The selective oxidation of 1,2-propanediol over gold, palladium and platinum heterogeneous catalysts

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

by

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ABSTRACT

Biodiesel is one of the most commonly used non petroleum-derived fuels in modern society. Glycerol, a by-product from bio-diesel manufacture, is an excellent starting material for the production of 1,2-propanediol by catalytic hydrogenolysis, which can be further oxidized to lactic acid - a major platform molecule which is used in the manufacturing of biodegradable polymers, food additives and moisturizing agents. Lactic acid can be produced by several routes, which are non-green and require the use of toxic and corrosive reagents, such as acetaldehyde and lactonitrile, as well as high-pressure apparatus, whereas the fermentation process is affected by low productivity and severe purification problems. In this work it is demonstrated that the oxidation of 1,2-propanediol can be carried out selectively under mild conditions using mono- and bimetallic catalysts comprising of Au and Pt group metals. These catalysts were obtained via the sol immobilization technique, while previous studies have used monometallic Au and Au-Pd alloyed catalysts at elevated temperatures and pressures. In fact, although it is known that 1,2-propanediol can be successfully oxidized to lactic acid, no literature is available for the oxidation of this compound under mild conditions and/or in the absence of a base. This prompted us to extend previous findings of 1,2-propanediol conversion and to investigate the possibility of "green" routes for lactic acid production.

A range of different Au, Pd and Pt activated carbon supported nanoparticles have been tested for 1,2-propanediol oxidation reaction. In the case of basic conditions, it was possible to reach 100% conversion with selectivity to lactate of *ca.* 96% using AuPt/C catalyst under 3 bar oxygen pressure and 40 °C, which are significantly lower parameter values than those reported in literature. Interestingly, a synergistic effect was observed when comparing the efficiency of monometallic catalysts and their bimetallic combinations. A series of tests with physical mixtures of Au/C and Pt/C catalysts proved that introducing the second metal led to an enhanced catalytic activity. It has also been shown that decreasing the amount of metal does not lead to drastic decreases in conversion. A range of activated carbons has been tested with the Darco KB-B (Sigma-Aldrich) giving the highest conversion values. This charcoal was used as a support for all further studies. Finally, it has been shown that when improving the reactor design by enhancing stirring capability, even air can be used as

an oxidant giving similar results to the ones when using molecular oxygen and pressurizing the system.

The possibility of base-free 1,2-propanediol oxidation has also been evaluated, and Au, Pd and Pt supported nanoparticles appeared also to be active giving *ca.* 75% conversion. Surprisingly, when the addition of the base is omitted, the reaction profile changes to the formation of another product, namely hydroxyacetone, which is the result of a secondary hydroxyl group oxidation. This trend was further investigated and a series of mechanistic studies have been carried out, including attempts to synthesize lactaldehyde. These results provided an insight into the origin of formic, acetic and pyruvic acids which are the by-products of the investigated reaction.

Finally, a full spectrum of C_4 isomeric diols have been screened to evaluate the activity of the catalysts having proved to be efficient for 1,2-propanediol oxidation. In the absence of a base, a similar trend was observed: both alcohol groups in diols were oxidized, though at different rates. Promising results were obtained for the oxidation of vicinal 2,3-butanediol to acetoin (100% selectivity). In fact, at present this compound can be produced by fermentation and a reusable heterogeneous catalyst can be advantageous.

ABSTRACT (Microfiche)

The selective oxidation of 1,2-propanediol to lactic acid over activated carbon supported Au, Pd and Pt catalysts and their bi- and trimetallic combinations is described and discussed. It has been demonstrated that this reaction can be carried out at high conversion values, *ca.* 99%, under room temperature, 1 to 3 bar oxygen pressure and in the presence of equimolar amount of sodium hydroxide.

The possibility of base-free oxidation of 1,2-propanediol is investigated. In the absence of a base the reaction profile is different from that of oxidation in the presence of a base. Hydroxyacetone appears to be the major product produced during the reaction, though lactic acid is also formed. Mechanistic studies are carried out using time-on-line experiments and the oxidation of all possible intermediates formed, giving an explanation of the formic, acetic and pyruvic acid formation.

The most promising catalysts used for 1,2-propanediol oxidation (Au, Pd and Pt mono- and bimetallic nanoparticles supported on carbon) are tested for the oxidation of the range of C_4-diols in the absence of base. 1,2-butanediol shows similar trend in product formation with that of 1,2-propanediol. 1,3-butanediol oxidation over Pt-containing catalysts results in the formation of unstaturated aldehyde as a by-product, besides the expected hydroxyacid and hydroxyketone. In the case of 1,4-butanediol it is possible to oxidize both hydroxy-groups giving *ca.* 16% of dicarboxylic acid. Finally, 2,3-butanediol could be oxidised to acetoin with 100% selectivity though giving no more than 10-12% conversion.

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Chapter 1: INTRODUCTION

1.1 Definition of catalysis and a catalyst

A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium, without being consumed overall in the process. Therefore catalysis is the change in rate of a chemical reaction due to the participation of a catalyst [1].

If a catalyst and reagents are in one phase, it is homogeneous catalysis. In this case a catalyst is uniformly distributed through the volume. The typical homogeneously catalysed processes are numerous reactions of hydration [2], hydrolysis [3], halogenation [4], esterification [5], condensation [6], liquid phase oxidation of hydrocarbons in a presence of salts of Co, Mn, Fe, Cu [7-9] etc.

A heterogeneous catalyst, in turn, is in a phase different from that of the reactants. The most well-known is the case when a solid catalyst accelerates the reaction between gases or reaction in a solution. Examples of the heterogeneously catalyzed processes can be the most important reactions of synthesis and oxidation of ammonia [10, 11], oxidation of SO_2 to SO_3 [12], dehydrogenation of alkanes into olefins and dienes [13, 14], oil cracking and reforming [15], and many others.

Finally, it also worth mentioning the case of heterogeneous-homogeneous catalysis. This applies to processes which start on the surface of a solid catalyst but carry on in a gaseous or liquid phase. These are usually exothermic radical chain reactions, for instance oxidation of methane to C_2H_4, CH_3OH or to CH_2O over oxide catalysts [16-18] and they are also known as heterogeneously initiated homogenous reactions.

1.2 History of catalysis

Different biocatalytic processes have been used since early ages, such as fermentation of grape or fruit juices for wine production or production of cheeses. In 17-18th centuries some catalytic reactions were discovered. In the 17th century a method for production of sulfuric acid was invented [19], and in 1793 Désormes and Clément finally proved the catalytic mechanism of this process, according to which nitrogen oxides interact with SO_2 and O_2 being homogeneous catalysts:

$NO_2 + SO_2 + H_2O \rightarrow NO + H_2SO_4$ (eq. 1.1)

$NO + ½\ O_2 \rightarrow NO_2$ (eq. 1.2)

Désormes and Clément pointed out two major principles of catalysis: non-stoichiometry and cyclicity of action of nitrogen oxides. The first heterogeneous reaction was probably observed by Johann Joachim Becher and further described by Joseph Priestley in 1778 [20] where ethylene appears to have been discovered by heating ethanol with sulfuric acid.

In the 1830s important conclusions had been made. In 1833 Michael Faraday showed that the "contact" effect of some substances was connected with physico-chemical properties, and these substances did not necessarily interact with the reagents. In 1834 Eilhard Mitscherlich suggested calling these reactions "contact reactions" to characterize a big group of reactions accelerated by metals. In 1835 Jöns Jakob Berzelius generalized data on a huge number of "contact" reactions known at that time and suggested calling this phenomenon "catalysis". In 1836 he identified the unknown reason that causes catalysis as a "catalytic force" [21]. This definition has generated a lot of discussions and in the middle of the 19th century the amount of work on catalysis increased significantly. Thus, Clemens Alexander Winkler solved a problem of catalytic oxidation of SO_2 to SO_3 in the presence of Pt-catalyst which gave an impulse for the development of a lot of branches of the chemical industry [22].

Between the end of 19th and the beginning of 20th centuries physical chemistry was formed as a separate branch of chemistry due to works of J. Vant-Hoff, S. Arrhenius and W. Ostwald, who generalized the data on catalysis taking into consideration chemical kinetics and thermodynamics. Between the years 1884-1909 Ostwald developed a catalytic route for ammonia oxidation, which became the basis of industrial nitric acid production [23]. This established proportionality between the rate of homogeneously catalysed reaction and the amount of catalyst, and gave a precise definition of a catalyst as "a substance that changes the rate of reaction without itself being consumed", as well as describing the interaction of catalysis with thermodynamics. This resulted in the first Nobel Prize for work on catalysis (1909).

One of the most important achievements of catalysis of that time was the discovery of an industrial way of ammonia production by Fritz Haber (Nobel Prize in 1918). In 1931 Carl Bosch was also awarded a Nobel Prize for the design of high pressure techniques for the production of fine chemicals.

Further achievements were the catalytic dehydration, isomerization and other reactions of hydrocarbons which were studied in detail by Zelinsky and his contemporaries [24]. Sergei Lebedev, a Russian/Soviet chemist, invented a way of producing polybutadiene synthetic rubber, the first commercially viable and mass-produced synthetic rubber of this type [25].

In the middle of the 20th century there were numerous debates on the mechanisms of catalysis. Thus, in 1928 Semyonov discovered branched chain reactions [26] and in 1956 together with Cyril Norman Hinshelwood was awarded a Nobel Prize for their work on mechanisms of chemical transformation.

The 1960-70s brought significant improvements in oil refining and in searching for alternative raw materials. Nowadays, the process of catalyst improvement still takes place with the aim of significantly increasing process efficiency, including enhanced selectivity to a desired product and maximized conversion of the starting material under mild

reaction conditions.

1.3 Catalysis and thermodynamics

According to the laws of thermodynamics the position of equilibrium attained in a chemical reaction is the same whether a catalyst is present or not, a catalyst does not shift the equilibrium of a chemical reaction. Consequently, for a reaction where a reactant A gives the product B, $A \rightleftharpoons B$ there cannot exist two different positions of equilibrium with two different free energy states. Therefore the catalyst must equally accelerate both forward A→B and backward B→A reactions.

As the equilibrium constant K at given temperature is determined from the equation:

$$\Delta G = -RT \ln K \qquad \text{(eq. 1.3)}$$

according to the law of mass action, the equilibrium constant equals:

$$K = k_A / k_B \qquad \text{(eq. 1.4)}$$

where k_A and k_B are forward and backward rate constants. Therefore, if a catalyst accelerates the rate constant of forward reaction k_A, it will accelerate the rate constant of backward reaction k_B as stated above.

1.4 Basic steps of catalysis

Catalytic reactions usually comprise the following steps: diffusion of the reagents to the catalyst surface, adsorption, the reaction itself (chemical transformations on the surface, usually several stages), desorption and diffusion of reaction products. Any of these steps

can be rate-determining. Because of their importance, particularly in heterogeneous catalysis, a brief description is reported here.

