5
180	20	0	7
220	20	6	15

2.5. References

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Chapter 3

Catalyst characterization and CO oxidation

3.1. Introduction

In this chapter, several characterization techniques, explained in detail in chapter 2 of this study, were employed to investigate the physical and chemical properties of the prepared supported gold catalysts. The catalytic activities of these catalysts resulting from preparation procedures explained in chapter 2 were studied for low temperature CO oxidation reaction. The results obtained of the characterization of the catalysts were evaluated with catalytic results for the low temperature CO oxidation reaction of these catalysts in order to study several parameters, such as: the selection of the support material, preparation method, and preparation parameters such as pH and ageing process, which can affect either the properties of these catalysts or their catalytic activities. After this, several experiments at high GHSV were employed to confirm the effect of the above mentioned parameters, and to correlate the low temperature CO oxidation reaction and alkane activation reactions over the prepared supported gold catalysts. This correlation will be presented and discussed in detail in chapter 5 of this research study.

3.2. Characterization

3.2.1. BET surface area

BET surface area values depend on the preparation procedure and on the support material. In the case of Au/ZnO, there was almost no different in BET surface area data of the support before and after calcination.

The BET surface area of Au/ZnO catalysts decreased when pH is $9 \leq$. In the case of Au/Fe_2O_3, there was a significant difference in BET data before and after calcinations when Au/Fe_2O_3 was prepared by precipitation with variable pH (method A), but no significant difference when Au/Fe_2O_3 was prepared by precipitation at constant pH (method B).

Table 3.1 BET analyses for ZnO, Au/Fe_2O_3, Au/ZnO and Au/Fe_2O_3 prepared by Method A.

Au / support	Preparation Procedure	Catalyst description	BET m^2/g	Treatment status
Au / ZnO	Method A (Variable pH)	pH 5	54	Uncalcined
		pH 6	51	
		pH 7	45	
		pH 8	58	
		pH 9	23	
		pH 10	23	
		No Ageing, pH 6	54	
		Aged 3 hrs, pH 6	30	
		Aged 5 hrs, pH 6	37	
		Aged 8 hrs, pH 6	40	
		Aged 12hrs, pH 6	40	
		No Ageing, pH 8	58	
		Aged 1 hrs, pH 8	54	
		Aged 3 hrs, pH 8	55	
		Aged 5 hrs, pH 8	82	
		Aged 8 hrs, pH 8	58	
		Aged 12hrs, pH 8	66	
Fe_2O_3		pH 8.2	225	Uncalcined
			94	Calcined
Au/Fe_2O_3			208	Uncalcined
			69	Calcined

Table3. 2 BET analyses for ZnO, Fe_2O_3, Au/ZnO and Au/ Fe_2O_3 prepared by Method B.

Au / support	Preparation Procedure	Catalyst description	BET m2/g	Treatment status
Au / ZnO	Method B (constant pH)	At pH 5	50	Uncalcined
		At pH 6	23	
		At pH 7	25.5	
		At pH 8		
		At pH 9	41	
		At pH 10	59	
		No Ageing , pH 6		
		Aged 1 hr, pH 6	30	
		Aged 3 hrs, pH 6	33	
		Aged 5 hrs, pH 6	39	
		Aged 8 hrs, pH 6	32	
		Aged 12hrs, pH 6	52	
Fe_2O_3		pH 9	42	Uncalcined
			29	Calcined
Au/Fe_2O_3		At pH 4	230	Uncalcined
		At pH 5	247	
		At pH 6	226	
		At pH 7	176	
		At pH 8	193	
		At pH 10	364	
		At pH 4	33	Calcined
		At pH 5	70	
		At pH 6	59	
		At pH 7	49	
		At pH 8	52	
		At pH 10	129	

Similar results were obtained for the above supported gold catalysts when they were prepared by the deposition-precipitation method. When Au/MgO was prepared by the deposition-precipitation method, the calcined support had a higher surface area compared with the uncalcined support, possibly due to the dehydration of MgO during the calcination. However, when gold was deposited on MgO, uncalcined and calcined catalysts had a lower surface area than the support material. The gold catalyst supported on MnO_X had a much higher surface area than the support itself.

Table 3.3 BET analyses for different supported gold catalysts prepared by the deposition-precipitation method

Catalyst	Support Prep. Method	BET m^2/g	Treatment status
ZnO	Precipitation. A (variable pH)	51	Uncalcined
		43	Calcined
Fe_2O_3		225	Uncalcined
		94	Calcined
MgO		21	Uncalcined
		310	Calcined
MnO_x		2	Uncalcined
		11	Calcined
ZnO	Precipitation. B (constant pH)	55	Uncalcined
		44	Calcined
Fe_2O_3		42	Uncalcined
		28	Calcined
MgO		43	Uncalcined
		252	Calcined
MnO_x		1	Uncalcined
		8	Calcined
Au/ZnO	Precipitation. A	39	Uncalcined
		36	Calcined
Au/ZnO	Precipitation. B	44	Uncalcined
		38	Calcined
Au/Fe_2O_3	Precipitation. A	201	Uncalcined
		107	Calcined
Au/Fe_2O_3	Precipitation. B	41	Uncalcined
		37	Calcined
Au/MgO	Precipitation. A	37	Uncalcined
		39	Calcined
Au/MgO	Precipitation. B	35	Uncalcined
		39	Calcined
Au/MnO_x	Precipitation. A	86	Uncalcined
		50	Calcined
Au/ MnO_x	Precipitation. B	28	Uncalcined
		25	Calcined

3.2.2. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopic analyses were undertaken for all the prepared gold supported catalysts to identify the effect of the preparation methods and parameters on the gold content in these catalysts. Fig. 3.1and Fig. 3.2 show the AAS for Au/ZnO catalysts prepared by coprecipitation at variable pH (method A) and at constant pH (method B) respectively. The gold content is strongly dependent on the pH, by increasing the pH the gold content decreases in the catalyst prepared by coprecipitation at variable pH (A) or at constant pH (B).

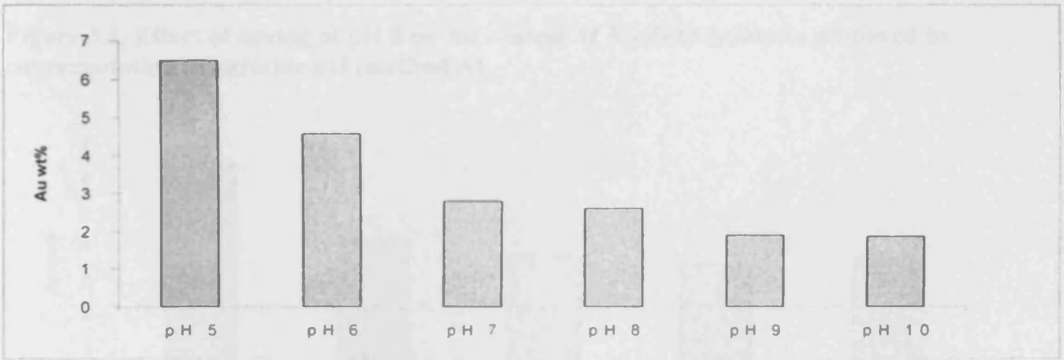

Figure 3.1. Effect of pH in method A on the Au content of Au/ZnO catalysts

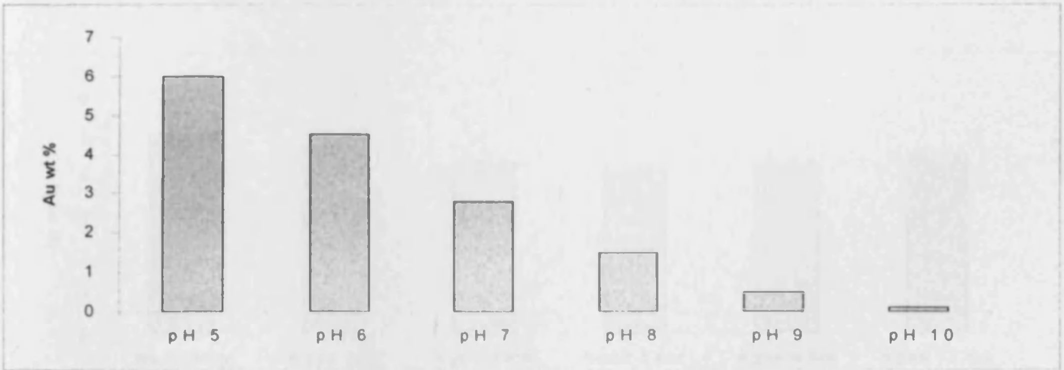

Figure 3.2. Effect of pH in method B on the Au content of Au/ZnO catalysts

The ageing process during the preparation led to a decrease in the gold content in the prepared catalysts. However, there was no large difference between the obtained gold contents in the catalysts aged at different times.

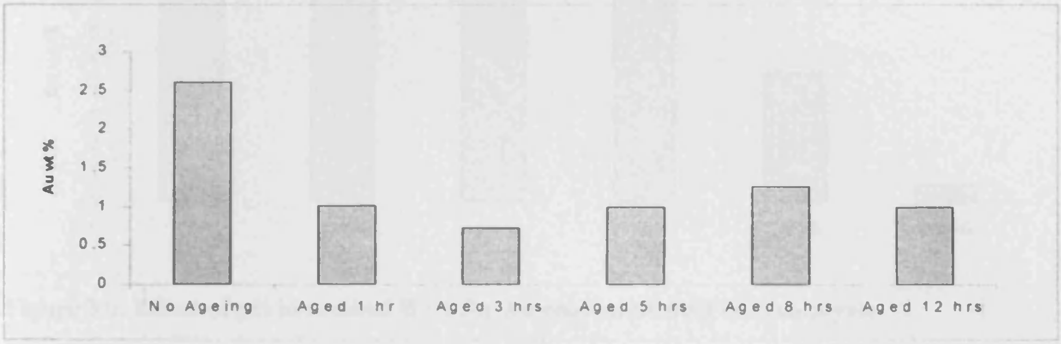

Figure 3.3. Effect of ageing at pH 8 on Au content of Au/ZnO catalysts prepared by coprecipitation at variable pH (method A)

Figure 3.4. Effect of ageing at pH 6 on Au content of Au/ZnO catalysts prepared by (method A)

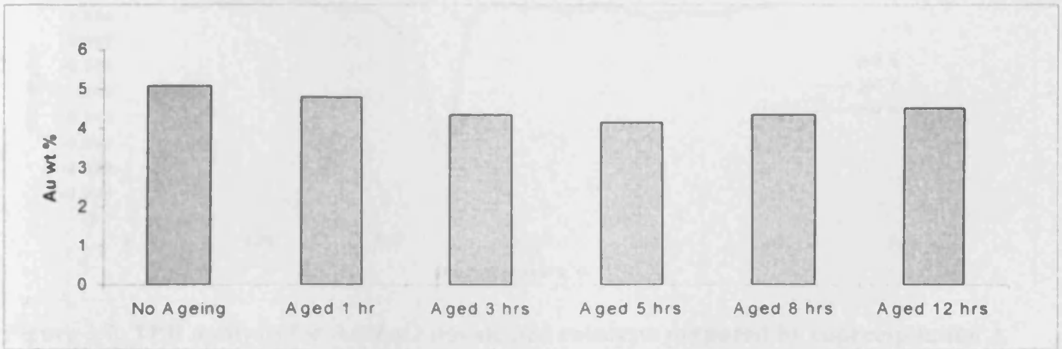

Figure 3.5. Effect of ageing at pH 6 on Au content of Au/ZnO catalysts prepared by (method B)

Au/Fe_2O_3 catalysts prepared by coprecipitation at constant pH showed some increase in gold content by increase the pH, but when pH reach 10, gold content decreased. Fig. 3.6. show the effect of pH on the gold content for Au/Fe_2O_3 catalysts.

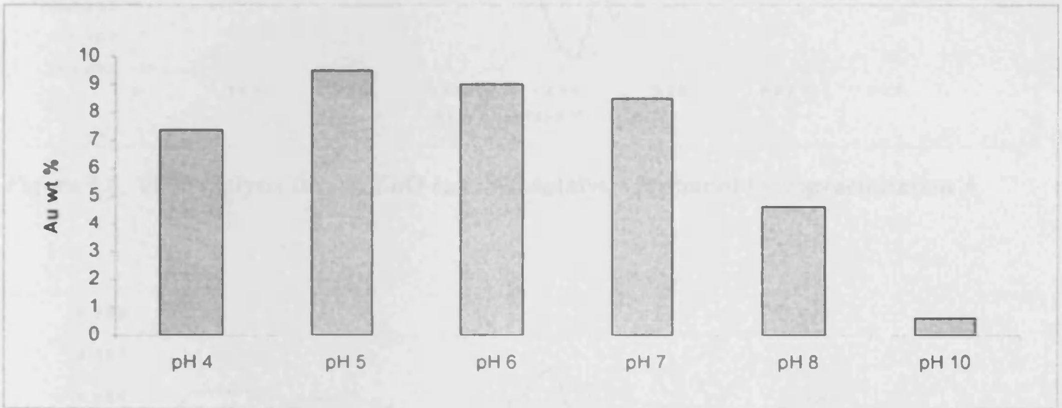

Figure 3.6. Effect of pH in method B on the Au content of Au/Fe_2O_3 catalysts

3.2.3. Temperature Programmed Reduction (TPR)

The aim of studying temperature programmed reduction analysis was to ascertain the effect of gold as promoter, and the effect of the preparation methods and preparation parameters on the reducibility of the supports. Several catalysts were tested for TPR and the results are in the figures below.

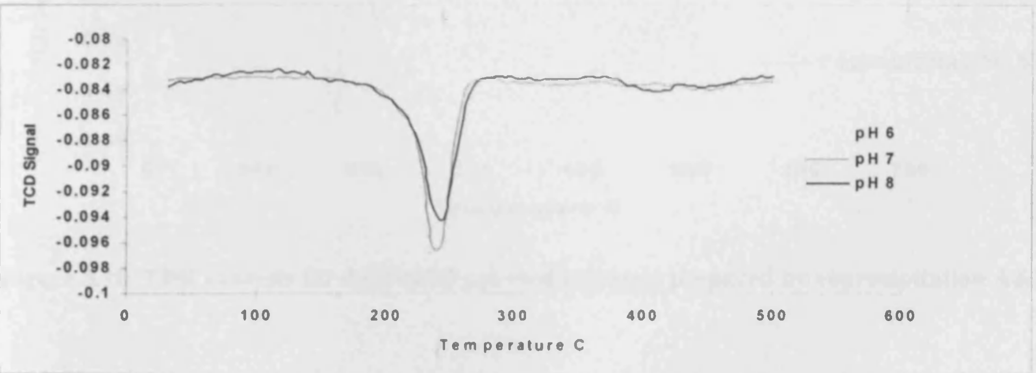

Figure 3.7. TPR analysis for Au/ZnO uncalcined catalysts prepared by coprecipitation A

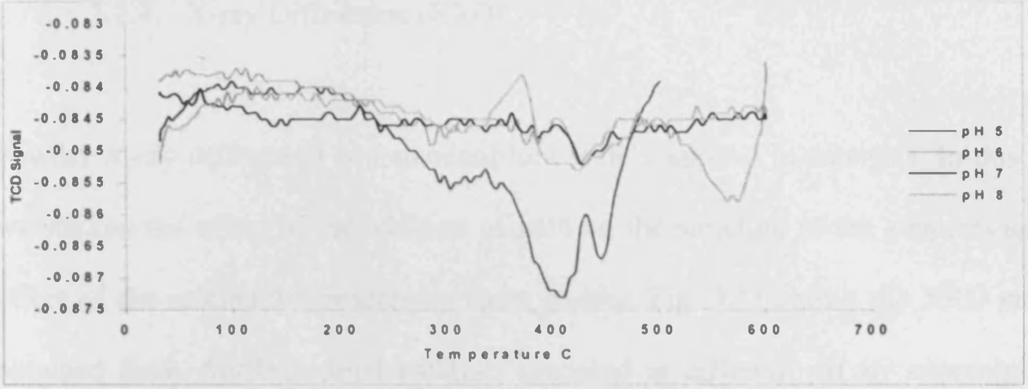

Figure 3.8. TPR analysis for Au/ZnO calcined catalysts prepared by coprecipitation A

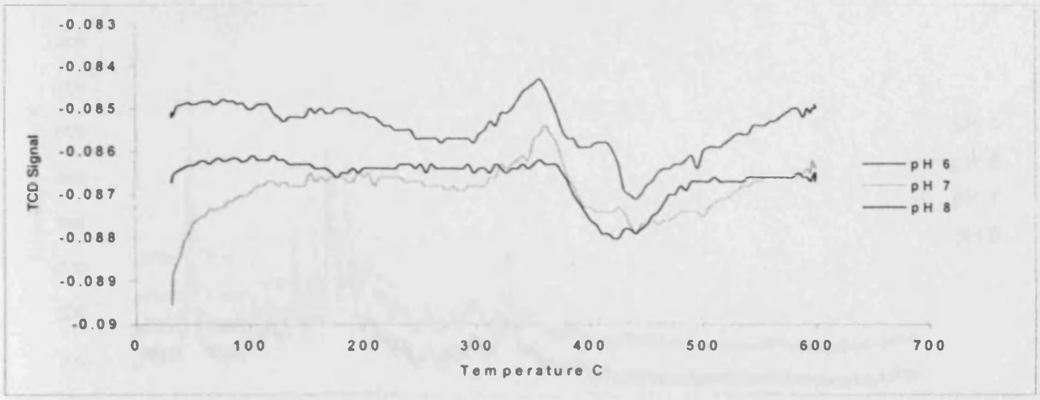

Figure 3.9. TPR analysis for Au/ZnO calcined catalysts prepared by coprecipitation B

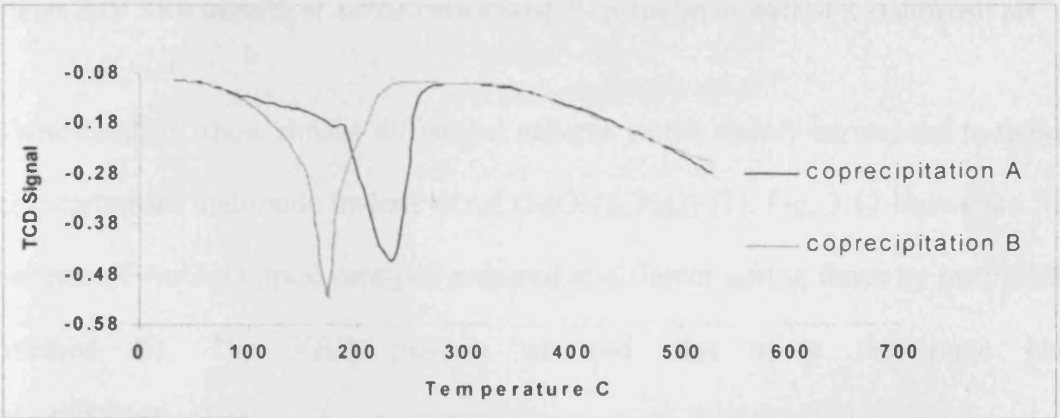

Figure 3.10. TPR analysis for Au/Fe2O3 calcined catalysts prepared by coprecipitation A&B

3.2.4. X-ray Diffraction (XRD)

Powder X-ray diffraction is a standard tool widely applied in catalysis. In this study we studied the effect of the addition of gold on the structure of the supports and the effect of the calcination process on these phases. Fig. 3.11 shows the XRD patterns obtained from Au/ZnO dried catalysts prepared at different pH by coprecipitation (method A).

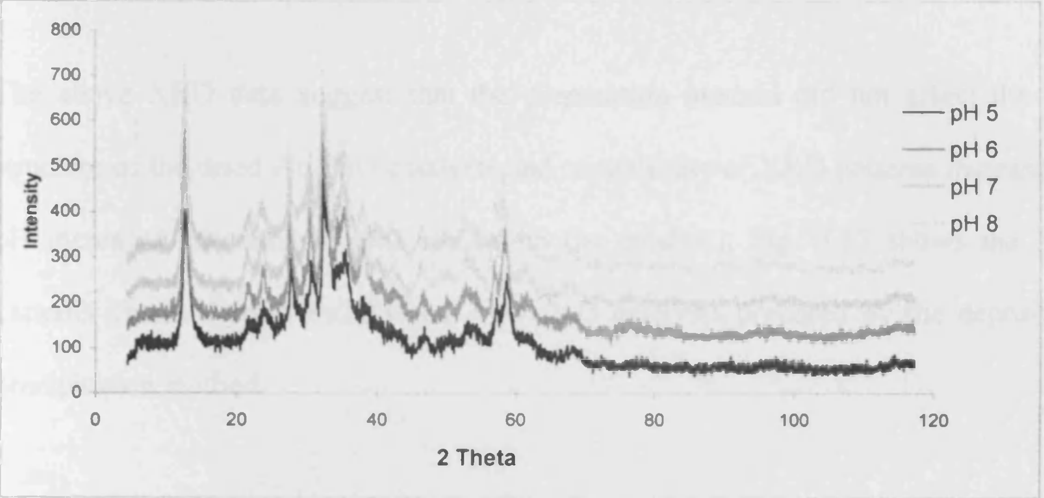

Figure 3.11. XRD patterns of Au/ZnO dried catalysts prepared by method A at different pH

These catalysts show similar diffraction patterns which mainly correspond to those of zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6.H_2O$) [1]. Fig. 3.12 shows the XRD patterns of Au/ZnO dried catalysts prepared at different ageing times by precipitation (method B). The XRD patterns obtained also show the same phase ($Zn_4CO_3(OH)_6.H_2O$).

