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LOW TEMPERATURE OXIDATION OF ETHANOL TO ACETIC ACID USING GOLD-BASED CATALYSTS

Steton Moses Tembe

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the Masters of Science.

Johannesburg, 2010

Declaration

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



……

Signature of candidate

……26……day of ……July……..2010

In memory of my late aunt and cousin

Bukobo Tembe and Thulisiwe Khumalo respectively.

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Publications and presentations arising from this work

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- Acetic acid production by selective oxidation of ethanol using Au catalysts supported on various metal oxide. (S.M. Tembe, G. Pattrick, M.S. Scurrell, *Gold Bull*., 2009, **42**, 321).

Presentations

1. Oral presentation

- Postgraduate symposium 2009, Wits University, Johannesburg, South Africa
- CATOMAT group meetings 2008-2009, Wits University, Johannesburg, South Africa
- AuTEK day 2008, Mintek, Randburg, South Africa
- AuTEK steering meeting 2010, Randburg, South Africa

2. Poster Presentation

- CATSA conference 2008, Parys, Free State, South Africa
- CATSA conference 2009, Stellenbosch, Western Cape, South Africa

Abstract

Over the past decades it has become clear that gold supported nanoparticles are surprisingly active and selective catalysts for several green oxidation reactions of oxygen-containing hydrocarbons, in particular alcohols using molecular oxygen as the stoichiometric oxidant.

In this research, ethanol was oxidized to acetic acid using molecular oxygen as oxidant in a presence of gold supported catalysts. Catalysts containing 1 wt.% Au supported on TiO_2, ZnO, Al_2O_3, C and $MgAl_2O_4$ were prepared using different methods which includes inverse deposition precipitation, incipient wetness impregnation and immobilization of metal sol. It was found that TiO_2 gave the most superior activity as support for gold in ethanol oxidation, followed by ZnO and Al_2O_3.

High ethanol conversion of 93% and selectivity of 97% to acetic acid was achieved when using TiO_2 as support for gold after 20 h reaction. The effect of using excess oxygen was also investigated in the study. It was noticed that at higher oxygen pressures it is possible to convert ethanol to 100% conversion. When excess oxygen was introduced into the autoclave, an ethanol conversion of 99.4%, selectivity of 99.8% and yield of 99.2% was achieved without altering any reaction conditions.

The catalyst recycling studies were also conducted on Au/TiO_2, The activity studies showed that the catalyst can only be used twice and still maintain the ethanol conversion of greater then 90%. When the catalyst was re-used for the third time it was noticed that the catalytic activity had dropped to 29% and this was due to leaching of gold on the catalyst which was observed in a third cycle.

The concentration of ethanol was varied from 5 – 40 wt.% and it was noticed that at high ethanol concentration, the formation of ethyl acetate was most favoured compared to acetic acid. Acetic acid was only favoured at low ethanol concentration.

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Abbreviation Meaning

AAS	Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
AcH	Acetaldehyde
AcOH	Acetic acid
BET	Brunauer-Emmett-Teller
CO_2	Carbon dioxide
DP	Deposition Precipitation
EDS	Energy Dispersive X-ray Spectroscopy
EtOH	Ethanol
EtOAc	Ethyl acetate
FID	Flame Ionization Detector
GC	Gas Chromatography
HRTEM	High Resolution Transmission Electron Microscopy
h	Hours
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
NO_x	Nitrogen oxides
O_2	Oxygen molecule
PGM	Platinum group metals
SCCM	Standard Cubic Centimeters per Minute
SiO_2	Silicon dioxide
SO_x	Sulphur oxides
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
TCD	Thermal Conductivity Detector
XRD	X-ray diffraction
XPS	X-ray Photoelectron Spectroscopy
UV/vis	Ultraviolet visible spectroscopy

Chapter 1

1. Introduction

1.1. Background

The cost of various fuels and chemicals is largely governed by the cost of the raw material and the efficiency of the processes involved. Oil resources are becoming far more expensive compared with biomass resources. It is potentially possible to convert biomass (e.g. bioethanol) to essentially all high-value commodity chemicals and fuels currently available from fossil resources. There could be more advantages in using biomass as a feedstock compared with fossil resources, for example, in the chemical industry the introduction of oxygen functionalities into hydrocarbons can be rather difficult, whereas many products derived from biomass already contain some oxygen [1]. However, this entails an increase in production costs for some of the non-oxygen containing products, such as gasoline [2]. It is possible to produce some chemicals more easily and in fewer steps from biomass than from fossil resources [3]. The use of biomass as a sustainable resource for production of fuels and commodity chemicals could offer an improved security in supply, since biomass can be grown in most parts of the world. BioEthanol could be one of the examples of a chemical derived from biomass that could be used in future as a feedstock, considering its availability.

The oxidation of many organic substrates leads to the production of many functionalized molecules that are of great commercial and synthetic importance. The selective oxidation of alcohols to carbonyl compounds or carboxylic acids is a fundamental transformation in organic chemistry as these compounds are widely used as intermediates for fine chemicals [4-6]. The traditional inorganic oxidants, such as permanganate and dichromate, however, are toxic and produce a large amount of waste. The separation and

disposal of this waste material increases cost in chemical processes. Therefore, from both economic and environmental viewpoints, there is an urgent need for greener and more efficient methods that will replace these traditional toxic oxidants with clean oxidants, such as O_2, and preferably, a separable and reusable catalyst. Many researchers have reported the use of molecular oxygen as an oxidant for alcohol oxidation using different catalysts [7-11] and a variety of solvents. Due to the volatile, flammable, and toxic nature of organic solvents [12-14], solvent free oxidation became the preferred method because it is environmental friendly and associated with a high atom efficiency.

1.2. Motivation of the study

Presently, acetic acid and other carbonaceous commodity chemicals are mainly produced from petrochemical sources, but due to a diminishing amount of fossil fuels it is important to investigate new routes. One possibility is to use renewable feedstocks such as bioethanol. The production of bioethanol is growing, and it could be economically feasible to convert bioethanol into acetic acid. Today, bioethanol is mainly used as a fuel or fuel additive, and it has also attracted significant interest as a source for hydrogen production [15]. However, it appears much more feasible to use ethanol as a feedstock for chemical production from both an economical and green perspective. In addition, the demand for acetic acid is increasing, which further indicates that it is time to find alternatives to the fossil fuel feedstocks. Furthermore the price of renewable feedstocks is decreasing, whereas the price of fossil fuels is increasing making the ethanol route even more interesting.

The main concern of government regarding the mass production of industrial chemicals from fossil fuels is the environmental impact associated with their application which results in production of greenhouse gasses. Thus there is growing pressure to find more “green” processes for the production of these chemicals. An obvious route to acetic acid production would be the fermentation of bioethanol, but thus far it seems that this is only cost effective for the production of vinegar not for acetic acid demand by the chemical

industry due to small volume. A better route would be the direct oxidation of bioethanol to acetic acid under mild conditions using molecular oxygen (from air). This process would produce enough acetic acid to meet the demand by the chemical industry, hence the process is facile and the starting materials are easy to get.

1.2.1 Acetic acid demand

Acetic acid is one of the simplest and most widely used carboxylic acids having many important chemical and industrial applications. Acetic acid has a world demand of about 6.5 million tonnes per year [16], of which about 5 million tonnes are produced by the methanol carbonylation process and by bacterial fermentation. The remaining 1.5 million tonnes come from recycling [17]. Since the methanol carbonylation process is highly dependant on natural gas which is a non-renewable resource, it will not be able to support the acetic acid industry indefinitely.

1.2.2 Availability of bioethanol

More than 80% of the world's energy consumption and production of chemicals originates from fossil resources (oil, gas and coal). The use of fossil resources coupled with concerns about global warming, as mentioned earlier in this chapter, results in a big drive to develop new technologies for the generation of energy and chemicals. In this respect, it has recently been considered that biomass could become a major source for the production of energy and chemicals [18].

Bioethanol can be obtained from the fermentation of biomass. It contains about 8-10 vol% of ethanol [19]. It can be concentrated up to 96 vol% by a distillation process [20]. The total world production of bioethanol is constantly increasingly and was estimated to be more than 12.1 billion gallons per year in 2005 [21]. The global production of bioethanol reached 13.5 billion gallons in 2006 from 12.1 billion gallons in 2005 [22].

Bioethanol currently accounts for more than 94% of global biofuel production, and mostly of it comes from sugar cane [23]. About 60% of the global bioethanol production comes from sugar cane as the resource and 40% from other agricultural crops [24]. Brazil and the United States are world leaders, which exploit sugar cane and corn, respectively, and they together account for about 70% of the world bioethanol production [22]. Bioethanol can be used as an alternative resource for producing chemicals like ethylene, acetaldehyde, butadiene, acetic acid etc. Today, the annual production of bioethanol is around 45 million tonnes [2], which is significant enough to replace the petrochemical products produced from fossil resources. The products produced from bioethanol must obviously be more valuable than bioethanol itself for the process to be economically valuable. Instead of using bioethanol for transporting fuel purposes where it seems to have relatively low value nowadays, it could be instead be used as a feedstock for other important chemical products which have a much higher value.

The use of bioethanol in the transport sector will most certainly have some positive influence on CO_2 emissions, but it might prove possible to achieve an additional benefit by using it as feedstock for the chemical industry. It seems realistic to produce, for example acetic acid from bioethanol with a proper catalytic reaction pathway. Such a reaction was recently proposed by a research group in Denmark, where ethanol was oxidised to acetic acid with air, in an aqueous-phase reaction over a gold catalyst [20]. The production of chemicals from bioethanol can actually lead to higher CO_2 savings than by using it as a fuel.

1.2.3 What is acetic acid?

Acetic acid is an organic chemical compound that is best recognized for giving vinegar its sour taste and pungent smell. When pure, acetic acid is a clear, colorless liquid with a sharp, irritating odor. Its structural formula can be represented by CH_3COOH. It has a freezing point that is slightly below room temperature at 16.7 °C. Concentrated solutions of acetic acid are very corrosive and can cause painful burns on contact with skin.

1.2.4 Importance of acetic acid

Acetic acid is a commodity chemical that has demonstrated relatively rapid growth in production volume and is used in several areas, which includes the production of vinyl acetate monomer which polymerizes to form polyvinyl acetate, which is used in water-based latex paints and in glues for paper and wood. It is an important industrial and chemical reagent that is used in the production of polyethylene terephthalate which is mainly used for making soft drink bottles; cellulose acetate for making photographic film; and as well as synthetic fibres and fabrics. Because vinegar is weakly acidic, it has a variety of properties that are useful around the house. Mineral deposits formed when hard water evaporates, such as those found on plumbing fixtures and in tea kettles, dissolve in acids, so vinegar can be used to remove those mineral deposits. Vinegar is also used as a food preservative, and the sour taste makes it popular as a flavoring in cooking and in salad dressings.

1.3. Aims of the study

The aim of the study was to repeat the very promising result on the oxidation of ethanol to acetic acid using $Au/MgAl_2O_4$ which was previously done by Christensen *et al.* [20], and then to set about discovering other new gold-based catalysts that will perform the reaction with high conversion and selectivity. Also included in the study would be comparison between the reactivity of standard AuTEK catalysts from Mintek (Au/TiO_2 and Au/ZnO and others). Wet chemical and deposition precipitation methods were proposed as initial methods to deposit gold on the support in the search for novel catalysts. In addition to standard catalysis studies, studies of the activity of the catalysts, parameter scans of temperature, O_2 pressure, ethanol concentration, and pH and catalyst selectivity will be investigated. The catalysts will be fully characterized by various methods including XRD, XPS, ICP, TEM, and TPR/O/D.

1.4. Dissertation outline

Chapter 1: presents, the background, motivation and aims of the study

Chapter 2: presents the literature review

Chapter 3: presents the experimental work carried out in the study for ethanol oxidation

Chapter 4: presents the results and discussion of the new findings on ethanol oxidation using gold supported catalysts.

Chapter 5: gives the general conclusions from all the work carried out and presented in this dissertation.

1.5. References

1. Dale, B. E. *J. Chem. Technol. Biotechnol.,* **2003**, 78, 1093.
2. Rass-Hansen, J.; Falsig, H.; Jørgensen, B.; Christensen, C.H. *J. Chem. Technol. Biotechnol.,* **2007**, 82, 329.
3. Kosaric, N.; Duvnjak, Z.; Farkas, A.; Sahm, H.; Bringer-Meyer, S.; Goebel, O. *et al*., Ethanol in *Ullmann's Encyclopedia of Industrial Chemistry* (7th edn). Wiley, Chichester, **2006**.
4. Mallat, T.; Baiker A. *Chem Rev.*, **2004**, 104, 3037.
5. Muzart, J. *Tetrahedron*, **2003**, 59, 5789.
6. Rafelt, J.S.; Clark, J.H. *Catal. Today*, **2000**, 57, 33.
7. Opre, Z.; Ferri, D.; Krumeich, F.; Mallat, T.; Baiker, A. *J. Catal.*, **2006**, 241, 287.
8. Bavykin, D.V.; Lapkin, A.A.; Kolaczkowski, S.T.; Plucinski, P.K. *Appl. Catal., A*, **2005**, 288, 175.
9. Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J Am Chem Soc*., **2004**, 126, 10657.
10. Ji, H.; Song, J.; He, B.; Qian, Y. *React. Kinet. Catal. Lett.*, **2004**, 82, 97.
11. Makwana, V.D.; Son, Y.C.; Howell, A.R.; Suib, S.L. *J. Catal.*, **2002**, 210, 46.
12. Kluytmans, J.H.; Markusse, A.P.; Kuster; B.F.; Marin; G.B.; Schouten; J.C. *Catal. Today*, **2000**, 57, 143.
13. Gangwal, V.R.; van der Schaaf, J.; Kuster, B.M.; Schouten, J.C. *J. Catal.*, **2005**, 232, 432.
14. Hutchings, G.J.; Carrettin, S.; Landon, P.; Edwards, J.K.; Enache, D.; Knight, D.W.; Xu, Y.; Carley, A.F. *Top. Catal.*, **2006**, 38, 223.
15. Deluga, G.A.; Salge, J.R.; Schmidt, L.D.; Verkios, X.E. *Science*, **2004**, 303, 993.
16. Shin, C.H.; Kim, J.Y.; Kim, J.Y.; Kim, H.S.; Lee, H.S.; Mohapatra, D.; Ahn, J.W.; Ahn, J.G.; Bae, W.J. *Journal of hazardous materials*, **2009**,162,1278.
17. Production report, *Chem. Eng. News*, July 11, **2005**, pp.67.
18. Dimitratos, N.; Lpoez-Sanchez, J.A.; Hutchings, G.H. *Top. Catal.*, **2009**, 52, 258.
19. Soetaert, W.; Vandamme, E.; Lens, P.; Westermann, P.; Haberbauer, M.; Morena, M.; (Eds.), *Biofuels for fuel cells, IWA publishing, London*, **2005,** 37.

20. Christensen, C.H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.K.; Hansen, S.M.; Hansen, M.R.; Andersen, H.C.; A. Riisager, *Angew.Chem. Int. Ed.*, **2006**, 45, 4648.
21. *Biofuels Strategy: Key Facts and Figures.* MEMO/06/05 European Commission, Brussels, **2005**.
22. *Renewable Fuels Association* (RFA), Ethanol industry statistics, Washington, DC, USA, **2007**. [cited; available from: <www.ethanolrfa.org>] 20 June 2007.
23. *International Risk Governance Council* (IRGC), Governing the risk and opportunities of bioenergy, IRGC's bioenergy Project, Geneva, Switzerland, **2007**. [Cited; available from <www.irgc.org>] 12 August 2007.
24. A. Dufey. Biofuels production, trade and sustainable development: emerging issues. Environmental Economics Programme, Sustainable Markets Discussion Paper No. 2, International Institute for Environment and Development (IIED), London, September, **2006**.

Chapter 2

2. Literature Review

2.1. Introduction

Heterogeneous catalysis plays a major role worldwide, not only from the economic point of view, but it also provides the necessary infrastructure for the well being of the society as a whole. It is hard to imagine what modern society would be like without chemicals, polymers, and pharmaceuticals, most of which are prepared industrially by catalytic chemistry. Without effective heterogeneous catalysis the manufacture of many materials such as, pharmaceuticals, foodstuffs etc. would not be possible. It is therefore not surprising; that heterogeneous catalysis is a subject that spans chemistry, chemical engineering and materials science in working together to break new ground. There is intense and broad interest in the design of new catalysts and as well as seeking to understand how these materials function as catalysts.

Since the pioneering discovery by Haruta and his coworkers that gold nanoparticles can catalyze CO oxidation effectively at low temperatures,[1] there has been tremendous interest in gold-catalyzed oxidation reactions [2,3]. In particular, the oxidation of alcohols has received significant attention, and rightfully so, since the reaction satisfies most of the demands for a modern, sustainable, and ‘‘green’’ reaction [4]. The high activity of the supported gold nanoparticles allows the use of air as the stoichiometric oxidant, thus ensuring optimal atom economy. Furthermore, the reaction has the potential to play an important role in the synthesis of both commodity and fine chemicals, where the use of a heterogeneous catalyst allows the isolation of product(s) by a simple separation [5]. This represents a major improvement in catalysis as compared with ‘‘traditional’’ oxidation

technologies used before, especially in the chemical industry, which often rely on stoichiometric amounts of heavy metals and/or halogens.

2.2. Reactions catalyzed by gold

Over the past decades it has become clear that supported gold nanoparticles are surprisingly active and selective catalysts for several green oxidation reactions of oxygen-containing hydrocarbons (for example, alcohol) using molecular oxygen as the stoichiometric oxidant.

In the fine chemical industry, and as well as in traditional organic chemistry, many oxidation reactions are carried out using inorganic oxidants. The application of these types of reagents often containing chromium or manganese, inevitably leads to the generation of huge amounts of metal waste. In recent years several new procedures have been developed wherein a catalyst is used to facilitate the oxidation of alcohols employing molecular oxygen as the stoichiometric oxidant [6–9]. In this emerging field of "green" oxidation chemistry, catalysts comprising gold nanoparticles have attained a very prominent role, [10] since they are often surprisingly active and sometimes exhibit different chemoselectivity than platinum group metal catalysts. Thus, from a fundamental point of view, gold catalysis is a topic of intense scientific interest; drawing attention from a very diverse group of researchers. So far, literature reports [11] that the selective oxidation of alcohols has focused primarily on oxidizing alcohols into:

- Aldehydes,
- Carboxylic acids or esters, and
- Oxidation of aldehydes to esters,
- Epoxidations of olefins,
- Activation of C–H bonds in alkanes,
- Oxidation of amines,
- Propene epoxidation and alkanes to alcohol

2.3. Green catalysis

The consumption of fossil fuels using existing pathways is likely to continue for some time. However, there are distinct sustainability issues with the availability of these fossil resources and there is now considerable interest in utilising bio-renewable feedstocks, which do not have sustainability issues associated with them. Bio-renewable feedstocks can provide a valuable new route to the production of platform chemicals on which the generation of finished products can be based. Although these materials (bio-renewable) can be gasified and pyrolysed to produce syngas and oil-like materials, that can be processed by existing technology to a desired fine product chemicals. Bio-renewable feedstocks have the potential to replace fossil resources; hence it is possible to convert them into syngas by using an appropriate technology, for example by gasification or pyrolysis as shown in Figure 2.1 below.

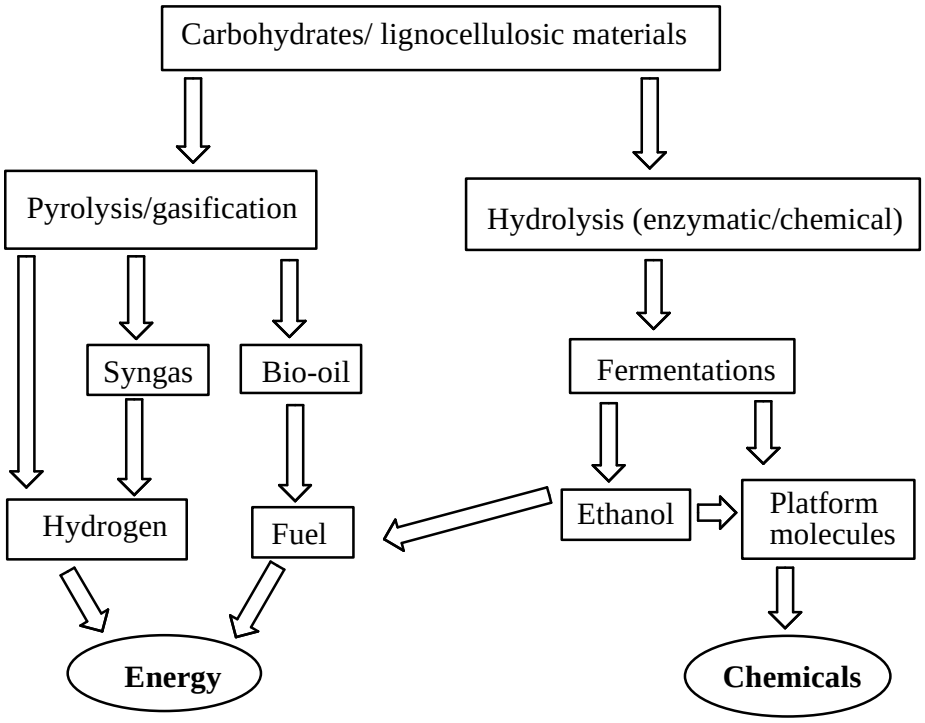

Figure 2.1: Scheme of biorefinery processes [12].

2.4. Biomass

During the growth of plants, water and carbon dioxide are absorbed and transformed into carbohydrates through the process of photosynthesis in the presence of sunlight. The organic matter that makes up these plants is known as biomass. Biomass contains a lot of energy that can be used to produce heat, transportation fuels, or chemicals depending on the processing technology used [13].

Human beings have used biomass as a source of energy for thousands of years, ever since human beings started burning wood to cook food or to keep themselves warm. Nowadays with a proper technology it is possible to convert biomass into chemicals such as acetic acid depending on the type of biomass used.

2.5. Bioethanol

Today, mankind faces two major air pollution problems i.e. global warming which is mainly caused by the emission of CO_2, and acid rain, caused by emissions of SO_x and as well as NO_x. Both problems are exacerbated by the use of fossil resources i.e. coal, petroleum, and natural gas which are non renewable resources. The use of renewable feedstocks is of crucial importance for a sustainable society. In this respect, catalysis represents a key approach to green chemistry in the activation and utilization of bio-renewable chemical feedstocks e.g. bioethanol. The use of bioethanol as feedstock for the production of chemicals is one of the ways that can be used to reduce both consumption of fossil resources and pollution of the environment by the chemical industry. The production of chemicals from fossil resources results in an increase of CO_2 concentration in the atmosphere, which contributes to global warming [14]. The combustion of fossil fuel contributes about 73% of the CO_2 released to the atmosphere [15]. More then 95% of carbonaceous chemicals are currently produced from fossil resources [16], which means that more CO_2 is being released to the atmosphere. Reducing the use of fossil fuels as the resource for chemicals would considerably reduce the amount of CO_2 produced, as well

as reduce the levels of pollutants [17]. To reduce the net contribution of greenhouse gases to the atmosphere, bioethanol has been recognised as the potential alternative resource to petroleum-derived fuel [18].

Bioethanol can be used as fuel or a fuel additive. The use of bioethanol as fuel offers many advantages which include higher octane rating, broader flammability limits, higher flame speeds and higher heats of vaporization than gasoline which is derived from fossil fuel [19]. Bioethanol can also be used as a fuel additive where it enhances the octane rating and improves the combustion, which reduces CO and ground level ozone emissions [20]. Using ethanol as a fuel additive offers many advantages because it is also less poisonous to the environment than other octane boosters such as lead and methyl *tert*-butyl ether (MTBE). Bioethanol is an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression–ignition engines [21]. The presence of oxygen facilitates the complete combustion of the hydrocarbon in the engine. Higher octane numbers are preferred in internal combustion engines. Using an oxygenate fuel such as bioethanol will provide a reasonable antiknock value, and combustion will be more efficient, reducing the hydrocarbons and particulates in the exhaust gases.

2.5.1 Challenges of using bioethanol

The only major problem with bioethanol production is the availability of raw materials for the production. The availability of feedstocks for bioethanol can vary considerably from season to season and depending on geographic location. The price of raw material for bioethanol production is also highly volatile, which can highly affect the production costs of bioethanol [22].

Ethanol has lower energy density than gasoline (bioethanol has 66% of the energy that gasoline has by volume %); it is corrosive, has a lower vapour pressure, is miscible with water and toxic to ecosystem [23]. Inspite of this the advantages of using bioethanol seem

to override its disadvantages. Today most hydrogen is produced by the steam reforming of natural gas. However this is not a solution to substantially decrease the emission of greenhouse gases to the atmosphere unless the natural gas is normally vented or flared instead. Bioethanol can be used in hydrogen production via catalytic steam reforming rather than using natural gas as feedstock which needs extensive purification. Many consider hydrogen to be a future energy source, especially for transportation sector and mobile devices [24]. The use of bioethanol in hydrogen production would offer a green route.

2.6. Production of acetic acid

Acetic acid can be produced both synthetically and by bacterial fermentation. At present, the main route for the production of acetic acid is by methanol carbonylation [25]. This process includes the use of metals as catalysts, while bacterial fermentation only uses enzymes or bacteria during the oxidation process.

2.6.1 Methanol carbonylation

This process involves the reaction of methanol with carbon monoxide in the presence of a rhodium complex catalyst at a temperature of 150 to 200 °C and a pressure of 30 to 60 atmospheres [26]. This process accounts for approximately 60% of the total world acetic acid manufacturing capacity [25].

$$CH_3OH + CO \xrightarrow{\text{Rhodium complex}} CH_3COOH \quad \text{.....2.1}$$

This process (Eq. 2.1) exhibits high selectivity to acetic acid based on methanol (99%) and carbon monoxide (85%) [27]. Carbonylation of methanol, catalyzed by rhodium, was invented by Monsanto in the 1960s, and this process worked for about 25 years as the

leading technology for the production of acetic acid. In the early 1990s, the difference in the prices of rhodium (US$ 500/oz) and iridium (US$ 60/oz) was the driving force for the replacement of rhodium with iridium.[25]. In 1996 a new, more efficient, process was announced by BP Chemicals for the carbonylation of methanol, and this time using iridium as catalyst [26]. The potential use of iridium instead of rhodium was identified in the early work done by Monsanto [25]; however, the reaction rate exhibited by the rhodium catalyst system was superior to that of iridium. It was disclosed that the combination of the iridium catalyst with a metal promoter such as ruthenium increases the activity of the catalyst and minimizes the product impurities more than previously reported iridium systems without a promoter [26]. The major problem facing the chemical industry in using this process is that it is highly dependent on fossil resources as feedstock, and it uses a PGM catalyst. Due to an increase in oil prices and PGM catalysts, there is obviously economic pressure on acetic acid production. It is therefore imperative for scientists to look for alternative routes for the production of acetic acid, which will be cheaper and economically valuable rather than using expensive PGM catalysts.

