The Selective Oxidation of Bioderived Molecules by Gold Catalysts

Thesis submitted in accordance with the requirements of Cardiff University for the degree of Doctor of Philosophy

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2012

Acknowledgements

Firstly, I would like to thank my supervisors Graham Hutchings and Stuart Taylor and to both Dave Willock and Dave Knight for their support, confidence and guidance throughout the duration of my studies.

Next on the list would be my post docs, Pete Miedziak, for his expertise, honesty and wittiness, and Nick Dummer for his wisdom and optimism.

I must also thank the members of the glycerol challenge consortium and my direct industrial supervisors Don Leanord and Charles Farrar from Tessenderlow/Tennants fine chemicals for their technical insights, organic chemistry and use of their GCMS facilities.

A special mention must be made to the technical staff of Cardiff University, Steve Morris, Alun Davies and Rob Jenkins for their patience, reactor building (and post explosion reassembly) and the other miracles they have performed.

My time during this work would not have been so enjoyable without my friends in the office and labs. A special mention goes out to Cat Davies who has kept me fuelled for chemistry with a variety of tasty baked goods. And to Mark who has kept me sane, focussed and hopeful during the writing of this work, I am truly grateful.

Finally, I would like to thank my family for the support they have given me throughout my education.

Abstract

The selective oxidations of the bioderived molecules, 1,2-propanediol, 1,3-propanediol and glycerol, were investigated using gold based catalysts. These reactions were carried out in both low pressure glass reactors and high pressure autoclaves. The reaction conditions such as temperature and amount of base were investigated to order to achieve the optimum conditions.

The gold based catalysts used were prepared by sol immobilisation and impregnation methods. The supports tested were activated carbon, titania, ceria and magnesium oxide. The ceria supported catalyst was demonstrated to be extremely selective for the oxidation of 1,2-propanediol in methanol in which methyl lactate is the desired product. The addition of palladium to the gold catalyst led to an increase in activity for all supports, however, in the case of the ceria supported catalyst a decrease in selectivity was observed.

The use of a magnesium oxide support was found to be advantageous in the oxidation of 1,3-propanediol and model compounds 1,4-propanediol and butyrolactone. An increase in activity and selectivity to the desired products, dimethyl malonate and dimethyl succinate, was demonstrated when this catalyst support was used. The structure of the support was found to be $Mg(OH)_2$ when the catalyst was prepared by sol immobilisation. When prepared by impregnation methods the support retained its periclase MgO structure but was found to be far less selective than the $Mg(OH)_2$ support.

The use of this support for the oxidation of glycerol was investigated. When gold is alloyed with platinum on this support it is possible to achieve high conversions of glycerol and good selectivities to glyceric acid in base free conditions.

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1 Introduction

1.1 Catalysis

The term catalysis was first used in 1835 by J.J. Berzelius whilst reviewing unexplained observations in scientific work[1]. He noted that certain compounds in low concentrations appeared to exert a force on other reactants in order to decompose them. He called this the catalytic force. A catalyst is now defined as:

> "A catalyst is a body or material which can induce the phenomenon of catalysis. It enhances the rate of reaction, and while being intimately involved in the reaction sequence, it is regenerated at the end of it."[2]

Catalysts have been utilised in a number of applications, ranging from the Davy lamp to the Haber process[2] and to the production of fuels. Enzymes are biological catalysts, responsible for reactions within the human body and all other living things. Usually based on proteins they are substrate and product specific. Man made synthetic catalysts strive to replicate the specificity of enzymes. There are two main classes of synthetic catalysis; homogeneous and heterogeneous. Homogeneous catalysts operate in the same phase as the reactant, for example, the destruction of ozone by chlorine radicals. Heterogeneous catalysts act in a separate phase to the reactant. An example of this is the use of a solid iron catalyst in the Haber process where ammonia is synthesised from nitrogen and hydrogen gases.

The surface structure of the catalyst is critical to the activity and selectivity of the catalyst. This is due to the process of catalysis in which there are a number of steps

- Diffusion – this step involves the movement of the liquid or gas substrate molecules to the catalyst surface
- Adsorption – the substrate molecules then bond to the catalyst surface
- Surface diffusion – the substrate may then travel over the surface
- Dissociation – the reactants may then dissociate
- Surface reaction – the adsorbed species on the surface react together, this is often the rate determining step

- Desorption – the product molecule leaves the catalyst surface

This process offers a lower energy pathway for the reaction to occur.

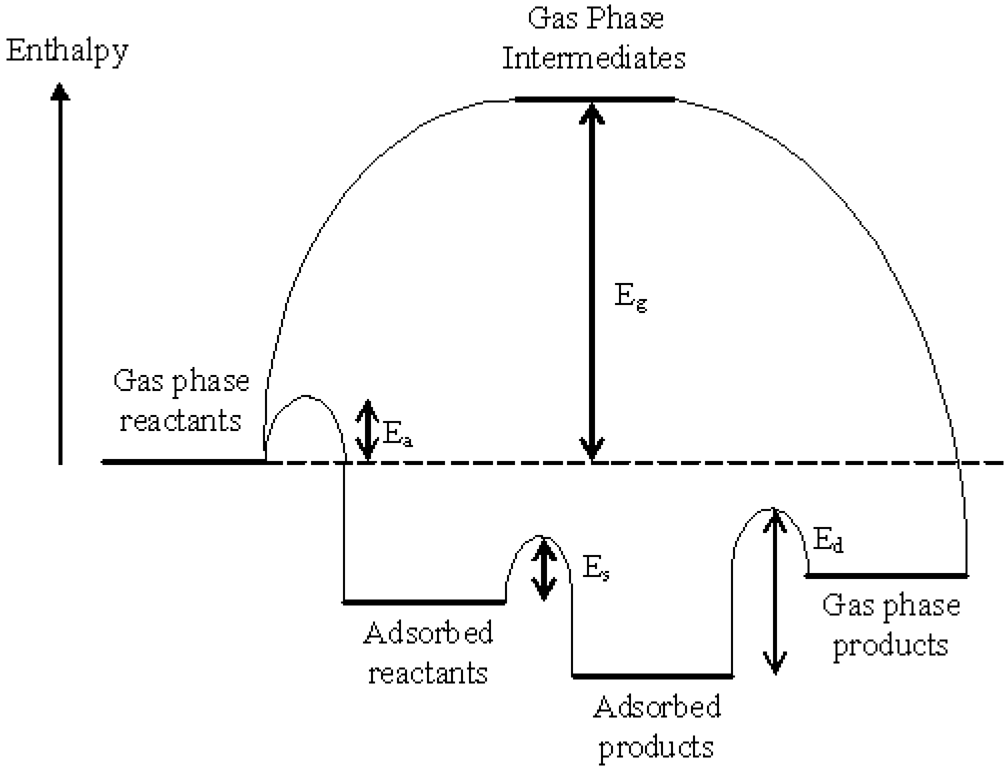


Figure 1-1 the energy diagram of a catalysed and uncatalysed gas phase reaction. The activation energies of adsorption E_a, surface reaction E_s, desorption E_d and gas phase reaction E_g are shown

Figure1.1, shows the energy diagram for a gas phase catalysed reaction. The first step in the gas phase is the breaking of bonds, this requires a lot of energy and therefore leads to a high energy intermediate before bonds are created and the low energy products are formed. During the catalysed reaction the bond breaking occurs whilst the reactant molecules are adsorbed on the catalyst surface. This stabilises the intermediates, thereby creating a lower energy pathway for the reaction. The rate at which equilibrium concentration is reached is increased, the position of which is not altered by the presence of the catalyst.

1.2 A brief history of heterogeneous gold catalysis

Historically gold has been used in organometallic and coordination chemistry but was considered to be catalytically inactive until recently[3]. Bond *et al.* were first to report the high activity of supported gold catalysts for the hydration of olefins[4]. However, almost a decade passed before interest in heterogeneous gold catalysis was renewed. Haruta *et al.* demonstrated the superiority of gold catalysts for CO oxidation[5]. These catalysts were supported on iron oxide. In this work the effect of preparation method was investigated and it was found that this had a considerable effect on the activity of the catalyst. It was established that the preparation method dictated the size of the gold particles in the catalyst and this particle size was the important parameter for catalysis. The control of particle size is vital for high activity catalysts.

Around the same time Hutchings demonstrated that supported gold catalysts showed enhanced activity for the hydrochlorination of ethyne to vinyl chloride[6]. Later, Haruta *et al.* applied gold catalysis to the industrially important oxidation of propene to propylene oxide, in this case a titania support employed[7]. Since this work, gold catalysts have been proven to be active for the selective oxidation of alcohols as demonstrated by Prati and Rossi[8]. Carbon was the support selected for the gold catalysts for the oxidations of ethylene glycol and 1,2-propanediol. The next major breakthrough in the world of heterogeneous gold catalysis was the application for the direct synthesis of hydrogen peroxide under non explosive conditions[9].

Throughout the work on gold catalysis it has been shown that a number of factors are important for synthesising an active and selective catalyst; these include preparation method, particle size and support. Another factor to consider is the alloying of gold to another metal.

1.2.1 Preparation method

The method by which the catalyst is prepared influences the particle size and distribution of the gold particles. Nanoparticulate gold is needed for good catalyst activity. The choice of support also contributes to the size and nature of the metal in the final catalyst.

The simplest of preparation methods is the impregnation method in which a gold precursor solution is simply stirred with the chosen support and then calcined. Catalysts prepared by impregnation have been applied to the oxidation of alcohols[10, 11] and the direct synthesis of hydrogen peroxide[12], amongst others. The impregnation method leads to a bimodal distribution of particles, small (2-10 nm) and larger particles (>20 nm)[10].

The use of the deposition precipitation, DP, method leads increased control over particle size. In this methodology, the catalyst support is stirred in a solution of the metal precursor. The pH of the solution is varied by the addition of base. The nature of the catalysts produced by this method is dependent on a number of variables including concentrations of precursor solutions, pH, stirring time and calcination conditions[13]. Prati *et al.* compared supported gold catalysts prepared by impregnation and deposition precipitation for alcohol oxidations. It was found that the catalysts prepared by deposition precipitation had a smaller average gold particle size than those prepared by impregnation when gold was supported on both carbon (8 and 20 nm respectively) and alumina (7 and 12 nm respectively)[8]. The DP catalysts were also shown to be more active and selective than the impregnation catalysts.

Another preparation method which leads to the formation of small nanoparticles on metal oxides is co-precipitation. In this method the support is produced during the catalyst preparation. Sodium carbonate is added to a mixture of gold precursor and metal nitrate. This leads to a good dispersion of gold. The rate of precipitation determines the gold particle size[14].

Chemical vapour deposition (CVD) involves the reaction of a volatile organogold compound with a support. The vapour of dimethylgold acetylacetonate can be deposited on oxide and carbon supports at 306 K. This technique produces small nanoparticles (< 6 nm) but with a larger size distribution than the deposition precipitation method[14].

Colloidal gold has been observed for over a hundred years[15]. In earlier work solutions of $HAuCl_4$ were reduced with toxic white phosphorus to produce colloidal solution of metallic gold[15] ranging in colour from ruby red to blue. These gold nanoparticles were observed to have a wide particle size distribution, from 20 – 220 nm[16]. Particle size is an important variable for the activity of gold catalysts[5] and control of this is desirable in the design and synthesis of gold catalysts. In 1985 Baschong *et al.* produced gold particles which were homogeneous in size with an average diameter of 2.6 nm[17]. In this work the aurochloric gold solution was reduced with sodium thiocyanate to form a gold colloid for use in protein labelling.

The sol immobilisation technique is a relatively new technique for the preparation of supported catalysts. This involves forming a gold colloid and immobilising polymer stabilised particles on a support. Before the immobilisation step the gold is chemically reduced from 3+ to 0. By using this method a narrow particle distribution is achieved[10]. In 1993 Duff *et al.* reported the synthesis of supported gold colloid which showed activity for CO oxidation[18]. The gold particles were synthesised by the reduction of $HAuCl_4$ by partially hydrolysed tetrakis(hydroxymethyl)phosphonium chloride ($P(CH_2OH)4Cl$, THPC). It was found that the volume of reducing agent used influences the gold particle size. The mean particle size was 1.5 nm (cluster nuclearity of 170) under standard conditions, as determined by STEM analysis. Later, sols prepared by the same method were supported on TiO_2, ZrO_2 and Al_2O_3 by stirring at pH 2 (HCl in water) which is below the isoelectric point of the support materials. After immobilisation on the support the average particle size was 2.0 nm, retaining the small particle size created in the colloid. These supported catalysts were found to be active for CO oxidation without calcination, unlike catalysts prepared by impregnation and deposition precipitation, which leads to sintering of the gold particles.

Another method to create a gold colloid with small particle size is the use of a polymer, such as polyvinyl alcohol (PVA)[19], as a stabilising agent and sodium borohydride ($NaBH_4$) as the reducing agent[20]. This procedure is particularly advantageous to create Au/C carbon catalysts[21]. By adjusting the initial concentration of the $HAuCl_4$ solution the gold particle size was controlled. High activities and selectivities for the oxidation of ethylene glycol to glycolate were achieved.

These methods have been modified to produce bimetallic colloids of AuPd[22] and AuPt[23]. Both unsupported and supported bimetallic nanoparticles show a synergistic effect when compared with the monometallic sols. The supported particles have been shown to be random homogeneous alloys[10].

Catalysts prepared by this method have been shown to be more active than those prepared by impregnation and have been shown to be effective for a number of alcohol oxidations[24, 25].

1.3 Gold catalysts for selective oxidation

Gold catalysts have been shown to be extremely active for oxidation reactions, from hydrocarbons to alcohols and hydrogen gas to form hydrogen peroxide among others. They are more stable and selective than traditional oxidation catalysts such as platinum and palladium[23]. Gold has a high electrode potential (E= +1.69 V), for this reason gold is stable and has a high resistance to oxygen and other poisons.

1.3.1 The direct synthesis of hydrogen peroxide

Oxidation is a key industrial process. Currently, the use of stoichiometric oxidising agents such as sodium percarbonate[26], metallic peroxides and percarboxylic acids leads to low atom efficiency[27]. Molecular oxygen is the preferred oxidant however elevated temperatures are needed in order to achieve substrate activation. Hydrogen peroxide is a green oxidant as the only by-product from its use as an oxidant as is water. Hydrogen peroxide has many applications, such as bleaches, for hairdyes and disinfection, and in a number of industrial processes[28].

At present hydrogen peroxide is synthesised in the anthraquinone cycle. However this method has a number of problems including cost and the hydrogenation of anthraquinone. The process is only viable on a large scale which creates high concentrations of hydrogen peroxide which is undesirable for use in chemical syntheses where relatively small amounts are used. Therefore, the development of a smaller scale, greener process is desirable. One route to this is the synthesis of hydrogen peroxide from hydrogen and oxygen under non explosive conditions.

The earlier research into the direct synthesis of hydrogen peroxide from hydrogen and oxygen utilised palladium catalysts[29, 30]. Hutchings *et al.* were first to demonstrate that gold catalysts were effective for this reaction[9]. An alumina support was selected to prepare Au, Pd and AuPd catalysts by incipient wetness impregnation. The rate of hydrogen peroxide synthesis on the gold catalyst was more than 4 times that produced by the palladium catalyst. The bimetallic AuPd/Al_2O_3 showed a considerable improvement over both monometallic catalysts with a hydrogen peroxide production rate of 2.9 times that of the gold catalyst as shown in table 1-1.

Table 1-1 Formation of H_2O_2 from the reaction of H_2/O_2 over Au and Pd catalysts

Catalyst	Solvent	Temperature /°C	Pressure /Mpa	O_2/H_2 mol ratio	H_2O_2 mmol g(catalyst)$^{-1}$h^{-1}
Au/Al_2O_3	methanol	5	3.7	1.2	1530
Au:Pd (1:1)/Al_2O_3	methanol	5	3.7	1.2	4460
Pd/Al_2O_3	methanol	5	3.7	1.2	370

Rate of H_2O_2 formation averaged over 30 min experiment.

This work was extended to include titania as a support[12] this is displayed in table 1-2. The titania support was shown to be superior to the previous alumina support in terms of rate of formation of hydrogen peroxide. This work compared the impregnation and deposition precipitation preparation methods for monometallic Au/TiO_2 catalysts. The impregnation method synthesised the best catalyst for H_2O_2 production. This may be explained by comparing the gold particle sizes created by each method. It was noted that the impregnation method produced larger particle sizes than the deposition precipitation method. Again, the synergistic effect from the addition of palladium to the gold catalyst was demonstrated on the titania catalyst. The ratio of these two metals, Au:Pd, was 1:1 wt and 4:1 wt. The 1:1 wt ratio was proven to be twice as productive as the 4:1 wt ratio for the synthesis of hydrogen peroxide with productivities of 64 and 28 molh^{-1}kg^{-1} respectively.

Other supports that have been investigated are zeolites[31], Fe_2O_3, carbon and silica[28]. For monometallic catalysts the Au/TiO_2 was the most productive catalyst. The activated carbon support was superior to the others when bimetallic AuPd catalysts were compared. The catalysts have been characterised and it was found that bimetallic AuPd/C has a different metal nanoparticulate structure to the other supports. The carbons support exhibits homogeneous random alloy particles whereas other supports display a core shell structure with palladium rich shell and gold core.

Table 1-2 Comparison of hydrogen peroxide productivity and CO conversion for catalysts prepared by deposition–precipitation (DP) and impregnation (Imp)[12].

Catalyst (wt %)	Preparation method	Pre-treatment	Productivity (molH_2O_2 h^{-1} kg^{-1}_{cat})	H_2O_2 (wt %)	CO conversion (%)
5% Au/TiO_2[a]	D.P.	Air, 25 °C	0.229	0.002	85
5% Au/TiO_2[a]	D.P.	Air, 120 °C	0.482	0.005	76
5% Au/TiO_2[a]	D.P.	Air, 400 °C	0.388	0.004	40
5% Au/TiO_2[a]	Imp	Air, 400 °C	7.1	0.014	<1
4% Au-1% Pd/TiO_2[b]	Imp	Air, 400 °C	28	0.057	<1
2.5% Au-2.5% Pd/TiO_2[b]	Imp	Air, 400 °C	64	0.128	<1
5% Pd/TiO_2[b]	Imp	Air, 400 °C	31	0.061	<1

Reaction conditions as described in text; reaction time for H_2O_2 synthesis 30 min; reaction time for CO oxidation following achievement of steady state: 1–6 h.Mass of catalyst for H_2O_2 synthesis: [a] 50 mg, [b]10 mg

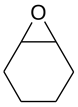
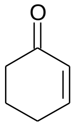
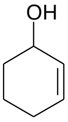
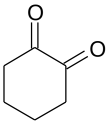
1.3.2 Selective oxidation of hydrocarbons

There is significant interest in the selective oxidation of hydrocarbons such as methane, propene and cyclohexane. Propene oxide is traditionally manufactured by the chlorohydrin and hydroperoxide processes[32]. These methods are not environmentally friendly and the development of a green catalytic process is very desirable. As discussed earlier Haruta *et al*[33]. demonstrated the activity of gold catalysts for this reaction in the presence of O_2 and H_2. Titania supported gold, palladium and platinum catalysts were compared and it was found that the gold catalyst was the only catalyst to give high selectivity to propene oxide. The palladium and platinum catalysts were more selective to the hydrogenation product, propane. It has been hypothesised that the gold catalyst is selective to propene oxide due to the formation of hydroperoxo species on the gold surface, which aids the desorption of propene oxide from the catalyst surface.

Another epoxidation reaction that is catalysed by gold is the selective oxidation of cyclohexene. Hutchings *et al.*[34] investigated this transformation with a Au/C catalyst under mild conditions. A selectivity of 50 % to the epoxide was achieved at 29.7 % conversion after

24 h. The reaction was carried out in 1,2,3,5-tetramethylbenzene as a solvent with TBHP as an initiator. The reaction temperature was 80 °C and molecular oxygen was the oxidant. No C6 products were observed in non polar solvents.

Table 1-3 Effect of solvent on selective oxidation of cyclohexene using a 1% Au/carbon catalyst

		Selectivity /%					yield /%
Solvent	Conversion /%					C6 products	C6 products
Water	100	0	0	0	0	0	0
Methanol	27.1	0	0	0	0	0	0
THF	5.8	0	0	0	0	0	0
Hexane	26.1	Trace	Trace	Trace	0	0	0
Toluene	29.1	Trace	35.1	25.1	0	60.2	17.5
1,4-Dimethyl benzene	53.5	0	12	0	43.5	55.5	29.7
1,3,5-Trimethyl benzene	8	Trace	78.1	Trace	0	78.1	6.2
1,2,4,5-Tetramethyl benzene	29.7	50.2	26.3	0	0	76.3	22.7
1,2,4,5-Tetramethyl benzene /1,4-dimethylbenzene	23.1	26	42	9.1	0	77.1	17.8
Quinoline	33.2	0	10.5	0	0	10.5	3.5
hexafluorobenzene	29.1	0	47.1	26.8	0	73.9	21.5
1,4-Difluorobenzene	15.8	8.9	36.1	2.5	0	47.5	7.5

Reaction conditions: 1% Au/C (0.22 g), C_6H_{10} (0.012 mol), 80 °C, 24 h, solvent (20ml). For polar solvents, t-butyl hydroperoxide, TBHP (5 mol% based on C_6H_{10}) was added.

Gold has also been shown to catalyse the oxidation of alkanes. Zhao *et al*[35] first demonstrated that ZSM-5 supported gold catalysts promoted C-H activation for the oxidation of cyclohexane. The reaction was carried out in solvent free conditions at 150 °C in oxygen (1 MPa). A conversion of 16 % was achieved with 67 % selectivity to cyclohexanone which is an important starting material in the pharmaceutical and insecticide industries. The effects of metal[36], solvent[37] and reaction additive have been investigated. Other alkane oxidation catalysed by gold include methane and propane[38].

1.3.3 Selective oxidation of alcohols

The oxidation of alcohols provides a route to carboxylic acid acids which are components in many chemical syntheses. Biella and Rossi investigated the gas phase oxidation of a number of primary and secondary alcohols[39] with a gold on silica catalyst. Very high selectivities to aldehydes (> 94 %) and ketones (> 84 %) were achieved. It was found that secondary alcohols were more susceptible to oxidation with gold catalysts and the oxidation occurred at lower temperatures.

In liquid phase oxidation reactions with gold catalysts, base has been proven to be essential for activation of the alcohol molecule[40], which is not the case for Pd and Pt catalysts. Gold has an advantage over traditional palladium and platinum oxidation catalysts in terms of selectivity. Prati *et al.*[8] tested Au/C catalysts for ethylene glycol and propanediol. Gold catalysts were more selective to primary oxidation products and more stable in reusability and leaching tests. This work was expanded to glycerol[41] in which the preparation method was investigated. Later work utilised the same active Au/C for the oxidation of the primary mono-alcohols, butanol and propanol, under mild conditions (3 kPa of O_2 at 70 °C)[42]. Gold catalysts were once again shown to be more selective than palladium catalysts. Au/C was prepared by impregnation, deposition precipitation and sol immobilisation. These catalysts had average particle sizes of 18.5, 13 and 7.5 nm gold particles respectively. The activity for ethylene glycol oxidation was found to decrease with increasing gold particle size. The catalyst prepared by sol immobilisation was the most active with a TOF of 1000 h^{-1} and most selective to glycolate (98 %).

Corma *et al.* reported that the use of nanaocrystalline ceria as a support for gold catalysts was superior to TiO_2, Fe_2O_3 and C supports for the oxidation of 3-octanol[43]. This

Au/CeO_2 catalyst was found to be active in the absence of solvent[44] and base, unlike gold catalysts prepared on other supports[40]. The gold on this catalyst is formed in the form of Au^{3+}, Au^{+} and Au^{0}. The cationic gold is stabilised by the ceria surface, creating Ce^{3+} species. The catalyst was then tested for a number of alcohol oxidations in the presence of solvent and base. High conversions of both primary and secondary alcohols were achieved with good selectivities to the corresponding aldehydes and ketones. As reported previously, secondary alcohols were more reactive to oxidation[39] and underwent oxidation in solvent free conditions.

The oxidation of benzyl alcohol with gold catalysts also leads to the selective formation of an aldehyde[45]. Benzaldhyde is used in the pharmaceutical and food additive industries. Enache *et al.* demonstrated the activity for supported gold, palladium and bimetallic AuPd catalysts[46]. A range of zeolite and titania supports were selected for screening. It was found that the more acidic supports were detrimental for benzaldehyde selectivity. The addition of palladium to the gold catalyst led to an increase in benzyl alcohol conversion and selectivity to the aldehyde. Further investigations into support effects for gold catalysts were made by Choudhary *et al.*[47]. The most active support was ZrO_2, followed by MnO_2 and SmO_2. Gallia supported gold catalysts were also shown to be very active[48]. The selectivities to benzaldehyde were > 75 %. The Au:Pd ratio was investigated in detail by Enache *et al.* with titania supported catalysts[11]. The highest activity with a bimetallic catalyst was achieved with a 1:1 wt ratio of Au:Pd. The palladium catalyst was the most active at short reaction times but showed deactivation, it was also the least selective to benzaldehyde. The monometallic gold catalyst was the most selective. With regards to selectivity for the bimetallic catalysts, the more gold rich the catalyst the higher the selectivity to benzaldehyde. Recent advances have been made in oxidising benzyl alcohol with supported AuPd catalysts in milder conditions, with low oxygen pressures (1 bar)[49].

Table 1-4 The effect of AuPd ratio on the rate of benzyl alcohol oxidation[11]

Catalyst	TOF (h^{-1})[a]	
	Au-Pd catalysts	Au-Pd physical mixtures
5% Au/TiO_2	33,700	33,700
4% Au-1% Pd/TiO_2	47,600	42,300
3% Au-1% Pd/TiO_2	48,700	50,800
2.5% Au-1% Pd/TiO_2	65,400	55,100
2% Au-3% Pd/TiO_2	65,100	59,400
1% Au-4% Pd/TiO_2	64,000	67,900
5% Pd/TiO_2	76,500	76,500

[a] Determined at 0.5 h reaction time

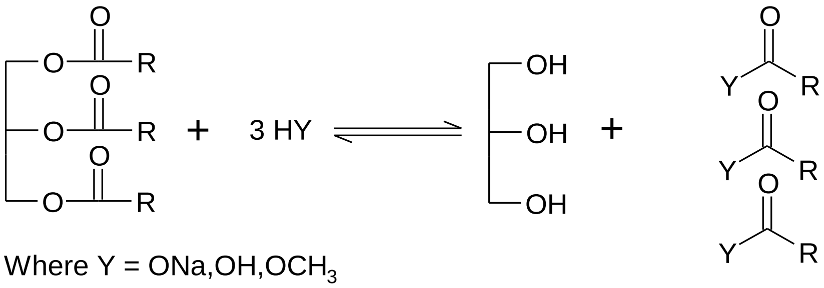
1.4 Biodiesel production

Since the industrial revolution, energy has become vital to encourage economic growth and make significant scientific and engineering advances. In earlier times coal was the major source of the energy needed. Petroleum became more popular in the twentieth century with the development of electricity, cars and airplanes. In 2006, coal, petroleum and natural gas made up 83.7 % of global energy sources[50].

The depletion of fossil fuel reserves has brought the need of new renewable fuels. Biofuels are fuels which have been derived from biomass, such as corn, sugarcane and soya amongst others. Biofuels also aim to be carbon neutral, in that the carbon released through their combustion is counter-balanced by the carbon that is absorbed during the re-growth of the biomass for further fuel production. Biofuels are a cleaner fuel as they contain less particulate matter such as sulphur, soot and aromatics[51].

Biodiesel can be produced from the trans-esterification of triglycerides, which are found in plants such as soybean and rapeseed as well as animal fats. Biodiesel is the most common biofuel in Europe. Biodiesel is a promising new biofuel, as its physical properties are close to that of traditional diesel. When burned in combustion engines, less engine wear occurs than when traditional diesel is used. Other advantages of biodiesel include cost, availability and improved lubrication properties[52]. The emissions of burning biodiesel show a 99 % reduction in SO_2 emissions, a 20 % decrease in CO, hydrocarbons and soot are reduced by 32 % by 50 % respectively and particulates are decreased by 39 %. Another advantage of biodiesel is its biodegradability. In the case of a spill, 90 % of the biodiesel will have degraded in 3 weeks; therefore, there is a significant decrease in the impact on the environment including wildlife[53]. From 1980 to 2005, the worldwide production of biofuels has increased dramatically from 4.4 to 50.1 billion litres[54]. The manufacture of biodiesel has also risen recently from 11.4 million litres in 1991 to 3.9 billion litres in 2005[54]. Studies have shown that the average net reduction in greenhouse gases for biodiesel is 54 %, as calculated from a full lifecycle analysis. This includes, greenhouse gases released in agriculture, biorefining, delivery and consumption[55].

However, there is some controversy surrounding biofuels. Increasing biodiesel production means more biodiesel plants need to be grown and places for this agriculture must be found. The conversion of non-agricultural land and forestry areas to biodiesel plantations is occurring around the globe. In Malaysia, rain forests and peat lands are being displaced in favour of palm plantations and in forrest clearing in the Amazon for the growing of soybean plants is reducing the biodiversity of the area. The clearing of these areas by burning also impacts the environment by increasing greenhouse gases[56]. The ground used for growing plants for biofuel production could be used for crops, leading to the “food vs. fuel” debate[57]. Biofuels have already been observed to have caused increases in food prices[55].



Scheme 1-2 The production of biodiesel[58]

As is demonstrated in Scheme 1-2 from one triglyceride molecule, 3 ester molecules are produced along with 1 molecule of the by-product, glycerol. The yield of glycerol is 10 % by weight. The EU issued a directive that stated that by 2010 5.75% of travel fuels must come from bio-derived renewable sources. The increase in the production and use of biodiesel has caused the market value of glycerol to plummet (1300 €t^{-1} in 2000-2003 to 500€t^{-1} in 2004-2006)[58].The production of glycerol is anticipated to increase steadily and the question is raised as whether glycerol can be converted to value added chemicals.

Glycerol itself has a number of applications in cosmetics, pharmaceuticals and foods[59]. However, the crude glycerol produced by this process has very few uses. The glycerol in this form contains water, methanol, inorganic salts, fatty acids, unreacted glycerides and methyl esters. The purity of the glycerol in its crude state can be as low as 50 % depending on the manufacturing method used[59]. Due to the methanol content of crude glycerol it is deemed hazardous waste, and consequently its disposal is difficult. The purification process involves neutralisation of the by products with phosphoric acid followed by separation of the components and vacuum flashing to remove the methanol. The resulting glycerol is 80 – 90 % pure and is generally resold to glycerol purification plants where it undergoes vacuum distillation and/or ion exchange to yield a glycerol purity of 99.5 – 99.7 %. This process is an expensive one and it has been suggested that the projected volume of glycerol will outweigh the commercial demand for its traditional applications. Therefore there is a need for new glycerol processes to utilise this highly functionalised molecule.

1.5 Transformations of glycerol

Due to recent increase in availability and low market value there has been significant interest in the conversion of this highly functionalised molecule into more desirable value added products. Zhou *et al.* have recently written a review on these transformations[59].

1.5.1 Fuels from glycerol

Hydrogen gas has a number of applications, from fuel cells to the Haber process[60] and the global market for hydrogen is estimated to be approximately 45 million tonnes per annum. Aqueous phase reforming is a process in which glycerol is converted to hydrogen and carbon monoxide[61]. This is achieved at low temperatures (225 – 300 °C) with the use of platinum-Rhenium catalysts in a one pot process[62].

$$C_3H_8O_3 + 3H_2O \longrightarrow 3CO_2 + 7H_2$$

Equation 1-1

This synthesis gas can be used in the Fischer-Tropsch process or methanol synthesis to produce fuels and chemicals. The use of glycerol in these processes offers an alternative to the traditional source of syngas, fossil fuels. Monometallic platinum catalysts supported of alumina have been utilised in a similar aqueous phase reaction to yield higher concentrations of H_2 with low CO formations[63]. This reaction was shown to require lower amounts of energy than standard methane reforming to produce hydrogen gas and is extremely cost effective. The low temperature is favourable for the water-gas shift reaction to take place, therefore producing small amounts of CO. Huber *et al.* demonstrated that a Raney nickel catalyst was also active for this reaction. The selectivity of the catalyst was tuned with the addition of tin to yield lower concentrations of CO.

The formation of synthesis gas from glycerol can be directly used in a Fischer-Tropsch reaction in a single two bed reactor[64]. This reaction can take place at temperatures as low as 225 °C. Glycerol is converted to synthesis gas as per equation 1-2 below;

$$C_3O_3H_8 \longrightarrow 3CO + 4H_2$$

Equation 1-2

This syngas process is coupled with the Fischer- Tropsch reaction to produce liquid fuels suitable for combustion engines for transportation. The overall reaction equation is shown below

$$C_3O_3H_8 \longrightarrow \frac{7}{25}C_8H_{18} + \frac{19}{25}CO_2 + \frac{37}{25}H_2$$

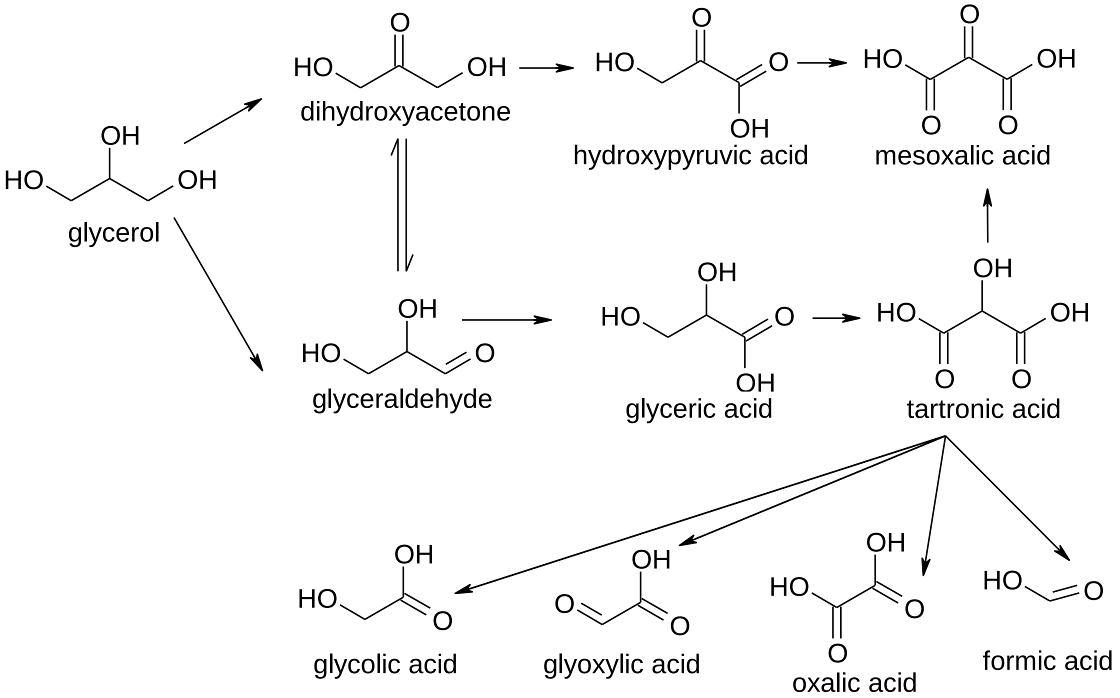
Equation 1-3

A number of variables were investigated for this reaction including feed concentration, pressure and effect of water. PtRe/C catalysts were employed for the conversion of glycerol and Ru/TiO_2 for Fischer-Tropsch process. The pyrolysis of glycerol at 700 °C also leads to the formation of syngas[60].

1.5.2 Glycerol oxidation

Glycerol can be oxidised with heterogeneous catalysts to produce a range of oxygen added molecules with applications in polymer building, cosmetics, food additives, and organic synthesis as shown in scheme 1-3.

It was first shown by Rossi and Prati that supported gold nanoparticles were effective for alcohol oxidation in the presence of base[8, 65] to give glyceric acid as the primary product. The C3 products are the most desirable but undergo C-C cleavage during the reaction. The primary oxidation product is glyceric acid which is oxidised to tartronic acid, which itself undergoes decarboxylation to glycolic acid. The glycolic acid can be oxidised to oxalic acid. Another route to the C2 product glycolic acid is from the fragmentation of glyceric acid which also produces the C1 molecule formic acid.



Scheme 1-3 The oxidation pathway of glycerol

It has been hypothesised that the role of base is as an initiator of the reaction, activating the glycerol molecule for dehydration of the hydroxyl group[41, 66]. It was shown that gold catalysts are inactive without the presence of base[40]. The amount of base has a large effect on both conversion of glycerol and selectivity to glycerate[67]. Carrettin *et al.* investigated the effects of a number of reaction variables, including base concentration, oxygen pressure and glycerol/metal ratio. The catalyst used was Au/C. It was demonstrated that in higher concentrations of NaOH, high selectivities of glycerate are achieved. Increasing the oxygen pressure increased the conversion of glycerol. However, increased concentrations of the secondary oxidation product, tartronic acid, were detected. The same trend was observed when the amount of catalyst was increased (s/m). Again it was demonstrated that supported gold catalysts are superior to platinum catalysts.

The role of base in the oxidation of glycerol with Au, Pd and Pt catalysts was investigated in detail by the same authors[40]. A number of bases we tested for the reaction with a Pt/C catalyst. Although the reaction proceeds without base a marked improvement in conversion was observed with all bases tested (NaOH, $NaNO_3$, KOH, LiOH, RbOH and CsOH. The selectivity to glyceric acid was increased when NaOH, KOH and LiOH were used. The use of NaOH provided the highest yield of glyceric acid. When $NaNO_3$ was used a high selectivity to oxalic acid (85 %) was achieved. As shown previously the use of the gold catalyst in the presence of base leads to 100 % selectivity to glyceric acid.

Prati *et al.* investigated the effect of preparation method with carbon supported gold catalysts. Catalysts were prepared by impregnation and sol immobilisation[41]. It was found that the catalysts prepared by sol immobilisation showed the highest activity. It was found that this preparation method produced small (4-5 nm) well dispersed gold particles. The drawback to the high activity of these catalysts is the oxidation of the desired product glyceric acid over time. This occurred less when impregnation catalysts are employed this is most likely due to the larger particle size of these catalysts (>10 nm). The same effect was observed for titania supported gold catalysts[68]. In this work catalysts prepared by sol immobilisation were compared with those synthesised by deposition precipitation.

The next breakthrough came when Prati *et al.* synthesised bimetallic carbon supported AuPd and AuPt catalysts[23]. The bimetallic AuPd/C catalyst showed a higher activity (1.5 times) than both monometallic Au/C and Pd/C for the oxidation of glycerol at 30 °C. A physical mixture of Au/C and Pd/C was also tested; the activity of this mixture was comparable to that of a monometallic gold catalyst. It was suggested that the alloying of the 2 metals was the key to the enhancement in activity displayed by the bimetallic catalysts. This was confirmed when a bimetallic catalyst in which the metals were not in an alloyed phase failed to display the same activity as the alloyed bimetallic catalysts. The selectivity to glyceric acid was also increased when a bimetallic AuPd catalyst was used. The same activity trend was observed for the bimetallic AuPd as the monometallic gold catalyst in which the second highest selectivity is to the C3 product tartronic acid. The total selectivity to C3 products at 30 °C was > 88.9 % at 90 % conversion. The same trends were observed when graphite was chosen as the support[69].

The alloying of gold and platinum also led to an increase in activity in relation to Au/C and Pt/C, in the order of 1.4 times. The use of the bimetallic AuPt/C catalyst led to decrease in glyceric acid selectivity and an increase in the formation of the C2 product glycolic acid. Platinum catalysts have been shown to promote C-C cleavage previously[40]. The selectivity to C3 products at 30 °C was reduced to between 55.0 and 63.4 % at 90 % conversion.

Later investigations compared the effect of changing bimetallic AuPd particle sizes on the conversion of glycerol and selectivity to glyceric acid[22]. These particles were synthesised by the sol immobilisation method and supported on carbon. Once again, the metal particles with the smallest diameter, < 2 nm, proved to be the most active. As the particle size increased the activity decreased as is the case with monometallic gold catalysts. The selectivity trend is also echoed, the larger the bimetallic particles the higher the selectivity to glyceric acid, as smaller particles promote over oxidation which leads to tartronic and glycolic acid.

Dimitratos *et al.*[10]. also showed the synergistic effect of palladium addition to gold catalysts. In this work both preparation method and support was investigated. Au, Pd and AuPd catalysts supported on titania and carbon were synthesised by the impregnation and sol immobilisation method. The impregnation catalysts were prepared in 1 % and 5 % weight metal contents. There was a difference in the structure of the bimetallic particles on the titania and carbon supports. The bimetallic structures supported on titania were of a core-shell morphology with a palladium rich shell and gold rich core and the particles on the carbon support were homogeneous alloys. Once again, the bimetallic catalysts showed a dramatic increase in activity, a factor of 1.5 for carbon supported and 4 for titania supported. The monometallic catalysts on carbon were more active than the titania supported catalysts. This trend is reversed for the bimetallic catalysts. The selectivities were compared at iso conversion and it was found that the AuPd/TiO_2 was more selective to glycerate than the bimetallic carbon catalyst which showed higher selectivities to C2 product glycolic acid and C1 formic acid.

A comparison was made between the impregnation and sol immobilisation methods. The catalysts prepared by sol immobilisation were considerably more active than those prepared by impregnation. It has been discussed previously that metal particle size is a major factor in the activity of gold and gold palladium catalysts[22] for the selective oxidation of glycerol. The catalysts prepared by sol immobilisation have a smaller particle size distribution than the impregnation catalysts. The bimetallic particles prepared by the sol immobilisation method are small random homogenous alloys. Again, the bimetallic catalysts show a significant improvement in activity when compared with monometallic Au and Pd catalysts.

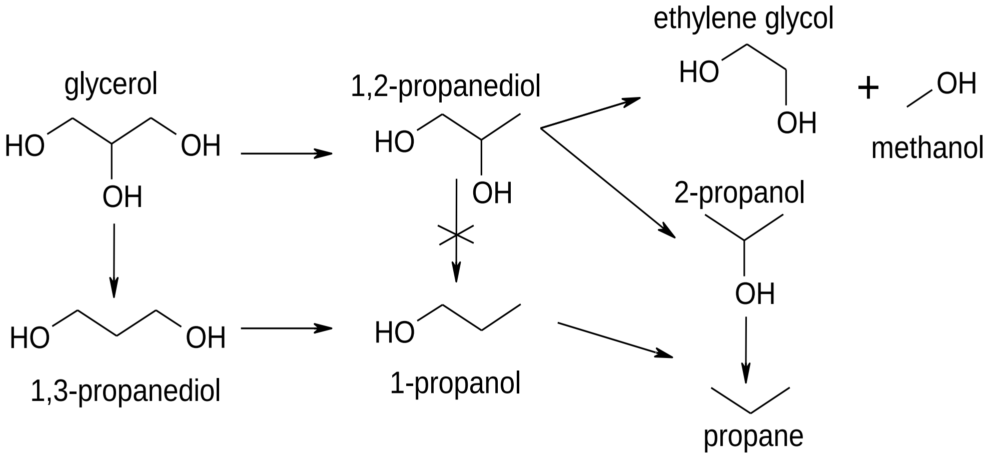
Recently advances have been made in the base free oxidation of glycerol. Platinum catalysts have been shown to be effective for this reaction[70, 71]. However, these platinum catalysts have been shown promote carbon-carbon cleavage resulting in formation of carbon dioxide and formic acid[40]. Prati *et al.* were the first to demonstrate that gold based catalysts supported on carbon were active for glycerol oxidation in base free conditions[72]. Low conversions of glycerol (< 10 %) were achieved by using monometallic gold catalysts supported on activated carbon, titania and H-mordenite. The experiments were carried out at 100 °C with 3 bar O_2 pressure. Only the H-mordenite supported catalyst showed a high selectivity to glyceric acid (70 %). The other supports resulted in high selectivities to C1 products (32-51 %). Bimetallic AuPd and AuPt catalysts were prepared supported on activated carbon. Both catalysts showed an improvement of activity and selectivity to glyceric acid when compared with monometallic catalysts. The gold-platinum catalyst was significantly more active than the AuPd catalyst, showing conversions of 58 and 12 % respectively. The platinum catalyst also resulted in an improved selectivity to glyceric acid. A AuPt/H-mordenite catalyst was also prepared and tested for the reaction This support was superior to the activated carbon support and yielded 83% selectivity to glyceric acid and 70 % glycerol conversion at 100 °C after 2 h.

Since the first investigations a number of variables have been investigated, such as catalyst preparation method[73], support[10] and metal particle size[74]. It has been shown that under basic conditions bimetallic gold palladium catalysts are more active than monometallic gold and palladium catalysts, thereby demonstrating a synergistic effect. Catalysts prepared by the sol immobilisation method are more active than catalysts prepared by other methods.

1.5.3 Selective hydrogenolysis of glycerol

The hydrogenolysis of glycerol leads to the formation of ethylene glycol, 1,2- and 1,3-propanediol as depicted in scheme 1-4. 1,2-propanediol is an important commodity chemical with applications in cosmetics, foods and the synthesis of pharmaceuticals. It is also utilised as a non-toxic de-icer for water supplies[75]. The traditional industrial method for the manufacture of 1,2-propanediol is from the hydration of propylene oxide[59] which is obtained from petroleum.

The selective hydrogenolysis of glycerol to 1,2-propanediol has been commercialised[76]. To produce propanediol from glycerol a copper chromite catalyst is utilised in the 2 stage reaction which can take place at 200 °C at less than 10 bar of hydrogen pressure[77]. This reaction proceeds *via* hydroxyactone which is then hydrogenated. The yield of 1,2-propanediol is >90 %. The production of 1,2-propanediol form glycerol is significantly less costly than the traditional method[61]. There is another new process currently in operation to transform glycerol into 1,2-propanediol; the vapour phase hydrogenation of glycerol[78].



Scheme 1-4 The hydrogenolysis of glycerol[59]

1,3-propanediol is a raw material in the synthesis of specialist polyester fibres which exhibit modified characteristics, such as chemical resistance and elastic recovery[79]. 1,3-propanediol is traditionally produced from fermentation, via hydration of acrolein or from the hydroformylation of ethylene oxide[59].

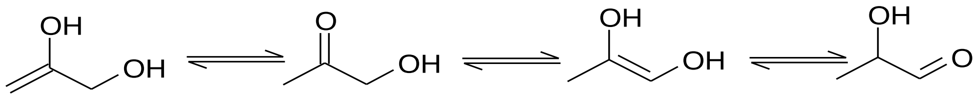
1.5.3.1 Selective oxidation of 1,2-propanediol

The oxidation of 1,2-propanediol has been carried out with supported gold catalysts to yield Lactic acid, acetic acid and formic acid[80]. Lactic acid has a number of uses in food, cosmetics and pharmaceutical industries[81]. Lactic acid is the building block for polylactic acid which is a polymer which has a number of applications in medicine[82], for example as biocompatible sutures and tissue engineering[83]. Polylactic acid can also be utilised as a biodegradable thermo plastic. Due to these important applications, the demand for lactic acid is expected to reach 200000 MT per year by the end of 2011[81]. Lactic acid can also be produced from the fermentation of glucose by lactic acid bacteria.

In 1998 Prati *et al.* reported the first oxidation of 1,2-propanediol by gold catalysis, using gold on carbon catalyst prepared by impregnation and deposition precipitation[8]. The experiments were carried out at 70 °C, with 300 kPa of O_2 with a substrate to metal ratio (s/m) of 1000. These reactions were carried out in the presence of a base, NaOH (1:1 molar ratio with substrate). Under these conditions this catalyst was found to give 100 % selectivity to lactic acid at 78 % propanediol conversion after 1 h. A comparison to commercial Pd/C and Pt/C was made, the gold catalyst was found to be superior in terms of selectivity (100 % selectivity to lactate for gold catalysts, ~90 % for both palladium and platinum catalysts). Deuterium exchange experiments were also conducted in order to probe the mechanism of oxidation. The mechanism is shown in scheme 1-6.

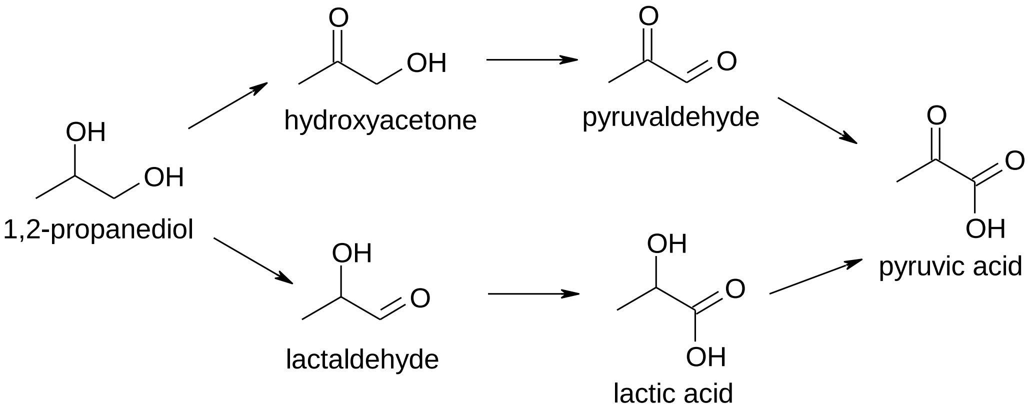
One route to lactic acid is the oxidation of the primary hydroxyl group of 1,2-propanediol this yeilds lactaldehyde and subsequently latate. The second route leads from the oxidation of the secondary hydroxyl group to form hydroxacetone which is rapidly transformed under basic conditions to form 2 different enols, as shown in scheme 1-5. The reaction then proceeds *via* pyruvic aldehyde which undergoes an intramolecular cannizaro reaction which spontaneously yields lactate under basic conditions. A small amount of pyruvate was also detected when palladium and platinum catalysts were employed at pH 8.