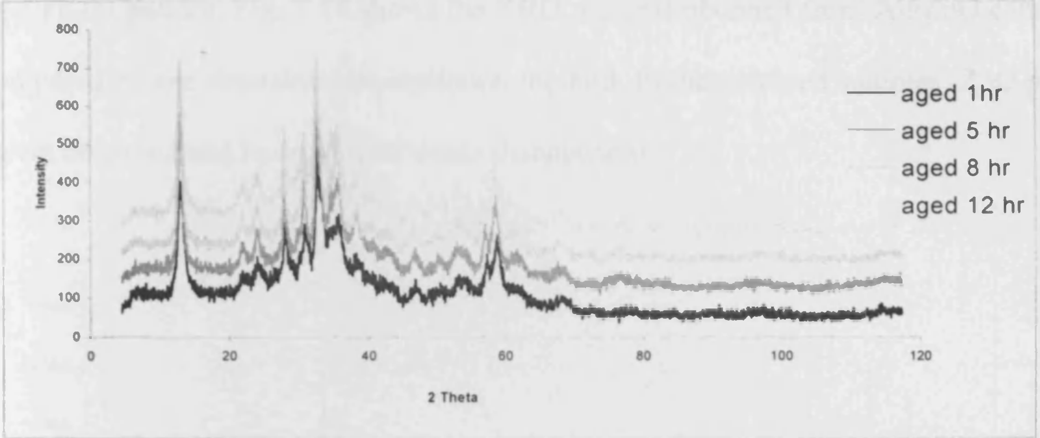

Figure 3.12. XRD patterns of Au/ZnO dried catalysts prepared by method B at different ageing times

The above XRD data suggest that the preparation method did not affect the bulk structure of the dried Au/ZnO catalysts and crystallinity of XRD patterns increased as pH increased (decreasing gold content in the catalyst). Fig. 3.13 shows the XRD patterns obtained from Fe2O3 and Au/Fe2O3 catalysts prepared by the deposition-precipitation method.

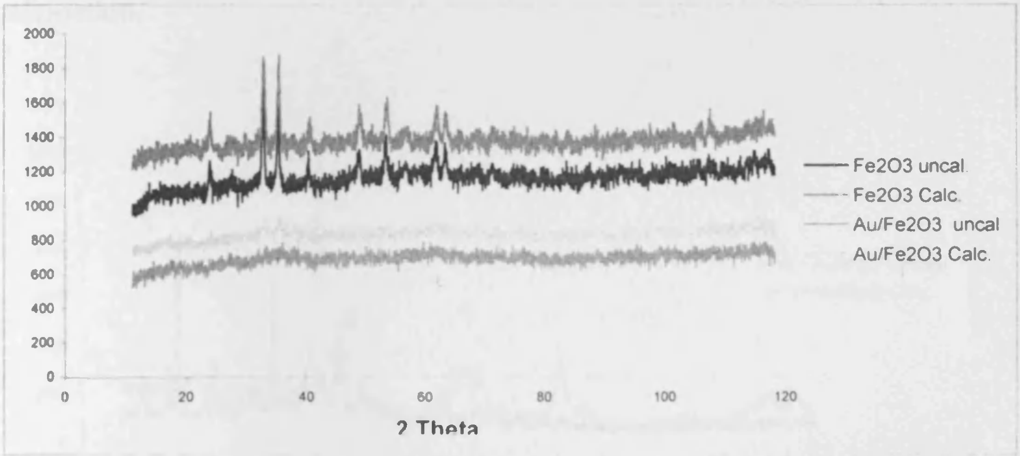

Figure 3.13. XRD patterns of Fe2O3, Au/Fe2O3 catalysts prepared by deposition-precipitation

Deposition of gold on Fe_2O_3 led to a decrease in the crystalline diffraction the Fe_2O_3 pattern while the pretreatment of the materials increases the crystalline diffraction of the Fe_2O_3 pattern. Fig. 3.14 shows the XRD patterns obtained from Au/ZnO catalysts prepared by the deposition-precipitation method. In the calcined samples, ZnO peaks were observed and hydrozincate peaks disappeared.

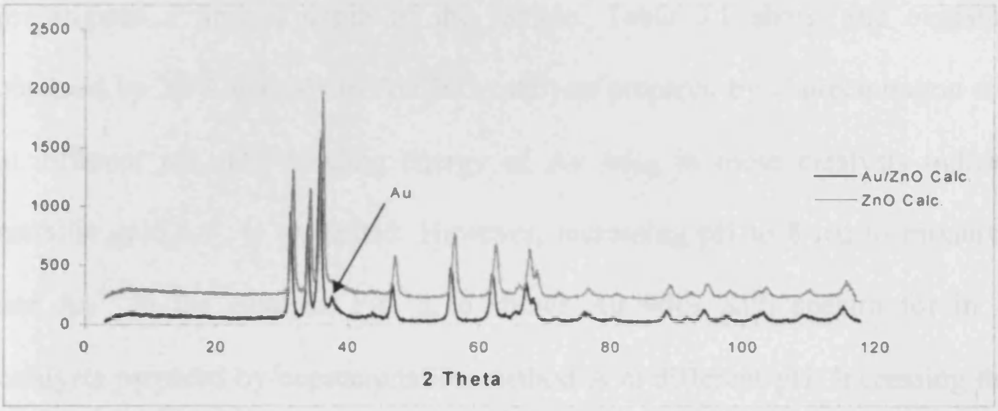

Figure 3.14. XRD patterns of Zn, Au/ZnO catalysts prepared by deposition-precipitation

Fig. 3.15 shows the XRD patterns obtained from Au/MgO catalysts prepared by the deposition-precipitation method. XRD patterns become more crystalline by calcination.

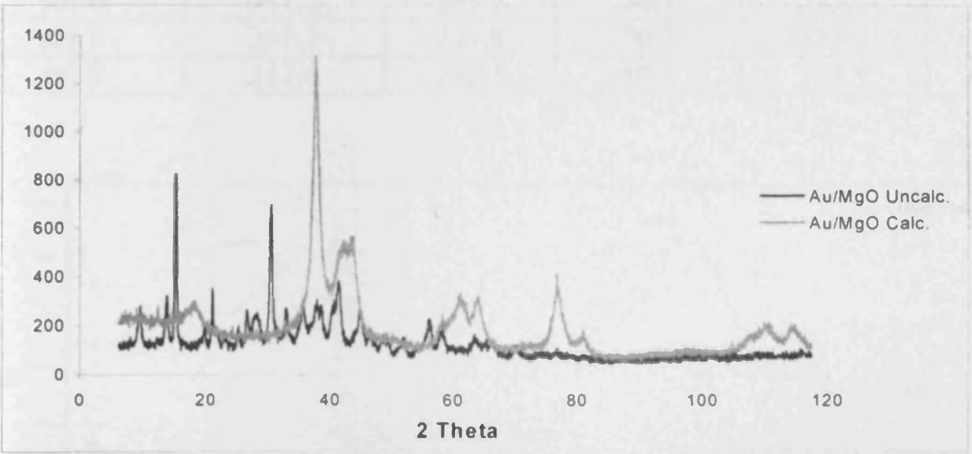

Figure 3.15. XRD patterns of Au/MgO catalysts prepared by deposition-precipitation

3.2.5. X-ray photoelectron spectroscopy (XPS)

To develop new catalytic systems it is very important to study change in surface electronic, chemical and structural properties during a particular process. XPS is one of the most suitable analytical techniques for the analysis of surfaces, because it investigates a limited depth of the sample. Table 3.1 shows the oxidation state obtained by XPS analysis in Au/ZnO catalysts prepared by coprecipitation method A at different pH. The binding energy of Au $4d_{5/2}$ in these catalysts indicates that metallic gold,Au^0, is presented. However, increasing pH to 8 led to mixture of Au^0 and Au^{+x} in the catalyst. Fig. 3.16 shows Au $4d_{5/2}$ XPS spectra for in Au/ZnO catalysts prepared by coprecipitation method A at different pH. Increasing the pH of the prepared samples led to decrease in intensity of gold species, which disappeared when pH > 8.

Table 3.4 XPS analysis of Au/ZnO uncalcined catalysts prepared by method A at different pH

Catalyst	Au $4d_{5/2}$ (B. Energy)	C_{1s} (B. Energy)	Au 4 $d_{5/2}$ - C_{1s}	Au $4d_{5/2}$ (Calibrated)	Au oxidation state
pH 5	341.4	291.5	49.9	334.9	Au^0
pH 6	341.3	291.2	50.1	335.1	Au^0
pH 7	342.1	291.8	50.3	335.3	Au^0
pH 8	342.6	292.1	50.5	335.5	Au^0- Au^{+x}

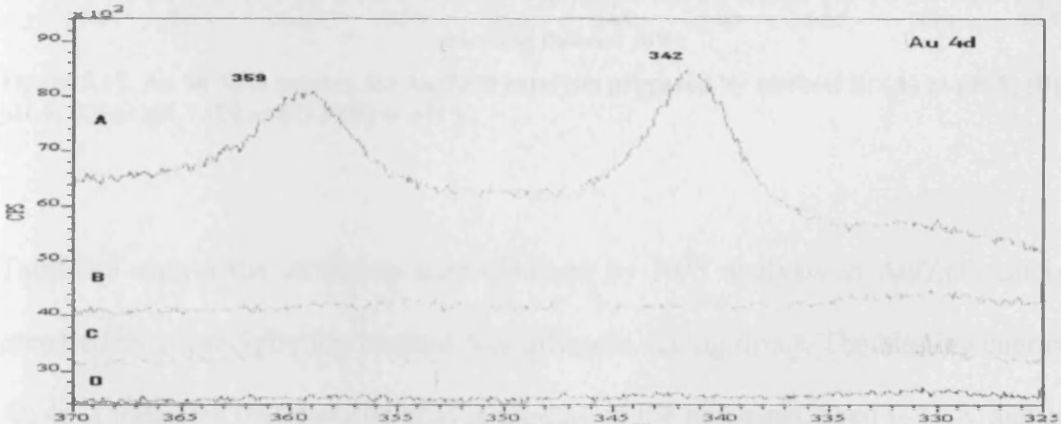

Figure 3.16. Au 4d XPS spectra for Au/ZnO catalysts prepared by method A: (A) at pH 5; (B) at pH 6; (C) at pH 7 (D) at pH 8

Table 3.2 shows the oxidation state obtained by XPS analysis in Au/ZnO catalysts prepared by coprecipitation method B at different pH. The binding energy of Au 4d$_{5/2}$ in these catalysts indicates metallic gold,Au^0, is present.

Table 3.5 XPS analysis of Au/ZnO uncalcined catalysts prepared by method B at different pH

Catalyst	Au 4d$_{5/2}$ (B. Energy)	C$_{1s}$ (B. Energy)	Au 4 d$_{5/2}$ - C$_{1s}$	Au 4d$_{5/2}$ (Calibrated)	Au oxidation state
pH 5	341.9	291.7	50.2	335.2	Au^0
pH 6	341.2	291.4	49.8	334.8	Au^0
pH 7	340.9	290.8	50.1	335.1	Au^0
pH 8	341.4	291.5	49.9	334.9	Au^0

Fig. 3.17 shows Au 4d$_{5/2}$ XPS spectra for Au/ZnO catalysts prepared by coprecipitation method B at different pH.

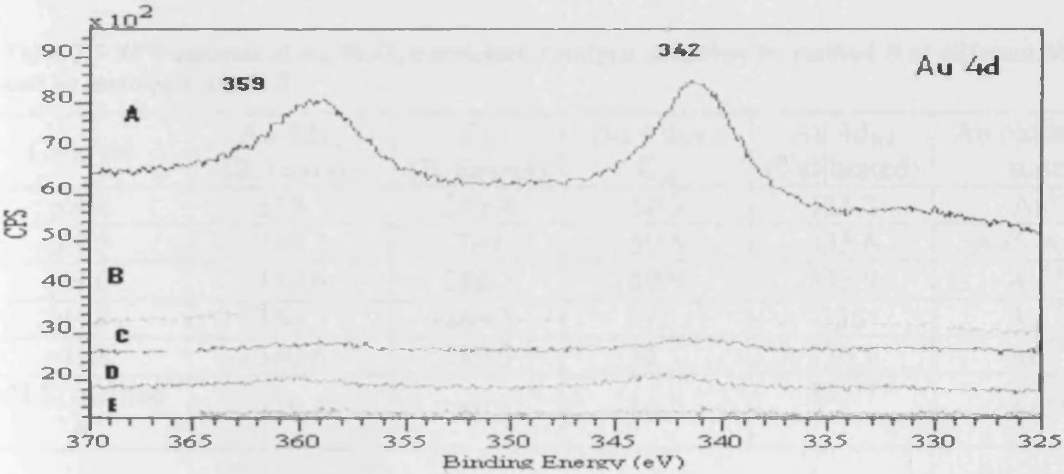

Figure 3.17. Au 4d XPS spectra for Au/ZnO catalysts prepared by method B: (A) at pH 5; (B) at pH 6; (C) at pH 7 (D) at pH 8 (E) at pH 9

Table 3.3 shows the oxidation state obtained by XPS analysis in Au/ZnO catalysts prepared by coprecipitation method A at different ageing times. The binding energy of Au 4d$_{5/2}$ indicates that metallic gold is presenting the non-aged, aged for 1 h, and aged for 8 h catalysts, and mixture of metallic and cationic gold is present in catalysts aged for 3 h, 5 h, and 12 h.

Table 3.6 XPS analysis of Au/ZnO uncalcined catalysts prepared by method A at different ageing times

Catalyst	Au $4d_{5/2}$ (B. Energy)	C_{1s} (B. Energy)	Au 4 $d_{5/2}$ - C_{1s}	Au $4d_{5/2}$ (Calibrated)	Au oxidation state
No ageing	341.3	291.2	50.1	335.1	Au^0
Aged 1 h	341.6	291.4	50.2	335.2	Au^0
Aged 3 h	341.9	291.3	50.6	335.6	Au^0- Au^{+x}
Aged 5 h	341.1	290.5	50.6	335.6	Au^0- Au^{+x}
Aged 8 h	342.6	292.9	49.7	334.7	Au^0
Aged 12 h	342.1	291.6	50.5	335.5	Au^0- Au^{+x}

Table 3.4 shows the oxidation state obtained by XPS analysis in Au/Fe_2O_3 catalysts prepared by coprecipitation method B at different pH. The binding energy of Au $4d_{5/2}$ indicates that at pH higher than 5, oxidized gold was present in these catalysts.

Table 3.7 XPS analysis of Au/Fe_2O_3 uncalcined catalysts prepared by method B at different pH and by method A at pH 8

Catalyst	Au $4d_{5/2}$ (B. Energy)	C_{1s} (B. Energy)	Au 4 $d_{5/2}$ - C_{1s}	Au $4d_{5/2}$ (Calibrated)	Au oxidation state
pH 4	339.7	289.4	50.3	335.3	Au^0
pH 5	340.2	289	50.6	335.6	Au^0- Au^{+x}
pH 6	339.6	288.7	50.9	335.9	Au^{+x}
pH 7	340.3	289.3	51	336	Au^{+x}
pH 8	340.6	289.5	51.1	336.1	Au^{+x}
pH 8, method A	339.8	289.1	50.7	335.7	Au^{+x}

While Au 4f XPS spectra for Au/ZnO catalysts lacked clarity, they were clear in the case of Au/Fe_2O_3 catalysts. Fig. 3.18 shows Au 4f XPS spectra for Au/Fe_2O_3 catalysts prepared by coprecipitation method B at different pH. Au^{+x} 4f peaks' intensity decreased as pH increased.

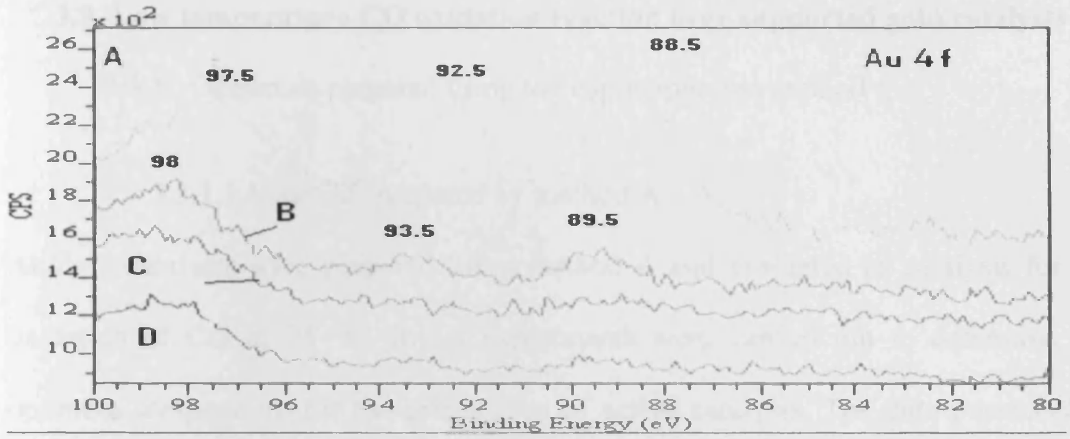

Figure 3.18. Au 4d XPS spectra for Au/Fe2O3 method B: (A) at pH 5; (B) at pH 6; (C) at pH 7 (D) at pH 8

XPS analysis of gold catalysts prepared via the deposition-precipitation method using four different supports (ZnO, Fe_2O_3, MgO, and MnO_2) gave some idea of the oxidation state of gold particles. Table 3.5 shows the oxidation state obtained by XPS analysis in gold catalysts prepared by deposition-precipitation method and supported on ZnO, Fe_2O_3, MgO, and MnO_x. The binding energy of Au $4d_{5/2}$ indicates that metallic gold is present in Au/ZnO catalyst, oxidized gold is presented in Au/ Fe_2O_3 and Au/ MgO had, and a mixture of metallic and oxidized gold is present in Au/MnO_x.

Table 3.8 XPS analysis of uncalcined supported gold catalysts prepared by the DP method

Catalyst	Au $4d_{5/2}$ (B. Energy)	C_{1s} (B. Energy)	Au 4 $d_{5/2}$ - C_{1s}	Au $4d_{5/2}$ (Calibrated)	Au oxidation state
Au/ZnO	336.2	286.4	49.8	334.8	Au^0
Au/Fe_2O_3	340.6	289.4	51.2	336.2	Au^{+x}
Au/MgO	342.5	291.3	51.2	336.2	Au^{+x}
Au/MnO_x	339	288.4	50.6	335.6	Au^0- Au^{+x}

3.3. Low temperature CO oxidation reaction over supported gold catalysts

3.3.1. Materials prepared using the coprecipitation method

3.3.1.1. Materials prepared by method A

Au/ZnO catalysts were prepared using method A and evaluated as catalysts for the oxidation of CO at 25 °C. Initial experiments were carried out to determine the optimum temperature for the preparation of active catalysts. The data presented in Fig. 3.19 are for the materials dried at 90 °C with no additional ageing step in the preparation, i.e. the material was filtered as soon as pH = 6.0 had been reached. These data show that active catalysts can be prepared with temperatures in the range 60 – 80 °C, but at higher temperature inactive materials are formed. In view of this, we standardised subsequent preparations at a controlled temperature of 80 °C.

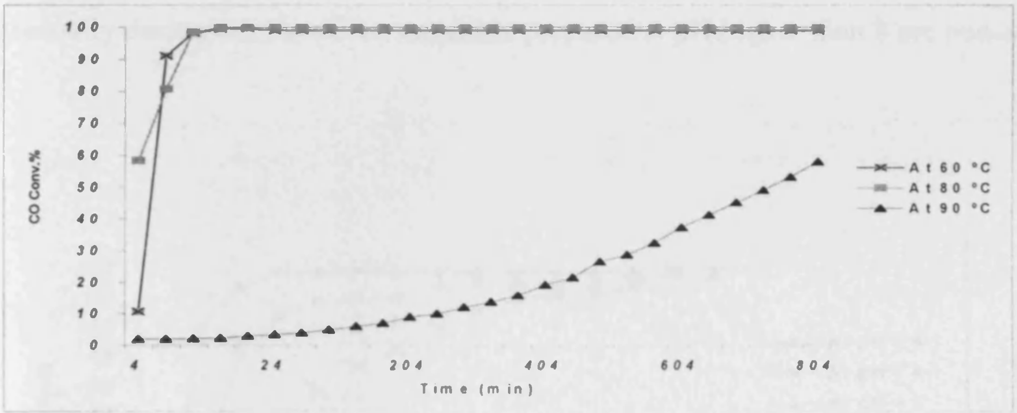

Figure 3.19. Effect of temperature of precipitation for dried Au/ZnO using coprecipitation method A at 60, 80, 90 °C

The Au/Fe_2O_3 catalyst was prepared in the same manner at 80 °C. Both catalysts were re-produced and re-evaluated for CO oxidation reaction. Fig. 3.20 shows the results of these catalysts.

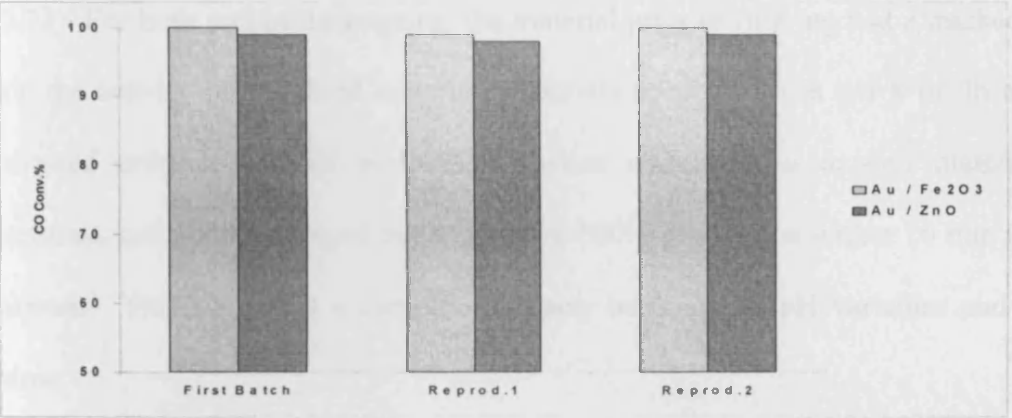

Figure 3.20. Reproducibility of supported gold catalysts prepared by coprecipitation A at 80 °C

The effect of the final pH was investigated at 80 °C. The results clearly indicated that pH had a marked effect on uncalcined catalyst activity, Fig. 3.21. Active catalysts were prepared with a final pH between of 5-6. At a pH higher than 6, catalytic activity gradually decreased. However, materials prepared at pH higher than 8 are non-active.