2.6.2 Bacterial fermentation

Typically, vinegar contains about 4 to 8% acetic acid. As the defining ingredient of vinegar, acetic acid has been produced and used by humans since before the dawn of recorded history. Vinegar used to be produced from dilute solutions of alcohol, such as wine, apple cider and fermented grain, malt and rice, through the action of certain bacteria in the presence of oxygen. These bacteria require oxygen, and the overall chemical change is the reaction of ethanol with oxygen to form acetic acid and water as indicated in equation 2.2.

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \quad \text{.....2.2}$$

Due to an increase in applications for acetic acid in the chemical industry this process could not meet demand for acetic acid and this has resulted in exploration of new alternative routes for the production of acetic acid.

2.7. Alcohol oxidation

The selective oxidation of alcohols is one of the most important transformations in organic synthesis [28]. Although a number of methods have been developed, the search for new facile, cost-effective and environmentally friendly procedures that avoid the use of large excess, toxic and expensive metal oxidants are required [28]. An attractive and promising alternative route is the direct oxidation of alcohols catalyzed by reusable heterogeneous solid catalysis, using molecular oxygen (O_2) [10]. The catalytic oxidation of alcohols with air has attracted significant attention as a "green" chemistry reaction [29] in catalysis. The catalysts used include mainly palladium and platinum and have shown some promising results in alcohol oxidation [29]. However these metal catalysts generally suffer from rapid deactivation due to leaching as a consequence of over-oxidation of the metal active sites [30]. One of the major problems associated with the use of these catalysts in oxidation reactions is product selectivity, since a broad range of products often exist at the end of reaction. For example, in glycerol oxidation, there are six potential C_3 oxygenated products as demonstrated in Figure 2.2 below. Selective versus nonselective oxidation is, therefore, the big challenge and requires the design of new effective catalysts that will provide a high selectivity to the desired product.

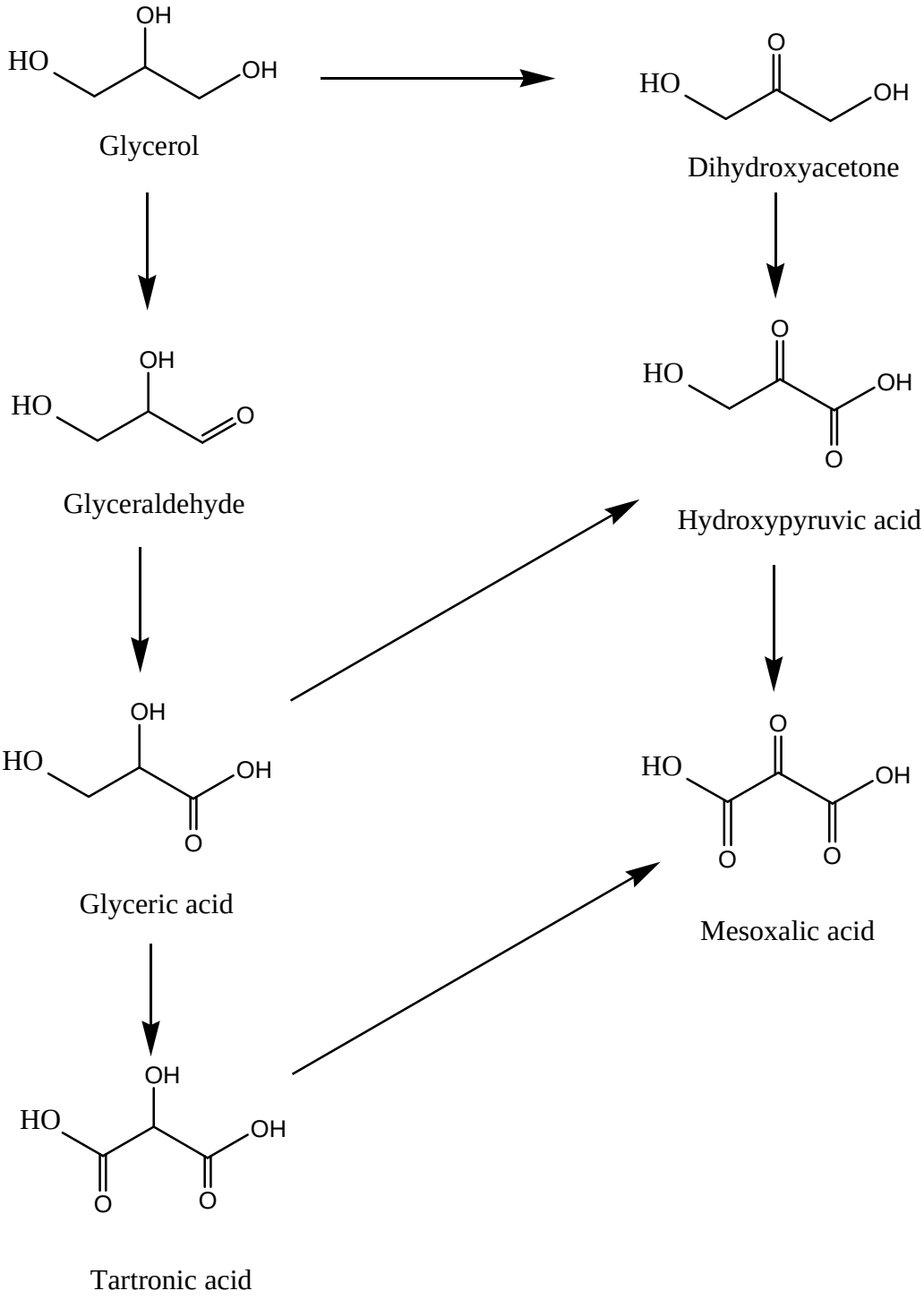

Figure 2.2: Different oxygenated products arising from glycerol oxidation [31].

2.7.1 The superior performance of gold catalysts over platinum group metal catalysts in alcohol oxidation

The oxidation of glucose has been investigated using Pt group metals as the catalyst; although these catalysts have been reported to suffer from rapid deactivation due to metal leaching, self-poisoning and over-oxidation [32]. The use of bi-and tri-metallic catalysts have been proposed to overcome these effects. In particular, Bi promoted catalysts showed the best performance for improving the catalyst activity [33]. However, the catalytic activity of these catalysts did not surpass the activity of the gold catalyst for glucose oxidation as shown in Figure 2.3 below. The gold catalyst showed an outstanding performance for glucose oxidation as compared to Pt group metal catalysts. Gold catalysts showed a much better selectivity and high resistance to poisoning compared to Pt group metal catalysts [34].

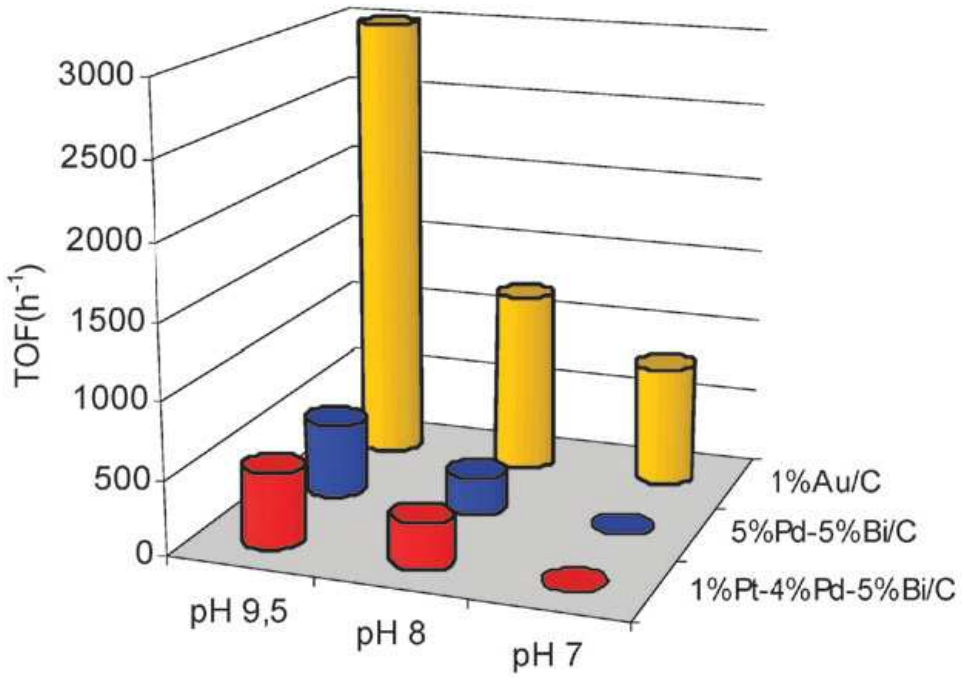

Figure 2.3: Catalytic performance of different catalysts in glucose oxidation [34]

Pd nanoparticles supported on hydroxyl apatite (Pd/apatite) has recently been reported by Kaneda and co-wokers as one of the most active catalysts for the aerobic oxidation of alcohols [35]. In contrast Abad *et al.* reported Au/CeO_2 as the most active catalyst for alcohol oxidation compared to palladium supported catalysts as shown in Figure 2.4 [30].

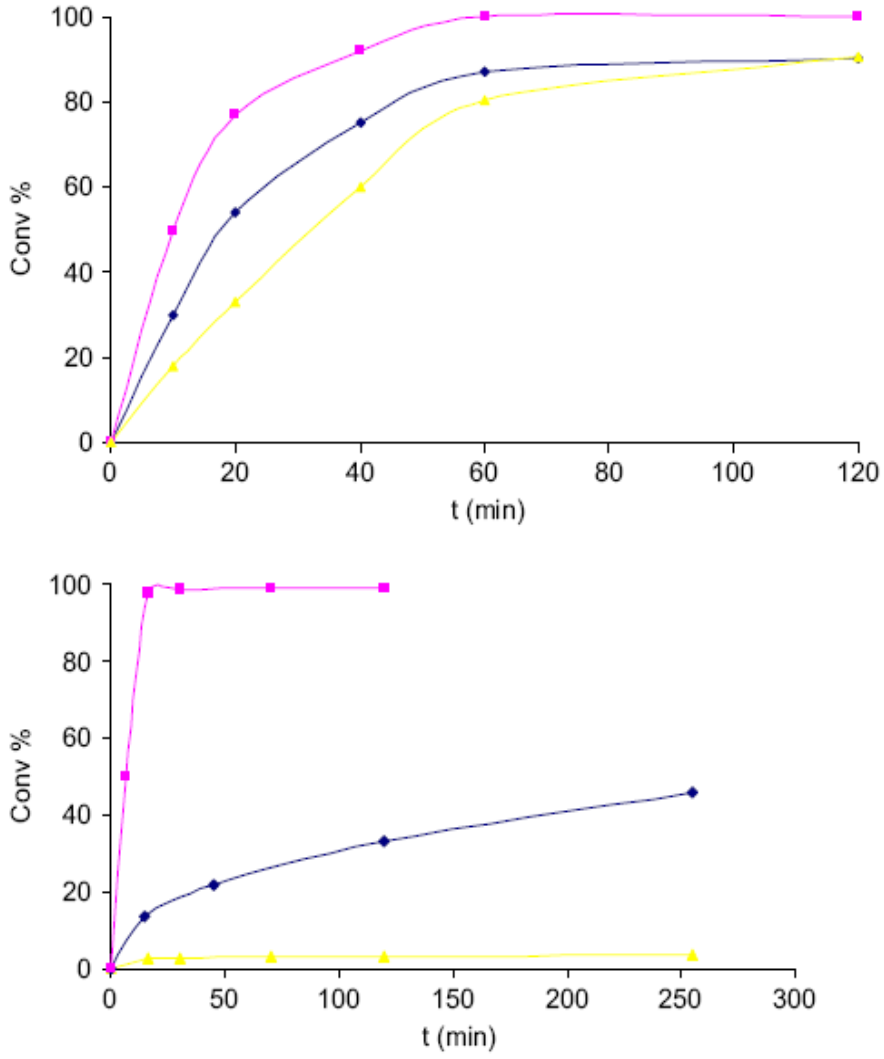

Figure 2.4: Comparison of catalytic activity of Pd/CeO_2 (▲yellow), Au/CeO_2 (■ pink), and Pd/apatite (♦ navy) for the aerobic oxidation of alcohols. Top: 1-phenylethanol. Bottom: 3-octanol [30].

2.7.2 Ethanol oxidation by gold catalysis

It has recently been shown that acetic acid can be synthesized directly from aqueous phase oxidation of ethanol using gold based catalysts [29]. The supported gold nanoparticles have attracted considerable attention recently as promising new materials for alcohol oxidation owing to their higher selectivity and lower susceptibility to leaching as compared to platinum group metal catalysts [36].

$$CH_3CH_2OH + O_2 \xrightarrow{\text{Gold catalyst}} CH_3COOH + H_2O \quad \text{.....2.3}$$

There is a significant amount of work that has been done on ethanol oxidation using gold catalysis, amongst this work, it is reported that if the reaction is taking place in aqueous solution the formation of carboxylic acid is favoured as the main product over the aldehyde, but in solvent-free experiments, aldehyde formation is favoured as the major product [30]. Idriss *et al.* investigated the effect of temperature in the gas-phase oxidation of ethanol over Au/CeO_2 catalyst in the temperature range of 100-800 °C and the study revealed that the product changed significantly with varying temperature [37]. At low temperatures the acetaldehyde was the main product. Christensen *et al.* reported that, the highest yield of acetic acid can be achieved when ethanol is oxidized in aqueous phase at moderate temperatures and pressures [29]. The highest yield of 90-95% was reported with a proper selection of reaction conditions when using a gold supported catalyst [38].

The catalysts that have been used before to attempt the aqueous phase oxidation of ethanol to acetic acid include palladium and platinum in homogeneous phase reaction. The use of these catalysts in ethanol oxidation showed some promising results [39, 40]. Though there was a problem associated with them, which was poor selectivity towards acetic acid formation. Secondly they produced a significant amount of acetaldehyde [29]. The catalytic activity of Pt, Pd and Au was also studied in the aqueous phase oxidation of ethanol. The results showed that all catalysts had the same catalytic activity [29], but the only difference was that the gold catalyst showed a high selectivity to acetic acid.

The effect of support was also investigated. Gold was loaded in different supports, such as magnesium-aluminium oxide ($MgAl_2O_4$) and titanium oxide (TiO_2). The results reported in the study showed that there was no significant difference between the two metal oxide supports [38], but if the supports used were non-metal oxides the effect could have been very different; and this has been reported in selective oxidation of glucose [41].

2.8. Factors affecting alcohol oxidation

The gold particle size is considered to be of the paramount importance for aerobic oxidation of alcohol [42]. It has been shown that support may also play a key role in determining the catalytic activity and selectivity of the reaction [30, 43]. For example, certain reactions reach an optimum activity and /or selectivity at larger particle diameters of the catalysts while other reactions show superior performance at smaller particle diameters. The shape and symmetry of the particle itself can influence the site population and geometry [44]. Some studies have also shown that the addition of a base can highly affect the oxidation of alcohol [45].

2.8.1 Effect of metal oxide support

The catalytic properties of supported gold have been shown to depend very sensitively on a number of factors such as particle size; pretreatment, calcination temperature and preparation method. The nature of support material and its physical state seem to play one of the critical central roles in gold catalysis [46, 47]. Transition metal oxides are generally used as support in heterogeneous catalysis. The overall performance of a supported gold nanoparticle is highly dependent on the structure and properties of oxides supports, and the gold-oxide interface interactions [48, 49]. A wide range of metal oxides and other materials have been studied as supports for various reactions in alcohol oxidation over supported gold catalysts.

The supports studied include C [31], TiO_2 [38, 41, 50], Al_2O_3 [51], $MgAl_2O_4$ [29], SiO_2, CeO_2 [50, 52-54], γ-Ga_2O_3, Ga_2O_3 [55]. However there is still a lot that needs to be done in order to understand the mechanism as to how this catalyst works in alcohol oxidation reactions.

2.8.2 Effect of gold particle size

It has been shown both experimentally and theoretically that the activity of Au nanoparticles in the oxidation of CO increases with decreasing particle size and is strongly affected by the type of support used [56-58]. However, bulk Au has been employed in certain oxidation reactions as well indicating that, the presence of larger Au particles can be favourable for certain oxidation reactions [59].

Some studies have shown the effect of the size of gold particles in alcohol oxidation using CeO_2 and TiO_2 as support for the aerobic oxidation of benzyl alcohol. The gold particle size prepared was in the range of 1.3 to 11.3 nm. The catalysts were then tested for aerobic oxidation of benzyl alcohol. The results showed that there was a huge effect of gold particle size in alcohol oxidation. The optimal activity was observed for the catalysts with an average particle size of 6.9 nm, whereas smaller and bigger particles showed a poor activity. This behavior was observed irrespective of the support (CeO_2 or TiO_2) and of the reaction conditions applied [50]. Similar results were also reported by Zheng and Stucky for aerobic oxidation of ethanol using gold supported on silica [54]. Three SiO_2–supported catalysts with 3.5, 6.3, and 8.2 nm gold particles were prepared by depositing the nanoparticles on chromatography silica gel from their corresponding chloroform solutions. The catalytic screening of the three catalysts was performed on ethanol oxidation at 200 °C using molecular oxygen as the oxidant. The results showed that Au particle size has a crucial role in alcohol oxidation as shown in Figure 2.5.

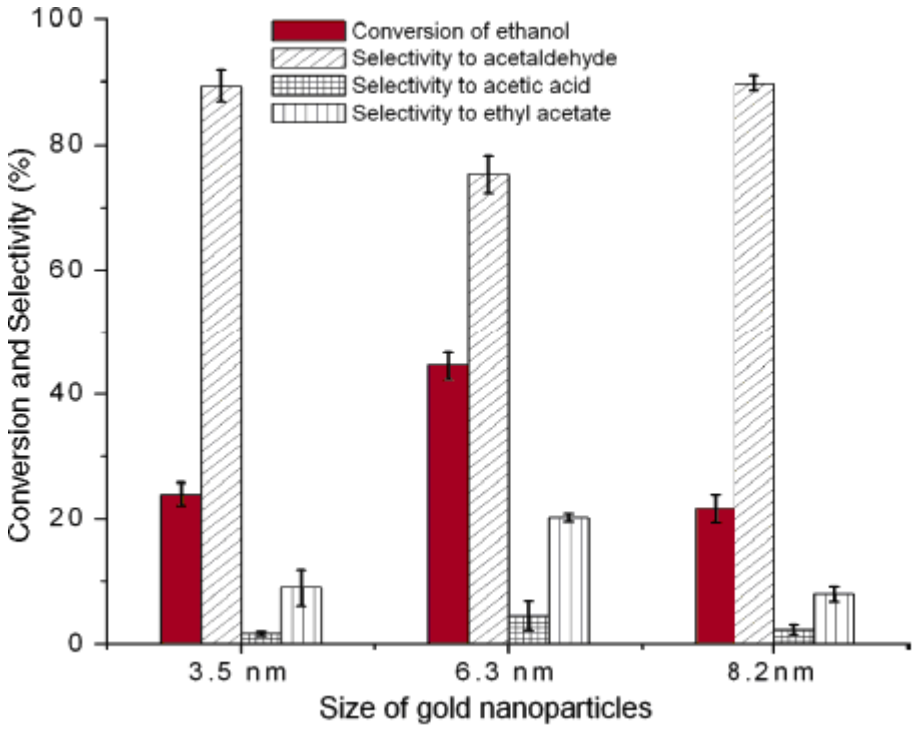

Figure 2.5: Different gold particles size supported on SiO_2, and their ethanol conversions [54].

The catalytic study of three catalysts with different Au particle size, showed that the smallest gold nanoparticles (3.5 nm) did not exhibit as high a catalytic activity as 6.3 nm gold nanoparticles (45% EtOH conversion). Both 3.5 and 8.2 nm nanoparticles showed lower ethanol conversions of 24% and 22% respectively [54]. Sun *et al.* [52] also reported the effect of gold particle size on ethanol oxidation using gold on silica prepared by immobilization of metal sol. The results of the study showed that, gold particles with an average diameter of 5 nm had a high activity for ethanol oxidation, about 3 times higher than that of smaller (3 nm), and 15 times higher than that of larger (10-30 nm) gold particles.

2.8.3 Effect of a base in alcohol oxidation

The oxidation of alcohols to acids and aldehydes using gold catalysts has been one of the success stories in gold catalysis, following the seminal studies of Prati and Rossi [39, 40, 60]. It has been shown that heterogeneous ceria supported gold catalysts are able to oxidize several higher alcohols to their corresponding carboxylic acids using air as an oxidant [7]. Prati and Rossi were the first to show that alcohols, specifically diols and sugars can be oxidized to the corresponding acids with gold catalysts but only when base is present [39, 40]. A similar observation was also reported by Carretin *et al*. where 100% selectivity of sodium glycerate was observed in glycerol oxidation reaction when the reaction was carried out with an addition of NaOH [61]. In the absence of NaOH, no glycerol conversion was observed. The presence of a base is essential for some reaction to take place in alcohol oxidation, for example as shown in Figure 2.6 addition of 10% KOH promoted the oxidation of benzyl alcohol to methyl benzoate [45].

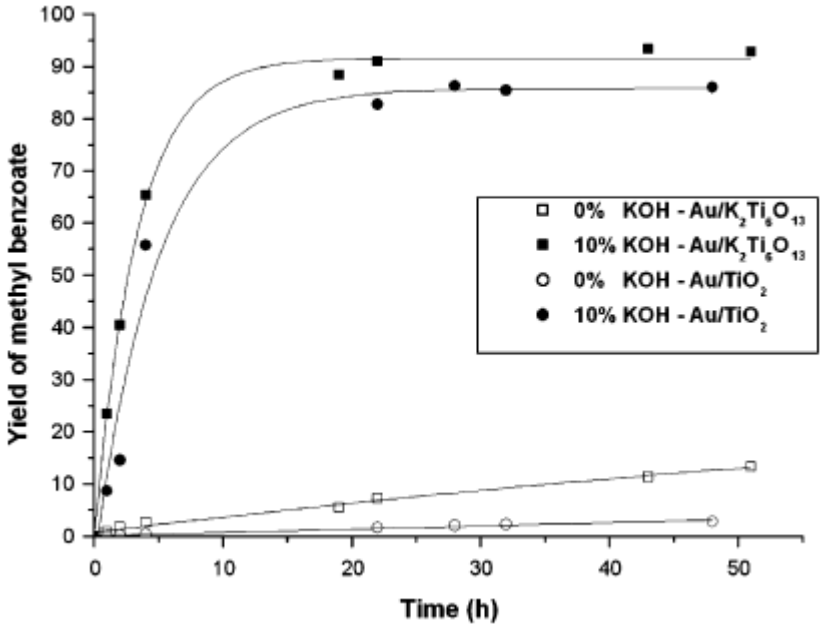

Figure 2.6: The effect of a base added in alcohol oxidation reaction [45].

The presence of small amount of base (KOH) promoted the reaction to give a higher yield of methyl benzoate. Less then 5% yield of methyl benzoate was observed when the base (KOH) was not added, but when the base was added the yield exceeded 80% as shown in Figure 2.6. On the contrary it was noted that catalysts such as Au/Ga_3O_9 can also perform aerobic oxidation of alcohols at room temperature without a base being added [62].

The effect of having a base in alcohol oxidation is critical for some reactions to take place. Some reactions require a bit of a base to take place, while some do not need a base at all. For example, for the oxidation of ethanol to acetic acid, no base is required [4, 8, 61].

2.9. Gas phase oxidative dehydrogenation of ethanol

The vapour- phase oxidative dehydrogenation of ethanol has been considered as the most important process for the production of acetic acid and acetaldehyde, the process includes dehydrogenation of ethanol over copper-chromium supported catalyst, vanadium based catalysts etc. The majority of the known processes for preparing acetaldehyde from ethanol are generally incapable of producing acetic acid as co-product except by a sequential operation wherein the acetaldehyde formed by dehydrogenation is further oxidized to acetic acid in a separate reactor. This represents a significant limitation on the efficiency of acetic acid production using these processes. On the other hand, those ethanol dehydrogenation processes which are known to produce acetic acid and acetaldehyde directly from ethanol are generally either characterized by very low selectivities to acetic acid or are operated under conditions which are impractical in large scale application. For example U.S. Pat. No. 1,636,952 describes a process whereby a mixture of air and ethanol in a ratio of 14:1 (air: ethanol) is passed over a vanadium oxide catalyst resulting in the production of about 10% acetic acid and 70% acetaldehyde. Although the reaction produces both acetic acid and acetaldehyde at relatively high quantities, it does this by using an extremely high oxygen to ethanol mole ratio, which

results in the feed being diluted to a point where the energy requirements for pumping the resulting large volume of feed gas through the catalytic reactor becomes a serious problem which affects the overall process economics. Working with large volumes of gas feed which contains O_2 and a hydrocarbon is not an easy thing to handle, because it is often associated with explosions and fire. So oxidation of ethanol in aqueous phase reaction using gold supported catalysts overcomes the problem of the high energy requirements for pumping the large volume of feed gas required in these systems. In gold catalysis systems no large volumes of air are required for oxidation to take place; only a 1:1 mole ratio of ethanol to air is required for the reaction. The use of gold catalysts offers many advantages which include high alcohol conversions and selectivity to the required products based on the reaction conditions chosen.