The first step is the diffusion of the molecules to the surface. The majority of catalysts are either granular or porous bodies; in both cases it is important to deliver the reagents to the catalyst surface. There exist two diffusion limitations: external diffusion regime when the reaction is limited by delivering the reagents to the catalyst surface; and internal diffusion regime when the mass transport inside of the catalyst pores is the rate limiting step. Some other examples will also be provided in the current thesis (Chapter 3).

After diffusion the substrate is adsorbed onto the catalyst surface. This process can be classified as physisorption (characteristic of weak van-der-Vaals forces) and chemisorption (characteristic of covalent bonding) and it is often the rate-determining step in a catalytic reaction. Then the reaction itself takes place. Finally, the product desorption occurs and the reaction products are released from the catalyst surface and diffuse back into the gas/liquid phase.

1.5 Kinetics of catalytic reactions

The kinetics of catalytic reactions deals with how fast the reaction proceeds, therefore determination of kinetic parameters, such as reaction order or activation energy, is essential. This is important, because knowing these parameters may help to understand the reaction mechanism, which can further lead to the design of catalysts with enhanced performance. In addition, knowing the rate-determining step also helps to further design the catalytic reactor taking into account, for instance, diffusion limitations.

As mentioned above, a catalyst is a substance that changes the rate of the reaction without itself undergoing any change. Therefore the primary effect of the catalyst is to speed up the rate of reaction. The reaction rate is connected with temperature *via* the Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad \text{(eq. 1.5)}$$

Or

$$\ln k = \ln A - E_a/RT \qquad \text{(eq. 1.6)}$$

Where

k = rate constant,

A = pre-exponential factor or frequency factor,

E_a = activation energy,

R = gas constant,

T = temperature (measured in Kelvin)

It follows that, by using eq. 1.6, the activation energy can be determined as the slope from a series of measurements by plotting the logarithm of rate constant against the reciprocal temperature.

The use of a catalyst provides an alternative molecular reaction pathway with lower activation energy, thus increasing the reaction rate.

As described in section 1.4, a catalytic reaction consists of a reaction cycle formed by a series of elementary reaction steps. Hence the rate expression is in general a function of many parameters. In heterogeneously catalysed reactions reactants are adsorbed on the catalyst surface, undergo chemical modifications on the surface to give adsorbed products and these products finally desorb. The overall catalyst activity, selectivity and turnover frequency are determined by the composition and the structure of its surface, therefore it is important to give definitions of these terms.

The selectivity *s* defines how much of a given product, is obtained versus the others that can be obtained (if any). This parameter describes the relative rates of two or more competing reactions on a catalyst [27], and for the case of a product *i* it can be defined as:

$$s_i = r_i / \Sigma_i r_i \qquad \text{(eq. 1.7)}$$

where s_i is the selectivity for the product *i* and r_i the reaction rate to product *i*.

In other words, selectivity is the ability to direct a reaction to yield preferentially a particular product, and it is an essential feature for every catalyst. One of the main purposes of this thesis work is to identify catalysts with enhanced selectivity.

The turnover frequency (TOF) represents the number of molecules of substrate converted per catalyst active site per time, and it can be used as an average value of the overall catalytic activity [28], it is defined as:

$$TOF = \frac{N_{Av}}{\theta} dN_i / dt \qquad \text{(eq. 1.8)}$$

where N_{Av} is Avogadro's number, and θ represents the number of sites in the experimental system and can be presented as

$$\theta = L \cdot A \qquad \text{(eq. 1.9)}$$

where L is the number density of sites (per unit area) and A is the area of the catalyst. A TOF has units of reciprocal time.

In view of this, another parameter often used to define the catalytic activity is the turnover number (TON), which considers the number of molecular reactions, or reaction cycles, up to the decay of activity, and it is defined as:

$$TON = TOF\ [time^{-1}] \cdot t_L\ [time] \qquad \text{(eq. 1.10)}$$

Where t_L is the lifetime of the catalyst. It is immediately apparent that TON unlike TOF is a dimensionless parameter.

1.6 Classification of catalytic processes and catalysts by mechanisms and choice of catalyst

There is no uniform theory to select a catalyst or even more importantly to predict the catalytic properties of substances. In catalysis, like in non-catalytic kinetics, in most cases it is impossible to calculate the activity, and hence the reactivity of a substance, due to unknown constants in the elementary steps of the reaction. Therefore, in most cases, empirical correlations between activity or reactivity and physical or chemical properties of substances are used.

In view of this, nearly all catalysed reactions can be divided into two major classes: redox (single-electron) reactions and acid-base (ionic) reactions.

The first class comprise processes involving electron transfer: oxidation, reduction, hydrogenation, dehydrogenation, decomposition of oxygen-containing compounds like H_2O_2, N_2O, $KClO_4$ [29-31]. Typical catalysts for these reactions are metals or metal oxides, *i.e.* substances generally capable of quickly, and reversibly, switching between two different oxidation states by possession of highly mobile electrons. The most widely spread catalysts of this class are: i) transition metals, especially 8-10th group metals (Pt, Pd, Rh, Ru, Fe, Co, Ni) and 11th group (Cu, Ag, Au); ii) transition metal oxides (V_2O_5, MnO_2, Cr_2O_3, MoO_3, Nb_2O_5), iii) and mixed oxides, like spinels (Fe_3O_4, $CuCr_2O_4$, $ZnCr_2O_4$), perovskites ($CaTiO_3$, $NaNbO_3$, $NiLaO_3$), sulfides (MoS_2, WS_2, NiS, Co_9S_8) and some semiconductors like ZnO or ZnS.

The second class comprises acid-base interaction reactions, for which the most common are catalytic cracking, hydration, dehydration, hydrolysis, some isomerisation reactions, polymerization and polycondensation reactions [32-34]. Typical catalysts for these

processes are the substances that possess acidic (Al_2O_3, ThO_2, zeolites, heteropolyacids) and basic (MgO, CaO) properties. Usually they are crystals-insulators or amorphous non-conducting solids.

One more important class of reaction is catalysis by coordination complexes. A coordination bond is a dipolar bond in a complex, and both transition and non-transition elements are capable of forming it. The energy of this bond is usually lower than a pure covalent bond, thus favouring the formation and participation of the metal complex compounds in catalytic reactions. Catalysis by complexes usually occurs at low temperatures which is typical of homogeneous catalysis. A remarkable industrial case of heterogeneously catalyzed reactions following the coordination mechanism non mediated by electron transitions is the Ziegler-Natta polymerization of olefins by solid $TiCl_3$, it requires the presence of $Al(C_2H_5)_3$ to trigger the process.

In reality, the final choice of catalyst is a highly complex process, because the same reaction can follow either homolytic redox or heterolytic acid-base mechanisms depending on reaction conditions. Thus, dehydrogenation of isopropyl alcohol to acetone [35]:

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2 \qquad \text{(eq. 1.11)}$$

can proceed via homolytic C-H and O-H bond cleavage in a redox process, at the same time CaO and MgO can catalyze this reaction leading to the heterolytic C-H and O-H bond cleavage.

It should then be clear that a range of different factors define the catalytic activity of any substance. Therefore it is hard to establish correlations between activity and any specific property of the material used as a catalyst prior the catalytic test.

1.7 Catalysis by gold, palladium and platinum

For long time gold was considered to be poorly active as a catalyst. This is true for the bulk material, but when nanometer sized gold clusters are used, it can be an oxidation catalyst with intrinsic activity [36, 37]. It is now used for a large variety of reactions ranging from oxidation of carbon monoxide [38], propene to propylen oxide [39], cyclic aliphatic alkenes [40], sugars [41], mono- and polyfunctional alcohols [42, 43].

In contrast palladium and platinum have been used as catalysts since much earlier and with a longer tradition of being used in both heterogeneous and homogeneous catalysis as well as in electrochemistry. Both metals can be used together in catalytic converters to control automotive hydrocarbon and C and N monoxide emissions [44]. A high number of results have been reported for the oxidation of aliphatic alkanes, methane and propane [45-47]. Homogeneous Pd catalysts are widely used for carbonylation, cross coupling reactions and fine chemicals synthesis [48]. Electrooxidation of methanol and ethanol [49, 50] is also widely spread and occurs on both supported and unsupported Pd and Pt catalysts.

In this chapter our attention will focus on the oxidation of different mono- and polyfunctional alcohols over heterogeneous supported gold, palladium and platinum catalysts and how these catalysts can be used in the wider context of alcohol oxidation.

1.7.1 Oxidation of monofunctional alcohols

The purpose of this section is two-fold: to bridge the gap between the limited literature in 1,2-propanediol oxidation, and to introduce the specific features of the reactivity of alcohols over gold, palladium and platinum catalysts, that will be useful also for the substrates used in this thesis. In view of this, the reactivity of monofunctional alcohols is described and discussed, with the aim to identify common trends that will be used to explain the choices carried out in 1,2-propanediol oxidation, including the use of

bimetallic systems, different supports and the presence and the absence of base.

1.7.1.1 Oxidation of methanol

Methanol is the simplest of the monofunctional alcohols and it can be oxidized into different compounds according to the equations:

$CH_3OH + ½\ O_2 \rightarrow HCHO + H_2O$ (eq. 1.12)

$CH_3OH + ½\ O_2 \rightarrow 2H_2 + CO_2$ (eq. 1.13)

$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$ (eq. 1.14)

The process described by the equation 1.12 is industrially known as methanol steam reforming and it is performed using silver or iron molibdate catalysts. It should be noted that also formic acid can be produced from methanol by sequential addtion of CO and water. However, this is a route maily promoted over silver catalyst, and therfore it will not be described here. Yet, further studies [51] of this reaction showed that when using gold catalysts methanal was formed, but it should be noted that small amounts of hydrogen have been formed due to methanol decomposition.

Hydrogen production from methanol is a very important process. This gas is considered to be the source of carbon free energy carrier in future and methanol can be very attractive due to its availability and the high hydrogen-to-carbon ratio, with gold based catalysts playing a major role to achieve this target. In fact, hydrogen can be produced by partial oxidation of methanol over supported gold, palladium or platinum catalysts. This process can be carried out in different ways: methanol decomposition [52], partial oxidation [53] (eq. 1.13) or steam reforming [54] (eq. 1.12).

Hydrogen can be produced by partial oxidation of methanol over supported gold, palladium or platinum catalysts. Thus, Au/TiO_2 can be used to oxidize methanol [55].

Another important parameter that may influence the product selectivity is the O_2/CH_3OH molar ratio. When increasing the ratio from 0.1 to 0.5 the conversion increased from 41% to 100% suggesting that introduction of oxygen is helpful to enhance catalytic activity. Interestingly, hydrogen selectivity increases when increasing the O_2/CH_3OH ratio from 0.1 to 0.3 but drops down when going further up to 0.5 as methane and carbon monoxide are observed. This was explained by dissociation of hydrogen on gold surface, producing atomic hydrogen, which in turn reacts with methanol, and methane is produced as a result of this reduction process. High temperatures are also favourable for high methanol conversion and hydrogen selectivity (Fig. 1.1) [55].