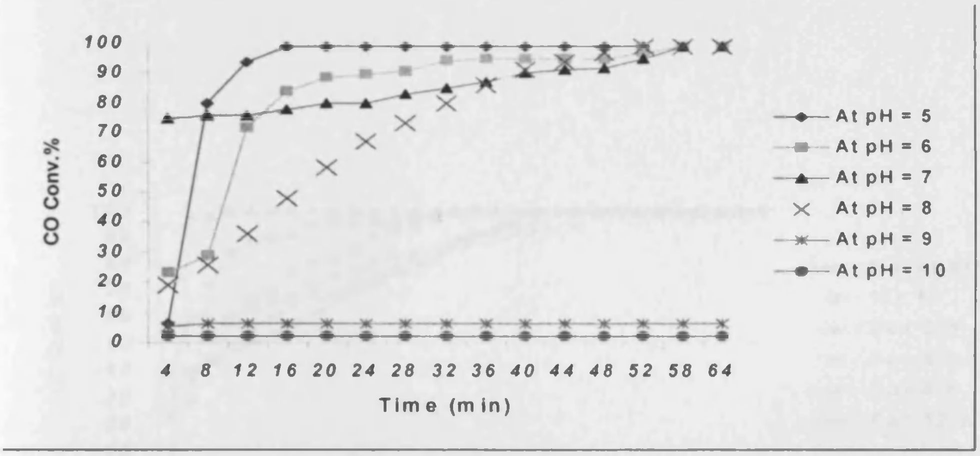

Figure 3.21. Effect of pH on the activity of dried Au/ZnO prepared by coprecipitation A at 80 °C

The effect of ageing was then examined at two pH values (pH 8, Fig. 3.22; pH 6 Fig. 3.23). For both sets of data ageing, the material prior to filtering had a marked effect on the activity of the dried material. Materials aged for 1h at pH 8 or 3h at pH 6 showed enhanced initial performance when compared to unaged materials. In contrast, calcination of aged materials gave 100% conversion within 10 min time on stream. This suggested a complex interplay between the pH variables and ageing time.

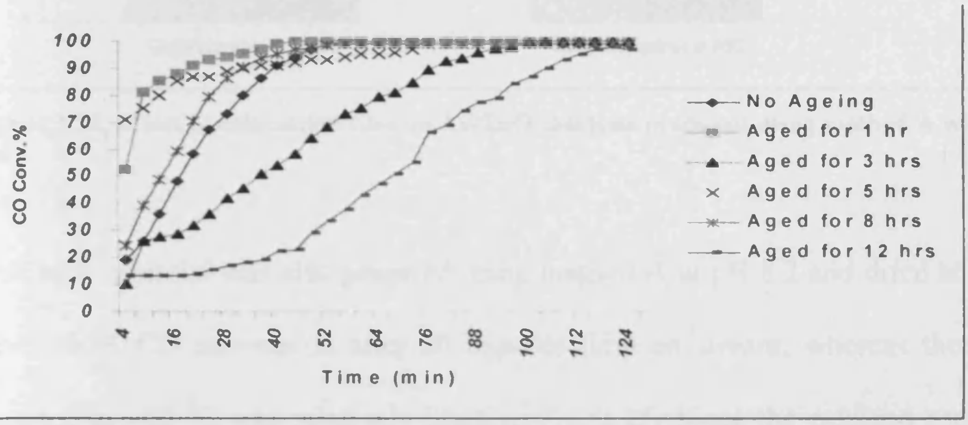

Figure 3.22. Effect of ageing on the activity of dried Au/ZnO catalysts prepared using method A with a final pH 8.0. no ageing, 1h, 3h, 5h, 8h, 12h

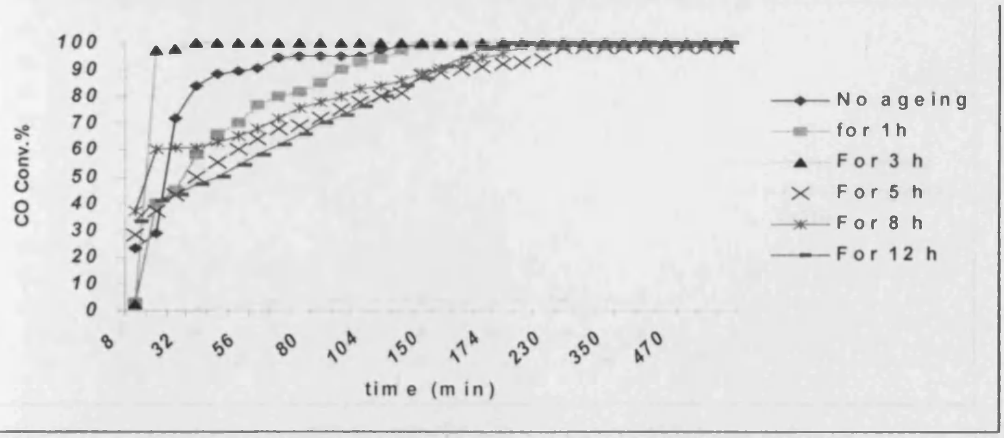

Figure 3.23. Effect of ageing on the activity of dried Au/ZnO catalysts prepared using method A with a final pH 6.0. no ageing, 1h, 3h, 5h, 8h, 12h

The effect of the calcination time was studied on Au/ZnO catalyst prepared by coprecipitation A, Fig. 3.24.

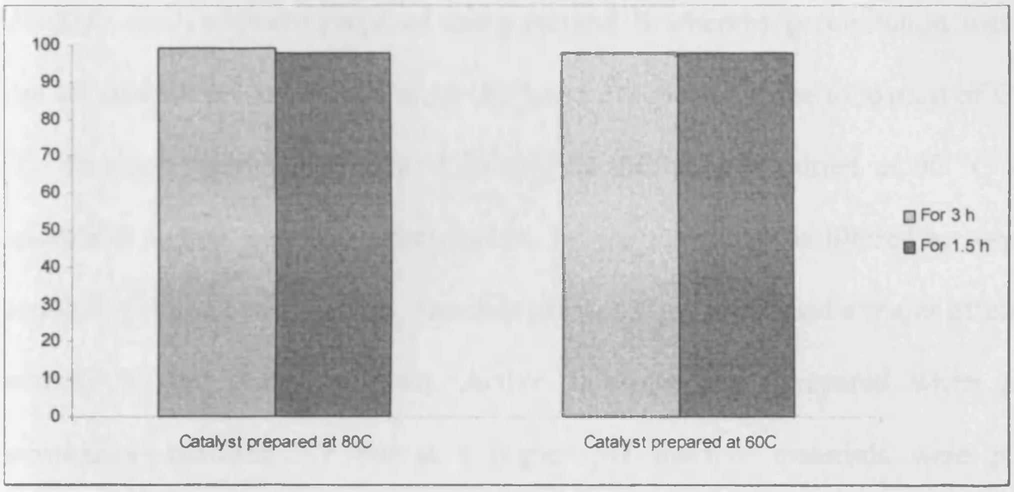

Figure 3.24. Effect of calcination time on Au/ZnO catalysts prepared using method A with a final pH 6

Au/Fe_2O_3 material was also prepared using method A at pH 8.2 and dried at 90 °C. It gave 100% CO conversion after 30 minutes time on stream, whereas the material calcined at 400 °C was relatively inactive Fig. 3.25. Since the calcined sample was more active than Fe_2O_3 prepared in the absence of Au, this suggested that the Au was exhibiting some catalytic effect.

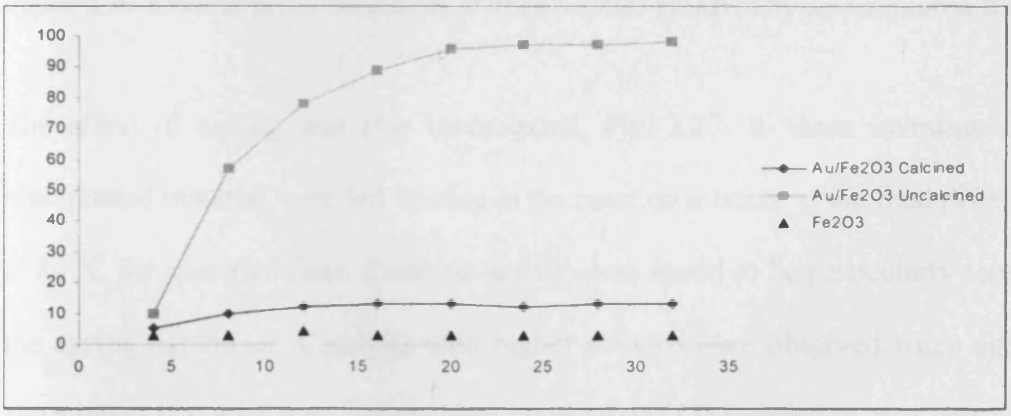

Figure 3.25. Catalytic evaluation for Fe2O3 and Au/Fe2O3 dried and calcined catalysts prepared using method A with a final pH 8.2

3.3.1.2.Materials prepared using method B

Au/ZnO catalysts were prepared using method B whereby precipitation was carried out at constant pH and temperature (80^{0}) and evaluated for the oxidation of CO at 25 °C. The data presented in Fig. 3.26 are for the materials dried at 90 °C with no additional ageing step in the preparation, i.e. the material was filtered as soon as the required pH had been reached. The data showed that the pH had a major effect on the activity of the dried materials. Active catalysts were prepared when pH was maintained between 5-7 but at a higher pH inactive materials were prepared. Calcination of materials prepared at pH 5-7 at 400 °C gave catalysts that were active immediately, whereas the dried materials required a short activation time.

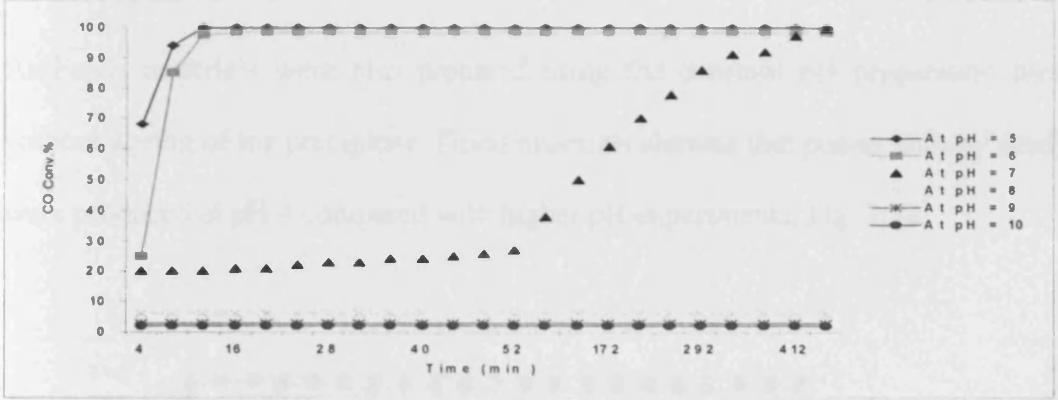

Figure 3.26. Effect of pH on the activity of dried Au/ZnO prepared by coprecipitation B at 80 °C

The effect of ageing was also investigated, Fig. 3.27. In these investigations, the precipitated material were left stirring in the reaction mixture at the final pH = 6.0 and at 80 °C for specified time. Catalytic activity was found to be particularly sensitive to the ageing parameter. Catalysts with higher activity were observed when aged for a short time (1h). And then, ageing over longer times (3h) tended to give catalysts with poorer initial activity, although the initial activity of catalysts aged for (5h) was better than the activity of catalysts aged for (3h). In addition, ageing for (8h) tended to produce catalysts with initial activity almost similar to unaged and (1hr) aged catalyst. Finally, ageing for much longer (12h) produced catalysts with lower initial activity.

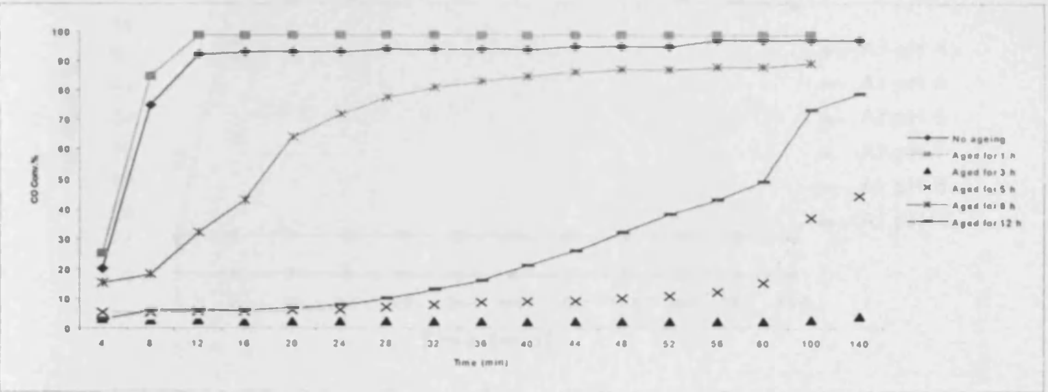

Figure 3.27. Effect of ageing on the activity of dried Au/ZnO catalysts prepared using method B with pH 6.0. no ageing, 1h, 3h, 5h, 8h, 12h

Au/Fe_2O_3 materials were also prepared using the constant pH preparation method without ageing of the precipitate. Dried materials showed that poorer activity catalysts were produced at pH 4 compared with higher pH experiments, Fig. 3.28.

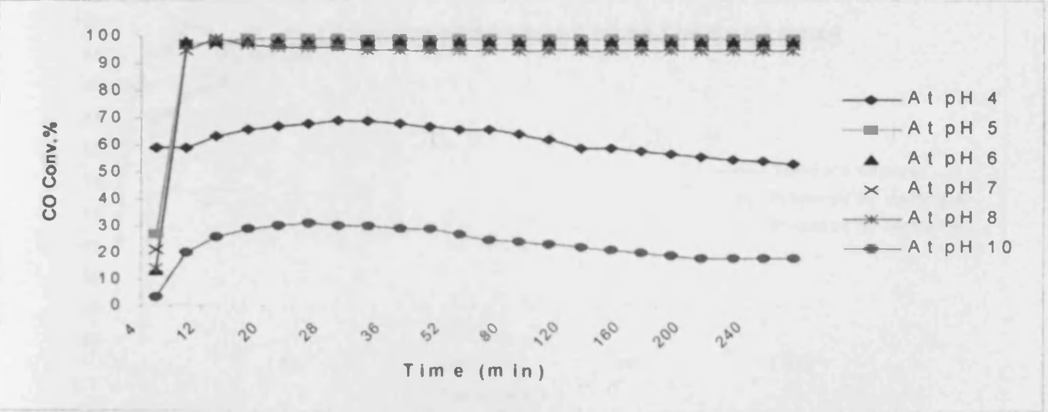

Figure 3.28. Effect of pH on the activity of dried Au/Fe_2O_3 prepared by coprecipitation B

Materials calcined at 400 °C showed a similar activity pattern, except that highest activity materials were prepared at pH ≥ 6, Fig. 3.29.

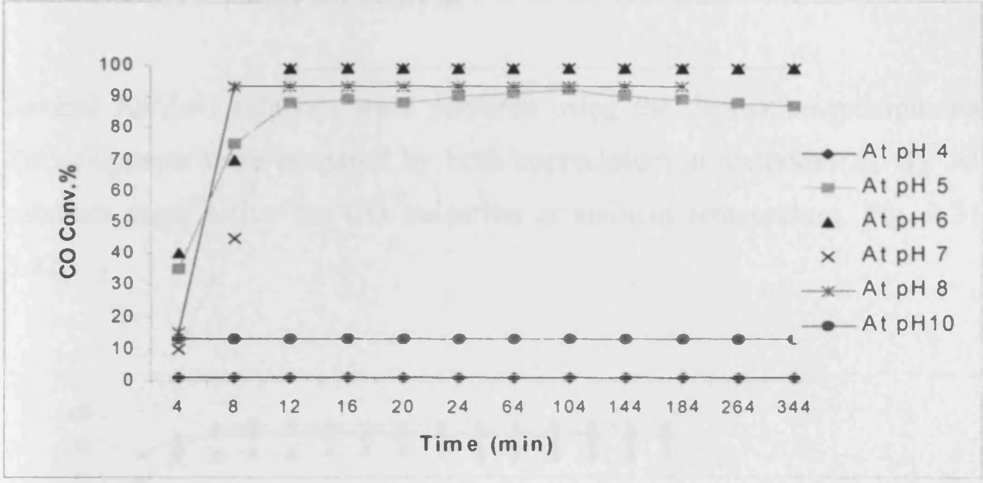

Figure 3.29. Effect of pH on the activity of calcined Au/Fe_2O_3 prepared by coprecipitation B

In order to compare the catalytic activity observed with the Au/ZnO and Au/Fe_2O_3 catalysts in this study and that of standard catalysts supplied by the World Gold Council were reacted and the results are shown in Fig. 3.30. Evaluation of standard catalyst was performed under the same conditions of our data.

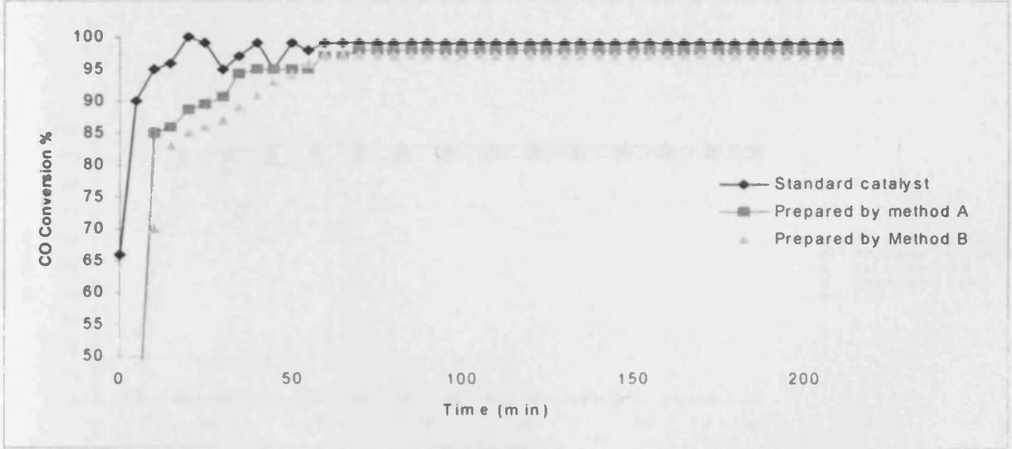

Figure 3.30. Comparison between standard Au/ZnO and our catalysts

3.3.2. Materials prepared using the deposition-precipitation method

3.3.2.1. Au/ZnO catalysts

Several Au/ZnO catalysts were prepared using the deposition-precipitation method. ZnO Supports were prepared by both coprecipitation methods (A, B). All Au/ZnO catalysts were active for CO oxidation at ambient temperature, Fig. 3.31 and Fig. 3.32.

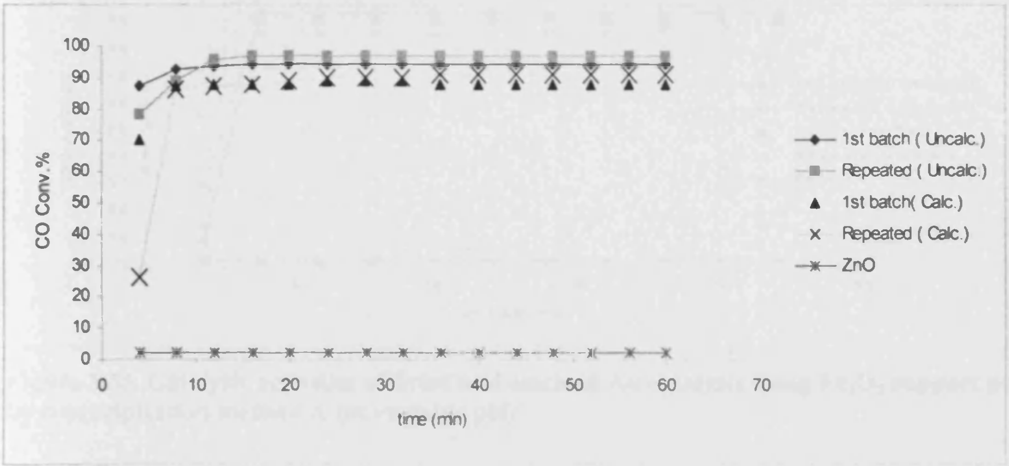

Figure 3.31. Catalytic activities of dried and calcined Au catalysts using ZnO support prepared by coprecipitation method A (at variable pH)

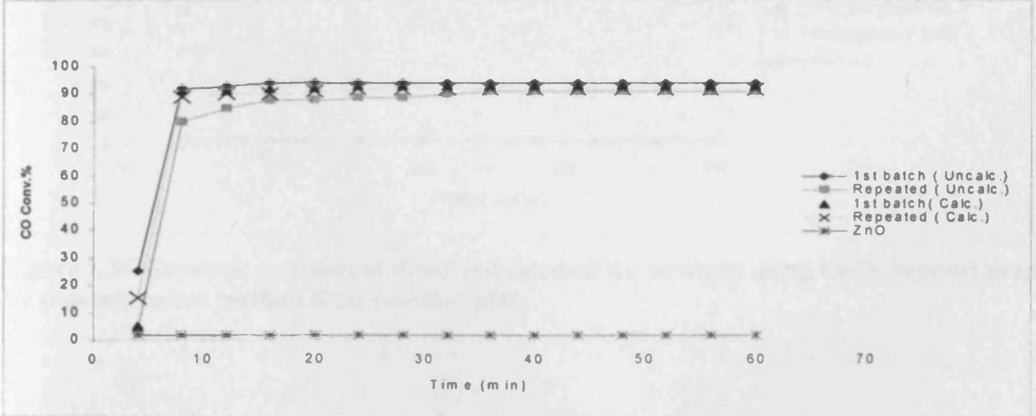

Figure 3.32. Catalytic activities of dried and calcined Au catalysts using ZnO support prepared by coprecipitation method B (at constant pH)

3.3.2.2. Au/Fe_2O_3 catalysts

Several Au/Fe_2O_3 catalysts were prepared using the deposition-precipitation method. Supports (Fe_2O_3) were prepared by both coprecipitation methods (A, B). All Au/Fe_2O_3 catalysts were active for CO oxidation at ambient temperature, Fig. 3.33 and Fig. 3.34.