2.10. References

1. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.*, **1987**, 16, 405.
2. Hashmi, A.S.K.; Hutchings, G.J. *Angew. Chem., Int. Ed.*, **2006**, 45, 7899
3. Edwards, P.P.; Thomas, J.M. *Angew. Chem., Int. Ed.*, **2007**, 46, 5480.
4. Mallat, T.; Baiker, A. *Chem. Rev.*, **2004**, 104, 3037.
5. Ishida, T.; Haruta, M. *Angew. Chem., Int. Ed.*, **2007,** 46, 7154.
6. Ebitani, K.; Motokura, K.; Mizugaki, T.; Kaneda, K. *Angew. Chem., Int. Ed.*, **2005**,44, 3423.
7. Abad, A.; Concepci´on, P.; Corma, A.; Garcia, H. *Angew. Chem., Int. Ed.*, **2005**, 44, 4066.
8. Christensen, C.H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.K.; Hansen, M.R.; Andersen, C.H.; Riisager, A. *Angew. Chem., Int. Ed.*, **2005**, 44, 4648.
9. Enache, D.I.; Edwards, J.I.; Landon, P.; Solsona-Espriu, B.; Carley, A.F.; Herzing, A.A.; Watanabe, M.; Kiely, C.J.; Knight, D.W.; Hutchings, G.J. *Science*, **2006**, 311, 362.
10. Hashmi, A.S.K.; Hutchings, G.J. *Angew. Chem., Int. Ed.*, **2006**, 45, 7896.
11. Klitgaard, S.K.; Egeblad, K.; Mentzel, U.V.; Popov, A.G.; Jensen, T.; Taarning, E.; Nielsen, I.S.; Christensen, C.H. *Green Chem.*, **2008**,10, 419.
12. Dimitratos, N.; Lopez-Sanchez, J.A.; Hutchings, G.J. *Top. Catal.*, **2009**, 52, 258.
13. Chang, J.; Leung, D.Y.C.; Wu, C.Z.; Yuan, Z.H. *Renewable and Sustainable Energy Reviews*, **2003**, 7, 453.
14. Dermibas, F.; Bozbas, K.; Balat, M. *Energy Explor Exploit.*, **2004**, 22, 355.
15. Wildenborg, T.; Lokhorst, A. Oil Gas Sci Technol Rev IFP, **2005**, 60, 513.
16. Rass-Hansen, J.; Falsig, H.; Jørgensen, B.; Christensen, C.H. *J. Chem. Technol. Biotechnol.*, **2007**, 82, 329.
17. Demirbas, A. *Energy Sources B*, **2006**, 1, 75.
18. Govindaswamy, S.; Vane, L.M. *Bioresource Technol.*, **2007**, 98, 677.
19. Balat, M.; Balat, H.; Öz, C. *Progress Energy Combust Sci.*, **2008**, 34, 551
20. Shapouri, H.; Duffield, J.A.; Wang, M. *Trans ASAE*, **2003,** 46, 959.

21. Hansen, A.C.; Zhang, Q.; Lyne, P.W.L. *Bioresouce Technol.*, **2005**, 96, 277.
22. Yoosin, S.; Sorapipatana, C. *Int J Sci Technol.*, **2007**, 12, 69.
23. Maclean, H.L.; Lave, L.B. *Prog Ener Combust Sci.*, **2003**, 29, 1.
24. Jacobson, M. Z.; Colella, W.G.; Golden, D.M. *Science*, **2005**, 308, 1901.
25. Yondela, N.; Kusano, S.; Yasui, M.; Pujado, P.; Wilcher, S. *Appl. Catal. A: Gen.*, **2001**, 221, 253.
26. Jones, J.H. *Platinum Metals Reviews*, **2000**, 44, 94.
27. Howard, M.J.; Jones, M.D.; Roberts, M.S.; Taylor, S.A. *Catal. Today*, **1993**, 18, 325.
28. Hundlucky, M. Oxidation in organic chemistry, American Chemical Society, Washington, DC, **1990**.
29. Christensen, C.H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.K.; Hansen, S.M.; Hansen, M.R.; Andersen, H.C. Riisager, A. *Angew. Chem. Int. Ed.*, **2006**, 45, 4648.
30. Abad, A.; Almela, C.; Corma, A.; Garcia, H. *Tetrahedrone*, **2006**, 62, 6666.
31. Carretin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Kiely; C.J.; Attard, G.A.; Hutchings, G.J. *Top. Catal.*, **2004**, 27, 131.
32. Biella, S.; Prati, L.; Rossi, M. *J. Catal.*, **2002**, 206, 242.
33. Besson, M.; Gallezot, P. *Catal. Today*, **2000**, 57, 127.
34. Pina, C.D.; Falletta, E.; Prati, L.; Rossi, M. *Chem. Soc. Rev.*, **2008**, 37, 2077.
35. Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.*, **2004**, 126, 10657.
36. Venema, F.R.; Peters, J.A.; van Bekkum, H.; Mol, J. *Catal.*, **1992**, 77, 75.
37. Sheng, P.Y.; Bowmaker, G.A.; Idriss, H. *Appl. Catal. A: Gen.*, **2004**, 261, 171.
38. Jørgensen, B.; Christiansen, S.E.; Thomsen, M.L.D.; Christensen, C.H. *J. Catal. A: Gen.*, **2007**, 251, 332.
39. Prati, L.; Rossi, M. *J. Catal. A: Gen.*, **1998**,176, 552.
40. Bianchi, C.; Porta, F.; Prati, L.; Rossi, M. *Top. Catal.*, **2000**, 13, 231.
41. Mirescu, A.; Berndt, H.; Martin, A.; Pruβe, U. *Appl. Catal. A: Gen.*, **2007**, 317, 204.

42. Tsunoyama, H.; Sakurai, H.; Negishi, Y.; Tsukuda, T. *J. Am. Chem. Soc.*, **2005**, 127, 9374.
43. Choudhary, V.R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B.S. *Green Chem.*, **2005**, 7, 768.
44. Hansen, T.W.; Hansen, P.L.; Dahl, S.; Jacobsen, C.J.H. *Catal. Lett.*, **2002**, 84, 7.
45. Klitgaard, S.K.; DeLa Riva, A.T.; Rebecka, S.H.; Werchmeister, M.; Christensen, C.H. *Catal. Lett.*, **2008**, 126, 213.
46. Bond, G.C.; Louis, C.; Thompson, D.T. *Catalysis by Gold*, Imperial College Press London, **2006**.
47. Russo, N.; Fino, D.; Saracco, G.; Specchia, V. *Catal. Today*, **2006**, 117, 214.
48. Haruta, M. *CATTECH.* **2002**, 6, 102.
49. Campbell, C.T. *Science*, **2004**, 306, 234.
50. Haider, P.; Kimmerle, B.; Krumeich, F.; Kleist, W.; Grunwaldt, J.D.; Baiker, A. *Catal. Lett.*, **2008**, 125, 125.
51. Bianchi, C.; Porta, F.; Prati, L.; Rossi, M. *Top. Catal.*, **2000**, 3, 231.
52. Sun, K.Q.; Luo, S.W.; Xu, N.; Xu, B.Q. *Catal. Lett.*, **2008**, 124, 238.
53. Penkova, A.; Blanes, J.M.M; Cruz, S.A.; Centeno, M.A.; Hadjiivanov, K.; Odriozola, J.A. *J. MicroMeso.*, **2009**, 117, 530.
54. Zheng, N.; Stucky, G.D. *J. Am. Chem. Soc.*, **2006**, 128, 14278.
55. Su, F.Z.; Chen, M.; Wang, L.C.; Huang, X.S.; Liu, Y.M.; Cao, Y.; He, H.Y.; Fan, K.N. *Catal. Commun.*, **2008**, 9, 1027.
56. Grisel, R.; Weststrate, K.J.; Gluhoi, A.; Nieuwenhuys, B.E. *Gold Bull.*, **2002**, 35,39.
57. Remediakis, I.N.; Lopez, N.; Nørskov, J.K. *Appl. Catal. A: Gen.*, **2005**, 291, 13.
58. Bond, G.C.; Thompson, D.T. *Gold Bull.*, **2000**, 33, 41.
59. Zhu, B.L.; Angelici, R.J. *J. Am. Chem. Soc.*, **2006**, 128, 14460.
60. Dimitratos, N.; Porta, F.; Prati, L.; Villa, A. *Catal. Lett.*, **2005**, 99, 181.
61. Carretin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Kiely; C.J.; Hutchings, G.J. *Phys. Chem.*, **2003**, 5, 1329.
62. Su, F.Z.; Wang, L.C.; Huang, X.S.; Liu, Y.M.; Cao, Y.; He, H.Y.; Fan, K.N. *Angew. Chem., Int. Ed.*, **2008**, 47, 334.

Chapter 3

3. Experimental

3.1. Materials

The gold precursor $HAuCl_4.xH_2O$ was obtained from Next Chimica and contained 50.0 ± 0.5% by weight of gold. During the preparation of all catalysts, deionized water was used to prepare the solution of 2.54×10^{-1} M of $HAuCl_4$. Titanium oxide used was obtained from Degussa as 7711 P-25 with a reported surface area of 50 m^2/g and containing 80% of anatase and 20% of rutile. The zinc oxide used was obtained from Süd-Chemie as G72 D. The base, sodium carbonate, used to adjust the pH during the preparation of the catalysts was obtained from SAARCHEM. Nitric acid (32%) was obtained from MERCK chemicals. Sodium citrate that was used during the preparation of gold catalyst supported on carbon was obtained from SIGMA ALDRICH.

Activated carbon derived from coconut was obtained from SIGMA ALDRICH. Aluminium oxide (gamma phase) and silver nitrate were purchased from MERCK chemicals. Ethanol was of the highest purity (99.6%) from Fluka and was used without any further purification. The nitrogen and hydrogen gas used for reductive pre-treatment of the catalysts were obtained from AFROX. The reactant gases for oxidation reaction were obtained from AFROX i.e. air (20% oxygen balanced with nitrogen), and pure oxygen (99.9% oxygen). Ethanol was added to the reactor at the beginning of the reaction.

3.2. Preparation of catalysts

There are several methods actually available to prepare gold supported catalysts: coprecipitation [1], deposition-precipitation [2], chemical vapour deposition [3], impregnation of phosphine complexes [4] and the recently introduced immobilisation of gold sols [5-6]. However, the choice of the preparation method depends on the type of support material employed.

Deposition-precipitation (Dp) method is the most effective method for the preparation of gold supported on metal oxides. The advantage of using Dp in catalyst preparation is that, it offers good dispersion of gold on metal oxide. It has been shown that, Dp is not a suitable method for the preparation of gold supported on carbon. The most useful method that has been shown to be the best for preparing gold supported on carbon is immobilization of gold sols; this method provides good dispersion of gold metal on the carbon support [7]. When using this method the choice of protecting agent is paramount in order to get a good metal dispersion and particle size on the carbon [8]. The methods used for the preparation of the catalysts used in the study include inverse deposition precipitation, incipitient wetness impregnation and immobilization of the metal sol.

3.2.1 Inverse deposition-precipitation

The gold catalysts supported on metal oxide were prepared by inverse deposition-precipitation technique with intended gold loading of 1 wt.% with respect to material support. The catalysts prepared using this method includes Au/TiO_2, Au/Al_2O_3 and Au/ZnO. These three catalysts were supplied to us as standard by AuTEK. During the preparation of these catalysts, the standard conditions of the inverse deposition precipitation technique were used, which involve contacting 13.5 mL of gold containing solution per gram of support material. The concentration of gold present in the solution is varied depending on the loading required and the loading efficiency for a particular metal oxide at a specified pH value.

During catalyst preparation, 50g $_{Au/l}$ $HAuCl_4$ was added to the necessary amount of deionised water and heated to 70°C. The pH of the solution was altered to pH = 7.5 (Degussa, 7711 P25, TiO_2) and (Süd-Chemie, Al_2O_3) or pH = 8.5 (Süd-Chemie, G72D, ZnO), over a period of 10 minutes using a 0.5 M Na_2CO_3 solution. The gold bearing solution and catalyst support material were contacted for one hour at 70°C while the pH was kept constant using 0.5 M Na_2CO_3 and 2 M HNO_3. After the prescribed ageing time the material was filtered and washed using 5 mL/g $_{cat}$ of deionised water for five minutes. The material was then filtered with this procedure being repeated with fresh wash water a total of five times. The catalyst was then dried at 120 °C for a period of 16.5 h in a fan assisted oven.

A reductive pre-treatment was performed by passing 5% H_2 in N_2 over a packed bed of 500 g of catalyst at a flow of 525 SCCM and a temperature of 120 °C for a period of 1 h.

3.2.2 Gold on activated carbon

Gold supported on activated carbon was prepared by immobilizing gold sol as described below. An aqueous solution of gold chloride of 2.54×10^{-1} M was prepared. To this was added the solution of the protecting agent, sodium citrate (0.15 M $Na_3C_6H_5O_7.2H_2O$), while stirring vigorously. The molar ratio of gold to citrate was kept constant at 1:6 throughout the synthesis. Sodium citrate served both as protecting and reducing agent for the gold into metallic state. Immobilization of gold was carried out by simply adding carbon support to the metal dispersion while stirring vigorously until the solution was clear.

3.2.2.1 Gold sol preparation

The gold sols were synthesized by adding 2 mL of 2.54×10^{-1} M $HAuCl_4$ solution into 300 mL of distilled water contained in a beaker of LABMAX instrument. The temperature was raised up to 65 °C, and then allowed it to equilibrate for a few minutes. The pH of the solution inside beaker was 2.1. Then the solution of sodium citrate was added into the beaker, and the solution mixture was aged for an hour while stirring. The stirring rate was maintained constant throughout synthesis at 400 rpm. After an hour the solution changed from yellow to reddish-pink in colour. The pH was measured to be 5.8. The carbon support (about 10 g) was then added into the reddish-pink solution of gold nanoparticles. The solution was then aged for 30 minutes on stirring before immobilizing the gold nanoparticles on carbon. After the addition of activated carbon the pH increased to 6.5.

3.2.2.2 Sol immobilization

The gold sol was immobilised by simply dipping the carbon support in the reddish-pink solution that had a metal sol contained in a beaker of LABMAX instrument. After the addition of the carbon, the reddish-pink solution turned clear, implying that all the gold particles had already been adsorbed on the carbon. The catalyst was calculated to have a final gold loading of 1 wt.%.

The gold nanoparticles were immobilized by decreasing the pH of the solution from pH 6.5 to 3.7 using 2 M nitric acid. The solution mixture was aged for 10 minutes while stirring. The catalyst was then filtered and thoroughly washed with about 2 liters of distilled water adjusted to a pH of 4.1. The catalyst was dried overnight at 80 °C. A reductive pre-treatment was performed by passing 5% H_2 in N_2 over a packed bed of 10 g of catalyst at a flow of 100 SCCM and a temperature of 200 °C for a period of 90 minutes.

3.2.3 Incipient Wetness Impregnation Method

The calculated amount of metal salt (i.e. copper nitrate or silver nitrate) was dissolved in 20 mL distilled water and subsequently added drop-wise to 10 g of TiO_2 contained in a 500 mL beaker, while slowly stirring. The resulting slurry was placed under continuous stirring on a hot plate kept at room temperature for about an hour. The resulting mixture was dried at 120 °C overnight and then collected as dry powder. It was then calcined in a furnace at 400 °C for 16 h in the presence of air. The total concentration of loaded metal was about 1 wt.% with respect to support material.

3.3. Feed preparation (5 wt. % ethanol)

The selective oxidation of alcohols is fundamentally important in the chemical industry, and it has recently attracted significant attention to researchers around the world [9]. In particular, ethanol is considered to be a promising renewable resource for replacing decreasing petrochemical reserves. As mentioned in chapter two, ethanol can be produced from biomass via fermentation with possible applications as alternative fuels, solvents, fuel cells and as a feedstock for producing bulk chemicals via selective oxidation [10].

The feed was prepared by diluting concentrated ethanol (99.6 wt.%) with distilled water up to 5 wt.% ethanol (i.e. 5mL ethanol + 95 mL water). Typically bioethanol contains about 8-10% ethanol [11]. It has been reported in the literature that at low ethanol concentration, acetic acid is favored as the main product for the reaction, while at high ethanol concentrations greater then 60 wt.%, ethyl acetate is formed as the main product [11].

3.4. Catalyst characterization

3.4.1 Surface area determination (BET).

This method was used to determine the specific surface areas and pore volumes of the catalyst samples. The measurements were done via isothermal adsorption of nitrogen at normal boiling point of liquid nitrogen. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method.

The analysis of the samples was performed on a TRISTA 3000 Micromeritics analyzer. The TRISTA 3000 is an automated gas adsorption analyzer which contains three ports, allowing the analysis of up to three samples simultaneously. It consists of the TRISTA analyzer and a FLOWPREP 060 Degasser.

The FLOWPREP 060 Degasser prepares samples for the adsorption analysis. It uses flowing gas passed over a heated sample to remove moisture and other contaminants. The degasser has six heating stations for degassing samples and six cooling stations. The desired temperature is set on the temperature controller pad located at the front of the instrument.

3.4.2 Powder X-ray Diffraction (PXRD)

The synthesized catalysts were analyzed using the PXRD to see whether gold was deposited on the catalysts. The PXRD gives the diffraction pattern of different elements in a particular region. The powder samples were loaded on the sample holder that has eight chambers for sample loading. This was performed on a D800 Brucker Powder X-ray diffractometer using Cu as a target.

3.4.3 High Resolution Transmission Electron Microscope (HRTEM)

The gold particles size distribution on the catalysts was determined using a TECH NEI NOVA SPIRIT Transmission Electron Microscope operating at a voltage of 120 kV. The powdered samples were ground and mixed with methanol and placed for few minutes in a sonicator for thoroughly mixing. A drop of sample was then placed on a copper grid and allowed to dry for a few minutes, and then the copper grid was mounted onto the probe of the microscope. The micrographs were then taken and recorded.

3.4.4 Inductively Coupled Plasma (ICP)

In this method, the determination of trace concentrations of elements in a sample was achieved using atomic emission spectroscopy (AES). The atomic spectroscopy method is based on the measurement of the amount of electromagnetic radiation absorbed or emitted by an analyte atom to determine the concentration of the sample. The liquid products were analyzed using the ICP to investigate the leaching of gold from the catalyst.

3.5. Catalysts evaluation for ethanol oxidation

3.5.1 Catalytic activity measurements

The experiment was conducted in 75 mL stainless steel autoclave reactor (Figure 3.1) which was made by the "*Institute for Industrial and Macromolecular Chemistry research,*" in Aachen University (Germany) which is the inhouse workshop of the Institute.

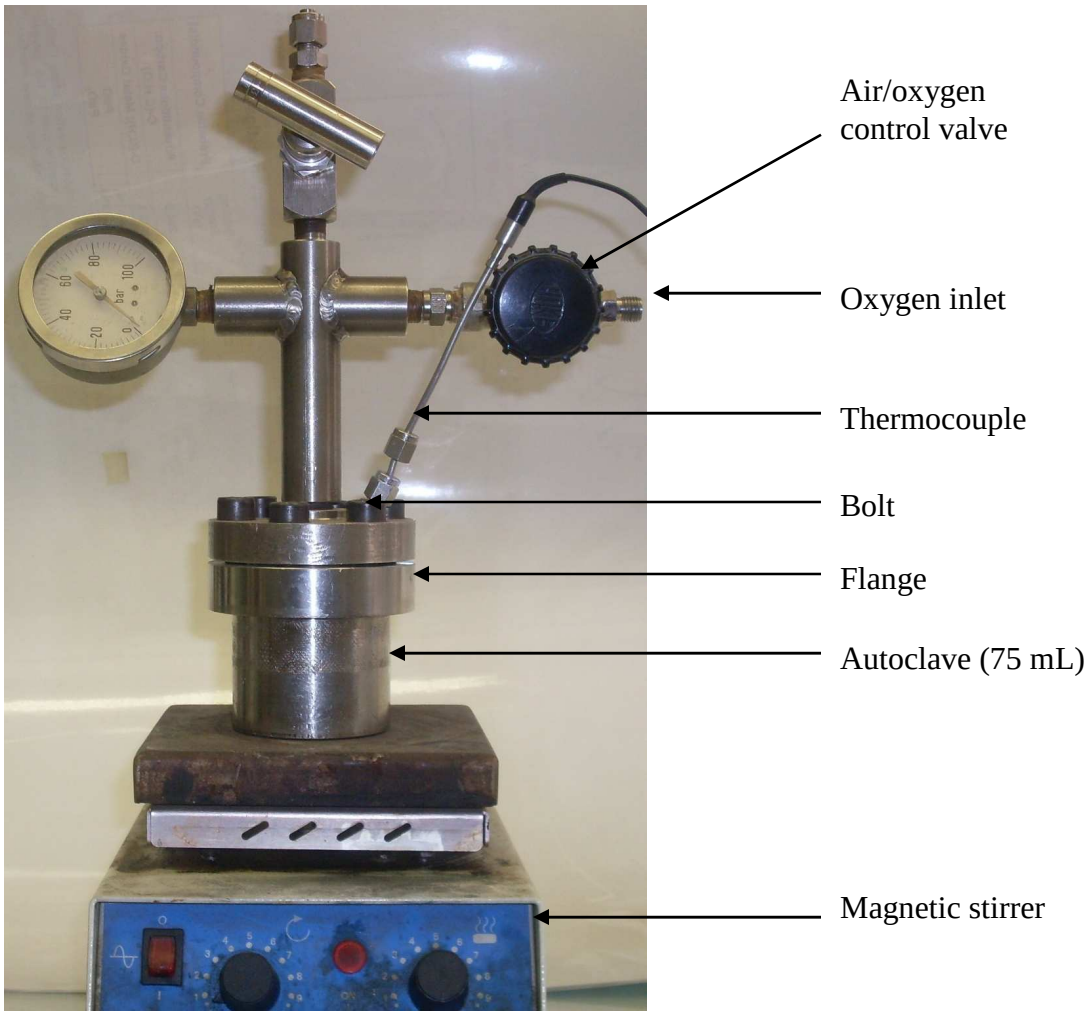

Figure 3.1: Picture of autoclave used for ethanol oxidation

The magnetic stirrer was only used for stirring the liquid mixture inside the autoclave not for heating purposes. The autoclave was surrounded by a heating coil jacket, which was then connected to a temperature controller together with a thermocouple to control the inside temperature of the autoclave.

The autoclave was charged with 10 mL of aqueous ethanol of desired concentration ranging from 5-40 wt.% ethanol diluted with water, and 150 mg of the catalyst. It was then closed and charged with technical air (80 vol% N_2, 20 vol% O_2) at the required pressure of 30 bar. The autoclave was then heated to the desired reaction temperature of 150 °C under stirring conditions for a required reaction time (5-25 h). It was noticed that after the autoclave was heated to150 °C the pressure inside the autoclave went to 48 bar and this was due to partial pressure of air, water and ethanol at 150 °C in the autoclave. The stirring rate was kept constant at for all reactions. After each reaction, the autoclave was cooled with an ice-water mixture to a temperature below 5 °C, to ensure that the volatile products such as acetaldehyde do not escape before analysis. At the end of each run, the liquid reaction mixture was separated from the catalyst by centrifuge, and then analyzed using a gas chromatograph equipped with a Carbowax column (2m × 2mm I.D. glass) and FID detector. At the end of reaction the autoclave was depressurized, and the gas from autoclave was collected with a gas collector for analysis using a gas chromatograph equipped with a TCD detector. This was done to check for the presence of gaseous products from the reaction, for example CO_2.

To investigate the effect of excess O_2 in the reaction, the autoclave was charged with 30 bar air, and then the reaction was allowed to run until all the O_2 had been used up. This was recognised by the constant conversion of ethanol after 20 h. After 20 h the autoclave was depressurized to atmospheric pressure and then recharged again with air to 30 bar and the reaction was performed for the required time; the products were then analysed.

Figure 3.2 shows a typical spectrum for liquid products obtained from FID gas chromatography (GC), after offline analysis of liquid mixture from the autoclave.

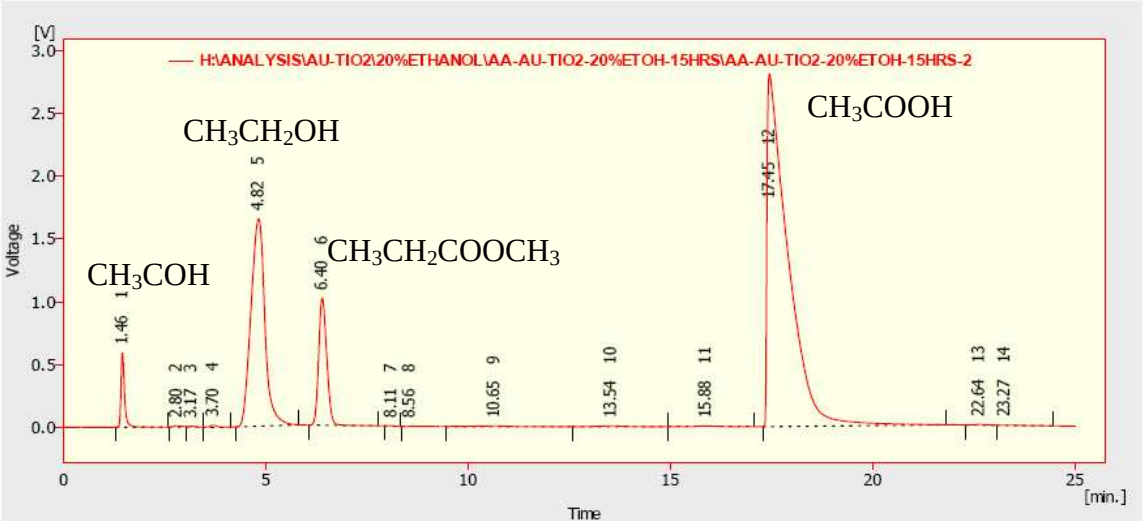

Figure 3.2: GC trace from ethanol oxidation

Figure 3.3 shows the schematic diagram of how all reactions were carried out in the study for the oxidation of ethanol.