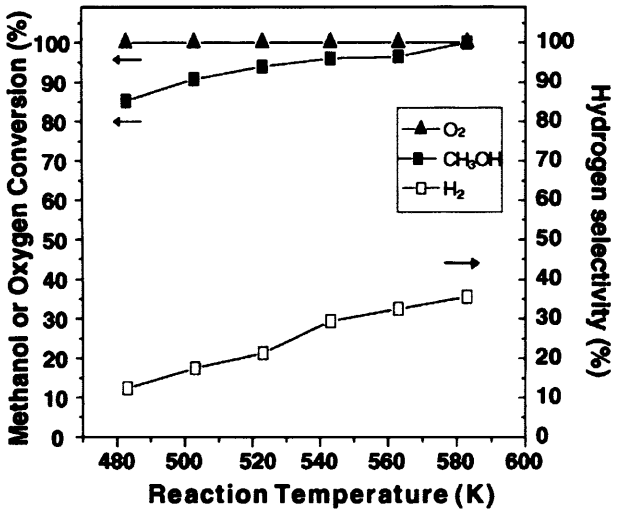


Figure 1.1. Effect of reaction temperature on methanol conversion, oxygen conversion and hydrogen selectivity for partial oxidation of methanol over 0.7 wt% Au/TiO_2 catalysts.

Thus, when increasing the reaction temperature from 482K to 583K it was possible to reach 100% conversion and 35% selectivity, whereas at lower temperatures the values were 85% and 12% respectively.

Au/TiO_2-MO_x (where M= Fe, Co, Zn) composite-oxide catalysts, prepared by deposition-precipitation, were also tested at 423-548 K using a microreactor [53]. The main products observed were hydrogen and carbon dioxide with traces of carbon monoxide (<1.5%) and

methane (<0.1%) also being detected. Interestingly, methanol conversion was almost the same for both Au/TiO_2 and Au/TiO_2-MO_x catalysts, but the hydrogen selectivity was different. For TiO_2 supported catalyst the selectivity was *ca.* 35% but when introducing additional metal oxide support (Fe_2O_3, Co_3O_4 or ZnO) the selectivity increased up to 70% with the most active catalyst being Au/TiO_2-Fe_2O_3. Taking into account that the mean diameters of Au particles were almost the same for both TiO_2 and TiO_2-MO_x catalysts, it is clear that introducing the composite metal-oxide additional support plays an important role in improving catalytic activity.

Palladium supported on zinc oxide can also be efficiently used as a catalyst for partial methanol oxidation [56, 57]. Within temperature range of 503-543 K the conversion reached 40-80% and with the increasing temperature conversion values rose as well.

Catalytic combustion of methanol and its decomposed derivatives over gold, palladium and platinum catalysts supported on metal oxide supports have also been reported in the literature [58]. Catalysts have been prepared by either co-precipitation, or deposition-precipitation, or impregnation and tested in a fixed bed reactor with five gases, namely CH_3OH, HCHO, HCOOH, H_2 and CO, passing through the catalyst. It was shown that methanol and all its derivatives can be oxidized at temperatures lower than 100 °C. Once more, Au/Fe_2O_3 is more active for CO oxidation than Pd and Pt supported on alumina, but these two catalysts are much more active for H_2 oxidation. For the oxidation of methanol, formaldehyde and formic acid the catalytic activity decreases in the order: $Pd/Al_2O_3 > Au/Fe_2O_3 > Pt/Al_2O_3$. Finally, the catalytic activity of gold catalysts strongly depends on the pH of starting solution for catalyst preparation and metal loading.

Gas phase oxidative coupling is a reaction that should not be ruled out when carrying out alcohol oxidation. In fact, it was also possible to carry out over nanoporous Au catalyst under continuous flow conditions and at ambient pressures [59]. At room temperature and stoichiometric ratio O_2/CH_3OH the coupling product methyl formate is produced nearly exclusively at 10% conversion. When increasing temperature up to 80 °C the selectivity decreases to 97% with the remaining 3% being CO_2 formed, but the conversion increases

up to 60% (Fig. 1.2) [59].

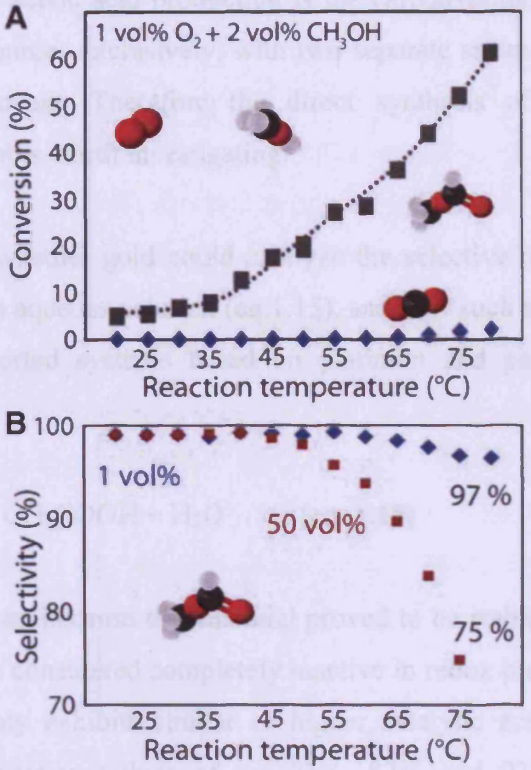


Figure 1.2. Catalytic oxidation of methanol on nanoparticulate gold catalysts.

The reusability tests also have been carried out showing stability for more than 7 days at mild conditions (<60 °C). At higher temperatures the activity decreased at the rate of ~ 6% per 24 hours, though after a week a catalyst was still active and could even be reactivated.

This description of methanol oxidation gives ground for further experiments on selective alcohols and aldehydes cross-coupling over nanoporous gold catalysts.

1.7.1.2 Oxidation of ethanol

Since e*thanol*, the second monofunctional alcohol, can be oxidized into different classes of products over gold, palladium or platinum as catalysts, the oxidation of this substrate is

described here. Ethanol oxidation leads to acetic acid, acetaldehyde and ethyl acetate. One of the routes of acetic acid production is the carbonylation of methanol [60]. This route uses fossil resources exclusively, with two separate steam-reforming steps usually involved in the process. Therefore the direct synthesis of acetic acid from the corresponding alcohol is worth investigating.

It was studied [61] whether gold could catalyze the selective oxidation of ethanol into acetic acid with air in aqueous solution (eq.1.15), and how such a catalyst would compare with previously reported systems based on platinum and palladium on a $MgAl_2O_4$ support.

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \qquad \text{(eq. 1.15)}$$

This oxide was chosen because this material proved to be stable at high water pressures and because it can be considered completely inactive in redox processes. Remarkably, the gold catalyst not only exhibits similar or higher catalytic activity than palladium or platinum (with conversion values of *ca.* 97%, 82% and 93% respectively) but, in particular, a significantly higher selectivity towards acetic acid than both of these well-known catalysts resulting in the yields of 83%, 16% and 60% respectively (Table 1.1) [61].

Table 1.1. Comparison of $MgAl_2O_4$-supported Au, Pt, and Pd catalysts for oxidation of aqueous ethanol to acetic acid with air[a].

Catalyst	Temperature [K]	Pressure [MPa]	Time [h]	Conversion [%]	Yield [%]
Au [b]	453	3	4	97	83
Pt	453	3	4	82	16
Pd	453	3	4	93	60

[a] Conditions: 150 mg catalyst, 1 wt% of metal, 10 mL of 5 wt% aqueous ethanol, [b] Corresponding to 0.07 mol% Au.

The major by-product for the gold catalyst is CO_2, whereas the Pd and Pt catalysts also produce significant amounts of acetaldehyde.

Different supports can be used for ethanol oxidation over gold catalysts. Comparison of TiO_2 and $MgAl_2O_4$ was carefully investigated [62]. For both catalysts, the yield of acetic acid was >90% at high conversion; it was slightly higher (95%) for the Au/TiO_2 catalyst than for the $Au/MgAl_2O_4$ catalyst, but with the difference was close to the experimental uncertainty. Interestingly, the two curves on plots temperature versus conversion and time versus conversion do not exhibit exactly the same shape, providing a first indication that the reaction proceeds *via* intermediates (acetaldehyde and one unknown) [63].

The influence of the gold particle size on the catalytic activity has been also studied [64]. Colloidal Au particles with average sizes of 3–30 nm were prepared by immobilization on an inert support (SiO_2) to evaluate the Au size effect on the aerobic oxidation of ethanol in aqueous solution. Interestingly, Au particles with an average diameter of 5 nm showed a real activity that was about three times that of the smaller (3 nm), and 15 times that of larger (10–30 nm) Au particles.

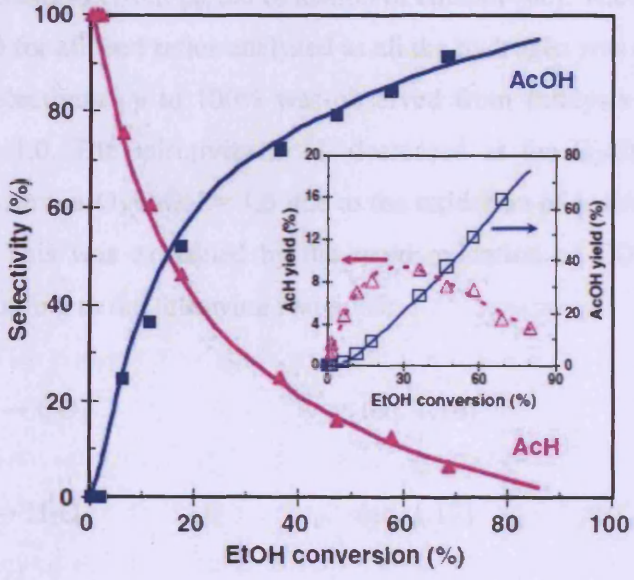


Figure 1.3. Dependence of product selectivity on ethanol conversion. Insert: relationship between product yields and ethanol conversion.

Studies on the dependence of product yields on ethanol conversion over Au particles with different sizes helped to understand that the yield of acetic acid increases always with the

ethanol conversion, while that of acetaldehyde passes through a maximum at an ethanol conversion of 20–30% (Fig. 1.3) [64], thus demonstrating that acetaldehyde is the intermediate product in the oxidation of ethanol to acetic acid.

Interesting results can be obtained when using platinum supported on different oxides. The catalytic oxidation of ethanol over Pt/SiO_2 catalysts prepared by the ion exchange of $[Pt(NH3)_4]^{2+}$ cations for terminal hydroxyl protons result in higher rates of acetic acid formation than those prepared by standard H_2PtCl_6 impregnation methods [65]. This was explained by a synergistic effect of the support. Pre-treatment in air results in a greater yield of acetic acid, while pre-treatment in H_2 increases the rate of CO_2 formation, which was due to a higher degree of support dehydroxylation following pre-treatment in H_2.