From these results in was established that the gold catalyst selectively oxidises the primary hydroxyl group of 1,2-propanediol, whereas, the palladium and platinum catalysts are not selective to either hydroxyl group and will oxidise both.



Scheme 1-5 Equilibria of hydroxyacetone under basic conditions[8]

This work also compares 2 preparation method for the oxidation of ethane-1,2-diol oxidation. With regards to the gold catalysts, the carbon supported catalysts were superior in terms of conversion to the alumina supported catalysts for both impregnation and deposition precipitation methods. It was found that larger gold particles were formed on the alumina support in both preparation methods. The DP catalysts were more active and selective to glycolate that those prepared by impregnation. It was shown that these DP catalysts have significantly smaller gold particles, suggesting that catalyst activity is related to metal particle size.



Scheme 1-6 reaction scheme of 1,2-propanediol[8]

The reuesability of Au/C, Pd/C and Pt/C was also investigated. The recycling tests showed that after 5 uses the gold and platinum catalyst showed minimal deactivation compared with palladium (from 75 – 50 % conversion after 5 runs). The only catalyst to maintain a high selectivity to lactate was the gold catalyst. Therefore it was shown that gold supported catalysts are superior to palladium and platinum catalysts in terms of selectivity and reusability.

The alloying of gold with palladium has been shown to lead to a 25 fold increase in activity of gold catalysts for the solvent free oxidation of alcohols[84]. Dimitratos *et al.* compared monometallic gold, palladium and bimetallic gold-palladium catalysts for the selective oxidation of 1,2-propanediol. Two supports, carbon and titania, and two preparation methods, impregnation and sol immobilisation, were compared. In this work the reactions were carried out in an autoclave reactor at 60 °C with 10 bar O_2 pressure. The substrate to metal ratio was 500 and 2 equivalents of NaOH was used (mol/mol).

The dispersion and structure of the supported metal particles is considerably different between the two preparation methods. The catalysts prepared by impregnation had particle sizes ranging from 2-24 nm with occasional rare large particles of ~25 nm, whereas the particles prepared by sol immobilisation had a much smaller size distribution of 4-7 nm. The nature of the bimetallic AuPd particles synthesised was also different. The catalysts prepared by impregnation displayed a core shell structure. For the titania supported catalyst a palladium rich shell with a gold core was observed. The particles supported on carbon were found to be homogeneous alloys, as were both catalysts prepared by sol immobilisation.

The comparison of the monometallic gold and palladium catalysts prepared by impregnation show that show that the gold catalyst is more active than palladium for both carbon and titania supports. When the two metals are alloyed the activity increased 2 fold in the case of the carbon supported and 3 fold for titania supported catalysts. For the carbon supported catalysts the bimetallic catalyst shows a considerable improvement for the selectivity to lacate (Au – 73.7, Pd-77.9 and AuPd – 95.4 %).The titania supported catalysts show higher selectivities to lactate than carbon supported catalysts. More C2 and C1 products resulting from C-C cleavage are observed in the case of carbon supported catalysts.

Table 1-5 Effect of the metal composition and nature of support on the liquid phase oxidation of 1,2-propanediol with O_2 using Au and Pd catalysts synthesised by impregnation[a]

		Selectivity (%)			
Catalyst	Conv. (%)	Lactate	Acetate	Formate	TOF (h^{-1}) [b]
1%Au/C_I	16	73.7	23.2	3.1	20
1%Pd/C_I	11	77.9	20.7	1.4	13
2.5%Au2.5%Pd/C_{Iw}	32	95.4	4.0	0.7	40
1%Au/TiO_{2I}	15	80.9	17.7	1.4	18
1%Pd/TiO_{2I}	6	99.7	0.0	0.3	7
5%Au/TiO_{2I}	27	91.5	6.0	1.6	34
5%Pd/TiO_{2I}	3	92.0	7.5	0.5	4
2.5%Au2.5%Pd/TiO_{2Iw}	91	96.3	3.6	0.1	114

[a] Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 500, NaOH/1,2-propanediol molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 4h. [b] TOF (h^{-1}) at 4 hours of reaction. TOF numbers were calculated on the basis of total loading of metals.

The catalysts prepared by the sol immobilisation were tested with a much lower substrate metal ratio (2000) than the impregnation catalysts. These catalysts are shown to be 10-20 times more active than the catalysts prepared by impregnation. The trend of reactivity of the metals is the same that is observed with the impregnation catalysts (Pd < Au < AuPd).

Table 1-6 Catalytic activity of Au, Pd and Au-Pd supported catalysts prepared by sol-immobilisation in liquid phase oxidation of 1,2-propanediol with O_2[a]

Catalyst	Conv. (%)	Selectivity (%) Lactate	Acetate	Formate	TOF (h^{-1})[b]
0.5%Au/TiO_{2SI}	58	96.0	4.0	0	1156
0.5%Pd/TiO_{2SI}	7	98.5	1.5	0	135
1%AuPd/TiO_{2SIm}	94	95.9	4.1	0	1880
1%Au/C_{SI}	31	92.0	7.2	0.8	619
1%Pd/C_{SI}	3	97.3	1.1	1.6	60
1%AuPd/C_{SIm}	53	99.3	0.3	0.5	1066

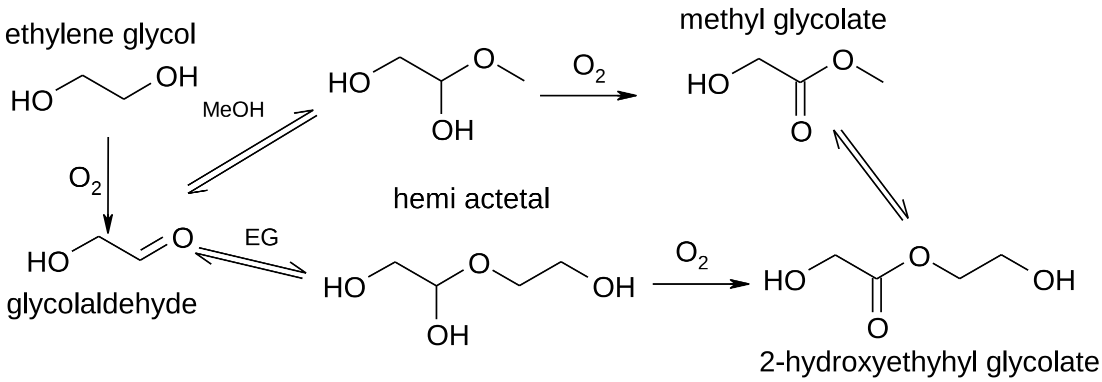
[a]Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 2000, NaOH/1,2-propanediol molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 1h. [b]TOF (h^{-1}) at 1 hour of reaction. TOF numbers were calculated on the basis of total loading of metals.

In summary, the use monometallic gold catalysts over that of palladium and platinum catalysts is advantageous in terms of activity and selectivity to desired C3 products. The alloying of gold with palladium produces a synergistic effect resulting in vast improvements on the activity and selectivity of the monometallic catalysts. Small AuPd nanoparticles which are random homogeneous alloys formed by the sol immobilisation method are favourable to the slightly larger core shell structures prepared by impregnation. The use of a carbon support led to an increase in C-C cleavage resulting in the formation of formic acid. The titania support was demonstrated to be superior in terms of activity and selectivity to lactic acid.

1.6 Oxidations in methanol

Carretin *et al.* demonstrated that gold catalysts are not active for the oxidation of glycerol without base[40]. It has been suggested that 2 molar equivalents of sodium hydroxide provides the optimal conversion of 1,2-propanediol and selectivity to lactic acid[80]. However, the use of stoichiometric reagents is not desired industrially. The formation of glycerol occurs in a base containing methanol solution as described in scheme 1.5.1-1. This fact raises the question as to whether this solution itself could provide a route to value added products.

Hayashi *et al.*[85] carried out the oxidation of alcohols using methanol as the solvent to produce esters, thereby negating the need of stoichiomatic amounts of base. In this publication ethanol, n-propanol, n-butanol, allyl alcohol, diethylene glycol, methallyl alcohol, ethylene glycol and 1,3-propanediol were oxidised in methanol. The oxidation of these alcohols was carried out in an autoclave charged with a catalyst, alcohols and oxygen gas (0.1–5 MPa). The reaction was carried out at 50–150 °C for 1–10 h. A comparison was made between oxide supported gold, palladium and ruthenium catalysts for the oxidative esterification of ethylene glycol. The reaction products were the desired product, methyl glycolate, and methyl formate. The gold catalyst was proven to be superior to both other catalysts tested displaying both the highest conversion of ethylene glycol and selectivity to methyl glycolate. For diols ethylene glycol and 1,3-propanediol it was found that only one hydroxyl group was reactive. A mechanism for the oxidative esterification of ethylene glycol was suggested.



Scheme 1-7 mechanism proposed for the oxidation of ethylene glycol in methanol[85]

It was hypothesised that the reaction proceeds via a hemiacetal and that the rate determining step, as in aqueous oxidations, is the removal of hydrogen from a hydroxyl group. The proposed reaction pathway is shown in scheme 1-7.

Nielsen *et al*[86]. investigated the oxidation of primary alcohols in methanol. A gold catalyst was chosen and the effect of pH was studied. It was found that the addition of acid was detrimental to the conversion of 1-hexanol, whereas, the addition of a base, $NaOCH_3$, was seen to increase the rate of conversion of 1-hexanol and hence yield of methyl hexanoate.

Further work on the oxidation of alcohols in methanol in the presence of catalytic base, sodium methoxide, was conducted by Taarning et *al.*[87]. In this publication the oxidative esterification of glycerol, 1,2-propanediol and 1,3-propanediol was achieved with titania and iron oxide supported gold catalysts. 1,2-propanediol was reported to react slower than glycerol and 1,3-propanediol, to compensate for this the substrate to metal ratio was reduced from 112 to 56. The observed products resulting from the oxidation of glycerol were methyl glycerate, dimethyl tartronate and dimethyl mesoxalate. It was suggested that the first step proceeds via hydroxyacetone and glyceraldehyde which are in equilibrium. The iron oxide supported catalyst was more active, it was also more selective to the final product, dimethyl mesoxalate as the conversion of methyl glycerate occurs faster with Au/Fe_2O_3 when compared to the titania supported catalyst.

The oxidation of 1,2-propanediol is hypothesised to proceed via lactaldehyde which is tautomerised to hydroxyactone or oxidised to methyl lactate. The final product is methyl pyruvate which arises from the oxidation of hydroxyacetone. This mechanism is in agreement with the aqueous scheme proposed by Prati *et al.*[8]. The oxidation of 1,3-propanediol is very selective, as seen by Hayashi *et al.*[85], only one hydroxyl group is oxidised to give methyl-3-hydroxypropionate with 90 % selectivity. The other products observed are dimethyl malonate and methyl acrylate. Again the first step on the reaction is the formation of an aldehyde, in this case 3-hydroxypropanal.

Homogeneous catalysts have been successful in oxidising both hydroxyl groups of 1,8-octanediol, 1,9-nonanediol and 1,12-dodecandiol[88]. An iridium complex and 2-(methylamino)ethanol (MAE) were utilised to achieve 55 % selectivities to the monoesters and 45 % selectivity to the diesters of these diols. The diols were reacted with the catalysts $[CpIrCl_2]_2$ and MAE, acetone and methanol at room temperature for 24 h.

In summary, the oxidation of alcohols in methanol with catalytic amounts of base represents a new route to value added products from biomass. Industrially significant chemicals can be synthesised by this method in which the use of stoichiometric amounts of base is not required.

1.7 The Aims of the project

The Aim of this project is to achieve value added chemicals from the bio derived molecule glycerol, thereby utilising a renewable resource, with the ultimate aim of producing industrially important oxidation products in a green manner by employing monometallic and bimetallic precious metal catalysts.

The first reaction to be investigated is the oxidation of 1,2-propanediol to yield lactic acid, with a view to reducing the current standard amount of base, 2 equivalents mol/mol. As gold catalysts are inactive in base free conditions, the prospect of catalytic base in methanol as a solvent will be investigated.

The second reaction is the oxidation of 1,3-propanediol, again with catalytic base. The literature reviewed has revealed that this reaction is difficult and the use of model compounds may be implemented in order to further understand the reaction mechanism to improve the yield of the desired product, dimethyl malonate.

The oxidation of glycerol is a well known reaction; however, there is currently the need for stoichiometric amounts of base in order to observe activity of gold catalysts for this reaction. This is undesirable for industrial applications due to the formation of chloride salts as a result of neutralisation. Novel precious metal catalysts will be employed under base free conditions with the aim of high and activity and selectivity to glyceric acid.

1.8 References

1. M. Berzelius, *Journal of the Franklin Institute*, 1836, **22**, 331-334.
2. M. Bowker, *The basis and applications of heterogeneous catalysis*, Oxford University Press, 1998.
3. A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896-7936.
4. G. Bond and P. Sermon, *Gold Bulletin*, 1973, **6**, 102-105.
5. M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, 405-408.
6. G. J. Hutchings, *J. Catal.*, 1985, **96**, 292-295.
7. T. Hayashi, K. Tanaka and M. Haruta, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, 1996, **41**, 71-74.
8. L. Prati and M. Rossi, *Journal of Catalysis*, 1998, **176**, 552-560.

9. P. Landon, P. J. Collier, A. J. Papworth, C. J. Kiely and G. J. Hutchings, *Chem. Commun. (Cambridge, U. K.)*, 2002, 2058-2059.
10. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.
11. D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2007, **122**, 407-411.
12. J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely and G. J. Hutchings, *Journal of Catalysis*, 2005, **236**, 69-79.
13. F. o. Moreau, G. C. Bond and A. O. Taylor, *Journal of Catalysis*, 2005, **231**, 105-114.
14. G. C. Bond, C. Louis and D. T. Thompson, *Catalysis by Gold*, Imperial College Press, 2006.
15. M. Faraday, Editon edn., 1857, vol. 147, pp. 145-181.
16. J. Wiesner and A. Wokaun, *Chemical Physics Letters*, 1989, **157**, 569-575.
17. W. Baschong, J. M. Lucocq and J. Roth, *Histochemistry and Cell Biology*, 1985, **83**, 409-411.
18. D. G. Duff, A. Baiker and P. P. Edwards, *Journal of the Chemical Society, Chemical Communications*, 1993, 96-98.
19. H. Hirai, Y. Nakao and N. Toshima, *Journal of macromolecular science. Chemistry*, 1979, **A13**, 727-750.
20. F. Porta, L. Prati, M. Rossi, S. Coluccia and G. Martra, *Catalysis Today*, 2000, **61**, 165-172.
21. L. Prati and G. Martra, *Gold Bulletin*, 1999, **32**, 96-101.
22. N. Dimitratos, J. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati and A. Villa, *Catalysis Letters*, 2006, **108**, 147-153.
23. C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, *Catalysis Today*, 2005, **102-103**, 203-212.
24. S. Meenakshisundaram, E. Nowicka, P. J. Miedziak, G. L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor, D. W. Knight, D. Bethell and G. J. Hutchings, *Faraday Discussions*, 2010, **145**, 341-356.
25. J. A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G. L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R. L. Jenkins, A. F. Carley, D. Knight, C. J. Kiely and G. J. Hutchings, *Nat Chem*, 2011, **3**, 551-556.

26. A. R. Vaino, *The Journal of Organic Chemistry*, 2000, **65**, 4210-4212.
27. S. Lee and P. L. Fuchs, *Journal of the American Chemical Society*, 2002, **124**, 13978-13979.
28. J. K. Edwards, A. Thomas, B. E. Solsona, P. Landon, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2007, **122**, 397-402.
29. R. Meiers, U. Dingerdissen and W. F. HÃ¶lderich, *Journal of Catalysis*, 1998, **176**, 376-386.
30. S.-E. Park, L. Huang, C. W. Lee and J.-S. Chang, *Catalysis Today*, 2000, **61**, 117-122.
31. G. Li, J. Edwards, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2006, **114**, 369-371.
32. M. John R, *Applied Catalysis A: General*, 2001, **221**, 73-91.
33. M. Haruta, B. Uphade, S. Tsubota and A. Miyamoto, *Research on Chemical Intermediates*, 1998, **24**, 329-336.
34. M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132-1135.
35. R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang and J. Suo, *Chemical Communications*, 2004, 904-905.
36. S. Golunski, R. Rajaram, N. Hodge, G. J. Hutchings and C. J. Kiely, *Catalysis Today*, 2002, **72**, 107-113.
37. Y.-J. Xu, P. Landon, D. Enache, A. F. Carley, M. W. Roberts and G. J. Hutchings, *Catalysis Letters*, 2005, **101**, 175-179.
38. B. E. Solsona, T. Garcia, C. Jones, S. H. Taylor, A. F. Carley and G. J. Hutchings, *Applied Catalysis A: General*, 2006, **312**, 67-76.
39. S. Biella and M. Rossi, *Chemical Communications*, 2003, 378-379.
40. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2003, **5**, 1329-1336.
41. F. Porta and L. Prati, *Journal of Catalysis*, 2004, **224**, 397-403.
42. L. Prati and F. Porta, *Applied Catalysis A: General*, 2005, **291**, 199-203.
43. A. Abad, P. Concepción, A. Corma and H. García, *Angewandte Chemie International Edition*, 2005, **44**, 4066-4069.
44. A. Corma and M. E. Domine, *Chemical Communications*, 2005, 4042-4044.
45. D. I. Enache, D. W. Knight and G. J. Hutchings, *Catalysis Letters*, 2005, **103**, 43-52.

46. G. Li, D. Enache, J. Edwards, A. Carley, D. Knight and G. Hutchings, *Catalysis Letters*, 2006, **110**, 7-13.
47. V. R. Choudhary, A. Dhar, P. Jana, R. Jha and B. S. Uphade, *Green Chemistry*, 2005, **7**, 768-770.
48. F.-Z. Su, M. Chen, L.-C. Wang, X.-S. Huang, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, *Catalysis Communications*, 2008, **9**, 1027-1032.
49. P. Miedziak, M. Sankar, N. Dimitratos, J. A. Lopez-Sanchez, A. F. Carley, D. W. Knight, S. H. Taylor, C. J. Kiely and G. J. Hutchings, *Catalysis Today*, 2011, **164**, 315-319.
50. S. Lim and L. K. Teong, *Renewable and Sustainable Energy Reviews*, **14**, 938-954.
51. N. Rahmat, A. Z. Abdullah and A. R. Mohamed, *Renewable and Sustainable Energy Reviews*, **14**, 987-1000.
52. A. S. M. A. Haseeb, M. A. Fazal, M. I. Jahirul and H. H. Masjuki, *Fuel*, **90**, 922-931.
53. K. r. W, *Renewable Energy*, **16**, 1078-1083.
54. http://www.pecc.org/food/pfso-singapore2006/PECC_Annual_06_07.pdf.
55. L. P. Koh and J. Ghazoul, *Biological Conservation*, 2008, **141**, 2450-2460.
56. J. Fargione, J. Hill, D. Tilman, S. Polasky and P. Hawthorne, Editon edn., 2008, vol. 319, pp. 1235-1238.
57. S. Sunderasan, *Renewable Energy*, 2009, **34**, 950-954.
58. A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chemistry*, 2008, **10**, 13-30.
59. C.-H. Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. Lu, *Chemical Society Reviews*, 2008, **37**, 527-549.
60. T. Valliyappan, N. N. Bakhshi and A. K. Dalai, *Bioresource Technology*, 2008, **99**, 4476-4483.
61. M. P. a. M. Rossi, *The Future of Glycerol*, RSC Publishing, 2008.
62. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angewandte Chemie International Edition*, 2007, **46**, 4434-4440.
63. R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964-967.
64. D. A. Simonetti, J. Rass-Hansen, E. L. Kunkes, R. R. Soares and J. A. Dumesic, *Green Chemistry*, 2007, **9**, 1073-1083.
65. S. Biella, L. Prati and M. Rossi, *Journal of Catalysis*, 2002, **206**, 242-247.
66. S. Demirel-Gülen, M. Lucas and P. Claus, *Catalysis Today*, 2005, **102-103**, 166-172.

67. S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G. J. Hutchings, *Chemical Communications*, 2002, 696-697.

68. N. Dimitratos, A. Villa, C. L. Bianchi, L. Prati and M. Makkee, *Applied Catalysis A: General*, 2006, **311**, 185-192.

69. N. Dimitratos, F. Porta and L. Prati, *Applied Catalysis A: General*, 2005, **291**, 210-214.

70. J. Gao, D. Liang, P. Chen, Z. Hou and X. Zheng, *Catalysis Letters*, 2009, **130**, 185-191.

71. D. Liang, J. Gao, J. Wang, P. Chen, Z. Hou and X. Zheng, *Catalysis Communications*, 2009, **10**, 1586-1590.

72. A. Villa, G. M. Veith and L. Prati, *Angewandte Chemie International Edition*, 2010, **49**, 4499-4502.

73. W. C. Ketchie, M. Murayama and R. J. Davis, *Topics in Catalysis*, 2007, **44**, 307-317.

74. N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati and A. Villa, *Catalysis Letters*, 2006, **108**, 147-153.

75. A. Corma, S. Iborra and A. Velty, *Chemical Reviews*, 2007, **107**, 2411-2502.

76. http://senergychem.com/.

77. M. A. Dasari, P.-P. Kiatsimkul, W. R. Sutterlin and G. J. Suppes, *Applied Catalysis A: General*, 2005, **281**, 225-231.

78. , WO2007010299A1, 2007.

79. P. Gallezot, *Green Chemistry*, 2007, **9**, 295-302.

80. N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chemistry*, 2009, **11**, 1209-1216.

81. G. Reddy, M. Altaf, B. J. Naveena, M. Venkateshwar and E. V. Kumar, *Biotechnology Advances*, **26**, 22-34.

82. A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardini and R. M. Filho, *Biotechnology Advances*.

83. B. Gupta, N. Revagade and J. Hilborn, *Progress in Polymer Science*, 2007, **32**, 455-482.

84. D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, Editon edn., 2006, vol. 311, pp. 362-365.

85. T. Hayashi, T. Inagaki, N. Itayama and H. Baba, *Catalysis Today*, 2006, **117**, 210-213.

86. I. Nielsen, E. Taarning, K. Egeblad, R. Madsen and C. Christensen, *Catalysis Letters*, 2007, **116**, 35-40.

87. E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, Editon edn., 2008, vol. 10, pp. 408-414.

88. N. Yamamoto, Y. Obora and Y. Ishii, *The Journal of Organic Chemistry*, 2011, **76**, 2937-2941.

2 Experimental

2.1 Chemicals – Source and Purity

The chemicals were used as received.

Water HPLC, Aldrich
Methanol HPLC, Aldrich
Hydrogen tetrachloroaurate trihydrate, Aldrich
Palladium chloride, Johnson Matthey
Platinum chloride, Johnson Matthey
Ceria, VP AdNano ceria, Evonik Degussa GmbH
Carbon, Aldrich G60, Darco
Titania, P25 Degussa
Magnesium oxide, Nanoscale Corporation
Polyvinyl alcohol, 99 % hydrolysed, Aldrich
Sodium borohydride, 98 %, Sigma
Tetrakis(hydroxymethyl)phosphonium chloride (THPC), 80% in water, Aldrich
Glycerol, ≥ 99 %, Sigma-Aldrich
1,2-propanediol, ≥ 99 %, Sigma-Aldrich
1,3-propanediol, ≥ 99.6 %, Sigma-Aldrich
1,4-butanediol, ≥ 99 %, Aldrich
Butyrolactone, ≥ 98 %, Aldrich
Ethylene glycol, ≥ 99 %, Sigma-Aldrich
Sodium hydroxide, ≥ 97 % powder, Sigma-Aldrich
Sodium methoxide, 25 wt. % in methanol, Sigma-Aldrich

2.2 Definitions

$$\boldsymbol{Conversion}\ (\%) = \frac{\boldsymbol{moles\ of\ reactant\ converted}}{\boldsymbol{initial\ moles\ of\ reactant}} \times \mathbf{100}$$

$$\boldsymbol{Selectivity}\ (\%) = \frac{\boldsymbol{moles\ of\ product}}{\boldsymbol{moles\ of\ reactant\ converted}} \times \mathbf{100}$$

$$\boldsymbol{TOF} = \frac{\boldsymbol{moles\ of\ reactant\ converted/moles\ of\ metal\ on\ catalyst}}{\boldsymbol{time}\ (\boldsymbol{h})}$$

The turn over frequency can be expressed as the concentration of active sites on the catalysts. However, in this work the number of active sites is unknown; therefore the TOF is calculated using the total number of moles of metal in the catalyst amount used.

The oxidation reactions were carried out using the same amount of precious metals, irrespective of the catalyst loading. This was achieved by using a standardised substrate:metal ratio.

$$\boldsymbol{s\!:\!m = \frac{number\ of\ moles\ of\ substrate}{number\ of\ moles\ of\ metal\ on\ catalyst\ used}}$$

2.3 Catalyst Preparation

2.3.1 Sol immobilisation

The sol immobilisation technique is a relatively new technique for the preparation of supported catalysts. This method involves forming a stabilised gold based colloid and immobilising the particles on a support. Before the immobilisation step the gold is chemically reduced from 3+ to 0. After the support is added the pH of the solution is reduced to lower than the isoelectric point of the support with an acid to achieve good wetting of the support.

2.3.1.1 Au,Pd,Pt, Au-Pd and Au-Pt catalysts by sol immobilisation

Monometallic and a range of bimetallic catalysts were prepared supported on activated carbon (AC), magnesium oxide and titania using the sol immobilisation method. The detailed procedure for the preparation of 0.5wt%Au-0.5wt%Pd/support (1g) follows. A colloid was formed by adding polyvinyl alcohol (PVA) to an aqueous solution (400 mL) of $HAuCl_4.xH_2O$ (0.408 mL of 12.25 mg/mL solution) and palladium chloride (0.5mL of 10mg/mL solution). The metals were then reduced using $NaBH_4$ (2.539 mL of 0.1M aqueous solution). The solution was left to equilibrate (30 min) before adding carbon support (0.99 g) and acidifying (0.1M H_2SO_4). After 1 h the solution was filtered, washed with water (800 mL) and dried (16 h, 110 °C). In the case of magnesium oxide supported catalysts the solution was not acidified after the support was added.

2.3.1.2 Ceria Supported Au, Pd and Au-Pd Catalysts by Sol Immobilisation

Ceria supported Au, Pd and Au-Pd were prepared using the sol immobilisation using a different method. The detailed procedure for the preparation of 0.5wt%Au- 0.5wt%Pd/ceria (1g) follows. Sodium hydroxide (2.4 mL of 0.2M aqueous solution) and Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 1.427 mL of 10% vol aqueous solution) were added to water (47 mL) and stirred for 3min. Aurochloric acid (0.408 mL of 12.25 mg/mL solution) and palladium chloride (0.5 mL of 10 mg/mL solution) were added and the solution was left to equilibrate (30 min) before adding ceria support (0.99 g) and acidifying to pH1 (0.1M H_2SO_4). After 1 h the solution was filtered, washed with water (800 mL) and dried (16 h, 110 °C).

2.3.2 Impregnation methods

2.3.2.1 Au,Pd and Au-Pd Catalysts by Wet Impregnation

Mono metallic and bimetallic catalysts were prepared supported on activated carbon (AC), silica, titania and ceria by wet impregnation. The detailed procedure for the preparation of 2.5wt%Au- 2.5wt%Pd/support (1g) follows. Palladium chloride (41.66 mg) was dissolved in an aqueous solution of aurochloric acid (4.08 mL of 12.25 mg/mL solution). Support (0.95 g) was then added and the mixture was stirred and heated until a paste was formed. The catalyst was then dried (110 °C, 16 h). After this time the catalyst was ground and calcined at 400 °C for 3 hours with a ramp rate of 20 °C/min.

2.3.2.2 Modified impregnation method.

A bimetallic 0.5wt%Au- 0.5wt%Pd/MgO catalyst was prepared by a modified impregnation method. A 50 ml round bottom flask fitted with a magnetic stirrer bar was charged with aurochloric acid (5.6 mL of a 8.9 mg/mL solution) and an acidic $PdCl_2$ solution (8.3 mL of a 6mg/mL in a 0.58 M HCl solution). The volume of the solution was adjusted using deionised water to a total volume of 16 ml. The solution was stirred vigorously (1000 rpm) and the temperature of the oil bath was raised from 27 ^oC to 60 ^oC over a period of 10 min. After this time MgO support was added (1.98 g) over a period of 8-10 min with constant stirring. After completion of the addition of the support, the slurry was stirred at 60 ^oC for an additional 15 min. Following this, the temperature of the oil bath was raised to 95 ^oC and the slurry was stirred at that temperature for 16 h. Subsequently, the solid powder was transferred into a mortar and pestle and was ground thoroughly to form a uniform mixture. After this time the catalyst was calcined at 400 °C for 3 hours under a steady flow of 5 %H_2 in Ar with a ramp rate of 10 °C/min.

2.4 Catalyst Evaluation

The substrates used in this study are ethylene glycol, 1,2-propanediol, 1,3-propanediol, glycerol, butyrolactone and 1,4-butanediol.

2.4.1 Oxidation of Alcohols in Water – Standard Reaction Conditions in Autoclave Reactor

A 50 mL autoclave was charged with an aqueous solution of the chosen alcohol (0.6 M, 20 mL), sodium hydroxide (0.96 g) and catalyst (s:m=2000). The reactor was then sealed, pressurised (10 bar O_2) and purged 3 times. The oxygen inlet remained open so that oxygen was replenished as it was consumed. The reactor was then heated to the required temperature. The stirrer speed was set to 1500 rpm. The reaction duration was 4 hours. Samples were taken periodically and analysed by high performance liquid chromatography.

2.4.2 Oxidation of Alcohols in Water – Standard Reaction Conditions in Glass Reactor

A 50 mL Colover glass reactor was charged with an aqueous solution of the chosen alcohol (0.3M, 10 mL), sodium hydroxide (0.24 g) and catalyst (s:m=2000). The reactor was then sealed, pressurised (3 bar O_2) and purged 3 times. The oxygen inlet remained open so that oxygen was replenished as it was consumed. The reactor was then heated to the required temperature. The stirrer speed was set to 1000 rpm. The reaction duration was 4 h. Samples were taken periodically and analysed by high performance liquid chromatography.

2.4.3 Oxidation of Alcohols with Hydrogen Peroxide

A 50 mL round bottom flask fitted with condenser was charged with an aqueous solution of the the chosen alcohol (0.3M a, 20 mL), sodium hydroxide (0.48 g) and catalyst (s:m=2000). Hydrogen peroxide was added (4 equivalents). The reactor was then heated to the required temperature. The stirrer speed was set to 1000 rpm. The reaction duration was 4 h. Samples were taken periodically and analysed by high performance liquid chromatography.

2.4.4 Oxidation of Alcohols with Bubbling Oxygen

A 50 mL round bottom flask fitted with condenser was charged with an aqueous solution of the the chosen alcohol (0.3M a, 20 mL), sodium hydroxide (0.48 g) and catalyst (s:m=2000). The reactor was then heated to the required temperature. The stirrer speed was set to 1000 rpm. Oxygen gas was bubbled through the solution at a chosen flow rate. The reaction duration was 4 h. Samples were taken periodically and analysed by high performance liquid chromatography.

2.4.5 Oxidation of Alcohols in Methanol – Standard Reaction Conditions in Autoclave Reactor

A 75 mL HEL autoclave was charged with the chosen alcohol (8 mMol), methanol (35mL) sodium methoxide (1.6 mMol, 25% wt. in methanol) and catalyst (s:m=1000). The reactor was then sealed, pressurised (10 bar O_2) and purged 3 times. The oxygen inlet remained open so that oxygen was replenished as it was consumed. The reactor was then heated to the required temperature. The stirrer speed was set to 1000 rpm. The reaction duration was 24 h. Samples were taken periodically and analysed by gas chromatography equipped with a CP-wax column.

2.4.6 Oxidation of Alcohols in Methanol– Standard Reaction Conditions in Glass Reactor

A 50 mL colover glass reactor was charged with the chosen alcohol (3 mMol), methanol (15mL) sodium methoxide (0.6 mMol) and catalyst (s:m=500). The reactor was then sealed, pressurised (3 bar O_2) and purged 3 times. The oxygen inlet remained open so that oxygen was replenished as it was consumed. The reactor was then heated to the required temperature. The stirrer speed was set to 1000 rpm. The reaction duration was 24 h. Samples were taken periodically and analysed by gas chromatography equipped with a CP-wax column.

2.4.7 Catalyst Stability

2.4.7.1 Filtration Experiments

To establish whether any metal was leached from the catalyst during the reaction and is therefore capable of initiating a homogeneously catalysed reaction, the reaction was carried out as normal for a specific time. After this time the catalyst was removed by filtration, a sample was taken and the reaction vessel was charged with the remaining reactant solution. The standard reaction protocol was followed for the same amount of time. The pre- and post filtration reaction samples were analysed by the appropriate method and compared to discover whether a homogeneous reaction was taking place.

2.4.7.2 Reuse Experiments

To establish the stability of the catalyst, the catalyst (2x normal mass) was tested under the standard conditions, recovered and retested under the standard conditions.

2.5 Catalyst characterisation

2.5.1 Scanning Transmission Electron Microscopy (STEM)

Electron microscopes can be used to observe catalyst surfaces. In this way it is possible to determine the size and composition of supported particles. In transmission electron microscopy (TEM), an electron beam between 100-400 KeV is directed at a sample, the transmitted electrons form a 2D image of the catalyst surface which a can be magnified to produce a bright field image and the electrons which are diffracted by the sample particles produce a dark field image.

In scanning electron microscopy (SEM), a narrow beam of electrons are rastered over a catalyst surface. The electron beam displaces some of the surface electrons, which are known as secondary electrons and are low energy, these are detected to provide an image of the catalyst surface. Some of the incident electrons are backscattered by atomic nuclei and provide information on the elemental composition of the sample, as the amount of scattering is dependent upon atomic weight.

Scanning transmission electron microscopy combines both techniques. Elemental analysis is possible due to the emission of X-rays from the sample when it is bombarded with electrons. These X-rays are analysed by energy dispersive analysis of X-rays, EDX.

2.5.1.1 Scanning Transmission Electron Microscopy (STEM) Experimental

STEM was carried out at Lehigh University centre for advanced materials and nanotechnology. Samples for transmission electron microscopy (TEM) analysis were prepared by dipping a carbon-coated copper TEM grid directly into the finely ground dry catalyst powder. Bright-field diffraction-contrast imaging was used to determine particle size distributions with a JEOL 2000FX TEM operating at 200 kV. Scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) imaging was used to image the nanoparticles at atomic resolution with an aberration corrected JEOL 2200FS STEM operating at 200 kV. STEM X-ray energy dispersive spectroscopic (XEDS) imaging was performed in an aberration-corrected FEI Titan 80-300 (S)TEM equipped with a 4pi Revolution EDX system.

2.5.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface sensitive technique which can be utilised to establish elemental make up of a catalyst surface. It also provides information on the oxidation states of the elements present[1]. This technique relies on the principles of the photoelectric effect, in which a photon of energy hv is absorbed by an atom. As a consequence, an electron with binding energy E_b is ejected from the atom with kinetic energy E_k. φ is the work function of the spectrometer.

$$E_k = hv - E_b - \varphi$$

Equation 2-1

In this technique Al Kα (1486.3 eV) X-rays are fired at the catalyst surface to achieve this effect. The intensity and kinetic energy of the ejected electrons (photoelectrons) are measured. Each element has a characteristic binding energy and the photoelectrons can therefore be assigned to a specific element.

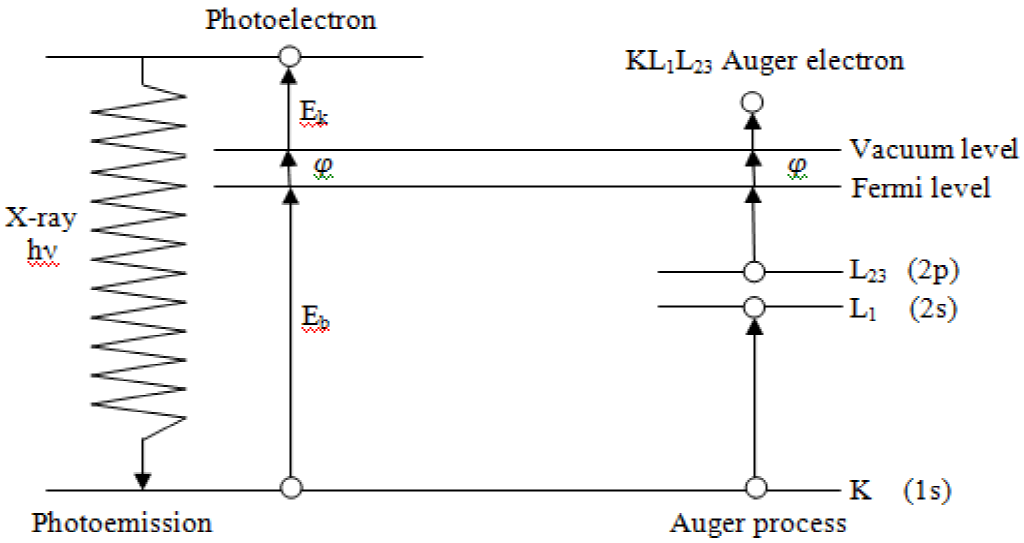


Figure 2-1 XPS processes of photoemission and the Auger Process

It is possible to establish the oxidation state of the element by looking more closely at the binding energy of the atom. The electronic energy states of an atom are altered when the oxidation state is changed. This is due to the attractive force from the nucleus exerted on the electrons being shared over differing numbers of electrons. The fewer electrons there are, the stronger the pull of the nucleus and therefore the binding energy is increased.

The Auger process is described in figure 2-1. Auger electrons arise from the absorption if the X-ray photon emitted by the photoemmision process by another electron in the atom. If the energy of the photon is greater than the binding energy of the electron the electron is ejected from the atom, in an autoionisation mechanism[2]. A typical spectra is shown below in figure 2.2.

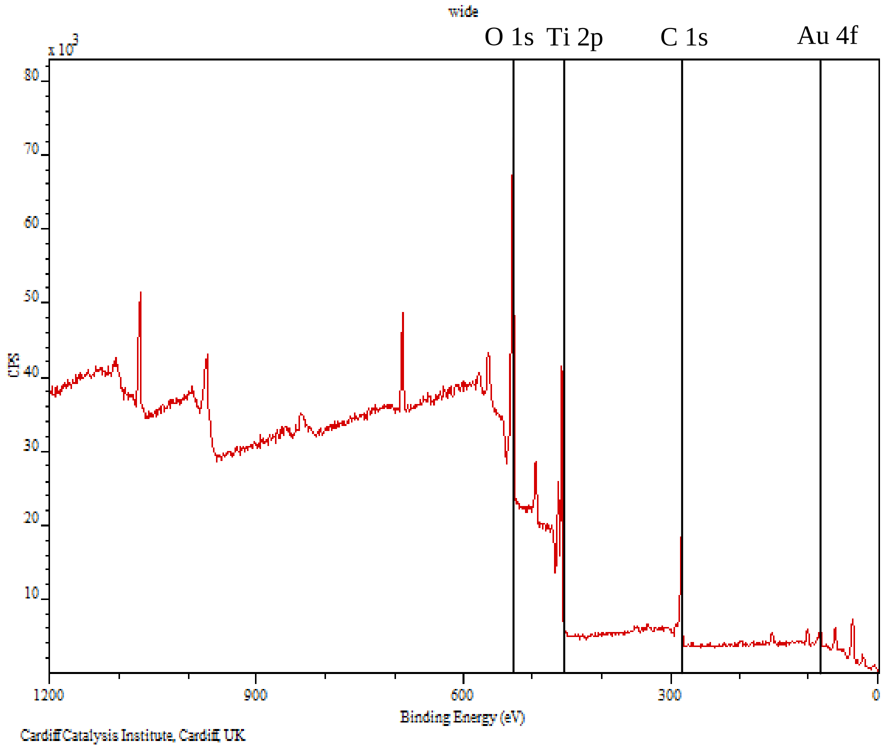


Figure 2-2 the XPS spectra of a 1.5% Au/TiO$_2$ catalyst

2.5.2.1 X-ray Photoelectron Spectroscopy (XPS) Experimental

The XPS analysis within this report was conducted at the Cardiff University XPS analysis centre using a VG EscaLab 220i spectrometer equipped with an AlKα X-ray 300 W source. The binding energies were standardised against a C 1s reference (284.7 eV).

2.5.3 X-ray Diffraction (XRD)

XRD is a technique used to probe the bulk crystalline properties of catalyst samples. It is possible to identify crystalline phases present and establish particle sizes within a powder sample[1].

To produce the X-rays, a copper target is bombarded with high energy electrons. Characteristic Kα (8.04 keV, 0.154nm) and Kβ X-rays are emitted, resulting from excited electrons in the copper target returning to the ground state. The Kβ X-rays are filtered out and the remaining Kα photons are elastically scattered by atoms in the catalyst sample. The scattered X-rays are measured using a moving detector and those that are in phase interfere constructively to give higher intensity reflections. To calculate lattice spacings d, the Bragg equation is used which relates wavelength of the x-rays, λ, the angle between incident x-rays and the normal plane, θ, and the order of reflection, n.

$$n\lambda = 2d\sin\theta$$

Equation 2-2 Bragg's law[3]

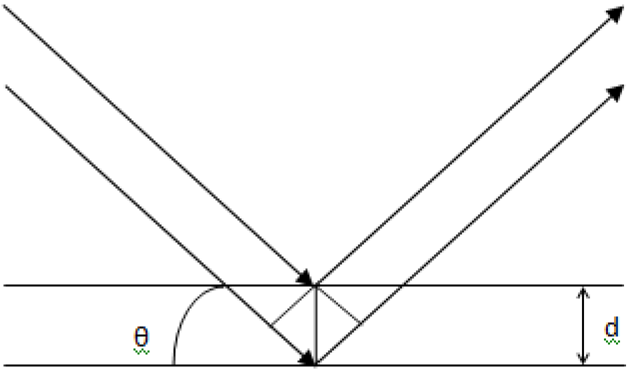


Figure 2-3 diagrammatical representation of Bragg's law

These characteristic lattice d spacings can then be used to identify the compounds present. Information about crystallite size can also be obtained from XRD. When long range order is present in a sample the diffraction peaks are clear and sharp. Broadening occurs when this order is disrupted and subsequently there is incomplete destructive interference. The scherrer equation links crystallite size, $\langle L \rangle$, to line width, β.

$$< L >= \frac{K\lambda}{\beta cos\theta}$$

Equation 2-4 Scherrer equation

Where λ is the wavelength of the x-rays, θ is the angle between incident x-rays and the normal plane, and K is a constant, usually 1.

2.5.4 Characterization and phase analysis of MgO catalysts

XRPD spectra were acquired using a X'Pert PanAlytical diffractometer operating at 40 kV and 30 mA selecting the Cu K_{α} radiation using a Ni filter. Detailed set-up conditions were: soller slits 0.04 radians, mask 15 mm, divergence and receiving slits $1/4^{o}$, step scan mode from 10 to 80^{o} 2θ in 33 min. Analysis of the spectra was carried out using X'Pert HighScore Plus software for the full pattern analysis and Specview software for the analysis of the line broadening.

Phase analysis was based on the following JCPDS entries: $Mg(OH)_2$ (brucite) entry file: 07-0239, MgO (periclase) entry file: 45-0946, $MgCO_3$ (magnesite) entry file: 08-0479 and $Mg_2CO_3{\cdot}2H_2O$ (barringtonite) entry file: 18-0768.

Product analysis

2.5.5 Gas chromatography (GC)

Gas Chromatography (GC) is a commonly used technique for separating chemical mixtures. Liquid or gas samples are vaporised in an injector port after which a carrier gas, helium, transports the now gaseous sample to the chromatography column where the components are separated by differing interactions with the stationary phase. Each component is then carried to the flame ionisation detector (FID). The products are combusted with air and hydrogen to produce cations which are analysed by an anode detector.

The carrier gas is most often helium which is compatible with most detectors resulting in good resolution and separation of peaks. A liquid sample is injected through a rubber septum into the GC injection port using a syringe. Inside the injection port is a salinised glass liner. The carrier gas then transports the now vapourised sample to the chromatography column. This column, the stationary phase, is usually a viscous liquid chemically bonded to the inside of the capillary column or on the surface of solid particles packed into the column or can be the solid particles themselves. In general non-polar columns are used to separate non polar mixtures and polar columns, polar solutions.

The Gas chromatographs used in this work utilised flame ionisation detectors (FID), however other detectors are available such as thermal conductivity detectors which are universal but are less sensitive than FID and electron capture detectors which is primarily used for halogen containing molecules[4]. In an FID the separated components of the solution are combusted in a mixture of air and hydrogen gases. Carbon (except carbonyl and carboxyl) atoms produce CH radicals which it has been suggested form CHO^+ ions in the flame.

$$CH + O \rightarrow CHO^+ + e^-$$

The number of ions produced is proportional to the number of carbon atoms entering the flame. Electrons flow from the anode to the cathode where they neutralise the CHO+ in the flame, this creates a current which is the detection signal.

2.5.5.1 Experimental

GC analysis was carried out using a Varian 3800 chromatograph equipped with a CP8400 autosampler and CP-wax 52 column. Products were identified by comparison with authentic samples. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used. Calibration curves are attached as an appendix.

2.5.6 Gas Chromatography Mass spectrometry (GCMS)

Gas chromatography mass spectrometry can be used to separate and identify chemical components in a volatile solution. The compounds are separated by gas chromatography as described above, subsequently; each component is identified by ionisation and detection in mass spectrometry. Mass spectrometry is very compatible with gas chromatography as low concentrations of analyte are needed for analysis. Mass spectrometry is used to determine the masses of atoms, molecules and fragments of the latter.

As molecules leave the GC they are ionised by electron ionisation. A hot filament emits electrons which are then accelerated through a potential (70 V). These electrons interact with the molecules from the GC causing ionisation usually by the loss of an electron. If one electron is removed the remainder of the molecule is the positively charged molecular ion. This ion may have enough energy to undergo further fragmentation.

A positively charged plate repels the ions towards the analyser tube. The ions are then separated by their mass to charge ratios (m/z). The two most common types of detector are the time of flight detector and the quadrapole mass analyser. In the former ions are accelerated by an electrical field so that all ions have the same kinetic energy. The velocities at which the ions reach the detector can be used to determine the mass to charge ratio of the ions. Lighter ions travel faster than heavier ones, therefore, all ions with the same m/z ratio arrive at the detector at the same time. The separation is shown below in equation 2.6.2-1 where E is the pulse potential, s is the tube length, d is the length of field free driftzone and t is the time of flight of the ion.

$$\frac{m}{z} = 2eEs\left(\frac{t}{d}\right)^2$$

Equation 2-5 TOF separation

The second technique, the quadrupolar analyser, separates the ions of differing mass to charge ratio with the application of oscillating electric field. The quadrupole consists of four metal rods which have a current applied across them along with alternating radio frequencies. The movement of the ions through the poles depends upon the electric fields as only specific m/z ratios will have a stable trajectory through the detector. As the fields change ions of differing m/z are allowed to reach the detector.

The separated ions can be detected by a number of methods including an electron multiplier and Faraday cup. An electron multiplier uses a vacuum tube to multiply charges. A charged particle collides with an emmisive material with induces the emission of secondary electrons. These electrons are accelerated to strike a second diode to create more electrons. This greatly amplifies the signal received.

The Faraday cup uses the production of a current to detect the ions. The ions strike a metal plate, the transfer of charge between the two creates a small current. The size of this current is dependent on the number of ions which can therefore be determined.

2.5.7 High Performance liquid chromatography (HPLC)

Aqueous product mixtures which are not volatile enough to use gas chromatography were separated and quantified by reverse phase HPLC. In this technique mixtures are separated by forcing them through very fine solid particles at high pressures. Liquid product mixtures were injected into the injector port where it is mixed the polar mobile (eluent) phase.

This mobile phase can be isocratic or gradient in nature. Isocratic elution uses just one solvent, if the single solvent is not adequate to separate the components in a reasonable timeframe more than one solvent can be used in differing concentrations as the chromatography run is underway.