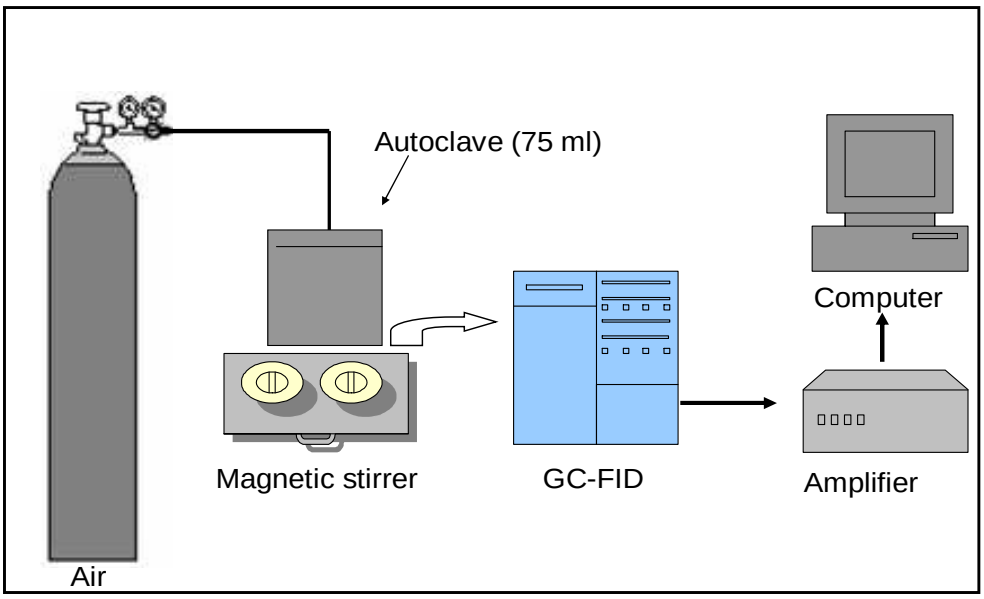

Figure 3.3: Schematic diagram of ethanol oxidation flow chart.

3.6. Calculations

a). % Ethanol conversion = $\frac{EtOH_{in} - EtOH_{out}}{EtOH_{in}} \times 100\ \%$

b). Selectivity (%) = $\frac{Product_{formed}}{EtOH\ conversion} \times 100\ \%$

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

Where:

$EtOH_{in}$ = peak area of ethanol for the inlet ethanol obtained from chromatogram

$EtOH_{out}$ = peak area of ethanol for the outlet ethanol obtained from chromatogram

M_{Au} = molecular weight of gold

M_{sup} = molecular weight of support

3.7. References

1. Hutchings, G.J. *Gold Bull*. **1996**, 29, 123.
2. Tsubota, S.; Cunningham, D.A.; Bando, Y.; Haruta, M. in: *Preparation of Catalysts VI*, Vol. 91, eds. Poncelet, G.; Martens, J.; Delmon, B.; Jacobs, P.A; Grange, P. **1995**, p. 227.
3. Okumura, M.; Nakamura, S.; Tsubota, S.; Nakamura, T.; Azuma, M.; Haruta, M. *Catal. Lett*. **1998**, 51, 53.
4. Kozlov, A.I.; Kozlova, A.P.; Liu, H.; Iwasawa, Y. *Appl. Catal.* A **1999**, 82, 9.
5. Grunwaldt, J.D.; Kiener, C.; Woegerbauer, C.; Baiker, A. *J. Catal.* **1999**,181, 223.
6. Prati, L. and Martra, G. *Gold Bull*. **1999**, 32, 105.
7. Bianchi, C.; Biella, S.; Gervasini, A.; Prati, L.; Rossi, M. *Catal. Lett*, **2003**, 85, 91.
8. Coluccia, S.; Martra, G.; Porta, F.; Prati, L.; Rossi, M. *Catal. Today*, **2000**, 61, 165.
9. Sheldon, R.A.; Arends, I.W.C.E.; ten Brink, G.J.; Dijksman, A. *Acc. Chem. Res*. **2002**, 35, 744.
10. Christensen, C.H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.K.; Hansen, S.M.; Hansen, M.R.; Andersen, H.C.; Riisager, A. *Angew.Chem. Int. Ed.* **2006**, 45, 4648.
11. Jørgensen, B.; Christiansen, S.E.; Thomsen, M.L.D.; Christensen, C.H. *J. Catal. A: Gen.* **2007**, 251, 332.

Chapter 4

4. Results and Discussion

Oxidation of ethanol to acetic acid using gold-based catalysts

4.1. Introduction

In this chapter we explain the results obtained on ethanol oxidation using gold-based catalysts, and show how the outstanding properties of nanogold can be used in new processes based on alcohol oxidation using molecular oxygen as oxidant. The catalytic properties of nanogold in the selective oxidation of organic compounds represent a recent but exciting contribution to the art of heterogeneous catalysis.

The selective oxidation of alcohols is one of the most important reactions in organic synthesis [1], and is applied on an industrial scale in the production of numerous base chemicals and down to laboratory scale in the production of various fine chemicals [2-4]. Recently, there has been a considerable interest on focusing on aerobic oxidation reactions of alcohols, using air or pure oxygen as the oxidant rather than using classical metal oxides as the oxidizing reagent. The use of conversional transition metal oxides and salts such as permanganate, chromate, bromate or other stoichiometric oxidants generates a high amount of toxic wastes [5] as mentioned earlier. Although these reagents are quite general in scope, they cannot be appropriate in “green” chemistry, because the oxidation reaction requires them in stoichiometric amount and they produce problematic by-products which are difficult to handle [6].

The main reason for this new approach for alcohol oxidation can be attributed to the low cost of oxygen and the fact that oxygen is a "green" oxidant leading to water as the only by-product. There is no doubt that from the "green" chemistry point of view molecular oxygen is an ideal oxidizing reagent for oxidation of alcohol, since water is the only by-product of the reaction (Eq. 4.1).

$$CH_3CH_2OH + O_2 \xrightarrow[\text{Aerobic oxidation of alcohols}]{\text{Supported catalysts}} CH_3COOH + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

Previous investigations on ethanol oxidation have focused on metals such as platinum [7, 8], ruthenium [9], palladium [10, 11] and molybdenum [12]. Recently there has been an increase in interest in gold catalysis which followed the two seminal discoveries of Haruta *et al.* [13] and Hutchings [14] in CO oxidation and acetylene hydro-chlorination respectively. It has been found that Au supported catalysts are selective and stable for oxidation of various alcohols to their corresponding aldehydes, acids and ketones [15-17].

The results presented in this chapter, are based on ethanol oxidation using gold catalysts supported on different metal oxide supports, ranging from acidic to basic oxide supports. The support materials used include TiO_2, ZnO, Al_2O_3, $Au/MgAl_2O_4$ and activated C. Silver supported on titanium oxide was used to compare the catalytic activity of gold with other transition metal belonging to the same group. An $Au/MgAl_2O_4$ catalyst was used as the reference catalyst to start off with, as it was reported elsewhere to work very well for ethanol oxidation [15]. No detailed study was conducted on this catalyst.

4.2. Catalyst activity tests

The catalytic activity of different catalysts was conducted at 5 wt.% ethanol, and later in this chapter (section 4.8) the results showing the effect of ethanol concentration will be

presented. The metal loading of all catalysts was 1% by mass of support material. The reaction conditions were kept constant for all reactions, and the duration of the reaction was varied from 5-25 h in 5 hour intervals. The conversion of ethanol using each of these catalysts will be discussed under the subheadings below. Figure 4.1 presents the catalytic test results on ethanol oxidation using different catalysts at 150 °C and 30 bar pressure of air.

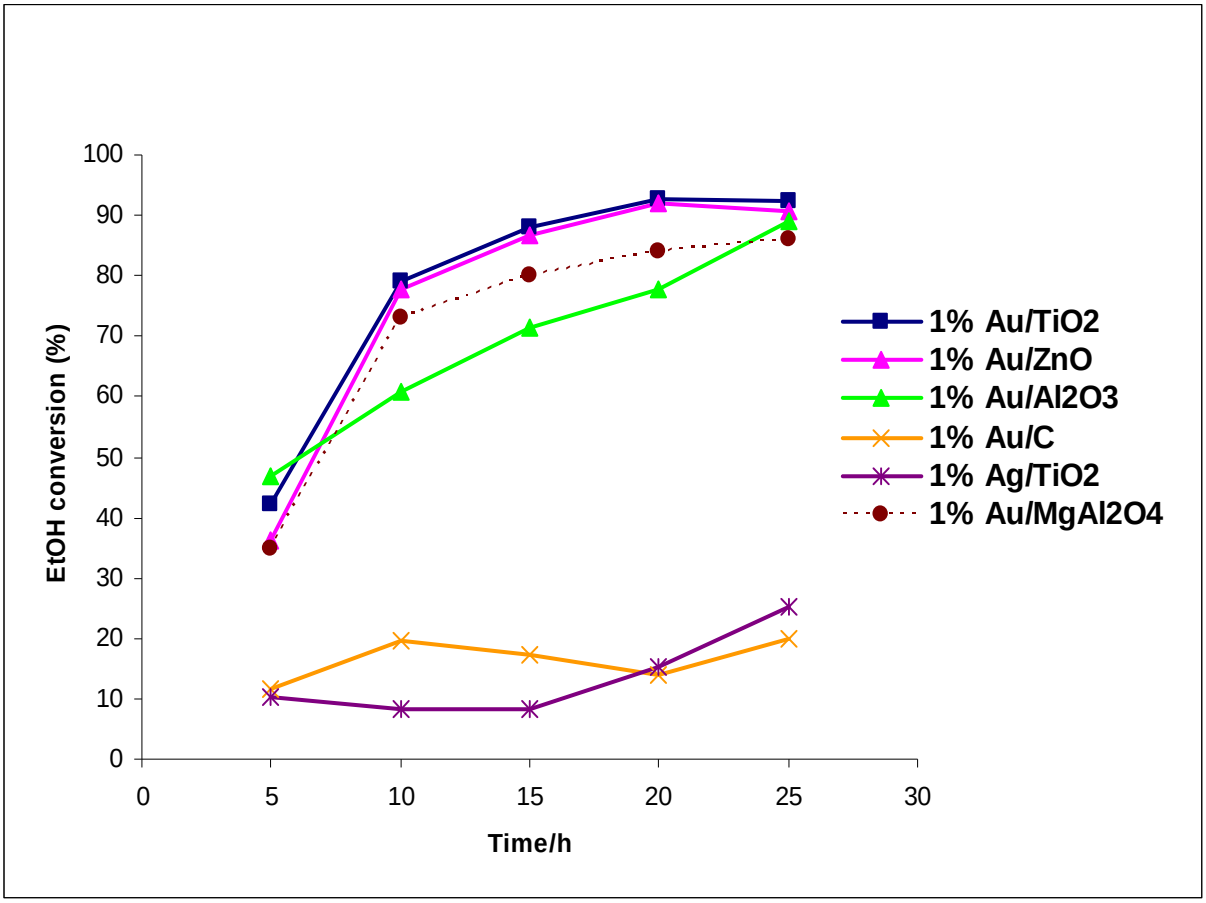

Figure 4.1: The conversion of ethanol with gold supported catalysts

4.2.1 The activity study of Au/TiO_2 and Au/ZnO

The study investigated the conversion of ethanol using gold metal supported on different metal oxide supports. The catalytic activity of different catalysts was plotted as a function

of reaction time. The result observed when gold was supported on titanium and zinc oxides showed a high activity towards ethanol oxidation as shown in Figure 4.1. An ethanol conversion of > 90% after 20 h was achieved without altering any reaction conditions. After 10 h about 80% of ethanol conversion was observed, and this ethanol conversion was also reported by Christensen *et al.* where 1% $Au/MgAl_2O_4$ was used as a catalyst [15]. Ethanol conversion of 93% was observed after 20 h when using 1% Au/TiO_2, and then it remained constant afterwards and this was attributed to insufficient of oxygen being present in the autoclave. Only about 7% of ethanol remained unreacted in the autoclave after 20 h. No other products were observed since the catalyst has an intrinsic selectivity to acetic acid after 20 h. The insufficient of oxygen was confirmed by calculating the number of moles of oxygen required to fully oxidize 10 mL ethanol present in the autoclave. The constant conversion of ethanol after 20 h was expected as the number of moles of oxygen calculated at 30 bar pressure of air was less than the number of moles of ethanol in 10 mL. In order to achieve 100% conversion of ethanol, an equal number of moles of ethanol and oxygen is required in the system. Since the overall reaction has the reactant mole ratio of 1:1 (Eq. 4.1) provided that the products are only acetic acid and water.

4.2.2 The activity study of Au/Al_2O_3

The catalytic activity behavior observed when gold was supported on aluminium oxide was a bit different from the other metal oxide supports. Ethanol conversion was observed to increase linearly with increasing reaction time as shown in Figure 4.1. This catalyst showed lower conversion of ethanol compared to other metal oxide catalysts (i.e. Au/TiO_2 and Au/ZnO) when reaction time was kept small i.e. < 25 h, but after 25 h ethanol conversion was almost the same for all the catalysts. The difference was insignificant.

4.2.3 The activity study of Au/C and Ag/TiO_2

The catalyst showed a poor activity towards ethanol oxidation, though it has been reported that this catalyst showed some good catalytic activity for the oxidation of glycerol to glycerate [18]. The corresponding selectivity of 100% to sodium glycerate was observed after 3 h when the catalyst was used [18]. Other examples where gold supported on carbon showed some good catalytic activity includes the higher selectivity (up to 97%) for the formation of 1, 2, 3, 5-tetramethylbenzene and 90% selectivity to epoxide [19]. The literature revealed that the catalyst is good for the oxidation of alcohol, but this was in contrast with our findings for ethanol oxidation. The conversion of ethanol observed when Au was supported on carbon was less then 20% after 25 h which was the lowest compared to the other catalysts used. The activity of Ag/TiO_2 was also tested for ethanol oxidation, and the results observed showed a poor activity with a corresponding conversions of < 30% after 25 h (Fig. 4.1).

4.3. Catalysts selectivity

The selectivity of the catalysts was calculated based on the mol of products i.e. acetic acid (AcOH), ethyl acetate (EtOAc) and acetaldehyde (AcH) in the liquid phase. The direct oxidation of ethanol to acetic acid resulted in other side products such as acetaldehyde and ethyl acetate. These chemicals are used by the chemical industry quite extensively as the starting material for the synthesis of fine chemicals, for example, acetaldehyde can be directly oxidized to acetic acid by the use molecular oxygen. Hence studying their selectivity would be of great interest for the future. The selectivity of each catalyst will be discussed under the subheadings below.

4.3.1 Selectivity of Au/TiO_2

The oxidation of ethanol using gold supported on titanium oxide showed a good selectivity of 97% to acetic acid after 20 h. When the reaction time was kept short (i.e. ≤ 5 h), it was noticed that the selectivity of 7% to acetaldehyde and 11% to ethyl acetate was achieved. It was noticed that as the reaction time increases the selectivity of the side products decreases to almost zero as shown in Figure 4.2 below, and this showed that all side products were oxidized into acetic acid with time. After 25 h the catalyst was highly selective to acetic acid.

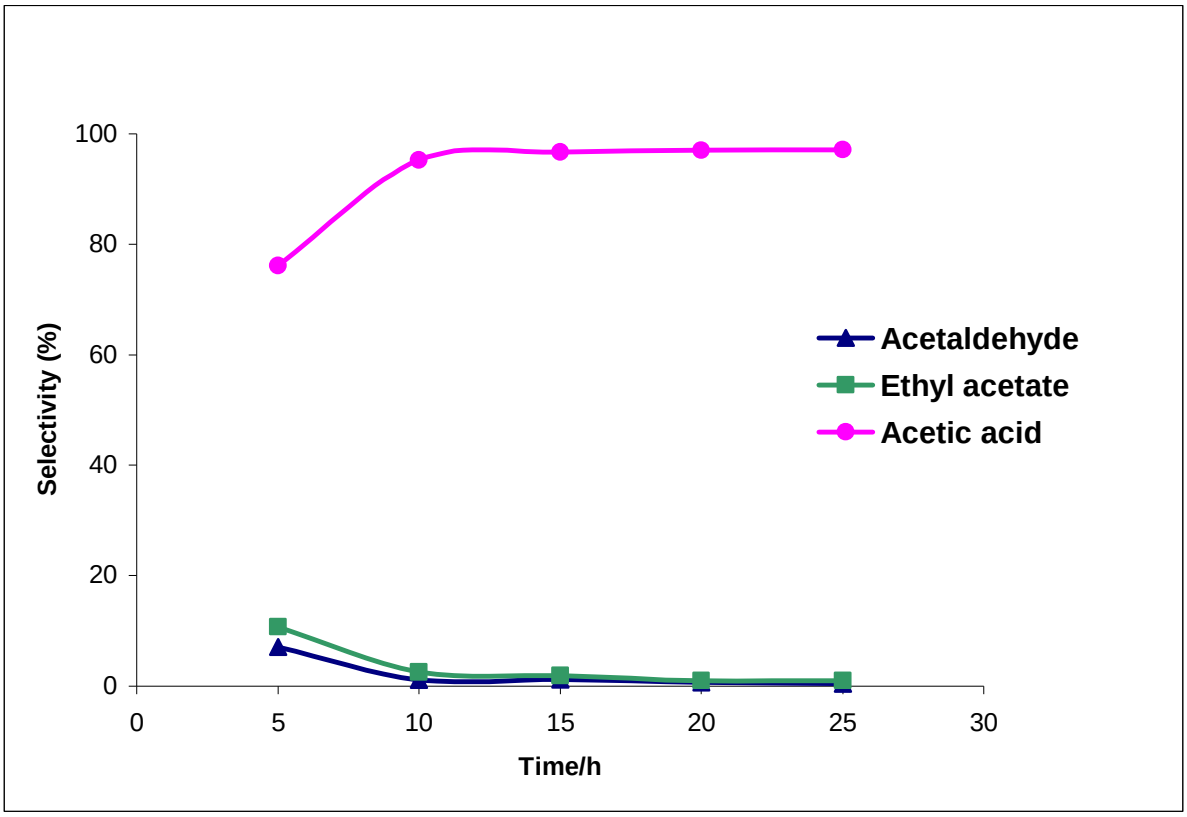

Figure 4.2: Selectivity of Au/TiO_2 on ethanol oxidation

4.3.2 Selectivity of Au/ZnO

Ethanol oxidation using gold supported on zinc oxide showed a good catalytic activity with a high selectivity to acetic acid. The selectivity to acetic acid of 96% was achieved after 20 h. The selectivity to acetaldehyde and ethyl acetate was observed when the reaction time was kept short, but as the reaction time increases their selectivity dropped to about < 1% as shown in Figure 4.3.

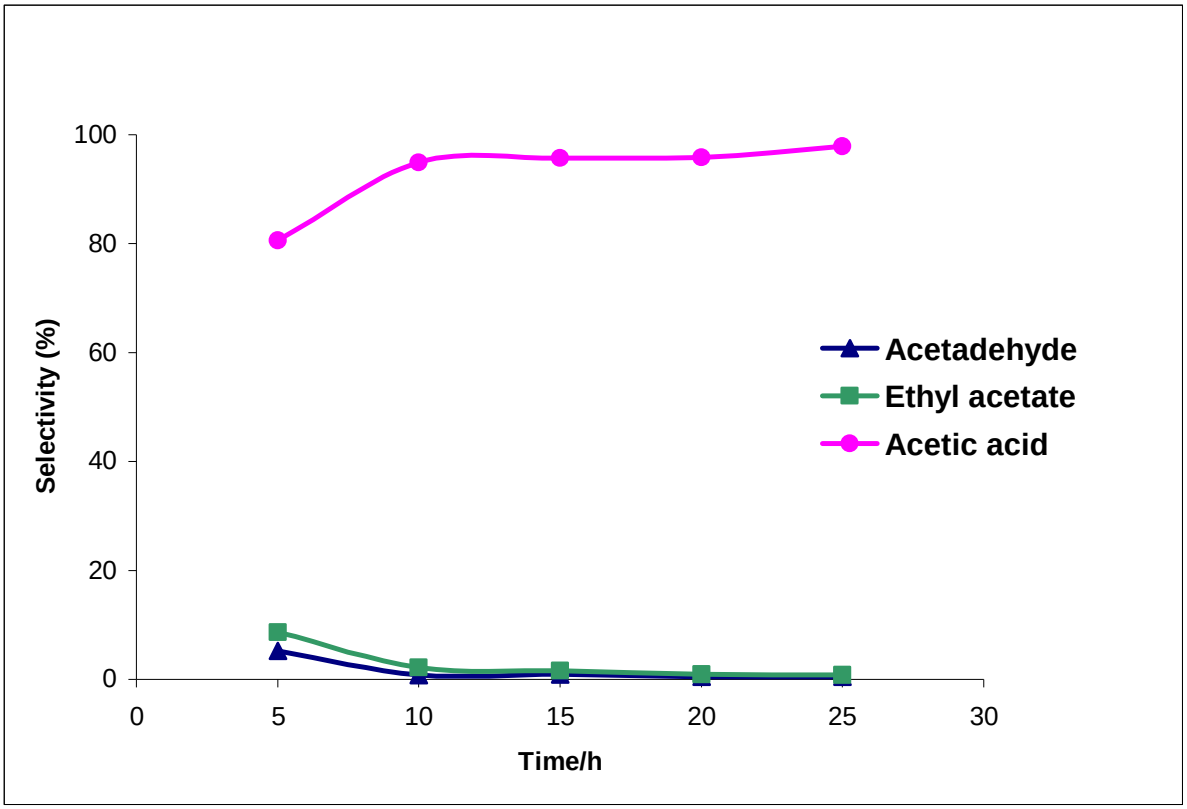

Figure 4.3: Selectivity of Au/ZnO on ethanol oxidation

4.3.3 Selectivity of Au/Al_2O_3

The oxidation of ethanol using gold supported on alumna, showed similar behavior to the other metal oxide supports. A selectivity to acetic acid of 81% was observed after 5 h, but as the reaction time increased the selectivity increased to about 95% after 25 h. All gold catalysts supported on basic metal oxides showed a good selectivity to acetic acid as compared with acidic oxides.

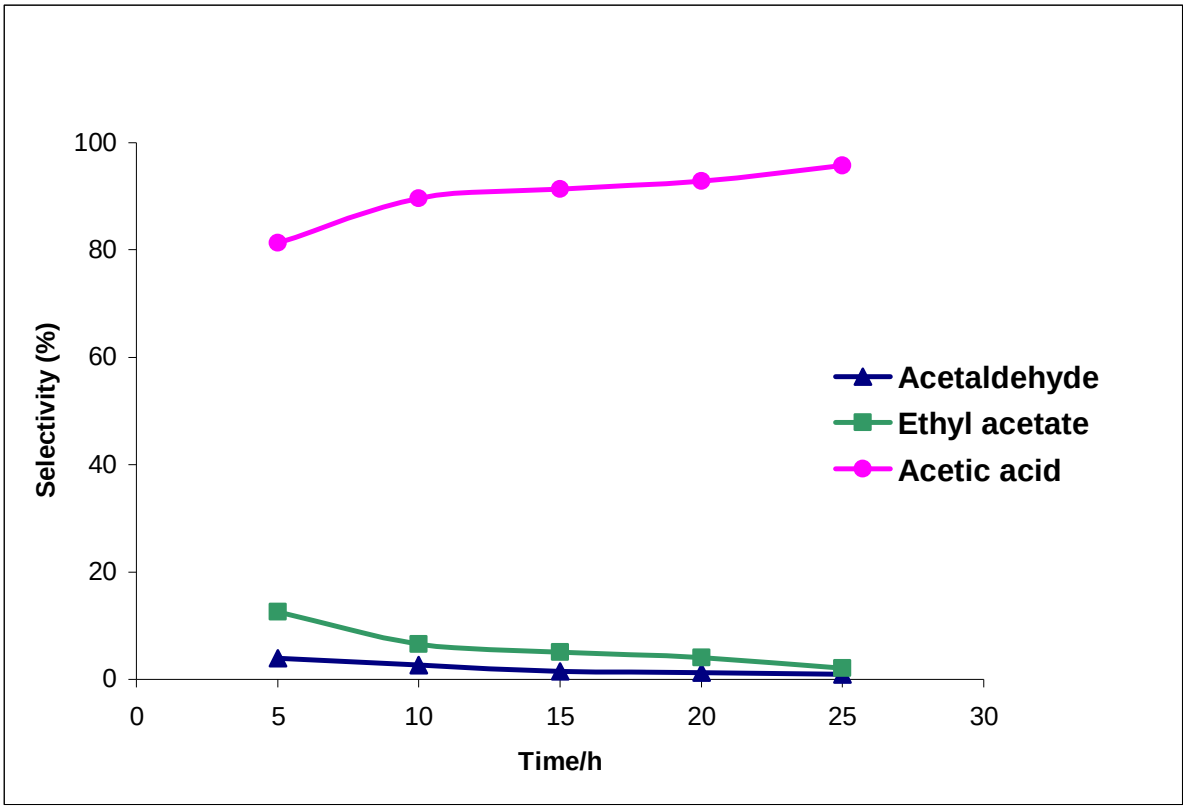

Figure 4.4: Selectivity of Au/Al_2O_3 on ethanol oxidation

4.3.4 Selectivity of Au/C

Gold supported on activated carbon showed a poor selectivity to acetic acid as the reaction time increases. A progressive increase of selectivity to acetic acid was observed from 5 - 20 h, thereafter was a suddenly drop of selectivity to acetic acid favoring the formation of ethyl acetate.