Platinum supported on alumina, zirconia and zinc oxide, prepared either by incipient wetness impregnation or sol-gel method, were tested to evaluate the possibility of hydrogen generation from partial oxidation of ethanol [66]. The selectivity was negligible over Pt/ZnO for all feed ratios analyzed as all the hydrogen was oxidized to water. A high hydrogen selectivity up to 100% was observed from catalysts Pt/Al_2O_3 and Pt/ZrO_2 at $O_2/EtOH = 1.0$. The selectivity to H_2 decreased as the $O_2/EtOH$ ratio decreased and approached zero at $O_2/EtOH = 1.5$ due to the oxidation of hydrogen via the high content of oxygen. This was explained by the rapid oxidation of CO and H_2 at high oxygen content according to the following reactions:

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2 \qquad \text{(eq. 1.16)}$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \qquad \text{(eq. 1.17)}$$

The best catalyst was a Pt/ZrO_2 catalyst which was able to oxidize ethanol at a low temperature of *ca.* 370 K, almost excluding CO formation and with the selectivity to hydrogen > 90%. These results can possibly make this catalyst a good candidate to use for fuel cell systems.

Complete oxidation of ethanol is also possible at 400 °C over Pt/Al_2O_3 catalyst [67]. Alumina as an acidic catalyst promotes formation of ethylene and diethyl ether, Pt/Al_2O_3 results in formation of partially oxidized compounds. In turn, alkali-promoted Pt/Al_2O_3 does not produce acetic acid or acetaldehyde and in general are more active than unpromoted catalysts. The most efficient catalyst was alkali promoted Pt/Al_2O_3 (K/Al = 0.10), with complete oxidation of ethanol to CO_2 achieved at 220 °C, while complete oxidation of ethanol over the unpromoted catalyst was obtained at 280 °C.

1.7.1.3 Oxidation of propanol

Propanol, the next monofunctional alcohol, already has two isomers, namely 1-propanol and 2-propanol. Both alcohols can be oxidised to corresponding carbonyl compounds.

1-propanol, as well as 2-propanol, can be successfully oxidized in gas phase over Au/SiO_2 to propionaldehyde and acetone respectively [68]. The reactivity of both primary and secondary hydroxyl groups was compared showing that the activation of secondary alcohols occurs at lower temperature (423K vs. 573K). In the case of primary alcohols, Au on the support acts mainly as a surface modifier: the acidic centres of the support address the reaction to a more extended substrate oxidation. In the oxidation of secondary alcohols, gold acts also as a strong activator of the organic substrates as silica support is almost inactive at this temperature (413K).

Pt can be also used as a catalyst for oxidation of isomeric alcohols. 5%Pt/C was used as an oxidative catalyst at mild temperature (313K) in supercritical CO_2 [69]. The main reaction products observed are acetone or propionic aldehyde and propionic acid.
Compared to conversions in aqueous solution, catalyst stability is significantly enhanced in supercritical CO_2 and depends on the oxygen concentration. Platinum catalysts with nanoporous silica (MCM-41, silicalite-1) as a support were also active for the oxidation of 2-propanol in supercritical carbon dioxide.

Catalytic combustion was possible over gold on ceria catalysts [70]. Though the support itself was able to promote oxidation of 2-propanol, the presence of gold seemed to enhance the catalytic activity.

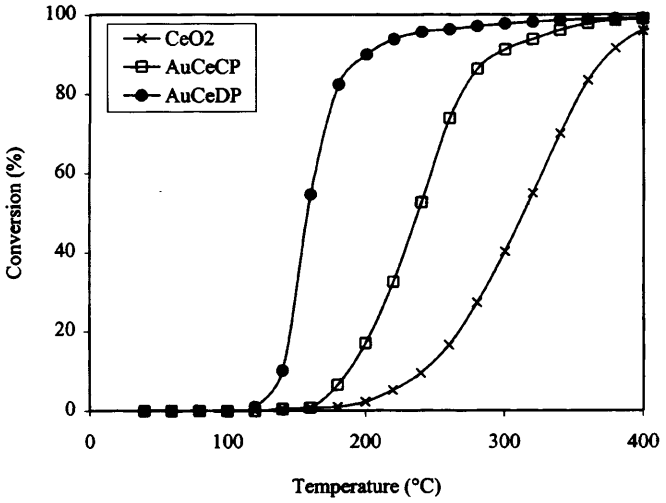


Figure 1.4. Conversion of propanol on Au/CeO_2 catalysts.

It should be noted, that the products formed were only acetone, CO_2 and water, with the former being produced at low temperatures with high selectivity and the last two compounds were observed at higher temperatures. After experiments comparing CeO_2 and Au/CeO_2 (Fig. 1.4) [70], it was suggested that the catalytic activity of the Au/CeO_2 system is related to the capability of gold nanoparticles to weaken the surface Ce–O bonds adjacent to Au atoms, thus enhancing the reactivity of the CeO_2 surface capping oxygen which is involved in the volatile organic compounds oxidation through a Mars-van Krevelen reaction mechanism [71].

Au/Fe_2O_3 catalyst prepared by coprecipitation is also very active for 2-propanol oxidation [72]. Figure 1.5 shows the distribution of products for this reaction.

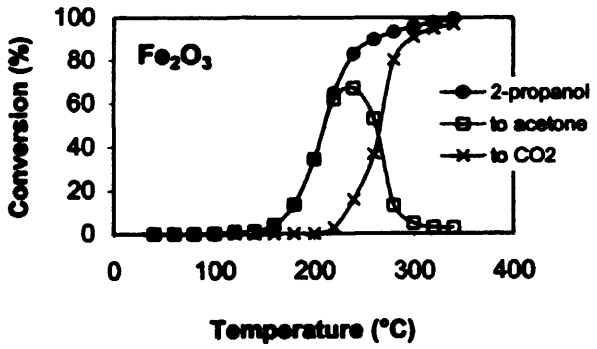
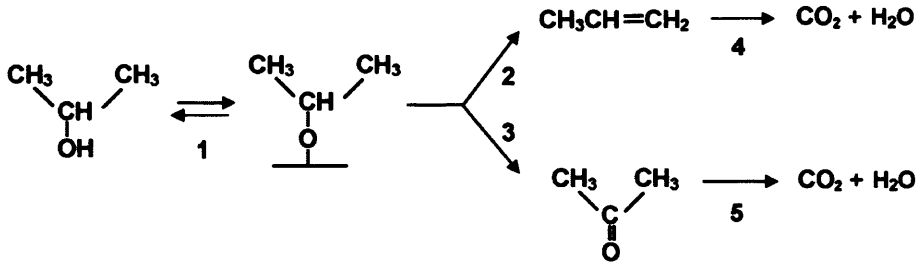


Figure 1.5. Conversion of 2-propanol and products distribution on Au/Fe_2O_3.

The high activity of this catalyst is probably related to the ability of highly dispersed gold to activate the oxygen of the iron oxide weakening the Fe–O bonds located nearby the gold atoms.

Interesting results can be obtained using gold/titanium oxynitride catalysts [73]. Introducing nitrogen atoms into the support seems to exert a negative role in the total combustion to CO_2, but a positive one in the partial oxidation to acetone. This can be possibly explained by the presence of $Au^{\delta+}$ surface species detected in these solids. On the contrary, the higher the gold surface concentration and the lower the gold particle size, the higher the oxidation performances of the catalysts, especially in the partial oxidation reaction to acetone.

The mechanistic insights are also explored and the possible reaction pathway was suggested [74]. The reaction pathway of the 2-propanol oxidation begins with the adsorption of gaseous 2-propanol as 2-propoxide surface species (step 1), suggesting possible dissociative adsorption of 2-propanol (Scheme 1.1) [74]. The decomposition of 2-propanol after the formation of 2-propoxide species proceeds by two parallel reactions: (1) via propene formation (step 2), dehydrogenation to acetone (step 3). These compounds are further decomposed to CO_2 and H_2O.



Scheme 1.1. Reaction mechanism of 2-propanol oxidation.

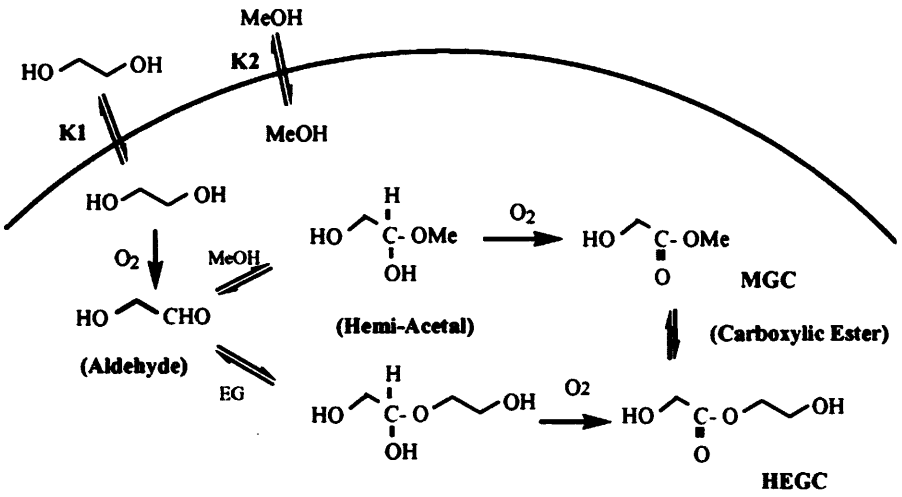
1.7.1.3 Oxidation of higher alcohols

Higher alcohols, primary and secondary, aliphatic or benzylic, can also be oxidized using Au and Pd heterogeneous catalysts [75]. 1% Pd/MgO catalyst is found to be a highly active heterogeneous catalyst for the oxidation of alcohols using molecular oxygen at a moderate temperature of 70–80 °C. The following compounds were selectively oxidized without the presence of any added base or excess organic solvents: 2-propanol, 2-butanol, 1-pentanol, 2-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, cyclohexanol, cyclopentanol and higher aliphatic and cyclic alcohols. Reusability tests of this catalyst revealed no appreciable loss of activity and product selectivity. The activity of the catalyst is ascribed to the reducible nature of the support, which can act as a ligand for the metal that helps in the oxygen transfer through the formation of a metal–alcoholate intermediate [76].

1.7.2 Oxidation of diols

1.7.2.1 Oxidation of ethylene glycol

Ethylene glycol – the simplest diol - can be oxidized to carboxylic acid, namely glycolic acid, over Au/Al_2O_3 catalyst [77] or in methanol to form corresponding ester – methyl glycolate [78]. The mechanism of the final product formation is the following: ethylene glycol – aldehyde – hemiacetal – carboxylic ester (Scheme 1.2) [77], with the rate determining stage probably being an abstraction of α–hydrogen from alcohol.