The sample in the mobile phase is then pumped to the non polar column. The most common type of stationary phase support is microporous particles of silica. These particles are permeable to solvent and have a high surface area of hundreds of meters per gram. In liquid-liquid partition chromatography, the silica sometimes has covalently bonded silanol groups on its surface.

The components and solvent molecules compete for binding sites on the stationary phase. Each component equilibrates within the column and elutes at a different time, at which time it is pumped to the detectors. Elution occurs when the solvent displaces the solute from the column. In this way the products are identified by comparison with authentic samples.

The refractive index detector measures the refraction of a beam of light through the liquid being pumped through the detector. The refractive index is altered by the composition of the liquid. The refractive index detector is used for detecting non ionic, non UV active non fluorescent molecules.

The sample is then pumped to the second detector, the ultra violet - visible (UV-vis) detector which is equipped with deuterium and quartz halogen lamps (190-900 nm). This detector is around 1000 times more sensitive that the RI detector. Many compounds absorb radiation in this range, including aromatics and compounds containing carbonyl groups. The intensity on the UV light is measured before and after the sample to establish the absorbance. Absorbance, A, is proportional to concentration, c.

$$A = \varepsilon l c$$

Equation 2-6

Where ε is molar absorptivity and l is path length

Therefore, by constructing calibration curves the concentration of reactants and products it is possible to calculate the conversion of reactants and yields of products.

2.5.7.1 Experimental

Analysis was carried out using Varian 920 HPLC with ultraviolet and refractive index detectors. Reactants and products were separated using a Metacarb 67H column. The eluent was an aqueous solution of H_3PO_4 (0.01M) and the flow was 0.3 ml/min. Samples of the reaction mixture by a factor of 10 using the eluent. Products were identified by comparison with authentic samples. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used.

2.5.8 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy is one of the most widely used analytical techniques in modern chemistry due to its applications in determining the structure of unknown molecules. NMR spectroscopy is based on the principle that electrons and some nuclei have spin angular momentum also known as a magnetic moment[5] (when spin quantum number, I, is not 0). Outside of a magnetic field all energy levels are degenerate, this changes with the application of an external magnetic field.

An electron, for instance, has spin quantum number s = ½, in an electron field this electron has two possible orientations $m_s = +½$ (denoted α or ↑) or $m_s = -½$ (β or ↓). The alignment of the electron is determined by the value of m_s and the magnetic field B and the energy of each orientation is given by equation 2-10 below[3]. Where g_e is the g-value of the electron (2.0023 for a free electron) and γ is the gyromagnetic ratio of the electron given by equation 2-11.

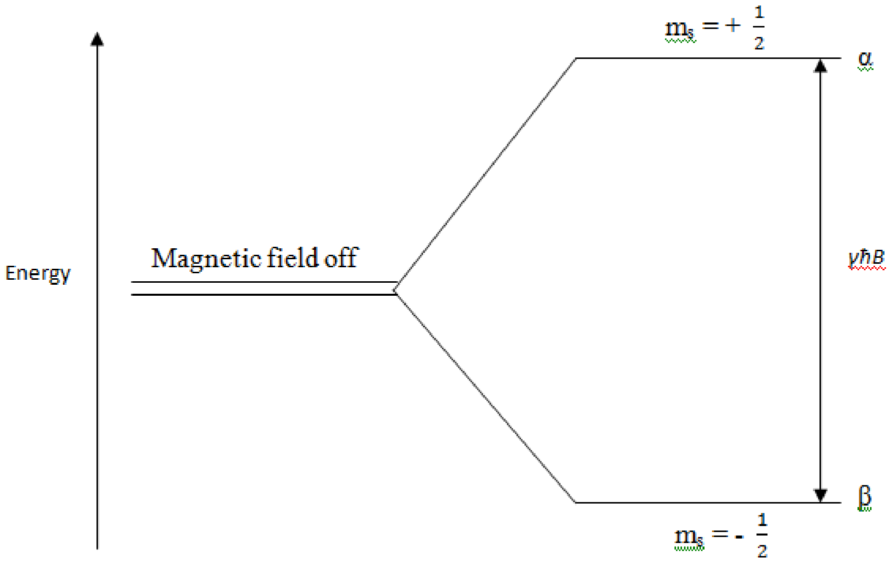


Figure 2-7 The energy levels of a spin ½ nucleus in a magnetic field.

$$E_{m_s} = -g_e\gamma\hbar B m_s$$

Equation 2-8

$$\gamma = -\frac{e}{2m_e}$$

Equation 2-9

By irradiating the nucleus with energy matching that of the energy difference between the two energy states, it is possible to promote a nucleus from the lower energy level to the higher one. The extra energy is dissipated by spin-spin or spin-lattice relaxation.

The chemical shift of a nucleus is the difference between its resonance frequency and that of a reference standard[3]. This chemical shift increases with increasing magnetic field strength in a proportional relationship. Another factor which effects chemical shift is the shielding effects of surrounding atoms. This chemical shift is indicative of neighbouring groups.

The area underneath each resonance signal is proportional to the number of nuclei in that particular “environment”. To further understand the nature of the molecule under investigation the fine structure of the spectrum must be considered. The resonances signals themselves undergo splitting arising from the contribution of each nucleus to the local field experienced by other nuclei. This is known as spin-spin coupling and is denoted by the constant, J (Hz). This constant is specific to the molecule and is unaffected by magnetic field strength. The amount of splitting is dependent on the number of neighbouring spin active nuclei. In general, *N* equivalent nuclei spin=1/2 nuclei split the resonance of a neighbouring atom into *N*+1 lines, with intensity distributions of Pascals triangle[3].

2.5.8.1 Experimental

The ^{13}C and ^{1}H NMR spectra were obtained using a Bruker 'Avance' 400 MHz DPX spectrometer, equipped with Silicon Graphics workstation running 'X win 1.3' with results reported in ppm with number of protons, multiplicity and assignment. All chemical shifts for ^{1}H NMR were recorded in deuterated chloroform (*d*-$CDCl_3$) or deuterated dimethylsulfoxide (d_6-DMSO).

2.5.9 Atomic Absorption Spectroscopy (AAS)

In atomic spectroscopy techniques, a substance to be probed is ionised in a flame, furnace or plasma. It is possible to measure the relative concentrations of each element in the sample by absorption or emission of radiation of specific wavelengths[4]. These wavelengths are characteristic to particular energetic transitions within atoms of a specific element.

The spectrometer uses a premix burner to mix the fuel, oxidant and sample before introduction to the flame. The most common oxidant is air and fuel is acetylene, this produces a flame temperature of 2400 – 2700 K. The mixture is sprayed into the flame and vapourised. The liquid in the sample is evaporated and the solids are decomposed into atoms.

Hollow cathode lamps are used to produce the spectrum, they contain a vapour of the element under analysis and either Ne or Ar. A voltage is applied between the anode and cathode, and the gas is ionised with the positive ions accelerated towards the cathode to produce a current (2-30 mA). The energy of these ions sputters metal ions from the cathode into the gas phase. These gaseous ions collide with high energy electrons to emit monochromatic photons, which can be absorbed by same metal in the analyte solution. The lamp is pulsed on and off to distinguish between signals from the lamp and flame and flame emission. The subtraction of which gives the signal due to metal in the analyte.

Concentrations of the element can be calculated as the amount of absorption is proportional to the amount of the element present.

2.5.9.1 Experimental

Atomic absorption spectroscopy was performed using a Perkin–Elmer 2100 atomic absorption spectrometer equipped with a magnesium (hollow cathode) lamp and air acetylene flame. The wavelength was 202.5 nm. An external calibration was carried out using known concentrations of Magnesium (10-100ppm) in order to quantify levels of magnesium in reaction mixtures. The reaction mixtures were analysed for magnesium after filtration.

References

1. J. W. Niemantsverdriet, *Spectroscopy in Catalysis: An Introduction*, John Wiley & Sons, 2008.
2. G. Attard and C. Barnes, *Surfaces*, Oxford University Press, 1998.
3. P. W. Atkins and J. D. Paula, *Elements of physical chemistry*, W. H. Freeman, 2009.
4. D. C. Harris, *Quantitative chemical analysis*, W.H. Freeman and Co., 2003.
5. A. K. Brisdon, *Inorganic spectroscopic methods*, Oxford University Press, 1998.

3 Catalyst Characterisation

A number of techniques were employed to probe the nature of the metals on the catalysts and the catalyst supports.

3.1 X-ray diffraction of MgO supported catalysts

XRD was carried out in order to probe the catalyst support to determine whether the different preparation methods affected the nature of the support.

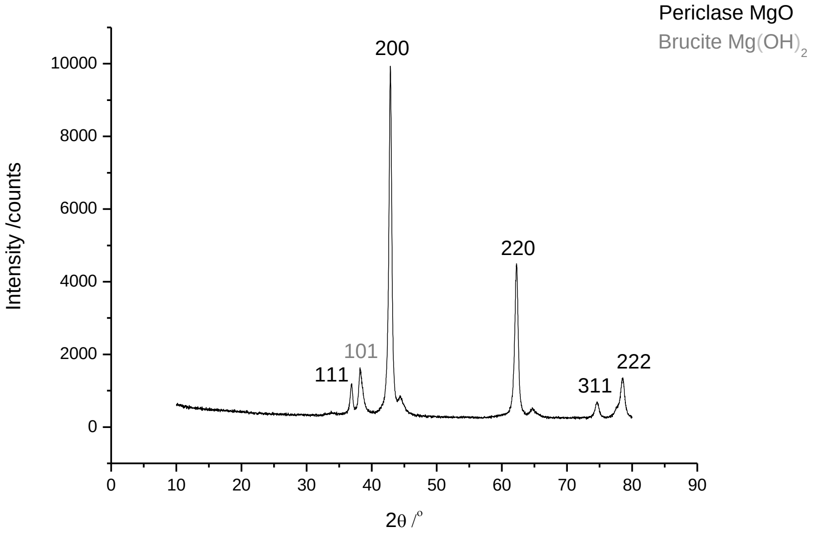


Figure 3-1 The XRD spectrum of AuPd/MgO prepared by the impregnation method

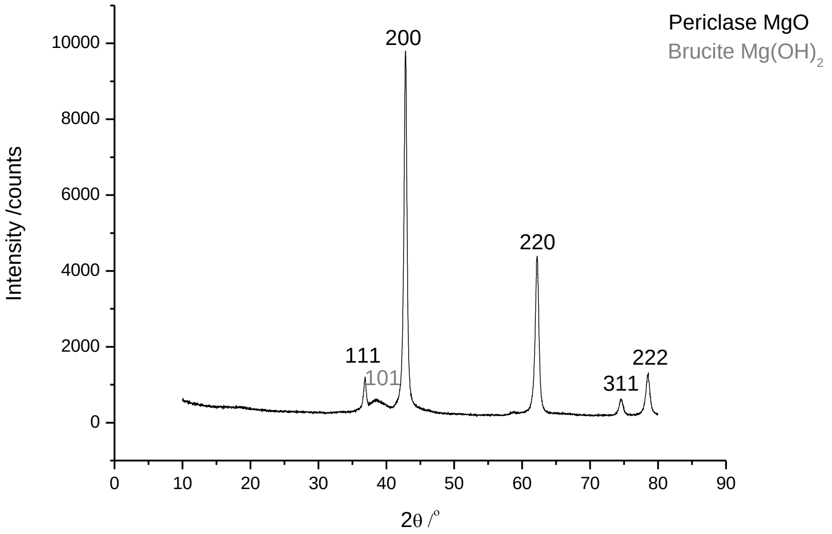


Figure 3-2 The XRD spectrum of AuPd/MgO prepared by the modified impregnation method

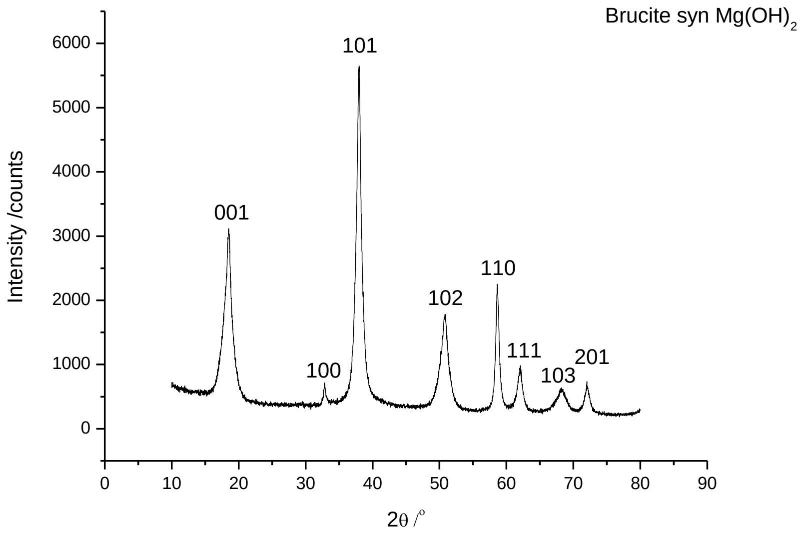


Figure 3-3 The XRD spectrum of AuPd/MgO prepared by the sol immobilisation method

The impregnation methods have largely retained the Periclase MgO structure of the bare support, a small amount of the Brucite $Mg(OH)_2$ (101) phase is evident (figures 3-1 and 3-2). The catalyst prepared by the sol immobilisation method has a very different structure. The support appears to be entirely $Mg(OH)_2$ with the brucite structure. All diffraction patterns seen can be attributed to this brucite material (figure 3-3).

3.2 UV analysis

The unsupported bimetallic Au-Pd colloidal sol (1:1 wt) was analysed by UV-visible spectroscopy in order to detect unalloyed gold.

The UV spectrum (figure 3-4) shows an absence of the gold surface plasmon band (490 -520 nm). This indicates the formation of alloy between gold and palladium.

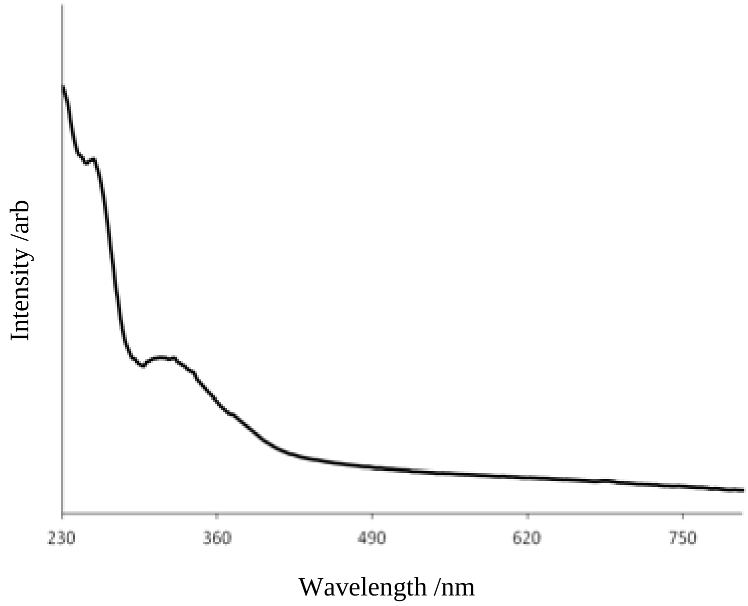


Figure 3-4 The UV-visible spectrum of the gold palladium sol prepared by the THPC/NaOH method

3.3 XPS

3.3.1 Carbon and titania supported catalysts

X-ray photoelectron spectroscopy was carried out to determine the nature of the metallic groups on the catalyst surface and to quantify the metal loadings. The bimetallic AuPd catalysts prepared by sol-immobilisation supported on carbon and titania are indicated to be random alloys as no surface enrichment of either metal is evident. The palladium present is in both Pd^{2+} and Pd^0 states with the metallic palladium in higher concentrations.

3.3.2 Ceria supported catalysts

XPS analysis of Au/CeO_2 prepared using the THPC/NaOH method (figure 3-5) revealed that the gold is present in both metallic and cationic states (binding energies of 83.9 and 85.5 eV, respectively in *ca.* 80:20 ratio). The gold metal loading is 0.5 %. The monometallic palladium catalyst also has a % weight of around loading of 0.5 %. The palladium in this catalyst is present as Pd^{2+} (binding energy of 337.3).

The bimetallic catalyst is approximately the expected Au:Pd ratio of 1:1 (*ca.* 0.2 wt% each) and the gold is metallic in this case. The Pd signal is extremely weak, however the signal is seen to undergo a reduction of intensity during X-ray analysis, suggesting the Pd is present as Pd^{2+} (binding energy *ca.* 338 eV) as shown in figure 3-6. Previous studies using THPC/NaOH methodology have shown that single particles contained both metals and the presence of inhomogeneous alloy was evident with the formation of PdO[13].

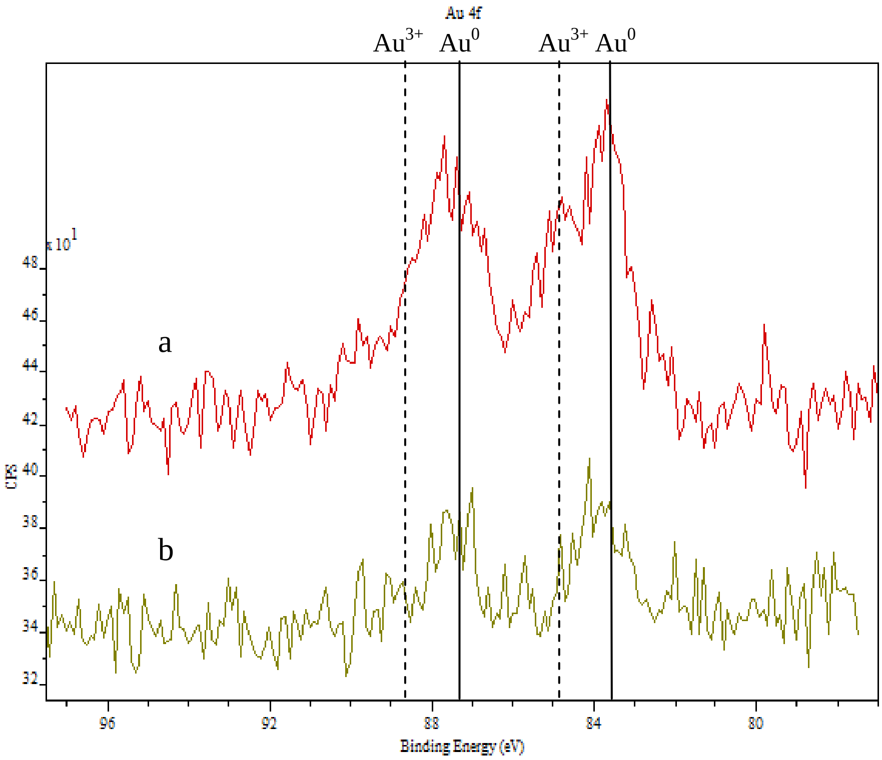


Figure 3-5 The XPS Au 4f spectra of a) Au/CeO$_2$ and b) AuPd/CeO$_2$

The Pd/CeO$_2$ catalyst shows some evidence of support reduction. The Ce 3d XPS spectra of Au, AuPd and Pd/CeO$_2$ are shown below in figure 3-8. The V’ peak from Ce^{3+} can be seen as a shoulder of the V peak from Ce^{4+}. This is indicative of oxygen vacancies on the surface of the ceria.

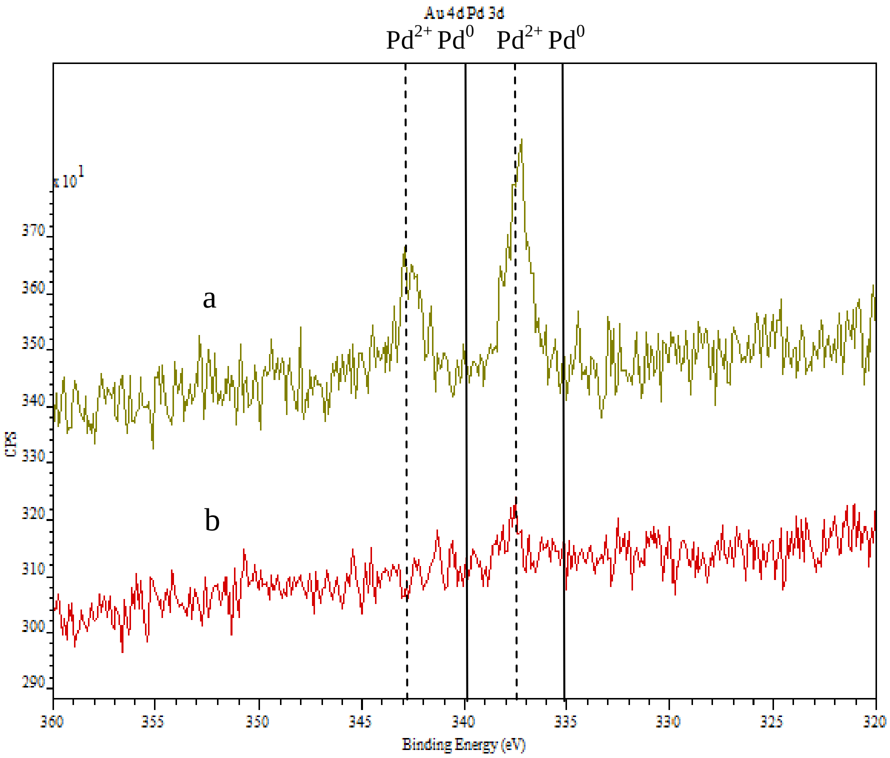


Figure 3-6 The Pd 3d spectra of a) Pd/CeO_2 and b) $AuPd/CeO_2$

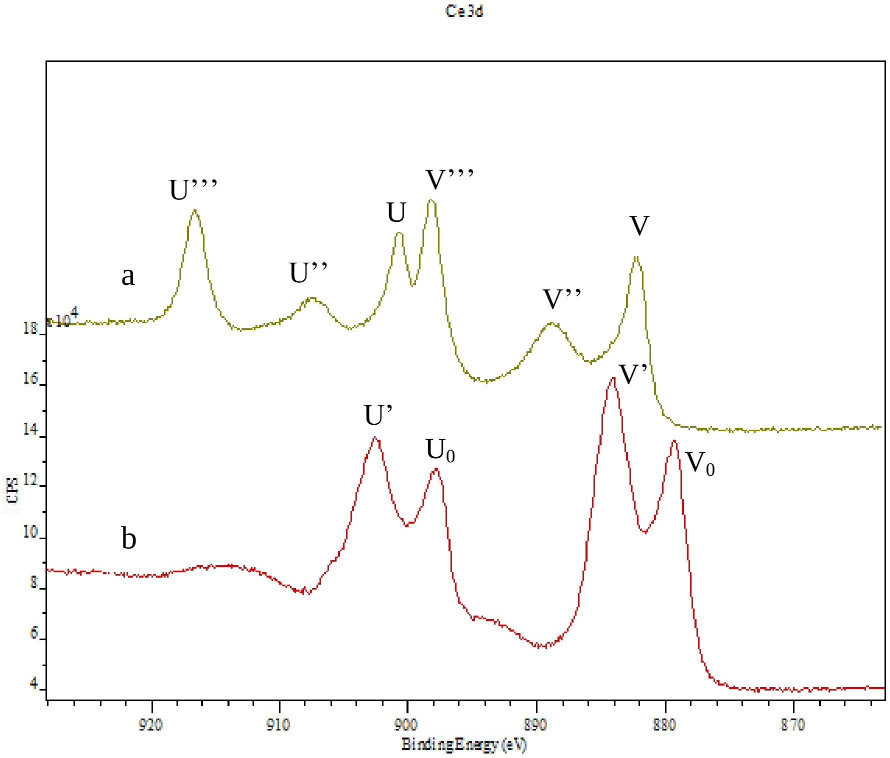


Figure 3-7 XPS Ce 3d spectra of cerium oxide. a) Ce^{4+} (CeO_2) and b) Ce^{3+} (Ce_2O_3).

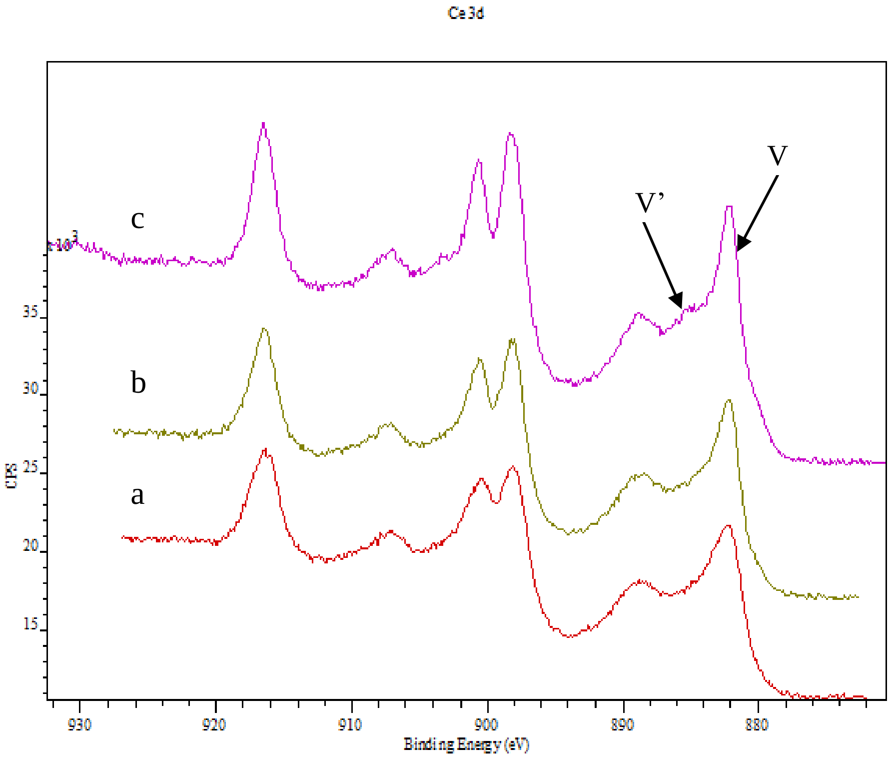


Figure 3-8 the XPS Ce 3d spectra for ceria supported catalysts. a) Au/CeO_2, b) AuPd/CeO_2 and c) Pd/CeO_2

3.3.3 Magnesium oxide supported catalysts

Probing the nature of the metals on the MgO support material using XPS is difficult as the magnesium Auger peaks mask the palladium 3d peaks as shown in figure 3-10. The gold appears to be present in the zero oxidation state in the catalysts prepared by all three preparation methods; sol immobilisation, impregnation and modified impregnation (figure 3-9).

The 1% AuPd/$Mg(OH)_2$ (1to1 molar) prepared by sol immobilisation was tested for the oxidation of butyrolactone. The catalyst was analysed by XPS after the reaction had taken place in order to observe any changes to the catalyst surface. Both Au 4f (figure 3-11) and 3d regions show very little change after reaction.

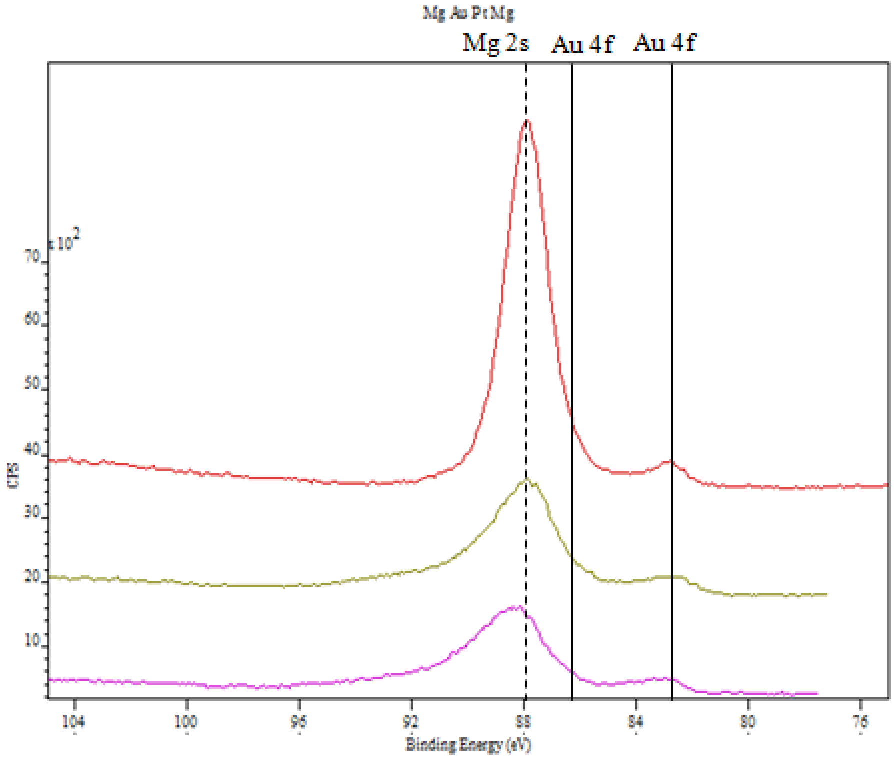


Figure 3-9 the XPS spectra of the Au 4f region of AuPd/Mg(OH)$_2$ catalysts prepared by a) sol immobilisation, b) impregnation and c) modified impregnation

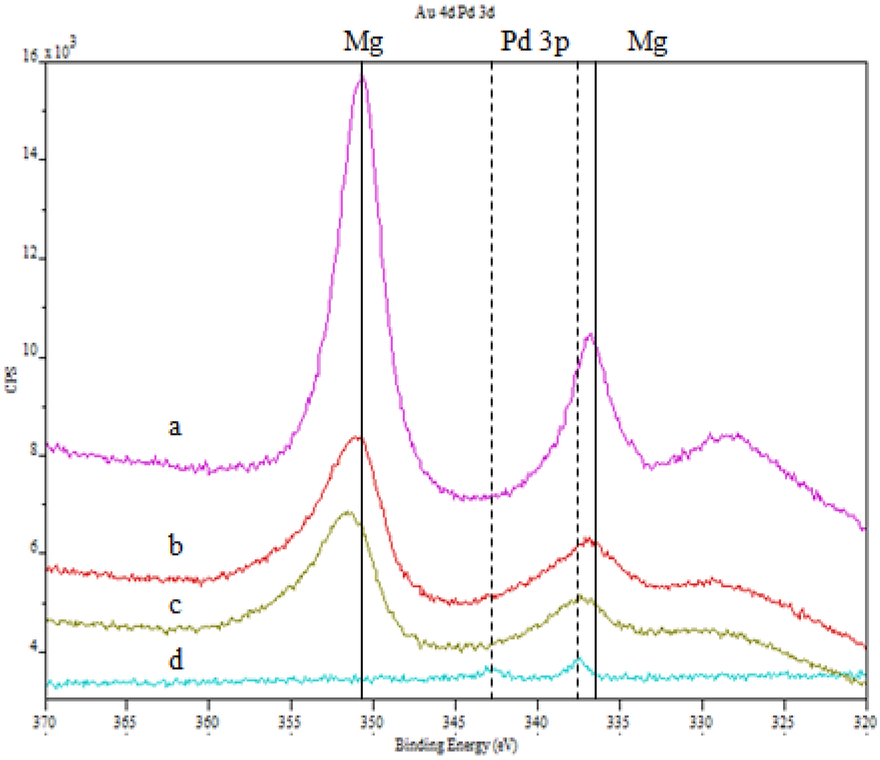


Figure 3-10 XPS spectra of the Pd 3d region of AuPd/Mg(OH)$_2$ catalysts prepared by a) sol, b) imp and c) modified imp and d) Pd/CeO$_2$ prepared by sol immobilisation

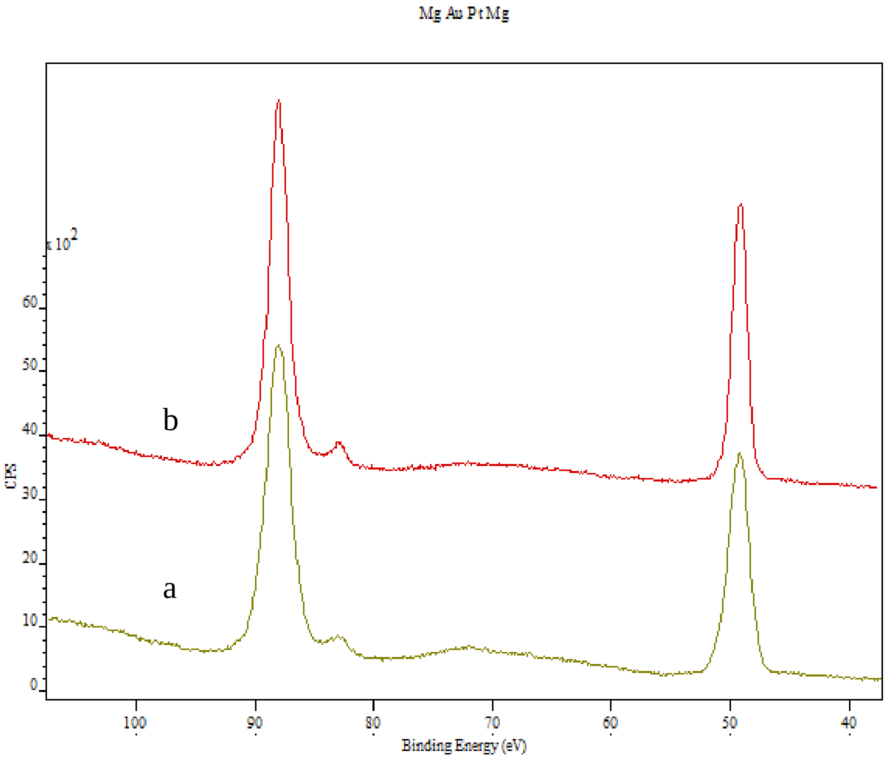


Figure 3-11 the XPS Au 4f spectra of 1% AuPd/Mg(OH)$_2$ prepared by sol immobilisation a) before and b) after reaction.

3.4 Scanning Transmission Electron Microscopy

Carbon, titania ceria and magnesium hydroxide supported catalysts by sol immobilisation and magnesium hydroxide prepared by the modified impregnation method have been characterised by scanning transmission electron microscopy. The particle size distribution data was calculated using bright field TEM micrographs. The nature of the bimetallic particles was probed using STEM-HAADF imaging. Z contrast in this method allows for identification of metals by atomic mass. It is therefore possible to determine the AuPd particle structure in the bimetallic catalysts.

3.4.1 Carbon and titania supported catalysts

3.4.1.1 Monometallic catalysts

The median gold particle size is around 4 nm for both Carbon and titania supports (figures 3-12 and 3-13 respectively). The Pd/TiO$_2$ has a slightly smaller median particle size of 3.8 nm (figure 3-14). No large particles are detected when this preparation method is used, this is in agreement with other literature[7, 14].

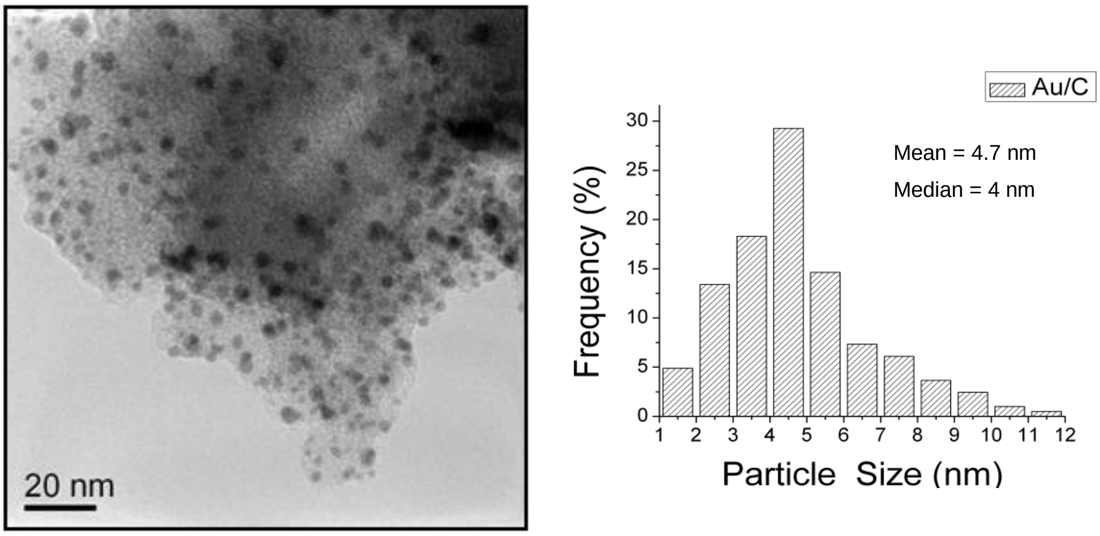


Figure 3-12 The Particle size distribution data, as determined from bright field TEM micrographs for Au/C prepared by sol immobilisation.

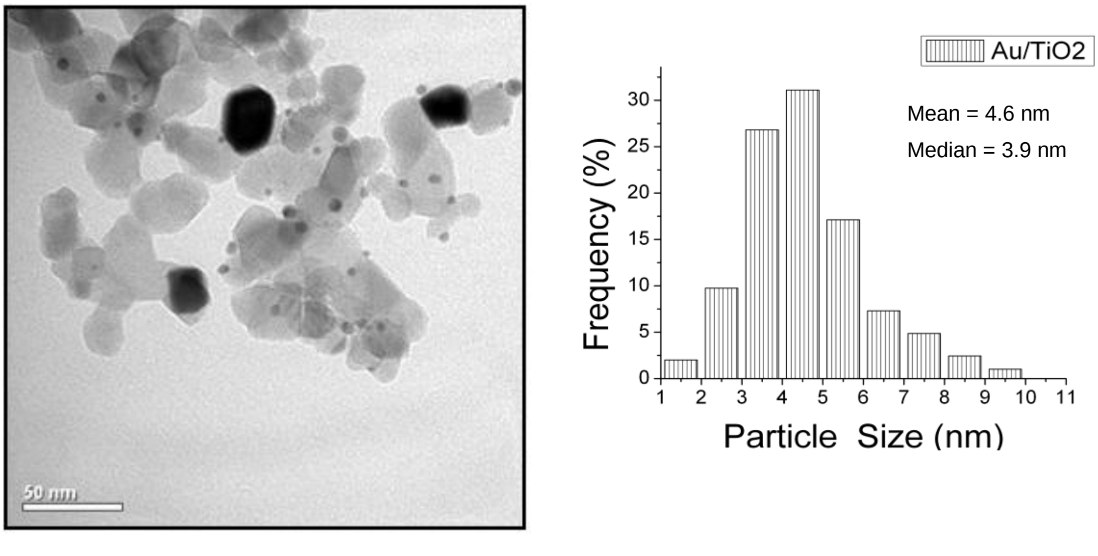


Figure 3-13 Particle size distribution data, as determined from bright field TEM micrographs for Au/TiO_2 prepared by sol immobilisation.

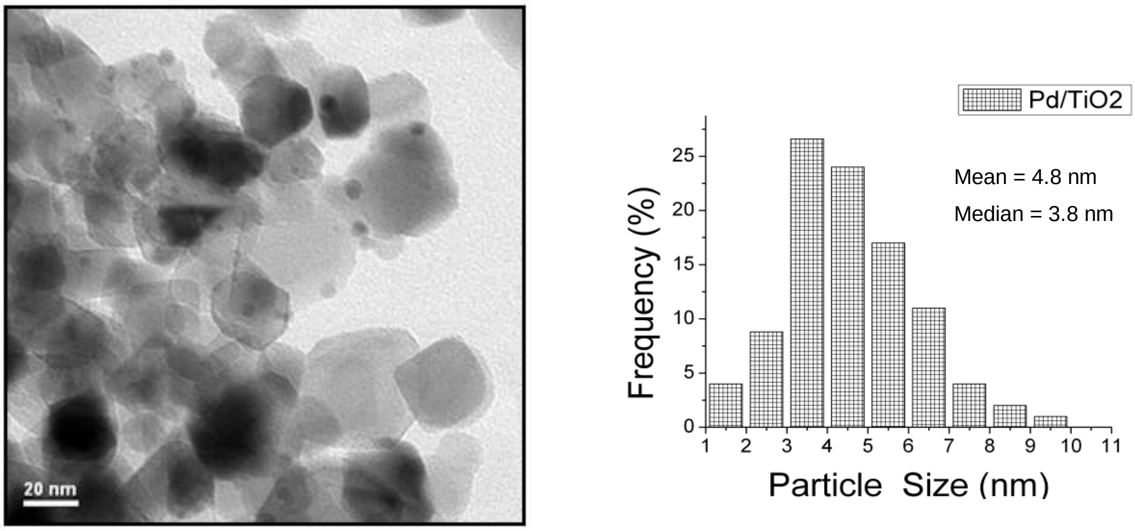


Figure 3-14 Particle size distribution data, as determined from bright field TEM micrographs for Pd/TiO_2 prepared by sol immobilisation.

3.4.1.2 Gold-palladium (1:1 wt) catalysts

Images of the bimetallic AuPd particles were achieved from STEM-HAADF experiments.

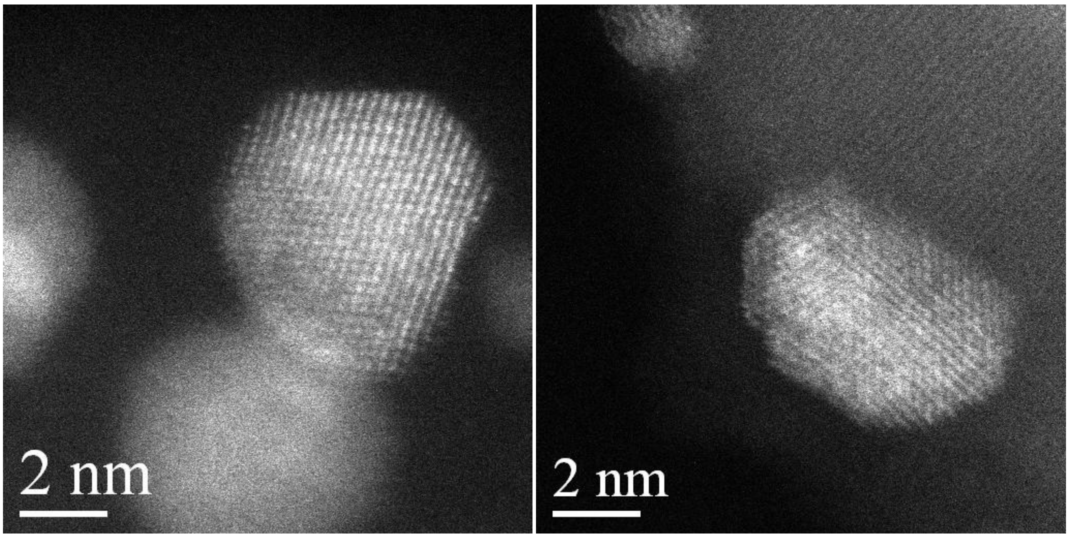


Figure 3-15 STEM-HAADF images of catalysts prepared by sol immobilization. AuPd/C (left), and AuPd/TiO_2 (right).

From the STEM-HAADF images it is possible to determine the structure of the bimetallic particles due to the z-contrast, which is based on mass, of gold (z=79) and palladium (z=46). There is no segregation of the two metals into a core-shell structure. We can therefore assume that the particles formed are random homogeneous alloys.

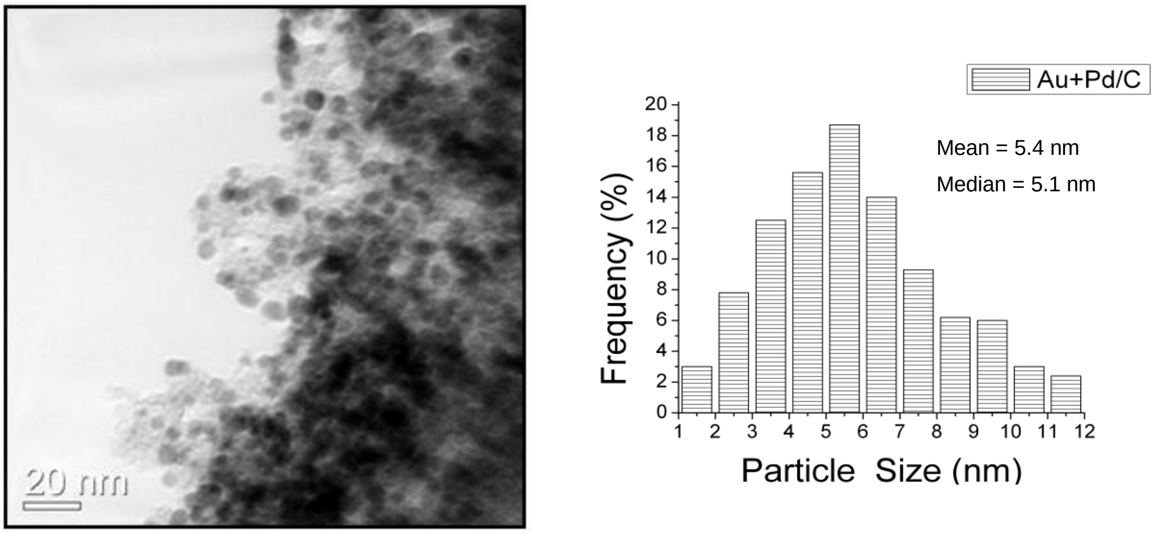


Figure 3-16 The Particle size distribution data, as determined from bright field TEM micrographs for AuPd/C prepared by sol immobilisation.

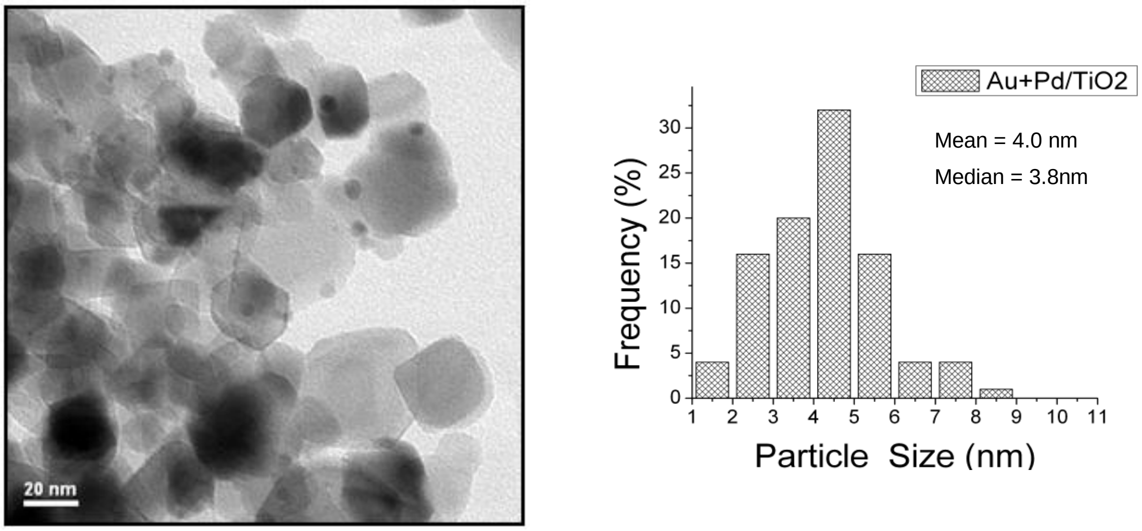


Figure 3-17 Particle size distribution data, as determined from bright field TEM micrographs for for AuPd/TiO_2 prepared by sol immobilisation.

The majority of the colloidal particles before the immobilisation step were icosahedral or decahedral (multiply twinned), whereas a small percentage of the particles were cuboctahderal. The shape of the particles differ when immobilised on different supports. When supported on carbon particles retained their spherical shape and showed a lower ability to wet the amorphous carbon support (figure 3-15). When supported on titania, it was observed that the particles were highly faceted with a cuboctahedral structure or singly twinned morphology. In addition, it was observed that the particles formed an extended flat interface structure with the crystalline titania structure. The average bimetallic particle size is larger when supported on carbon, (figure 3-16) 5.1 nm compared with 3.8 nm for titania (figure 3-17).