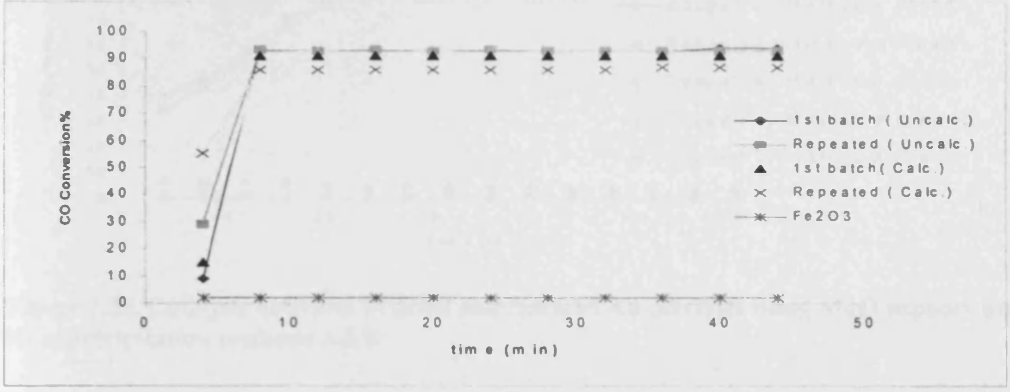

Figure 3.33. Catalytic activities of dried and calcined Au catalysts using Fe_2O_3 support prepared by coprecipitation method A (at variable pH)

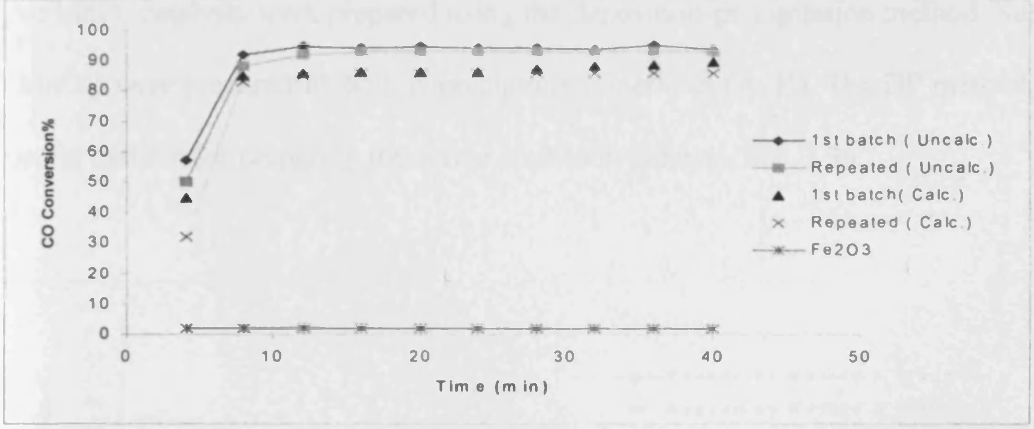

Figure 3.34. Catalytic activities of dried and calcined Au catalysts using Fe_2O_3 support prepared by coprecipitation method B (at constant pH)

3.3.2.3.Au/MgO catalysts

Au/MgO catalysts were prepared using the deposition-precipitation method. Supports (MgO) were prepared by both coprecipitation methods (A, B). the Au/MgO catalyst was active only at 25 °C using the support prepared by coprecipitation method A-uncalcined catalyst, Fig. 3.35.

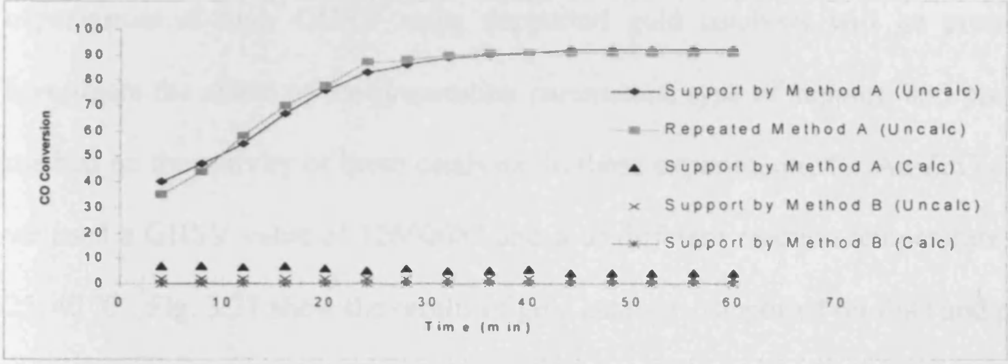

Figure 3.35. Catalytic activities of dried and calcined Au catalysts using MgO support prepared by coprecipitation methods A&B

3.3.2.4.Au/MnO$_2$ catalysts

Au/MnO$_2$ catalysts were prepared using the deposition-precipitation method. Supports (MnO$_x$) were prepared by both coprecipitation methods (A, B). The DP method is not useful method for preparing the active Au/MnO$_x$ catalyst, Fig. 3.36.

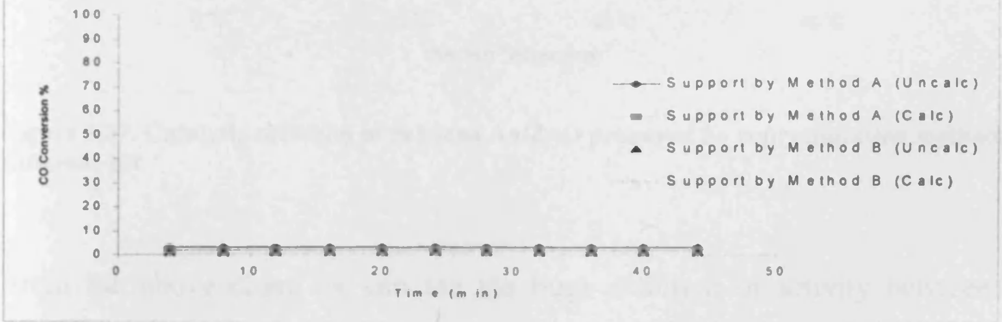

Figure 3.36. Catalytic activities of dried and calcined Au catalysts using MgO support prepared by coprecipitation methods A&B

3.4. CO oxidation at high gas hourly space velocity (GHSV)

After we obtained very good results for most of the prepared supported gold catalysts, we studied the difference in the activity of these catalysts, particularly catalysts that gave high CO conversion. In this subsection, a number of CO oxidation reaction experiments at high GHSV using supported gold catalysts will be presented to investigate the effect of the preparation parameters, type of support, and preparation method on the activity of these catalysts. In these experiments, for Au/ZnO catalysts, we used a GHSV value of 126000h^{-1} and four different reaction temperatures, 0, 15, 25, 40 °C . Fig. 3.37 show the results of gold catalysts supported on ZnO and prepared via coprecipitation A at different pH.

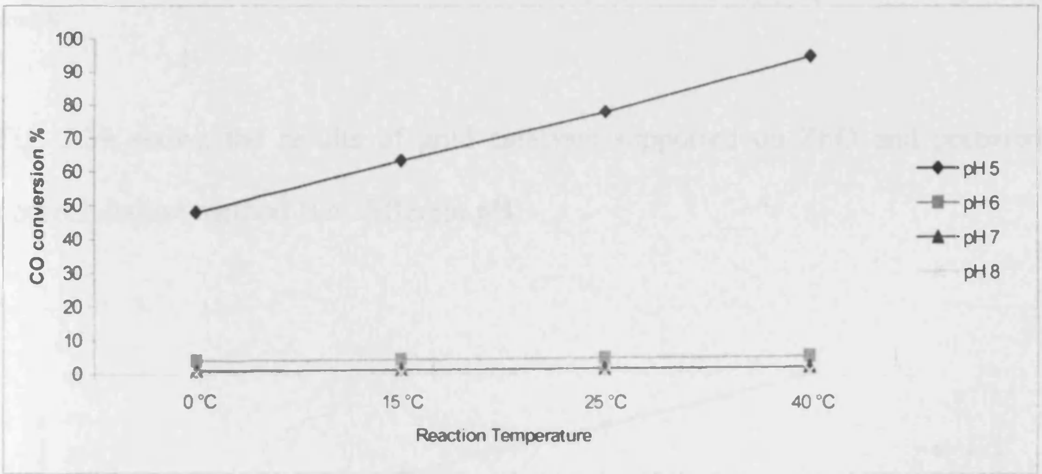

Figure 3.37. Catalytic activities of calcined Au/ZnO prepared by coprecipitation methods A at different pH

From the above chart we can see the huge different in activity between catalyst prepared at pH 5 and other catalysts prepared at higher pH, confirming the previous catalytic and characterization studies of these catalysts, namely, that the lower pH the higher catalytic activity of Au/ZnO catalysts. Fig. 3.38 presents the catalytic data for Au/ZnO prepared via coprecipitation A at pH 6, 7, and 8 respectively indicating that the lower the pH is the higher the catalytic activity. However, all catalysts obtained activity lower than 6%.

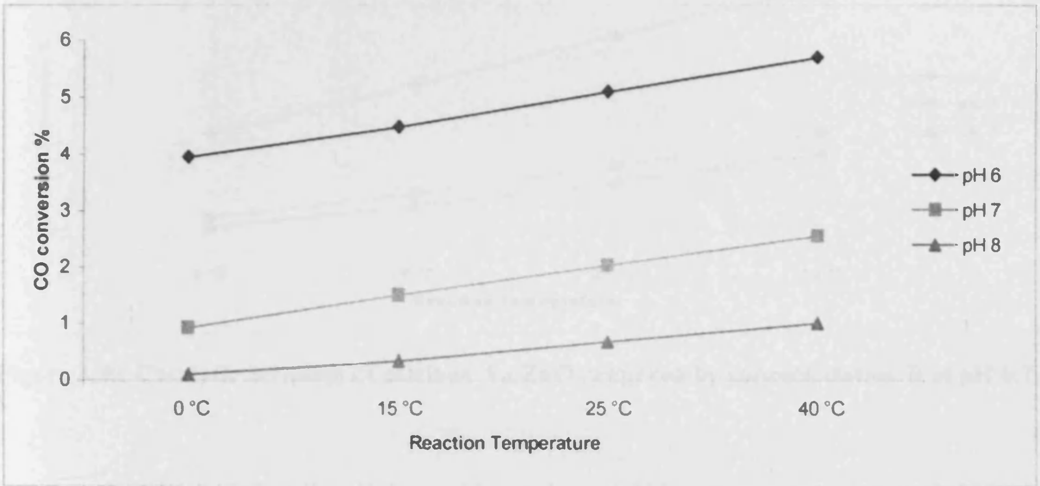

Figure 3.38. Catalytic activities of calcined Au/ZnO prepared by coprecipitation A at pH 6,7, and 8

Fig. 3.39 shows the results of gold catalysts supported on ZnO and prepared via coprecipitation method B at different pH.

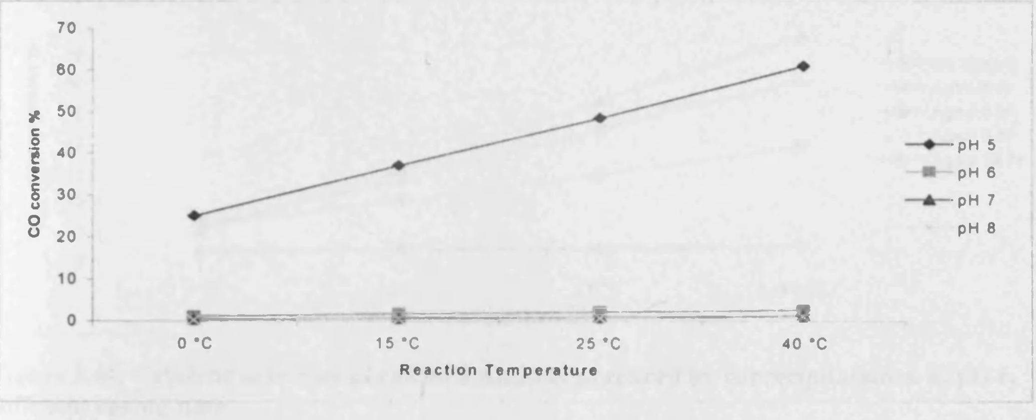

Figure 3.39. Catalytic activities of calcined Au/ZnO prepared by coprecipitation methods B at different pH

As in Fig. 3.38, Fig. 3.40 presents the catalytic data of Au/ZnO prepared via coprecipitation B at pH 6, 7, and 8 respectively without the catalyst prepared at pH 5 for the same reasons.

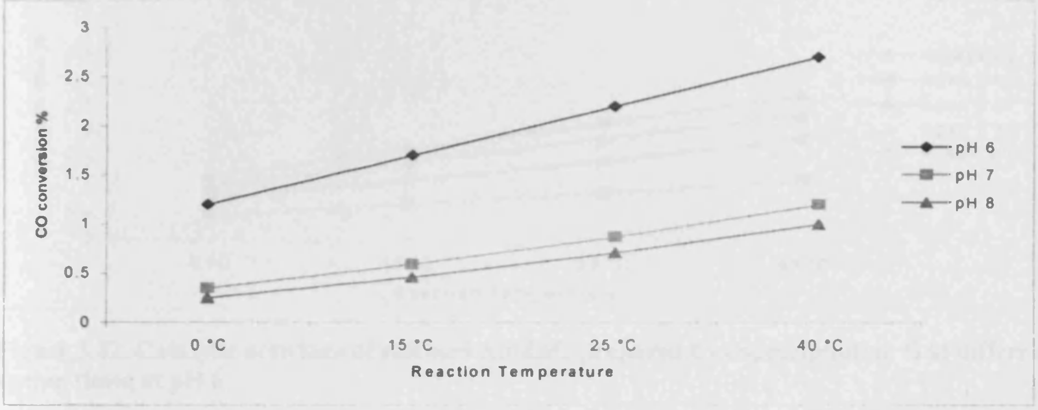

Figure 3.40. Catalytic activities of calcined Au/ZnO prepared by coprecipitation B at pH 6,7, and 8

Fig. 3.41 show the results of gold catalysts supported on ZnO and prepared via coprecipitation A at different ageing times at pH 6.

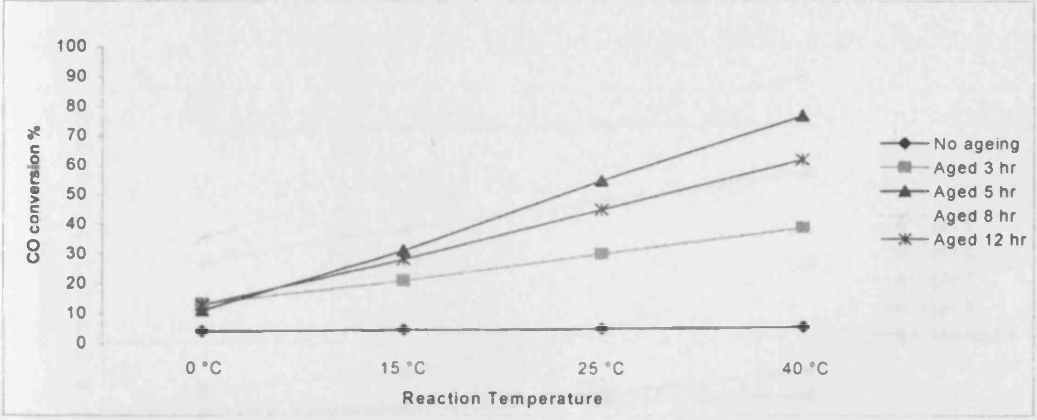

Figure 3.41. Catalytic activities of calcined Au/ZnO prepared by coprecipitation A at pH 6, different ageing time

Fig. 3.42 show the results of gold catalysts supported on ZnO and prepared via coprecipitation B at different ageing times at pH 6.

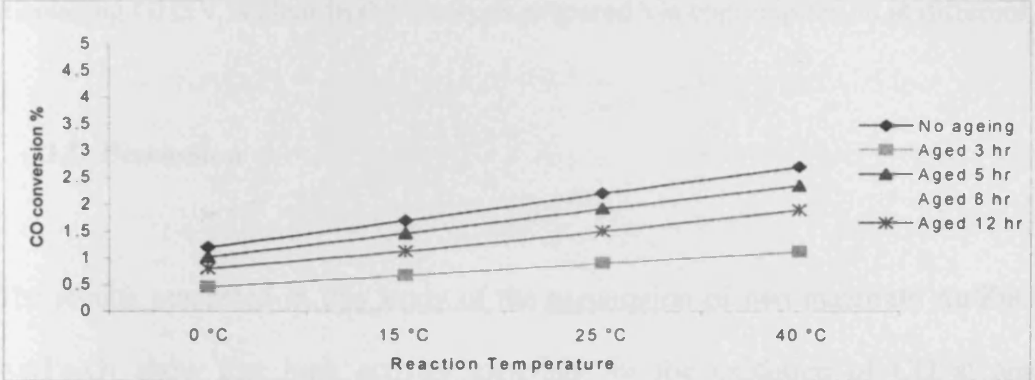

Figure 3.42. Catalytic activities of calcined Au/ZnO prepared by coprecipitation B at different ageing times at pH 6

Au/Fe_2O_3 catalysts prepared by coprecipitation method B were much higher catalytic activities than Au/ZnO catalysts. Therefore, GHSV value used for Au/Fe_2O_3 catalysts experiments, 480000 h^{-1}, were higher than those used for Au/ZnO catalysts , 126000 h^{-1}. The effect of an increasing GHSV on the catalytic activities of Au/Fe_2O_3 was studied and presented in Fig. 3.43.

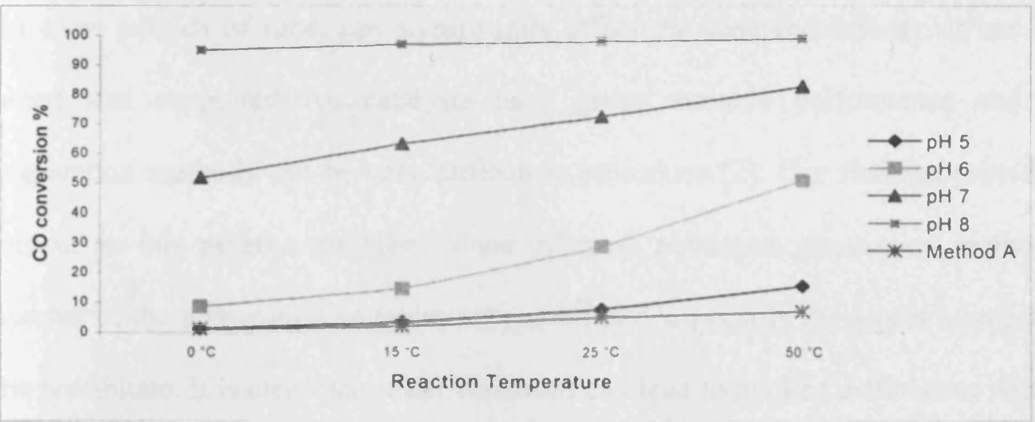

Figure 3.43. Catalytic activities of calcined Au/Fe_2O_3 prepared by coprecipitation A& (B at different pH)

The Au/Fe_2O_3 catalyst prepared by coprecipitation method A was non-active whereas catalysts prepared via coprecipitation method B were active, as already obtained in the results of CO oxidation at the standard reaction conditions, Fig. 3.29. The effect of increasing GHSV is clear in the catalysts prepared via coprecipitation at different pH.

3.5. Discussion

The results presented in this study of the preparation of two materials Au/ZnO and Au/Fe_2O_3 show that high activity materials for the oxidation of CO at ambient temperature can be readily prepared for both calcined and non-calcined materials using two different coprecipitation procedures. These results are comparable with the results obtained from the standard catalysts supplied by the World Gold Council tested under the same reaction conditions, Fig. 3.30. However, the most important observation is the potential sensitivity of these preparation methods to slight variations in the procedure when the materials are examined as catalysts for ambient temperature CO oxidation. For example, use of temperatures $\geq$ 80 °C led to inactive catalysts (Fig. 3.19). Variation in the ageing of the precipitate prior to filtration, even for short periods of time, can significantly affect the observed activity. It has been noted that supported Au catalysts have given variable performance and that preparation methods can be very difficult to reproduce [2]. Our findings provide an answer to this putative problem, since in many published preparation methods a number of the preparation variables are not defined, especially the aspect of ageing of the precipitate. It is clear that small variations can lead to marked differences with the dried catalyst. Calcined catalysts are, however, not particularly affected by the reaction conditions, since the use of the elevated temperature leads to the formation of particulate Au with the same characteristics, and this is relatively insensitive to the starting structure.

Precipitation method A has been well studied previously and has been the main coprecipitation method used to prepare Au catalysts with ZnO and Fe_2O_3 as supports. Indeed, Hutchings at al. [3, 4] previously made a detailed transmission electron microscopy study of the materials made using this method, namely Au/ZnO and Au/Fe_2O_3, and correlated the data with the catalytic performance for CO oxidation. The non-calcined materials, in both cases, were found to comprise nanocrystalline forms of the ZnO and FeOOH supports, respectively, but no nanocrystals of Au could be observed, suggesting that the Au particles if present were very small. ^{197}Au Mossbauer spectroscopy [5] confirmed that a significant proportion of the Au was present in cationic form in the dried materials. For materials calcined at 400 °C, orthorhombic nanocrystals of Au were observed and using ^{197}Au Mossbauer spectroscopy no cationic gold was found to be present. Similar structural observations have been found for the materials prepared in this study. The dried Au/Fe_2O_3 materials were found to be very effective for CO oxidation whereas the Au/ZnO materials were relatively inactive. In contrast the calcined Au/ZnO materials were found to be very effective for CO oxidation whereas the calcined Au/Fe_2O_3 materials were relatively inactive. The present study has widened the earlier study and shown that active catalysts can be prepared for both dried and calcined materials as long as the precipitation conditions are closely controlled, in particular the pH, the temperature and the ageing time.

With precipitation method A, the final pH is an important variable since the components present in the reaction mixture precipitate at different pH values [6]. For example, the onset of precipitation of Zn^{2+} is *ca.* pH7, whereas the onset of precipitation of Fe^{3+} is *ca.* 3. Hence using precipitation procedure A the iron oxide/hydroxide/carbonates precipitates very early in the preparation procedure, and conversely the zinc oxide/hydroxide/carbonates precipitate relatively late in the procedure. This implies the preparation of Au/Fe_2O_3 materials using procedure A, is similar to deposition precipitation since the support is precipitated prior to the active component. This is not the case for Au/ZnO materials. However, it is clear that a calcination step ensures the formation of an active catalyst and the cationic gold is reduced and forms uniform nanocrystals [3, 4].