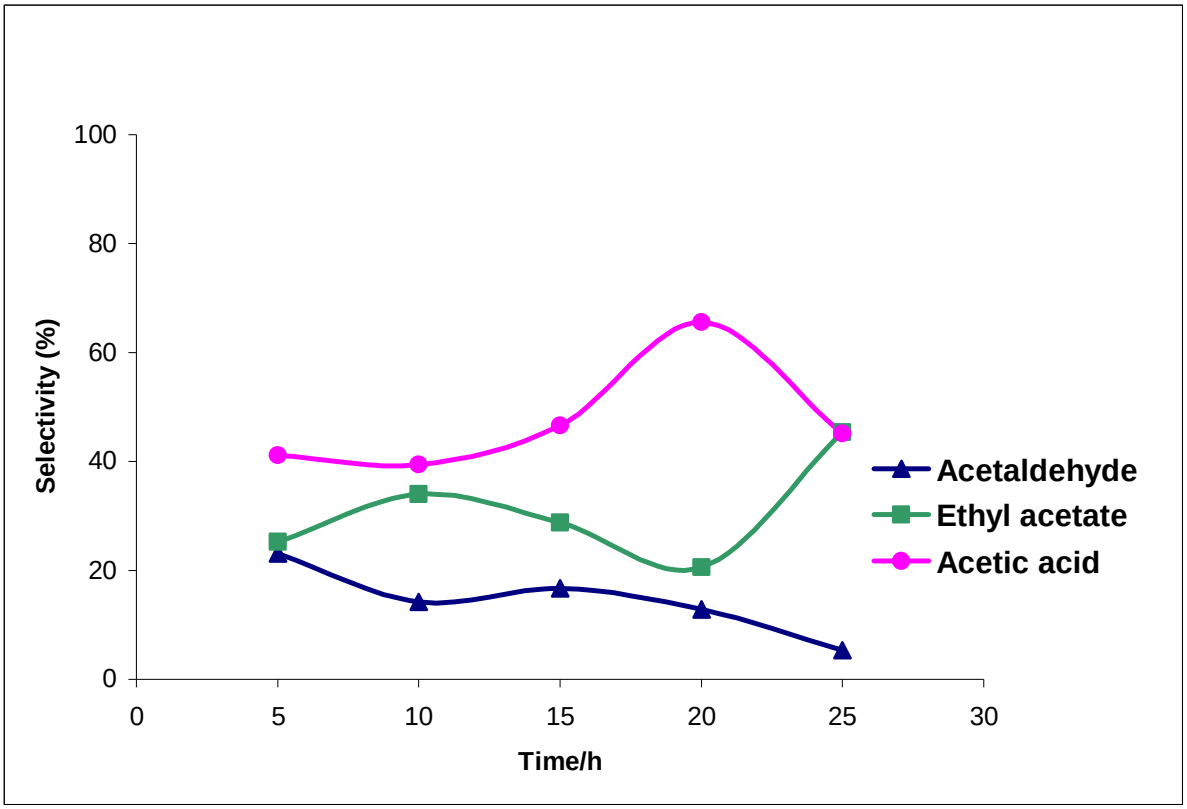

Figure 4.5: Selectivity of Au/C on ethanol oxidation

4.3.5 Selectivity of Ag/TiO_2

The selectivity of silver metal supported on titanium oxide was studied on ethanol oxidation. After 5 h the silver catalyst showed a selectivity of about 60% to acetic acid and it kept increasing up to 95% after 15 h, and then it drops after wards. The drop in selectivity was attributed to acetic acid reacting backwards with ethanol to form ethyl acetate. It was noticed that as the acetic acid selectivity drops, the ethyl acetate selectivity increases counter acting the drop in acetic acid.

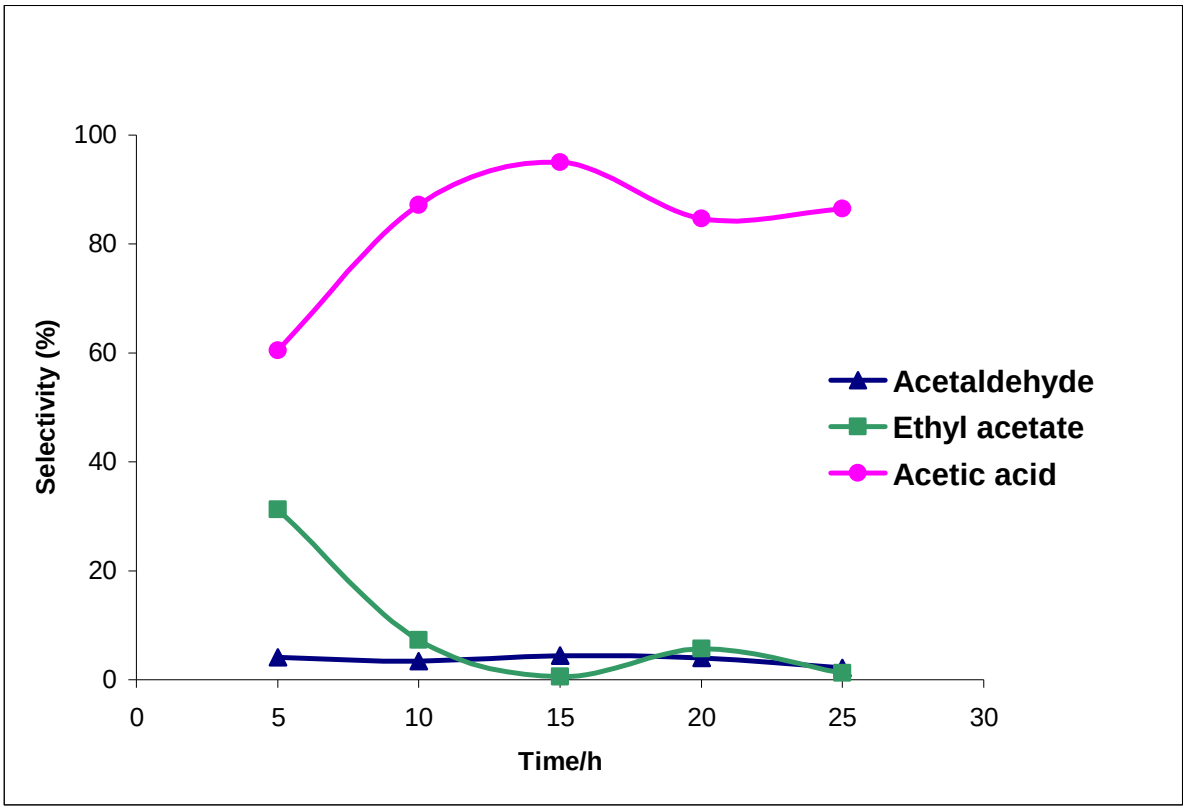

Figure 4.6: Selectivity of Ag/TiO_2 on ethanol oxidation

4.4. The yield of acetic acid produced

The yield of acetic acid was determined for all the catalysts used for ethanol oxidation. Gold catalysts supported on zinc and titanium oxides showed higher ethanol conversions and selectivity to acetic acid as discussed earlier. After 20 h about 89-90% yield of acetic acid was achieved when using Au/ZnO and Au/TiO_2. Other catalysts showed a good selectivity to acetic acid but poor yield, for example, Ag/TiO_2 had a selectivity of 60% after 5 h with corresponding yield of 6%.

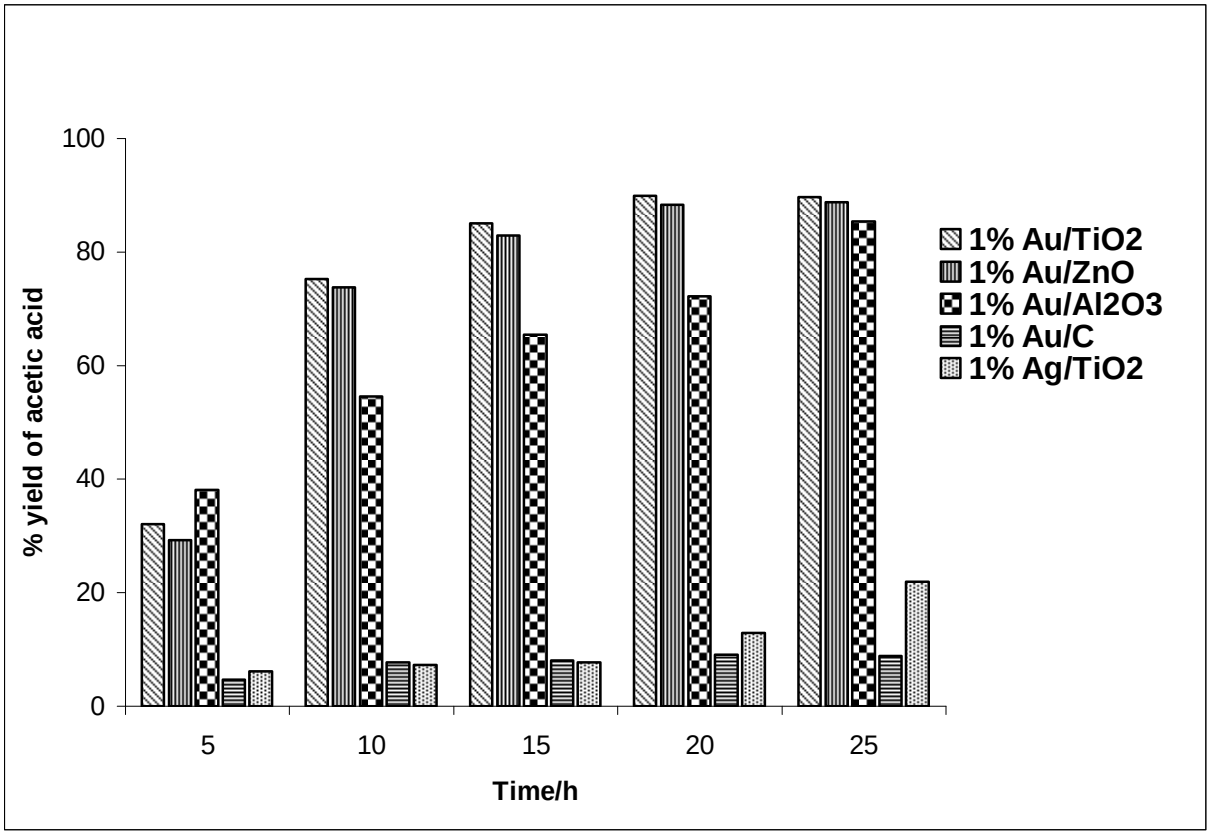

Figure 4.7: Percentage yield of acetic acid versus time using different catalysts

4.5. Comparison of catalysts selectivity to acetic acid, acetaldehyde and ethyl acetate using different catalysts

4.5.1 Acetic acid

It was very important to determine the selectivity of acetic acid in this study, as it was the product of interest. The selectivity order to acetic acid was arranged as follows, starting from highly selective one to a least selective catalyst.

Au/TiO_2 >Au/ZnO >Au/Al_2O_3 >Ag/TiO_2 >Au/C.

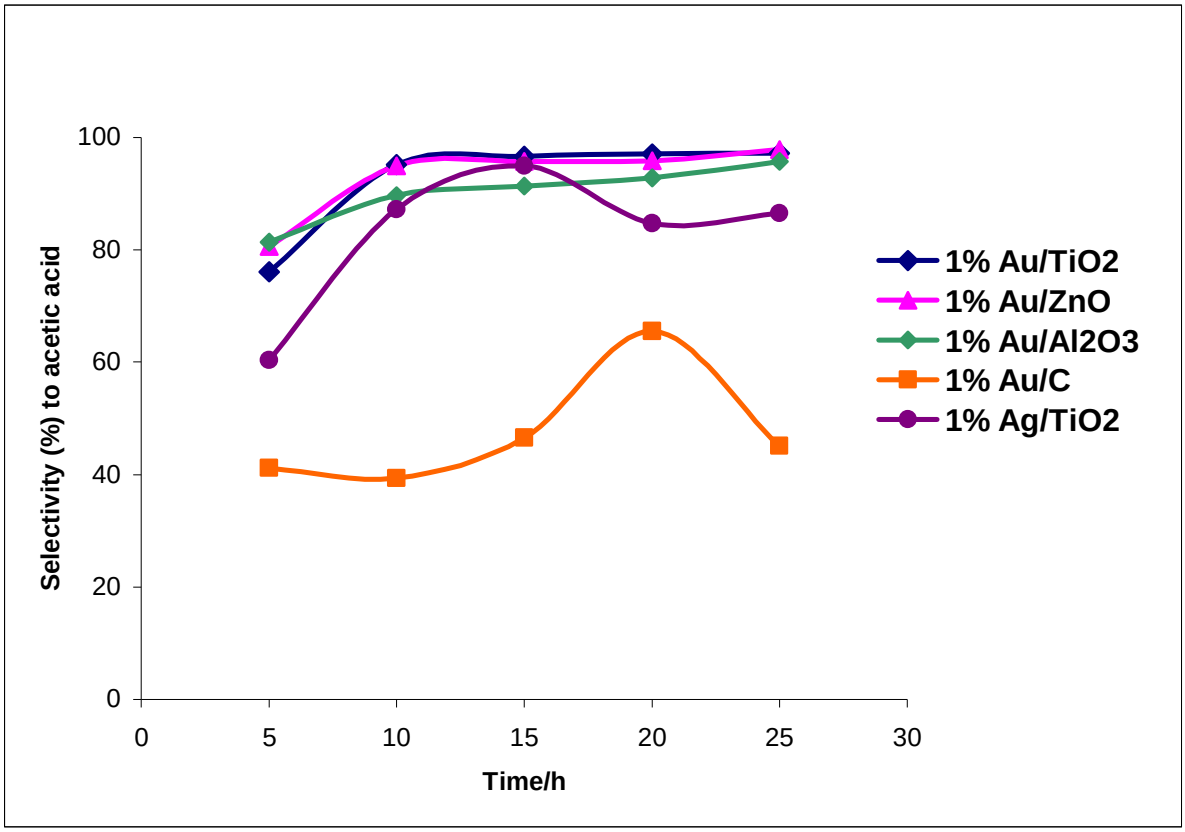

Figure 4.8: Comparison of selectivities to acetic acid

4.5.2 Acetaldehyde

Acetaldehyde was typically produced by partial oxidation of ethanol during the reaction. The catalyst that showed good selectivity to acetaldehyde formation was Au/C. After 5 h the selectivity of 23% to acetaldehyde was observed, and then it dropped to 5% with increasing reaction time to 25 h. The reason for the drop in selectivity was because with increasing reaction time all the acetaldehyde was full oxidized into acetic acid. Other catalysts showed a poor selectivity to acetaldehyde as shown in Figure 4.9.

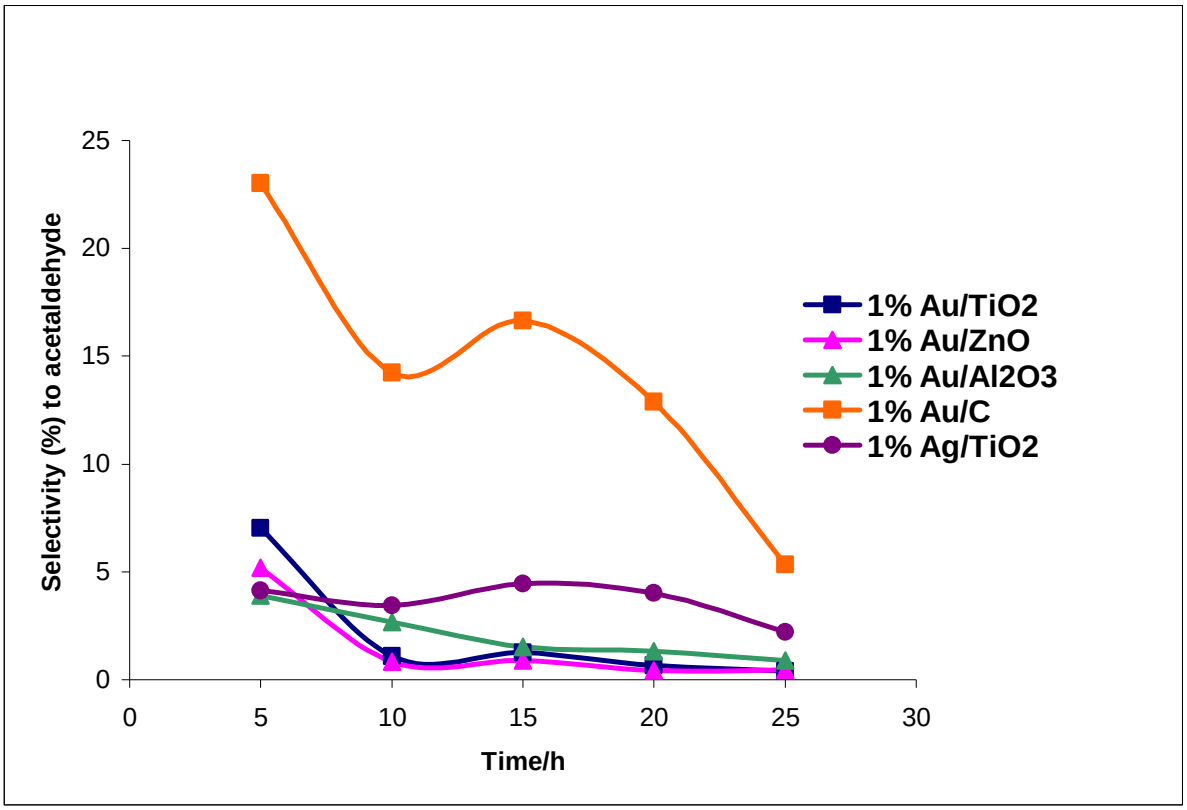

Figure 4.9: Comparison of selectivities to acetaldehyde

4.5.3 Ethyl acetate

Ethyl acetate was typically produced by esterfication of acetic acid during the reaction. This chemical has got a wide range of applications, for instance, in the paint industry and is also gaining the interest as the substitute for methyl ethyl ketone, for example, in the food industry [20]. In Figure 4.10, gold supported on activated carbon showed a selectivity of 45% to ethyl acetate after 25 h, while other gold supported catalysts showed poor selectivity to esters.

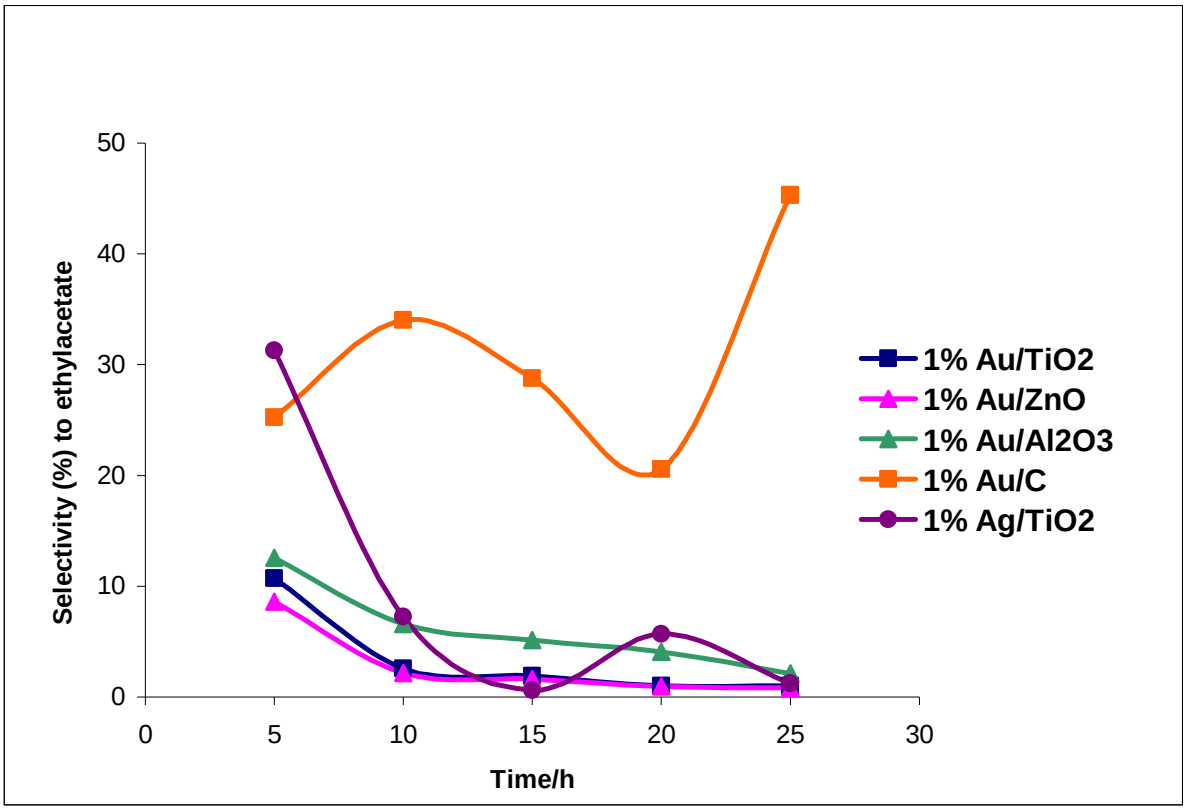

Figure 4.10: Comparison of selectivities to ethyl acetate

4.6. Products characterization

4.6.1 Inductively Coupled Plasma (ICP-AES).

All the products were characterized by ICP-AES at the end of each reaction in order to see whether gold leaching was taking place from the catalysts or not. Metal leaching in the catalysts might result in severe catalysts deactivation. It has been reported that oxidation catalysts, for example, the one based on platinum metals, may undergo irreversible deactivation due to modification of the catalyst structure by metal leaching, or reversible deactivation due to poisoning of the metal surface by strongly adsorbed species such as oxygen, impurities, products, or by-products [21]. It was therefore important to do a test for metal leaching in the study. Before metal leaching analysis was conducted on product samples with IPC-AES, the colour differences in the products was noticed as shown in Figure 4.11.

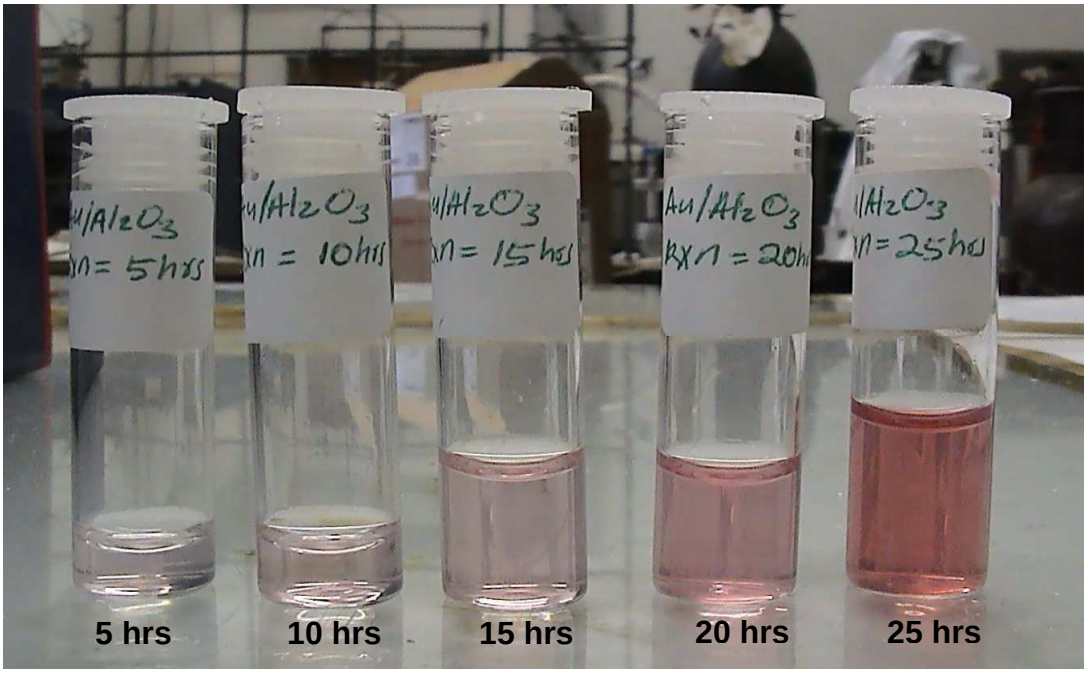

Figure 4.11: The colour of product from Au/Al_2O_3 reaction.

The results obtained from ICP-AES showed that indeed there was gold leaching on the alumina support (Au/Al_2O_3). The concentration of gold in the product was determined by ICP-AES and results for all catalysts are shown in Figure 4.12 below. The ICP-AES results revealed that the concentration of gold in the product increased exponentially with increasing reaction time for the alumina support.

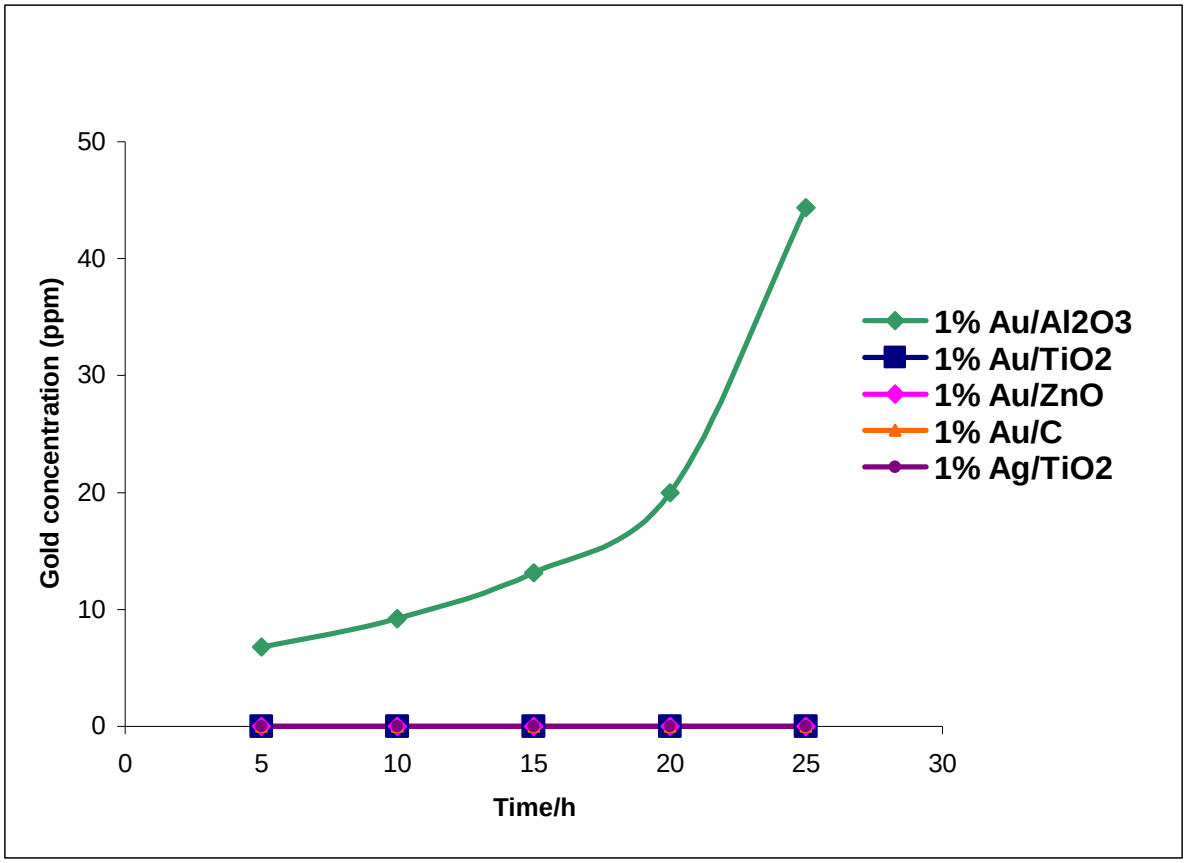

Figure 4.12: Gold leaching on alumina support at 5 wt.% ethanol.