3.4.2 Ceria supported catalysts

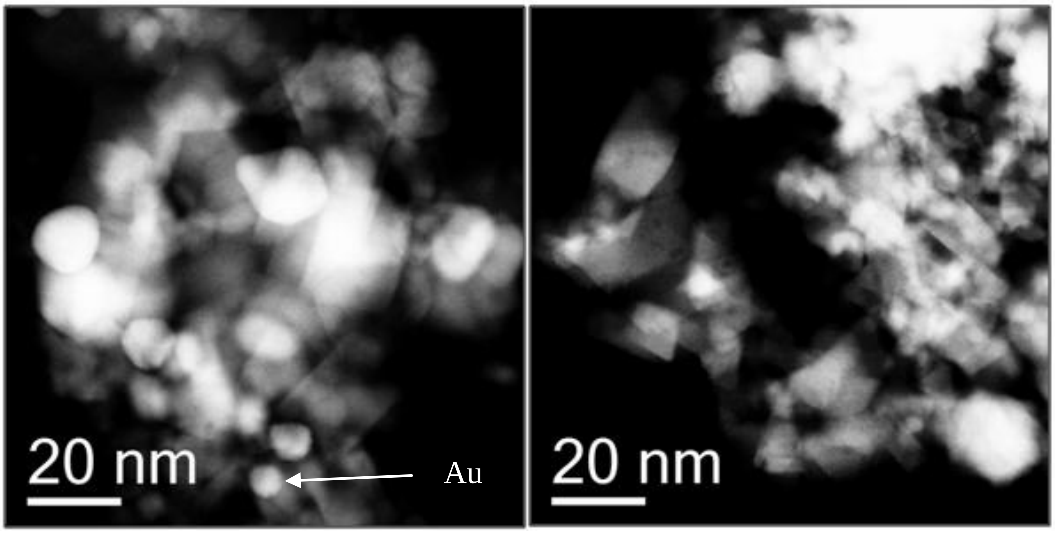


Figure 3-18 the STEM-HAADF images of Au/CeO_2 (left) and AuPd/CeO_2 (right)

Unfortunately due to the low gold loadings and the size and nature of the nanoceria support it was difficult to observe the similarly sized supported Au and AuPd nanoparticles using this technique. The few gold particles observed appear to be round in contrast to the faceted nature of the ceria (figure 3-18).

3.4.3 Magnesium hydroxide supported catalysts

3.4.3.1 Gold palladium catalysts

The AuPd/$Mg(OH)_2$ (1:1 mol) catalyst prepared by the modified impregnation method shows small bimetallic particles, which are random homogeneous alloys, with some larger monometallic gold and palladium structures (figure 3-20). The bimetallic particles formed were found to be irregular with differing compositions. The average metal particle size is 3 nm as shown in figure 3-19.

All MgO supported catalysts prepared by sol immobilisation displayed a platelet structure characteristic of material that has been derived from an $Mg(OH)_2$ precursor. This is consistent with the findings from the XRD data in section 3.1 above.

The sol immobilisation method also leads to the formation of small bimetallic alloy structures, the average particle size of these particles is 3.1 nm (figure 3-21) for the AuPd/Mg(OH)$_2$ (1:1 mol). No monometallic particles were detected.

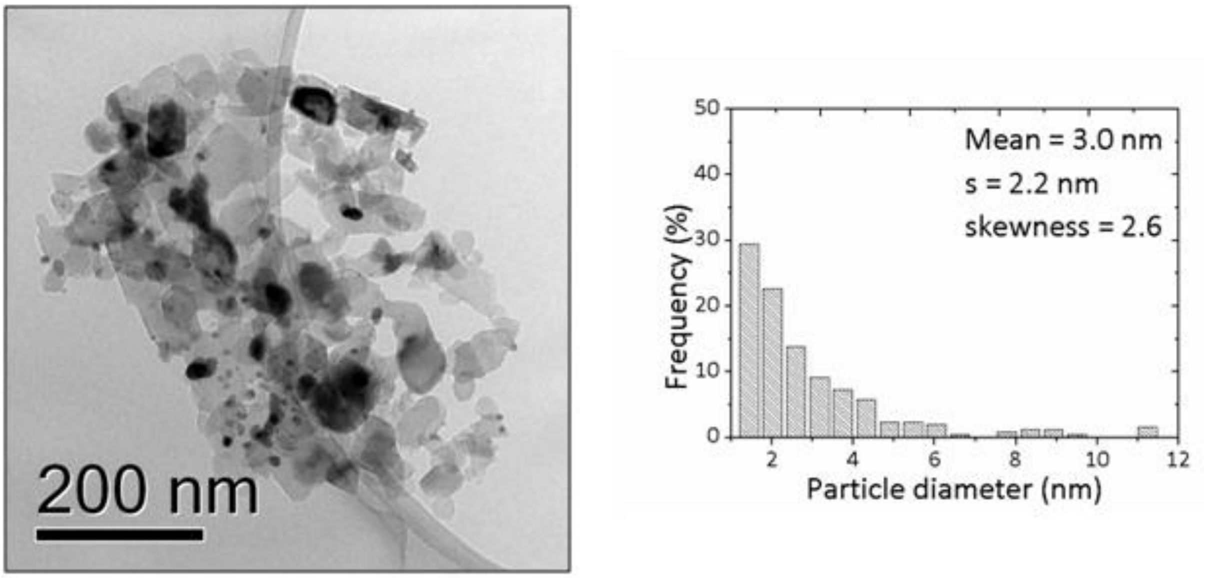


Figure 3-19 The Particle size distribution data, as determined from bright field TEM micrographs for AuPd/MgO prepared by modified impregnation.

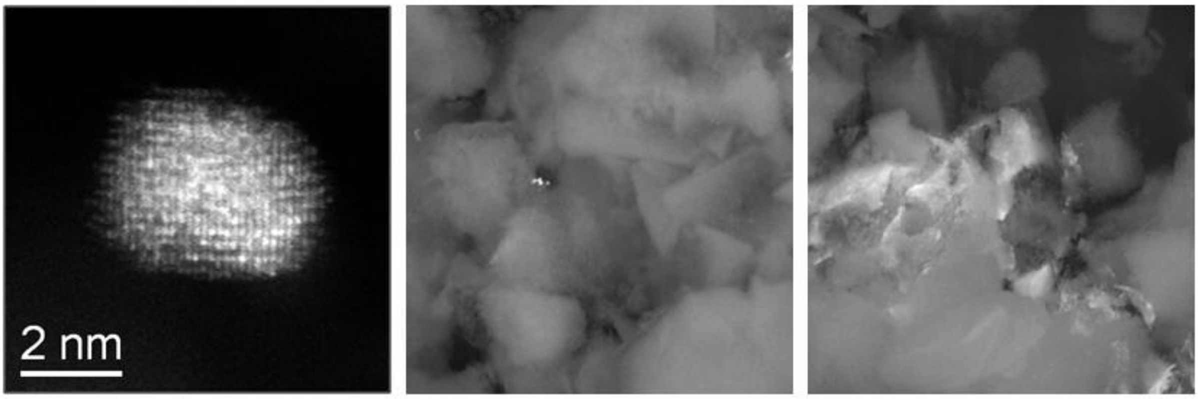


Figure 3-20 STEM-HAADF images of catalysts prepared by modified impregnation. Bimetallic nanoparticle (left), evidence of larger gold (middle) and palladium particles (right).

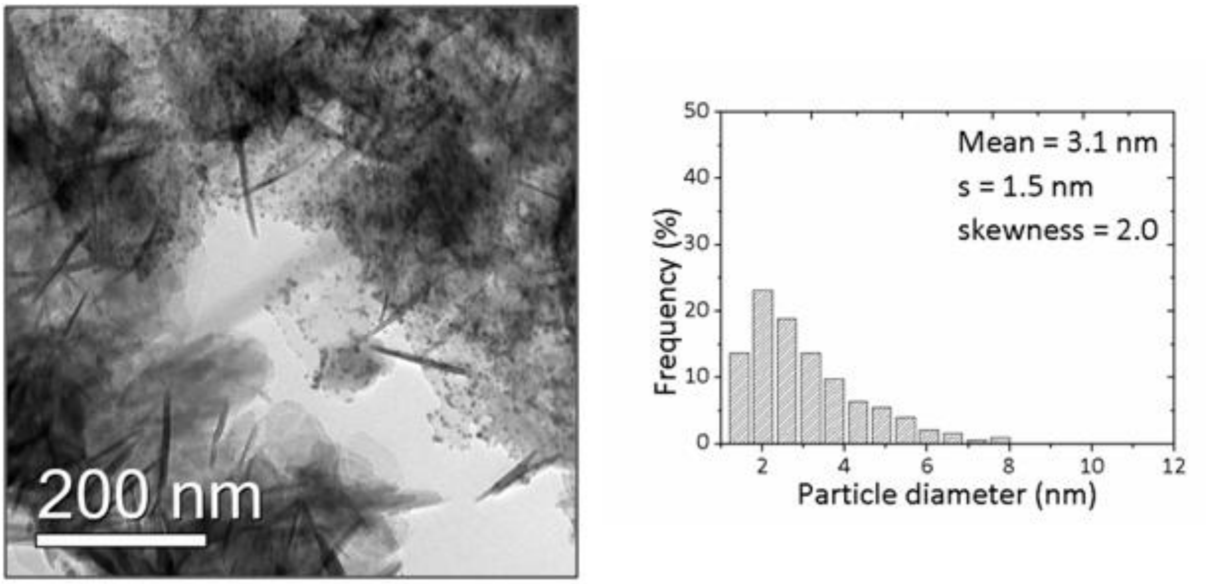


Figure 3-21 The Particle size distribution data, as determined from bright field TEM micrographs for AuPd/MgO prepared by sol immobilisation.

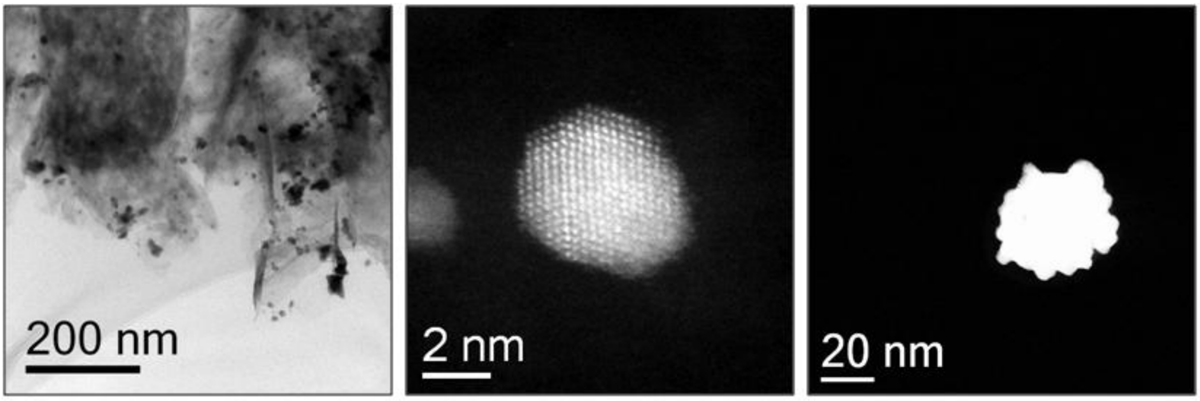


Figure 3-22 bright field TEM micrograph and STEM-HAADF images of a remaining bimetallic nanoparticle and large gold rich particle formed from scintering

After one use in the oxidation of butyrolactone in methanol the catalyst prepared by sol immobiliation shows an increase in particle size from considerable sintering. Some small particles (2-5 nm) remain. The large particles formed appear to be gold rich in nature (figure 3-22).

A 1:1 wt and 1:3 mol AuPd/$Mg(OH)_2$ were also prepared. The AuPd/ $Mg(OH)_2$ catalyst was calcined at 150 and 200 °C. From analysis of the TEM micrographs of the AuPd/MgO catalyst prepared by sol immobilisation with a 1:1 wt ratio of Au:Pd, it was found that in both cases, of the fresh and calcined catalysts, the metallic particles were fully alloyed, and showed a homogeneous dispersion on the support. The median AuPd particle size was found to be 4.1 nm on the dried support (figure 3-23) compared with to 4.8 nm after calcination at 200 ^{o}C (figure 3-24). The AuPd/MgO catalyst that was prepared with a 1:3 molar ratio exhibited the same average particle size of 4.1 nm (figure 3-25).

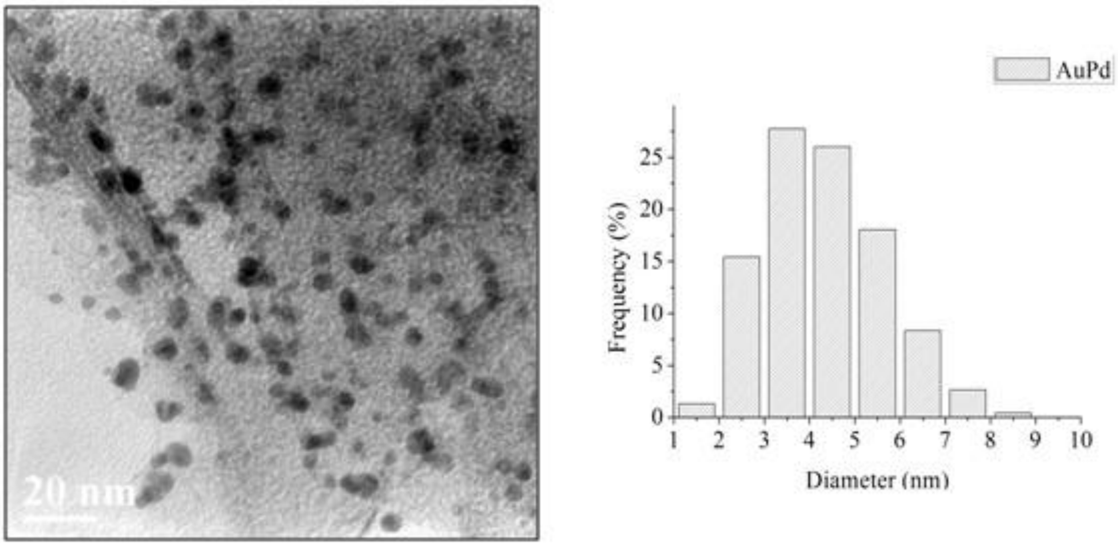


Figure 3-23 The Particle size distribution data, as determined from bright field TEM micrographs for AuPd/Mg(OH)$_2$ (1:1 wt), prepared by sol immobilisation.

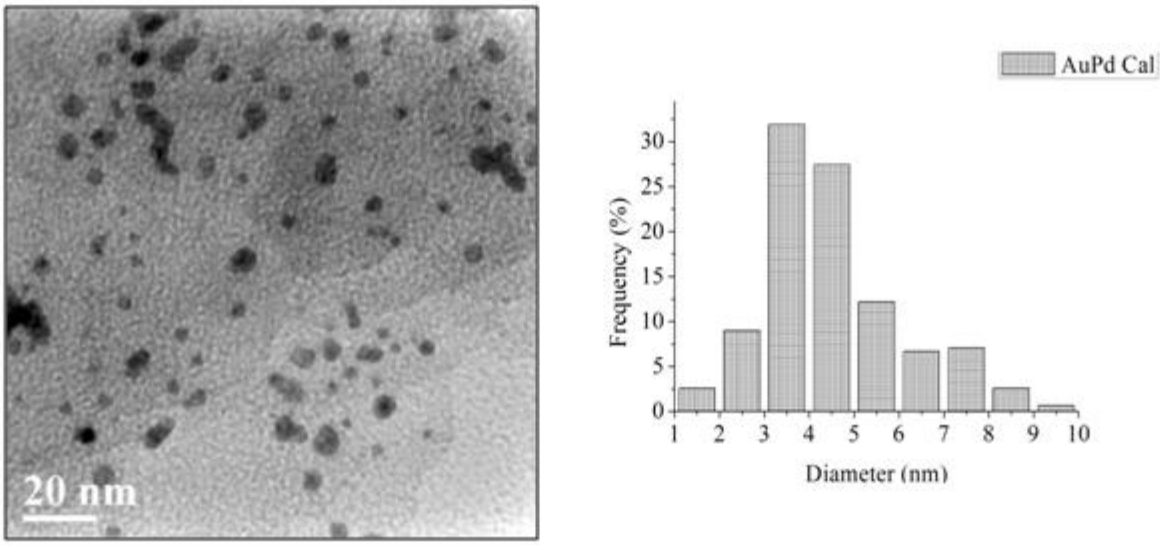


Figure 3-24 The Particle size distribution data, as determined from bright field TEM micrographs, for AuPd/Mg(OH)$_2$ (1:1 wt) calcined at 200°C.

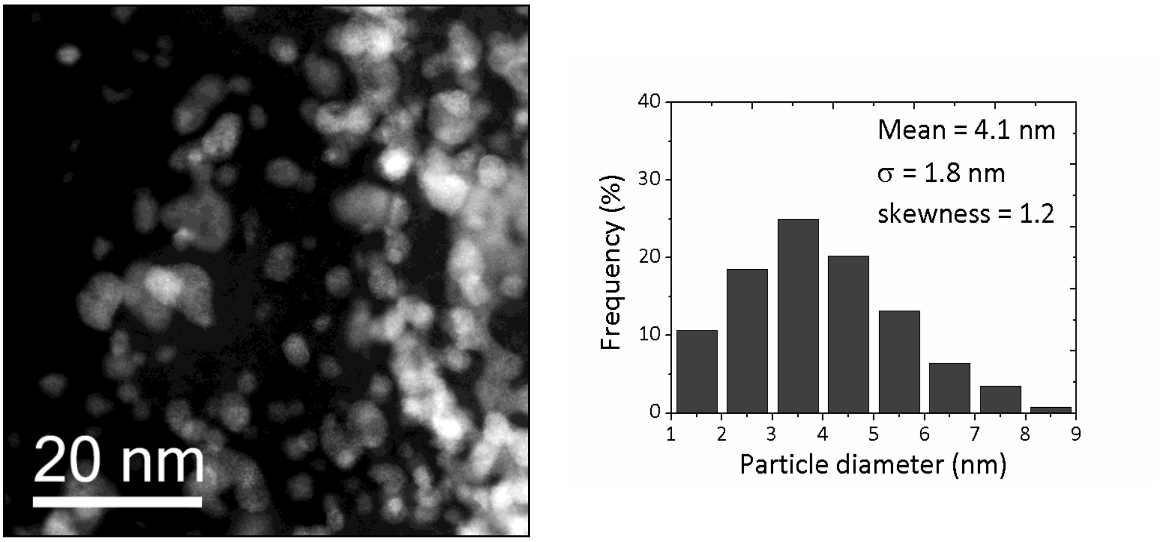


Figure 3-25 Low magnification STEM-HAADF image and corresponding particle size distribution of AuPd(1:3)/$Mg(OH)_2$

3.4.3.2 Gold platinum catalysts

The AuPt/MgO support has the same platelet structure as the AuPd catalysts. The Au-Pt metal nanoparticles were also found to be fully alloyed and well dispersed on the support.

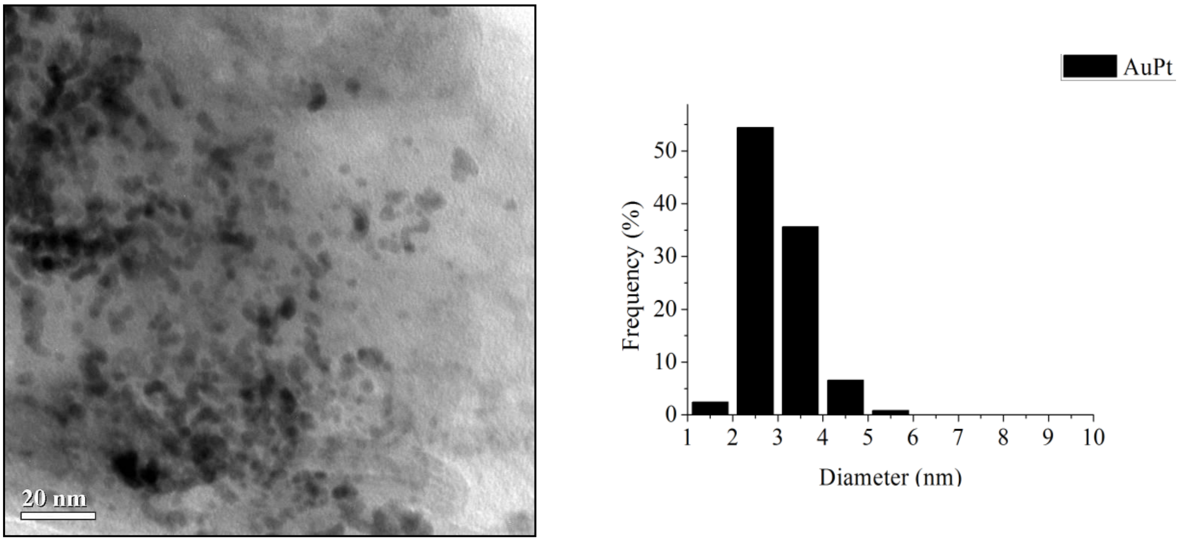


Figure 3-26 The Particle size distribution data, for AuPt/$Mg(OH)_2$ (1:1 wt), prepared by sol immobilisation.

For the AuPt/$Mg(OH)_2$ catalyst with a 1:1wt ratio the particle size distributions indicate a median particle size of 2.8 nm (figure 3-26) which increases to 3.4 nm for the sample calcined at 200 °C (figure 3-27).

The AuPt/MgO catalyst with 1:3 molar ratio of the metals has larger metal particles than the 1:1 catalysts, with a mean particle size of 4 nm (figure 3-28).

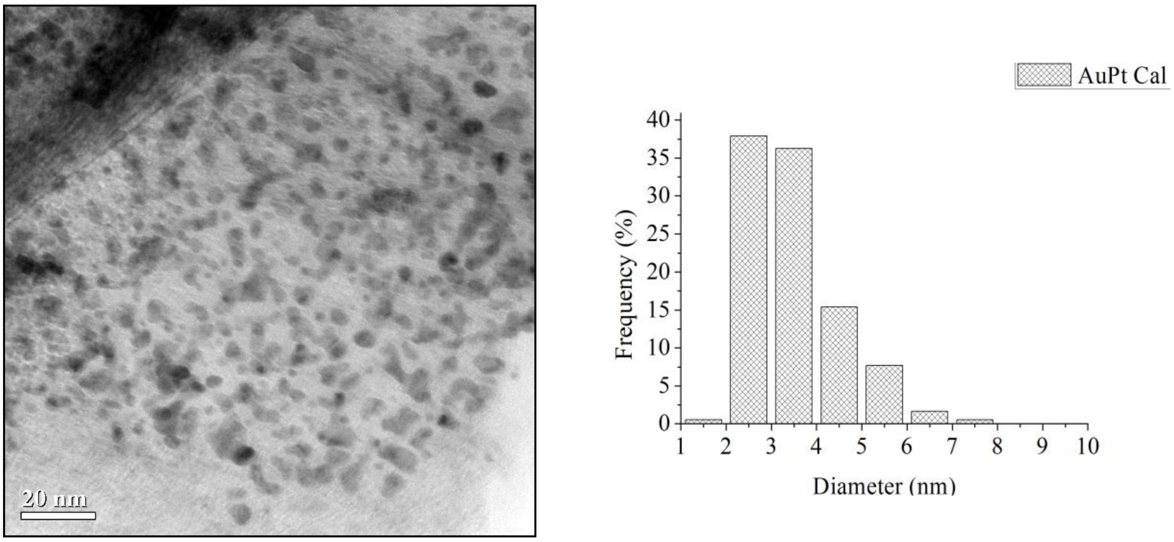


Figure 3-27 The Particle size distribution data, as determined from bright field TEM micrographs, for AuPt/$Mg(OH)_2$ prepared by sol immobilisation and subsequently calcined at 200 °C.

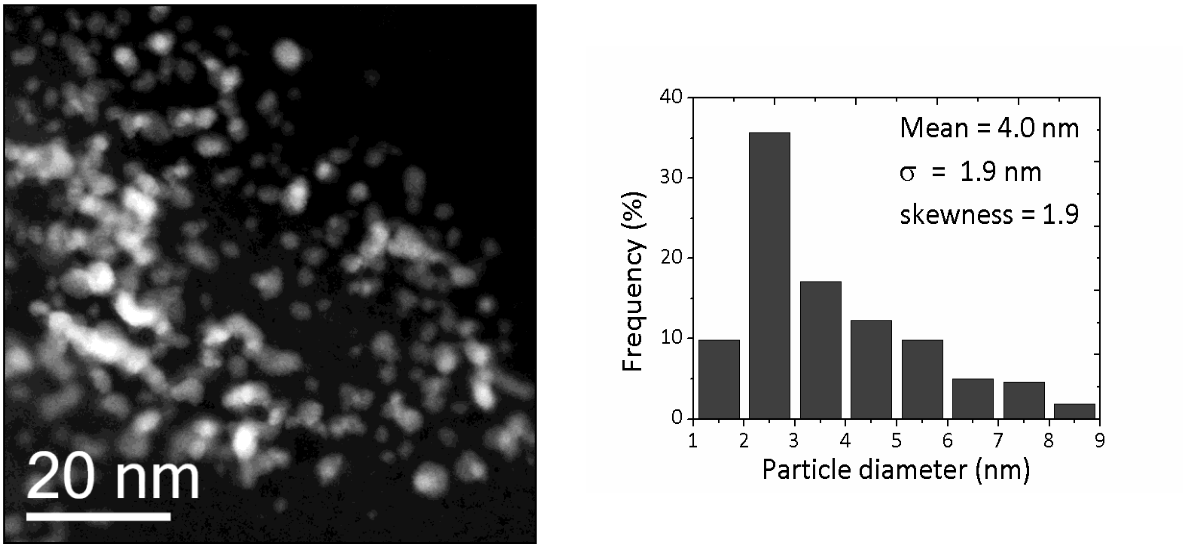


Figure 3-28 Low magnification STEM-HAADF image and corresponding particle size distribution of 1% AuPt(1:3)/$Mg(OH)_2$

A summary of the mean particle sizes of these catalysts is below in table 3-1

Table 3-1 Summary of particle size data of supported catalysts

Catalyst	Mean particle size of dried sample /nm	Particle size after calcination at 200 °C nm
1% Au/C	4.7	
1% AuPd/C (1:1 wt)	5.4	
1% Au/TiO_2	4.6	
1% Pd/TiO_2	4.8	
1% AuPd/TiO_2 (1:1 wt)	4.0	
1% AuPd/$Mg(OH)_2$ (1:1 wt)	4.1	4.8
1% AuPd/$Mg(OH)_2$ (1:1 mol)	3.1	
1% AuPd/$Mg(OH)_2$ (1:3 mol)	4.1	
1% AuPt/$Mg(OH)_2$ (1:1 wt)	2.6	3.4
1% AuPt/$Mg(OH)_2$ (1:3 mol)	4.0	

These catalysts will now be applied to a number of oxidation reactions in chapters 4, 5 and 6.

3.5 References

1. S. Marx and A. Baiker, *The Journal of Physical Chemistry C*, 2009, **113**, 6191-6201.
2. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.
3. N. Dimitratos, J. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati and A. Villa, *Catalysis Letters*, 2006, **108**, 147-153.

4 Oxidation of 1,2-propanediol

4.1 Introduction

1,2-propanediol can be synthesised from hydrogenolysis of glycerol, therefore increasing the usage of a renewable source[1]. The transformations of 1,2-propanediol have recently attracted attention from the scientific community with applications in the synthesis of fine chemicals[2-4].

Gold supported nanoparticles have shown high catalytic activity for a variety of polyol oxidations[5, 6]. The influence of preparation method has been studied for the synthesis of active supported metal catalysts, such as impregnation, deposition-precipitation and colloidal methods. The colloidal methods typically produce small metallic particles with a narrow particle size distribution. These nanoparticles have been shown to be more active than larger ones prepared by impregnation methods which lead to a bimodal distribution of particles[6, 7] including small particles and larger (< 40 nm) particles. Alloying gold with another metal such as platinum or palladium has been shown to create a synergistic effect, enhancing activity, selectivity to the desired products[8].

It has been shown that the oxidation of 1,2-propanediol in aqueous conditions is catalysed by gold and gold palladium catalysts to yield lactic acid[2, 8]. Lactic acid is polymerised to produce polylactic acid (PLA) which can be utilised as biodegradable plastic [9]. The reaction scheme for the oxidation of 1,2-propanediol is shown below in scheme 1.1-1.

The oxidation of 1,2-propanediol can be performed using methanol as the solvent in order to produce lactic acid esters[10]. Catalytic amounts of base are used in the reaction, in comparison to 2 or more equivalents (mol/mol) in aqueous oxidation. Therefore, the reaction is greener as there is less waste from the reaction itself and from the subsequent acidification of the sodium lactate.

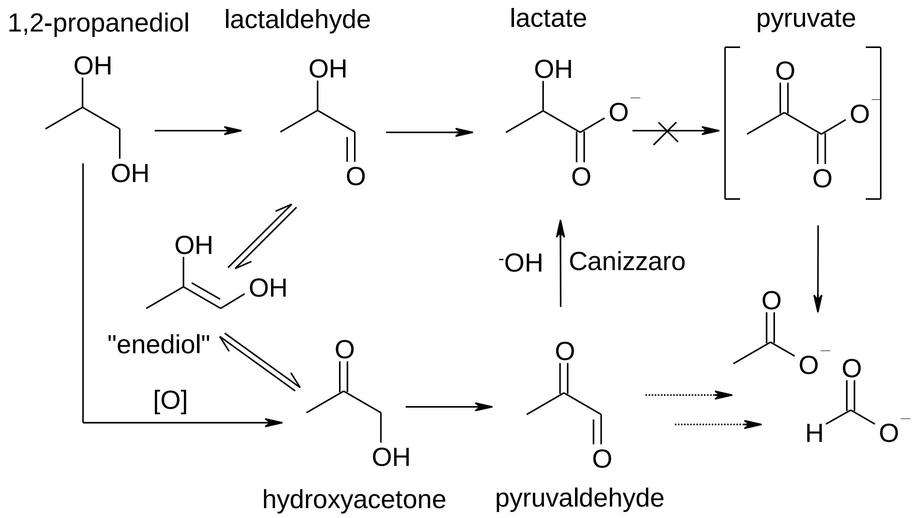


Figure 4-1 The oxidation of 1,2-propanediol[8]

4.2 Results and discussion

4.2.1 Aqueous oxidation

Prati *et al*[2] have shown that Au/C is an active catalyst for alcohol oxidations. In this work it was shown that catalysts with smaller gold particles are more active for the oxidation of 1,2-propanediol. The sol immobilisation method has been shown to produce the most active Au/C catalysts[8] due to their narrow particle size distributions. Therefore this catalyst was chosen to test for aqueous oxidation of 1,2-propandiol.

4.2.1.1 Effect of oxygen flow rate

The oxidation of 1,2-Propanediol was carried out at 60 °C in a glass reactor with 2 equivalents of base (NaOH) using a 1% Au/C catalyst prepared by sol immobilisation. The substrate metal ratio was 2000. Oxygen was bubbled into the reactant solution with varying speeds. The reaction time was 3 hours.

As the oxygen flow rate is increased the conversion of 1,2-propanediol increases (figure 4-2), this is most likely due to the increase in oxygen concentration in the solvent and hence the catalyst surface. It has been shown that the conversion increases with increasing oxygen flow rate. At low oxygen flow rates, between 25 and 50 mL/min, when the oxygen flow rate is doubled the conversion almost doubles (1.88 times). When the flow rate increases from 50 to 100 mL/min the conversion increases by a factor of 1.86. The tripling of the flow rate from 25 to 75 mL/min sees the conversion increase three fold (3.10).

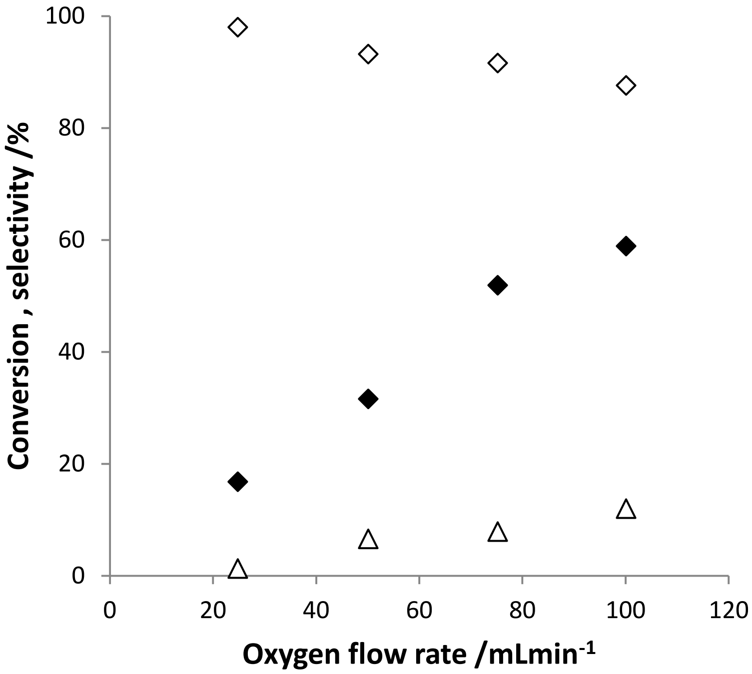


Figure 4-2 The effect of oxygen flow rate on the conversion of 1,2-propandiol (◆) and selectivity to lactic acid (◇) and acetic acid (∆). 1,2-propanediol:metal = 2000, 1,2-propanediol:base = 2, T=60 °C, reaction time = 3 h.

This shows that the transport of the oxygen to the catalyst surface is operating in the kinetic regime and the catalyst surface is not saturated in this range of flows. Increasing the flow of air[5] and increasing the concentration of oxygen in nitrogen[11] have also been proven to increase the conversion of alcohol oxidation[5].

The selectivity to lactic acid decreases with increasing oxygen flow rate, under these conditions lactic acid is oxidised to acetic acid and traces of formic acid via the sequential oxidation pathway described in scheme 4-1.

4.2.1.2 The effect of base

1,2-Propanediol (0.3M) was oxidised at 60 °C under atmospheric pressure in a glass reactor for 3 hours using hydrogen peroxide (4 equivalents) as the oxidant. The amount of base (sodium hydroxide) was varied from 0 to 4 equivalents. The same 1% Au/C catalyst was tested with substrate:metal ratio of 2000. The results are shown in figure 4-3.

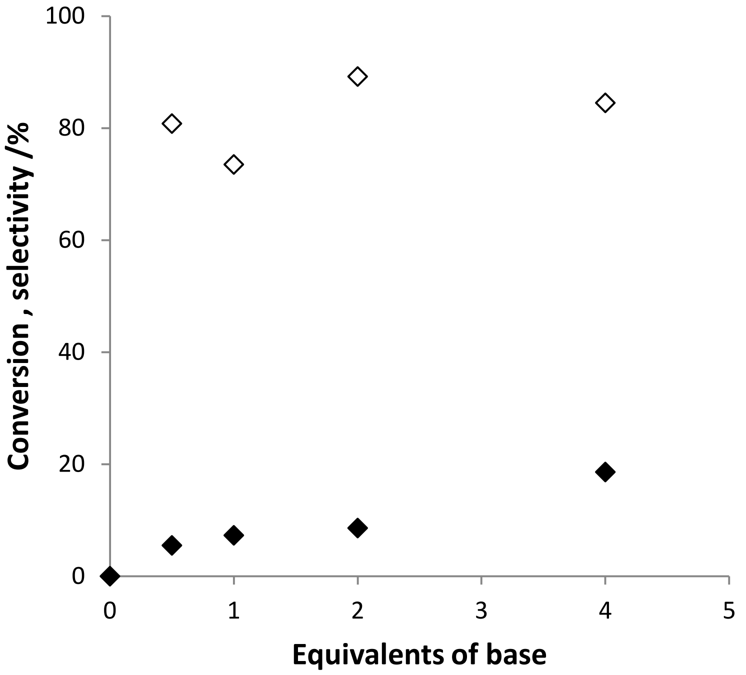


Figure 4-3 The effect of base on the conversion of 1,2-propandiol (◆) and selectivity to lactic acid (◇). Reaction conditions; 1,2-propanediol:metal = 2000, 1,2-propanediol:base = 0-2, 1,2-propanediol:H_2O_2 = 4 , T=60 °C, reaction time = 3 h.

As the amount of base increases, the conversion of 1,2-propanediol increases. When no base is present the reaction does not proceed. The optimal amount of base for high selectivity is 2 equivalents. This same trend has been observed when 1,2-propanediol is oxidised in an autoclave using molecular oxygen as the oxidant[8].

It is thought that the role of base in polyol oxidation with gold catalysts, is as an initiator. Hutchings *et. al.* hypothesised that the hydroxyl ion from NaOH was responsible for the activation of a glycerol molecule under oxidising conditions[5], thereby facilitating the deprotonation of the primary hydroxyl group, forming glyceraldehyde which is rapidly oxidised to glyceric acid.

Without the presence of base the monometallic gold catalyst was unable to catalyse the oxidation of 1,2-propanediol, this is in agreement with other polyol oxidation work[6, 12]. The addition of base was also shown to enhance selectivity to the primary oxidation product, lactic acid. The same trend had been seen with other substrates.

4.2.2 Oxidations in methanol

The oxidation of diols in methanol has been catalysed by a range of oxide supported gold catalysts[13]. These catalysts have been shown to be more active and selective than monometallic Pd and Ru catalysts. Christensen *et al.* oxidised 1,2-propanediol using methanol as the solvent using the world gold council catalysts (WGC) 1.5% Au/TiO_2 and 5%Au/Fe_2O_3[10]. In this work the substrate metal ratio was a very low 56, therefore the following work was undertaken to investigate the reaction at a more desirable ratio.

4.2.2.1 Reaction profile

A reaction was performed at 100 °C in a glass reactor at 3 bar in methanol using a 1.2%Au/TiO_2 world gold council catalyst. Samples were taken periodically to establish a reaction pathway (figure 4-4). The substrate metal ratio was 500.

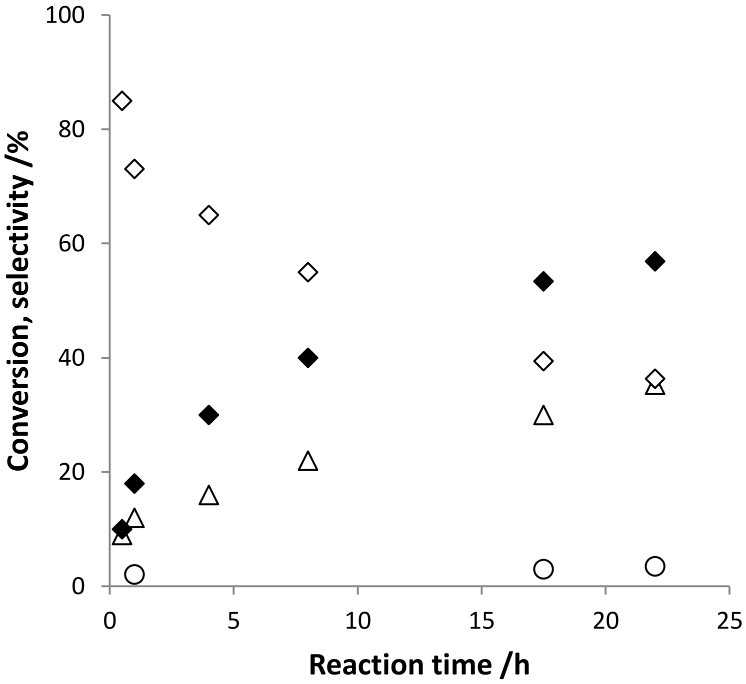


Figure 4-4 The reaction profile of 1,2-propanediol oxidation. Conversion of 1,2-propanediol (◆), selectivity to hydroxyacetone (◇) selectivity to methyl lactate (Δ), and methylpyruvate (○). 1,2-propanediol:Au = 500, 1,2-propanediol:NaOMe = 10, T = 100 °C, P(O_2) = 3 bar

The primary oxidation product appears to be hydroxyacetone, which is subsequently oxidised to methyl lactate. It is unclear where the small amount of methyl pyruvate originates from. This is in agreement with the scheme proposed by Christensen *et al*[10]. However the selectivity to methyl lactate is lower than in referenced work (78 %). This could be a result of the decrease in the catalyst amount or oxygen pressure (3 bar in contrast with 5 bar in the literature). The reaction vessel is also different, autoclave versus glass reactor.

To further understand the chemistry involved, the intermediates, hydroxyacetone and methyl lactate, were oxidised under the same conditions as 1,2-propanediol above for 24 hours (table 4-1).

Table 4-1 Oxidation of intermediates

		Selectivity /%		
Substrate	Conversion /%	Methyl lactate	Hydroxyacetone	Methyl pyruvate
Hydroxyacetone	99.8	70.5	-	29.5
Methyl lactate	96.4	-	-	90.6

Reaction conditions; substrate:Au = 500, substrate:NaOMe = 10, T = 100 °C, $P(O_2)$ = 3 bar

Table 4-1 shows that hydroxyacetone is mainly oxidised to methyl lactate and to a lesser extent methyl pyruvate. However, the small amount of pyruvate present is likely to be from the oxidation of methyl lactate as when methyl lactate was oxidised under the same conditions the major product was methyl pyruvate.

Additional experiments were carried out in order to prove whether methyl lactate can also be formed from the reaction of lactic acid with methanol. The reaction was carried out under the same conditions with Au/TiO_2 World Gold Council catalyst. It is also possible that the mechanism includes reaction of 1-methoxy-1,2-propanediol and pyruvaldehyde in a Canizzaro reaction, which could form methyl lactate and hydroxyacetone.

There are four different pathways proposed to produce methyl lactate: via lactaldehyde (2), which is rapidly oxidised under basic conditions; via hydroxyacetone (4), formed by direct oxidation of 1,2-propanediol (1) or by base-induced tautomeric equilibrium with the intermediate enediol derived from lactaldehyde. The third is via the formation of 1-methoxy-1,2-propanediol (7) from lactaldehyde and methanol and then a Cannizaro reaction takes place to form methyl lactate and hydroxyacetone. Finally, the formation of methyl lactate via lactic acid (5) and methanol is feasible. These are shown in scheme 4-5.

Table 4-2 The esterification of lactic acid

Substrate	Time /h	Yeild of methyl lactate /%
Lactic acid	1	3.3
	4	6.7
	24	35.2

Reaction conditions; substrate:Au = 500, substrate:NaOMe = 10, T = 100 °C, $P(O_2)$ = 3 bar

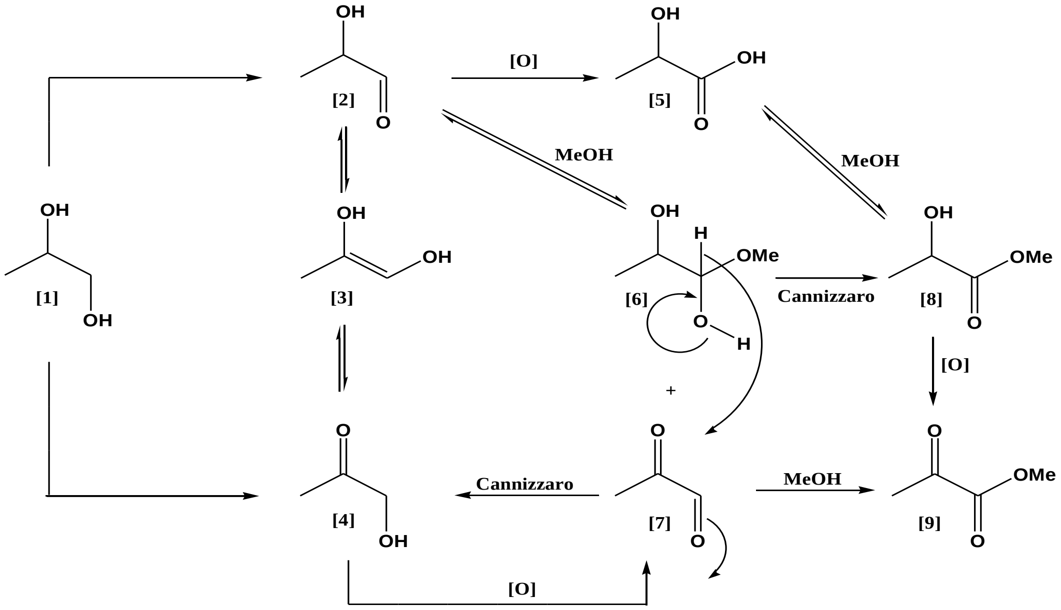


Figure 4-5 The reaction scheme of 1,2-propanediol oxidation in methanol. (1) 1,2-propanediol, (2) lactaldehyde, (3) enediol, (4) hydroxyacetone, (5) lactic acid, (6) 1-methoxy-1,2-propanediol, (7) pyruvaldehyde, (8) methyl lactate, (9) methyl pyruvate.

4.2.2.2 Effect of substrate metal ratio

The effect of substrate to metal ratio on the reaction was investigated using the same Au/TiO_2 catalyst as above. As is shown below in figures 4-6 and 4-7, the conversion increases with decreasing s:m, *i.e.* more catalyst. This is in agreement with other catalytic reactions[14].

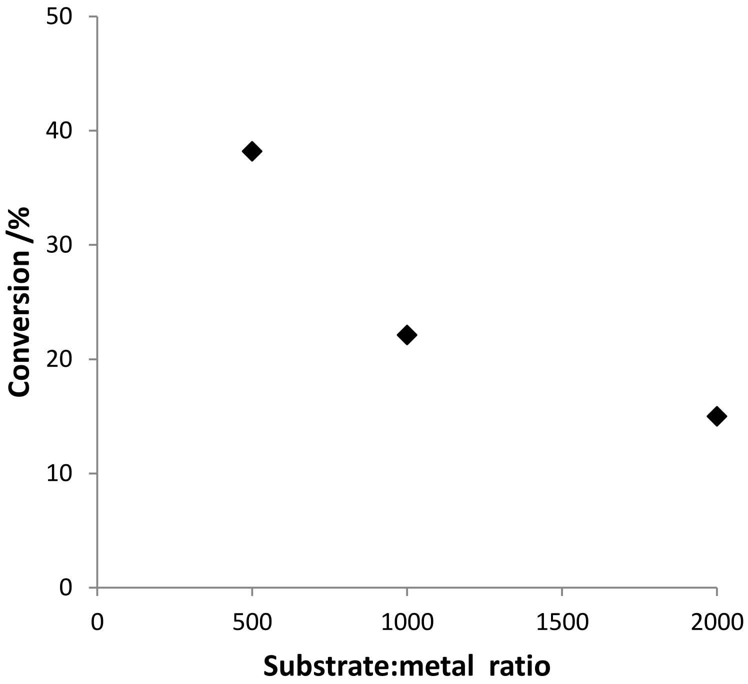


Figure 4-6 The effect of substrate metal ratio on the conversion of oxidative esterification of 1,2-propanediol. Reaction conditions 1,2-propanediol:Au = 500-2000, 1,2-propanediol:NaOMe = 10, T = 100 °C, P(O_2) = 3 bar

When the catalyst amount is doubled from s:m = 2000 to 1000 the conversion increases by a factor of 1.5, from 1000 to 500 the conversion increases by a factor of 1.73. This result shows that the reaction is mass transport limited and therefore not operating in the kinetic regime. To achieve high conversions in catalyst screening experiments, a substrate metal ratio of 500 has been chosen. As can be seen in figure 4-8, the substrate metal ratio has little effect on selectivity and is likely to be similar at isoconversion.

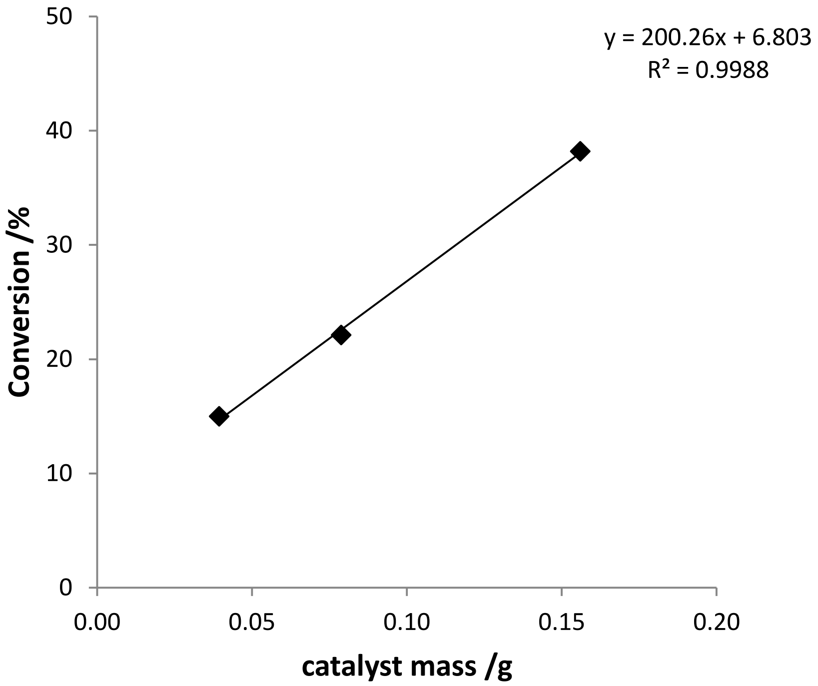


Figure 4-7 The effect of catalyst mass on the conversion of oxidative esterification of 1,2-propanediol

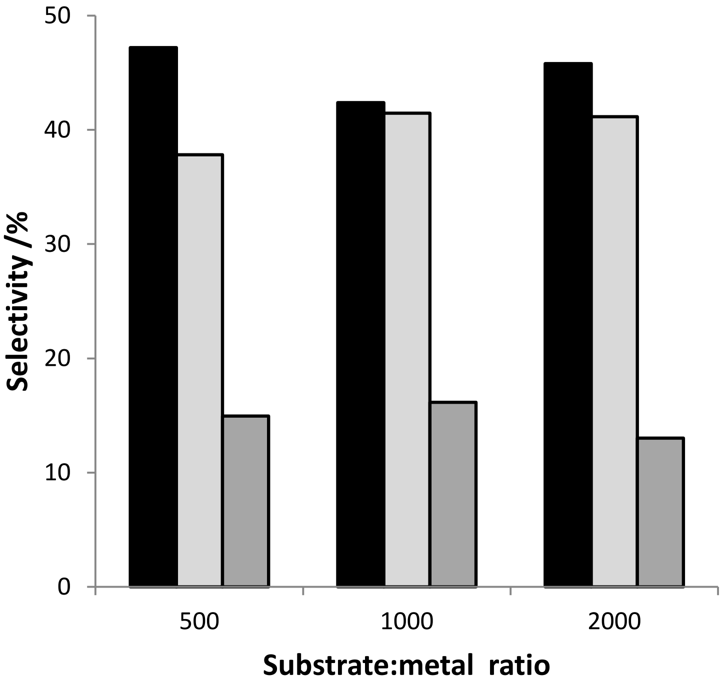


Figure 4-8 The effect of substrate metal ratio on the selectivity to hydroxyacetone (■) methyl lactate (□) and methyl pyruvate (▨)

4.2.2.3 Effect of catalyst support

A series of gold catalysts were screened for this reaction (figure 4-9). Two were the world gold council catalysts Christensen used in his work[10], the others were prepared by the sol immobilisation method (sol) using PVA and sodium borohydride, excepting the ceria supported which were prepared using a THPC/sodium hydroxide synthesis method.