Scheme 1.2. The proposed mechanism of ethylene glycol oxidation in methanol over Au catalysts.

The best results of 62% conversion and 88% selectivity to methyl glycolate were achieved at 90 °C and MeOH/ethylene glycol ratio = 15.

However, it is worth to be mentioned that the final products of the reaction strongly depend on the amount of substrate used. In fact, in case of 1:1 ratio between aldehyde and methanol the hemiacetal will be obtained, while the excess of methanol will lead to the acetal formation.

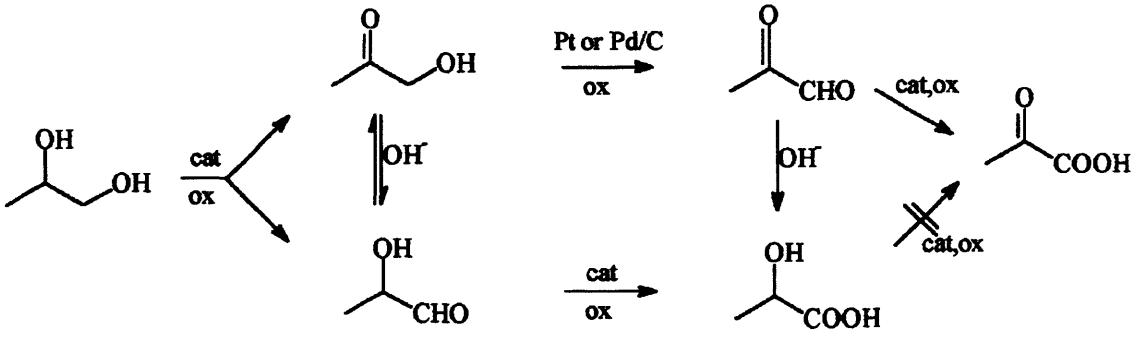
1.7.2.2 Oxidation of 1,2-propanediol

1,2-propanediol can also be oxidized selectively to corresponding acids over Au, Pd and Pt heterogeneous catalysts. Thus, an attempt to synthesize pyruvic acid is reported by using Pd/C and PdPb/C catalysts [79]. Palladium catalysts seemed to be ineffective in propylene glycol oxidation, resulting in low yields and selectivities, but the introduction of lead increased to yield of pyruvate up to 40%. Interestingly, hydroxyacetone (an intermediate in1,2-propanediol oxidation) was oxidized to pyruvic acid suggesting the formation of dicarboxylic acid *via* hydroxyketone, though lactic acid itself was also possible to transform into pyruvate [79]. However contraddictory results were obtained

by Prati and Rossi [80] as desribed in the next paragraphs.

These studies have been extended by investigating the effect of promoter addition on the reactivity of 1,2-propanediol to form lactic acid [81]. The same reaction mechanism of the pyruvic acid formation was proposed, one path *via* hydroxypropanal and lactic acid, another - *via* hydroxyacetone and methyl glyoxal. The effects of the promoters Pb, Bi and Sn were studied on both activity and selectivity. It appeared that the promoted catalysts were more easily de-activated by over-oxidation, presumably because they are less noble than platinum. Pb, Bi and Sn enhance the oxidation of lactic acid resulting in higher yields of pyruvic acid and suppression of acetic acid formation.

In turn, another mechanism of 1,2-propanediol oxidation over carbon supported Au, Pd and Pt catalysts under basic conditions was proposed [80]. A general reaction scheme under basic conditions (see scheme 1.3) includes lactic acid production either by oxidation of the primary hydroxyl group via lactaldehyde or by the intramolecular Canizzaro reaction of pyruvic aldehyde (methyl glyoxal). The latter can be formed by oxidation of propanediol at the secondary hydroxyl group giving hydroxyacetone, but the lactaldehyde and hydroxyacetone could also be in equilibrium *via* their enols.

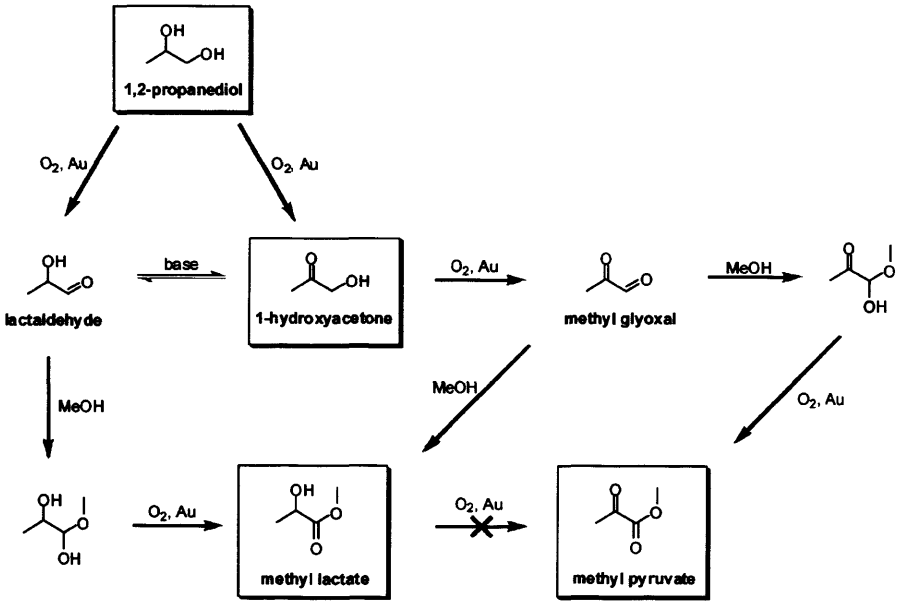


Scheme 1.3. Reaction scheme for propane-1,2-diol under alkaline conditions.

Regarding the catalytic test results, Au/C converted diol to lactic acid with 100% selectivity (and 30% conversion), whereas when using platinum and palladium on carbon catalysts hydroxyacetone and pyruvate were also detected (24% and 4% respectively).

From these data, one can conclude that gold shows an intrinsic high selectivity to the primary hydroxylic group oxidation, whereas Pd and Pt are not selective between primary and secondary hydroxyls. Therefore, the high selectivity shown by palladium and platinum catalysts under stronger basic conditions can be explained by rapid equilibria and the intramolecular Canizzaro reaction favouring the formation of lactate also from pyruvic aldehyde.

The catalytic oxidative esterification of 1,2-propanediol in methanol over Au/TiO_2 and Au/Fe_2O_3 was also studied [82]. After 1 hour it was possible to reach 87% conversion with two products observed – methyl lactate and hydroxyacetone. Interestingly, after 21 hours the conversion was >98% and selectivity to methyl lactate decreased to 72% as methyl acetate also was formed. However, it should be stressed that such high amount of methyl acetate is likely to derive from methanol solvent. The proposed reaction mechanism is similar to that of Prati (Scheme 1.4) [82].



Scheme 1.4. Reaction scheme for oxidative esterification of 1,2-propanediol in the presence of base. The observed products are highlighted in boxes.

The reaction pathway first involves oxidation of 1,2-propanediol to either lactaldehyde or

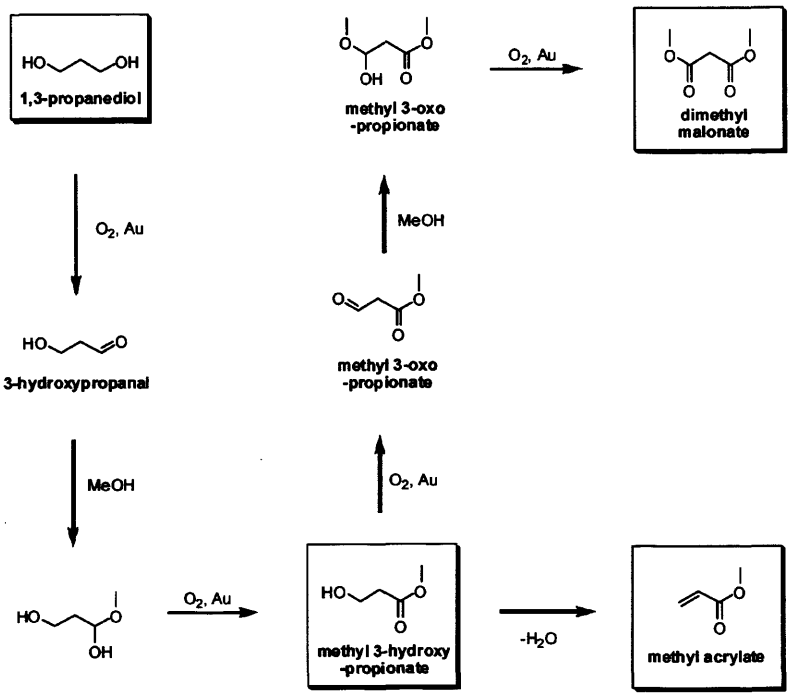
1-hydroxyacetone. Lactaldehyde is then oxidized rapidly to give methyl lactate, whereas 1-hydroxyacetone can give either methyl lactate or methyl pyruvate.

Au and AuPd sol immobilized catalysts were successfully used for 1,2-propanediol oxidation under basic conditions [83]. Thus, after 1 hour it was possible to reach 23% conversion with 96% selectivity to lactate, other 4% being selectivity to acetic and formic acid. Addition of the second metal, palladium, enhanced the activity and retained the high selectivity to lactate using O_2 as oxidant giving 96% lactate selectivity at 94% conversion after 4 hours reaction time.

Homogeneous oxidation of 1,2-propanediol was possible over stabilized gold nanocolloids combined with a membrane base catalyst separation [84]. It appeared that the activity of the sol catalysts was the same with stabilized nanoparticles deposited on carbon. These catalysts could be easily recycled by means of nanofiltration both from water and organic solvents with the best membrane being cellulose acetate and poly(dimethyl)siloxane. Further recycling tests proved the catalytic activity to retain the same after a few consecutive runs.

1.7.2.3 Oxidation of 1,3-propanediol

Very limited literature is available on the oxidation of *1,3-propanediol*. Thus, oxidative esterification of this substance was carried out in the presence of base over Au catalyst [82].