The leaching of metals when gold is supported on alumina in aqueous phase oxidation was also reported in the literature. Mallat *et al.* [22] showed by XPS and ICP-AES measurements that there was a loss of platinum and bismuth after oxidation of L-sorbose on $Pt\text{-}Bi/Al_2O_3$ catalysts. No leaching of platinum or bismuth from Pd-Bi/C catalysts was observed in glucose oxidation carried out at basic pH [23], nor from Pt-Bi/C catalysts employed in the oxidation of glycerol even at slightly acidic pH [24]. The leaching of

metals when supported on alumina might be due to instability of alumina in the reaction medium. Our study also showed the leaching of gold on catalyst supported on alumina and this could also be attributed to instability of alumina in the reaction medium. Gold supported on other metal supports did not show any gold leaching by ICP-AES. All products were clear transparent solutions when using other catalysts. As an example, the products for Au/ZnO are shown in Figure 4.13 below.

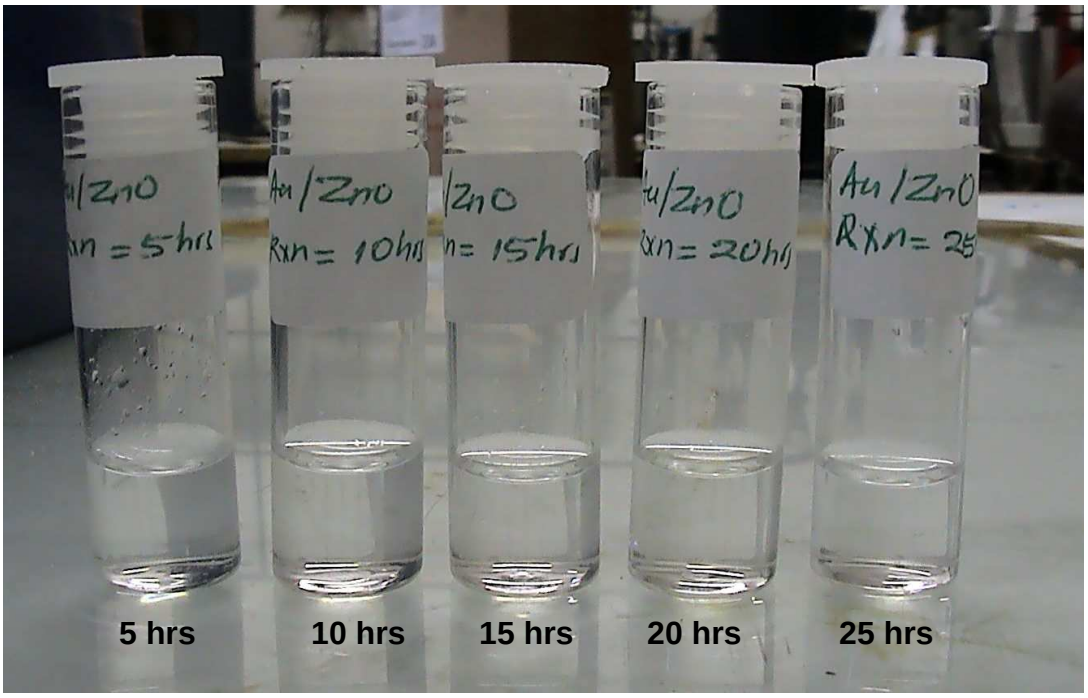

Figure 4.13: The colour of product from Au/ZnO[a].

[a] The colour of products from other catalysts was clear transparent solutions like in the case of Au/ZnO.

4.6.2 Products characterization using UV-vis spectrometry

The UV-visible spectrometry was used to determine whether there was aggregation of gold nanoparticles after leaching into solution (in Au/Al_2O_3 reaction). Gold nanoparticles have a tendency to aggregate in solution if they are not stabilized or protected. In order to protect gold nanoparticles from aggregation in solution, a capping agent is required which will stabilize them in solution and prevent them from coming together. In the present study no capping agent was used and so aggregation of gold could be expected following the leaching from the alumina support.

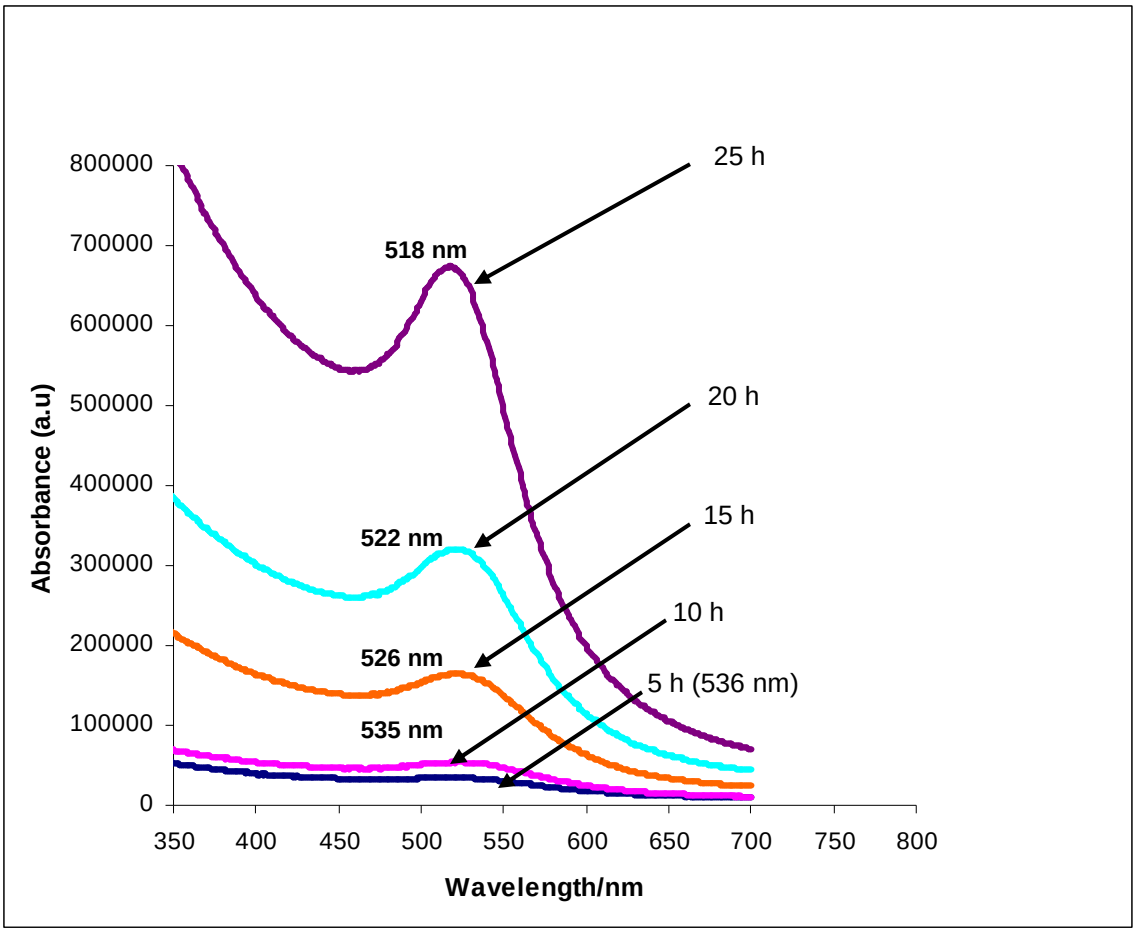

Figure 4.14: UV-vis spectra of product from Au/Al_2O_3 reactions[b].

[b] Reaction time in Figure 4.14 was varied from 5- 25 h to see the leaching effect.

The results from UV-vis showed something opposite from what was anticipated to happen. No aggregation of gold nanoparticles was observed on UV-vis results. The results showed that gold nanoparticles were decreasing in size as the reaction time increases (Figure 4.14). The UV-vis peaks shifted to low wavelengths with increasing reaction time indicating that there was a decrease in size of gold nanoparticles with increasing reaction time. If aggregation had taken place during the reaction, the peaks would be expected to shift to the far right with increasing reaction (leaching) time. The decrease in the size of gold nanoparticles with increasing reaction time could be attributed to the formation of acetic acid. As the concentration of acetic acid was increasing with increasing reaction time, it is believed that acetic acid stabilised the gold nanoparticles in solution, hence no aggregation of gold nanoparticles was observed during leaching.

4.7. Catalysts characterization

4.7.1 X-ray diffraction pattern of gold supported catalysts (1% Au loadings)

The X-ray diffraction patterns of Au catalysts supported on different metal oxides and the carbon support are shown in Figure 4.15 below. The diffraction lines due to gold are noticed at 2θ = 38.1, 44.2, 65.5, 77.5 and 81.4 and were only observed in one catalyst i.e. Au/C. No diffraction lines of gold were observed for the other Au supported catalysts, however this did not rule out the possibility that Au was present. The reason could be because the metal loading was very small below the detection limit of the instrument. Further characterization such as HRTEM was conducted to confirm the presence of gold in those catalysts for which XRD did not detect the presence of gold metal.

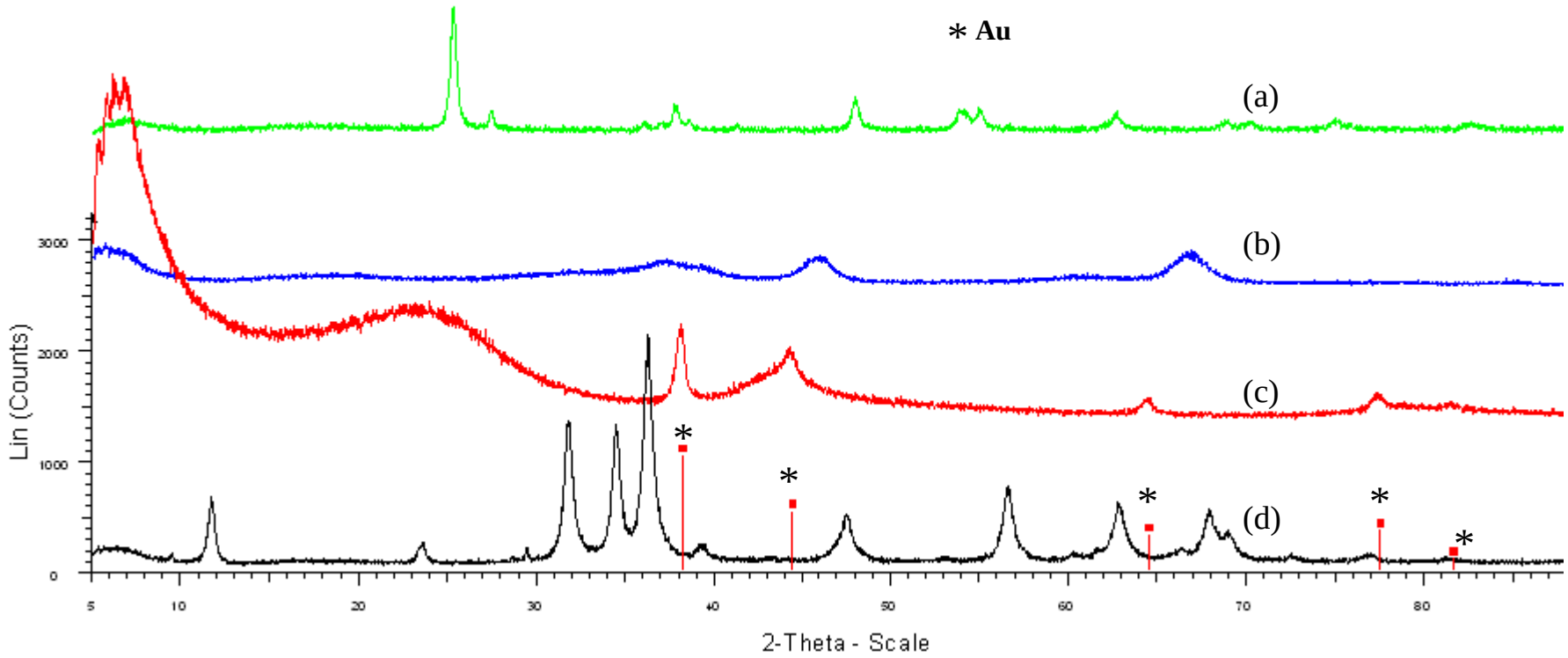

Figure 4.15: X-ray diffractograms of (a) Au/TiO_2, (b) Au/ZnO, (c) Au/C and (d) Au/Al_2O_3.[c]

[c] Diffractograms in figure 4.15 were off-set for clarity, vertical red lines represent powder diffraction pattern of gold.

4.7.2 High resolution transmission electron microscope (HRTEM)

The HRTEM studies of Au supported catalysts confirmed that indeed gold was present in all catalysts as shown in Figure 4.16.

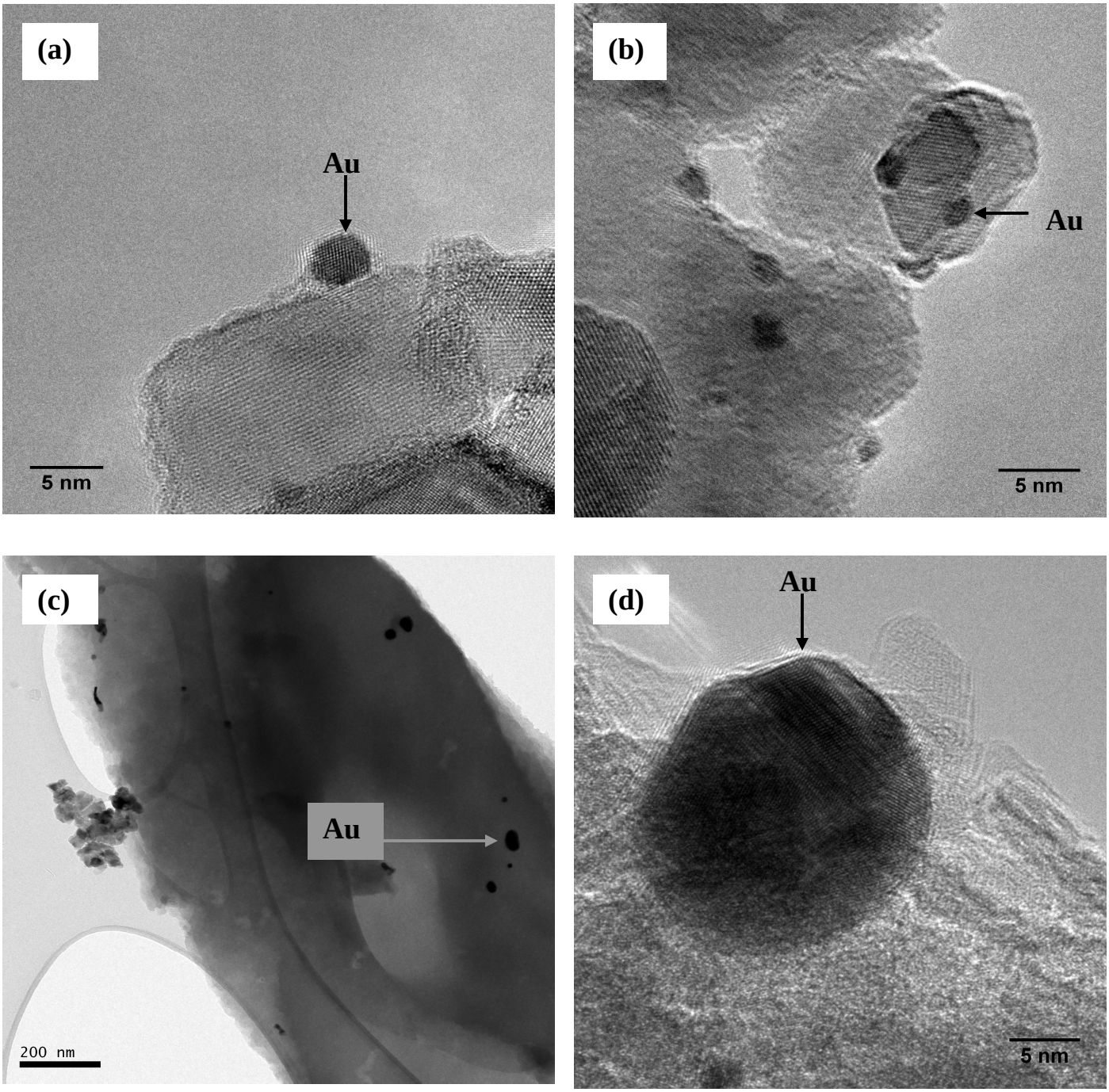

Figure 4.16: HRTEM images of (a) Au/TiO_2, (b) Au/ZnO, (c) Au/C and (d) Au/Al_2O_3

4.7.3 Energy dispersive X-ray spectroscopy (EDS)

EDS accompanied by HRTEM technique was used to confirm the presence of gold in all catalysts. Although the EDS spectra of all catalysts were not shown in this chapter but only one was shown as example of how the presence of gold was confirmed in all catalysts. The EDS spectrum of Au/Al_2O_3 is shown below in Figure 4.17.

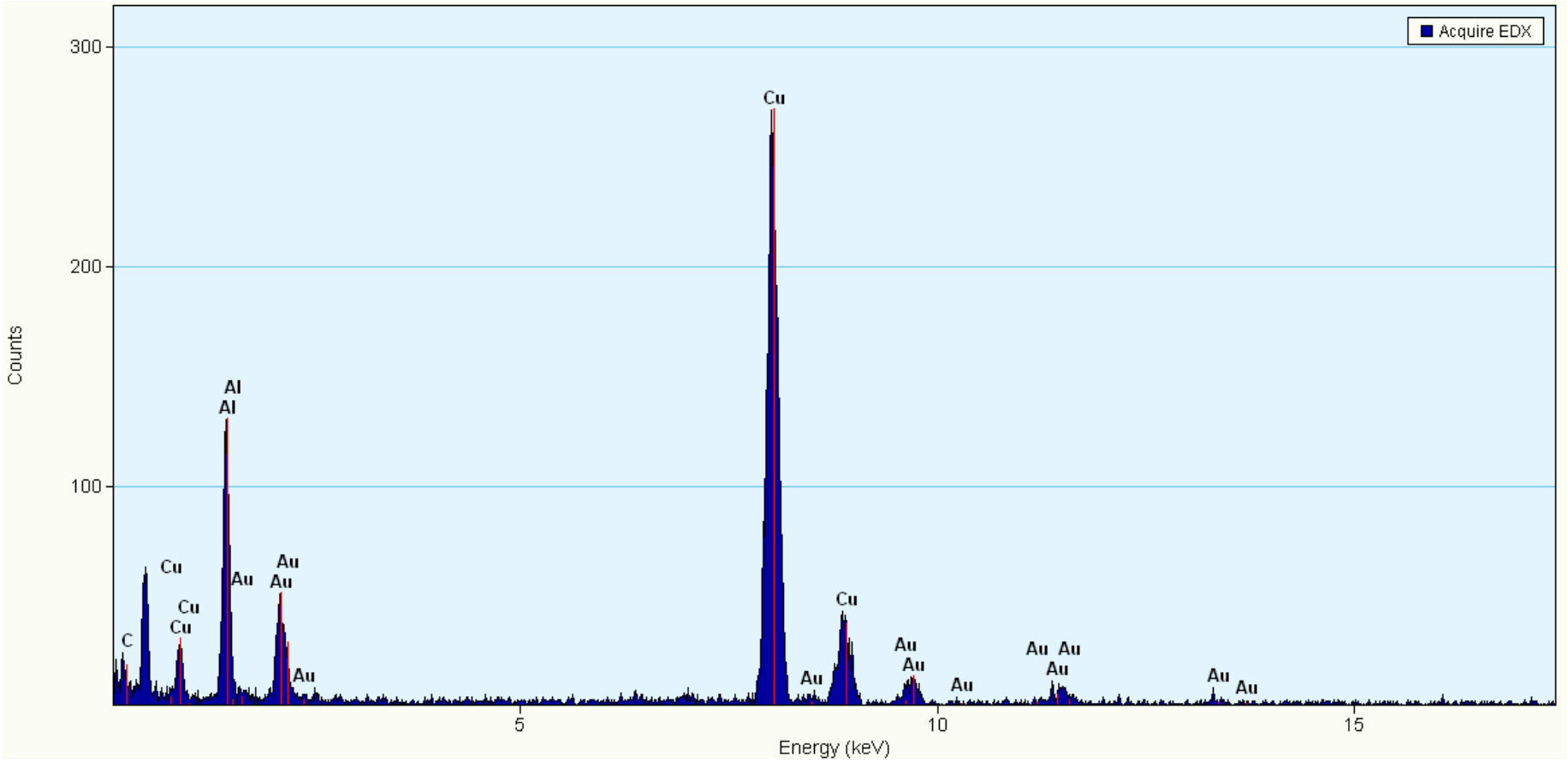

Figure 4.17: EDS spectrum of Au/Al_2O_3[d].

[d] Only Au/Al_2O_3 EDS spectrum was included in the dissertation not for all the catalysts

4.7.4 Gold particle size distribution

The gold particle size distribution was estimated from TEM images using image-j software. The particle size distribution of Au/TiO_2 and Au/ZnO was very narrow with the most of the particles being in the size range of 2 to 3 nm. Other catalysts showed a broad range of gold particle size distribution >10 nm.

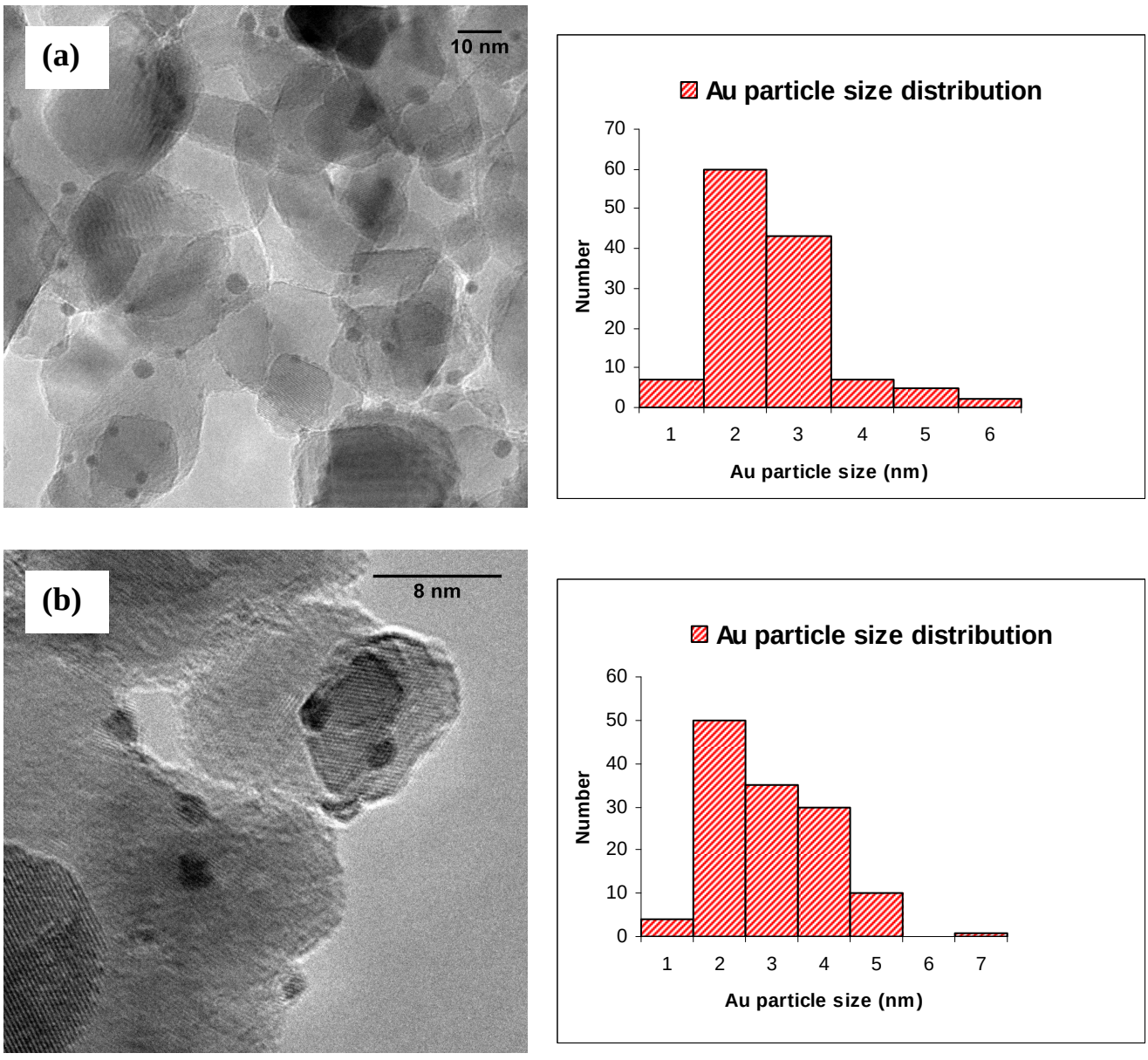

Figure 4.18: Gold particle size distribution on (a) Au/TiO_2 and (b) Au/ZnO

4.7.5 Gold on carbon support (Au/C)

Deposition-precipitation (Dp) is a highly favoured method for the preparation of highly dispersed gold nanoparticles on metal oxide supports such as TiO_2, ZnO and Al_2O_3, but unfortunately it fails with carbon, since it gives large aggregates of gold [25]. Dp is not suitable for loading gold on supports that have a zero point charge at low pH, for example C ~ 4 and SiO_2 ~ 2 [26]. Dp requires the adjustment of pH value within the range of 6~10, and at this pH the activated carbon behaves as negatively charged surface and gold species exists mostly as $Au(OH)_3$ which makes it difficult to adsorb the negatively charged gold on the negatively charged carbon surface. This is also applicable to hydrophobic supports such as WO_3 [27].