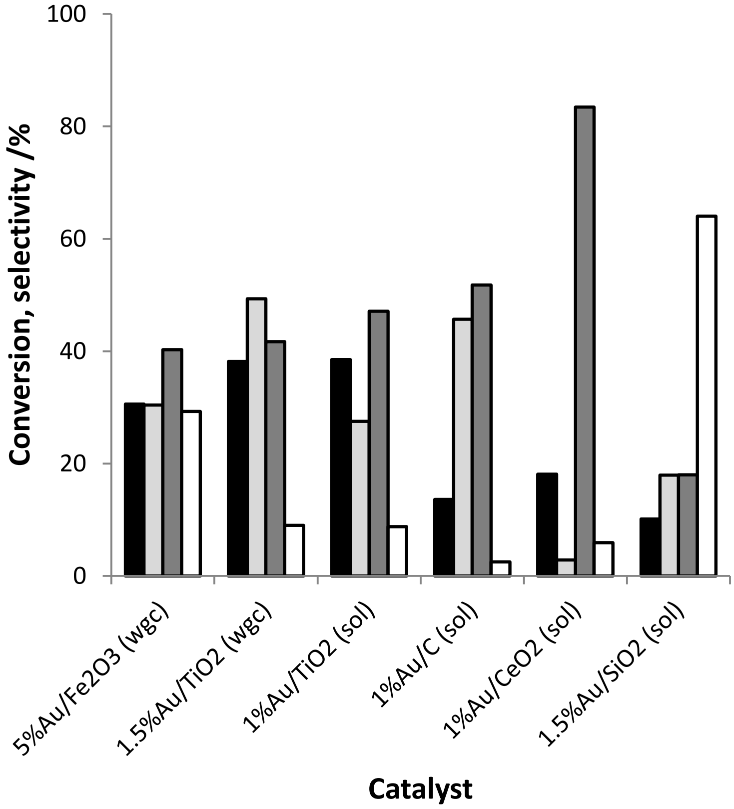


Figure 4-9 Effect of support on the conversion of 1,2-propanediol (■) and selectivity to hydroxyacetone (■) methyl lactate (■) and methyl pyruvate (□). Reaction conditions 1,2-propanediol:Au = 500, 1,2-propanediol:NaOMe = 10, T = 100 °C, $P(O_2)$ = 3 bar

The nature of the catalyst support effects both conversion of 1,2-propanediol and the product distribution. Gold supported on carbon has been previously shown to give high conversions of 1,2-propanediol in the aqueous phase with high selectivity to lactic acid[2, 15]. In methanol the carbon support was less active than most metal oxide supports tested but did show the lowest selectivity to methyl pyruvate which is formed from the oxidation of methyl lactate.

The titania supported catalysts were the most active with the World Gold Council catalyst and the catalyst prepared by sol immobilisation showing very similar conversions, 38.2 % and 38.5 % respectively, this is most likely due to the similar gold particle size of these catalysts (WGC – 3.6 nm an sol immobilisation – 3.8 nm). The sol catalyst shows an enhancement in the selectivity to methyl lactate, 47.1 % compared with 41.7 % of the World Gold Council catalyst.

The Au/SiO_2 catalyst shows the lowest activity with 10.1 % conversion of 1,2-propanediol. The main product in this case was methyl pyruvate at 64.0 % with 17.9 % hydroxyacetone and 18.0 % methyl lactate. The other World Gold Council catalyst, Au/Fe_2O_3 shows comparably high conversion 30.6 %. This catalyst also showed a high selectivity to methyl puyuvate (29.3 %) showing that this catalyst oxidised the methyl lactate under reaction conditions. The selectivity to methyl lactate itself was 40.3 %. By far the most selective catalyst to methyl lactate was the ceria supported catalyst. The selectivity to hydroxyacetone after 24h was exceptionally low (2.8 %) with the methyl lactate selectivity at 83.5 %.

Taking into account that the particle size is in a similar range for all the gold supported catalysts (3-7 nm, as shown in chapter 3) for the gold supported nanoparticles the difference in activity and selectivity of the catalysts could be attributed to metal-support interactions, active sites in the metal-support interface the shape of the gold particles and oxidation state. In the case of the Au/CeO_2 catalyst a lower catalytic activity was observed with an enhanced selectivity to methyl lactate. The lower activity and enhanced selectivity to methyl lactate could be attributed to the presence of cationic gold (20%) which has been demonstrated by XPS measurements in chapter 3. It seems that presence of metallic and cationic gold is beneficial for the improvement in the selectivity of methyl lactate. However, it has been suggested that Au^{3+} is susceptible to poisoning from strong binding carboxylic acids[16]. Carrettin *et al.* have demonstrated that the activity of a Au/CeO_2 and Au/Yt_2O_3 for the oxidation of CO is directly proportional to the concentration Au^{3+} ions on the catalyst surface[17]. These two supports were found to stabilise the Au^{3+} species.

It is well known that ceria is an oxygen donator[18]. It is possible that these properties aid the transformation of hydroxyacetone to methyl lactate. Ceria supported catalysts have been used previously by Corma *et al.* for the esterification 5-hydroxymethyl-2-furfural[19]. In this work it was shown that ceria supported catalysts were more active than other metal oxide supports in base free conditions. The ceria supported catalyst was also more selective to the diester product, 2,5-dimethylfuroate, than other oxide supported catalysts, Fe_2O_3 and TiO_2 and carbon supported catalyst. The same authors also demonstrated that ceria supported gold catalysts were more active and selective for the oxidation of oximes, such as cyclohexanone oxime to cyclohexanone than those supported on carbon and titania supports[20]. The presence of ceria has also been shown to promote the oxidation of alcohols with silver catalysts[21].

Corma *et al.* have suggested a mechanism for oxidation by Au/CeO_2[16]. It was suggested that the first step is the physisorption of an oxygen molecule at an oxygen defect on the ceria surface. This interaction leads to the formation of a metal peroxyl radical, Ce^{4+}-O-O. The Au^{3+} species on the catalyst surface form gold-alcoholate structures. It has been proposed that the metal peroxyl radical and gold-alcoholate combine to form a ketone and metal hydroperoxide which is decomposed by the gold.

The difference in preparation method must also be addressed. It is not possible to create ceria supported catalysts by the $PVA/NaBH_4$ sol immobilisation method. It has been shown by Prati *et al.* that Au colloids prepared by the THPC/NaOH have slightly smaller particles than when prepared by the $PVA/NaBH_4$ method[22] (2.02 nm compared with 2.45 nm). However, it has also been shown that when these colloids are supported on carbon the gold particle sizes are similar and both catalysts show similar activity for the oxidation of ethylene glycol[23]. A comparison of Au/TiO_2 prepared by the two different sol immobilisation has also been made for the oxidation of glycerol[24]. It was demonstrated that the THPC/NaOH preparation yielded smaller nanoparticles (2-3 nm) than the $PVA/NaBH_4$ method (4-5 nm). The THPC/NaOH was more active and more selective (increase of 12 %) to further oxidation products at iso conversion (90 %).

The ceria supported catalyst is more selective to methyl lactate than the other supports, it is likely this is due to a combination of the presence of cationic gold, preparation method and oxygen donation properties of the support. The question is posed whether the conversion can be improved whilst maintaining the high selectivity.

4.2.2.4 Effect of palladium addition

The addition of palladium to a gold catalyst has been shown to have a positive effect on conversion and selectivity of oxidation reactions. A 0.5%Au0.5%Pd/TiO_2 has been shown to be extremely active and selective for aqueous 1,2-propanediol oxidation[8].

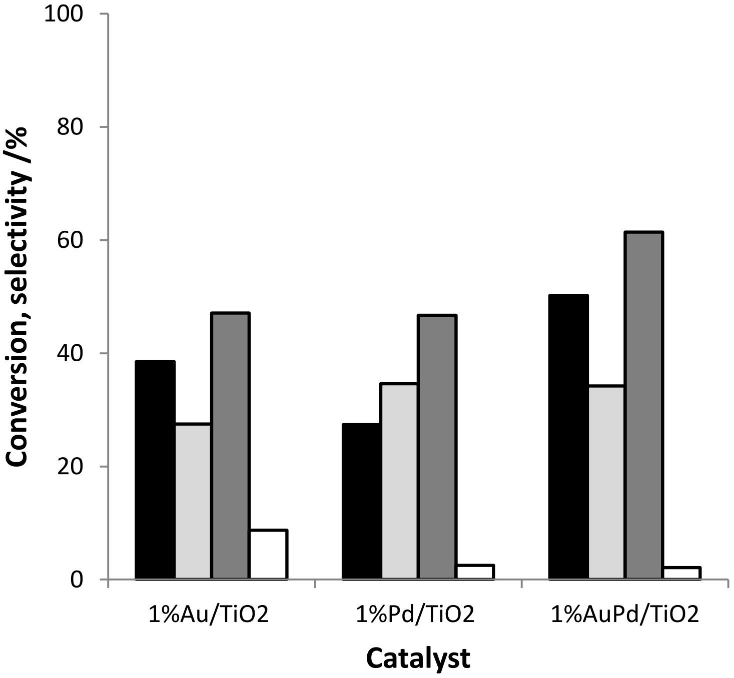


Figure 4-10 effect of metal on the conversion of 1,2-propanediol (■) and selectivity to hydroxyacetone (▨) methyl lactate (▩) and methyl pyruvate (□). Reaction conditions 1,2-propanediol:metal = 500, 1,2-propanediol:NaOMe = 10, T = 100 °C, $P(O_2)$ = 3 bar

As shown in figure 4-10 both Au/TiO_2 and Pd/TiO_2 are active for the oxidation of 1,2-propanediol in methanol. The monometallic gold catalyst is more active than palladium but both catalysts show a similar selectivity to methyl lactate. When these metals are combined to create a bimetallic AuPd/TiO_2 a synergistic effect is demonstrated. The conversion increases by 12 % (Au/TiO_2) and selectivity to methyl lactate by 14 %. This has been previously observed in the aqueous phase oxidations on 1,2-propanediol[8] and glycerol[7]. In light of these results a range of Au-Pd bimetallic catalysts in a 1:1 wt ratio were prepared.

This addition of palladium to the gold catalysts was also observed to be beneficial for the other supports tested (figure 4-11). The most significant increase in activity was apparent on the carbon support, where the conversion rose from 13.6 % to 50.2 %. However, the selectivity to methyl lactate was not enhanced by the addition of palladium to the carbonsupported catalyst. The same is true of the ceria supported catalyst; the conversion was enhanced by the addition of palladium but the selectivity to methyl lactate decreased.

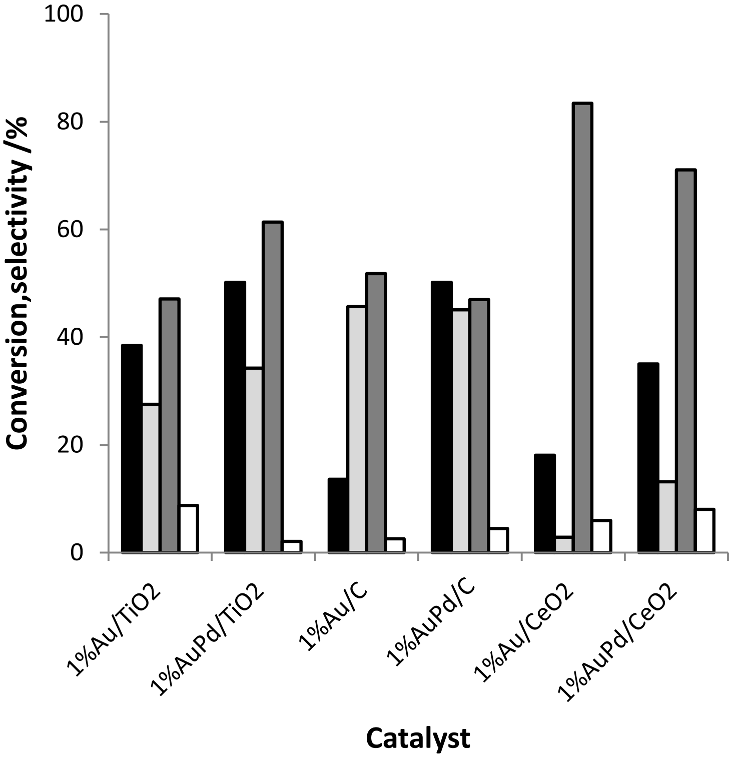


Figure 4-11 Effect of palladium addition to the gold catalyst on the conversion of 1,2-propanediol (■) and selectivity to hydroxyacetone (■) methyl lactate (■) and methyl pyruvate (□). Reaction conditions 1,2-propanediol:metal = 500, 1,2-propanediol:NaOMe = 10, T = 100 °C, P(O_2) = 3 bar

Due to the excellent selectivity to methyl lactate of the ceria supported catalysts, this support was chosen to investigate the systematically study the effect of changing the Au:Pd ratio (figure 4-12 and 4-13).

It was found that monometallic Pd/CeO_2 is active for the reaction (56 % conversion), however, the selectivity to methyl lactate is significantly lower than that of the gold catalyst (54 % compared with 83.5 %). This trend has been observed previously by Corma *et al* for the oxidation of a number of alcohols. The palladium catalyst showed evidence of cerium reduction in the XPS sprectrum (chapter 3). It is possible that this surface reduction during the preparation contributes to the enhanced activity of this catalyst. It has been suggested that the higher the concentration of Ce^{3+}, the higher the number of oxygen defects which increases the oxygen uptake potential of the support and hence the activity of the catalyst[16].

Three bimetallic catalysts were prepared with different Au:Pd molar ratios. Increasing the amount of palladium led to an linear increase in conversion of 1,2-propanediol. As can be seen in figure 4-13 when the palladium content of the catalyst in the reaction is doubled from 4 to 8 μmol, the conversion almost doubles (from 22 % to 40 %). When gold and palladium are alloyed it is possible to achieve an increased conversion whilst maintaining a high selectivity to methyl lactate.

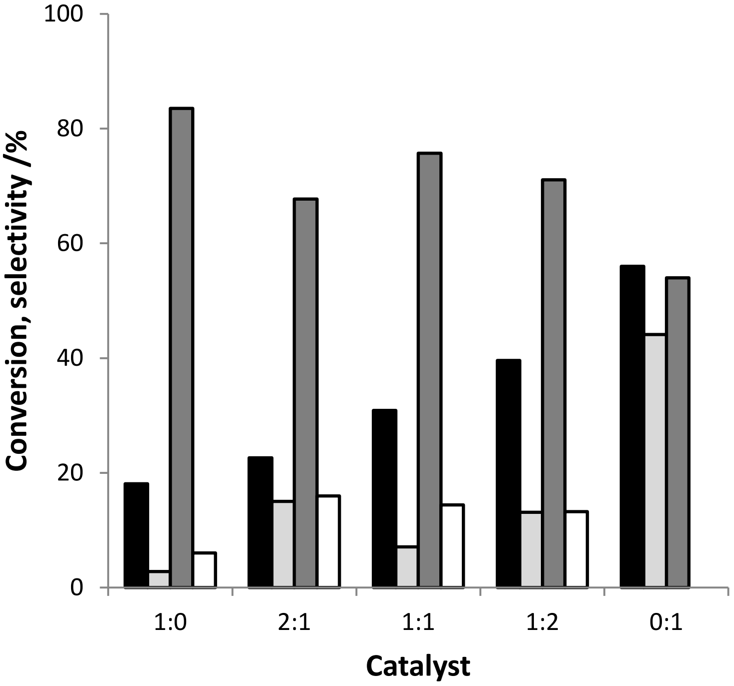


Figure 4-12 The effect of Au-Pd ratio on the conversion of 1,2-propanediol (■) and selectivity to hydroxyacetone (▫) methyl lactate (▪) and methyl pyruvate (□) with CeO_2 supported catalysts. Reaction conditions; 1,2-propanediol:metal = 500, 1,2-propanediol:NaOMe = 10, T = 100 °C, $P(O_2)$ = 3 bar

This effect has been observed previously when a physical mixture of gold and palladium catalyst were utilised by Enache *et al.* for the solvent free oxidation of benzyl alcohol with titania supported catalysts[25]. The most selective bimetallic catalyst was the 1:1 molar which yielded a selectivity of 75.7 %. This molar ratio of AuPd has been demonstrated to be the most selective in the esterification of 1-octanol to methyl at 78 % using polymer incarcerated catalysts[18] and for the solvent free oxidation of benzyl alcohol[25].

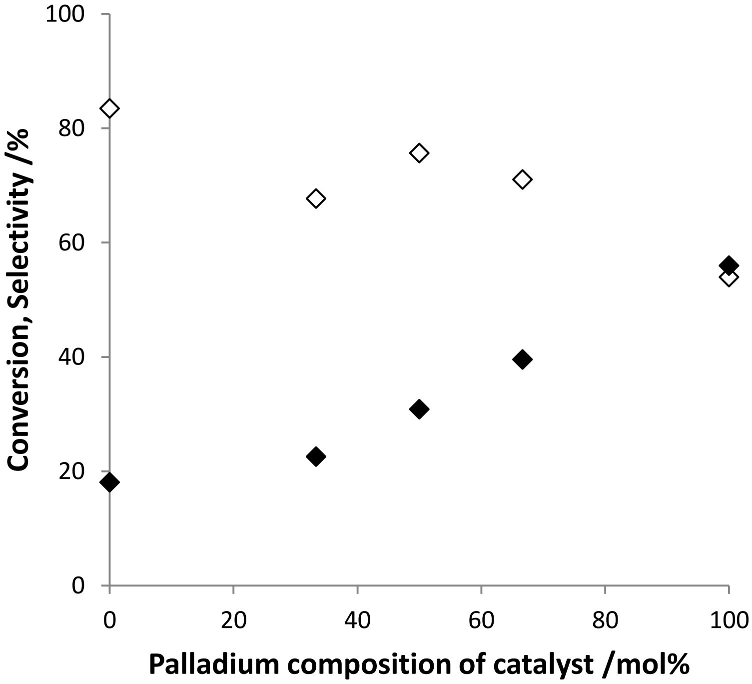


Figure 4-13 The effect of Palladium content of ceria supported catalysts on the conversion (◆) and selectivity to methyl lactate acid (◇)

4.3 Conclusions and future work

The oxidative esterification of 1,2-propanediol was investigated using gold and gold palladium nanoparticles supported on a range of supports. The reaction profile was investigated in detail. The major products were hydroxyacetone, methyl pyruvate and methyl lactate, the desired product.

The Au/CeO_2 and Pd/CeO_2 catalysts showed the highest selectivity and activity respectively. The gold catalyst contained 20 % Au^{3+} species which could account for the high selectivity when compared with the other monometallic gold catalysts tested. XPS analysis revealed that the Pd/CeO_2 catalyst showed partial reduction of the ceria surface, which has been linked to enhanced activity[16]. It was found that the addition of palladium to gold significantly enhanced the activity and retains the high selectivity to methyl lactate using O_2 as oxidant.

To extend this work the preparation of higher loaded AuPd/CeO_2 would be investigated, as at present the actual loading of the 1% catalysts is only 0.5%. Therefore the substrate/metal ratios are higher than calculated for a 1% catalyst. Investigations into optimising the catalyst by increasing the Au^{3+} and surface defects of the ceria would be undertaken.

The reaction could be carried out under more oxidising conditions, for example, in an autoclave at 10 bar pressure, which would likely give higher conversions as shown in the literature[7]. As the desired product is a sequencial oxidation product this may also lead to an increase in selectivity as demonstrated in the same work.

With further careful tuning to the catalyst, higher yields of methyl lactate could be achieved, thus providing a greener solution to the production of lactic acid esters and a route to value added chemical from biomass.

References

1. T. Miyazawa, Y. Kusunoki, K. Kunimori and K. Tomishige, *Journal of Catalysis*, 2006, **240**, 213-221.
2. L. Prati and M. Rossi, *Journal of Catalysis*, 1998, **176**, 552-560.
3. T. Tsyjino, S. Ohigashi, S. Sugiyama, K. Kawashiro and H. Hayashi, *Journal of Molecular Catalysis*, 1992, **71**, 25-35.
4. H. H. C. M. Pinxt, B. F. M. Kuster and G. B. Marin, *Applied Catalysis A: General*, 2000, **191**, 45-54.
5. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2003, **5**, 1329-1336.
6. C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, *Catalysis Today*, 2005, **102-103**, 203-212.
7. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.

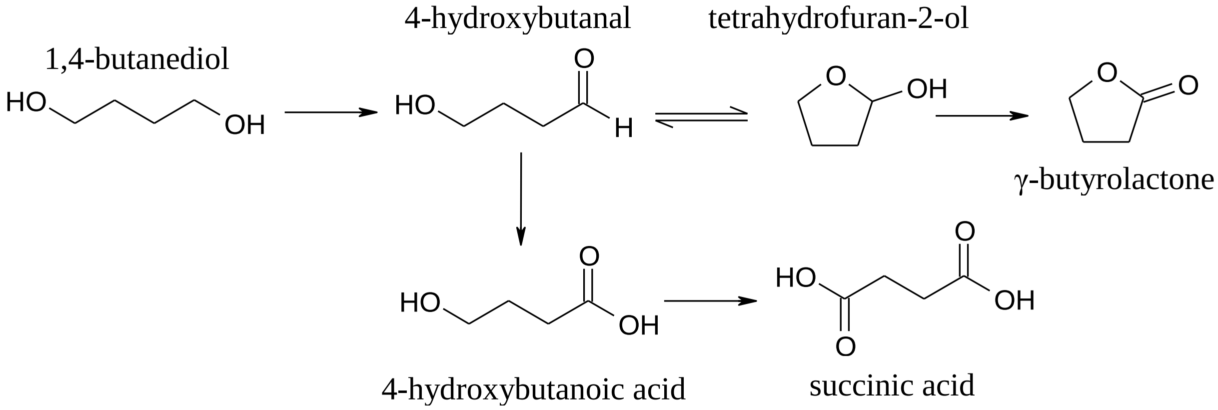
8. N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chemistry*, 2009, **11**, 1209-1216.
9. R. Datta and M. Henry, *Journal of Chemical Technology & Biotechnology*, 2006, **81**, 1119-1129.
10. E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, Editon edn., 2008, vol. 10, pp. 408-414.
11. W. Bang, X. Lu, A. M. Duquenne, I. Nikov and A. Bascoul, *Catalysis Today*, 1999, **48**, 125-130.
12. W. C. Ketchie, M. Murayama and R. J. Davis, *Topics in Catalysis*, 2007, **44**, 307-317.
13. T. Hayashi, T. Inagaki, N. Itayama and H. Baba, *Catalysis Today*, 2006, **117**, 210-213.
14. J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely and G. J. Hutchings, *Journal of Catalysis*, 2005, **236**, 69-79.
15. N. Dimitratos, F. Porta and L. Prati, *Applied Catalysis A: General*, 2005, **291**, 210-214.
16. A. Abad, C. Almela, A. Corma and H. GarcÃ-a, *Tetrahedron*, 2006, **62**, 6666-6672.
17. S. Carrettin, A. Corma, M. Iglesias and F. SÃ¡nchez, *Applied Catalysis A: General*, 2005, **291**, 247-252.
18. K. Kaizuka, H. Miyamura and S. Kobayashi, *Journal of the American Chemical Society*, 2010, **132**, 15096-15098.
19. O. Casanova, S. Iborra and A. Corma, *Journal of Catalysis*, 2009, **265**, 109-116.
20. A. Grirrane, A. Corma and H. Garcia, *Journal of Catalysis*, 2009, **268**, 350-355.
21. M. J. Beier, T. W. Hansen and J.-D. Grunwaldt, *Journal of Catalysis*, 2009, **266**, 320-330.
22. A. Villa, D. Wang, D. S. Su and L. Prati, *ChemCatChem*, 2009, **1**, 510-514.
23. F. Porta, L. Prati, M. Rossi, S. Coluccia and G. Martra, *Catalysis Today*, 2000, **61**, 165-172.
24. N. Dimitratos, A. Villa, C. L. Bianchi, L. Prati and M. Makkee, *Applied Catalysis A: General*, 2006, **311**, 185-192.
25. D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2007, **122**, 407-411.

5 Oxidative esterification of 1,3-propanediol and 1,4-butanediol

5.1 Introduction

1,3-propanediol can be produced from glycerol by hydrogenolysis of glycerol, a by-product of the biodiesel process[1]. Christensen *et al.* demonstrated that the oxidative esterification of 1,3-propanediol could be catalysed by supported gold catalysts[2] to yield dimethyl malonate which is a useful chemical in the perfume industry. Selectivity to this product was very low, 5 % and other studies have shown that esterification of both hydroxyl groups on a diol, for example ethylene glycol, is difficult[3]. The desired product in this case is dimethyl malonate and to further identify a route to increasing the yield of this product, the oxidation of 1,4-butanediol to dimethyl succinate was also studied.

Recently, there has been scientific interest in the liquid phase oxidation of 1,4-butanediol to lactones. These lactones are used for synthesising a variety of polymers and the product γ-butyrolactone is widely used in agriculture, the synthesis of resins and fibers, the petroleum industry and as a solvent[4, 5]. The dehydrogenation of 1,4-butanediol is the traditional route to butyrolactone, this is achieved using copper based catalysts at high temperatures[6, 7]. Huang *et. al.*, suggested that the oxidation of 1,4-butanediol proceeds via 4-hydroxybutanal and then via two alternative pathways, one through tetranhydrofuran-2-ol and subsequently γ-butyrolactone, and the second through 4-hydroxybutanoic acid leading to succinic acid[4]. This work was carried out with a Au/TiO_2 catalyst at 140 °C with 1.25 MPa of air.



Scheme 5-1 The oxidation of 1,4-butanediol by Huang *et al.*

In this work metal oxide supported catalysts prepared by deposition precipitation with a 3-10 % loading were shown to be active for the reaction. It was demonstrated that the 8 % weight loaded catalyst was the most active and selective. Recently it has been shown that unsupported Au-Pd nanoparticles in a substrate/metal ratio of 500 can catalyse the aqueous oxidation of 1,4-butanediol to butyrolactone at 62 °C with 100 % selectivity to butyrolactone at 84 % conversion[8]. Acid catalysts have also been shown to give high selectivities of butyrolactone from 1,4-butanediol[9]. It has been shown previously that it is possible to achieve a 45 % yield of the diesters from 1,8-hexanediol, 1,9-nonanediol and 1,12-decanediol[10].

5.2 Results and discussion

5.2.1 1,4-butanediol oxidative esterification – reaction conditions

5.2.1.1 Effect of temperature

A reaction was performed under standard conditions in a HEL autoclave (10 bar O_2) as outlined in chapter 2, using a 1.2% Au/TiO_2 World Gold Council catalyst. Samples were taken periodically to establish the reaction pathway. The results are shown in figures 5-2 to 5-5.

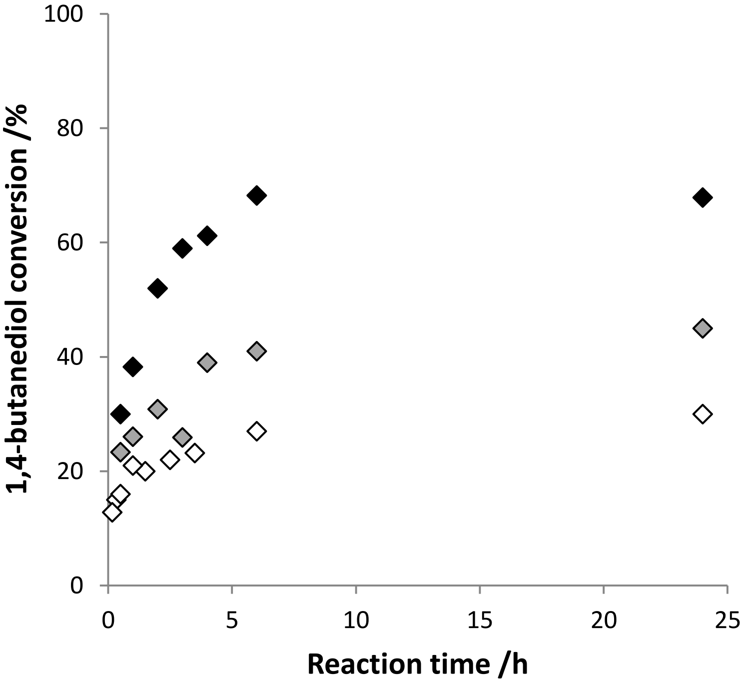


Figure 5-2 The conversion of 1,4-butanediol at 60 °C (◇), 80 °C (◈) and 100 °C (◆). Reaction conditions 1,4-butanediol:metal = 500, ,4-butanediol:NaOMe = 5, T = 60-100 °C, $P(O_2)$ = 10 bar.

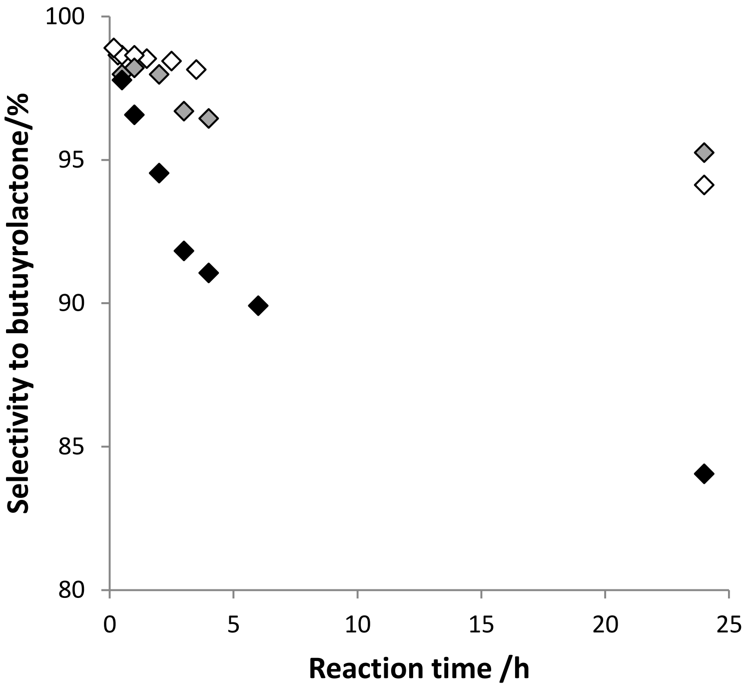


Figure 5-3 Selectivity to butyrolactone at 60 °C (◇), 80 °C (◈) and 100 °C (◆). Reaction conditions 1,4-butanediol:metal = 500, ,4-butanediol:NaOMe = 5, T = 60-100 °C, P(O_2) = 10 bar.

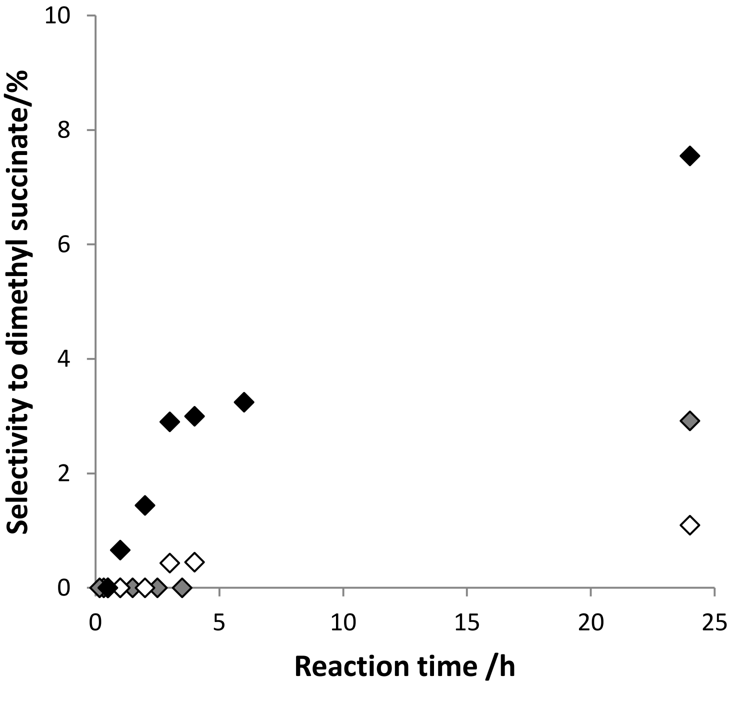


Figure 5-4 Selectivity to dimethyl succinate at 60 °C (◇), 80 °C (◈) and 100 °C (◆)Reaction conditions 1,4-butanediol:metal = 500, 1, ,4-butanediol:NaOMe = 5, T = 60-100 °C, P(O_2) = 10 bar.

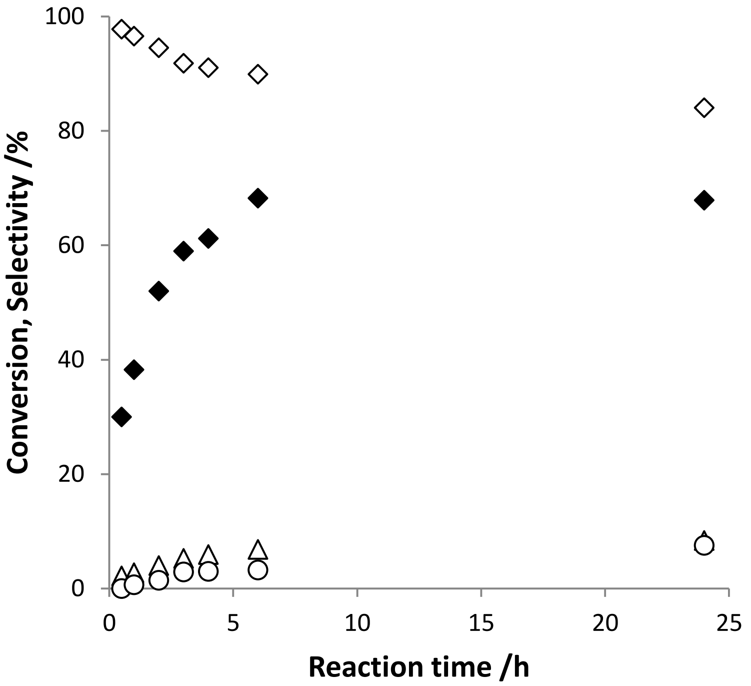


Figure 5-5 Reaction profile at 100 °C. Conversion (◆), selectivity to butyrolactone (◇) selectivity to dimethyl succinate (Δ), methyl-4-hydroxybutyrate (○).Reaction conditions 1,4-butanediol:metal = 500, 1,4-butanediol:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

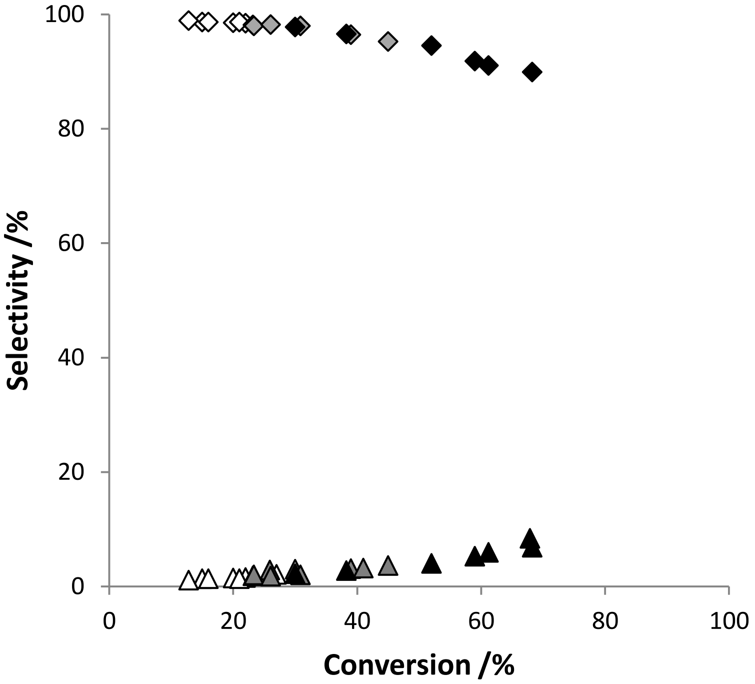
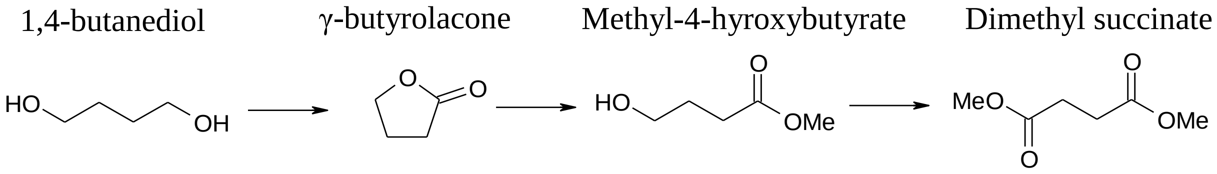


Figure 5-6 The selectivity to butyrolactone (◇) and dimethyl succinate (Δ) at 60 (□), 80 (■) and 100 °C (■)

1,4-butanediol was oxidised in methanol at 100 °C with a 1.5 % world gold council Au/TiO_2 catalyst (figure 5.5), samples were taken periodically to establish the reaction pathway. The major product was butyrolactone, the selectivity to which decreased over time. The selectivities to methyl-4-hydroxybutyrate and dimethyl succinate increased over time. It was confirmed that the oxidation of butyrolactone yielded primarily methyl-4-hydroxybutyrate, 58.1 % selectivity at 1h, and secondly the desired product dimethyl succinate, 41 % at 1h. The selectivity to butyrate decreases over time (29.9 % after 24 h) and the selectivity to succinate increases (70.1 % at 24 h), suggesting a sequential oxidation pathway. This is slightly different than the reaction route suggested by Huang *et al*[4] in aqueous conditions. Under these conditions it was suggested that the primary product was hydroxybutanol and from this molecule 2 reaction pathways lead, one to yield butyrolactone and the other 4-hydroxybutanoic acid and subsequently succinic acid. The mechanism does not state that succinic acid can be produced from the oxidation of butyrolactone in water.



Scheme 5-7 The reaction pathway of 1,4-butanediol oxidation in methanol

The effect of temperature on 1,4-butanediol oxidative esterification with a 1.5 % world gold council Au/TiO_2 catalyst was investigated. As expected, when kinetics are considered, the rate of reaction increased with increasing of temperature, after 24 h the conversion of 1,4-butanediol was 30, 45 and 68 % at temperatures of 60, 80 and 100 °C respectively. The product distribution varied with reaction temperature. The oxidation of butyrolactone occurred faster with increasing temperature. Consequently, the selectivity to the desired product, dimethyl succinate, increased with temperature. There is a clear correlation between temperature and selectivity to succinate – the higher the temperature the higher the selectivity to dimethyl succinate. It can be seen by plotting conversion versus selectivity, Figure 5-6, that the reaction follows the same reaction pathway at all temperatures, merely at a slower rate.

In light of these results the following reactions were carried out at 100 °C in an autoclave and 60 °C in glass due to safety reasons. The primary product of 1,4-butanediol oxidation appears to be butyrolactone, which is subsequently oxidised to methyl-4-hydroxybutyrate and dimethyl succinate.

5.2.1.2 Effect of base

5.2.1.2.1 The substrate base ratio

The effect of substrate base ratio on the reaction was investigated using the same Au/TiO_2 catalyst as above. The reaction was carried out at 100 °C in an autoclave reactor at 10 bar oxygen pressure.

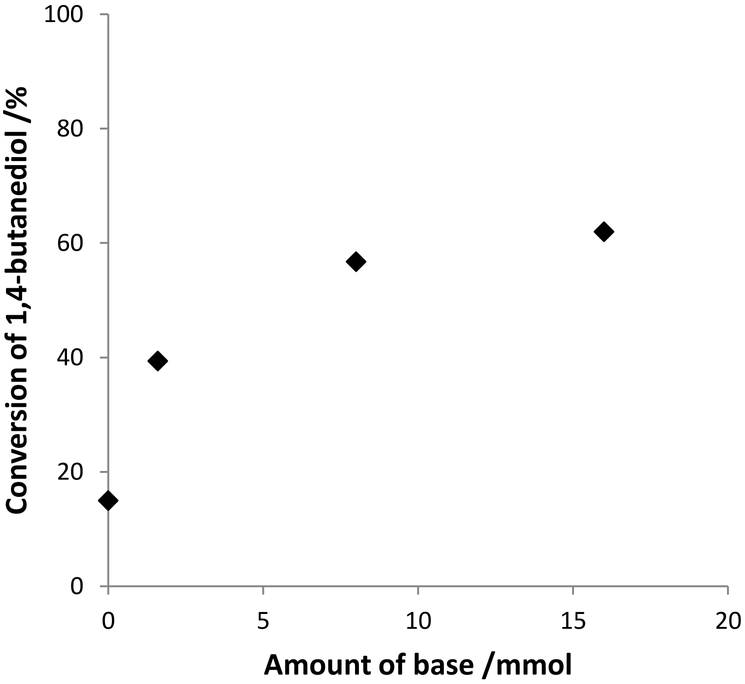


Figure 5-8 The effect of the amount of base on 1,4-butanediol oxidation at 1hour. Reaction conditions 1,4-butanediol:metal = 500, 1,4-butandiol:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

The amount of base has been shown to play a crucial role in the activation of the substrate for the oxidation of diols as has been displayed for other substrates[11,12,13]. For industrial applications it is important to consider the effect of the amount of base. The effect of substrate:base molar ratio on the reaction was studied using the same Au/TiO_2 catalyst. It is clear that the concentration of base significantly affected 1,4-butanediol conversion and also the yield of succinate. The reaction is able to proceed when no base is added, therefore indicating that base is not needed to activate the 1,4-butanediol molecule (figure 5-8). However increasing the amount of base did increase the initial reaction rate of reaction.

Further increase in the amount of base did not significantly increase the yield or selectivity to dimethyl succinate. In fact an excess of base appeared to be detrimental to succinate formation (figure 5-9).

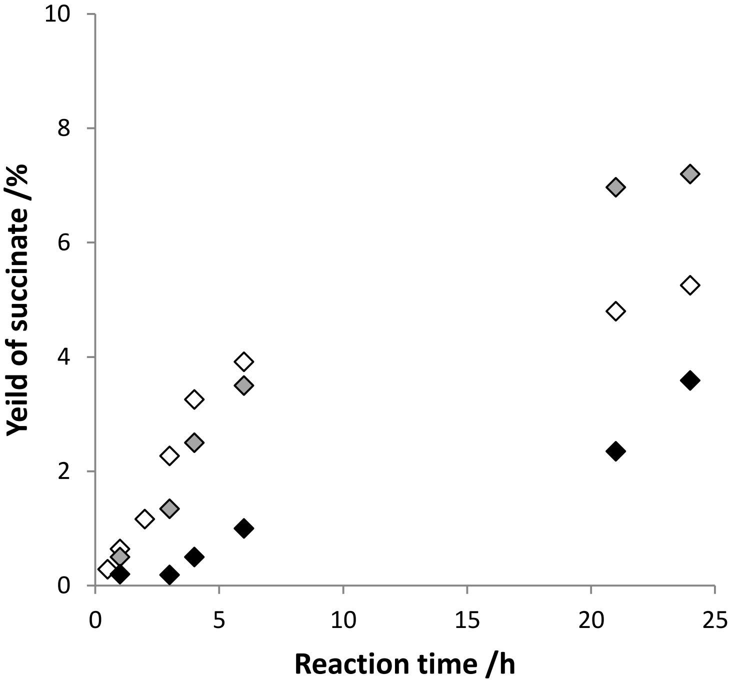


Figure 5-9 Yeild of succinate using substrate:base ratio 5:1 (◇), 1:1 (◈) and 2:1 (◆).Reaction conditions 1,4-butanediol:metal = 500, 1,4-butanediol:NaOMe = 5, T = 100 °C, $P(O_2)$ = 10 bar.

5.2.1.2.2 Effect of acid

The reaction was completed without base and in the presence of phosphotungstic acid (10%) supported on silica.

The addition of acid leads to significant changes to the product distribution as shown in figure 5-9. Initially the major product detected is methyl-4-hydroxybutyrate, it is likely that this arises from butyrolactone forming then ring opening in the presence of acid. Over time the selectivity to butyrate decreases. After 24 h the selectivity the butyrate dropped to 17.3 %. The addition of a solid acid into the reaction mixture has a marked effect on selectivity to dimethyl succinate – no succinate is detected.

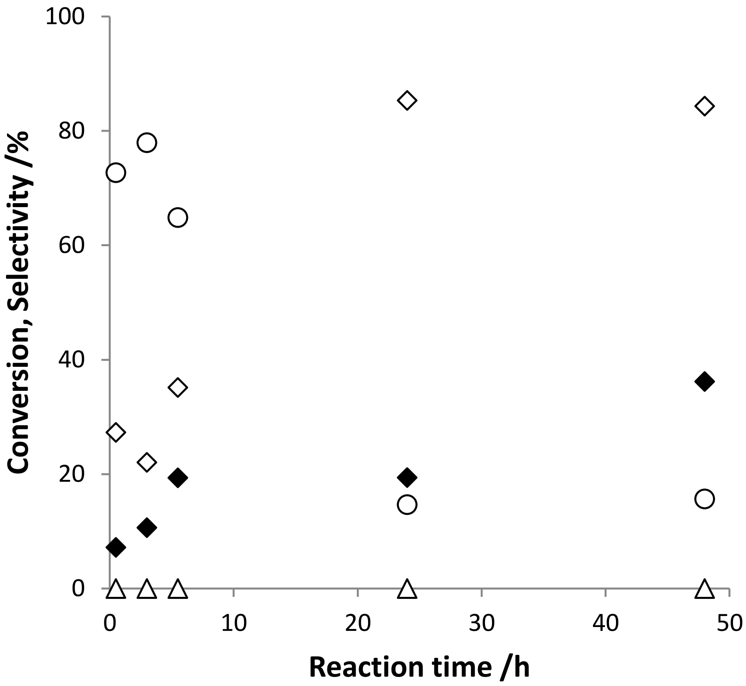


Figure 5-10 The effect of phoshotungstic acid addition on conversion of 1,4-butanediol (◆), selectivity to butyrolactone (◇), selectivity to dimethyl succinate (Δ), and methyl-4-hydroxybutyrate (○). s:m = 500, acid 0.1g, T = 100 °C, $P(O_2)$ = 10 bar.

The addition of a solid acid into the reaction mixture has a marked effect on selectivity. Early in the reaction methyl-4-hydroxybutyrate is the major product, selectivity decreases over time with the formation of more butyrolactone. No dimethyl succinate was detected.

5.2.1.3 Effect of added water

The reaction was carried out under the same conditions with 10 % water in methanol mix as the solvent. The results are shown below in figure 5-11.

When the solvent is changed from pure methanol to a 90:10 methanol/water mix by volume the conversion and selectivity are affected detrimentally (figure 5-11). The initial rate at 30 min is halved when water is added. The TOF is reduced from 403 to 200 h^{-1}. The selectivity has also been reduced from 3.2 % to 0.9 %.