In addition to the effects of temperature and pH, catalysts prepared using both procedures A and B are very sensitive to ageing of the precipitate. This is a topic that has received very limited attention in the academic literature. However, it is recognised by commercial suppliers of oxide catalyst precursors that many basic carbonates and hydroxides that are initially precipitated during the coprecipitation process partially redissolve, giving significant changes in morphology, and this is crucial for the eventual catalytic performance of the material. However, in the synthesis of most Au catalysts reported to-date this potentially crucial preparation step has not been investigated or has gone unreported. Previously, Hutchings at al. [7] have shown that ageing plays an important part in the activity of Au/CuO/ZnO catalysts for ambient temperature CO oxidation. Ageing of copper containing precipitates is known to be crucial and they have recently documented two cases in detail. First, they have shown the processes occurring in the transformation of CuO/ZnO precursors using detailed transmission electron microscopy, and demonstrated the effect on the activity for ambient temperature CO oxidation [8]. Also, they have shown that ageing can markedly affect the activity of $CuMnO_x$ hopcalite catalysts for CO oxidation [9, 10]. With $CuMnO_x$, the effect of ageing is complex as ageing initially decreases the observed catalytic activity, but at longer ageing times the catalyst becomes active again, and the morphological and structural changes were correlated with this change in activity. In the present case of Au/ZnO catalysts, this behaviour is also observed for both preparation methods, Fig. 3.44.

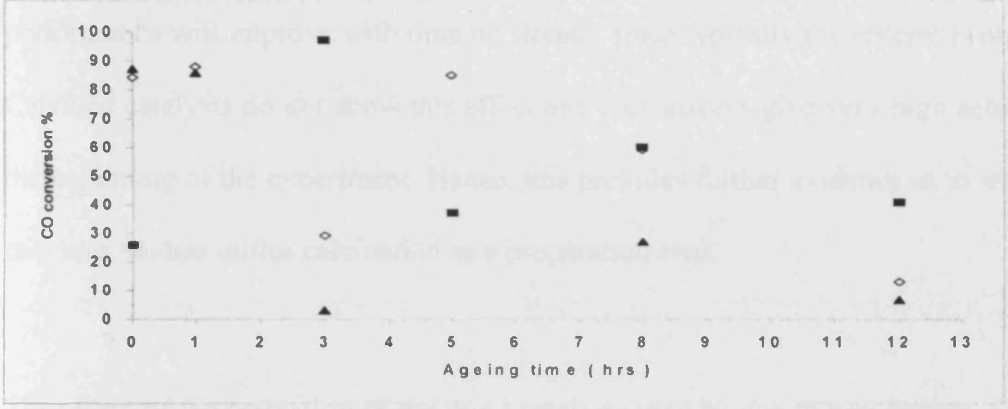

Figure 3.44. Effect of ageing time on the initial catalytic performance of Au/ZnO. Key: (◊) method A pH 8.0, (■) method A pH 6.0, (▲) method B final pH 6.0. Catalytic data recorded at 16 min time on stream.

In some cases, initially ageing the precipitate increases the activity for CO oxidation. For materials prepared using method B, the activity then declines with ageing and then subsequently increases for the dried catalysts. With calcined catalysts, this behaviour is not observed and all give active catalysts. The dried catalyst does not exhibit nanocrystals of Au and so transmission electron microscopy has not been helpful in this case. However, these data serve to emphasise that this step is crucial in the preparation of active Au catalysts that have not been calcined, and hence control of this parameter is essential if reproducible catalysts are to be obtained with this method of preparation.

One clear difference in catalytic performance is observed for dried and calcined catalysts. For the dried materials, in many cases, the catalytic performance is observed to increase with time on stream, and sometimes this effect may take several hours. Eventually, although, these materials usually gave 100% CO conversion. Variable catalytic performance is often observed with supported Au catalysts, since their initial activity is often observed as poor and, it is not immediately apparent that the catalytic performance will improve with time on stream, since typically the reverse is observed. Calcined catalysts do not show this effect and they always give very high activities at the beginning of the experiment. Hence, this provides further evidence as to why most previous studies utilise calcination as a preparation step.

The origin of the activation of the dried catalysts may be due to two factors. First, the exposure of the catalyst to CO, a reducing gas, may lead to the reduction of the cationic gold to metallic gold. Although it must be noted that a large excess of oxygen is present, but gold is typically inert to oxidation by dioxygen. Second, the effect may be due to non-optimal levels of moisture being retained in the catalyst, since they are dried at 90 °C, a relatively low temperature. The presence of water is known to be crucial in the reaction of CO on Au nanocrystals. Haruta and co-workers [11] showed that Au/TiO_2, Au/Al_2O_3 and Au/SiO_2 containing Au nanocrystals all increase in activity when low concentrations of water are cofed. It is possible that during the initial phase of the catalytic reaction, the optimal level of surface hydroxyl groups may be established for the dried materials.

X-ray diffraction patterns of the dried Au/ZnO catalysts as shown in Fig. 3.11 indicate that the metallic or oxide gold disappears in XRD patterns. This might be due to either the gold particles highly dispersed on the surface of the support or Au peaks were overlapped by hydrozincate and/or ZnO, or the amount of gold species is smaller than that detected by the XRD technique. However, in these catalysts, the presence of gold decreases the crystallinity of the support peaks. Fig. 3.13 shows x-ray diffraction patterns of Au/Fe_2O_3. The peaks showed lower intensity suggesting gold interacted with the support decreasing the crystallinity of the support. One possible explanation for this observation involves the formation of nanophase alloy (gold atoms surronnded by Fe_2O_3 atoms) during coprecipitation. The surface defects presented in the amorphous phase might increases the interaction between gold particles and support, which prevents gold agglomeration to bigger particles.

XPS analysis of dried Au/ZnO catalysts prepared by coprecipitation method A at different pH as shown in Table 3.4 indicates that metallic gold was obtained at lower pH and by increasing pH, a mixture of Au^{0}- Au^{x+} was obtained. Combining these results with CO oxidation results for Au/ZnO catalysts prepared by coprecipitation method A at different pH suggests that metallic gold was responsible for the catalytic activity of these catalysts. Further, increasing the pH of the prepared samples led to a decrease in the intensity of the gold species on the surface, which disappear at > pH 8.

This is in agreement with the results obtained from AA and CO oxidation. The same was observed for Au/ZnO catalysts prepared by coprecipitation method B at different pH. XPS analysis of dried Au/ZnO catalysts prepared by coprecipitation method A at different ageing times as shown in table 3.6 indicates that metallic gold was obtained at non-aged, 1h , and 8h aged catalysts while a mixture of Au^0- Au^{+x} was obtained for catalysts aged for 3h, 5h, 12h. This implies that the ageing process during the preparation of the catalyst had an influence; however, the effect of this process on the gold oxidation state on the surface is unclear as yet. XPS analysis of the dried Au/Fe_2O_3 catalysts prepared by coprecipitation method B at different pH as shown in Table 3.7 indicates that metallic gold was obtained at lower pH and by increasing pH, Au^{x+} was obtained. Combining these results with CO oxidation results for Au/Fe_2O_3 catalysts prepared by coprecipitation method B at different pH suggests oxidised gold was responsible for the catalytic activity of these catalysts. This is in agreement with the ^{197}MS study by Hutchings [5] concluding that Au^{x+} was responsible for the activity of gold catalyst supported on Fe_2O_3. The same XPS analysis results for Au/ZnO and Au/ Fe_2O_3 catalysts prepared by deposition-precipitation method indicated that the effect of this preparation method on the gold oxidation state was negligible.

TPR experiments reported in this study have shown that the reduction of the supports in the supported gold catalysts strongly depends on the preparation method and preparation parameters. In the case of Au/ZnO catalysts, the reduction of the uncalcined catalysts is dependent on the pH value, Fig. 3.7. The lower pH, the higher gold content, by AA, Fig. 3.1, the greater the decrease in oxidation of the surface. Calcined catalysts were reduced at higher temperature than the uncalcined, Fig. 3.8 and Fig. 3.9.

In the case of Au/Fe_2O_3 catalysts, it is well known that the reduction of bulk iron oxide by hydrogen proceeds through the following steps [12, 13]:

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe$$

Our TPR analysis suggested that a correlation exists between the reduction temperature and preparation method, Fig. 3.10. Au/Fe_2O_3 prepared by coprecipitation at variable pH is reduced at higher temperature than prepared via coprecipitation at constant pH. By correlation with BET analysis, Table.3.1, for both catalysts, it can be said that the higher the surface area the lower the reduction temperature. Our results are in agreement with the results of Galvagno *et.al.* [14]. They studied Au/Fe_2O_3 by TPR at higher temperatures and found that reduction to FeO occured at 657 °C. However, we did not reach this temperature since the maximum temperature in all of our studies is 500 °C, for alkane activation reactions, see chapter 4.

In the case of supported gold catalysts prepared by the deposition-precipitation method, four different supports were used for this study (ZnO, Fe_2O_3, MgO, MnO_2). We concentrated on the comparison between these catalysts and we did not go through the effect of the preparation parameters because they have been well studied previously [15-17]. It is important to note that all supports were prepared by two different coprecipitation methods at variable and constant pH to ascertain the effect of these methods on the support and then on the prepared supported gold catalysts. All supports were calcined and then used for preparation of the supported gold catalyst via the deposition-precipitation method.

Two Au/ZnO catalysts were prepared via the deposition-precipitation methods using two ZnO materials prepared by coprecipitation at variable and constant pH, respectively. The obtained results, Fig. 3.31 and Fig. 3.32 showed that Au/ZnO catalyst prepared via this method were highly active under our reaction conditions with both supports and in dried or calcined status. However, this was expected because BET surface area analysis of the supports showed no significant difference in the surface area, Table. 33, and XRD patterns showed the same. Further, XRD of the catalysts show that the calcined catalyst more crystalline than the dried catalysts and the gold pattern is clearly appear in the calcined catalyst, Fig. 3.14.

Two Au/ Fe_2O_3 catalysts were also prepared via deposition-precipitation methods using two Fe_2O_3 calcined materials prepared by coprecipitation at variable and constant pH respectively. The obtained results also showed Au/ Fe_2O_3 catalysts prepared via this method are highly active at our reaction conditions with both supports and in dried or calcined status.

By the same preparation method, two Au/MgO catalysts were prepared and tested for CO oxidation. The catalytic results showed the catalyst active only when in the dried status and support prepared by coprecipitation method at variable pH. The Au/MnO_2 catalyst was not active for CO oxidation under our reaction conditions.

The gold catalysts supported on ZnO and Fe_2O_3 prepared by coprecipitation methods A and B were evaluated for low temperature CO oxidation reaction at higher GHSV to investigate the parameters that affect their catalytic activities and to identify the difference in the catalytic activities of these catalysts. Au/ZnO catalyst prepared by coprecipitation procedure A at pH 5 showed higher activity compared with other catalysts prepared by the same procedure at pH 6 and higher, Fig. 3.37. The same results were obtained for Au/ZnO catalysts prepared by coprecipitation procedure B at pH 5, Fig. 3.39. However, Au/ZnO catalysts prepared by coprecipitation procedure A at pH 5 showed higher activities than those prepared by coprecipitation procedure B at the same pH value. The effect of the ageing process on Au/ZnO catalysts prepared by coprecipitation procedure A at pH 6 is very clear. Activities of aged catalysts were higher than non-aged one, Fig. 3.41. The ageing process had a very low influence on Au/ZnO catalysts prepared by coprecipitation procedure B, Fig. 3.42. Au/Fe_2O_3 catalysts prepared by coprecipitation B showed an increase in activity with an increase in pH value. Further, Au/Fe_2O_3 catalysts prepared by coprecipitation B at pH 8 showed very high activity, even at the highest limit of GHSV of our experiment (480000 h^{-1}) and also at 0°C. In contrast, Au/Fe_2O_3 catalysts prepared by coprecipitation method A were non-active catalysts. To reiterate, this study showed that Au/Fe_2O_3 catalysts prepared by coprecipitation B at pH 6 and higher were much more active than the most active gold catalyst supported on zinc oxide, namely, Au/ZnO catalysts prepared by coprecipitation procedure A and B at pH 5.

The CO oxidation at high GHSV experiments. confirmed the effect of the selection of the support material, preparation method. and preparation parameters such as pH and ageing process. Another very important finding for CO oxidation at high GHSV experiments is the correlation between CO oxidation reaction and alkane activation reaction over the prepared supported gold catalysts. see Chapter 5 of this research study.

3.6. References

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Chapter 4

Light alkane activation by supported gold catalysts

4.1. Introduction

Over the past twenty years, many researchers in both academic and industrial laboratories have studied the conversion of light alkane (C_1-C_4) to the corresponding olefins and/or oxygenates. The products of these reactions are important feedstocks widely used in numerous industrial processes. Methane is the principal component of natural gas, about 75% of natural gas is CH_4. Up until now, the route to utilise methane for commercial purposes has been indirect, via syngas (CO, H_2) formation by steam reforming. This process [eq. 4.1] has many disadvantages such as; high energy requirement, high H_2/CO ratio (> 4, which is not suitable for methanol and Fischer-Tropsch synthesis), and poor selectivity for CO.

$$CH_4 + H_2O \longrightarrow 3H_2 + CO \qquad 4.1$$

The catalytic oxidation of methane to syngas [eq. 4.2] has been suggested by both academic and industrial researchers as promising an alternative route because it is mildly exothermic, more selective, and produces more desirable H_2/CO ratio.

$$CH_4 + 1/2O_2 \longrightarrow 2H_2 + CO \qquad 4.2$$

Due to the advantages of the catalytic oxidation of methane, an active search has been under way in recent years to find selective catalytic systems for the direct conversion of methane to oxygenated compounds (methanol-formaldehyde) or C_2+ hydrocarbons via methane oxidative coupling (MOC) [eq. 4.3]. So far, the yields obtained through these routs have been insufficient to justify commercial applications [1].

$$2CH_4 + O_2 \longrightarrow C_2H_4 + 2H_2O \qquad 4.3$$

One of the major challenges facing methane catalytic activation in many catalytic systems is the high temperature required to activate it. The use of such high temperatures often leads to the production of deep oxidation products which are more thermodynamically stable than the other useful products.

Ethane and propane are also components of natural gas, in the range of 15% and 3% respectively. The current commercial route for their conversion corresponding olefins, ethylene and propylene, which are basic feedstock in the petrochemical industry, is steam cracking at high temperature [2]. However, this process has both chemical and industrial limitations. Partial oxidation of light alkanes represents a possible route for the conversion of natural gas into valuable chemicals [3]. In these processes, reactions are carried out in the presence of oxygen or air which makes the reaction heat exothermic. Also, the consumption of H_2 in the reaction zone shifts the equilibrium toward the products. Furthermore, these routes can be performed at lower temperatures by the selection of a proper catalytic system. Therefore, several catalytic systems have been employed in these routes and have exhibited promising activities and selectivities. While some researchers have previously studied CH_4 [4, 5] and C_3H_8 [6] activation over gold based catalysts supported on different supports at low temperature, no studies so far have been published on C_2H_6 catalytic activation via supported gold catalysts. In all previous studies on light alkane activation catalysed by supported gold catalysts, the main product has been CO_2. The aim of this study is to investigate CH_4 activation using supported gold catalysts at light temperatures and to study the effect of the preparation parameters, types of supports on the activities of these catalysts. Further, some of these catalysts were evaluated for C_2H_6 and C_3H_8 activation at light temperature.

4.2. Results

4.2.1. CH_4 activation results

The activity of supported gold catalysts for methane catalytic activation is presented in this subsection.

4.2.1.1. Au/ZnO catalysts

Fig.4.1 shows the results of methane conversion by gold catalysts supported on ZnO and prepared via coprecipitation method A at different pH.

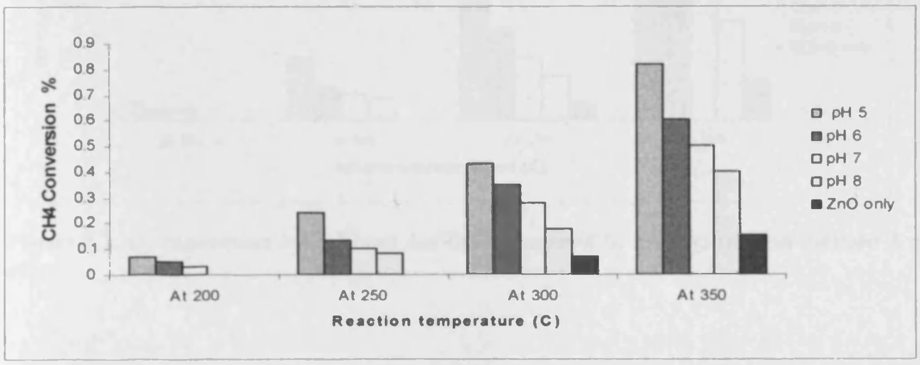

Figure 4.1. CH_4 conversion by calcined Au/ZnO prepared by coprecipitation methods A at different pH

Table 4.1 Initial activity temperature for Au/ZnO, method A, at different pH

Catalyst	initial activity temperature °C	CH_4 conversion %
Au/ZnO, pH 5	200	0.07
Au/ZnO, pH 6	200	0.05
Au/ZnO, pH 7	200	0.03
Au/ZnO, pH 8	250	0.08
ZnO	300	0.07

The initial activity temperatures for Au/ZnO prepared via method A and at different pH are listed in Table 4.1. These results indicate that the lower the pH is the lower the initial activity temperature. The greatest effect of pH was at pH 5, with higher CH_4 conversion. Activity of ZnO is only observed at 300 °C. The results of oxygen conversion by gold catalysts supported on ZnO and prepared via coprecipitation method A at different pH are presented in Fig. 4.2.

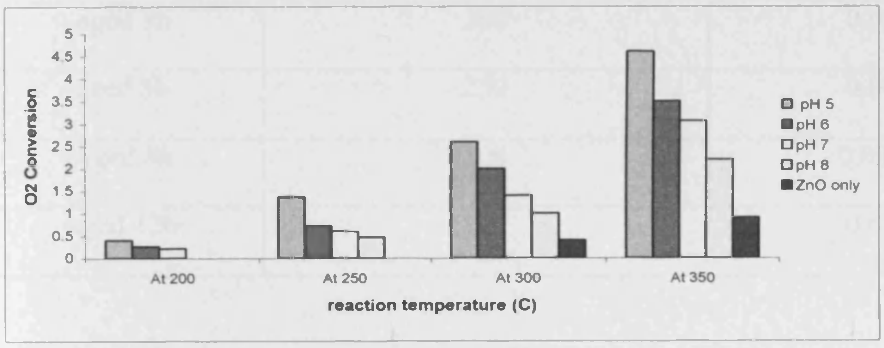

Figure 4.2. O_2 conversion by calcined Au/ZnO prepared by coprecipitation method A at different pH

Gold catalysts supported on ZnO and prepared via coprecipitation method A at pH 6 and at different ageing times were evaluated for CH_4 activation reaction. The results of CH_4 conversion are shown in Fig. 4.3.

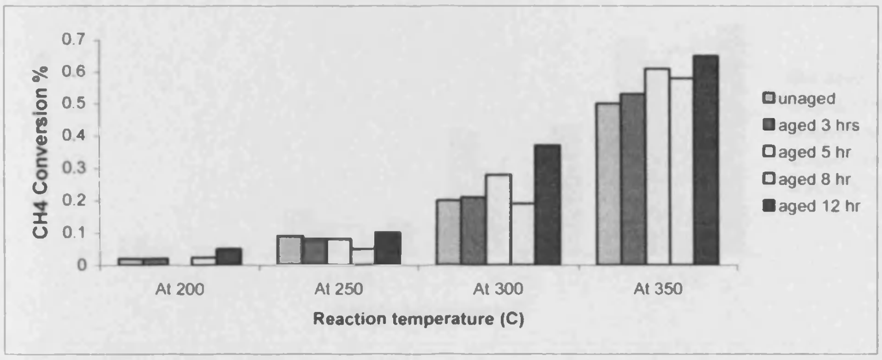

Figure 4.3. CH_4 conversion by calcined Au/ZnO prepared by coprecipitation A at different ageing times

Table 4.2 initial activity temperature for Au/ZnO, method A, at different ageing times.

Catalyst	initial activity temperature °C	CH_4 conversion %
no aging	200	0.02
aged 3h	200	0.02
aged 5h	250	0.08
Aged 8h	200	0.024
aged 12h	200	0.05

The initial activity temperatures for Au/ZnO prepared via method A and at different ageing times are listed in Table 4.2. These results showed that the catalyst aged for 5h has the highest initial activity temperature while the one aged for 12 h has the highest activity for CH_4 conversion at the low initial activity temperature. Oxygen conversion results by gold catalysts supported on ZnO and prepared via coprecipitation method A at different ageing times are presented in Fig. 4.4.

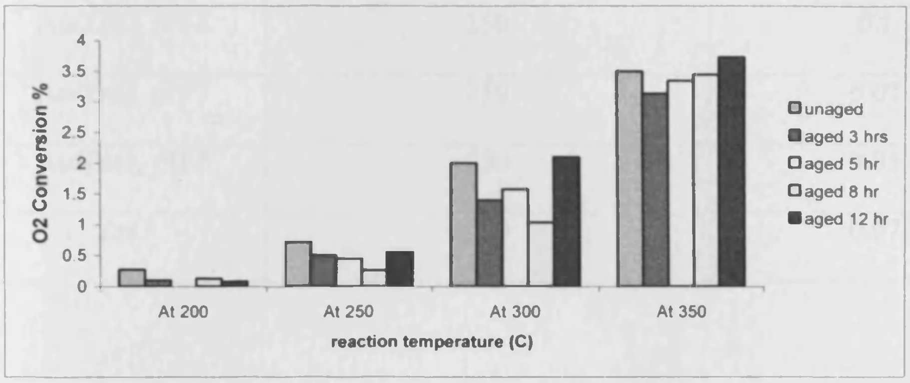

Figure 4.4. O_2 **conversion by of calcined Au/ZnO prepared by coprecipitation A at different ageing times**

From the above results it can be said that both CH_4 and O_2 conversions decrease as the pH of the catalysts increase. The ageing process also has an influence on the catalytic results. Gold catalysts supported on ZnO and prepared via coprecipitation B at different pH values were evaluated for CH_4 activation reaction. The results of CH_4 conversion are shown in Fig. 4.5.