The nature of both gold and carbon makes the classical preparation routes unsuitable for obtaining well dispersed gold on carbon. Thus, the use of metallic sols as precursors has been demonstrated to be advantageous when preparing gold on carbon catalysts. This method has demonstrated a good dispersion of gold on carbon [26].

Herein, we present the gold metallic sols that were prepared using citrate as protecting agent, and were characterized by UV-vis before immobilizing them on carbon support. The UV-vis spectrum of the prepared gold metallic sols is shown in Figure 4.19.

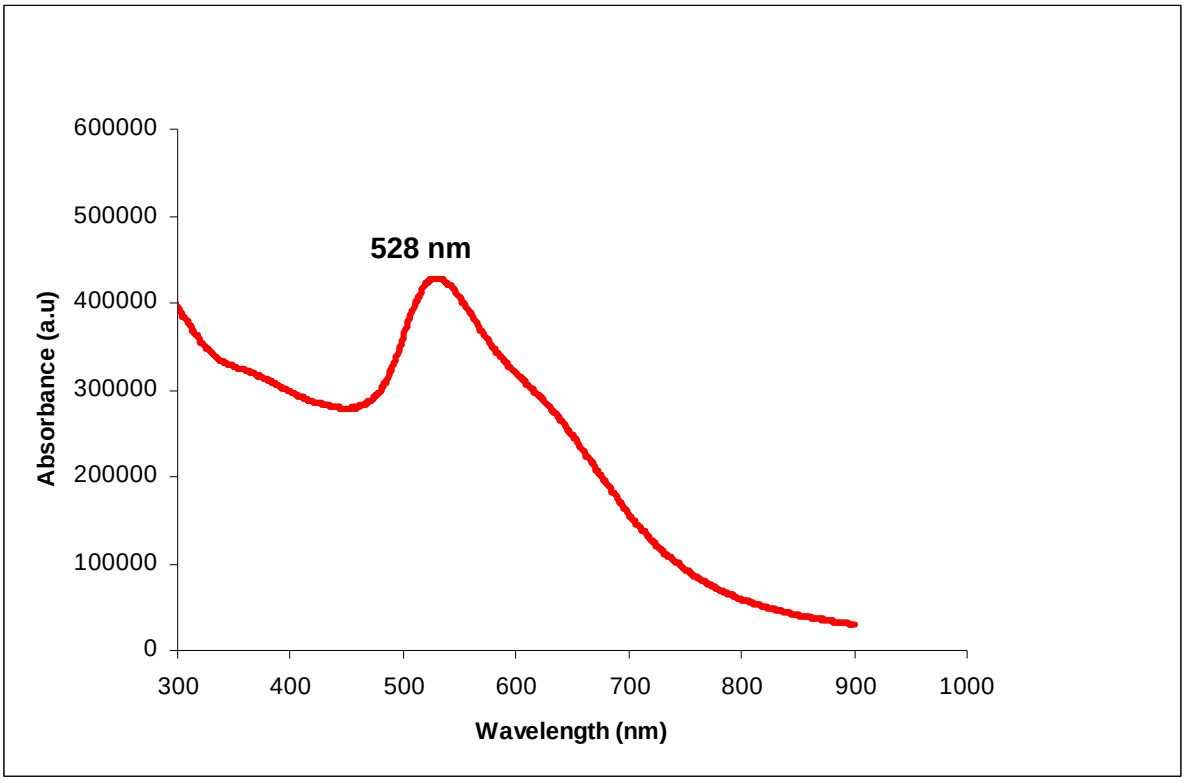

Figure 4.19: Gold nanoparticles protected by citrate ions.

The prepared gold nanoparticles showed absorption band at around 528 nm, and this indeed confirmed that gold nanoparticles were successfully synthesized by sol formation, which followed by immobilization of gold metallic sol on carbon support to form Au/C catalyst.

4.7.6 Surface area

The BET surface areas of the catalysts used in oxidation of ethanol in this study are reported in Table 4.1. The surface area of Au/TiO_2 was 44 m^2/g and this was the smallest surface area as compared to other catalysts used in the reaction. There was no correlation between the catalytic activity and the surface areas of the catalysts. Au/C was found to have the highest surface area of 942 m^2/g, but its catalytic activity for ethanol oxidation was very poor as compared to Au/TiO_2 with smallest surface area.

Table 4.1: The BET surface areas of catalysts used in ethanol oxidation

Catalyst	**BET surface area m^2/g**	**Pore volume cm^3/g**
1 wt.% Au/TiO_2	44	0.35
1 wt.% Au/ZnO	48	0.26
1 wt.% Au/Al_2O_3	245	0.67
1 wt.% Au/C	942	0.44
1 wt.% Ag/TiO_2	45	0.34

4.8. The effect of metal and support on ethanol oxidation

4.8.1 Effect of gold on ethanol oxidation

The most commonly used metals in oxidation reactions include Ag, Cu, Pd and Pt, and they are usually supported on metal oxides that are stable at high temperatures and chemically inert. These metals have been used for many years in the oxidation of alcohol until a recent discovery by Rossi and his co-workers, who were the first to show that alcohols can be oxidized to corresponding acids with gold catalysts [28, 29]. Since then the oxidation of alcohols using gold metal has been one of the best success stories in gold catalysis. Figure 4.20 shows the outstanding results for ethanol oxidation on gold as compared to other oxidizing metals.

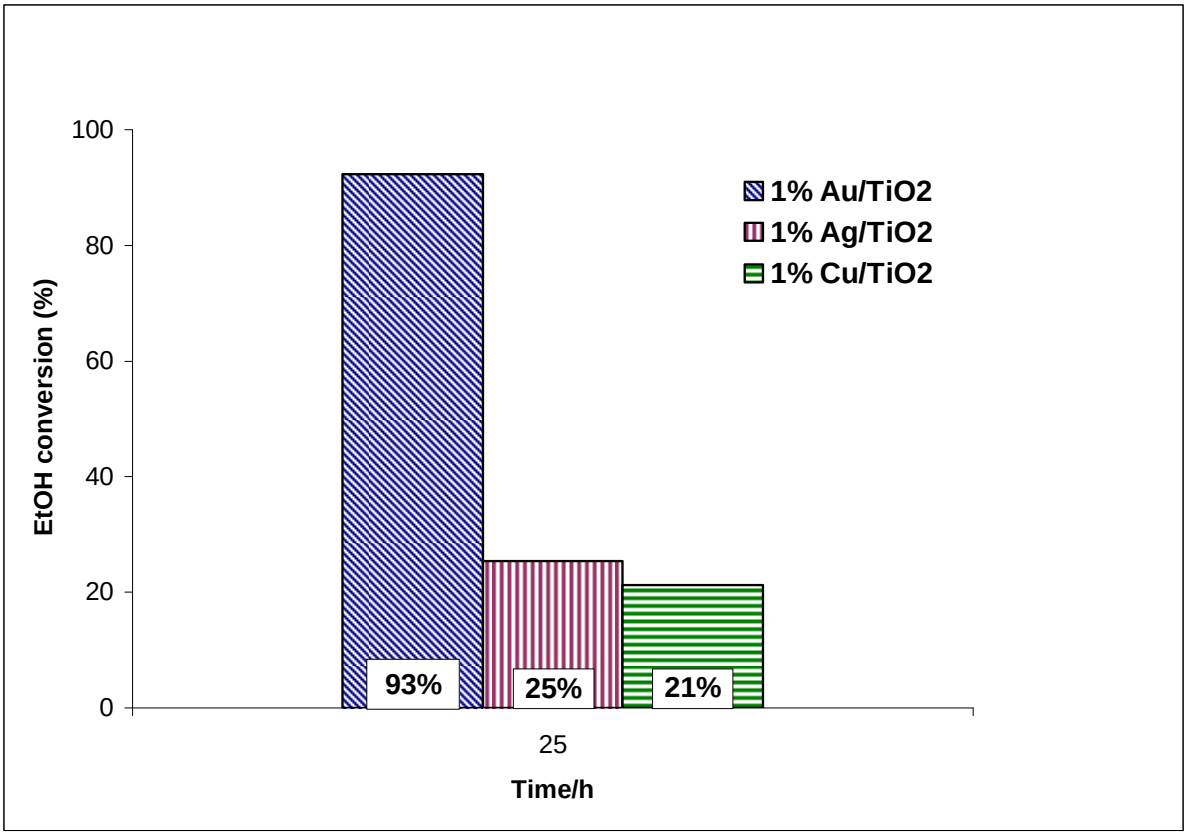

Figure 4.20: Effect of metal on ethanol oxidation reaction

After 25 h Cu and Ag supported catalysts showed ethanol conversions of 21 and 25% respectively, while the gold supported catalyst showed an ethanol conversion of 93%. The overall results obtained revealed that gold metal is more highly active for alcohol oxidation than other oxidizing metals.

4.8.2 The catalytic activity of Titania (TiO_2)

Titanium oxide was used as a catalyst for ethanol oxidation in order to see the effect of titania on gold supported catalysts. After 25 h reaction, titanium oxide (TiO_2) and gold supported on titanium oxide (Au/TiO_2) catalysts, showed ethanol conversion of 15% and 93% respectively. Thus TiO_2 contributes to the oxidation of ethanol.

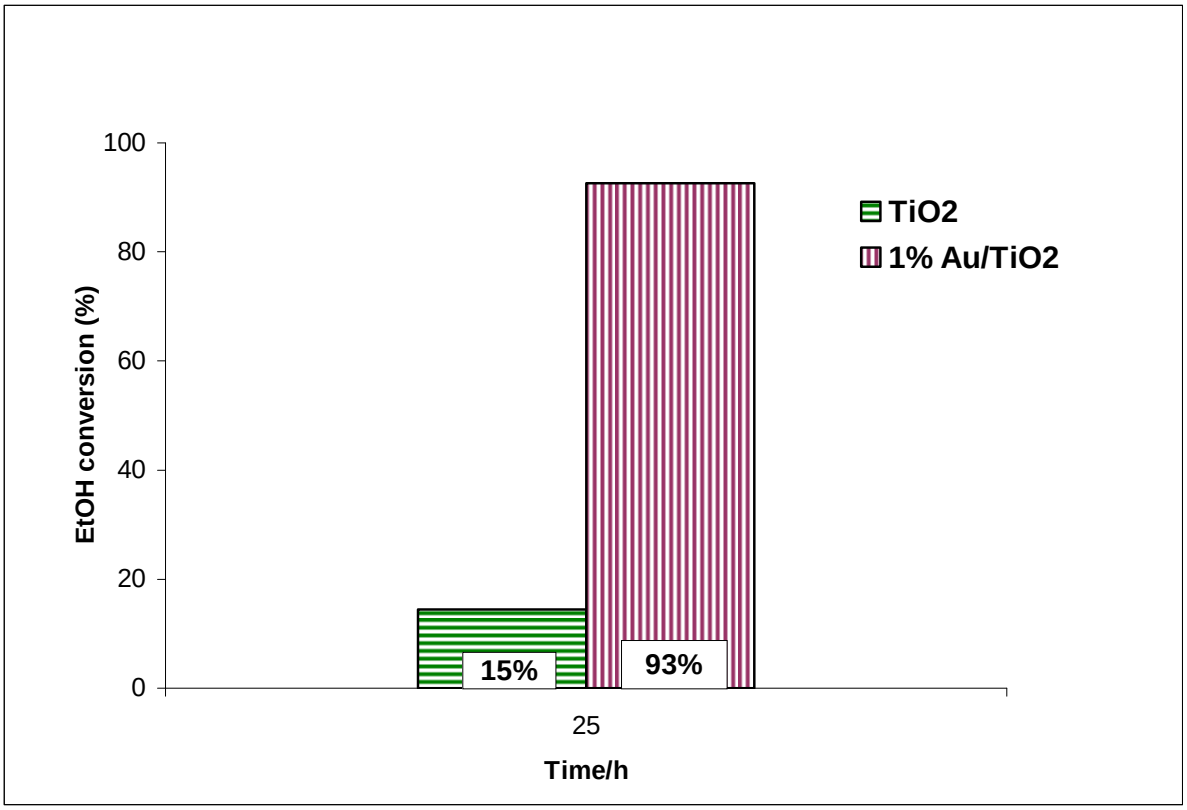

Figure 4.21: Conversion of ethanol with TiO_2 and Au/TiO_2

4.8.3 Effect of the properties of the metal support on ethanol oxidation

The catalytic properties of gold have been shown to depend extensively on a number of factors which include the oxidation state of the gold, the size of the gold particles, the redox properties of the support, preparation method, and pretreatment of the catalysts, although the discussion still remains open for several determinant aspects of these factors.

Schubert and his co-workers grouped the supports into two categories, the active (reducible) and inert (non-reducible) metal oxides [30]. They reported that gold catalysts with inert support (non-reducible) material such as Al_2O_3 and SiO_2 are intrinsically less active and the catalytic behavior is essentially a function of the size of the gold particles: higher activity is obtained when the gold particles are smaller. On the other hand, active supports which are reducible transition metal oxides, such as TiO_2, CeO_2, Fe_2O_2 have been described as the more appropriate ones for most reactions [31-33].

To investigate the effect of support on ethanol oxidation, three different types of supports were used i.e. TiO_2 (reducible metal oxide), Al_2O_3 (non reducible metal oxide) and C (acidic support). Gold was used as the active metal on investigating the effect of metal support. Different methods were used to load gold on supports. The results obtained from catalytic activity test of gold supported on these supports are presented in Figure 4.22.

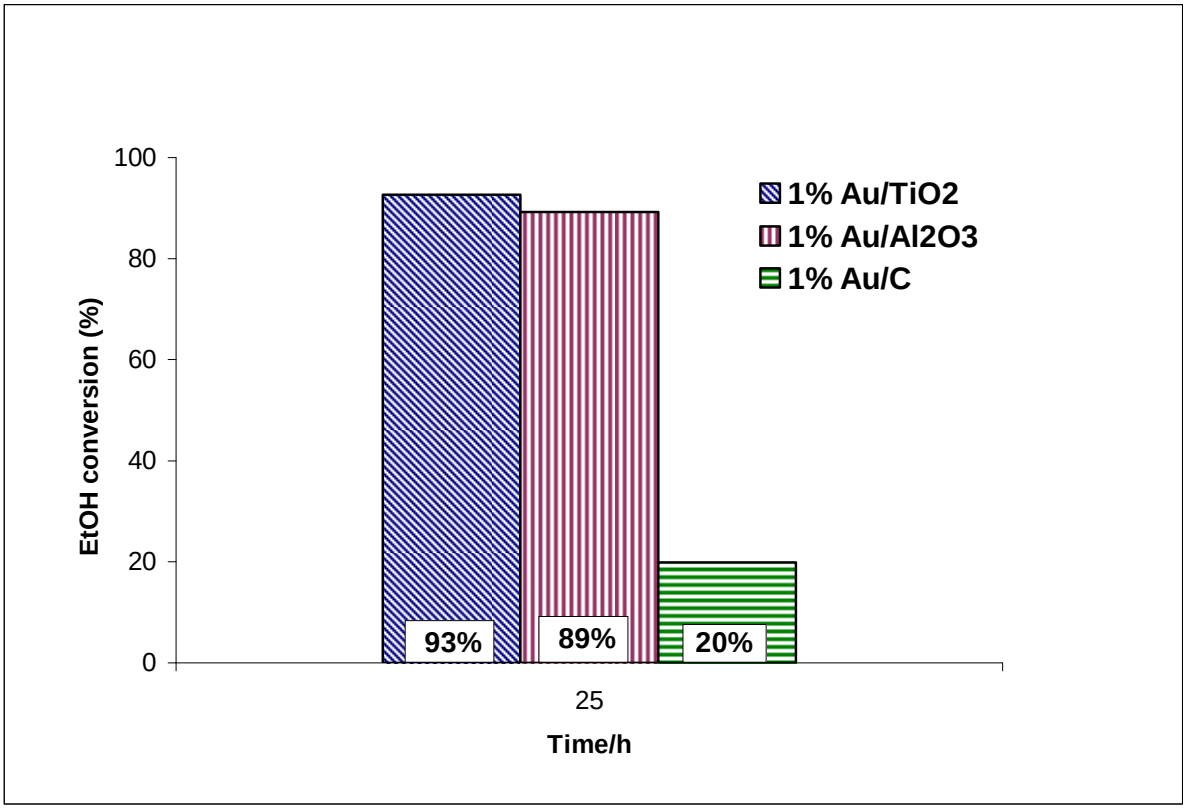

Figure 4.22: The effect of support on ethanol oxidation

Gold supported on reducible metal oxide i.e. TiO_2 showed a good catalytic activity of about 93% ethanol conversion after 25 h, followed by non-reducible metal oxide i.e. Al_2O_3 with 89% ethanol conversion and lastly by acidic support i.e. C which gave ethanol conversion of 20%. The overall results revealed that titanium oxide is the best catalyst support for gold in ethanol oxidation. The results obtained from basic hydroxide support i.e. TiO_2 and ZnO confirmed the explanation given in chapter two, that explains the effect of a base in alcohol oxidation. It was not a surprise to find that TiO_2 and ZnO support had a high activity in alcohol oxidation as compared to other supports. As explained in the literature in chapter two that the addition of a base promote alcohol oxidation. Therefore the activity of this two metal oxide supports in ethanol oxidation was expected to be high since they have basic properties which promote alcohol oxidation.

4.9. The effect of using excess oxygen on ethanol oxidation reaction

4.9.1 Catalytic test using 1% Au/TiO_2

The catalyst used for the test was chosen based on its higher catalytic activity towards ethanol oxidation as compared to other catalysts used in the study. It was noticed that the conversion of ethanol remained constant at 93% after 20 h, and this was attributed to a deficiency of oxygen inside the autoclave to react with ethanol rather than the catalyst deactivation. This was confirmed by running the reaction with excess oxygen in the autoclave. After 133 h, an ethanol conversion of 99.4% was achieved, without altering any other reaction conditions. The study revealed that it is possible to get 100% conversion of ethanol when enough oxygen is present in the system (autoclave).

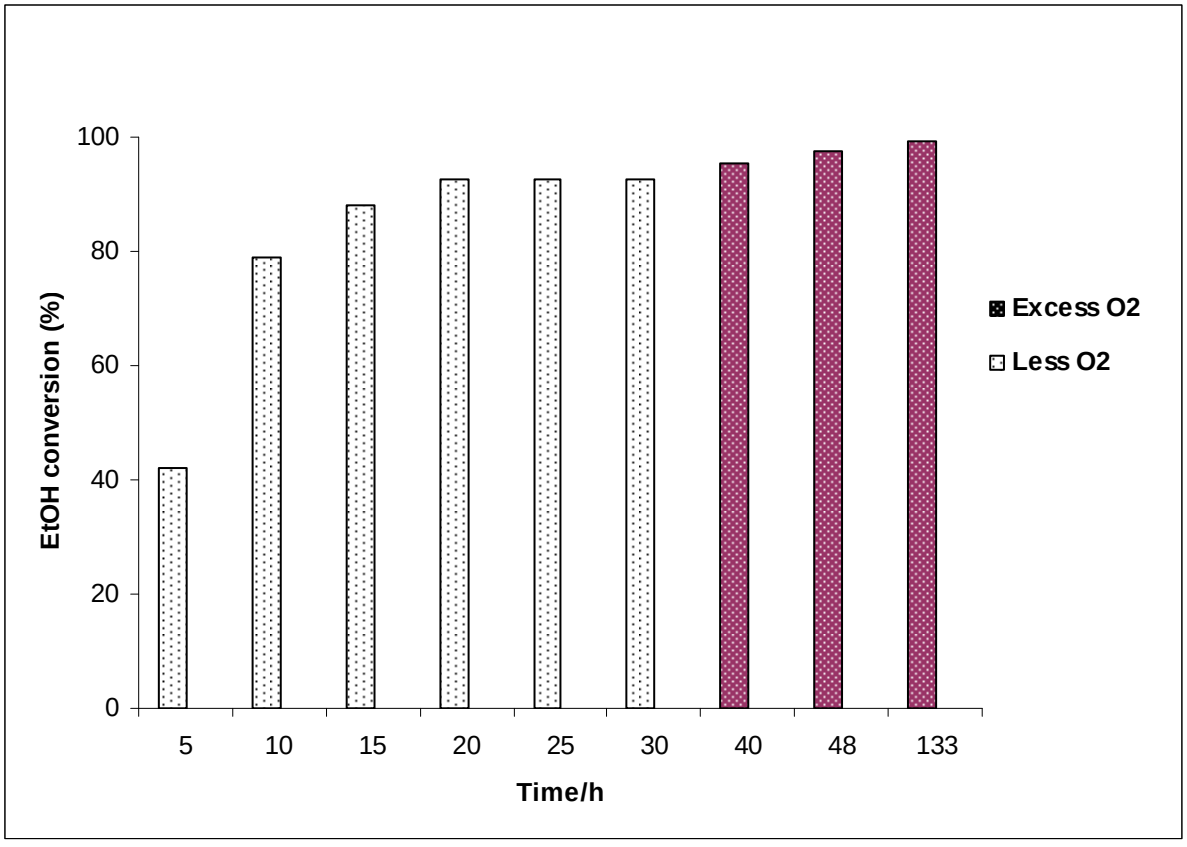

Figure 4.23: Conversion of ethanol with excess oxygen in the autoclave.

The yield and selectivity of acetic acid was also determined after the autoclave has been recharged with excess oxygen. The yield of acetic acid achieved was 99.2% while the selectivity was 99.8% (~ 100%) after 133 h as shown in Figure 4.24 below.

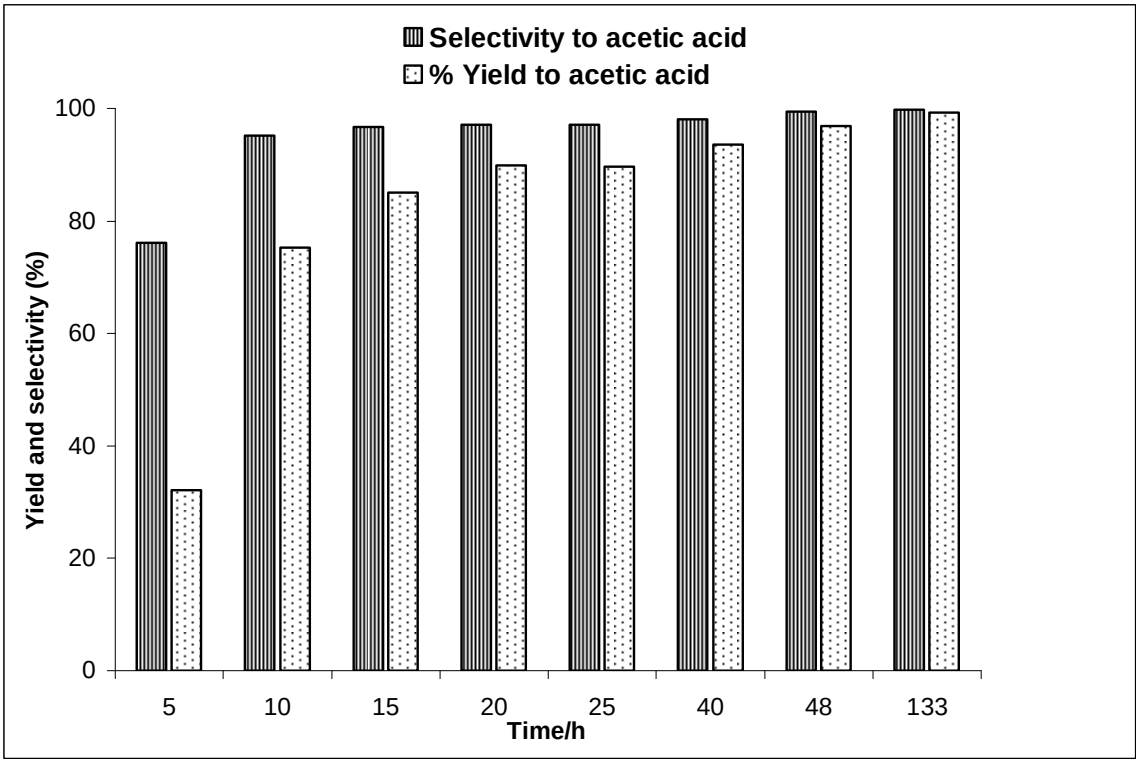

Figure 4.24: The yield and selectivity to acetic acid in excess O_2 using 1% Au/TiO_2

4.9.2 Product pH measurements for 1% Au/TiO_2

The pH studies of the products were measured at the end of each reaction run, in order to investigate the relationship between the pH of the product with increasing reaction time from 5 - 25 h. The pH of the product after 5 h for the Au/TiO_2 catalyst was measured to be 2.85, but after 10 h the pH dropped to approximately pH 2, thereafter the pH hardly changed with increasing reaction time. It remained almost constant at ~ pH 2

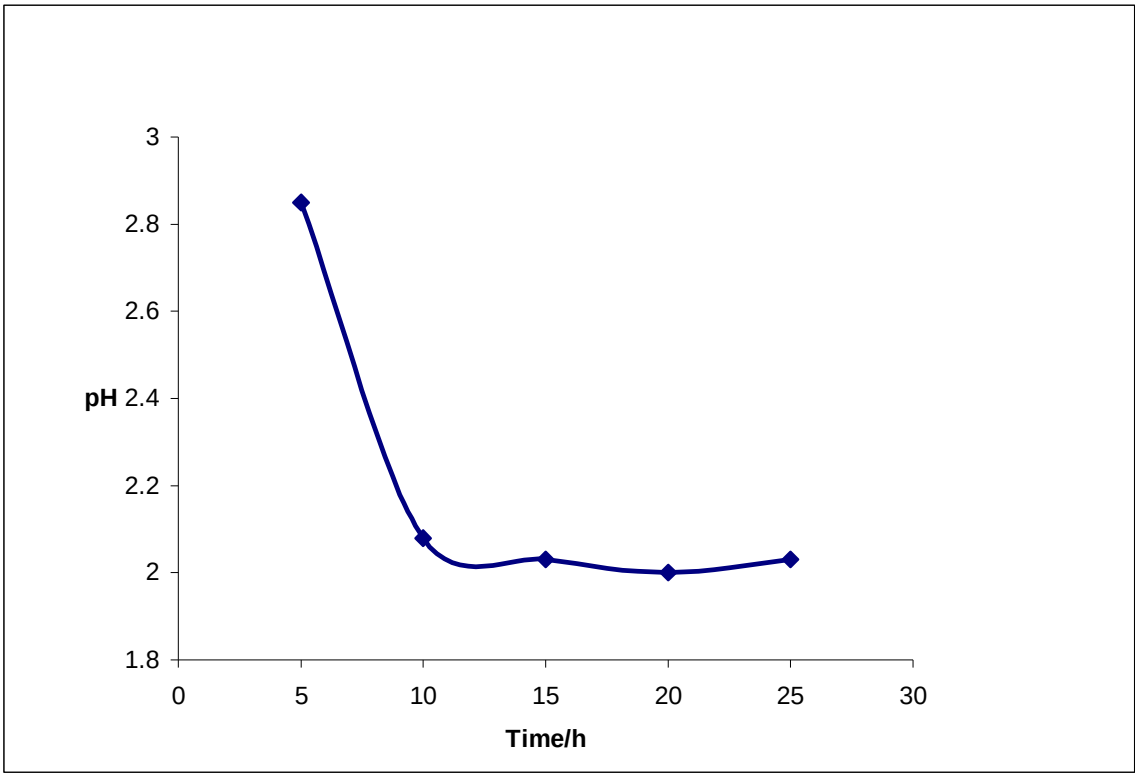

Figure 4.25: pH measurements of product from 1% Au/TiO_2 reactions

4.10. The effect of ethanol concentration

4.10.1 Conversion of ethanol (using 1% Au/TiO_2)

The study investigated the effect of ethanol concentration on the oxidation of ethanol. All other parameters i.e. temperature, pressure and the mass of ethanol were kept constant for all reactions while varying the concentration from 5 - 40 wt.% EtOH. The conversion of ethanol was observed to decrease with increasing ethanol concentration at a given point in time. The study revealed that as the concentration of ethanol increases, it affects the kinetics of the reaction by decreasing the rate of reaction. This was noticed after 20 h when 5 wt.% ethanol reaches a conversion of 93% while for 10, 20 and 40 wt.% ethanol, the conversion was still less then 90%. But when all reactions were run for a long time (i.e. 96 h), an ethanol conversion of 93% was achieved to all EtOH concentrations.