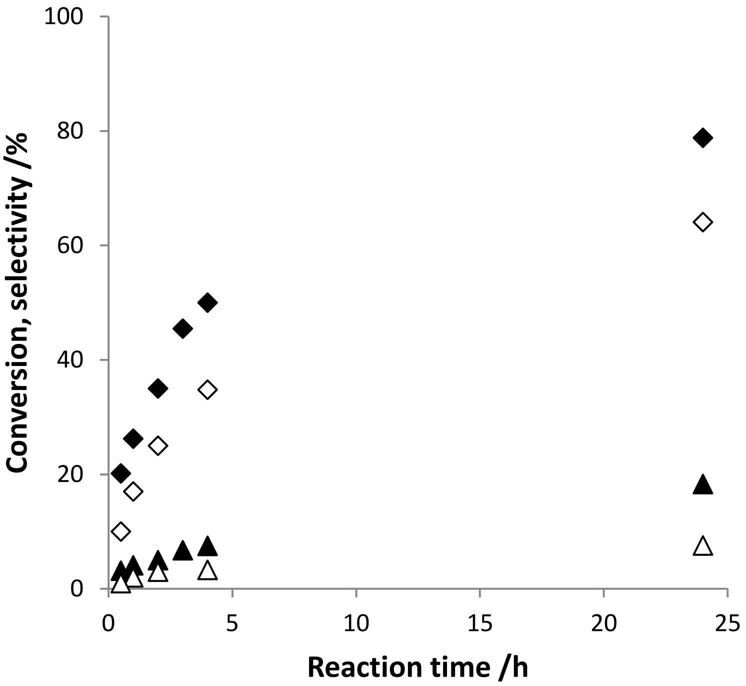


Figure 5-11 The effect of water addition of conversion and selectivity to succinate.Conversion dry (◆), conversion added water (◇), selectivity to dimethyl succinate dry (▲) and selectivity to dimethyl succinate with added water (∆)

The solubility of oxygen in water is lower than that in methanol; this may be one reason why the conversion has decreased in the modified solvent. Another factor to consider is the diffusion of the reactants to the catalyst. PFG NMR studies have been carried out to probe the diffusion properties of 1,4-butanediol in both solvents. It was found that the addition of water inhibits the adsorption of the 1,4-butanediol on the catalyst surface. At isoconversion it was found that at 35 % conversion the selectivity to dimethyl succinate in dry methanol is 5.3 % whereas in the 90:10 methanol/water mix the selectivity was reduced to 3.3 %.

5.2.2 Catalysis effects

5.2.2.1 Effect of catalyst support

Gold catalysts have been shown to be successful in oxidising alcohols[14]. Catalysts prepared by sol immobilisation have been shown to be more active than catalysts prepared by the impregnation method[15]. In light of this a range of oxide supported gold catalysts prepared by sol immobilisation were screened for 1,4-buatanediol oxidation in an autoclave at 100 °C.

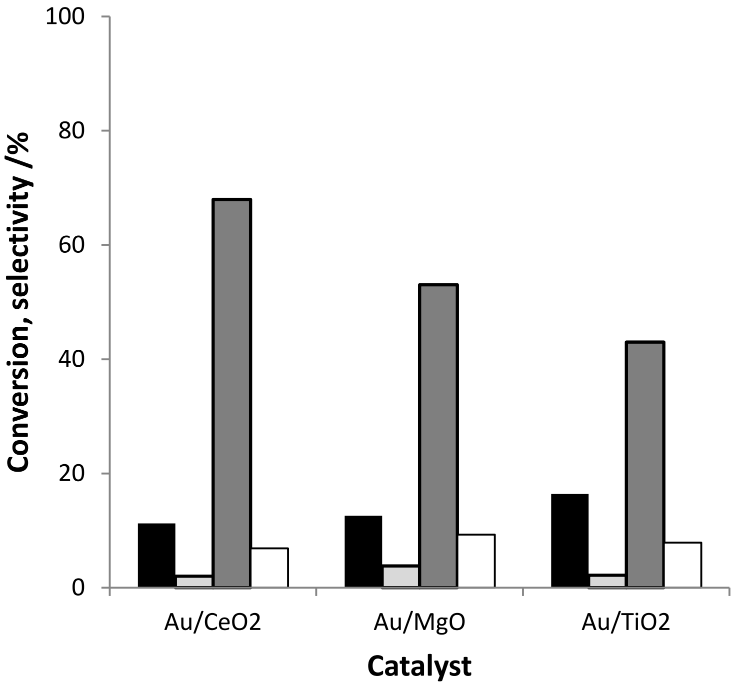


Figure 5-12 The effect of support on conversion of 1,4-butanediol at 4h (■) and 24h (■), and selectivity to dimethyl succinate after 0.5 h (■) and 24 h (□). s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

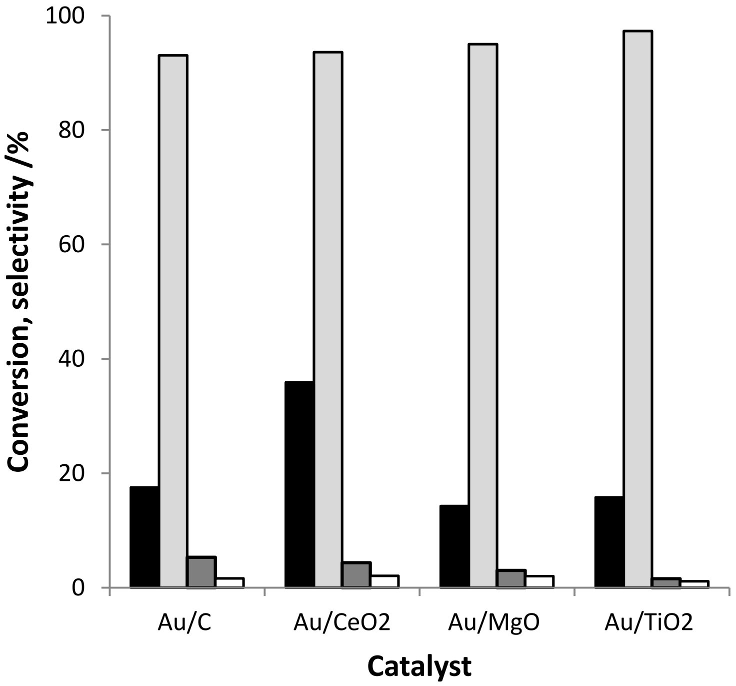


Figure 5-13 The effect of support on conversion of 1,4-butanediol (■) selectivity to butyrolactone (■), methyl-4-hydroxybutyrate (■) and dimethyl succinate (□) in a glass reactor at 24h. s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 3 bar.

Three gold metal oxide supported catalysts were tested for the reaction. The titania supported catalysts showed the fastest initial rate but showed less conversion than CeO_2 and MgO supports after 24 h (figure 5-12). The selectivities for TiO_2, CeO_2 and MgO at 24 h were 7.9, 6.9, and 9.3 % respectively. Although the World Gold Council Au/TiO_2 is more active than the sol immobilisation catalysts, if comparisons are made at isoconversion it is apparent that the sol immobilisation catalysts are more selective to dimethyl succinate. At 53 % conversion the WGC Au/TiO_2 catalyst shows a 4.0 % selectivity whereas the Au/MgO and Au/CeO_2 catalyst shows 9.3 % and 7.4 % selectivity to dimethyl succinate. At 40 % conversion the WGC catalyst shows a selectivity of 2.8 % the titania supported sol immobilisation catalyst shows a considerably higher selectivity of 7.9 %.

The reaction was also carried out in a glass reactor at 40 °C at 3 bar oxygen pressure (figure 5-13). When the reaction is carried out at a lower temperature and pressure there is a clear distinction between supports. Again the ceria support is by far the most active; the conversion of 1,4-butanediol at 24 h is double that of the other supports.

5.2.2.2 The effect of metal with ceria supported catalysts

Ceria supported catalysts have been shown to be the most selective for the oxidative esterification 1,2-propanediol to methyl lactate[16]. Monometallic palladium catalysts have been shown to be active for the oxidation of diols[17] and the addition of palladium to gold catalysts have been shown to considerably enhance activity[13, 15, 18]. In light of this information a ceria supported palladium catalyst and a bimetallic AuPd catalyst in a 1:1 wt ratio and tested under the same conditions.

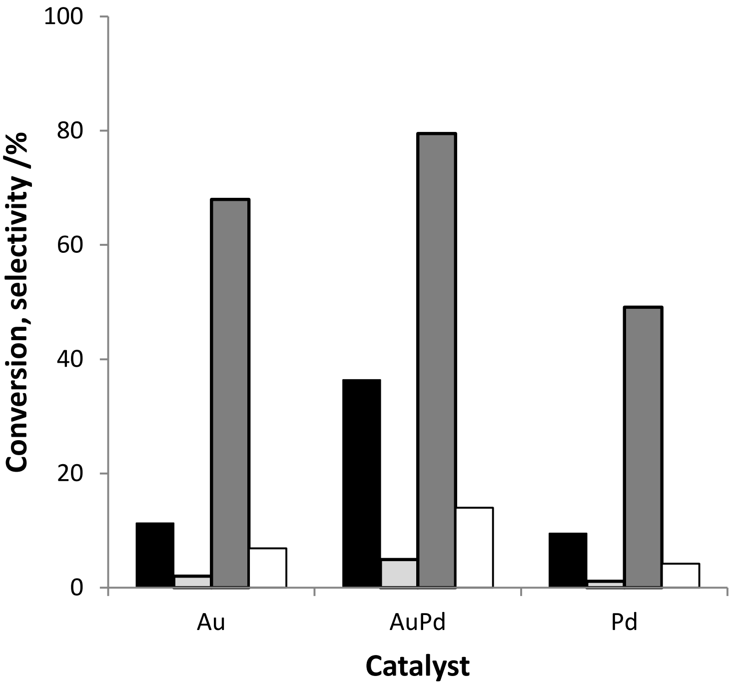


Figure 5-14 The effect of metal on conversion of 1,4-butanediol (4h (■) and 24h (■)), and selectivity to dimethyl succinate (0.5h (■) and 24h (□)) with ceria catalysts. s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

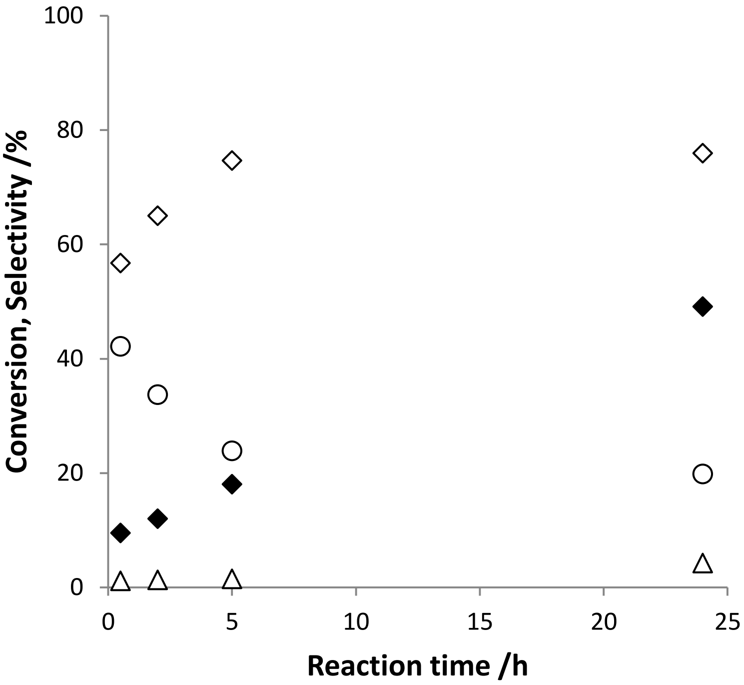


Figure 5-15 Reaction profile with Pd/CeO_2. Conversion (◆), selectivity to butyrolactone (◇) selectivity to succinate (△), methyl-4-hydroxybutyrate (○). s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

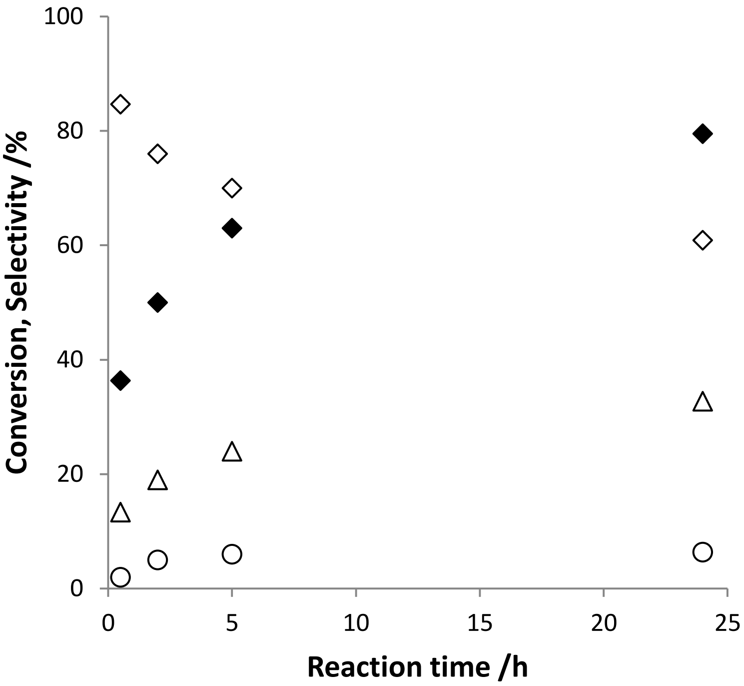


Figure 5-16 Reaction profile with AuPd/CeO$_2$. Conversion (◆), selectivity to butyrolactone (◇) selectivity to dimethyl succinate (Δ), methyl-4-hydroxybutyrate (○). s:m = 500, s:NaOMe = 5, T = 100 °C, P(O$_2$) = 10 bar.

The palladium catalyst tested was less active and less selective to dimethyl succinate than the monometallic gold catalyst (figure 5-14). The reaction pathway is similar to when acid is added to the reaction (figure 5-15). The selectivity to methyl-4-hydroxybutyrate is relatively high at early times but then the selectivity decreases over time, whereas, the selectivity to butyrolactone increases over time to a maximum of 75 % around 24 h. The selectivity to dimethyl succinate is a low 4.2 % after 24 h.

In the case of the bimetallic catalyst, the selectivity trend of the reaction is most similar to that of the gold catalyst; the initial highest selectivity was to butyrolactone which diminished over time giving rise to methyl-4-hydroxybutyrate and dimethyl succinate (figure 5-16). This catalyst shows an improvement in both activity and selectivity over both Au and Pd monometallic catalysts, demonstrating a synergergistic effect. The conversion at 30 min has increased threefold compared with the monometallic gold catalyst and is 3.8 times greater than the palladium catalyst. The Au, Pd and AuPd catalysts have TOFs at 30 min of 113, 95 and 364 respectively. The selectivity to dimethyl succinate after 24 h is double that of the gold catalyst (6.9 %) when palladium is added giving a selectivity of 14.0 %. The synergistic effect of gold and palladium is well known and has promoted other oxidation reactions[8, 17-19].

5.2.3 Mechanistic insights – the oxidation of butyrolactone

As the yields of succinate are not particularly high in the oxidation of 1,4-butanediol, mechanistic studies on the oxidation of the primary product butyrolactone were carried out.

5.2.3.1 Reaction Profile

A reaction was performed under standard conditions in an autoclave using the standard 1.2% Au/TiO_2 World Gold Council catalyst, as used previously for oxidations in methanol by Christensen *et al.*[2]. Samples were taken periodically to establish a reaction pathway.

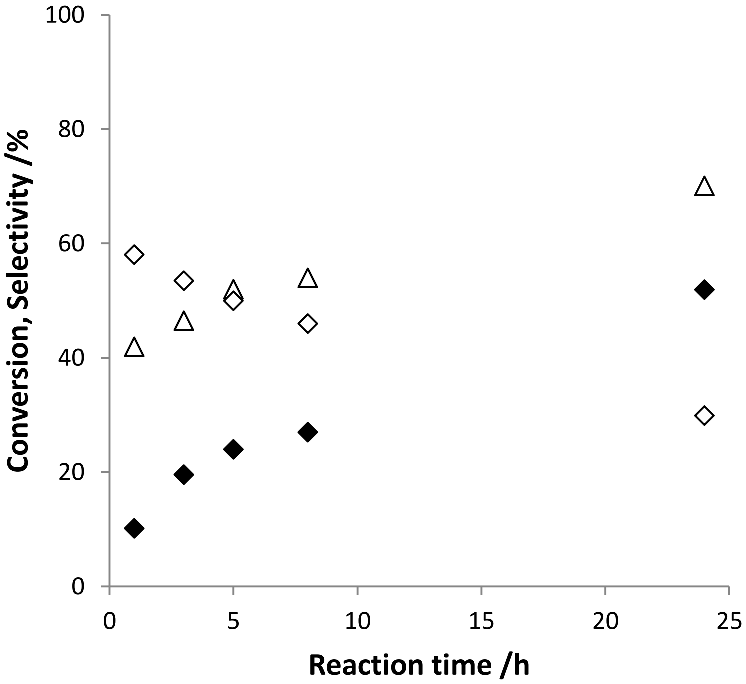


Figure 5-17 the reaction profile for the oxidation of butyrolactone. Conversion of butyrolactone (◆), selectivity to methyl-4-hydroxybutyrate (◇) and dimethyl succinate (△). s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

It can be seen that butyrolactone readily oxidises to methyl-4-hydroxybutyrate, which in turn is oxidised to the desired product, dimethyl succinate. After 24h the yield of succinate is 34.5 % compared with 5.7 % in the 1,4-butanediol oxidation.

5.2.3.2 Effect of acid addition

Butyrolactone was oxidised under the same conditions as 1,4-butanediol is section 5.2.1.2. Silica supported phosphotungstic acid (10%, 0.1g) was added to the reaction

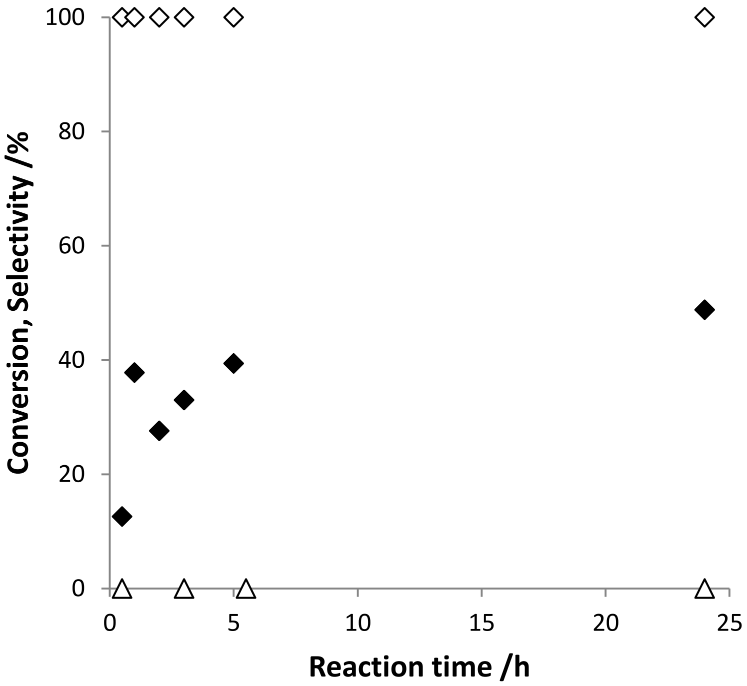


Figure 5-18 the effect of phosphotungstic acid addition on conversion of butyrolactone (◆), selectivity to methyl-4-hydroxybutyrate (◇) and selectivity to dimethyl succinate (△).s:m = 500, acid 0.1 g, T = 100 °C, $P(O_2)$ = 10 bar.

As with 1,4-butanediol, no dimethyl succinate is detected. The selectivity to methyl-4-hydroxybutyrate is 100 % throughout the reaction, proving that acidic conditions are detrimental to succinate formation.

5.2.3.3 Effect of support

A number of supports have been shown to be active for aqueous oxidations[13] and oxidations in methanol[3]. Prati *et al.* found that activated carbon was a very active support for glycerol oxidation[20]. A range of gold and palladium catalysts were screened for butyrolactone oxidation in glass reactors. The reaction time was 24h.

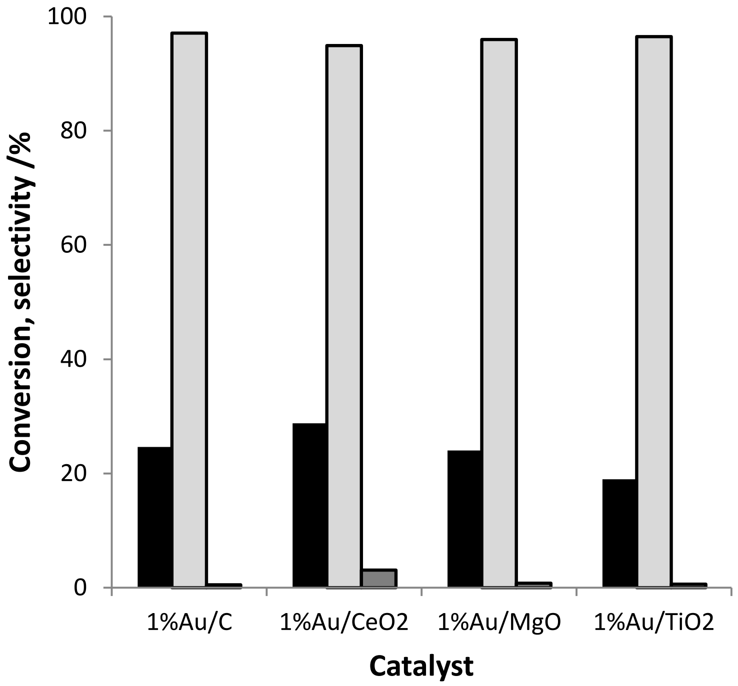


Figure 5-19 The effect of support on conversion of butyrolactone (■), selectivity to methyl-4-hydroxybutyrate (□) and dimethyl succinate (■) using gold catalysts after 24h. s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

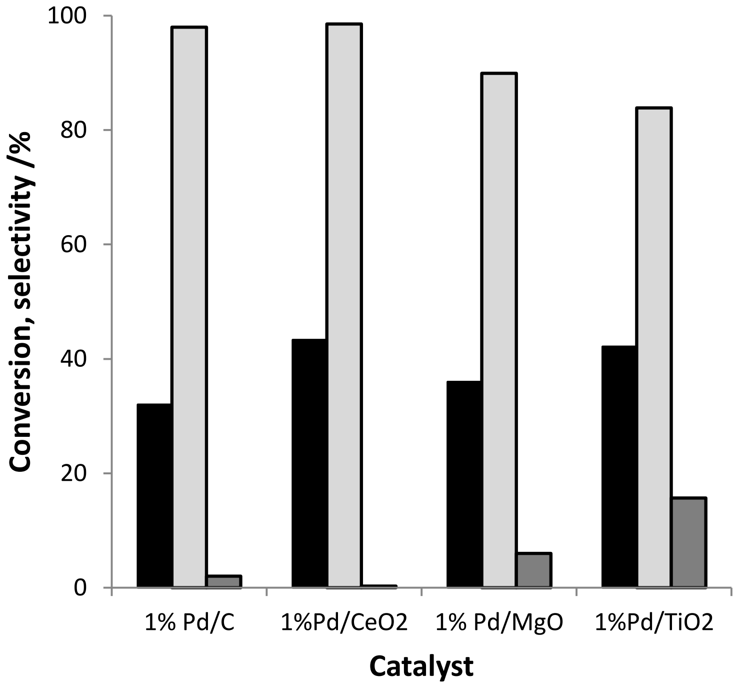


Figure 5-20 The effect of support on conversion of butyrolactone (■), selectivity to methyl-4-hydroxybutyrate (□) and dimethyl succinate (■) using Pd catalysts at 24h. s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 10 bar.

A range of gold catalysts were tested for the oxidation of butyrolactone. It was found that the ceria supported catalyst was both the most active and selective to dimethyl succinate (figure 5-19). It has been discussed previously in chapter 3 that XPS analysis has shown that this catalyst contains both metallic and cationic gold. The C, MgO and TiO_2 supported catalysts contain metallic gold only[15]. It is possible that the presence of this cationic gold promotes the selectivity to dimethyl succinate. In chapter 4 it was shown that the ceria supported gold catalysts gives the highest selectivity to the methyl lactate from 1,2-propanediol.

The palladium catalysts show a different story, the ceria supported catalyst is now the least selective to dimethyl succinate (5-20). However, it is still the most active. It could be suggested that the ceria support itself is activating the butyrolactone molecule. Corma *et al* have demonstrated that ceria supported gold catalysts are both active and selective for the esterification of 5-hydroxymethyl-2-furfural[21]. Without base present Au/CeO_2 was more active than Au/TiO_2 and Au/Fe_2O_3. The ceria supported catalyst also gave 100 % selectivity to the diester product after 5 h. In this work the oxidation was possible without oxygen present, it was suggested that this was due to the ceria support acting as an oxygen donator[22]. These reactions were carried at a relatively low pressure of 3 bar of oxygen, therefore these oxygen donator properties could be a factor in the high conversions of butyrolactone. Pd/TiO_2 shows greater selectivity to dimethyl succinate (15 % after 24h) than both the ceria (0.3 %) and MgO supported catalyst (5 %). All Palladium catalysts show higher conversions of butyrolactone than the gold catalysts. Magnesium doped alumina supported palladium catalysts have been shown to active for the oxidative esterification of aldehydes[23].

Bimetallic Au-Pd catalysts have been reported to catalyse a range of oxidation reactions[18, 19]. A 1:1 wt ratio has been proven to be effective for the oxidation of diols and polyols[13].A range of supported Au-Pd (1:1 wt) catalysts were synthesised and tested for the oxidation of butyrolactone the reaction time was 24h.

The bimetallic ceria supported catalyst showed the lowest selectivity to dimethyl succinate (figure 5-21). The titania and magnesium oxide supported catalysts show a synergistic effect when the metals are alloyed. In the case of the titania supported catalyst the monometallic gold catalyst shows the lowest conversion of butyrolactone and least selectivity to dimethyl succinate (figure 5-23). Pd/TiO_2 shows greater selectivity to dimethyl succinate (15 % after 24h) than the MgO supported catalyst (5 %). The bimetallic catalyst shows the highest selectivity to dimethyl succinate (20 %). It can be seen in that in the case of MgO supported catalysts the palladium and gold-palladium catalysts show comparable conversion under these conditions, whereas, the monometallic gold catalyst is much less active. The selectivity to dimethyl succinate is negligible for the monometallic gold catalyst. The palladium catalyst is more selective to succinate than the gold catalyst; however the selectivity to dimethyl succinate remains low. When the metals are alloyed there is a marked increase in selectivity to succinate (27 %).

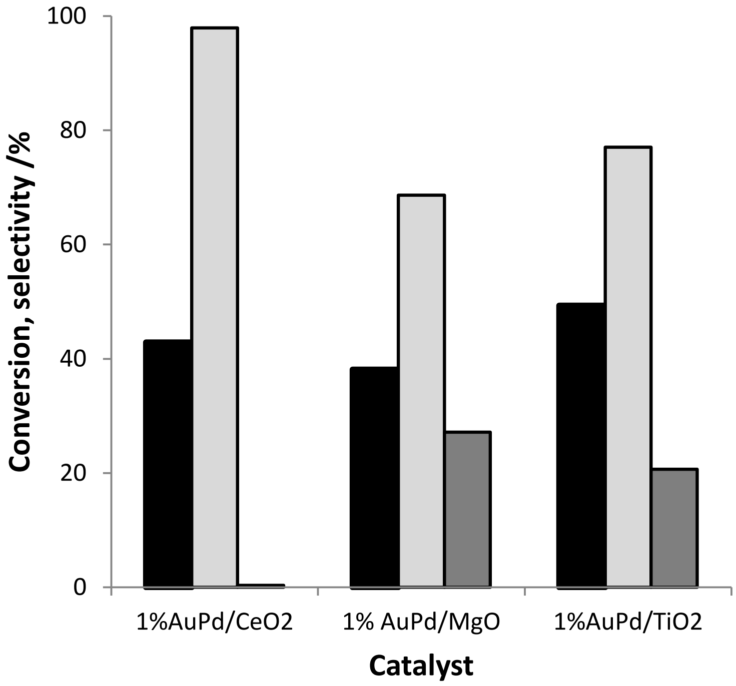


Figure 5-21 The effect of support using Au-Pd catalysts on conversion of butyrolactone (■), selectivity to methyl-4-hydroxybutyrate (□) and dimethyl succinate (▨).

The Au, Pd and Au-Pd data has been compared for MgO and Titania supports which give the highest selectivity to dimethyl succinate (figure 5-23). It can be seen in that in the case of MgO supported catalysts the palladium and gold-palladium catalysts show comparable conversion under these conditions, whereas, the monometallic gold catalyst is much less active. The selectivity to dimethyl succinate is negligible for the monometallic gold catalyst. The palladium catalyst is more selective to succinate (5 %) than the gold catalyst; however the selectivity to dimethyl succinate remains low. When the metals are alloyed there is a marked increase in selectivity to succinate (27 %).

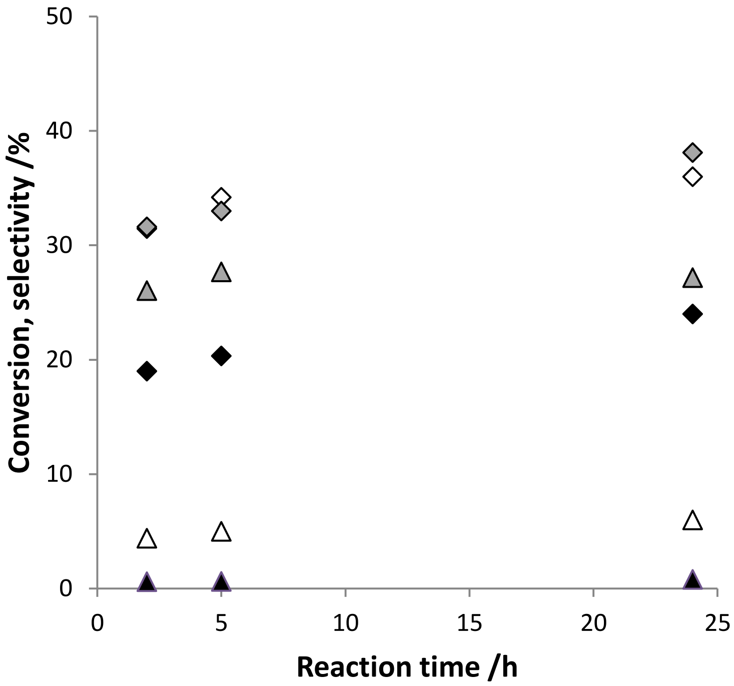


Figure 5-22 The conversion of butyrolactone and selectivities to succinate for Au/MgO (◆,▲), Pd/MgO(◇,Δ) and AuPd/MgO(◈,▲). s:m = 500, s:NaOMe = 5, T = 60 °C, $P(O_2)$ = 3 bar.

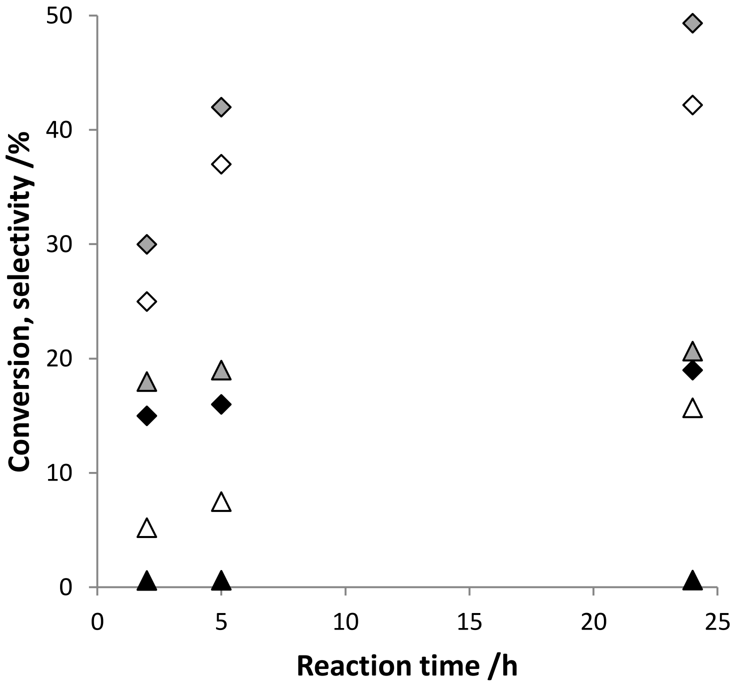


Figure 5-23 The conversion of butyrolactone and selectivities to succinate for Au/TiO_2 (◆,▲), Pd/ TiO_2 (◇,Δ) and AuPd/ TiO_2 (◈,▲). s:m = 500, s:NaOMe = 5, T = 60 °C, $P(O_2)$ = 3 bar.

1.1.1.1.The effect of Au-Pd ratio

In light of these results, the ratio of Au:Pd was varied in order to find the optimum. MgO was the chosen support of this investigation as it has shown the greatest selectivity to dimethyl succinate.

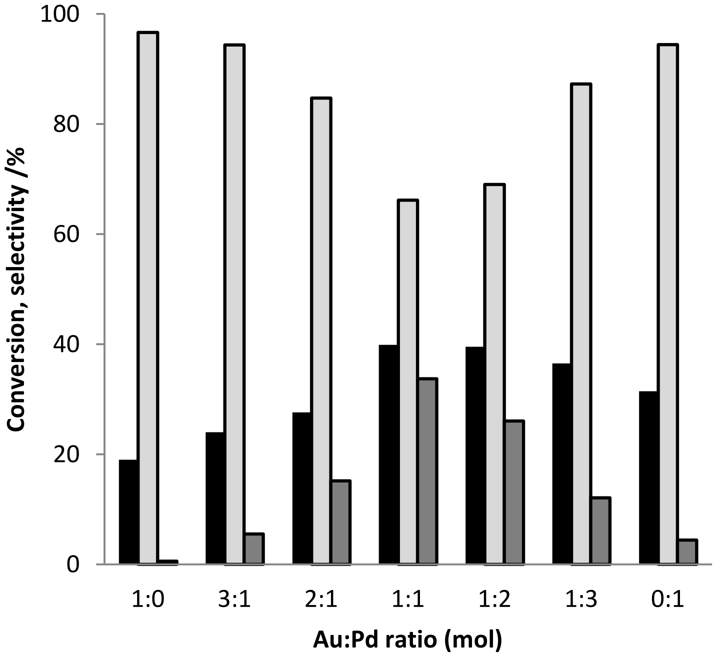


Figure 5-24 The effect of altering Au:Pd ratio on conversion of butyrolactone (■), selectivity to methyl-4-hydroxybutyrate (□) and dimethyl succinate (▨). s:m = 500, s:NaOMe = 5, T = 60 °C, P(O_2) = 3 bar.

The monometallic gold catalyst shows the lowest conversion. The addition of palladium to gold catalyst increases the conversion. The highest selectivity to succinate is achieved by using a 1:1 molar Au:Pd catalyst (figure 5-24). This trend has been shown previously for the oxidation of octan-1-ol in methanol[24] and the solvent free oxidation of benzyl alcohol[25].

5.2.3.4 Effect of substrate metal ratio

The effect of amount of catalyst was investigated in glass reactors using a 1:1 mol AuPd/MgO catalyst. The reaction time was 4h.

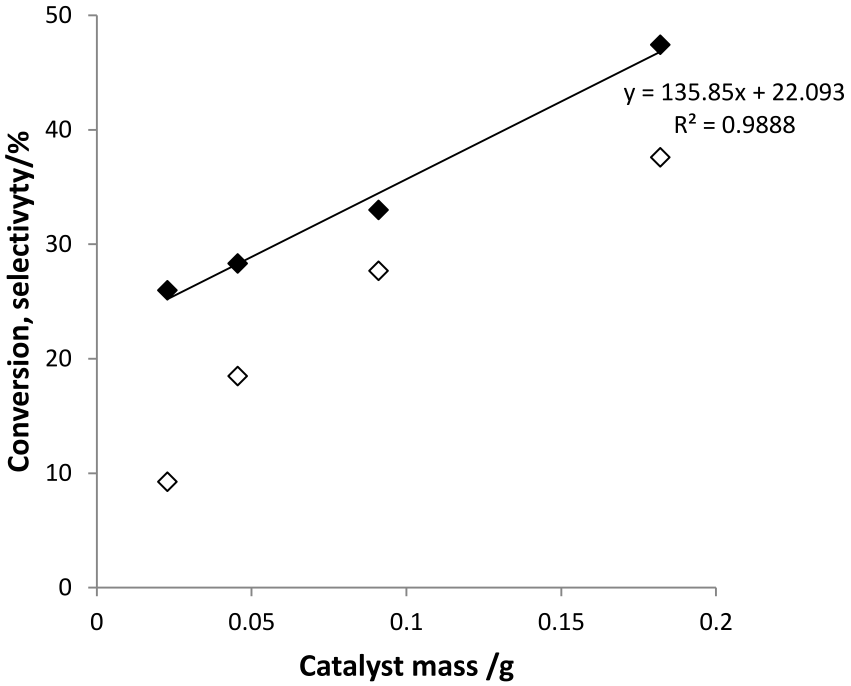


Figure 5-25 Effect of substrate:metal ratio on conversion of butyrolactone (◆) and selectivity to dimethyl succinate (◇) at 2h. s:m = 250-1000, s:NaOMe = 5, T = 60 °C, P(O_2) = 3 bar.

As expected when the catalyst amount is increased the conversion increases as shown in figure 5-25. When the catalysts mass is doubled the conversion does not double, the biggest increase is only by a factor of 1.3 times. What is more interesting is the selectivity to dimethyl succinate. At lower catalyst amounts (between s:m 2000 and 1000) the doubling of the catalyst does lead to a doubling (1.95 times) of the selectivity to succinate. Between s:m 1000 and 500 the selectivity to succinate increases by a factor of 1.8. At the higher catalyst amounts this factor has dropped to 1.5 times. It has been demonstrated in other oxidations that the more catalyst that is present the higher the selectivities to products that are further along the reaction profile[11].

5.2.3.5 Effect of solvent volume

Butyrolactone oxidation was carried out in a low pressure glass reactor using different volumes of methanol (5,10 and 15mL) as solvent.

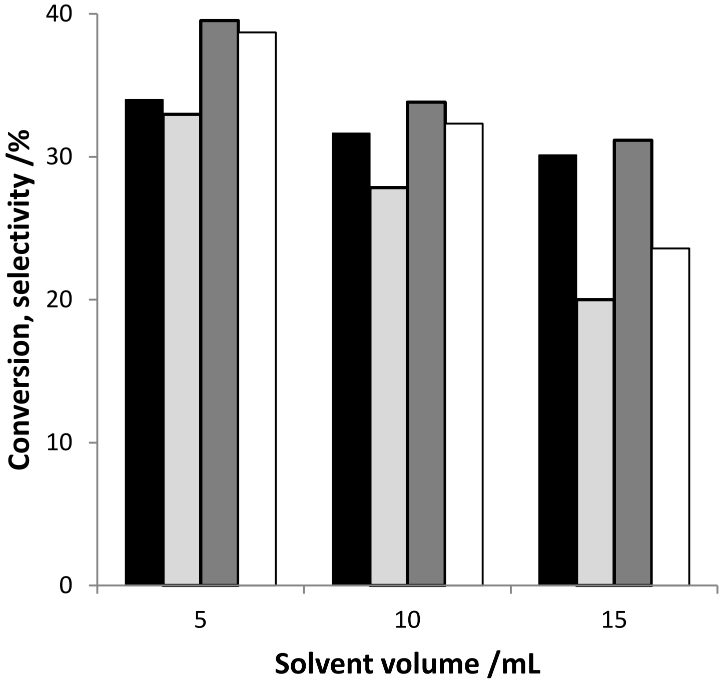


Figure 5-26 The conversion of butyrolactone at 2 (■) and 4h (■) and selectivities to succinate at 2 (■) and 4h (□) with varying volumes of solvent. s:m = 500, s:NaOMe = 5, T = 60 °C, P(O_2) = 3 bar.

An experiment was carried out where the volume of the methanol solvent was varied; this leads to a variation of concentration. It was found that the higher the solvent amount (lower the concentration) the lower the conversion of butyrolactone and selectivity to dimethyl succinate (figure 5-26). Conversely the lowest solvent amount yielded the highest conversion and selectivity to dimethyl succinate.

5.2.3.6 Reusability

AuPd/MgO (1:1 molar) was tested for reuseability. The catalyst was used once for 4h at 60°C, recovered and retested under the same conditions.

Table 5-1 Reusability of AuPd/MgO

			Selectivity /%		
AuPd/MgO (1:1 mol)	time /h	Conversion /%	Butyrate	Succinate	Acetic acid
Fresh	2	34.8	66.2	33.7	0.1
Fresh	4	39.9	56.6	43.3	0.1
Used once	2	35.5	93.6	6.1	0.3
Used once	4	40.3	90.6	9.1	0.3

s:m = 500, s:NaOMe = 5, T = 60 °C, $P(O_2)$ = 3 bar.

The using of the catalyst has little effect on conversion of butyrolactone. However, the selectivity to succinate is greatly decreased. The previous use of the catalyst appears to have hindered the conversion of methyl-4-hydroxybutyrate to succinate. It is possible that the active sited for this transformation have been blocked by irreversible adsorption of organic product intermediates as proposed by Zope *et al.*[26].

XPS and STEM analysis has been carried out to discover the nature of this deactivation (chapter 3). From STEM analysis it was observed that after a single use the catalyst contained larger gold structures as a result of sintering. Some small particles (2-5 nm) remained which could account for the preserved high activity. XPS revealed no changes to the to the gold on the catalyst surface. Another possibility is the poisoning of the active sites by organic compounds during the reaction.

5.2.3.7 The effect of the catalyst preparation method.

After considering the reusability problems of the catalyst prepared by sol immobilisation, two other preparation methods were investigated; impregnation and a modified impregnation method.

The catalyst prepared by sol immobilisation shows considerably higher selectivity to dimethyl succinate than either of the impregnation prepared catalysts (figure 5-28). The standard impregnation catalyst shows the lowest activity with a TOF of 225 h^{-1} compared with 295 h^{-1} and 312 h^{-1} of the sol immobilisation catalyst and modified impregnation respectively. It has been shown previously that catalysts prepared by impregnation are less active than those by sol immobilisation[15].

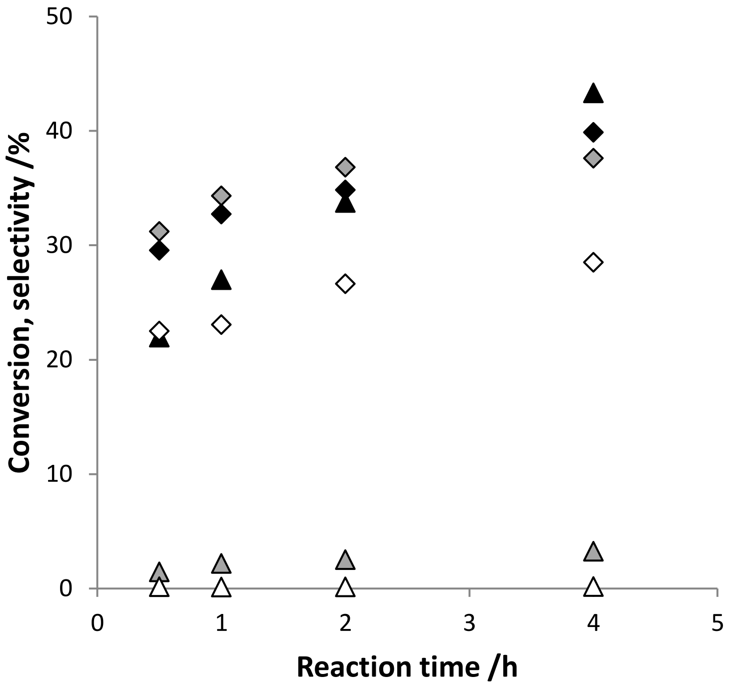


Figure 5-27 The conversion of butyrolactone and selectivity to dimethyl succinate with AuPd/MgO prepared by sol immobilisation (◆,▲), impregnation (◇,Δ) and modified impregnation (◆,▲). s:m = 500, s:NaOMe = 5, T = 60 °C, $P(O_2)$ = 3 bar.

It has been shown that impregnation catalysts contain large particles (20 nm) which are less active for oxidation than smaller particles. The catalysts prepared by sol immobilisation and modified impregnation have similar sized bimetallic particles (3.0 and 3.1 nm respectively) which are also similar in nature. However, the catalyst prepared by modified impregnation also contains some larger monometallic structures.

Another difference between these catalysts is the nature of the supports. The catalysts prepared by impregnation methods have a Periclase MgO support, whereas when prepared by sol immobilisation the catalyst support is altered to brucite $Mg(OH)_2$. Upon reuse the modified impregnation catalyst does not see a loss of activity or selectivity to dimethyl succinate. The difference in metallic structures and nature of the support could account for the difference in activity and selectivity of the MgO supported catalysts. It would appear that small bimetallic nanoparticular structures are needed for high conversions and the $Mg(OH)_2$ support is responsible for the high selectivity to dimethyl succinate.

5.2.4 1,3-propanediol oxidation.

5.2.4.1 Reaction with Au/TiO$_2$

The oxidation of 1,3-propanediol was carried out in a HEL autoclave reactor at 100 °C. The World Gold Council catalyst Au/TiO$_2$ was tested (table 1-2).

As can be seen in table 1-2 the selectivity to dimethyl malonate is very low even with the high substrate metal ratio used by Christensen *et al.*[2] of 112. The reaction conditions are very forcing with high temperature and pressure. To achieve higher conversions the oxygen atmosphere was refreshed by purging and pressurising every hour. In the case of 1,2-propanediol the addition of excess of increased the selectivity to dimethyl malonate.

Table 5-2 The oxidation of 1,3-propanediol

Catalyst	Substrate: base	Atm refreshment	s/m	Conversion /%	Selectivity /%	
					Methyl-3-hydroxypropionate	Dimethyl malonate
1.5% Au/TiO$_2$	10:1	No	112	68.4	100	0
1.5% Au/TiO$_2$	1:2	No	112	55.0	97.8	2.2
1.5% Au/TiO$_2$	1:2	Yes	112	88.3	98.1	1.9
1.5% Au/TiO$_2$	1:2	Yes	500	68.0	98.4	1.6

s:m = 500, T = 100 °C, P(O$_2$) = 10 bar.

1.1.1.2.Reaction with AuPd/MgO

The most selective catalyst for butyrolactone oxidation, 1% AuPd/MgO (1:1 mol), was tested for the oxidative esterification of 1,3-propanediol in a glass reactor at 60°C with 3 bar oxygen pressure substrate/base = 5:1 and substrate/metal = 500.

The oxidative esterification reaction proceeds via the monoester product, methyl-3-hydroxypropionate to which the highest selectivity is seen. The transformation of this product to the diester, dimethyl malonate is difficult[2]. By implementing the best catalyst and conditions for the oxidation of butyrolactone in the case of 1,3-propanediol the selectivity to the diester product, dimethyl malonate has been increased more than threefold with respect to the experiments carried out with Au/TiO$_2$ and literature work by Christensen *et al*[2]. The conversion is significantly lower under the more environmentally friendly conditions employed 10.6 % at 24 h compared with 94 % after 21 h. The temperature has been reduced from 100 to 60 °C and the oxygen pressure from 5 to 3 bar and the catalyst has been reduced by 4.46 times with s/m increased from 112 to 500.

Table 5-3 The oxidative esterification of 1,3-propanediol with AuPd/TiO_2

		Selectivity /%	
time /h	Conversion /%	propionate	malonate
2	5.5	85.8	14.2
5	8.0	67.9	13.6
24	10.6	80.6	18.6

s:m = 500, s:NaOMe = 5, T = 100 °C, P(O_2) = 3 bar.

The yields of both desired products, dimethyl succinate and dimethyl malonate is still low. A possible reason for this was thought to be preferential binding of the diester products to the catalyst surface. Thereby, these products act as a poison by blocking the active sites on the catalyst. However, when an experiment was carried out in which the stating reactant solution was doped with the observed quantities of the diester products no inhibition of the reaction was observed. The conversion and selectivities were consistent with the results under standard conditions.

5.3 Conclusions

The oxidative esterification of 1,4-butanediol was investigated using monometallic gold and palladium and bimetallic gold palladium nanoparticles supported on a range of supports. The major products were butyrolactone, which was subsequently oxidised to, methyl-4-hydroxybutyrate and the desired product dimethyl succinate. The yield of the desired product increased with increasing temperature, however, at iso conversion the selectivities to dimethyl succinate are the same. Therefore the selectivity to dimethyl succinate depends upon conversion, not temperature.

Base has been shown to have a large effect on the initial rate of the reaction. The rate increases with increasing base, however the yield of succinate is decreased when an excess of base is used. The addition of water to the reaction solvent detrimentally affects both the conversion of 1,4-butanediol and selectivity to dimethyl succinate.

The use of nano ceria support produced the most active catalysts but not the most selective. The highest selectivity to dimethyl succinate was seen when magnesium oxide was the catalyst support. It was found that the addition of palladium to gold significantly enhances the activity and selectivity to diemthyl succinate. An Au:Pd ratio of 1 to 1 molar supported on MgO gave the highest selectivity to dimethyl succinate. Both sol immobilisation and modified impregnation methods lead to the formation of small (~3 nm) bimetallic alloy particles which were observed to be needed for high conversions. The preparation of this catalyst by sol immobilisation leads to the formation of $Mg(OH)_2$ as the support material which is more active and selective than the MgO support prepared by the modified impregnation method.