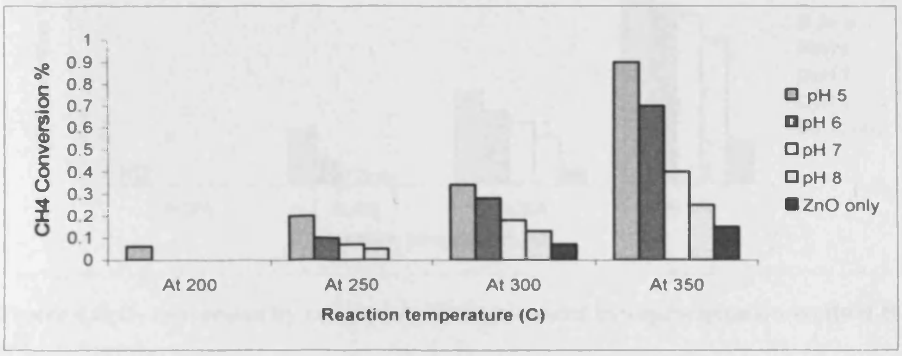

Figure 4.5. CH_4 **conversion by calcined Au/ZnO prepared by coprecipitation method B at different pH**

Table 4.3. initial activity temperature for Au/ZnO, method B, at different pH.

Catalyst	initial activity temperature °C	CH_4 conversion %
Au/ZnO, pH 5	200	0.06
Au/ZnO, pH 6	250	0.1
Au/ZnO, pH 7	250	0.07
Au/ZnO, pH 8	250	0.05
ZnO	300	0.07

The initial activity temperatures for Au/ZnO prepared via method B and at different pH are listed in Table 4.3. These results indicate that the lower the pH, the lower initial activity temperature. The greatest effect of pH was at pH 5, achieving the highest CH_4 conversion. ZnO Activity is observed only at 300 °C. Oxygen conversion results by gold catalysts supported on ZnO and prepared via coprecipitation B at different pH are presented in Fig. 4.6.

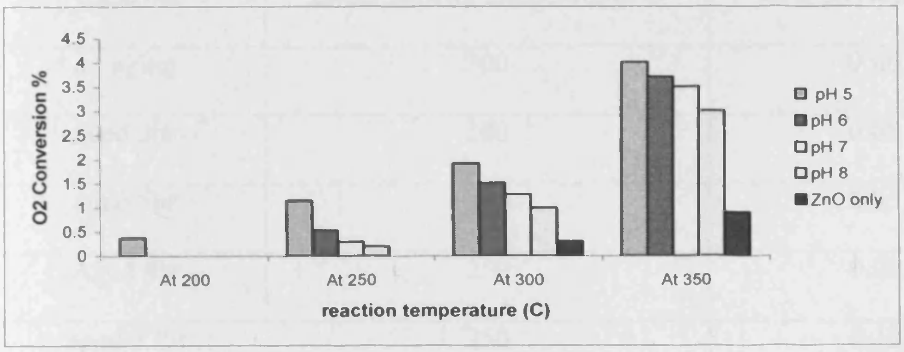

Figure 4.6. O_2 conversion by calcined Au/ZnO prepared by coprecipitation method B at different pH

From the above results, both CH_4 and O_2 conversions decrease as the pH of the catalysts increase. Morever, activity is less than that for catalysts prepared by coprecipitation at variable pH (method A). Gold catalysts supported on ZnO and prepared via coprecipitation method B at pH 6 and at different ageing times were evaluated for this reaction. The results of CH_4 conversion are shown in Fig. 4.7.

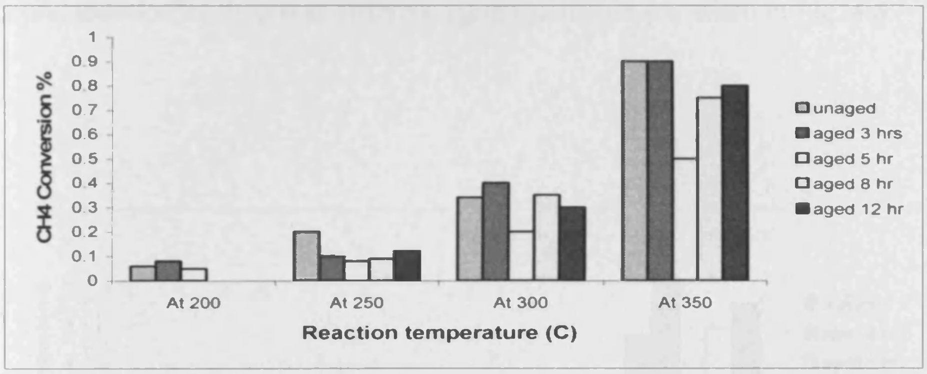

Figure 4.7. CH_4 conversion by calcined Au/ZnO prepared by coprecipitation method B at different ageing times

Table 4.4. initial activity temperature for Au/ZnO, method B, at different ageing times

Catalyst	initial activity temperature °C	CH_4 conversion %
no aging	200	0.06
aged 3hr	200	0.08
aged 5hr	200	0.05
Aged 8hr	250	0.09
aged 12hr	250	0.12

Low initial activity temperatures for Au/ZnO prepared via method B and at different ageing times are listed in Table 4.4. These results show that the catalyst aged for 3 h has the highest activity for CH_4 conversion at the lower initial activity temperature.

Oxygen conversion results by gold catalysts supported on ZnO and prepared via coprecipitation method B at different ageing times are presented in Fig. 4.8.

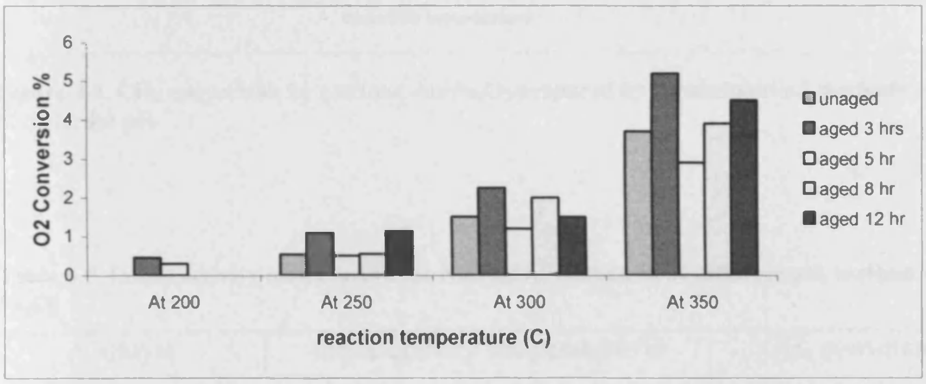

Figure 4.8. O_2 conversion by calcined Au/ZnO prepared by coprecipitation method B at different ageing times

As for catalysts prepared by method A, it can likewise be said that both CH_4 and O_2 conversions decrease as the pH of Au/ZnO catalysts prepared by method b increases. The ageing process also has an influence in the catalytic activity results.

4.2.1.2.Au/Fe_2O_3 catalysts

Gold catalysts supported on Fe_2O_3 prepared via coprecipitation methods A and B were evaluated for CH_4 activation reaction. CH_4 conversion results are shown in Fig. 4.9.

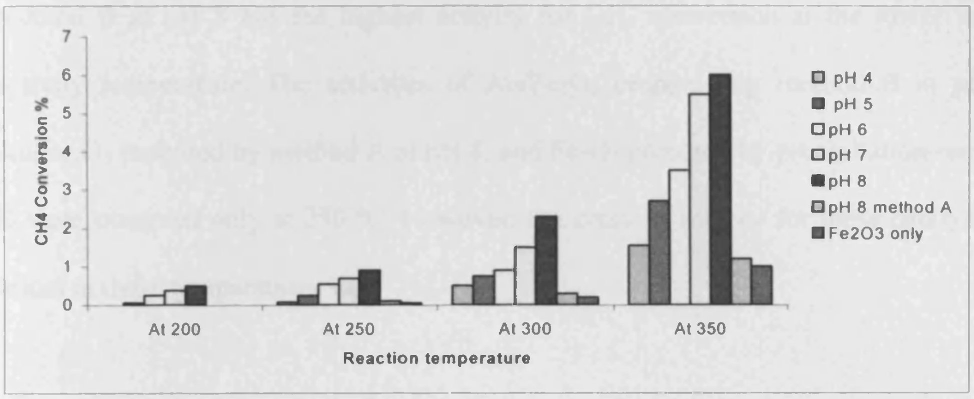

Figure 4.9. CH_4 conversion by calcined Au/Fe_2O_3 prepared by coprecipitation methods A and B at different pH

Table 4.5. Initial activity temperature for Au/Fe_2O_3, method B, at different pH, method A at pH 8, Fe_2O_3

Catalyst	initial activity temperature °C	CH_4 conversion %
Au/Fe_2O_3, B, pH 4	250	0.08
Au/Fe_2O_3, B, pH 5	200	0.06
Au/Fe_2O_3, B, pH 6	200	0.26
Au/Fe_2O_3, B, pH 7	200	0.38
Au/Fe_2O_3, B, pH 8	200	0.50
Au/Fe_2O_3, A, pH 8	250	0.10
Fe_2O_3, B	250	0.05

Low initial activity temperature for Au/Fe_2O_3 prepared via method B at different pH, Au/Fe_2O_3 prepared via method A at pH 8, and Fe_2O_3 prepared via precipitation method B are listed in Table 4.5. These results show that the catalyst prepared by method B at pH 8 has the highest activity for CH_4 conversion at the lower initial activity temperature. The activities of Au/Fe_2O_3 prepared by method B at pH 4, Au/Fe_2O_3 prepared by method A at pH 8, and Fe_2O_3 prepared by precipitation method B were observed only at 250 °C. However, the order of activity for these catalysts at initial activity temperatures was:

Au/Fe_2O_3 , method A(pH 8) > Au/Fe_2O_3, method B (pH4) > Fe_2O_3 (pH 8)

Oxygen conversion results by gold catalysts supported on Fe_2O_3 and prepared via coprecipitation methods A and B at different pH are presented in Fig. 4.10.

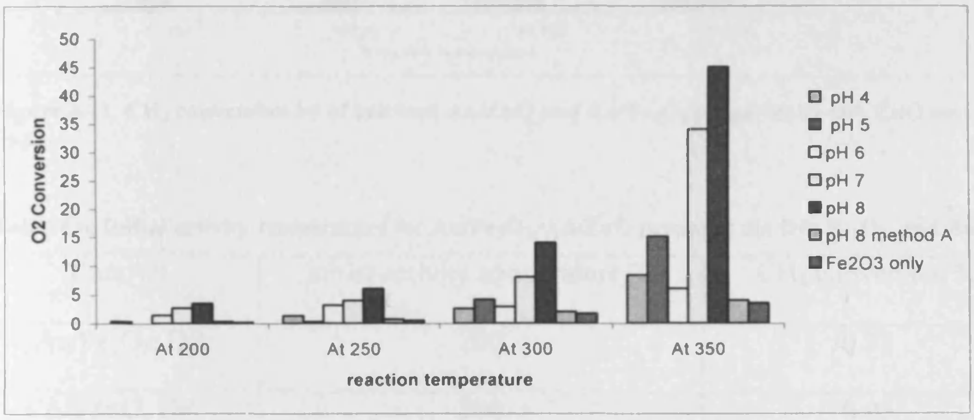

Figure 4.10. **O_2 conversion by calcined Au/Fe_2O_3 prepared by coprecipitation A and B at different pH**

CH_4 and O_2 conversions obtained for Au/Fe_2O_3 catalysts increased as pH value increased. However, the activity of Au/Fe_2O_3 prepared by method A was much lower than that prepared by method B.

4.2.1.3. Au/ZnO and Au/Fe_2O_3 prepared by DP method

Gold catalysts supported on ZnO and Fe_2O_3 prepared via the deposition-precipitation method are evaluated for CH_4 activation reaction. CH_4 conversion results are shown in Fig. 4.11.

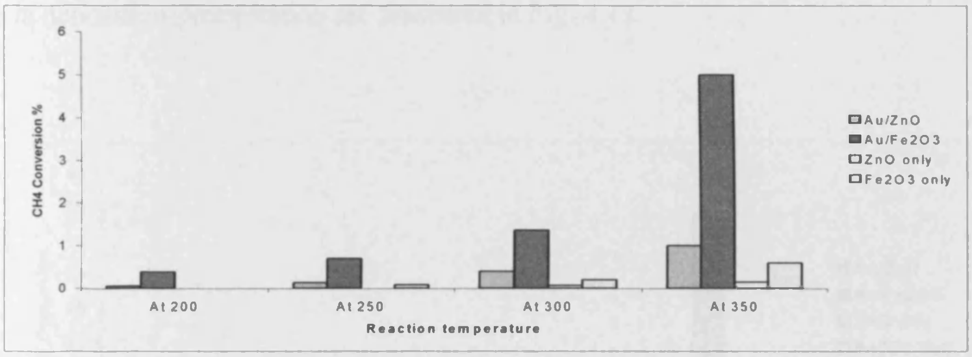

Figure 4.11. CH_4 conversion by of calcined Au/ZnO and Au/Fe_2O_3 prepared by DP, ZnO and Fe_2O_3

Table 4.6. Initial activity temperature for Au/Fe_2O_3, Au/ZnO prepared via DP, Fe_2O_3, and ZnO

Catalyst	initial activity temperature °C	CH_4 conversion %
Au/Fe_2O_3, DP	200	0.38
Au/ZnO, DP	200	0.05
Fe_2O_3, preci. B	250	0.08
ZnO, preci. A	300	0.07

Low initial activity temperatures for Au/Fe_2O_3 and Au/ZnO prepared via deposition-precipitation method, and Fe_2O_3 and ZnO prepared by precipitation method B and A respectively are listed in Table 4.6. These results show that the Au/Fe_2O_3 had the highest activity for CH_4 conversion at lower initial activity temperature. Fe_2O_3 Activity was observed at 250 °C, while ZnO activity was observed at 300 °C. The order of the activity for these catalysts at initial activity temperatures was:

Au/Fe_2O_3, DP > Au/ZnO, DP > Fe_2O_3, preci. B > ZnO, preci. A

Oxygen conversion results by gold catalysts supported on ZnO and Fe_2O_3 prepared via deposition-precipitation are presented in Fig. 4.12.

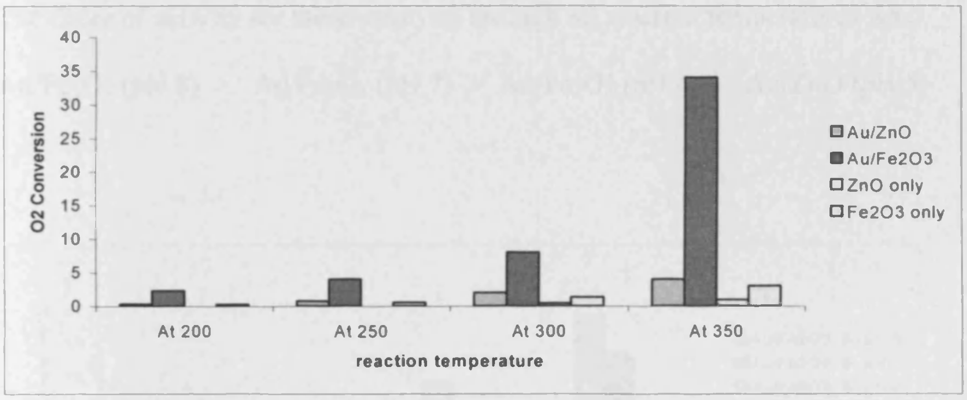

Figure 4.12. O_2 **conversion by calcined Au/ZnO and** Au/Fe_2O_3 **prepared by DP, ZnO and** Fe_2O_3

The above methane and oxygen conversion results on supported gold catalysts prepared via the DP method indicate that the gold catalyst supported on iron oxide is more active than that supported on zinc oxide. However, both are more active than the supports themselves.

4.2.2. Ethane and propane activation results

Only some catalysts were evaluated for ethane and propane catalytic activation. Some of these catalysts were chosen due to their high activities either for CO oxidation or CH_4 activation, while some were chosen for comparison with the high active catalysts for ethane and propane activation. These catalysts were Au/Fe_2O_3 prepared by coprecipitation at constant pH, method B, at pH 8, 7, 4 (see Chapter 2) and Au/ZnO prepared by coprecipitation at variable pH, method A, at pH 5. Au/Fe_2O_3 prepared at pH 8 had the highest activities for supported gold catalysts prepared and investigated in this study, while Au/ZnO prepared at pH 5 had the highest activity for gold on zinc oxide catalysts prepared and investigated in this study. The results of ethane conversion over the above selected supported gold catalysts are shown in Fig.4.13. The order of activity for these catalysts through all reaction temperatures was:

Au/Fe_2O_3 (pH 8) > Au/Fe_2O_3 (pH 7) > Au/Fe_2O_3 (pH 4) > Au/ZnO (pH 5)

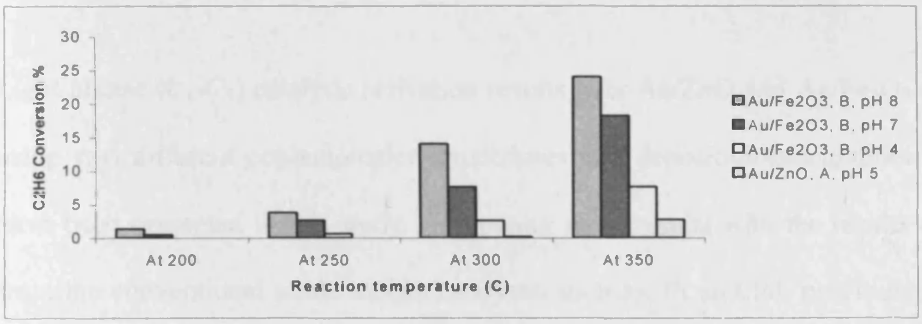

Figure 4.13. C_2H_6 conversion over supported gold catalysts at different temperatures

Propane conversion results over the above selected supported gold catalysts were in agreement with all previous CH_4 and C_2H_6 activation results over these catalysts.

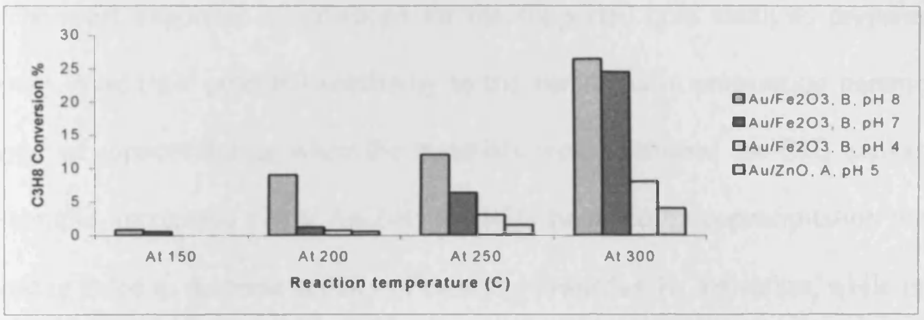

Figure 4.14. C_3H_8 conversion over supported gold catalysts at different temperatures

Propane conversion results are shown in Fig. 4.14. The order of activity for these catalysts through all reaction temperatures was:

Au/Fe_2O_3 (pH 8) > Au/Fe_2O_3 (pH 7) > Au/Fe_2O_3 (pH 4) > Au/ZnO (pH 5)

4.3. Discussion

Light alkane (C_1-C_3) catalytic activation results over Au/ZnO and Au/Fe_2O_3 catalysts using two different coprecipitation procedures and deposition-precipitation method have been presented in this study. Comparing these results with the results obtained from the conventional noble metals catalysts, such as; Pt and Pd, previously studied [7], the former indicated some activity for methane activation only above 300 °C, while this study's results showed supported gold catalysts can work at temperature lower than this. In this study, catalytic activity started at 200 °C for methane and ethane activation and even at 150 ° C for propane activation.

The most important observations for the supported gold catalysts prepared in this study were their potential sensitivity to the variations in preparation parameters and type of support during when the materials were examined for CH_4 activation. For example, increasing pH in Au/ZnO catalysts prepared by coprecipitation methods A and/or B led to decrease activity of catalysts towards CH_4 activation, while increasing pH in Au/Fe_2O_3 catalysts prepared by coprecipitation method B led to increase the activity of the catalysts towards CH_4 activation. Further, Au/Fe_2O_3 calcined catalysts prepared by coprecipitation method A were well known as non-active material for either CO oxidation [8] or CH_4 activation [4] while in this study, Au/Fe_2O_3 catalysts prepared by coprecipitation method B were very active for CO oxidation and showed the highest activity for CH_4 activation. Further, variation in the ageing times of the precipitate prior to filtration, even for a short period of time, can significantly affect the observed activity.

The obtained results of CH_4 activation over Au/ZnO and Au/Fe_2O_3 catalysts indicated that the final pH is an important variable since the components present in the mixture precipitate during the preparation at different pH values [9]. For example, the onset of precipitation of Zn^{2+} is *ca.* pH 7, whereas the onset of precipitation of Fe^{3+} is *ca.* 3. Hence using coprecipitation procedure A, the iron oxide/hydroxide/carbonates precipitate(s) very early in the preparation procedure and, conversely, the zinc oxide/hydroxide/carbonates precipitates relatively late in the procedure. This suggests the preparation of Au/Fe_2O_3 materials using procedure A is similar to deposition precipitation since the support is precipitated prior to the active component. This is not the case for Au/ZnO materials. However, pH in coprecipitation procedure B is constant throughout the coprecipitation process. This leads to the precipitation of the support and gold at the same time and then changes in the interaction properties between the support and gold during the calcination process. This is clear in the case of Au/Fe_2O_3 prepared by coprecipitation B. This method produces an active calcined catalyst while the calcined Au/Fe_2O_3 prepared via coprecipitation method A is non-active for either CO oxidation (Chapter 3) or CH_4 activation. This change in catalytic properties is clear also from the significant difference in the data obtained for the BET surface analysis of both Au/Fe_2O_3 catalysts prepared by coprecipitation A and B procedures (Tables 3.1 and 3.2, Chapter 3).