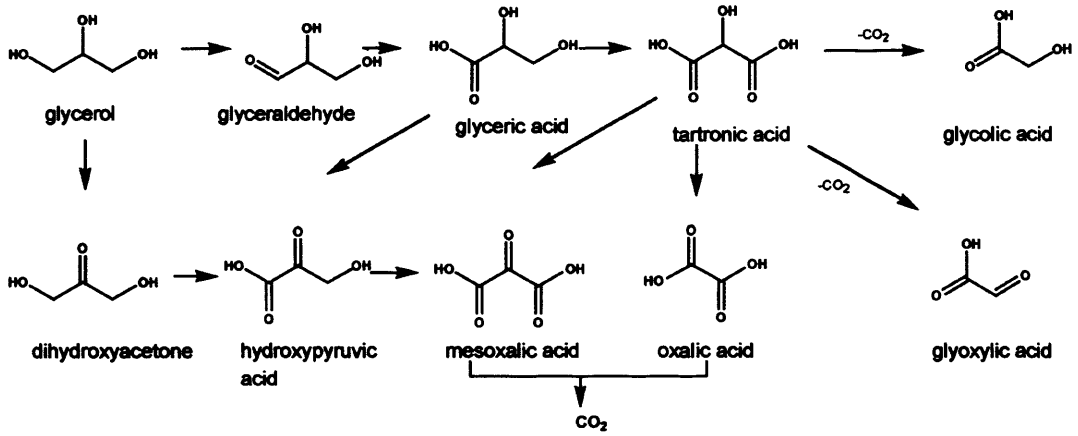
Scheme 1.5. Reaction scheme for oxidative esterification of 1,3-propanediol in the presence of base. The observed products are highlighted in boxes.

Oxidation of 1,3-propanediol follows the reaction pathway shown in the Scheme 1.5. Methyl 3-hydroxypropionate was formed at 94% conversion and 90% selectivity after 21 hours. Interestingly, the second alcohol group was very difficult to oxidize, resulting in formation of only 5% dimethyl malonate. Methyl acrylate, a result of dehydration of methyl 3-hydroxypropionate, was also formed after 21 hours reaction time (of *ca.* 5%).

Base-free oxidation of 1,3-propanediol was also possible over Au/CeO_2 catalysts [85]. The Au/CeO_2 cube catalyst performed high selectivity to methyl 3-hydroxypropionate (93.1% at 21.6% conversion) at the reaction temperature of 83 °C and the reaction time of 4 hours. Methyl 3-methoxypropionate was also possible to synthesize with a yield and selectivity of 37% and 40.2% respectively over Au/CeO_2 rod catalysts in the absence of base. The yield of methyl acrylate (38.4% yield with 41.6% selectivity) was also greatly improved using the Au/CeO_2 rods as catalysts. In turn, the Au/CeO_2 cubes were effectively recycled without losing gold particles.

1.7.3 Oxidation of triols

Glycerol is a renewable feedstock and it can be used for production of a large number of valuable compounds. The following products can be obtained by catalytic oxidation of glycerol over gold catalysts supported on carbon: dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid , hydroxypyruvic acid, mesoxalic, oxalic acid and tartronic acid [86].



Scheme 1.6. Reaction network of glycerol oxidation.

Recent research shows that by promoting gold catalysts with a second metal – platinum – it was possible to get a more active catalyst. Thus, it was possible to increase the selectivity to dihydroxyacetone from 26% to 36% at 50% conversion.

Other interesting results were obtained by using gold catalyst supported on graphite [87]. A series of catalysts with gold nanoparticles supported on graphite with 0.25, 0.5 and 1.0 wt% gold were tested for the oxidation of glycerol in the presence NaOH under autoclave conditions. 1%Au/C appeared to give ca. 56% conversion with 100% selectivity to glycerate, whereas catalysts with 0.5% and 0.25% gold loading resulted in 26% and 18% conversion and 61% and 54% selectivity to monoacid respectively. This selectivity drop can be probably explained by the removal of active sites capable of non-selective oxidation from the catalyst surface with the decrease of metal loading.

Bimetallic combinations of Au, Pd and Pt showed high activity in glycerol oxidation

when supported on activated carbon [88]. It was reported that by tuning the reaction conditions and by varying the nature of metal it was possible to direct the product distribution. It was proved, that either at 30 or 50 °C, bimetallic catalysts were more active than monometallic catalysts, which was indicative of a synergistic effect between Au and second metal (Pd or Pt). This effect was especially significant in the case of Pt as the monometallic was poisoned (possibly by glyceraldehyde) before reaching full conversion. In terms of selectivity to glyceric acid, AuPd catalysts showed in general better selectivity than AuPt catalysts, with Pd mainly promoting the formation of tartronic acid and Pt to glycolic acid. The overall selectivity to glyceric acid increased using bimetallic AuPd/C catalysts with respect to monometallics.

By varying the nature of the Pt precursor ("fresh" or "aged") and reducing agent ($NaBH_4$, N_2H_4 and H_2) in AuPt/C catalysts it was possible to enhance the catalytic performance in the aqueous glycerol oxidation [89]. Thus, reduction method by H_2 resulted in high activity and selectivity to glyceric acid for "fresh" Pt/C and $NaBH_4$ was a better reducing agent for "aged" Pt/C catalysts. Though for monometallic Pt/C catalyst a deactivation process was observed during the reaction. To overcome the deactivation problem, Pt/C catalysts were modified with addition of Au, resulting in higher activity and reaching full conversion. Finally, the most active bimetallic catalyst was obtained when using H_2 as the reducing agent for the Pt precursor.

Studies on comparison of the activity of monometallic Au and Pd catalysts and bimetallic AuPd/C catalysts with different metal ratios were also conducted [90].

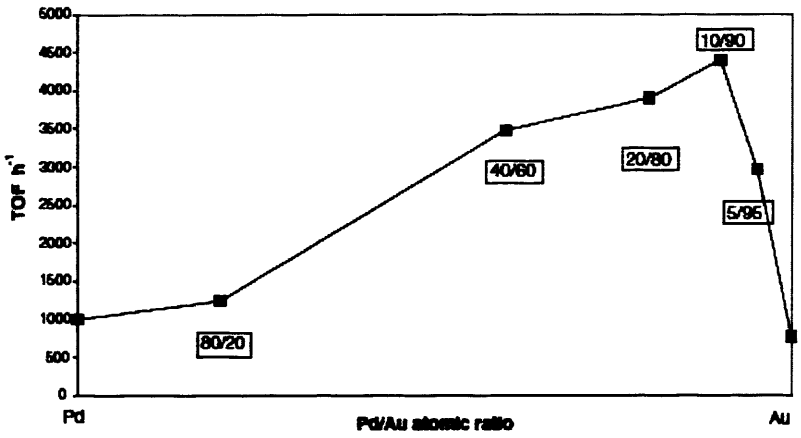


Figure 1.6. TOFs of bimetallic Au_xPd_y catalysts for glycerol oxidation.

From Fig. 1.6 [90] it is clear that all bimetallic catalysts are more active than monometallic ones. Comparing the Au/Pd ratio from 95/5 to 20/80 it was observed that the activity increased with increasing gold loading up to Au_{90}-Pd_{10}, thereafter it declines for higher gold content. Despite a noticeable change in activity of all catalysts tested, the change in selectivity to glyceric acid is not obvious: all bimetallic systems and pure Pd are more selective than gold.

Base-free glycerol oxidation was also possible using Pt/C catalysts with sizes from 1.5 to 26 nm [91]. The catalysts with different particle sizes were prepared by impregnation by varying the impregnation and reduction temperature, amount of reducing agent and the nature of support. The best results of 50% conversion and 47% selectivity were achieved when using catalysts with particle size less than 6 nm.

One more application of reactions with glycerol is gas-phase conversion to synthesis gas. [92]. This reaction is carried out over Pt catalysts at 623 K and atmospheric pressure. The following equations describe the process:

$$C_3O_3H_8 \rightarrow 3CO + 4H_2 \qquad \text{(eq. 1.18)}$$

The H_2/CO ratio for the above reaction is equal to 1.33. This ratio can be increased by the water–gas shift (WGS) reaction:

$CO + H_2O \rightarrow CO_2 + H_2$ (eq. 1.19)

The stoichiometry for conversion of glycerol to liquid alkanes, by the formation of synthesis gas coupled with Fischer–Tropsch synthesis, is:

$C_3O_3H_8 \rightarrow 7/25\ C_8H_{18} + 19/25\ CO_2 + 37/25\ H_2O$ (eq. 1.20)

This overall reaction to produce liquid fuels from glycerol is slightly exothermic, such that 96% of the energy content of the glycerol molecule is retained in the liquid alkane product.

The catalyst with the most acidic support, Pt/Al_2O_3, showed a period of apparently stable catalytic activity, followed by a period of rapid catalyst deactivation. The most basic catalyst support, MgO/ZrO_2, was rapidly deactivated. The most stable oxide-supported catalyst was Pt on CeO_2/ZrO_2; however, the performance of this catalyst is inferior to that of Pt supported on carbon. It was possible to reach 100% conversion into gas phase and TOF of 600 min^{-1} at 673 K and 1 bar pressure, thus demonstrating an efficient route of low-temperature transformation of glycerol into H_2/CO mixture.

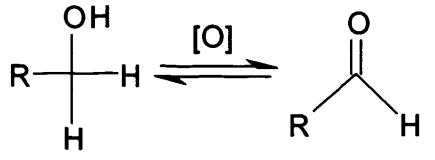
1.7.4 Summary on alcohols oxidation

The selective oxidation of alcohols is a very important target in green chemistry. The use of stoichiometric reagents is still widely spread, therefore new environmentally friendly approaches must be developed. From the overview on the catalytic alcohol oxidation it is clear that gold, palladium and platinum catalysts and their various combinations can be highly efficient systems for this purpose. It was shown that by using the appropriate support, metal or combination of metals, temperature, pressure or reaction media basicity, it was possible to tune the reactions to the formation of desired products, *i.e.* acids, aldehydes or ketones. As these nanoparticles proved to be effective for both mono- and polyfunctional alcohol group oxidation, they were chosen and further used in this work to

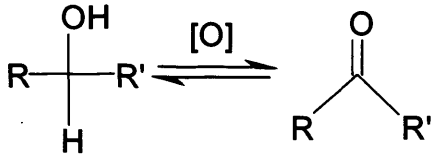
selectively oxidize 1,2-propanediol to form lactic acid.

1.8 Mechanistic aspects of the alcohol oxidation

Alcohol oxidation mechanisms are not as trivial as they may seem and include several steps, depending on the acidity/basicity of the media [93]. The first step is transformation of the OH^- functional group either into carbonyl or keto group (eq. 1.21-1.22).