The $AuPd/Mg(OH)_2$ catalyst was also selective to dimethyl succinate when 1,3-propendiol was oxidised in methanol. Christensen *et al.* achieved a selectivity of 5 % at 100 °C and 5 bar oxygen pressure. The conversion was 94 %. At the lower temperature of 60 °C and reduced pressure of 3 bar, a selectivity of 18.6 % was achieved at 10.6 % conversion.

This new $Mg(OH)_2$ support is superior in terms of selectivity to previous publications and fine tuning of this catalyst could lead to both higher conversions and selectivities to diester products. These products have important industrial applications and a source of these chemicals from bioderived routes is extremely desirable.

In the future, further work would be undertaken to to probe the nature of the deactivation of the 1% $AuPd/Mg(OH)_2$ catalyst prepared by sol immobilisation and to find a route to stabilise the bimetallic particles which are shown to sinter under reaction conditions.

The support material itself may be altered in the reaction process. More analysis into the nature of the reaction mechanism in the presence of the hydroxide support would lead to a better understanding of why this support is particularly selective, with a view to increasing the yields of the desired products and retard deactivation.

More forcing conditions such as higher temperatures and oxygen pressures have been shown to promote conversions and selectivity to sequential oxidation products in aqueous oxidations[13, 15]. Most of the reactions in this work were carried out under relatively mild conditions; increasing the severity of these conditions could lead to higher selectivities of dimethyl succinate and dimethyl malonate.

5.4 References

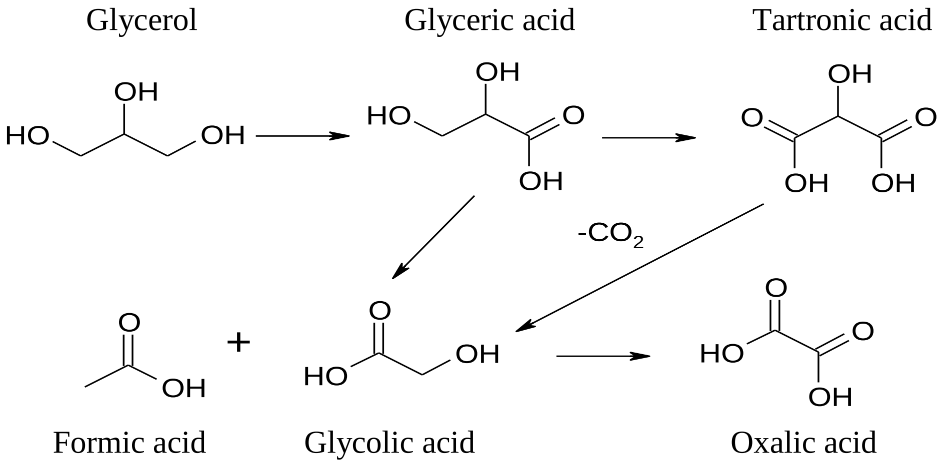
1. T. Miyazawa, Y. Kusunoki, K. Kunimori and K. Tomishige, *Journal of Catalysis*, 2006, **240**, 213-221.
2. E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, Editon edn., 2008, vol. 10, pp. 408-414.
3. T. Hayashi, T. Inagaki, N. Itayama and H. Baba, *Catalysis Today*, 2006, **117**, 210-213.
4. J. Huang, W.-L. Dai, H. Li and K. Fan, *Journal of Catalysis*, 2007, **252**, 69-76.
5. J. Huang, W.-L. Dai and K. Fan, *Journal of Catalysis*, 2009, **266**, 228-235.
6. , 5110954, 1992.
7. D. W. Hwang, P. Kashinathan, J. M. Lee, J. H. Lee, U. h. Lee, J.-S. Hwang, Y. K. Hwang and J.-S. Chang, *Green Chemistry*, **13**, 1672-1675.
8. W. Hou, N. A. Dehm and R. W. J. Scott, *Journal of Catalysis*, 2008, **253**, 22-27.
9. S. S. Lim, G. I. Park, J. S. Choi, I. K. Song and W. Y. Lee, *Catalysis Today*, 2002, **74**, 299-307.
10. N. Yamamoto, Y. Obora and Y. Ishii, *The Journal of Organic Chemistry*, 2011, **76**, 2937-2941.
11. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2003, **5**, 1329-1336.
12. F. Porta and L. Prati, *Journal of Catalysis*, 2004, **224**, 397-403.
13. N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chemistry*, 2009, **11**, 1209-1216.
14. A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896-7936.
15. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.

16. G. L. Brett, P. J. Miedziak, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, R. Tiruvalam, C. J. Kiely, D. W. Knight, S. H. Taylor, D. J. Morgan, A. F. Carley and G. J. Hutchings, *Catalysis Science & Technology*.
17. N. Dimitratos, F. Porta and L. Prati, *Applied Catalysis A: General*, 2005, **291**, 210-214.
18. S. Meenakshisundaram, E. Nowicka, P. J. Miedziak, G. L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor, D. W. Knight, D. Bethell and G. J. Hutchings, *Faraday Discussions*, 2010, **145**, 341-356.
19. P. Miedziak, M. Sankar, N. Dimitratos, J. A. Lopez-Sanchez, A. F. Carley, D. W. Knight, S. H. Taylor, C. J. Kiely and G. J. Hutchings, *Catalysis Today*, 2011, **164**, 315-319.
20. L. Prati and M. Rossi, *Journal of Catalysis*, 1998, **176**, 552-560.
21. O. Casanova, S. Iborra and A. Corma, *Journal of Catalysis*, 2009, **265**, 109-116.
22. Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, Editon edn., 2003, vol. 301, pp. 935-938.
23. Y. Diao, R. Yan, S. Zhang, P. Yang, Z. Li, L. Wang and H. Dong, *Journal of Molecular Catalysis A: Chemical*, 2009, **303**, 35-42.
24. K. Kaizuka, H. Miyamura and S. Kobayashi, *Journal of the American Chemical Society*, 2010, **132**, 15096-15098.
25. D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2007, **122**, 407-411.
26. B. N. Zope and R. J. Davis, *Green Chemistry*, 2011, **13**, 3484-3491.

6 Glycerol oxidation

6.1 Introduction

Glycerol is a bio-renewable feedstock that is a by-product of the manufacture of bio-diesel[1] and since there is an increasing drive towards greener fuels, the supply of glycerol as a sustainable raw material is anticipated to grow steadily. It was first shown by Rossi and Prati that supported gold nanoparticles are effective for alcohol oxidation in the presence of base[2, 3] to give glyceric acid as the primary product. The C3 products are the most desireable but undergo C-C cleavage during the reaction. The primary oxidation product is glyceric acid which is oxidised to tartronic acid, which itself undergoes decarboxylation to glycolic acid. The glycolic acid can be oxidised to oxalic acid. Another route to the C2 product glycolic acid is from the fragmentation of glyceric acid which also produces the C1 molecule formic acid. The reaction scheme is shown below in scheme 6-1



Scheme 6-1 The oxidation of glycerol

Since the first investigations a number of variables have been investigated, such as catalyst preparation method[4], support[5] and metal particle size[6]. It has been shown that under basic conditions bimetallic gold palladium catalysts are more active than monometallic gold and palladium catalysts, thereby demonstrating a synergistic effect. Catalysts prepared by the sol immobilisation method are more active than catalysts prepared by other methods.

It has been hypothesised that the role of base is as an initiator of the reaction, activating the glycerol molecule for dehydration of the hydroxyl group[7, 8]. It was shown that gold catalysts were inactive without the presence of base[9]. Recently advances have been made in the base free oxidation of glycerol. Platinum catalysts have been shown to be effective for this reaction[10, 11]. However, these platinum catalysts have been shown promote carbon-carbon cleavage resulting in formation of carbon dioxide and formic acid[9]. Prati *et al*. were the first to demonstrate that gold based catalysts supported on carbon were active for glycerol oxidation in base free conditions[12].

6.2 Results and discussion

6.2.1 The effect of palladium addition to a gold catalysts for glycerol oxidation in basic conditions

A 1% Au/TiO_2 and AuPd/TiO_2 (1:1 mol) ware prepared by sol immobilisation and tested for the oxidation of glycerol. These reactions were carried out in a glass reactor with 3 bar O_2 pressure at 60 °C and 2 equivalents of NaOH (mol/mol). The substrate:metal was 1000.

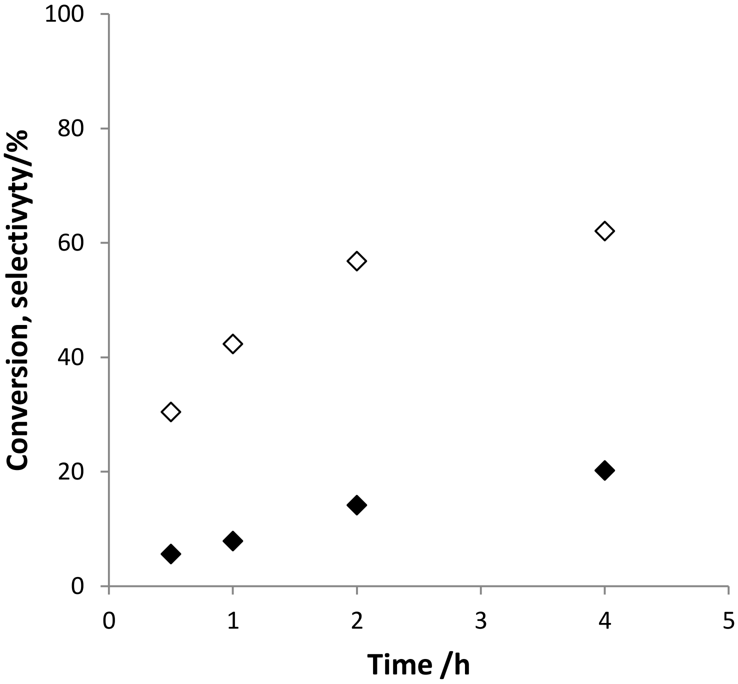


Figure 6-2 The conversion of glycerol with Au/TiO_2 (◆) and AuPd/TiO_2 (◇).

The addition of the palladium catalyst has increased the conversion of glycerol threefold (figure 6-2). This effect has been observed and discussed in literature studies[6, 13]. The selectivity to glyceric acid had also been increased (table -1).

Table 6-1 The oxidation of glycerol with Au/TiO_2 and AuPd/TiO_2

catalyst	time /h	conversion /%	selectivity /%					TOF /h^{-1}
			glycerate	oxalate	tartronate	glycolate	formate	
Au/TiO_2 dry 110°C	0.5	5.6	45.0	4.9	16.3	20.5	13.3	112.3
		7.9	39.7	4.4	13.5	23.7	18.6	78.8
		14.2	41.3	4.9	15.6	22.1	16.1	70.7
		20.2	44.5	5.6	18.9	29.0	1.9	50.5
AuPd/TiO_2 dry 110°C	0.5	30.5	52.2	3.3	27.5	11.6	5.4	608.7
		42.3	48.8	3.1	32.5	9.6	6.0	423.1
		56.8	46.8	3.4	33.2	10.6	6.0	283.9
		62.1	45.6	3.9	37.0	9.1	4.4	155.1

Reaction conditions: Gly (0.3 M), s:m=1000, s:NaOH=2, T=60 °C, P(O_2)=3bar, t=3h

6.2.2 Glycerol oxidation in base free conditions with gold palladium catalysts

In order to make the reaction more environmentally friendly, the possibility of oxidising glycerol without additional base was investigated. The removal of this aqueous base from the reaction significantly decreases the waste material and ensures that the catalytic oxidation is completed in a greener manner. The same titania supported gold-palladium catalyst was tested under the same reaction conditions but without base.

Table 6-2 The comparison of titania supported catalyst under basic and base free conditions

catalyst	base (NaOH)	time /h	conversion /%	Selectivity /%				
				glyceric acid	oxalic acid	tartronic acid	glycolic acid	formic acid
AuPd/TiO_2	2 eq.	3	59.9	46.2	3.5	36.0	9.0	5.3
AuPd/TiO_2	none	3	2.5	67.0	0.0	0.8	3.6	28.6

Reaction conditions: Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=3h

The removal of base from the glycerol oxidation reaction with AuPd/TiO_2 led to the expected reduction in glycerol conversion (table 6-2). The conversion fell from 59.9 % to a very low 2.5 %. It has been generally accepted that the role of the base in the oxidation of glycerol with gold base catalysts is as an initiator. The rate limiting step in the reaction is the removal of H^+ from the hydroxyl group[14], in the presence of base the step is easier to overcome[9] therefore promoting the oxidation of glycerol. There is also an effect on the selectivity of the reaction. The reaction without base produces a higher selectivity to the C1 product formic acid at the low conversion. The same effect has been seen by Prati *et al.*, a gold on carbon catalyst was tested in basic conditions at 90 °C[8] and in base free conditions at 100 °C[12]. In base free conditions after 2 h the conversion of glycerol was 3 %, the selectivity to glyceric acid was 39 % and the selectivity to C1 products was 51 %. In the presence of base the conversions are higher, at 50 % conversion, with the same Au/C catalyst, the selectivity to glyceric acid with 1 equivalent of base is 66 %, 2 is 57% and 4 equivalents of base yields a selectivity of 70 % despite the increased conversion. Therefore we can determine that the presence of base disrupts C-C cleavage during the reaction giving higher selectivities to C3 products.

6.2.2.1 Effect of support

Carbon and titania supported gold-palladium catalysts have been shown to be highly active for the oxidation of glycerol in basic conditions[5, 15]. Prati *et al.* have recently used a a carbon support for the base free oxidation of glycerol[12]. Three supported bimetallic Au-Pd catalysts were tested for the base free oxidation of glycerol. The reaction conditions were, 0.3 M glycerol at 100 °C, with oxygen pressure of 3 bar for 3 h. The metals were in a 1:1 wt ratio.

As can be seen is figure 6-3, the magnesium oxide support shows a considerable increase in activity compared with titania and carbon supports. The selectivity to glyceric acid is comparable for all three catalysts.

The effect of support on the oxidation of glycerol in basic conditions has been studied in detail[5, 9, 16]. Carbon supports have been shown to be more active than titania and iron oxide supports[5]. Monometallic Au, Pd and Pt supported on activated carbon have been shown to be active for glycerol oxidation in neutral conditions[12]. TiO_2, $MgAl_2O_4$ and H-mordenite supported gold catalysts also showed activity for glycerol oxidation in base free conditions. The addition of palladium to the gold catalyst was shown to increase this activity. This synergistic effect has been seen in the oxidation of glycerol in basic conditions[6, 13, 17].

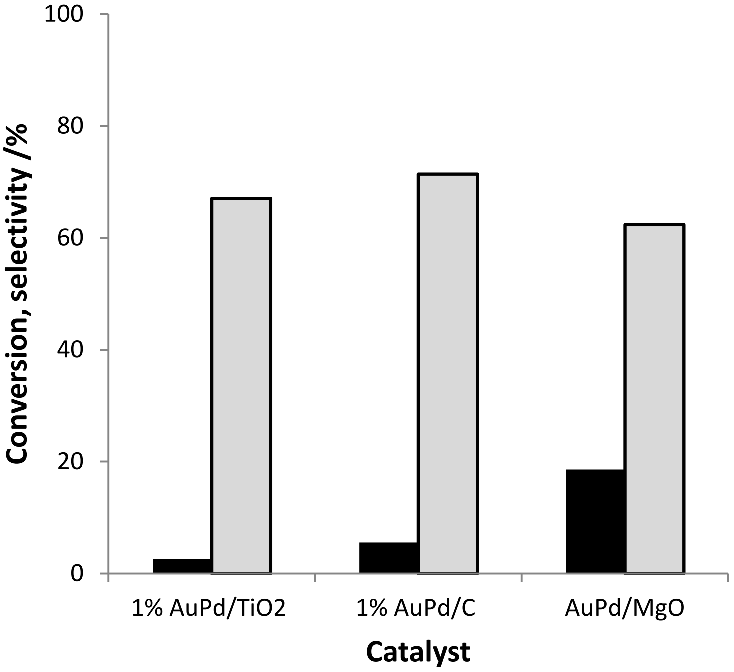


Figure 6-3 The effect of support on glycerol conversion (■) and selectivity to the major product glyceric acid (□). Reaction conditions: Gly (0.3 M), s:m=1000, s:NaOH=0, T=100 °C, $P(O_2)$=3bar, t=3h

Bimetallic AuPd catalysts in a 1:1 wt ratio were prepared by sol immobilisation. This AuPd ratio has been shown to be active under basic conditions[5]. Activated carbon, Titania and magnesium oxide were chosen as the support materials. The titania support shows the lowest activity at 2.6 % conversion, the carbon support was more active giving a conversion of 5.5 %. By far the most active catalyst was the AuPd/MgO catalyst at 18.6 %. The selectivities to glyceric acid were 67.0, 71.3 and 63.3 % respectively. The selectivity for the MgO supported catalyst is lower than that of the other catalysts, however the conversion is considerably higher. The selectivity to glyceric acid decreases with increasing conversion as it is oxidised to tartronic acid, glycolic, oxalic and formic acid. What is interesting when comparing these catalysts is the selectivity to the C1 product formic acid. The titania and carbon supports show selectivities to formic acid of 28.5 and 26.3 % respectively, however the selectivity to formic acid for the MgO supported catalyst is a relatively low 10.4 % Carbon supports have been shown previously to promote the formation of C1 products[5], it has been suggested that this is due to the acidic sites on the catalyst surface[18].

XRD analysis confirmed that the MgO support is hydrolysed during the sol immobilisation preparation method. The resulting support is in fact magnesium hydroxide, this is shown in chapter 3. The presence of hydroxyl groups on other supports has been shown to promote glycerol oxidation in base free conditions[10, 11]. Multiwalled carbon nanotube supports have been modified with HNO_3 to produce –OH groups on the surface of the support. This treatment has been reported to enhance the activity of supported platinum catalysts for base free glycerol oxidation. The conversion of glycerol at 6 h was increased from 48.2 to 64.6 % at 60 °C with the support modification. The substrate metal ratio was 445 and flowing oxygen was used at 150 mL/min. Again with this carbon support the selectivity to C1 products was higher than with the MgOH support at 17.8 %[10, 11]. This treatment has also been shown to promote glycerol oxidation under basic conditions[18], NaOH/glycerol = 2.

6.2.2.2 Effect of temperature with MgO supported catalysts

The AuPd/MgO (1:1 wt) prepared by sol immobilisation was tested at different temperatures under base free conditions with substrate:metal ratio =1000. The results are shown below in figure 6-4.

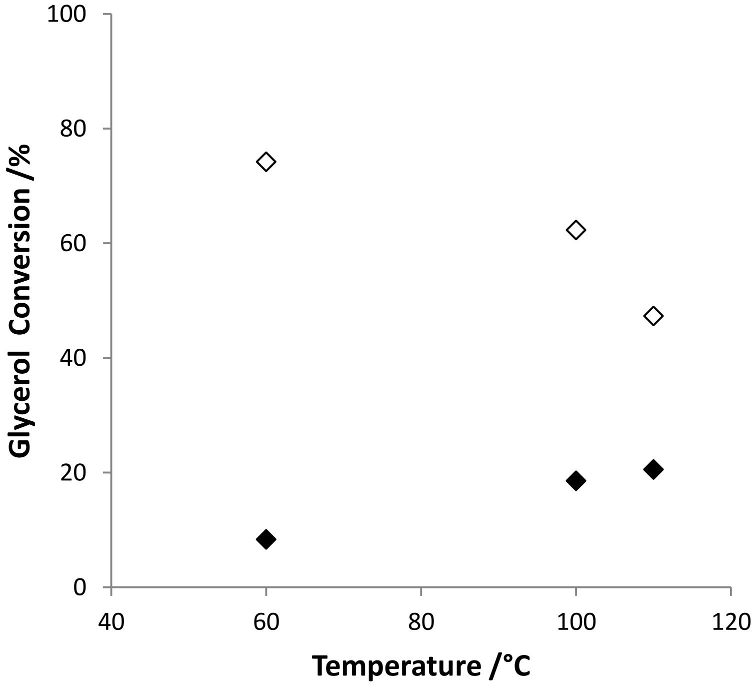


Figure 6-4 The effect of Temperature on glycerol conversion (◆) and selectivity to glyceric acid (◇). Reaction conditions: Gly (0.3 M), s:m=1000, s:NaOH=0, $P(O_2)$=3bar, t=3h.

As expected the conversion increases, and selectivity to glyceric acid decreases with increasing temperature[8]. Glyceric acid is oxidised at higher temperatures to give increased selectivities to tartronic acid, glycolic acid, oxalic acid and formic acid.

Glycerol oxidation reactions in basic conditions are generally reported at 60 °C or below[5, 19, 20]. The first literature report of base free glycerol oxidation with gold catalysts was by Prati *et al.*[12] The catalytic tests were conducted at 100 °C. The monometallic Au, Pd and Pt catalysts used in this publication were reported to be inactive at 50 °C. Monometallic Pt catalysts have been shown to be active in base free conditions, however the selectivity to glyceric acid is low and selectivities to undesirable C1 products is high[9]

The effect of temperature on base free oxidation of glycerol was investigated using a 1 % AuPd/MgO (1:1 wt) catalyst. When the temperature is increased from 60 to 110 °C the conversion increases from 8.4 % to 20.6 %. The selectivity to glyceric acid decreases from 74.2 % to 47.3 %. At higher temperatures the glyceric acid is oxidised mostly to tartronic acid, which is subsequently oxidised to form glycolic, oxalic acid and formic acid. This is in agreement with other literature[8]. In this case the highest increase in selectivity is for glycolic (4 to 12 %) and formic acid (8 to 12 %). Prati *et al.* reported a conversion of 12 % with a AuPd/AC (6:4 mol) carbon catalyst, at s/m =500[12]. The bimetallic AuPd/$Mg(OH)_2$ supported catalyst is far more active than the activated carbon supported catalyst, giving a higher conversion of 18.6 % with half the catalyst amount.

6.2.2.3 The effect of the Au:Pd ratio

Gold-palladium catalysts are extremely active for glycerol oxidation in basic media. As demonstrated above there is a synergistic effect when the two metals are alloyed. Carbon supported catalysts have been shown to be more active than titania supported catalysts[5]. Prati *et al.*[12] recently demonstrated that both monometallic (Au, Pd, Pt) and bimetallic (AuPd and AuPt) carbon supported catalysts were active for the oxidation of glycerol under base free conditions at 100°C. In light of the reported results, two AuPd/C catalysts were prepared by sol immobilisation. The Au:Pd ratios were 3:1 and 1:3. The reaction temperature was 60°C and s:m =500.

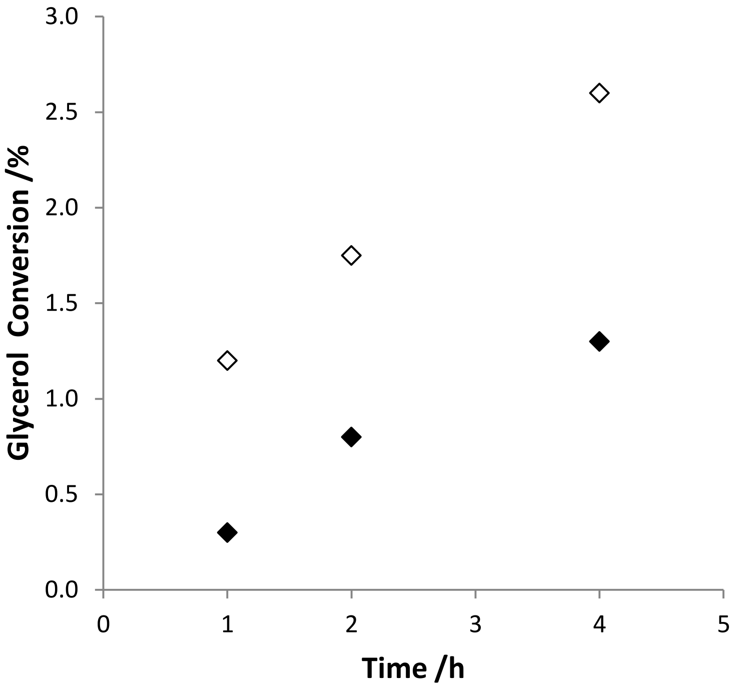


Figure 6-5 Glycerol conversion with 1% AuPd/C (3:1 molar) (◆) and 1%AuPd/C (1:3 molar) (◇). Reaction conditions: Gly (0.3 M), s:m=1000, s:NaOH=0, T=100 °C, P(O_2)=3bar, t=3h.

The conversions of glycerol are very low, however, there is a clear trend (figure 6-5). The palladium rich catalyst shows higher conversion than the gold rich catalyst. At 1 h the TOFs are 150 and 600 for the 3:1 and 1:3 Au:Pd ratios respectively.

1.1.1.3.Effect of Preparation method for AuPd/C

Two AuPd/C (1 to 3 and 3 to 1 molar) catalysts were prepared by impregnation and tested under base free conditions. The reaction temperature was 60 °C and s:m =1000. The catalysts prepared by impregnation were not active for the base free oxidation of glycerol at 60 °C as shown below in figure 6-6. The reactions were repeated at 110 °C, again there was no conversion of glycerol with the catalysts prepared by impregnation. With regards to the sol immobilisation catalysts, the more gold rich catalyst shows 100 % selectivity to C3 products glyceric and tartronic acid. The palladium rich catalyst shows a higher selectivity to glyceric acid but the selectivity to tartronic acid is diminished giving rise to increased concentrations of glycolic and formic acid, no oxalic acid was detected.

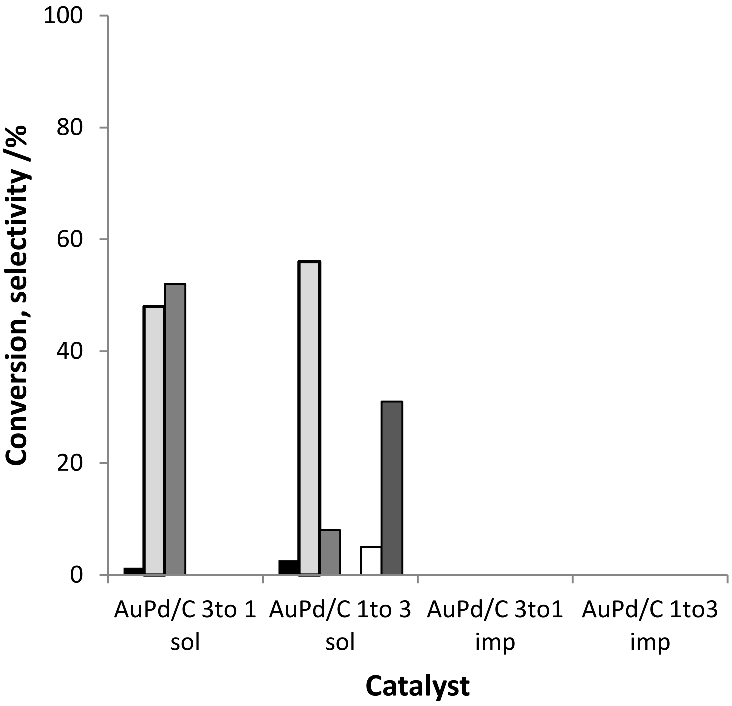


Figure 6-6 The conversion of glycerol (■) and selectivities to glyceric acid (■), tartronic acid (■), glycolic acid (□) and formic acid (■) with AuPd/C catalysts prepared by sol immobilisation and impregnation. Gly (0.3 M), s:m=1000, s:NaOH=0, T=100 °C, P(O_2)=3bar, t=3h.

6.2.2.4 Effect of catalyst support with AuPd ratio 1:3

Three supported bimetallic Au-Pd catalysts were tested for the base free oxidation of glycerol. The reaction conditions were, 0.3 M glycerol at 60 °C, with oxygen pressure of 3 bar for 4 h. The metals were in a 1:3 mol ratio and the substrate/metal ratio was 1000.

Again the magnesium oxide supported catalyst shows the both highest conversion of glycerol and highest selectivity to glyceric acid under base free conditions (figure 6-7). The other oxide support, ZnO, shows a higher conversion than the carbon supported catalyst however the selectivity to glyceric acid is just over half of the other catalysts tested, and the selectivity to formic acid is much greater.

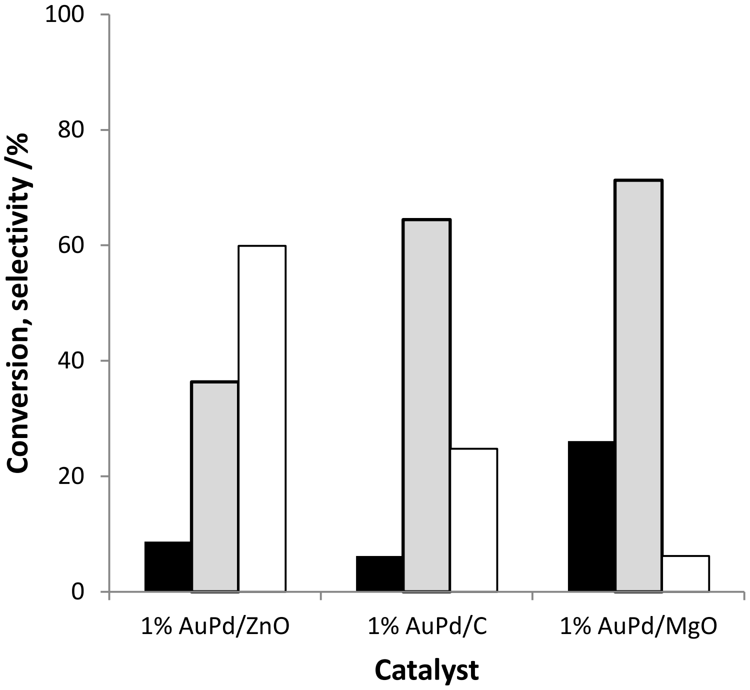


Figure 6-7 The effect of support on glycerol conversion (■) and selectivity to the major products glyceric acid (▨), and formic acid (□). Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=4h.

6.2.2.5 Effect of calcination

The 1% AuPd/MgO (1:3 molar) catalyst was calcined, following drying in an oven at 110 °C, under static air at 150 and 200 °C for 3 h with a ramp rate of 20 °C/min. These calcined catalysts were then tested. The reaction conditions were, 0.3 M glycerol at 60 °C, with oxygen pressure of 3 bar for 4 h. The metals were in a 1:3 mol ratio and the substrate/metal ratio was 1000, the results are shown below in figure 6-8.

The calcination of the sol immobilisation catalysts at both temperatures lead to an increase in activity of the catalyst, more so for the calcinations at 150 °C. The selectivity to glyceric acid has also been enhanced with the calcinations at 200 °C yielding the highest selectivity.

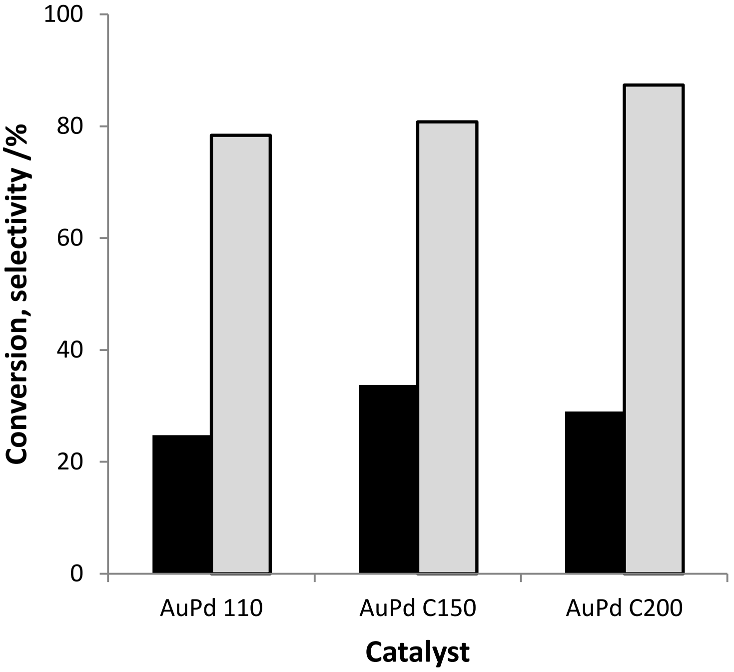


Figure 6-8 Effect of calcination. Conversion (■) and selectivity to glyceric acid (□). Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=4h.

The catalysts that have been calcined at 150 and 200 °C show an increase in activity and selectivity. The increase in activity is surprising when particle sizes of the metals are considered. The increase in the average particle size corresponds to a decrease in metal surface area, therefore the conversion of glycerol should decrease. It is possible that another effect is causing this phenomenon – the removal of the PVA ligand used in the sol immobilisation preparation, or possible changes to the surface morphology of the $Mg(OH)_2$ support on heating. The removal of the PVA ligand by washing has been shown to promote the oxidation of glycerol with Au/TiO_2 in basic conditions[21]. In terms of selectivity, larger particle sizes have previously been demonstrated to enhance selectivity to glyceric acid[6].

6.2.3 Gold platinum catalysts

6.2.3.1 The effect of metal combination with carbon supported catalysts

Two AuPt/C catalysts, 1:1 wt and 1:3 molar, were prepared by sol immobilisation and tested for the oxidation of glycerol in base free conditions at 60 °C. The s/m was 500.

The replacement of palladium with platinum on the carbon supported catalyst has lead to a vast increase in conversion (figure 6-9). The selectivity to glyceric acid has also been enhanced, whereas the undesirable C1 product, formic acid, has been reduced. Again, the 1:3 molar ratio is more active that the 1:1 ratio for the AuPt catalysts.

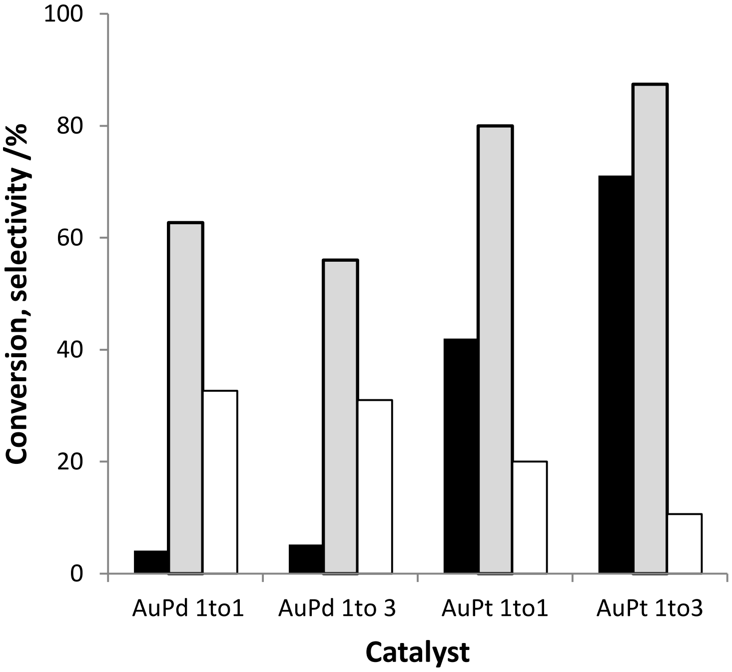


Figure 6-9 The effect of Au, Pd and Pt ratios on glycerol conversion (■) and selectivity to major products glyceric (▨) and formic acid (□) with carbon supported catalysts. Gly (0.3 M), s:m=500, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=4h.

6.2.3.2 Effect of Au-Pt ratio with MgO supported catalysts

A 1%Au/Pt/MgO (1:1 wt) catalyst was prepared and tested under the same conditions (s/m=1000) at 60 °C.

The AuPt catalysts show a significant enhancement in activity when compared to the AuPd catalysts (figure 6-10). The selectivity to glyceric acid after 4 h is comparable to that of the palladium catalysts despite the increased conversion. When comparing the Au:Pt ratio, again the catalyst with more platinum shows higher activity than the 1:1 AuPt catalyst.

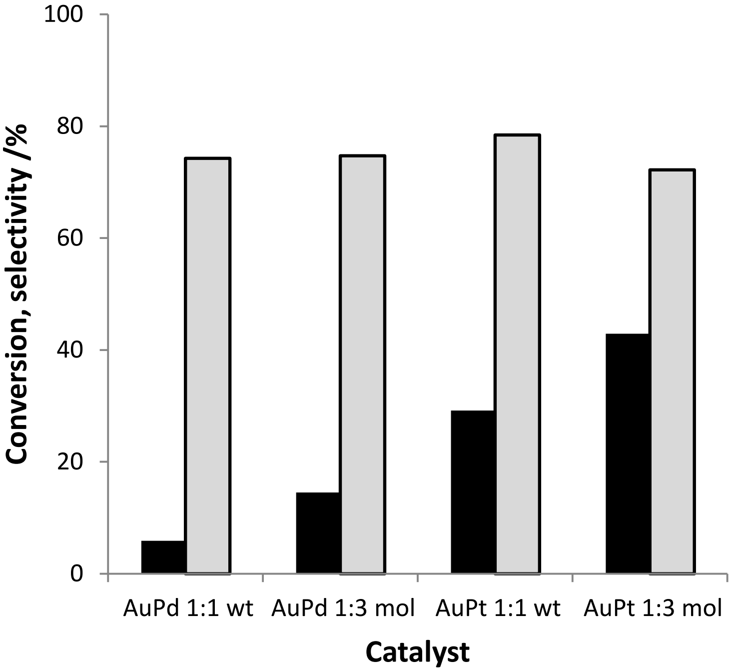


Figure 6-10 The effect of changing the metal combination on glycerol conversion (■) and selectivity to glyceric acid (□).Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=4h.

The Au:Pd ratio was investigated for the carbon supported catalyst. It was found that the more gold rich catalyst was less active than the palladium rich catalyst. When the molar percentage of palladium in the catalyst increases from 25 to 75 % the conversion doubles from 1.3 to 2.6 %. In the case of $Mg(OH)_2$ supported catalysts when the palladium amount is increased from 50 to 100 % the conversion of glycerol increases by a factor of 1.7 from 8.2 to 14.5 %. The same trend has been seen for the solvent free oxidation of benzyl alcohol by Enache *et al.*, the palladium rich AuPd bimetallic catalysts were shown to be the most active[22] when compared with gold rich monometallic catalysts supported on titania.

The gold to platinum ratio was also investigated. For carbon supported catalysts tested with s/m 500 the increasing of the platinum content from 50 mol % to 75 % lead to an increase in conversion of 1.7 times from 42.0 to 71.1 %. The selectivity to glyceric acid is also enhanced with an increase of 7 %. The same effect of conversion is seen when the metals are supported on $Mg(OH)_2$, increasing from 29.2 to 49.2 %. However, the selectivity to glyceric acid in this case is reduced by 6 %, due to the over oxidation to formic acid, showing an increase of 4.5 %.

6.2.3.3 Effect of temperature on glycerol oxidation with AuPt/MgO 1:3 mol

The AuPt/MgO (1:3 mol) catalyst is very active for the oxidation of glycerol in base free conditions at 60 °C. Experiments were carried out to determine if this catalyst is active at lower temperatures. The s/m was 1000. The results are shown below in figure 6-11.

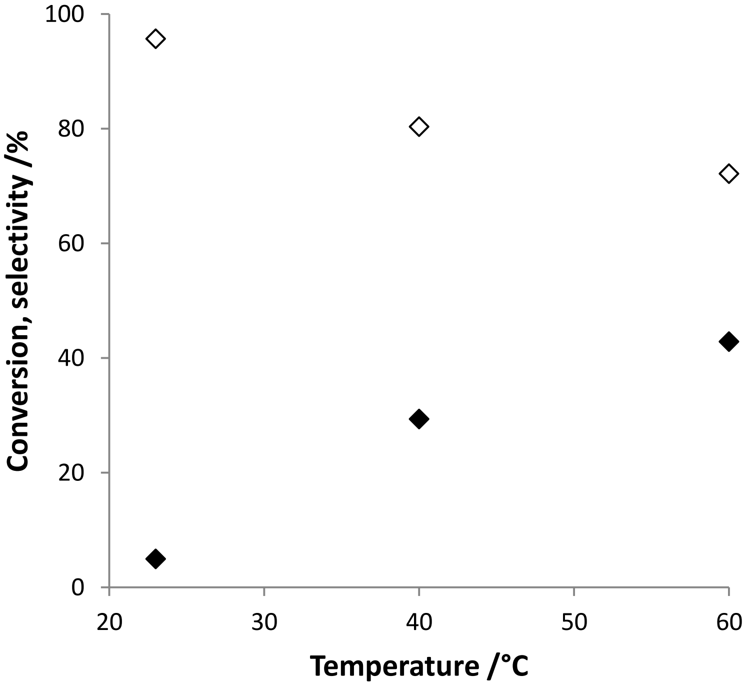


Figure 6-11 The effect of temperature on conversion of glycerol (◆) and selectivity to glyceric acid (◇) with AuPt/MgO (1:3 mol). Gly (0.3 M), s:m=1000, s:NaOH=0, $P(O_2)$=3bar, t=4h.

The catalyst shows some conversion (5.0 %) at ambient temperature, in this case 23 °C after 4 h. The selectivity to glyceric acid is incredibly high at 95.7 %. As expected the conversion increases with increasing temperature. The selectivity to glyceric acid decreases with temperature as observed with the AuPd catalysts.

The most active AuPt/$Mg(OH)_2$ (1:3 mol) catalyst was shown to be active at 60 °C, giving a glycerol conversion of 42.9 % after 4 h. The reaction temperature was reduced to 40 and 23 °C. The catalyst was active at both temperatures with conversions of 29.4 and 5.0 % respectively. As before, the selectivities to glyceric acid decreased with increasing temperature, from 95 % at 23 °C to 80.4 % at 40 °C to 72.2 % at 60 °C. Prati *et al.* reported AuPt nanoparticles supported on activated carbon and H-mordenite in a ratio of 6:4 molar.

The substrate metal ratio was 500, half that what has been used in the $Mg(OH)_2$ supported experiments here. The conversion at 100 °C of the carbon and H-mordenite supported catalysts were 58 and 70 % respectively.

Both AuPd and AuPt (1:3 molar) catalysts show activity at low temperatures in base free conditions, after 24 h at 23 °C the conversions of glycerol are 29.7 and 42.5 % respectively. This is the first report of the base free oxidation of glycerol at ambient temperatures.

6.2.3.4 Time online data for AuPt/MgO (1:1 mol)

A reaction was completed with AuPt/MgO at 60 °C for 6 h. The concentration of glycerol was 0.3 M, oxygen pressure was 3 bar and the substrate to metal ratio was reduced to 500 to achieve a high conversion.

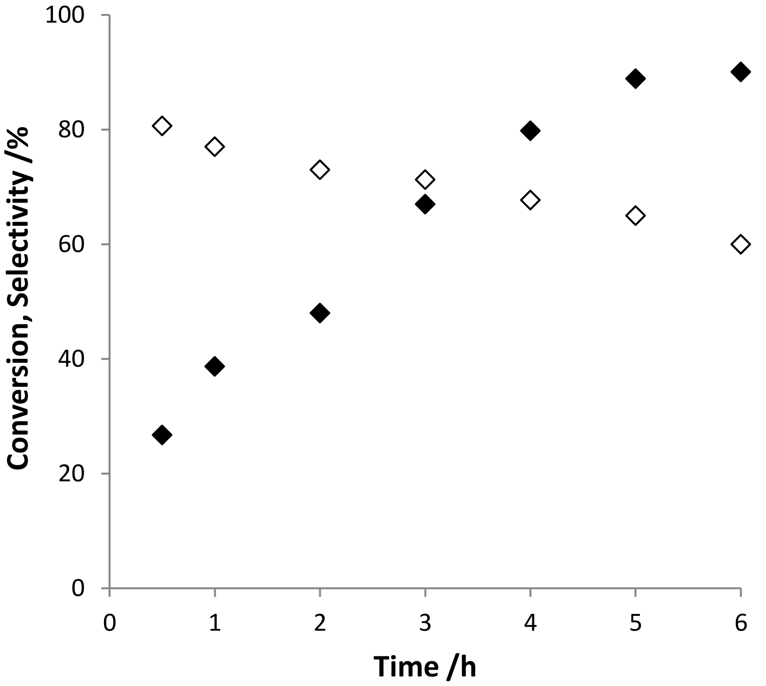


Figure 6-12 Time online data for AuPt/MgO (1:1). The conversion of glycerol (◆) and selectivity to glyceric acid (◇). Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, $P(O_2)$=3bar, t=4h.

The conversion of glycerol increases over time to a maximum of 90 % after 6 h, the rate of reaction is seen to decrease over time (figure 6-12). The selectivity to the desired C3 product glyceric acid decreases over time with increasing conversion. Selectivities to tartronic, oxalic and glycolic acids are increased with the oxidation of glyceric acid.

6.2.3.5 Physical mixtures

Au/MgO, Pd/MgO and Pt/MgO were synthesised by the sol immobilisation method. They were combined so that one mixed catalyst had the equivalent metal amounts of the AuPd/MgO (1:3 mol) catalyst and AuPt/MgO catalyst (1:3 mol). This experiment was undertaken to establish whether the synergistic effect is still in operation if the catalysts are not formed as alloys on a single catalyst. The reaction was carried out at 60 °C with substrate/metal=1000.

The physically mixed catalysts show some activity (figure 6-13). However, the conversions of the mixture catalysts are far less than the catalysts prepared in a single alloyed phase in the sol immobilisation preparation.

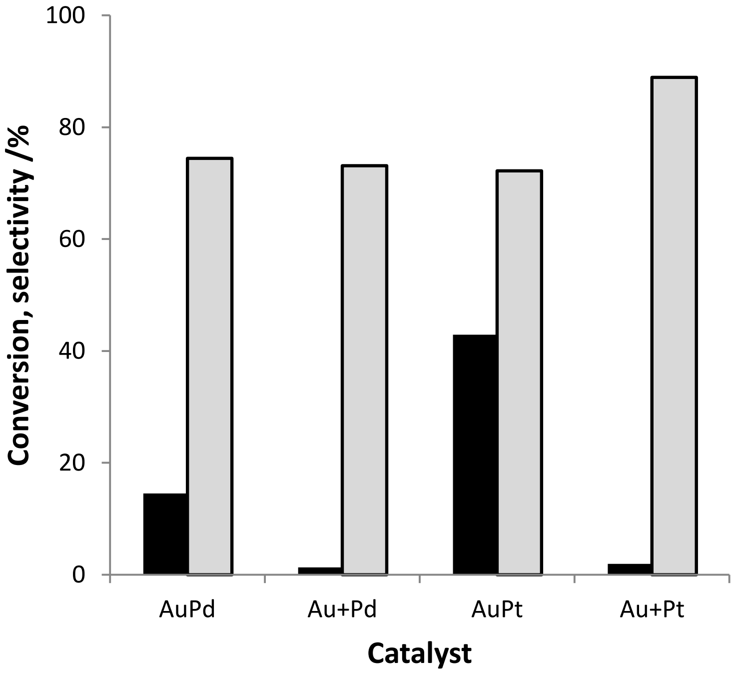


Figure 6-13 A comparison of physically mixed catalysts with bimetallic catalysts prepared in a single phase. Glycerol conversion (■) and selectivity to glyceric acid (□). Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, $P(O_2)$=3bar, t=4h.

6.2.3.6 Catalyst stability

6.2.3.6.1 Filtration experiments

To determine whether the AuPd/MgO catalyst was acting purely as a heterogeneous catalyst a filtration experiment was carried out. The reaction was conducted for 2 h, after which the catalyst was filtered out and the remaining reactant solution was reacted for another 2 h without catalyst. The results are shown in figure 6-14

After the catalyst was removed very little glycerol was oxidised. This indicates that no homogeneous reaction is in operation and implies that no gold or palladium has leached from the catalyst.

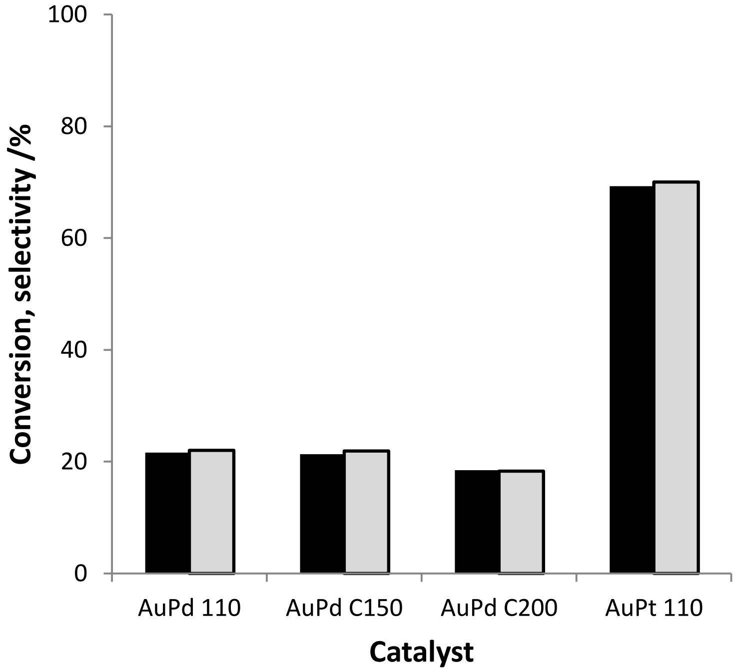


Figure 6-14 The conversion of glycerol at 2 h (■) and 4 h (□) in filtration tests with $Mg(OH)_2$ supported catalysts. Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, $P(O_2)$=3bar, t=2,4h.