An interesting result obtained for CH_4 activation over Au/Fe_2O_3 catalysts prepared by coprecipitation procedure B at pH 6 was that some methanol was observed at 300 °C, (Table 4.7). A possible explanation for this interesting result is that the gold particles are capable of selective reaction to methanol when prepared at this pH value, while at lower or higher pH value, gold particles block or poison the surface sites associated with the formation of methanol and then the yield of CO_2 is enhanced to perform the total oxidation process.

Table 4.7. CH4 activation results over Au/Fe2O3 at different pH, at 300 °C

	pH 4	pH 5	pH 6	pH 7	pH 8
CH_4 conversion %	0.5	0.75	0.9	1.5	2.3
CO_2 selectivity %	100	100	95	100	100
CH_3OH Selectivity %	0	0	5	0	0

Further, only the Au/Fe_2O_3 catalyst prepared by coprecipitation procedure B at pH 6 showed lower O_2 conversion than other Au/Fe_2O_3 catalysts prepared by coprecipitation procedure B at 300 °C, (Fig. 4.10), while O_2 conversions for other Au/Fe_2O_3 catalysts prepared by coprecipitation procedure B indicated that only total oxidation is observed.

In addition to the effects of the preparation method and pH, CH_4 activation results suggested that catalysts prepared using both procedures A and B are very sensitive to ageing of the precipitate (Fig. 4.3 and 4.7). The origin of the variation in activity and effect of the ageing process are not yet clear. However, it might be due to the difference in the dispersion of gold during the ageing process.

Au/ZnO and Au/Fe_2O_3 catalysts prepared via deposition-precipitation were evaluated for CH_4 activation due to their high activities in CO oxidation compared with other supported gold catalysts prepared by the deposition-precipitation procedure (Chapter 3) and to compare their results with Au/ZnO and Au/Fe_2O_3 catalysts prepared by coprecipitation A and B procedures. Fig. 4.15 shows CH_4 activation results over the most active catalysts prepared by both coprecipitation and deposition-precipitation procedures.

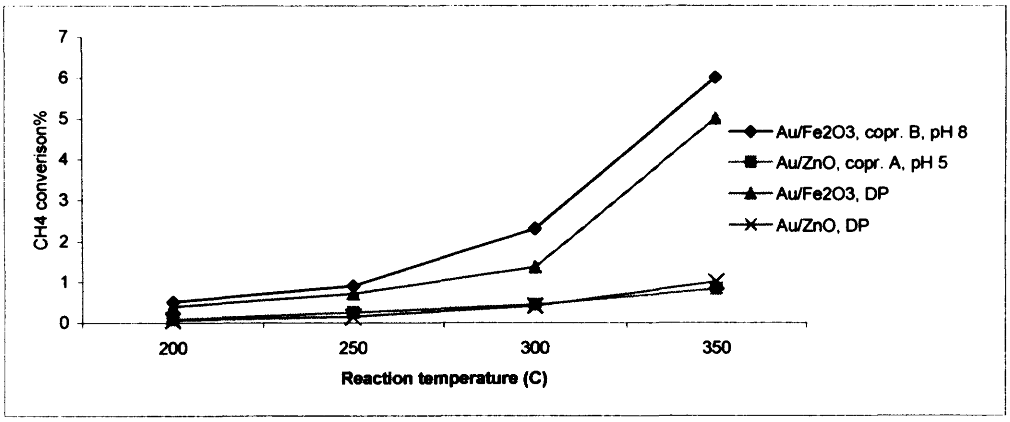

Figure 4.15. CH_4 conversion over supported gold catalysts at different temperatures

Au/Fe_2O_3 catalysts prepared by both coprecipitation B and deposition-precipitation procedures were more active than Au/ZnO catalysts prepared by both methods. However, Au/Fe_2O_3 catalysts prepared by coprecipitation B, a novel procedure for supported gold catalysts preparation, had the highest activity towards CH_4 activation reaction. The catalysts investigated in this study for CH_4 activation showed the following methane conversion scale:

Au/Fe_2O_3 coprecipitation B, pH 8 > Au/Fe_2O_3, DP > Au/ZnO coprecipitation A, pH 5 > Au/ZnO, DP

Au/Fe_2O_3 catalysts prepared by coprecipitation B, had the highest activity towards CO oxidation (Chapter 3) and CH_4 activation reaction was also the best catalyst for the activation of C_2H_6 and C_3H_8 (Fig. 4.13 and Fig. 4.14). C_2H_6 activation over supported gold catalysts has not been yet reported in literature; therefore, this study is an indication of supported gold catalysts contribution to this reaction. However, in this study, the main product was CO_2 which indicates that the supported gold catalyst is non-selective for this type of reaction. A comparison CH_4, C_2H_6, and C_3H_8 conversions over Au/Fe_2O_3 catalyst prepared by coprecipitation B is presented in Fig.4.16.

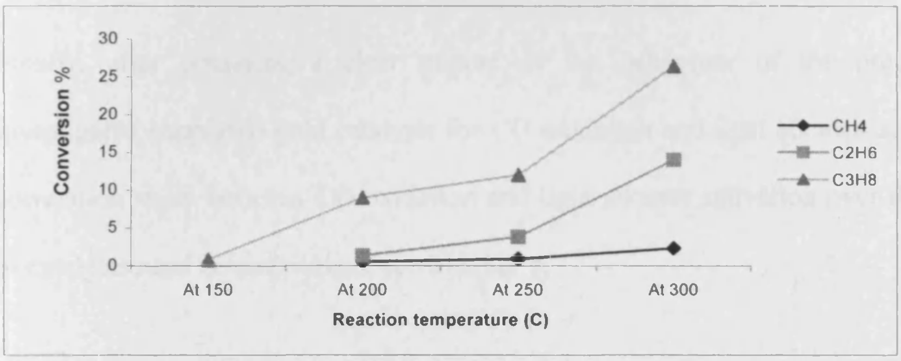

Figure 4.16. CH_4, C_2H_6, and C_3H_8 conversions over Au/Fe_2O_3 catalyst prepared by coprecipitation B

To determine the best catalyst, the activation of light alkane (C_1-C_3) was studied and the activity is as follows:

$$C_3H_8 > C_2H_6 > CH_4$$

As shown in Fig.4.16, the activity increases as the number of carbon atom in alkane increase, which indicates that the alkane conversion and then the rate of reaction depends on rupture of the C-H bond on the surface of the catalyst and not on rupture of the C-C bond. The energy of these bonds decreases from methane to propane as shown in (Table 4.7) [10]. From this table, it is clear that the C-H bond decreases from CH_4 to C_3H_8.

Table 8 C-C and C-H bonding energies for light alkanes

Hydrocarbon	C-C bonding energy KJ/mol	C-H bonding energy KJ/mol
CH_4	-	413
C_2H_6	330	410
C_3H_8	334	401

Finally, after obtaining a clear picture of the behaviour of the prepared and investigated supported gold catalysts for CO oxidation and light alkanes activation, a correlation study between CO oxidation and light alkanes activation over these types of catalysts need be undertaken, see Chapter 5.

4.4. References

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Chapter 5

Correlation between CO oxidation and Alkane activation

5.1. Introduction

CO oxidation over supported gold catalysts was studied in detail in Chapter 3. The studies investigated of CO oxidation at different GHSV and at different temperatures. Light alkane activation at different temperatures was studied in detail in Chapter 4. The work presented in this Chapter is comparing CO oxidation and alkane activation over supported gold catalysts. The activation energies of and the pre-exponential factors for the supported gold catalysts were calculated based on Arrhenius equation in order to determine the behaviour of supported gold catalysts for these two types of reactions.

5.2. Results

5.2.1. E_a over Au/ZnO prepared by coprecipitation method A at different pH

The activation energies and the pre-exponential factors of CO oxidation and CH_4 activation over Au/ZnO prepared via coprecipitation method A at different pH were calculated from the temperature dependency of the reaction at low conversion. Arrhenius plots for both reactions over Au/ZnO prepared via coprecipitation method A at different pH are shown in Figs. 5.1.and 5.2 respectively.

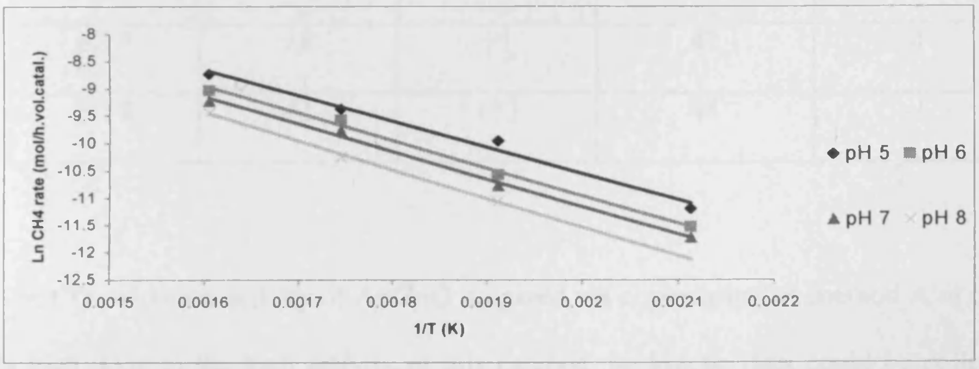

Figure 5.1. Arrhenius plots for CH4 activation over Au/ZnO prepared by coprecipitation method A at different pH

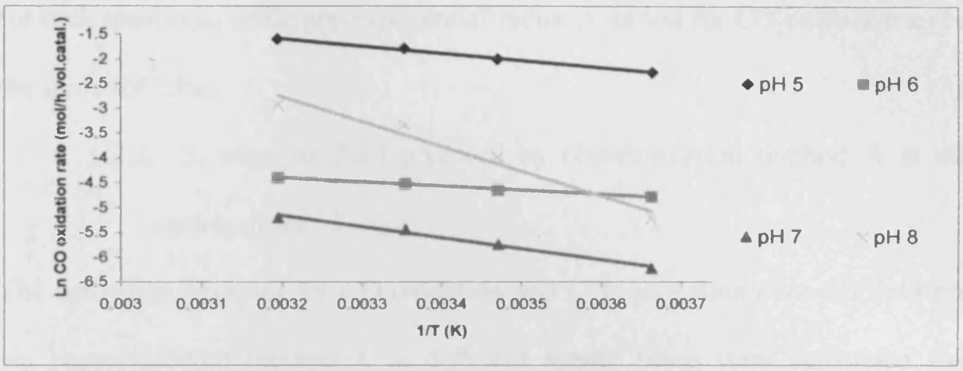

Figure 5.2. Arrhenius plots for CO oxidation over Au/ZnO prepared by coprecipitation method A at different pH

The activation energies E_a and the pre-exponential factor (A) for both reactions over Au/ZnO prepared via coprecipitation method A at different pH are shown in Table. 5.1.

Table 5.1 Activation energy for CO oxidation and CH4 activation over Au/ZnO, method A, at different pH.

Catalyst	Ea $_{CO}$ (kJ/mol)	Ln A $_{CO}$ (Arr. Eq. constant)	Ea $_{CH4}$ (kJ/mol)	Ln A $_{CH4}$ (Arr. Eq. constant)
pH 5	N/A	+3	39	-2
pH 6	12	-2	41	-1
pH 7	18	+1	42	-1
pH 8	42	+13	45	-1

The CO oxidation activity of Au/ZnO prepared via coprecipitation method A at pH 5 is high. Due to the high activity of this catalyst, no kinetic data could be collected under these conditions. However, increasing the pH led to increased activation energy for both reactions, while pre-exponential factor A varied for CO oxidation and almost the same for CH_4.

5.2.2. E_a over Au/ZnO prepared by coprecipitation method A at different ageing times

The activation energies for CO oxidation and CH_4 activation over Au/ZnO prepared via coprecipitation method A at different ageing times were calculated from the temperature dependency of the reaction at low conversion. The Arrhenius plots for both reactions over Au/ZnO prepared via coprecipitation method A at different ageing times are shown in Figs. 5.3.and 5.4 respectively.

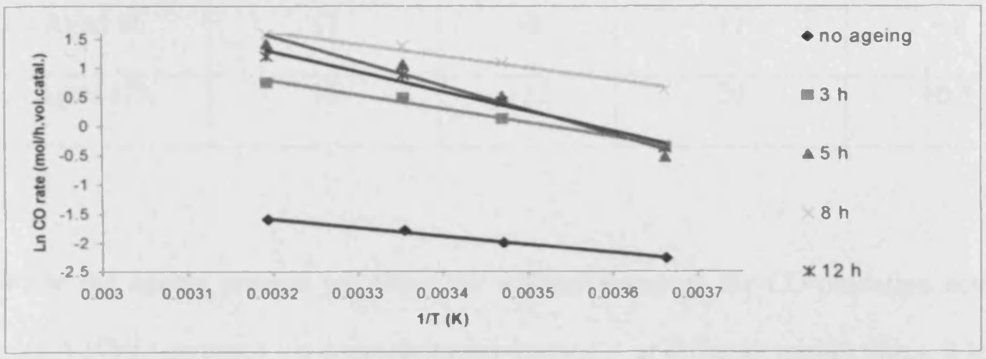

Figure 5.3. Arrhenius plots for CH4 activation over Au/ZnO prepared by copri. method A at different ageing times

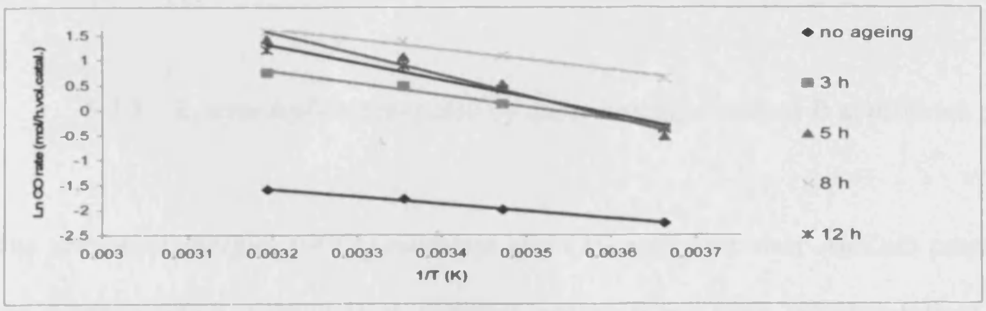

Figure 5.4. Arrhenius plots for CO oxidation over Au/ZnO prepared by copri. method A at different ageing times

The activation energies E_a and the pre-exponential factor (A) for both reactions over Au/ZnO prepared via coprecipitation method A at different ageing times are shown in Table. 5.2.

Table 5.2 Activation energy for CO oxidation and CH_4 activation, Au/ZnO, method A, at different ageing times

Catalyst	Ea $_{CO}$ (kJ/mol)	Ln A $_{CO}$ (Arr Eq constant)	Ea $_{CH4}$ (kJ/mol)	Ln A $_{CH4}$ (Arr Eq constant)
No ageing	12	-2	42	-1
Aged 3h	17	+8	20	+1
Aged 5h	15	+15	35	+2
Aged 8h	17	+8	17	+1
Aged 12h	16	+12	29	+0.5

While the ageing process increased the activation energy for CO oxidation activity over Au/ZnO prepared via coprecipitation method A at different ageing times, it led to a decrease in activation energy for CH_4 activation. The ageing process increased the pre-exponential factor for both reactions.

5.2.3. E_a over Au/ZnO prepared by coprecipitation method B at different pH

The activation energies for CO oxidation and CH_4 activation over Au/ZnO prepared via coprecipitation method B at different ageing times were calculated from the temperature dependency of the reaction at low conversions. The Arrhenius plots for both reactions over Au/ZnO prepared via coprecipitation method B at different pH are shown in Figs.5.5.and 5.6 respectively.

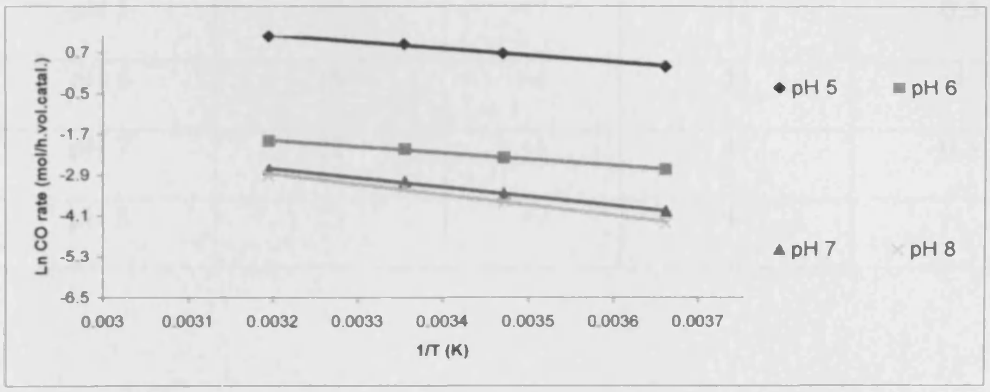

Figure 5.5. Arrhenius plots for CH4 activation over Au/ZnO prepared by coprecipitation methods B at different pH

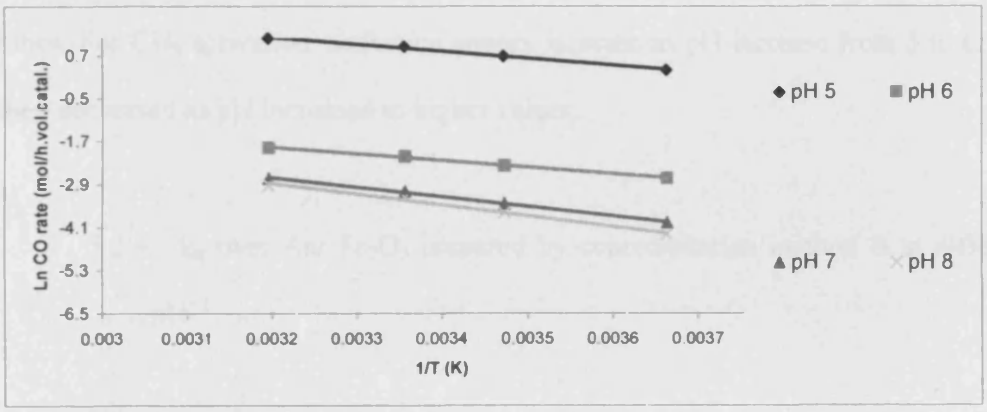

Figure 5.6. Arrhenius plots for CO oxidation over Au/ZnO prepared by coprecipitation methods B at different pH

The activation energies E_a and the pre-exponential factor (A) for both reactions over Au/ZnO prepared via coprecipitation method B at different pH are shown in Table. 5.3.

Table 5.3 Activation energy for CO oxidation and CH_4 activation over Au/ZnO, method B, at different pH

Catalyst	Ea $_{CO}$ (kJ/mol)	Ln A $_{CO}$ (Arr Eq constant)	Ea $_{CH4}$ (kJ/mol)	Ln A $_{CH4}$ (Arr. Eq. constant)
pH 5	15	+7	42	-0.5
pH 6	16	+4	53	-1
pH 7	22	+6	47	-0.3
pH 8	25	+7	44	-1

An increase the pH led to an increase the activation energy for the CO oxidation activity of over Au/ZnO prepared by coprecipitation method A at different ageing times. For CH_4 activation, activation energy increase as pH increase from 5 to 6, and then decreased as pH increased to higher values.

5.2.4. E_a over Au/ Fe_2O_3 prepared by coprecipitation method B at different pH

The activation energies and the pre-exponential factor (A) for CO oxidation and CH_4 activation over Au/Fe_2O_3 prepared via coprecipitation method B at different pH were calculated from the temperature dependency of the reaction at low conversion. Arrhenius plots for both reactions over Au/Fe_2O_3 prepared via coprecipitation method B at different ageing times are shown in Figs. 5.7.and 5.8 respectively.

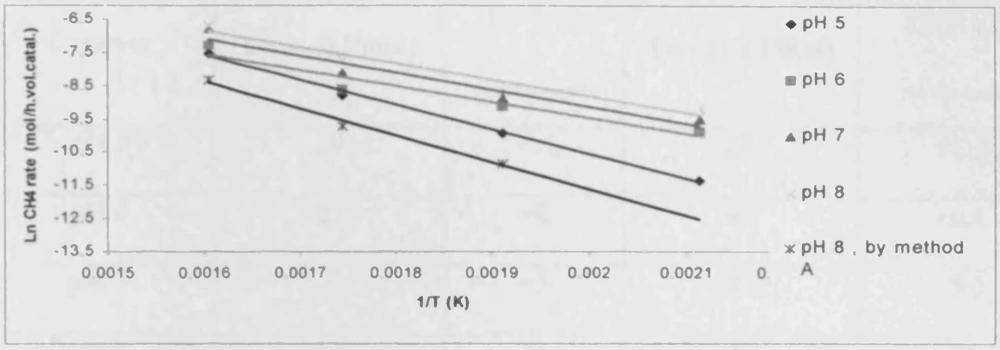

Figure 5.7. Arrhenius plots for CH4 activation over Au/Fe2O3 prepared by coprecipitation methods B at different pH

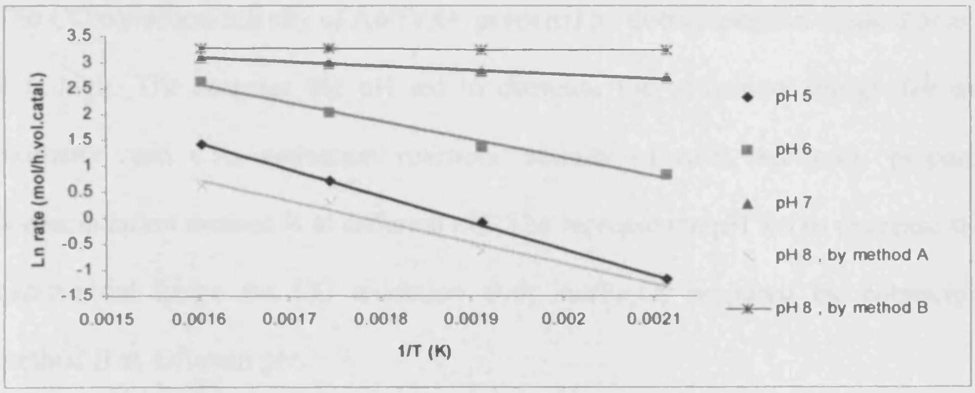

Figure 5.8. Arrhenius plot for CO oxidation over Au/Fe2O3 prepared by coprecipitation methods B at different pH

The activation energies E_a and the pre-exponential factor (A) for both reactions over Au/Fe_2O_3 prepared via coprecipitation method B at different pH are shown in table. 5.4.