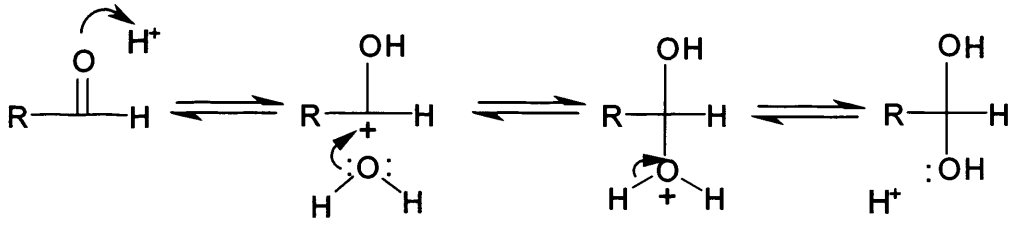


(eq. 1.21)



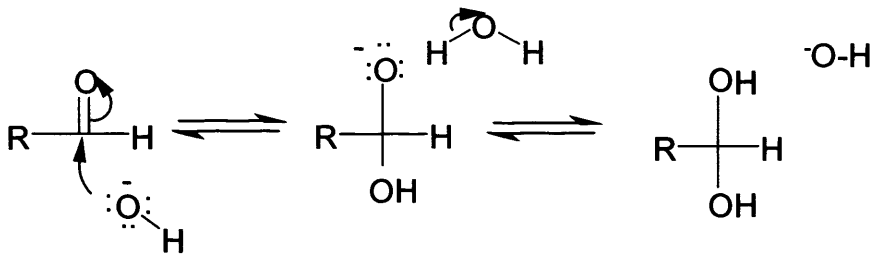
(eq. 1.22)

In the presence of acid, the carbonyl group of the aldehyde undergoes an addition reaction (scheme 1.7):



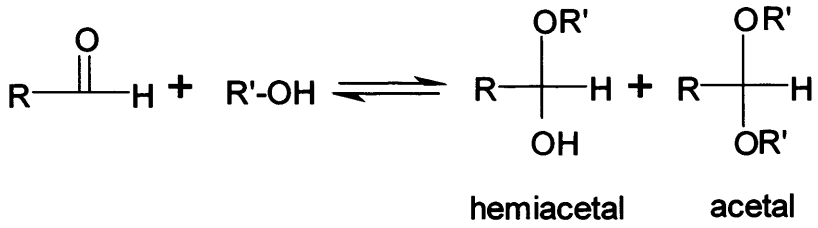
Scheme 1.7 Reaction mechanism of acid catalysed aldehyde transformation.

For the base catalysed reaction the mechanism is the following (scheme 1.8):



Scheme 1.8 Reaction mechanism of base catalysed aldehyde transformation.

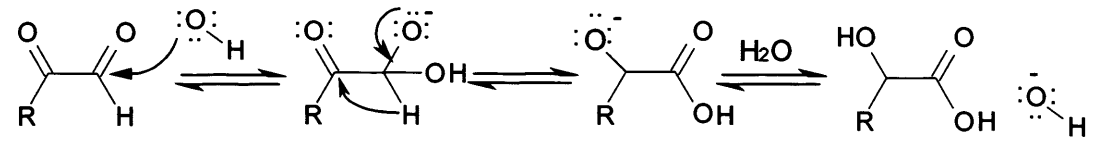
In the presence of alcohol, its hydroxyl group would act like OH group in water and the overall reaction will be (scheme 1.9):



Scheme 1.9 Reaction mechanism of hemiacetal and acetal formation.

The formation of hemiacetal or acetal strongly depend on the amount of the alcohol present in the reaction mixture.

Another important reaction that should be highlighted is intramolecular Canizzaro reaction (scheme 1.10). This redox transformation takes place when a non-enolizable aldehyde is heated in the presence of strong base (see papragraph 1.7.2.2)



Scheme 1.10 Intramolecular Canizzaro reaction mechanism.

This exactly what happens when methyl glyoxal is tranformed into lactic acid in the

presence of NaOH as one of the steps of 1,2-propanediol oxidation [80].

These reaction mechanisms are important not only for understanding the chemistry of alcohol oxidation, they could also occur on the activated carbon support surface (as this material is produced from carbonaceous source materials, and different functional groups will always be present on its surface), thus being one of the possible reasons of catalyst deactivation.

1.9 Outline of thesis

This work formed part of the Glycerol Challenge project where Cardiff Catalysis Institute was responsible for the diols oxidation section. The aim of the project in this thesis is to find novel catalysts for the selective oxidation of 1,2-propanediol to lactic acid under mild conditions and preferably base-free. The summarized outline of this work is described below:

Chapter 1: Introduction

This chapter gives an introduction into catalysis, its history and the basics of catalysis, thermodynamics and kinetics. An overview of the mono- and polyalcohols oxidation to the corresponding acids and aldehydes over gold, palladium and platinum supported catalysts is presented.

Chapter 2: Experimental

This chapter will describe the main techniques used for characterization of catalysts and reaction mixtures. These methods include: X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), nuclear magnetic resonance (NMR), and high-

performance liquid chromatography (HPLC).The protocols of catalyst preparation will be also explained as well as a full description of catalytic activity measurements in different types of the reactors.

Chapter 3: Oxidation of 1,2-propanediol in basic media

In this chapter the selective oxidation of 1,2-propanediol in the presence of base will be described. The choice of support, alloying metal and reaction conditions will be discussed. The possibility of using bi-and trimetallic catalysts as well as tests on physical mixtures of monometallic catalysts will be evaluated. Longer reaction times will be tested to achieve 100% conversion. Kinetic studies will be carried out to understand the reaction profile as well as to determine the reaction order and activation energy. Reusability tests will be conducted to assess catalyst viability. Finally, the characterization of catalysts mentioned across the chapter will be given.

Chapter 4: Base-free oxidation of 1,2-propanediol

The studies on oxidation of 1,2-propanediol in the absence of base will be presented. The influence of temperature, pressure and reactor type on the results of the oxidation reaction will be investigated as well as the possibility of using physical mixtures and catalysts with lower metal loadings. Tests on oxidation of all possible intermediates both in the presence and in the absence of catalyst will be conducted to understand the by-product formation and the reaction mechanism under base-free conditions. Finally, reusability tests will be carried out.

Chapter 5: Oxidation of C_4-diols

This chapter describes the attempts to oxidize longer-chain diols. The full range of C_4-diols will be tested using the most promising catalysts for 1,2-propanediol oxidation. An enhanced 2,3-butanediol oxidation will be carried out to reach higher conversion values and to understand the reaction mechanism.

Chapter 6: Conclusions and future work

The overall conclusions and possible perspectives of the research work described in the thesis are given in this chapter.

1.10 References

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Chapter 2: EXPERIMENTAL TECHNIQUES

2.1 Introduction

In this chapter the methodologies for catalyst preparation and the reactors used for diols oxidation are described, as well as the theoretical principles of the instrumental techniques used to characterize both catalysts and reaction products.

Furthermore, the experimental procedures used to prepare and characterize the specific materials reported in this work, as well as the product characterization and testing for the diols oxidation, are described in detail.

2.2 Catalyst preparation

All the catalysts used for diols oxidation were prepared using two preparation techniques: impregnation [1] and sol immobilization [2], which were applied to synthesise catalysts supported on titania and activated carbons respectively.

These two methods were chosen due to the need to synthesise materials comprising one metal as well as bimetallic and trimetallic catalysts, with high reproducibility in the preparation procedure. It is known that small variations in the preparation procedure might have a significant effect in the final catalytic performance [3, 4]. Therefore the impregnation method was used for its high reproducibility while the sol immobilization has the additional feature to lead to a narrower particle size distribution, which is another crucial factor to determine the catalytic activity [5,6].

2.2.1 Impregnation method

In the impregnation method, the metal precursor, usually in form of a salt, is dissolved in a solvent and impregnated in the support, which can be present either in form of powder or pellets or granules. Afterwards the sample is dried to eliminate the solvent and then calcined at a temperature within the range typically of 200 to 500 °C. This is the most important parameter to control in this procedure, as different calcination temperatures can lead to different activity [7,8]. In the current work a calcination temperature of 400 °C was used. A variation to this protocol is the incipient wetness impregnation [9]. In this case, the amount of solvent used is only to fill the pore volumes of the support.

The impregnation method is the most used in industrial context, mainly for economic reasons, due to full inclusion of precursor metal within the support material [10], which is not true for the deposition precipitation technique [11, 12] where metal nanoparticles are formed and deposited on the support by changing the pH of the precursor solution. Despite it is a widely used method to prepare metal nanoparticles over metal oxides, usually the final amount of deposited metal is less (up to 50%) of that of the original solution, particularly when gold is used [13].

2.2.1.1 Preparation of Au, Pd, and Au-Pd catalysts over titania

A series of catalysts were prepared supported on titania using an impregnation technique. 5 wt% Au/support, 5 wt% Pd/support, and a range of Au-Pd/support catalysts were prepared by impregnation of the support using aqueous solutions of palladium chloride and hydrogen tetrachloroaurate.

As an example, the detailed procedure for the preparation of the 2.5%Au-2.5%Pd supported catalyst is as follows: $PdCl_2$ (Johnson Matthey, 83.3 mg) was dissolved in a heated and stirred aqueous solution (5 ml) of $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey, 5 g, in 250 ml of deionised water). The resultant solution was added to the TiO_2 support

(Degussa, P25, 1.9 g) and the resulting slurry was dried at 100 °C for 16h. The obtained powder was ground and calcined (1g, 6 inch quartz boat) in static air at 400 °C for 3 hours at a ramp rate of 20 °C min^{-1}. The calcination temperature was chosen to have a final particles size distribution in the range of 20 nm.

All other catalysts were prepared by the same experimental procedure adjusting the amount of metal precursor in the starting solutions to give the desired metal loading.

2.2.2 Sol Immobilization method

In this preparation technique, metal nanoparticles are obtained by reducing the metal salt precursor and by stabilizing them with a suitable protecting agent in order to obtain a colloid, known as a sol [14]. The resulting solution is then impregnated, *i.e.* the metal nanoparticles are immobilized on the support in acid media. The catalyst is afterwards calcined at low temperature in air to remove the protecting agent. The most common reducing and protecting agents are $NaBH_4$ and polyvinyl alcohols respectively.

Unlike the impregnation method, where the particles size usually varies in a wide range of 2-30 nanometres [15], the sol immobilization method allows a much narrower interval, usually in the range of 2-5 nm [16], and this is useful to control the catalytic activity. Actually, while in the impregnation method the metal deposition on the support and the particle formation depend on the gradient concentration of the precursor solution inside the pores of the support, in the sol immobilization the nanoparticles are obtained before deposition, with clear advantage to a final uniform particle size distribution.

2.2.2.1 Preparation of Au, Pd, Pt, Au-Pd, Au-Pt, Pd-Pt and Au-Pd-Pt catalysts over activated carbons

A series of Au, Pt, Pd, Au-Pd, Au-Pt, Pd-Pt and Au-Pd-Pt catalysts supported on activated carbons were prepared using a sol-immobilisation method, using $NaBH_4$ as a

reductant, polyvinyl alcohol as a protecting agent and aqueous solutions of metal precursors of palladium chloride, hydrogen tetrachloroaurate and potassium tetrachloroplatinate. Different kinds of carbons were also used, namely: Aldrich G60, KB and KB-B, which differ in the surface area and the pH (water extract).