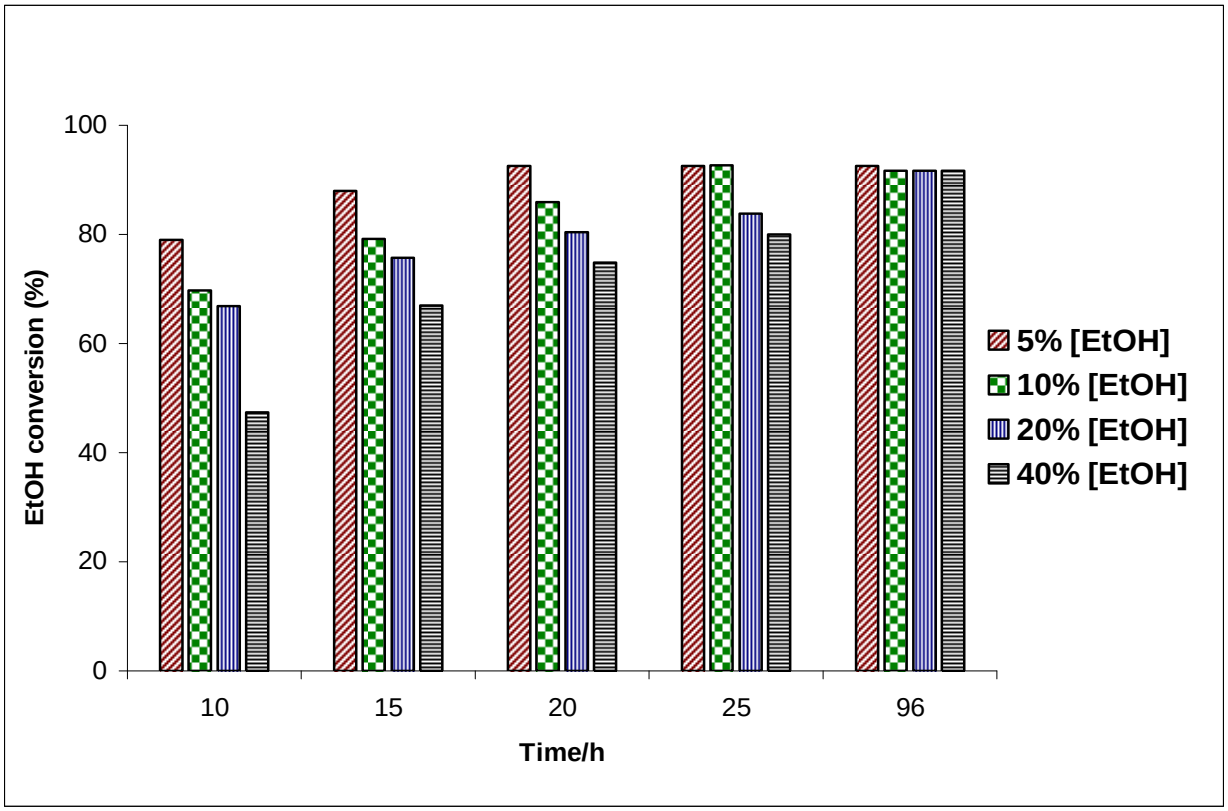

Figure 4.26: Effect of increasing ethanol concentration using 1% Au/TiO_2

4.10.2 Products distribution at higher ethanol concentration

At higher ethanol concentration, it was noticed that the reaction favors the formation of esters (i.e. ethyl acetate). This was in agreement with the findings of Jørgensen *et al.* [34]. The formation of acetic acid was not favored as the concentration of ethanol increased. The yield of acetic acid decreased from 75-19% when increasing the ethanol concentration from 5 – 40 wt.% respectively. The study revealed that, it is crucial to work at as a low concentration of ethanol as possible in order to achieve higher yields of acetic acid. At 40 wt.% ethanol concentration, it was noticed that the yield of ethyl acetate was even higher than the yield of acetic acid as shown in Figure 4.27.

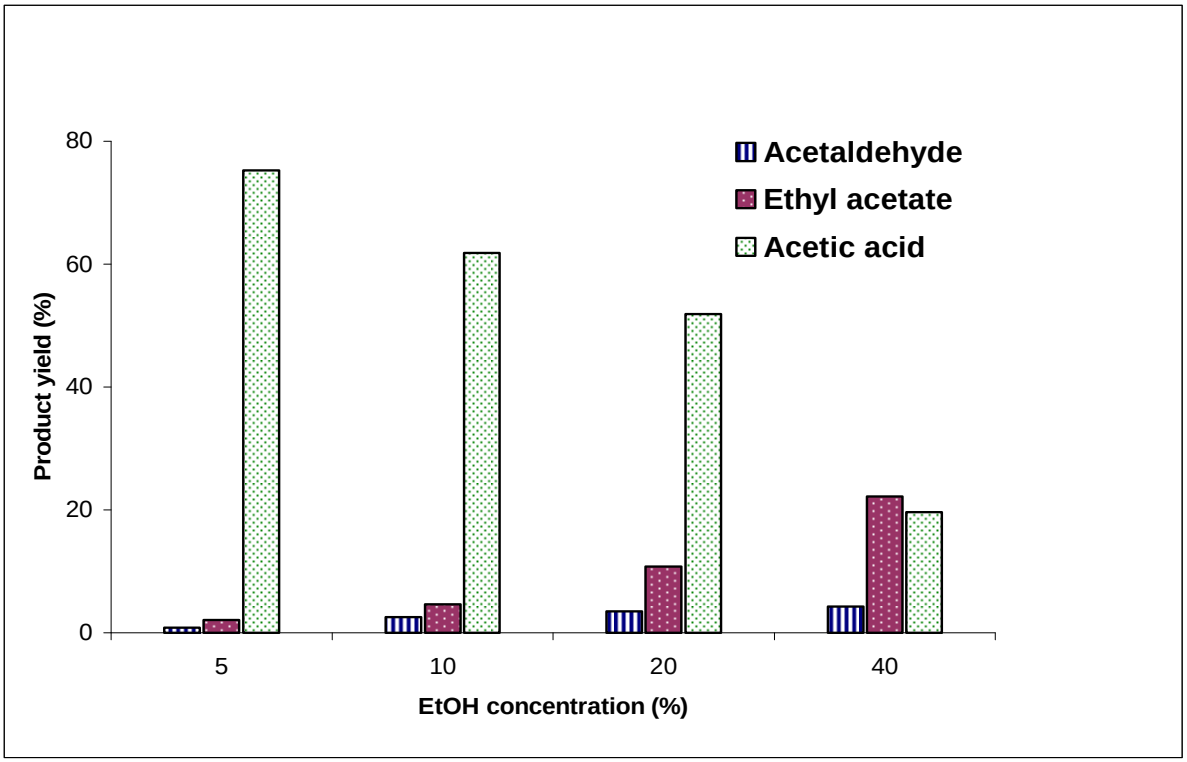

Figure 4.27: Products distribution with increasing ethanol concentration[5].

[5] In Figure 4.27 the reactions were run for 10 h.

4.10.3 Selectivities of product at higher ethanol concentration

The product selectivities were calculated based on the three products i.e. acetic acid, ethyl acetate and acetaldehyde as were the main products of the reaction. At higher ethanol concentration it was noticed that the selectivity of ethyl acetate was most favored as compared to other products. The selectivity of acetic acid was observed to decrease with increasing ethanol concentration and this was also reported by Jørgensen *et al.* [34].

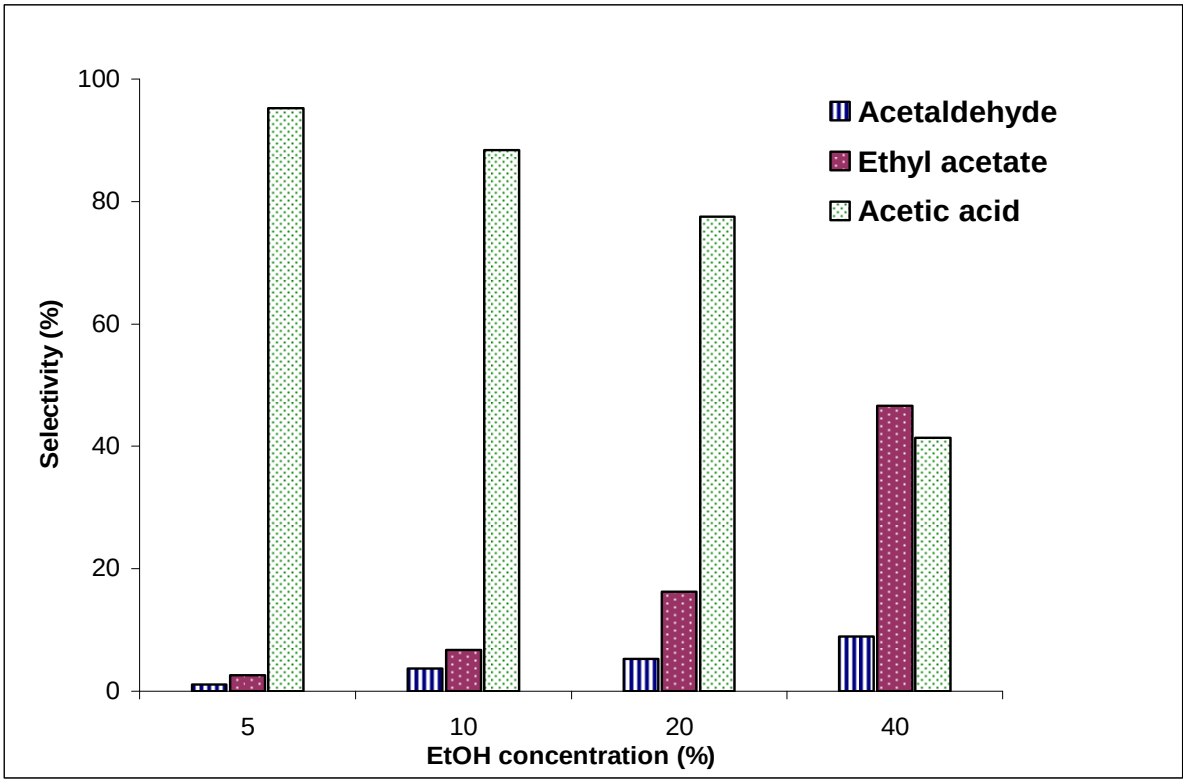

Figure 4.28: Products selectivities with increasing ethanol concentration[6].

[6] The data in Figure 4.28 the reactions were run for 20 h

4.11. The catalyst lifetime

4.11.1 Recycling test (1% Au/TiO_2)

Gold supported on titanium oxide was used to determine the catalyst recycling in aqueous phase oxidation of ethanol; since it was the most active catalyst for the reaction. There are many factors that contribute to catalyst deactivation in aqueous phase reactions. Firstly the metal catalysts could be deactivated by blockage of the surface by strongly adsorbed molecules either by impurities or reaction products that remain adsorbed on the surface of the catalyst, or adsorbed oxygen, since all reactions were conducted at 30 bar air. Secondly, the catalyst in the aqueous phase oxidation can be deactivated through leaching of metal into solution [6].

The catalyst recycling of 1% Au/TiO_2 was conducted in ethanol oxidation under the conditions described in the experimental section of this study. At the end of each run the resulting solution was separated from the catalyst by centrifuging and the products were analyzed using gas chromatography and the remaining catalyst was washed with water and transferred to the next run. All the reactions were run for 20 h. The conversion of ethanol in the first and second reaction cycles was 93%, but in the third cycle the activity of the catalyst dropped by almost threefold to about 29%, and this was attributed to the leaching of gold which was observed in the third reaction cycle (Figure 4.29-30). The study revealed that the catalyst can only be used twice and still maintain an ethanol conversion of 93%.



Figure 4.29: Colour of products from reaction cycle 1, cycle 2 (left) and cycle 3 (right)

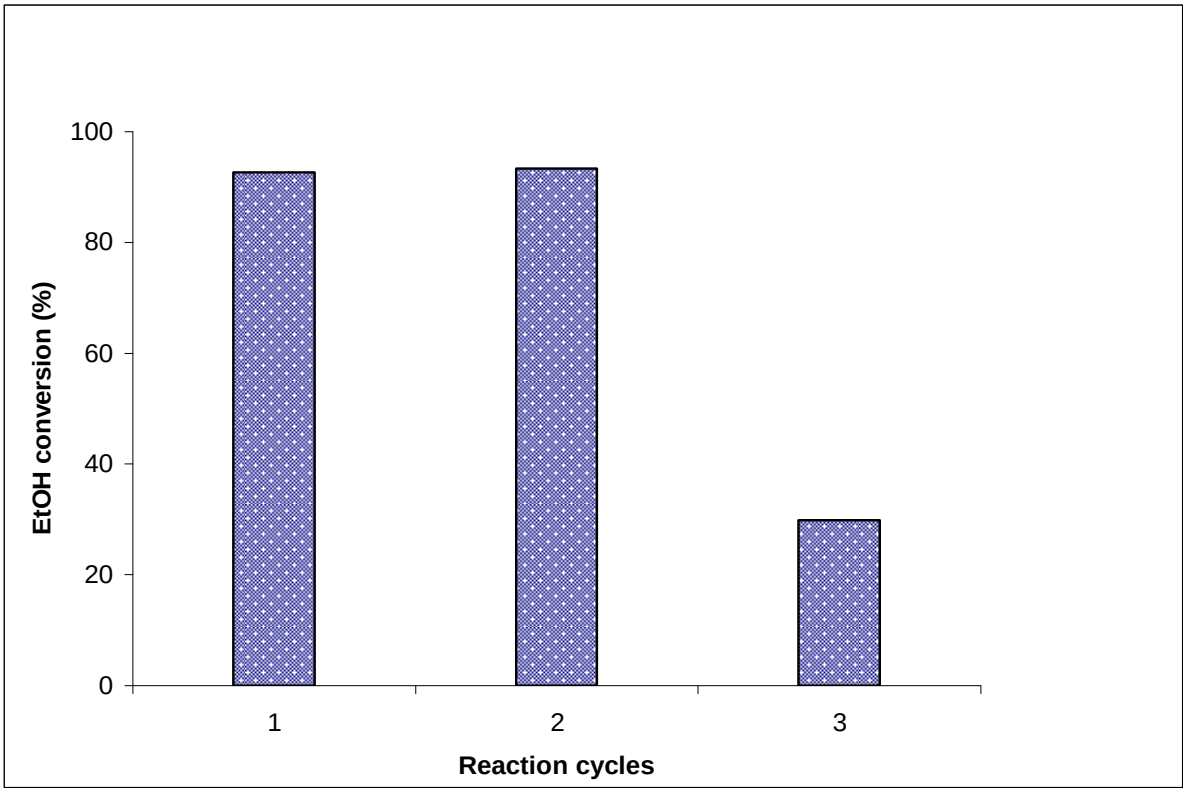

Figure 4.30: Recycling of 1% Au/TiO_2 in ethanol oxidation[7]

[7] In figure 4.30 each reaction was run for 20 h.

4.11.2 Quantitative analysis of gold leaching in reaction cycle three

The ICP-AES was used to determine the amount of gold leached in the reaction (Figure 4.29) when the catalyst was re-used for the third time. About 7.23 ppm of gold was detected by ICP in a solution mixture from reaction cycle three. No traces of gold were detected by ICP at the end of each reaction in cycles 1 and 2 when the catalyst was re-used for 20 h. This was amazing because when the reaction was run for 60 h without stopping, no gold leaching was observed, but when the catalyst was re-used 3× for 20 h reactions gold leaching was observed in the third reaction cycle (i.e. overall run time 60 h). It was noticed that gold leaching was only observed when the new feed was introduced into system, but when the reaction was run for long time no gold leaching was observed.

4.11.3 Hot filtration test

We also tested the reactivity of the hot filtrate on systems where gold leaching was observed i.e. Au-alumina and Au-titania systems, although with Au-titania system leaching was only observed when the catalyst was reused for the third time. While in the case of the Au-alumina system, gold leaching was observed when fresh catalyst was used for the first time in a reaction (ethanol oxidation).

The hot filtrate from each system was used as a catalyst for the next reaction, after gold leaching was observed. The results obtained from the study showed that the hot filtrate from both systems was not catalytically active when used as a catalyst for the next reaction. The hot filtration test results confirmed that the oxidation of ethanol was not taking place via homogeneous catalysis, but it reflected heterogeneous catalysis hence no positive results were obtained from the hot filtration test, in the absence of solid catalyst.

4.12. References

1. Hudly, M. Oxidation in organic Chemistry; American Chemical Society: Washington, DC, **1990**.
2. Besson, M.; Gallezot, P. *Catal Today*. **2000**, 57,127.
3. Mallat, T.; Baiker, A. *Catal Today*. **1994**, 19, 247.
4. Ishida, T.; Haruta M. *Angew Chem Int Ed*. **2007**, 46, 7154.
5. Corma, A.; García, H. Chem. Rev. **2002**, 102, 3837.
6. Kim, S.; Bae, S.W.; Lee, J.S.; Park, J.; *Tetrahedron*. **2009**, 65, 1461.
7. Lee, A. F.; Gawthrope, D. E.; Hart, N.J.; Wilson, K. *Surf. Sci.* **2004**,548,200.
8. Rajumon, M. K.; Roberts, M. W.; Wang F.; Wells, P. B. *J. Chem. Soc*., *Faraday Trans*. **1998**, 94, 3699.
9. Vessellie, E.; Baraldi, A.; Comelli, G.; Lizzit, S.; Rosei, R. *Chemphyschem.* **2004**, 5, 1113.
10. Bowker, M.; Holroyd, R. P.; Sharpe, R.G.; Corneille, J. S.; Francis, S. M.; Goodmanm, D. W. *Surf. Sci*. **1997**, 370, 113.
11. Davis, J. L.; Barteau, M. A. *Surf. Sci*. **1988**, 197, 123.
12. Chen, D. A.; Friend, C. M. *J. Am. Chem. Soc.* **1998**, 120, 5017.
13. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem Lett.* **1987**, 405.
14. Hutchings, G. J. *J. Catal*. **1985**, 96, 292.
15. Christensen, C.H.; Jørgensen, B.; Rass-Hansen, J.; Egeblad, K.; Madsen, R.; Klitgaard, S.K.; Hansen, S.M.; Hansen, M.R.; Andersen, H.C.; Riisager, A. *Angew. Chem., Int. Ed.* **2006**, 45, 4648.
16. Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanable, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, 311, 362.
17. Biella, S.; Rossi, M. *Chem. Commun*. **2003**, 378.
18. Carrettin, S.; McMorn, P.; Johnston, P.; Graffin, K.; Kiely, C. J.; Attard, G. A.; Hutchings, G. J.; *Top. Catal.* **2004**, 27, 131.

19. Huges, M. D.; Xu, Y.; Jenkins, P.; McMorm, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; Hutchings, G. J.; King, F.; Hugh Stitt, E.; Jonhson, P.; Graffin, K.; Kiely, C. J.; *Catal. Lett.* **2005**, 437, 1132.
20. Sakamuri, R.; Esters, Organic in Kirk-Othmer Encyclopedia of Chemical Technolgoy, online Version on Wiley InterScience.
21. Besson, M.; Gallezot, P. *Catal. Today*. **2000**, 57, 127.
22. Mallat, T.; Brönnimann, C.; Baiker, A. *Appl. Catal*. A **1997**, 149, 103.
23. Besson, M.; Gallezot, P.; Lahmer, F.; Flèche, G.; Fuertes, P. *J. Catal.* **1995**, 152, 116.
24. Garcia, R.; Besson, M.; Gallezort, P. *Appl. Catal.* A **1995**, 127,165.
25. Haruta, M. *Catalysis Surveys of Japan*, **1997**, 1, 61.
26. Prati, L.; *Gold Bull.*, **1999**, 32, 96.
27. Zheng, N.; Stucky, G. D. *J. Am. Chem. Soc*.; **2006**, 128, 14278.
28. Prati, L.; Rossi. M.; *J. Catal.* **1998**, 176, 552.
29. Bianchi, C.; Porta, F.; Prati, L.; Rossi, M.; *Top. Catal.* **2000**, 13, 231.
30. Moma, J.; PhD Thesis, University of the Witwatersrand, Johannesburg **2007**.
31. Boccuzzi, F.; Chiorino, A.; Manzoli, M.; Andreeva, D.; Tabakova, T.; *J.Catal.* **1999**, 188, 176.
32. Schubert, M. M.; Hackenburg, S.; van Veen, A. C.; Muhler, M.; Plzak, V.; Behm, R. J.; *J. Catal*. **2001**, 197, 113.
33. Romero-Sarria, L. M.; Martinez, T.; Centeno, M. A.; Odriozola, J. A. *J. Phys. Chem.* **2007**, 111, 14469.
34. Jørgensen, B.; Christiansen, S. E.; Thomsen, M. L. D.; Christensen, C. H. *J. Catal. A: Gen.* **2007**, 251, 332.

Chapter 5

5. Conclusions

- The main aim of the study was to repeat the very promising results found for the oxidation of ethanol to acetic acid using $Au/MgAl_2O_4$ which was previously reported by a research group in Denmark. This was successfully achieved by synthesizing a 1wt.% $Au/MgAl_2O_4$ catalyst using the deposition precipitation method. The catalyst activity test was conducted in air at 30 bar pressure, and an ethanol conversion of 86% was achieved after 25 h.

- The major target of the study was to discover whether gold supported on other metal oxides will catalyse the reaction (ethanol oxidation) with higher conversion and selectivity. This was successfully achieved by synthesizing different catalysts using various methods. The catalysts prepared include Au/TiO_2, Au/ZnO, Au/Al_2O_3, Au/C and Ag/TiO_2. The activity tests of the catalysts were conducted at 30 bar pressure of air. The AuTEK catalyst Au/TiO_2 showed higher activity performance on ethanol oxidation as compared to other catalysts used in the study. High conversions and selectivity was achieved when using this catalyst. After 20 h reaction, ethanol conversion of 93%, acetic acid selectivity of 97% and yield of 90% was achieved at moderate temperature and pressures.

- The effect of using excess oxygen was also investigated in the study. It was noticed that when greater quantities of oxygen were used it is possible to convert 100% of the ethanol. When excess oxygen was introduced into the autoclave, and ethanol conversion of 99.4%, selectivity of 99.8% and yield of 99.2% was achieved without altering any reaction conditions. We also noticed that working at higher temperatures favoured the conversion of ethanol.

- The effect of support was also investigated in the study, three different types of supports were used i.e. TiO_2 (reducible metal oxide or basic support), Al_2O_3 (non reducible metal oxide) and C (acidic support). It was noticed that when titanium or zinc oxides used as support high ethanol conversions (> 90%) were achieved. In the present study we conclude that basic hydroxide supports (i.e. TiO_2 and ZnO) are the best support for ethanol oxidation.

- The activity of Au for ethanol oxidation was compared with other oxidizing metal belonging to the same group with gold such as Cu and Ag. All three active metals were supported on TiO_2. After catalysts activity test, it was noticed that Au/TiO_2 was the most active catalyst for ethanol oxidation.

- The concentration of ethanol was varied from 5 – 40 wt.%. It was noticed that at high concentrations of ethanol, ethyl acetate was favoured as the main product. The formation of acetic acid was only favoured at low concentrations of ethanol. The high ethanol concentration was observed to affect the kinetics of the reaction. As the concentration of ethanol was increasing, it was noticed that the rate of ethanol conversion was becoming slow.

- The pH studies confirmed that indeed there was acetic acid in the product mixture before the analysis by GC. The pH of the product was analyzed using the pH meter at the end of each reaction. It was noticed that the pH of the product was approximately ~ 2.85 when the reaction time was kept short < 5 h, but when the reaction time was longer than 5 h the pH of the product remained at pH 2 throughout.

- The catalyst recycling study was conducted on Au/TiO_2, as it was found to be the most active catalyst for ethanol oxidation. The activity studies showed that the catalyst can only be used twice and still maintain an ethanol conversion of greater then 90%. When the catalyst was re-used for the third time it was noticed that the

catalyst had lost catalytic activity dropping to a value of 29% and this was due to leaching of gold from the catalyst which was observed in the third cycle.