Table 5.4 Activation energy for CO oxidation and CH_4 activation, Au/Fe_2O_3, method B, and pH 8 method A

Catalyst	Ea $_{CO}$ (kJ/mol)	Ln A $_{CO}$ (Arr Eq constant)	Ea $_{CH4}$ (kJ/mol)	Ln A $_{CH4}$ (Arr Eq constant)
pH 5	39	+10	61	+1.2
pH 6	27	+8	41	+0.1
pH 7	7	+3	42	+1.1
pH 8	0.6	+4	40	+4
pH 8, Method A	30	+7	67	+4.5

The CO oxidation activity of Au/Fe_2O_3 prepared by coprecipitation method B at pH 7, 8 is high. The increase the pH led to decrease the activation energy for the CO oxidation and CH_4 activation reactions activity of over Au/Fe_2O_3 prepared by coprecipitation method B at different pH. The increase the pH led to decrease the pre-exponential factor for CO oxidation over Au/Fe_2O_3 prepared by coprecipitation method B at different pH.

5.2.5. E_a study for C_2H_6 and C_3H_8 over selected supported gold catalysts

The activation energies for C_2H_6 activation over the best selected supported gold catalysts, Au/Fe_2O_3 prepared via coprecipitation method B at pH 7, and 8 and Au/ZnO at pH 5 were calculated from the temperature dependency of the reaction at low conversion. The Arrhenius plots for both reactions over these catalysts are shown in Fig. 5.9. The results show that Au/Fe_2O_3 prepared via coprecipitation method B at pH 8 was the lower activation energy, consistent with the results presented and discussed in Chapter 4.

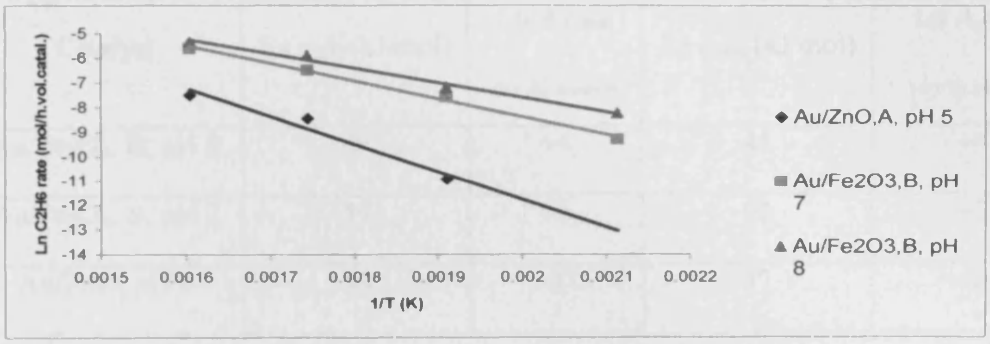

Figure 5.9. Arrhenius plots for C_2H_6 activation over the most active supported gold catalysts

The activation energies for C_3H_8 activation over the best selected supported gold catalysts, Au/Fe_2O_3 prepared via coprecipitation method B at pH 7and 8 and Au/ZnO at pH 5 were calculated from the temperature dependency of the reaction at low conversion. Arrhenius plots for both reactions over these catalysts are shown in Fig. 5.10.

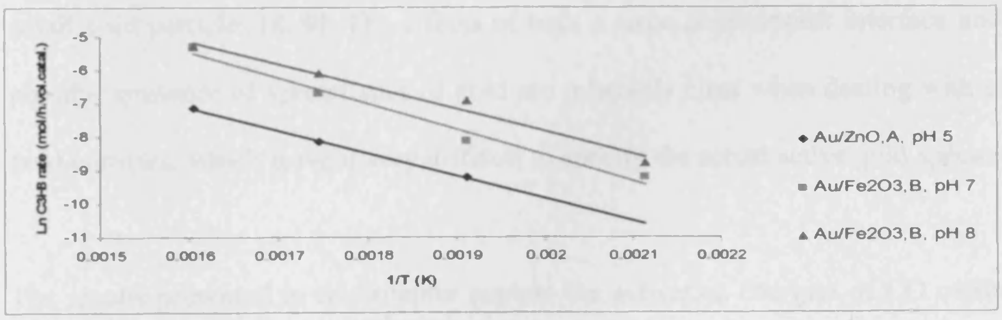

Figure 5.10. Arrhenius plot for C_3H_8 activation over the most active supported gold catalysts

The activation energies E_a and the pre-exponential factor (A) for C_2H_6 and C_3H_8 over the most active catalysts of the supported gold catalysts are shown in Table. 5.5.

Table 5.5. Activation energy for C_2H_6 and C_3H_8 activation over the most active supported gold catalysts

Catalyst	Ea $_{C2H6}$ (kJ/mol)	Ln A $_{C2H6}$ (Arr Eq constant)	Ea $_{C3H8}$ (kJ/mol)	Ln A $_{C3H8}$ (Arr Eq constant)
Au/Fe_2O_3, B, pH 8	49	+4	45	+4
Au/Fe_2O_3, B, pH 7	59	+6	53	+7
Au/ZnO, pH 5	53	+11	47	+6

5.3. Discussion

Small gold supported particles are beneficial for both low temperature CO oxidation [1-3] and CH_4 activation [4, 5]. This is ascribed to either the presence of a large total Au/support interface [6], the presence of special sites, such as a special electronic structure of very small gold particles [7], or ionic gold species specifically present on small gold particles [8, 9]. The effects of both a large gold/support interface and the possible presence of special sites of gold are relatively clear when dealing with small gold particles, which leave it very difficult to specify the actual active gold species.

The results presented in this chapter explain the activation energies of CO oxidation and light alkane (C_1-C_3) catalytic activation reactions over Au/ZnO and Au/Fe_2O_3 catalysts prepared via both coprecipitation procedures at variable and constant pH. When comparing supported gold catalysts, it is very important to consider the influence of the preparation parameters, type of support, and preparation procedure.

Comparing activation energies and pre-exponential factor (Arrhenius eq. constant) (A), which indicate active sites on the surface of the catalyst, for CO oxidation and CH_4 activation reaction over Au/ZnO catalysts prepared by coprecipitation method A at different pH, Table 5.1, shows that increasing pH led to an increase in the activation energies of both reactions. The pre-exponential factor (A) was increased by increasing pH in the case of CO oxidation reaction, whereas it remained almost stable for CH_4 activation reaction. Therefore, the effect of activation energy was higher than the pre-exponential factor (A) in the CO oxidation reaction, and activation energy only was affected by increasing pH in the case of CH_4 activation reaction because the pre-exponential factor had almost the same value over all these catalysts. However, the difference in activation energies for CH_4 activation over these catalysts was lower than that for CO oxidation. Further, the stability of the pre-exponential factor (A) for CH_4 activation over these catalysts suggests that the effect of pH in CH_4 activation was less than its effect in CO oxidation. This may be due to the high reaction temperature for CH_4 activation, which causes sintering of small supported gold particles, and the subsequent loss of some active sites, especially for catalysts prepared at low pH.

Comparing activation energies and the pre-exponential factor (Arrhenius eq. constant) (A) for CO oxidation reaction over Au/ZnO catalysts prepared by coprecipitation method A at different ageing times, tables 5.2, shows that variation in ageing times had no significant influence on the activation energies, while variation in the pre-exponential factor (A) had some influence. However, both E_a and the pre-exponential factor (A) were lower for aged catalysts than non-aged catalyst. In the case of CH_4

activation reaction, activation energies over the aged catalysts were lower than that over non-aged catalyst, while the pre-exponential factor (A) was almost the same for all the catalysts. This may be due to the high reaction temperature for CH_4 activation, which cause sintering of small supported gold particles and loss some active sites.

Comparing activation energies and the pre-exponential factor (Arrhenius eq. constant) (A) for CO oxidation and CH_4 activation reaction over Au/ZnO catalysts prepared by coprecipitation method B at different pH, Table 5.3, shows that increasing pH led to an increase in activation energy in CO oxidation reaction while variations in E_a for CH_4 over these catalysts were low. The effect of E_a on rate of CO oxidation reaction was higher than the effect of the pre-exponential factor (A) and, hence, increasing pH led to a decrease in E_a and then a decrease in the catalytic activity of these catalysts. Pre-exponential factor (A) values were much higher for CO oxidation reaction than CH_4 activation reaction. This may have been due to the high reaction temperature for CH_4 activation, which caused sintering of small supported gold particles, and then the loss of some active sites, especially for catalysts prepared at low pH.

Activation energies for CO oxidation over Au/ZnO catalysts prepared by coprecipitation method A prepared at different pH is lower than for CO oxidation over Au/ZnO catalysts prepared by coprecipitation method B prepared at different pH. These results are in agreement with the results presented in chapter 3, indicating that catalysts prepared by procedure A at different pH are more active than those prepared by method B at different pH. This confirms that the effect of E_a on CO oxidation reaction rate is higher than that of the pre-exponential factor (A). However, the effect of the factor is negligible in the case of CH_4 activation reaction.

Activation energy and pre-exponential factor (A) were examined for CO oxidation and CH_4 activation reaction over Au/Fe_2O_3 catalysts prepared by coprecipitation method B at different pH. Table 5.4 showed that increasing pH led to a decrease in activation energy in CO oxidation and CH_4 activation reactions. The effect of E_a on rate of CO oxidation reaction was higher than the effect of the pre-exponential factor (A) and, hence, increasing pH led to an increase in E_a and then an increase in the catalytic activity of these catalysts. Pre-exponential factor (A) values were much higher for CO oxidation reaction than CH_4 activation reaction. This may be due to the high reaction temperature required for CH_4 activation, which causes sintering of small supported gold particles, and then the loss of some active sites, especially for catalysts prepared at low pH. For Au/Fe_2O_3 catalysts prepared by coprecipitation method B at pH 8 for CH_4 activation reaction, there was agreement between E_a and pre-exponential factor (A) values, activation energy was low and the pre-exponential factor (A) was high, which means more active sites were obtained on this catalyst. This might be the reason for the highest activity obtained for this catalyst either for CO oxidation or CH_4 activation.

Activation energies and pre-exponential factors (A) were examined for C_2H_6 and C_3H_8 activation reaction over the most active supported gold catalysts, namely, Au/Fe_2O_3 prepared via coprecipitation B at pH 7 and 8 and Au/ZnO prepared via coprecipitation A at pH 5. Table 5.5 showed that the affect of activation energy was higher than that of the pre-exponential factor. The catalyst had the highest activity for both reactions, Au/Fe_2O_3 prepared by coprecipitation method B at pH 8, showed the lower activation energy and the lower pre-exponential factor (A) confirmed that the rate of both reactions depended on the activation energy. Further, Table 5.5 showed that E_a values for C_2H_6 over all selected catalysts were lower than that for C_3H_8 over these catalysts. This is because C-H bond in C_3H_8 is lower energy than C-H bond of C_2H_6.

5.4. References

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Chapter 6

Conclusion and future work

6.1. Conclusion

In this study, supported gold catalysts were found to activate CO and light alkanes at low temperatures. The selection of support materials and control of preparation parameters such as; pH, preparation temperature, ageing time are have been shown to be very important parameters for designing an active supported gold catalyst for both types of reaction. These catalysts exhibited excellent catalytic activity and stability compared with pure supports, ZnO and Fe_2O_3, and the best preparation temperature was 80 °C. Use of temperatures $\geq$ 80 °C led to inactive catalysts

The final pH is an important variable in the preparation of gold catalysts supported on ZnO and Fe_2O_3, since the components present in the reaction mixture precipitate at different pH values. The onset of precipitation of Zn^{2+} is pH 7, whereas the onset of precipitation of Fe^{3+} is pH 3. This might be the reason for the difference in activity between gold catalysts supported on both supports when pH increased. In the case of Au/ZnO, the increase in pH led to decrease the catalytic activity for low temperature CO oxidation and light alkanes activation as well. This might be because gold is precipitated at a lower pH than ZnO and then, as pH increase, gold particles become covered by Zinc particles, which leads to decrease the activity of the catalyst. The situation is different for Au/Fe_2O_3 catalysts, because Fe precipitates at pH 3, which is a lower pH than that for gold precipitation. Therefore, the increase in pH leads to an increase in the catalytic activity toward low temperature CO oxidation and light alkane activation.

Varying the ageing time of the precipitate prior to filtration, even for short periods of time, can significantly affect the observed activity. However, the origin of this effect is not yet clear.

Several characterisation techniques were used to study the properties of supported gold catalysts prepared in this study. Atomic absorption analyses showed that the content of gold is strongly dependent on the pH, the increase in the pH leading to a decrease gold content in the catalysts prepared by coprecipitation at variable pH (A) or at constant pH (B).

X-ray diffraction patterns of dried Au/ZnO catalysts showed that gold does not appear in XRD patterns, due to either to highly dispersion of gold particles are on the surface of the support or Au peaks overlapped by hydrozincate and/or ZnO or the amount of gold species is smaller than that detected by the XRD technique. In these catalysts, the presence of gold decreases the crystallinity of the support peaks. Further, the powder X-ray diffraction patterns of Au/ZnO as a function of Au content showed that Au peaks appeared only at lower pH, when the Au content is the highest in Au/ZnO catalysts. The phase detected for Au/ZnO before calcination was zinc carbonate hydroxide hydrate, $Zn_4CO_3(OH)_6.H_2O$, while after calcination it was zinc oxide, zincate (ZnO). X-ray diffraction patterns of Au/Fe_2O_3 peaks showed lower intensity suggesting that gold interaction with the support decreased the crystallinity of the support. The phase detected for calcined Au/Fe_2O_3 was hematite (Fe_2O_3), while uncalcined support was amorphous.

The reduction of the supported gold catalysts strongly depends on the preparation method and preparation parameters. In the case of Au/ZnO catalysts, the reduction of the uncalcined catalysts was dependent on pH. The lower pH, the higher the gold content, the more reduced by TPR. TPR analysis of calcined catalysts showed they reduced at a higher temperature than the uncalcined ones. In the case of Au/Fe_2O_3 catalysts, TPR analysis appeared to show a correlation existing between the reduction temperature and preparation method. Au/Fe_2O_3 prepared by coprecipitation method A was reduced at higher temperature than that one prepared via coprecipitation method B. BET surface area analysis showed that the active catalysts should have a BET surface area higher than 40 g/m^2.

Coprecipitation and deposition-precipitation methods obtained highly active gold catalysts supported on ZnO and Fe_2O_3 for low temperature CO oxidation. The Au/MgO catalyst, the only uncalcined catalyst was prepared by DP method. Support prepared by coprecipitation method A, was active at low temperature CO oxidation. DP method is not useful method to prepare active Au/MnO_x catalyst.

Supported gold catalysts showed activity towards light alkane (C_1-C_3) activation at reaction temperatures lower than those for other catalysts. Initial reaction temperature for methane and ethane activation was 200°C, and 150°C for propane activation. Further, the same behaviour of supported gold catalysts on low temperature CO oxidation was observed for light alkane (C_1-C_3) activation.

The obtained results of CH_4 activation over Au/ZnO and Au/Fe_2O_3 pointed to pH value as an important variable. In the case of Au/ZnO, the increase in pH led to the decrease the activity of this catalyst toward CH_4 activation, while for Au/Fe_2O_3 prepared by coprecipitation B, the increase in pH value led to the increase in the activity of this catalyst toward CH_4 activation. Au/Fe_2O_3 catalysts prepared by coprecipitation method A were non-active material for either CO oxidation or CH_4 activation. In contrast, Au/Fe_2O_3 catalysts prepared by coprecipitation method B were very active for CO oxidation and showed the highest activity for CH_4 activation over Au/Fe_2O_3 catalysts in this study. This preparation procedure has not been reported yet in the literature for Au/Fe_2O_3 catalysts. Thus, the novelty of these results obtained via this procedure is considerable. However, some methanol was observed at 300 °C over Au/Fe_2O_3 catalyst prepared by coprecipitation procedure B at pH 6.

In addition to the effects of preparation method and pH, the results of CH_4 activation showed that catalysts prepared using both procedures A and B are very sensitive to the ageing of the precipitate. The origin of the variation in activity and effect of the ageing process is not yet clear. However, it might be due to the difference in the dispersion of gold during the ageing process.

C_2H_6 and C_3H_8 activation reactions were studied over the supported gold catalysts prepared in this study. Au/Fe_2O_3 catalyst prepared by coprecipitation B, at pH 8, was also the best catalyst for the activation of C_2H_6 and C_3H_8. C_2H_6 activation over supported gold catalysts has not been yet reported in literature, so this study provides an indication to the likely behaviour of this reaction over this type of catalysts.

The main product observed for light alkane activation over supported gold catalysts was CO_2, suggesting that supported gold catalysts are non-selective catalysts for this type of reaction. However, comparison between the conversion of CH_4, C_2H_6, and C_3H_8 over the best catalyst, Au/Fe_2O_3 prepared by coprecipitation B at pH 8, showed that such activity increased as carbon atoms increased in the alkane.

Activation energies E_a and pre-exponential factor (A) for low temperature CO oxidation and light alkane activation reactions over supported gold catalysts were investigated in this study. A comparison of results showed some correlation between the behaviour of both types of reaction over the same catalyst. Both reactions strongly depend on preparation method, type of support, and preparation parameters such as; pH value, ageing time.

E_a results of CO oxidation and CH_4 activation over Au/ZnO catalysts prepared by coprecipitation method A and/or B prepared at different pH, showed that increasing pH led to an increase in the activation energy. The pre-exponential factor (A) was increased by increasing pH in the case of CO oxidation, whereas it remained almost stable for CH_4 activation. Therefore, the effect of activation energy was higher than the pre-exponential factor (A) in the CO oxidation reaction, and activation energy only was affected by increasing pH in the case of CH_4 activation reaction because the pre-exponential factor had almost the same value over all these catalysts. Further, the stability of the pre-exponential factor (A) for CH_4 activation over these catalysts suggests that the effect of pH in CH_4 activation was less than its effect in CO oxidation. This may be due to the high reaction temperature for CH_4 activation, which causes sintering of small supported gold particles, and the subsequent loss of some active sites, especially for catalysts prepared at low pH.

Variation in ageing times in Au/ZnO catalysts prepared by coprecipitation method A had no significant influence on the E_a, while variation in the pre-exponential factor (A) had some influence. However, both E_a and the pre-exponential factor (A) were lower for aged catalysts than non-aged catalyst. In the case of CH_4 activation reaction, activation energies over the aged catalysts were lower than that over non-aged catalyst, while the pre-exponential factor (A) was almost the same for all the catalysts. This may be due to the high reaction temperature for CH_4 activation, which cause sintering of small supported gold particles and loss some active sites.

E_a for CO oxidation and CH_4 activation over Au/Fe_2O_3 catalysts prepared by coprecipitation method B showed the lowest activation energies values of the supported gold catalysts prepared and investigated in this study, and this activation energy decreased as pH increased. However, the effect of E_a on rate of CO oxidation reaction was higher than the effect of the pre-exponential factor (A) and, hence, increasing pH led to an increase in E_a and then an increase in the catalytic activity of these catalysts. Pre-exponential factor (A) values were much higher for CO oxidation reaction than CH_4 activation reaction. This may be due to the high reaction temperature required for CH_4 activation, which causes sintering of small supported gold particles, and then the loss of some active sites, especially for catalysts prepared at low pH. For Au/Fe_2O_3 catalysts prepared by coprecipitation method B at pH 8 for CH_4 activation reaction, there was agreement between E_a and pre-exponential factor

(A) values, activation energy was low and the pre-exponential factor (A) was high, which means more active sites were obtained on this catalyst. This might be the reason for the highest activity obtained for this catalyst either for CO oxidation or CH_4 activation.

E_a for C_2H_6 and C_3H_8 activation reactions over the most active supported gold catalysts, Au/Fe_2O_3 prepared via coprecipitation B at pH 7, 8 and Au/ZnO prepared via coprecipitation A at pH 5, showed that the decreasing in activation energy was in order:

Au/Fe_2O_3 (pH 8) method B > Au/ZnO (pH 5) method A > Au/Fe_2O_3 (pH 7) method B

The effect of E_a was higher than that of the pre-exponential factor. The catalyst had the highest activity for both reactions, Au/Fe_2O_3 prepared by coprecipitation method B at pH 8, showed the lower activation energy and the lower pre-exponential factor (A) confirmed that the rate of both reactions depended on the activation energy. Further, E_a values for C_2H_6 over all selected catalysts were lower than that for C_3H_8 over these catalysts. This is because C-H bond in C_3H_8 is lower energy than C-H bond of C_2H_6.

6.2. Future work

Three supported gold catalysts were concluded as the best catalysts prepared and investigated in this study. These catalysts were Au/Fe_2O_3 (pH 8) method B, Au/Fe_2O_3 (pH 7) method B, and Au/ZnO (pH 5) method A. Further studies on these catalysts need to be undertaken to optimize their catalytic activity towards the desired reaction, obtaining useful products over these catalysts by promoting them with other materials to be selective catalysts. This optimization can be done as follows:

1. Characterization of the used catalysts needs to be studied. TPR analysis for used catalysts is important to show the change in oxidation of the catalyst during the reaction. TGA analysis is required to study the moisture in the dried catalysts. Further, the XPS technique is needed to study the oxidation state of the used catalysts.
2. A study of the addition of transition metal oxides, especially oxides with high oxygen storage capacity, to the supported gold catalysts, which may improve their catalytic activities towards the desired reactions. These types of oxides act as suppliers of oxygen and as structural promoters by stabilizing gold particles against sintering.
3. A study of the effect of variation in Au % loading within the range from 0.05 % to 5%.
4. A study of the deactivation of these catalysts.
5. Further studies of ageing.