6.2.3.6.2 The reuse of AuPt/MgO (1:3 mol)

The AuPt/MgO was tested under base free conditions for 30 min at 60 °C. The catalyst was then recovered and tested under the same conditions again. This was repeated so that the catalyst was tested 3 times to test the reusability of the catalyst. The substrate/metal was 1000.

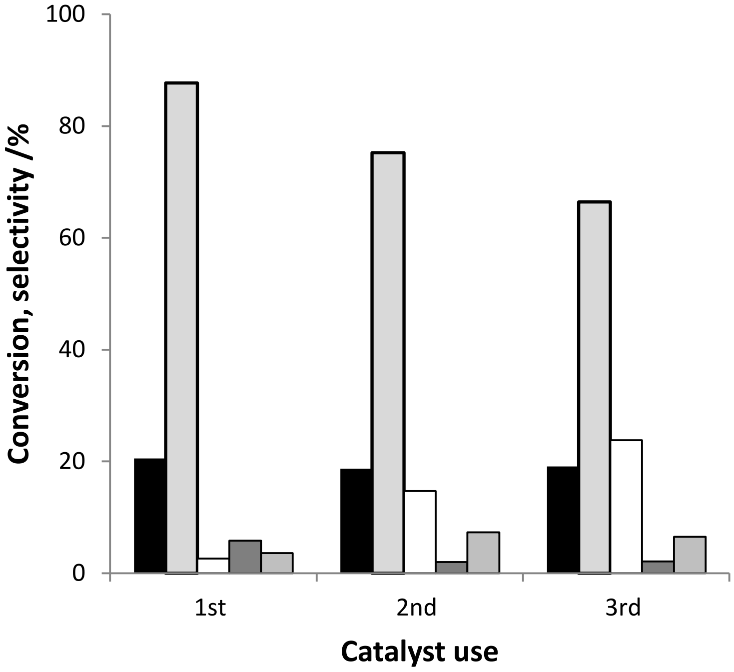


Figure 6-15 The effect of previous uses on the conversion of glycerol (■) and selectivities to glyceric (■), tartronic (□), glycolic (■) and formic acid. (■). Gly (0.3 M), s:m=1000, s:NaOH=0, T=60 °C, P(O_2)=3bar, t=0.5 h.

The conversion was not seen to diminish from the 1st use to the 3rd. The selectivity to glyceric acid was reduced every time the catalyst was used (87.5, 75.2 and 66.4 %), yielding higher selectivities of tartronic acid (from 2.6 fresh to 14.7 on 2nd use to 23.8% on 3rd use). The selectivity to formic acid has also increased by a lesser extent from 3.6 to 6.5 %.

6.2.3.7 Reactions at ambient temperature

6.2.3.7.1 The comparison of AuPd and AuPt catalysts

The oxidation of glycerol was carried out at room temperature (23°C) with s:m=500. The results are shown below in figure 6-16

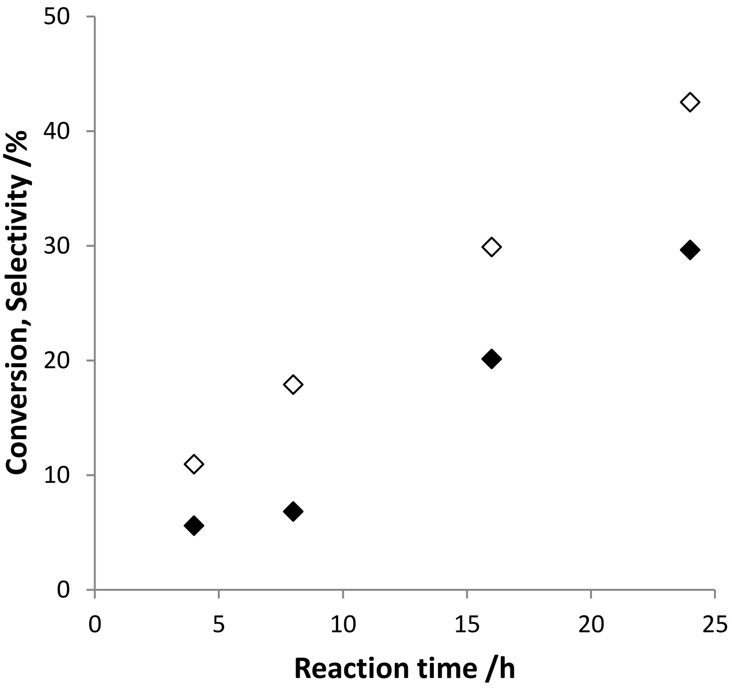


Figure 6-16 Glycerol conversion with 1:3 mol AuPd/MgO (◆) and AuPt/MgO (◇). Gly (0.3 M), s:m=500, s:NaOH=0, T=25 °C, P(O_2)=3 bar, t=24h.

6.2.3.7.2 Reuseability at ambient temperature

The AuPt/MgO (1:3 mol) catalysts was tested for reusability at room temperature 23°C with s/m = 500.

Table 6-3 The reusability of AuPt/MgO (sol) at ambient temperature

			selectivity /%				
catalyst	time /h	conversion /%	glyceric acid	oxalic acid	tartronic acid	glycolic acid	formic acid
AuPt/MgO (1:3 mol) fresh	24	41.5	85.1	0.2	3.8	4.8	6.1
AuPt/MgO (1:3 mol) used	24	39.1	83.1	0.3	5.7	4.4	4.7

Gly (0.3 M), s:m=500, s:NaOH=0, T=25 °C, P(O_2)=3 bar, t=24h.

As with the reactions at 60 °C, the reuse of the catalyst leads to the selectivity to glyceric acid is reduced and tartronic is increased (table 6-3). Both the conversion and selectivity to glyceric acid saw a decrease of 2 %. Once again the selectivity to tartronic acid increased on reuse. However this difference is in region of experimental error and is therefore not conclusively proven.

6.2.4 Atomic absorption spectroscopy

Two reactions were conducted with 1% AuPd/MgO and AuPt/MgO (1:3 mol) with substrate/metal 500. The reaction was carried out at 60 °C for 4h. The resulting solution was then tested for trace amounts of metals with atomic absorption spectroscopy. No gold, platinum or palladium metal was detected in this solution indicating that no metal had leached from the surface. Magnesium was detected in the amount of 77 ppm which signifies that 1.1 % of the MgO support had dissolved into the reaction medium. In order to establish whether this small amount of $Mg(OH)_2$ acts as an initiator to the reaction further experiments were carried out. 154 ppm of sodium hydroxide was added at the start of a reaction carried out under the same conditions. No significant increase in conversion of glycerol was seen.

Conclusions and future work

The use of magnesium hydroxide as a support is observed to enhance the selective oxidation of glycerol under base-free conditions using Au-Pd and Au-Pt catalysts that are prepared using a sol-immobilisation preparation method. The alloying of gold with platinum leads to a catalyst which is significantly more active than gold alloyed with palladium under base free conditions.

It was concluded that the surface composition of the nanoparticles requires a contribution from gold, however a larger fraction of the alloying metal, Pt or Pd, is required to observe high activity. Calcination of the sol-immobilised catalysts up to 200 ^{o}C leads to an increase in the activity with no apparent loss of stability, possibly due to the removal of the PVA ligands used in the preparation. This work is the first reported base free oxidation at low temperature. After 24 h a considerable conversion of glycerol is achieved with high selectivities to glyceric acid.

Further work on the optimisation of the catalyst could be undertaken. The $Mg(OH)_2$ support is not fully stable under reaction conditions as approximately 1 % of the support dissolves after 4 h at 60 °C. It may be possible to synthesise this catalyst by the alternative

THPC/NaOH method used in chapter 2 which has been shown to synthesise active catalysts on a number of oxide supports[23]. Other stabilising agents are also available such as PVP and citrate which has been reported to produce catalysts which give higher initial rates of glycerol conversion[15].

As the reaction only needs a small contribution from gold, it is possible that core shell metallic structures may provide an alternative to the low gold concentrated random homogeneous alloy structures. It is possible to produce metal particles with a gold rich core and palladium or platinum rich shell by a two step immobilisation preparation[24]. In this work metal structures with a palladium rich shell and gold rich core were shown to be particularly active for the oxidation of benzyl alcohol when supported on carbon and titania.

The removal of PVA from catalysts prepared by sol immobilisation by washing has been shown to increase activity of these catalysts for a number of oxidation reactions[21], it may be possible to apply this technique to the $Mg(OH)_2$ catalysts used in this work.

6.3 References

1. G. W. Huber and A. Corma, *Angewandte Chemie International Edition*, 2007, **46**, 7184-7201.
2. L. Prati and M. Rossi, *Journal of Catalysis*, 1998, **176**, 552-560.
3. S. Biella, L. Prati and M. Rossi, *Journal of Catalysis*, 2002, **206**, 242-247.
4. W. C. Ketchie, M. Murayama and R. J. Davis, *Topics in Catalysis*, 2007, **44**, 307-317.
5. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.
6. N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati and A. Villa, *Catalysis Letters*, 2006, **108**, 147-153.
7. S. Demirel-Gülen, M. Lucas and P. Claus, *Catalysis Today*, 2005, **102-103**, 166-172.
8. F. Porta and L. Prati, *Journal of Catalysis*, 2004, **224**, 397-403.
9. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2003, **5**, 1329-1336.

10. J. Gao, D. Liang, P. Chen, Z. Hou and X. Zheng, *Catalysis Letters*, 2009, **130**, 185-191.
11. D. Liang, J. Gao, J. Wang, P. Chen, Z. Hou and X. Zheng, *Catalysis Communications*, 2009, **10**, 1586-1590.
12. A. Villa, G. M. Veith and L. Prati, *Angewandte Chemie International Edition*, 2010, **49**, 4499-4502.
13. W. Hou, N. A. Dehm and R. W. J. Scott, *Journal of Catalysis*, 2008, **253**, 22-27.
14. J. H. J. Kluytmans, A. P. Markusse, B. F. M. Kuster, G. B. Marin and J. C. Schouten, *Catalysis Today*, 2000, **57**, 143-155.
15. N. Dimitratos, F. Porta and L. Prati, *Applied Catalysis A: General*, 2005, **291**, 210-214.
16. A. Tsuji, K. T. V. Rao, S. Nishimura, A. Takagaki and K. Ebitani, *ChemSusChem*, **4**, 542-548.
17. C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, *Catalysis Today*, 2005, **102-103**, 203-212.
18. E. G. Rodrigues, M. F. R. Pereira, X. Chen, J. J. Delgado and J. J. M. Órfão, *Journal of Catalysis*, **281**, 119-127.
19. A. Villa, C. Campione and L. Prati, *Catalysis Letters*, 2007, **115**, 133-136.
20. L. Prati, A. Villa, F. Porta, D. Wang and D. Su, *Catalysis Today*, 2007, **122**, 386-390.
21. J. A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G. L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R. L. Jenkins, A. F. Carley, D. Knight, C. J. Kiely and G. J. Hutchings, *Nat Chem*, 2011, **3**, 551-556.
22. D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley and G. J. Hutchings, *Catalysis Today*, 2007, **122**, 407-411.
23. N. Dimitratos, A. Villa, C. L. Bianchi, L. Prati and M. Makkee, *Applied Catalysis A: General*, 2006, **311**, 185-192.
24. R. C. Tiruvalam, J. C. Pritchard, N. Dimitratos, J. A. Lopez-Sanchez, J. K. Edwards, A. F. Carley, G. J. Hutchings and C. J. Kiely, *Faraday Discussions*, **152**, 63-86.

7 General Discussion, Conclusions and Future Work

7.1 General Discussion and Conclusions

Monometallic gold and gold based AuPd and AuPt bimetallic catalysts were applied to a number of alcohol oxidation reactions. Glycerol is a by-product of the biodiesel manufacturing process, which is an important process in the global development of renewable fuels. Glycerol itself undergoes hydrogenolysis to yield 1,2- and 1,3-propanediol which have a number of applications, including uses in foods, cosmetics and the synthesis of pharmaceuticals[1].

The base catalysed trans-esterification of triglycerides to produce biodiesel takes place in methanol as the solvent. A base/methanol mixture has been demonstrated to be suitable to perform catalysed oxidation reactions in[2-4]. The oxidative esterifications 1,2-propanediol, 1,3-propanediol and model compounds 1,4-butanediol and butyrolactone were investigated using methanol as a solvent and sodium methoxide as catalytic base.

For the oxidative esterification reactions a number of factors were found to be influential on activity and selectivity. Initial tests were conducted using supported monometallic gold catalysts. The catalysts were prepared by the sol immobilisation and compared with standard catalysts from the world gold council. It was shown that all catalysts had comparable gold particle sizes (3-7 nm) therefore it was shown that the nature of the support is important to achieve high yields of the desired products. In general it was found that metal oxide supported catalysts performed better than those supported on carbon. This is in opposition to oxidation reactions carried out in aqueous conditions[5, 6].

For the oxidative esterification of 1,2-propanediol, it was found that the titania supported gold catalysts were the most active, and that the catalyst prepared by the sol immobilisation method was more selective that the standard World Gold Council catalyst tested, these catalysts had different weight loadings (1% and 1.5 % respectively). The ceria supported catalyst showed a significantly higher selectivity to the desired product, methyl lactate. It was discovered that this particular catalyst contained both Au^0 and Au^{3+} species, unlike the other catalysts which display only metallic gold. It can therefore be suggested that this mixture (80/20) of gold oxidation states that may be a contributory factor to the high selectivity to methyl lactate. The ceria supported palladium catalyst showed a significantly higher conversion than the monometallic gold catalyst and the Pd/TiO_2 catalyst tested. It was observed from XPS analysis that the ceria support showed some reduction with indicates oxygen vacancies on the catalyst surface. This may be the reason that this catalyst shows such a high activity. The Pd/CeO_2 was demonstrated to be the most active catalyst tested, more so than any monometallic gold or bimetallic AuPd alloys.

The oxidative esterification of 1,4-butanediol to dimethyl succinate was investigated as a model compound for 1,3-propanediol which has been proven to be difficult to oxidise to dimethyl malonate[4]. The reaction pathway was investigated and it was shown that the reaction proceeds via butyrolactone and the mono-ester product methyl-4-hydroxybutyrate before yielding dimethyl succinate. The low yield of dimethyl succinate was found to be improved by increasing the temperature and by minimising the water content is the reactor. Again the highest selectivity to the desired product with a monometallic gold catalyst was observed with the Au/CeO_2 catalyst. The Pd/CeO_2 was also the most active catalyst for this reaction when palladium only catalysts were compared. A synergistic effect was observed when these metals were alloyed.

The most selective bimetallic catalyst was AuPd/MgO was investigated further by testing varying Au-Pd ratio. A 1:1 molar ratio of these metals proved to be the most active and selective for the oxidation of the intermediate molecule butyrolactone under the same conditions. This catalyst was probed by XRD and it was discovered that during the sol immobilisation preparation the MgO support is converted to $Mg(OH)_2$. Another 1:1 molar AuPd/MgO catalyst was prepared by a modified impregnation method which showed a similar average AuPd alloy particle size. This catalyst showed significantly lower selectivity to dimethyl succinate. The catalyst in this case retained the periclase MgO structure of the support material. Therefore it is likely that the support material plays a crucial role in the conversion of methyl-4-hydroxybutyrate to dimethyl succinate.

After one use the catalyst prepared by sol immobilisation shows significant decrease in selectivity. From STEM analysis it was concluded that significant sintering of the metal particles had occurred during the reaction.

Gold catalysts have been demonstrated to be inactive for the oxidation of glycerol without the presence of base[7]. The use of magnesium oxide as a support was observed to enhance the selective oxidation of glycerol under base-free conditions using Au-Pd and Au-Pt catalysts that were prepared using a sol-immobilisation preparation method. The alloying of gold with platinum led to a catalyst which was significantly more active than when gold was alloyed with palladium under base free conditions.

For the selective oxidation of glycerol under base-free conditions we conclude that the surface composition of the nanoparticles requires a contribution from gold, however a larger fraction of the alloying metal, *e.g.* Pd, is required to observe high activity. Calcination of the sol-immobilised catalysts up to 200 °C leads to an increase in the activity with no apparent loss of stability. Catalysts with Au/Pd and Au/Pt molar ratio 1:3 were active at ambient temperatures (25 °C).

These results show that it is possible to eliminate the use of NaOH from the glycerol oxidation reaction. In previous studies a strong base, usually NaOH, has been required with gold catalysts in at least stoichiometric quantities to observe any activity in the selective oxidation of glycerol. This new MgOH support is a solid base that replaces the additional homogeneous added base. This has immense benefits with respect to green chemistry since it will lead to the elimination of waste products associated with recovery of the products from basic solutions.

7.2 Future work

7.2.1 The oxidative esterification of 1,2-propanediol

The ceria supported gold catalyst was the most selective whereas the Pd/CeO_2 was the most active. It was concluded that the reasons for this may be the presence of Au^{3+} and a partially reduced ceria surface, respectively. Producing a catalyst with both of these features could potentially increase both the conversion of 1,2-propanediol and selectivity to methyl lactate. Therefore, the catalyst preparation could be modified to try and produce these characteristics.

The oxidation was carried out in a low pressure (3 bar) glass reactor. The use of more forcing conditions such as higher temperatures and pressures in an autoclave have been shown to increase conversions in alcohol conversions[8], at times at the expense of high selectivities. The use of an optimised catalyst under these conditions would increase the yield of the desired product methyl lactate.

Another possible route to increasing the yield of methyl lactate would be the use of a promoter ion, such as Zn^{2+}, Sm^{3+} which have been show to enhance the performance of ceria supported gold catalysts for CO oxidation[9].

7.2.2 The oxidative esterification of 1,4-butanediol and 1,3-propanediol

The most selective catalyst for the oxidation of 1,3-propaneidol and butyrolactone, a 1% AuPd/$Mg(OH)_2$ (1:1 molar) is not selective to the desired product, dimethyl succinate, after one use. It was found that after one use the metal particles had sintered to from larger particles. More work would be carried out to probe the nature of this deactivation and to find a route to stabilise the bimetallic particles.

The support material itself may be changed under the reaction conditions. More analysis into the nature of the reaction mechanism in the presence of the hydroxide support would lead to a better understanding of why this support is particularly selective, with a view to increasing the yields of the desired products.

Higher temperatures and oxygen pressures have been shown to promote conversions and selectivity to sequential oxidation products in aqueous oxidations[5, 6]. Most of the reactions in this work were carried out under relatively mild conditions; increasing the forcing nature of these conditions could lead to higher selectivities of dimethyl succinate and malonate.

7.2.3 The base free oxidation of glycerol

The most active catalyst for the base free oxidation of glycerol is the 1% AuPt/$Mg(OH)_2$ (1:3 molar) prepared by sol immobilisation. Modifications to the synthesis of this catalyst would be investigated such as the employment of other stabilising agents[10] or the application of the $NaBH_4$/THPC methodology as used in the synthesis of ceria supported catalysts.

Calcinations of the catalysts, led to an increase in conversion of glycerol and selectivity to glyceric acid. It is possible that this is due to the removal of the stabiliser, PVA. Lopez-Sanchez et al. demonstrated the removal of PVA by refluxing a catalyst prepared by sol immobilisation in water[11]. This method is likely to be superior to the calcination method as it leads to the sintering of the metal particles.

It was demonstrated by AAS that a small amount (1 %) of the support material had dissolved under reaction conditions. No precious metals were detected, however to achieve good reusability for industrial applications the support must be stabilised.

7.3 References

1. A. Corma, S. Iborra and A. Velty, *Chemical Reviews*, 2007, **107**, 2411-2502.
2. I. Nielsen, E. Taarning, K. Egeblad, R. Madsen and C. Christensen, *Catalysis Letters*, 2007, **116**, 35-40.
3. T. Hayashi, T. Inagaki, N. Itayama and H. Baba, *Catalysis Today*, 2006, **117**, 210-213.
4. E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, Editon edn., 2008, vol. 10, pp. 408-414.
5. N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, G. Brett, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2009, **11**, 4952-4961.
6. N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chemistry*, 2009, **11**, 1209-1216.
7. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Physical Chemistry Chemical Physics*, 2003, **5**, 1329-1336.
8. G. L. Brett, P. J. Miedziak, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, R. Tiruvalam, C. J. Kiely, D. W. Knight, S. H. Taylor, D. J. Morgan, A. F. Carley and G. J. Hutchings, *Catalysis Science & Technology*, 2011.
9. G. Avgouropoulos, M. Manzoli, F. Boccuzzi, T. Tabakova, J. Papavasiliou, T. Ioannides and V. Idakiev, *Journal of Catalysis*, 2008, **256**, 237-247.
10. A. Villa, D. Wang, D. S. Su and L. Prati, *ChemCatChem*, 2009, **1**, 510-514.

11. J. A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G. L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R. L. Jenkins, A. F. Carley, D. Knight, C. J. Kiely and G. J. Hutchings, *Nat Chem*, 2011, **3**, 551-556.

8 Appendix

8.1 The oxidative esterification of 1,2-propanediol – calibration curves

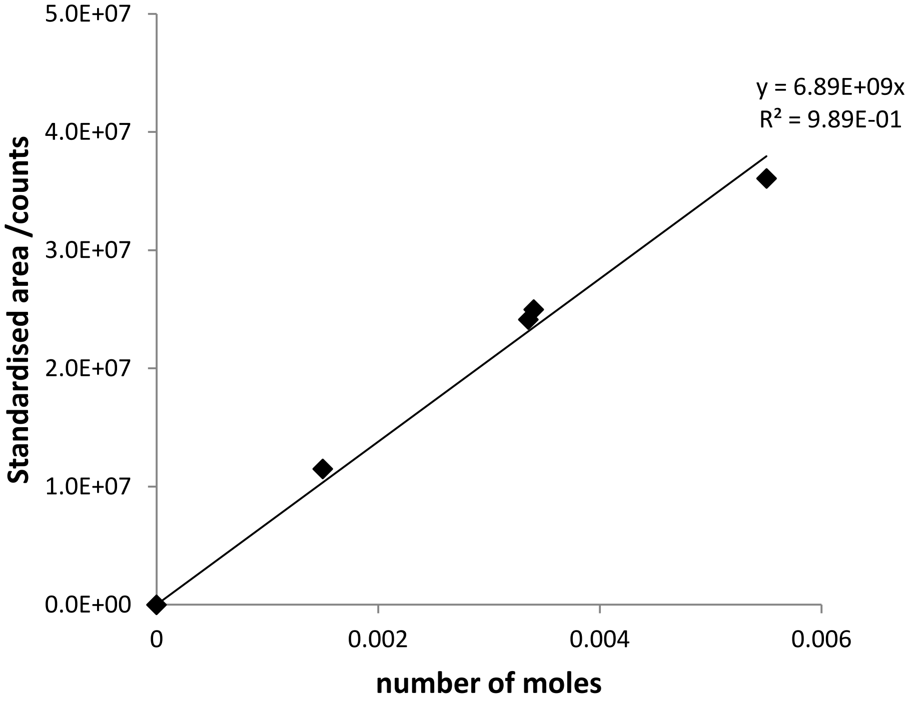


Figure 8-1 GC calibration curve for 1,2-propanediol

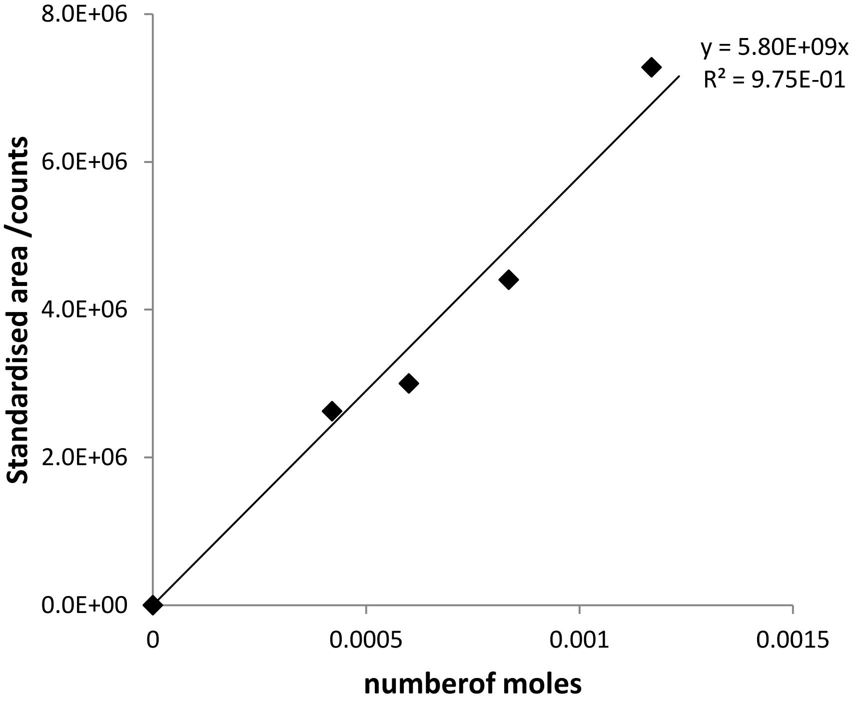


Figure 8-2 GC calibration curve for hydroxyacetone

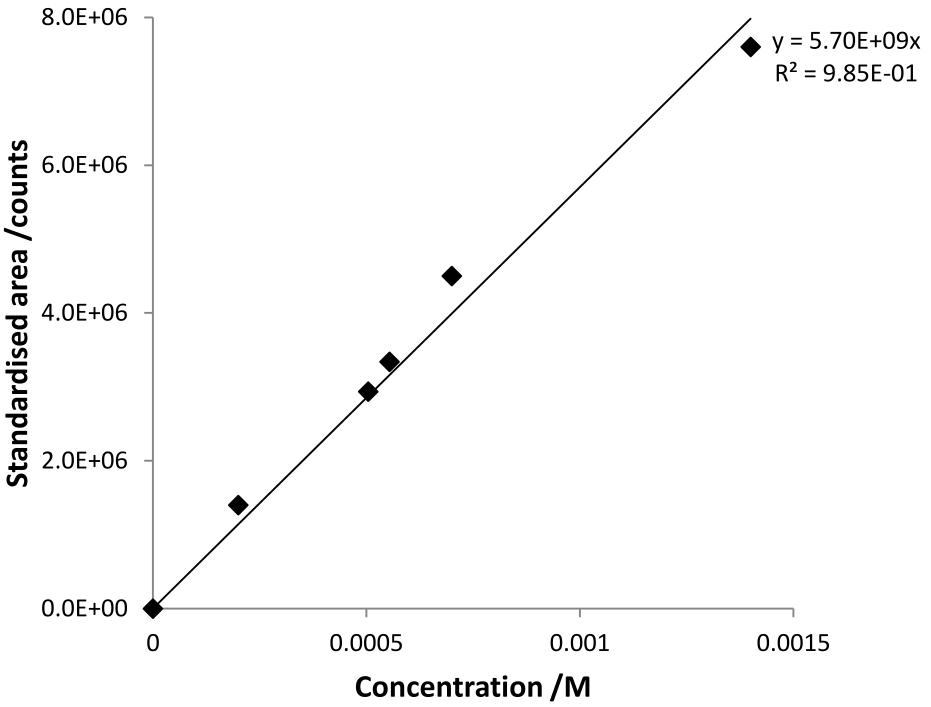


Figure 8-3 GC calibration curve for methyl lactate

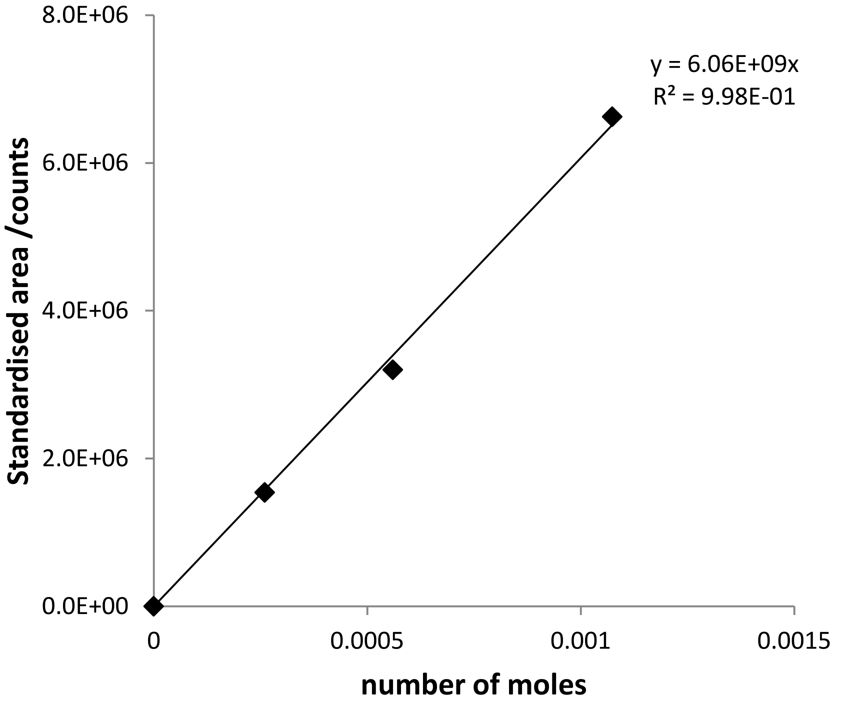


Figure 8-4 GC calibration curve for methyl pyuvate

8.2 The esterification of 1,4-butanediol

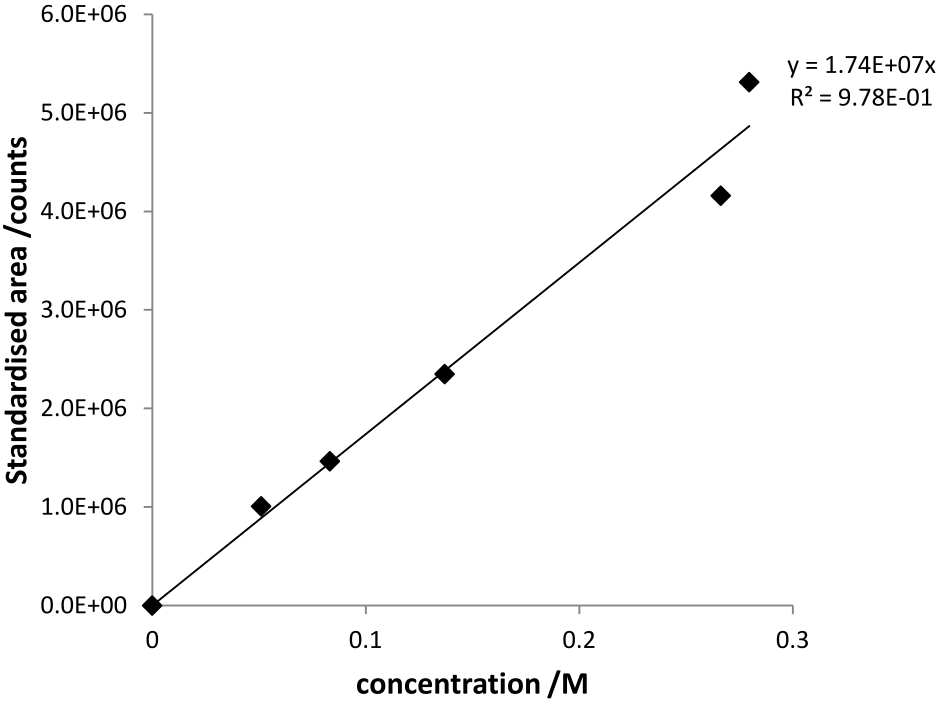


Figure 8-5 GC calibration curve of 1,4-butanediol

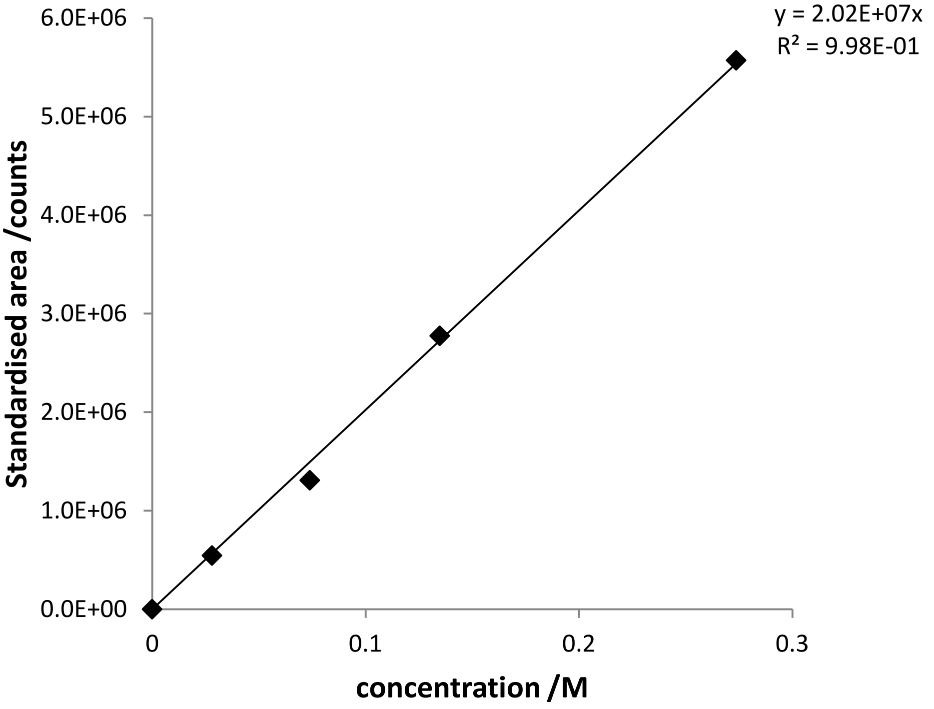


Figure 8-6 GC calibration curve of butyrolactone

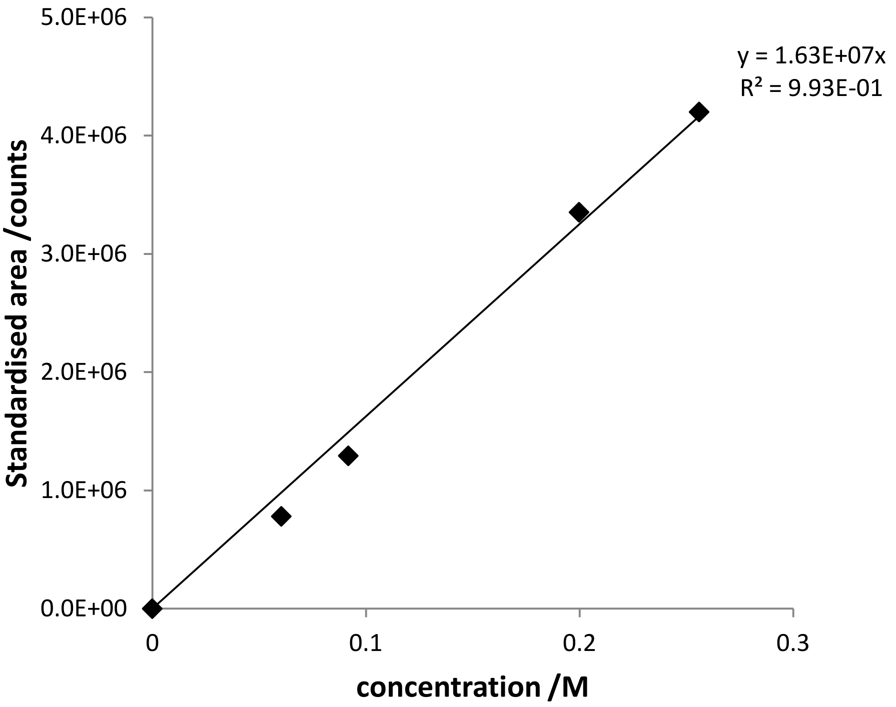


Figure 8-7 GC calibration curve of dimethyl succinate

8.3 Glycerol oxidation calibration curves

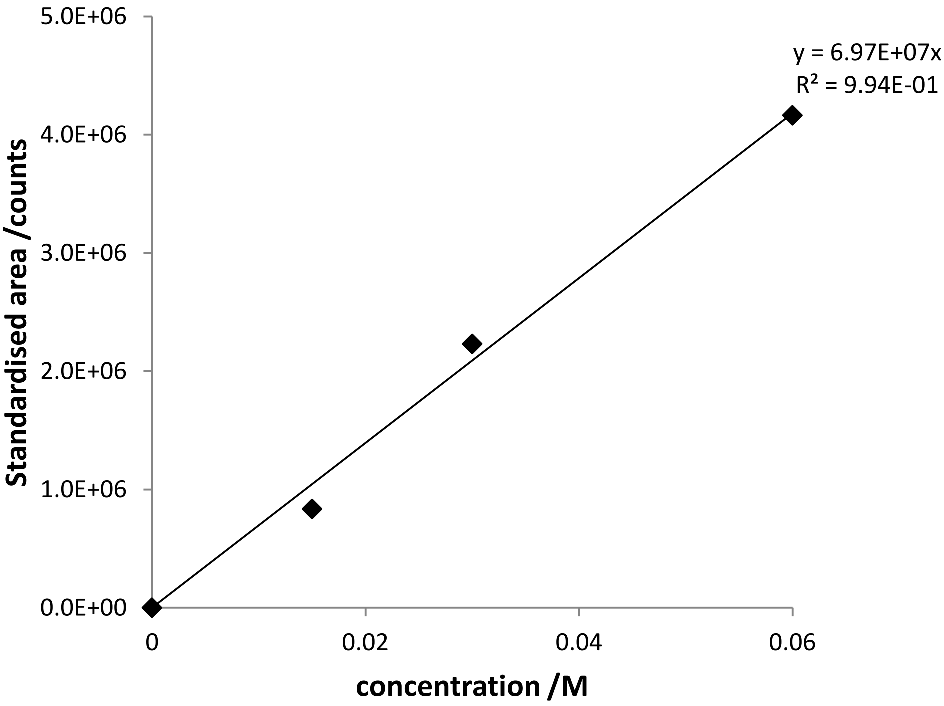


Figure 8-8 HPLC calibration curve for glycerol

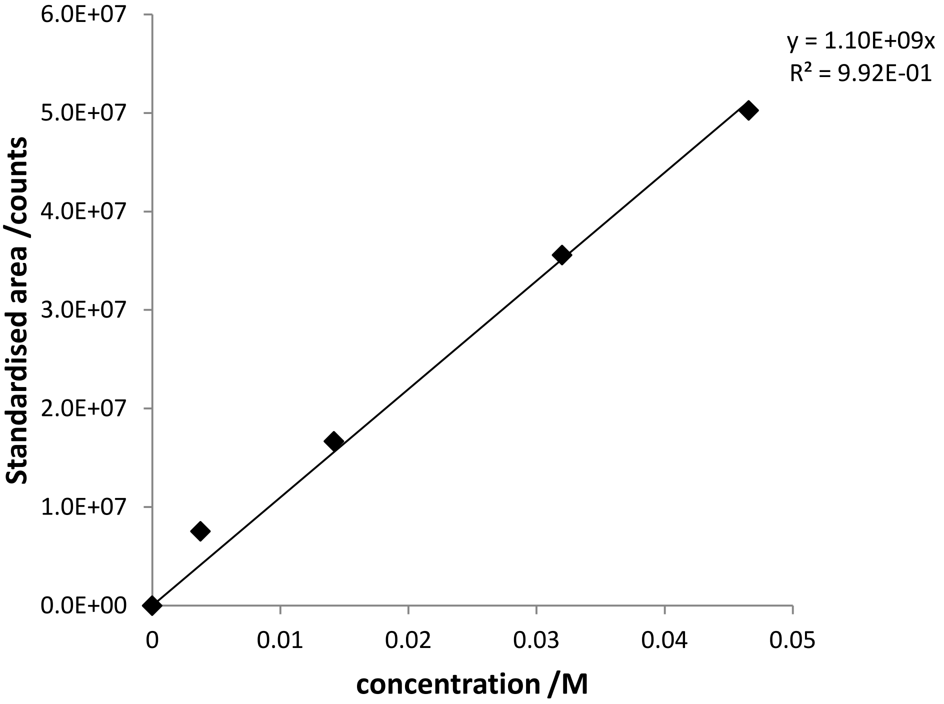


Figure 8-9 HPLC calibration curve for glyceric acid

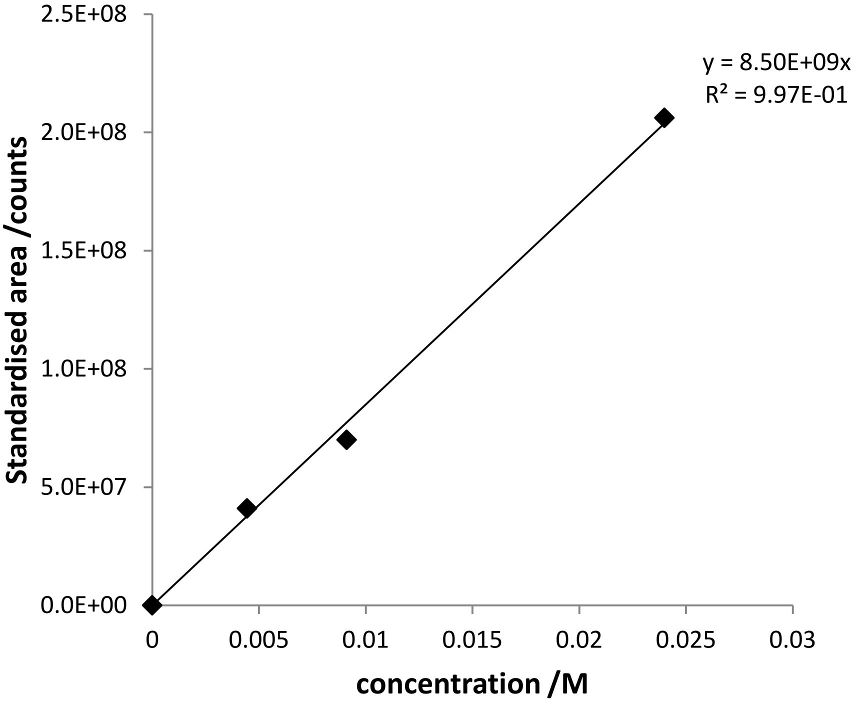


Figure 8-10 HPLC calibration curve for oxalic acid

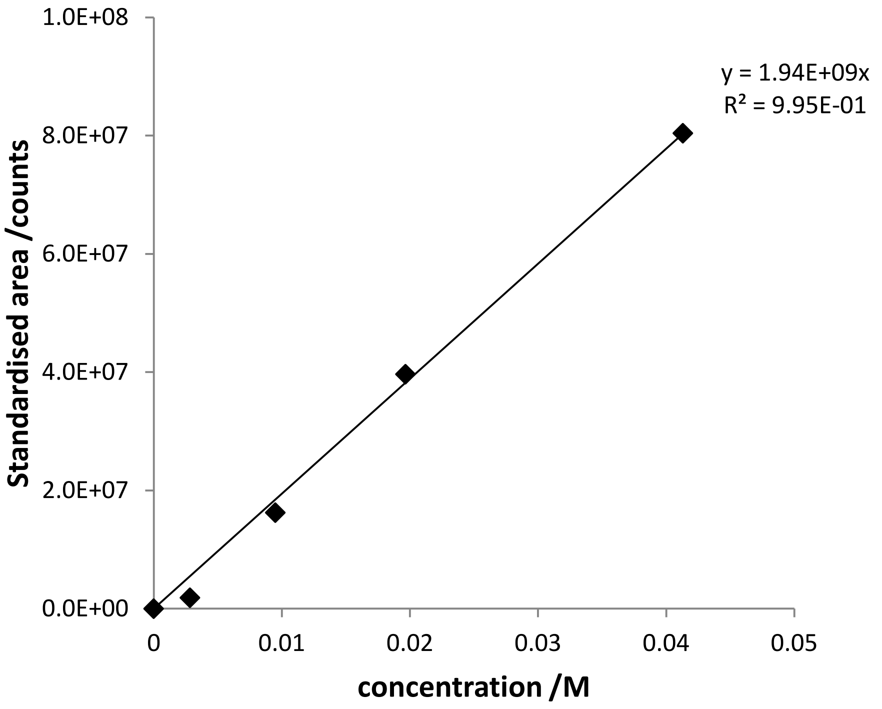


Figure 8-11 HPLC calibration curve of tartronic acid

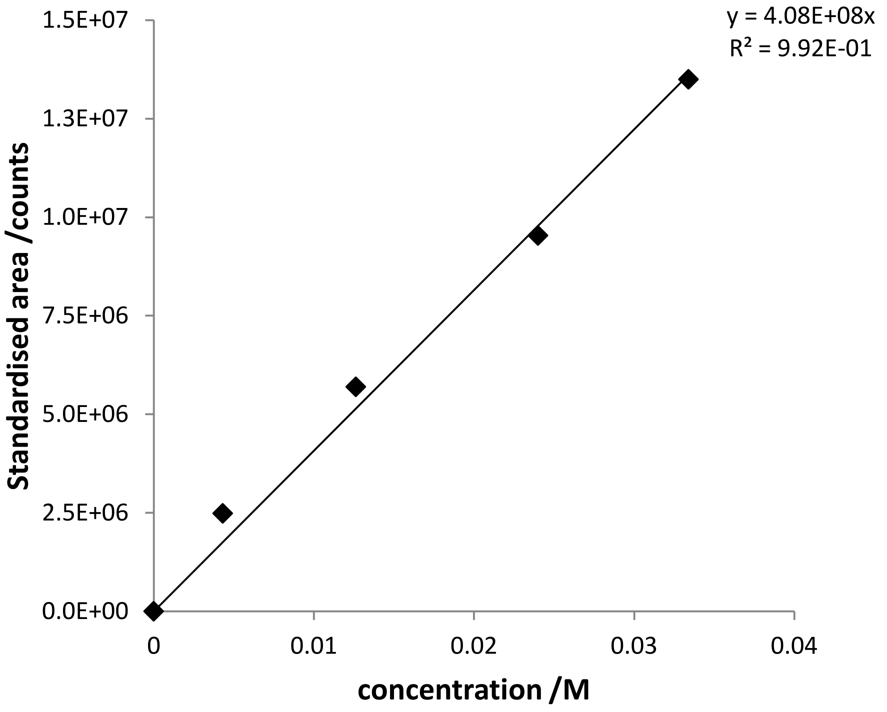


Figure 8-12 HPLC calibration curve of glycolic acid

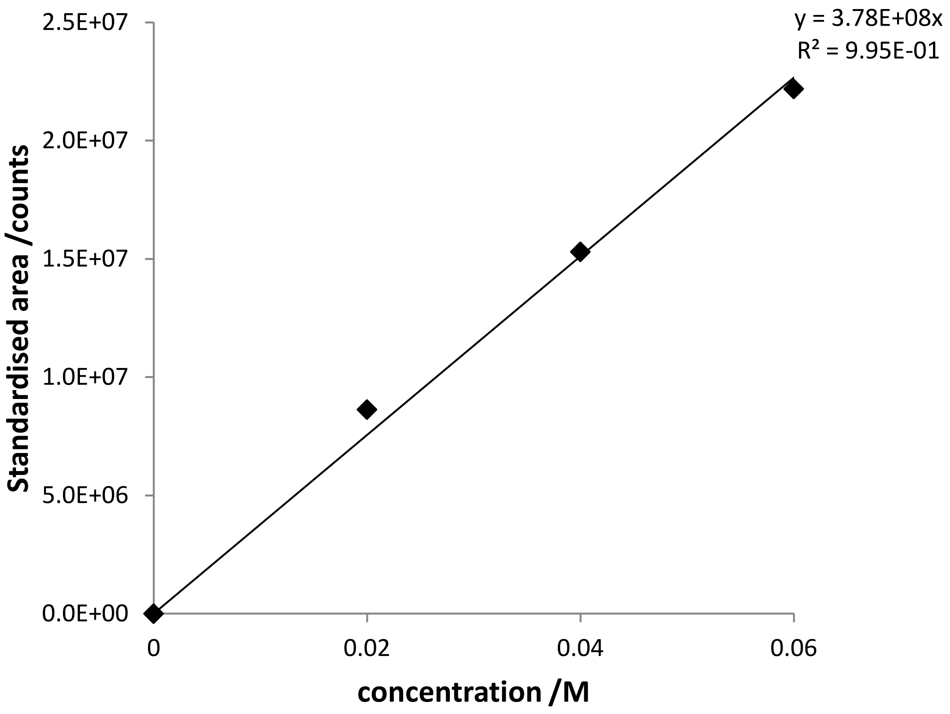


Figure 8-13 HPLC calibration of formic acid