As an example, the detailed procedure for the preparation of 2 grams of the 0.5% Pd - 0.5% Au supported bimetallic catalyst is as follows: $PdCl_2$ (Johnson Matthey, 5 g solution in 50 ml of deionised water) and $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey, 5 g solution in 250 ml of deionised water) were prepared. 0.816 ml of $HAuCl_4 \cdot 3H_2O$ and 0.417 ml of $PdCl_2$ were dissolved in 1 L of deionised water. To this solution polyvinyl alcohol (PVA) (Aldrich, 1 wt % solution, average molecular weight MW = 9,000-10,000 g/mol, 80% hydrolysed) was added (PVA/Au (wt/wt) = 1.2, 2,4 ml). Subsequently, a freshly prepared 0.1 M solution of $NaBH_4$ (Aldrich, assay > 96%), using a $NaBH_4$/Metal molar ratio of 5 (6.875 ml), was added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilised by adding 1.98 g of activated carbon (acidified to pH 1 by sulphuric acid) under vigorous stirring. The amount of support material required was calculated to give a total final metal loading of 1wt%. After 1 h the slurry was filtered, the catalyst washed thoroughly with distilled water and dried at 110 °C overnight.

The same experimental procedure was used to prepare other catalysts by adjusting the metal precursor solutions to the desired metal loadings. For catalysts containing platinum, K_2PtCl_4 (Johnson Matthey, assay 99%) was used as precursor.

Reproducibility of the catalyst coming from different batches was confirmed by a series of catalytic tests (3 repeated tests per any new batch). In all cases the catalyst had the same catalytic performance within 2-3% absolute error.

2.3 Catalyst characterization

The catalysts were characterized using different techniques aimed to identify: a) particle

size and morphology of the catalyst, b) surface area, c) control tests on metal leaching and d) the surface composition and oxidation state of the metal supported nanoparticles. The instrumental techniques used to perform the characterization, and the specific experimental conditions used for the catalyst prepared here are described.

2.3.1 X-ray diffraction

X-ray diffraction (XRD) is a bulk technique employed for several purposes, including: i) identification of crystal phases in minerals, catalysts, ceramic, ii) determination of crystallinity level in partially crystalline mixtures, iii) determination of the crystal structure of identified materials and iii) particle size determination [17].

In the presented thesis work an important variation of X-ray diffraction known as X-ray powder diffraction (XRPD) was used. This technique allows the analysis of the sample in the form of a powder, without the need of a single crystal [18]. This is particularly helpful in the analysis of heterogeneous catalysts which are often present in powder form.

2.3.1.1 X-ray generation and Bragg's law

A schematic of the X-ray generation process is reported in Figure 2.1. In this scheme, high energy electron interacts with the inner electrons of a target material removing an electron from the inner orbital. The electron vacancy created is immediately filled by an electron transition from an outer orbital. This transition process generates an X-ray photon of equal quantum energy to the transition.

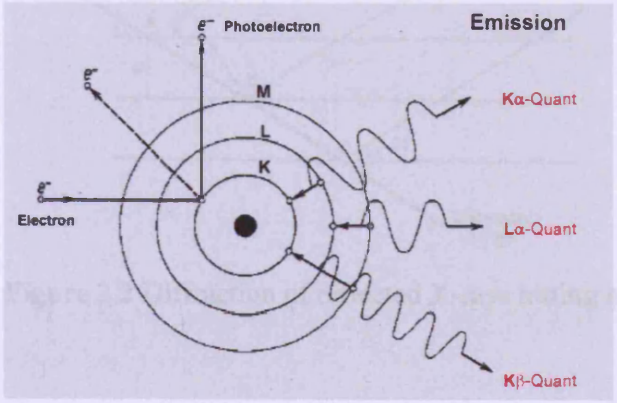

Figure 2.1 X-ray generation process

In common practice, X-rays can be obtained using three different procedures, namely: 1) generation by electrons: high energy electrons (known as a primary electron, usually generated by a hot tungsten filament) impact a metal target, the most common are made of Cu or Mo, and less frequently of Co, Fe or Cr, 2) generation by photons: by the use of photon radiation from an X-ray tube which ionises the sample atoms. The result is a photon emission known as X-ray fluorescence (XRF) and 3) by radioactive decay processes [17]. In this project the first method of using a Cu target source was used.

X-rays follow the same rules for all electromagnetic radiation, and therefore they are susceptible to diffraction. Obviously the necessary condition for diffraction is a long order range summed up with a distance between crystal planes in the same order of magnitude of the incident X-ray radiation. That is also why Cu, with a radiation wavelength for the K_α component of 1.54 Å, is widely used in generating X-rays.

In view of this, when an X-ray beam encounters a three dimensional lattice array of atoms, the X-rays will be scattered by adjacent atoms thus leading to both constructive and destructive interference. The first case occurs when the X-ray beams have a path difference equal to a whole wavelength number $n\lambda$, while for all other values destructive interference is present.

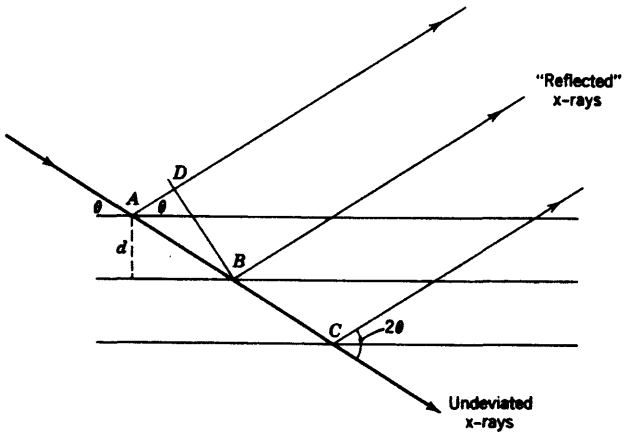

Figure 2.2 Diffraction of reflected X-rays hitting an ordered series of crystal planes

Using trigonometry (see Fig. 2.2) the path difference can be calculated as 2d *sin* θ, where *d* is the spacing between crystal planes and θ the incident angle of the radiation, (eq. 2.1) can be written as:

$$n\lambda = 2d \sin\theta \qquad \text{(eq. 2.1)}$$

This is known as Bragg's law [18]. Bragg's law is central to XRD practice and it can be applied to both single crystals and crystalline powders. However, in the latter case because of the random orientation of the crystallites forming the powder, it must be underlined that the resulting total diffraction is not a single diffracted beam, but a diffraction cone, as displayed in Fig. 2.3.

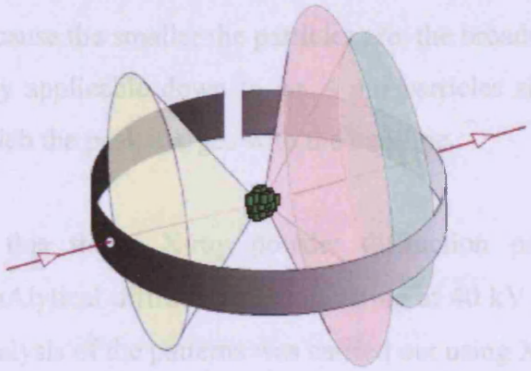

Figure 2.3: Diffraction cones from a powder crystalline sample.

This has implications for the geometry of the instruments used for single crystal or powder analysis, for which, the most important implication is that a 2-dimensional diffraction pattern from a powder sample is, in reality, a 2-dimensional section of a 3-dimensional diffraction cone.

2.3.1.2 Scherrer equation

One of the most common uses of X-ray powder diffraction in heterogeneous catalysis is

the determination of particle sizes, or crystallite size by the analysis of the width (broadening) of XRD peak. This effect is induced by the finite size of the crystallites, and becomes evident from particles sizes usually below 100 nm. Line broadening and crystallite sizes are correlated by the Scherrer equation [19], defined as:

$$L = \frac{K\lambda}{B\cos\theta} \qquad \text{(eq. 2.2)}$$

Where L is the diameter of the crystallite/particles (assumed to be spherical), K the shape factor and induces corrections for the shape of the particle (spherical, cubical tetrahedral or octahedral), θ is position of the reflection and *B* is the width of the XRD peak or 'total breadth of the reflection' in degrees.

Because the smaller the particles are, the broader the XRD peaks, the Scherrer equation is only applicable down to *ca.* 4 nm particles size as a lower determination limit, below which the peak merges with the baseline.

In this thesis X-ray powder diffraction patterns were acquired using an X'Pert PanAlytical diffractometer operating at 40 kV and 40 mA selecting the Cu K_α radiation. Analysis of the patterns was carried out using X'Pert HighScore Plus software. Crystallite sizes for the metal and metal oxide clusters were determined using the Scherrer equation assuming spherical particles shapes and a K factor of 0.89. The line broadening was determined using a Voigt profile function [20] convoluting the Gaussian and Lorentzian profile part of the reflection peak.

2.3.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is an analytical technique which allows determination of the structure of a solid sample down to atomic level, by means of the interaction of a high intensity electron beam (usually in the range of 200 KeV), which crosses the sample

and the electrons which are elastically scattered from the sample. This can be used to generate a two-dimensional image, which is typically acquired using fluorescence targets or charge-coupled device (CCD) cameras.

The typical resolution values of this method are nowadays in the range of 4-5Å [21], and if aberration corrected equipment is used, it is possible to reach angstrom or sub-angstrom resolution [22], with the incident radiation usually obtained by heated LaB_6 filaments [23].

Nowadays instruments coupled with energy dispersive X-ray spectrometers are also available [24], making then possible to build a chemical map of the sample.

Different instrumental designs can be used to obtain and acquire TEM images, but the most common is the one that uses the incident primary electron beam only (Fig. 2.4), in such case the resulting image is known as 'bright field image' and metal nanoparticles appear dark in a white background [24].

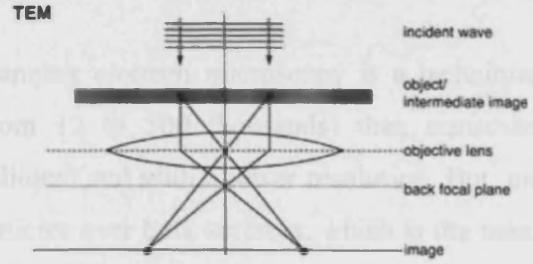

Figure 2.4. Primary electron beam crossing the sample for a bright field image [20].

If, in contrast, the detection occurs on scattered electrons, the resulting image is known as 'dark field image' and in this case metal nanoparticles appear as bright spots on a dark background. In the present work bright field images were acquired (Fig. 2.5).

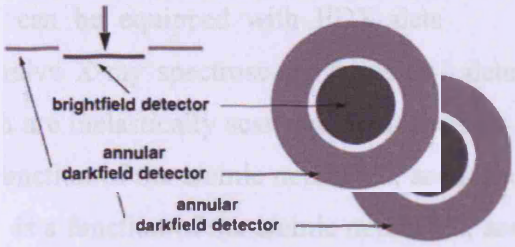

Figure 2.5. Signal detected from scattered electrons through the samples for a dark field image [20].

Taking into account the working principle of the instrument, although the samples do not require any particular pre-treatment, they need to be analysed at high vacuum. Most of the heterogeneous catalysts are prepared by grinding the samples in high purity methanol and then depositing a drop of this suspension onto a copper grid coated with a carbon film to hold the sample. A limitation of the method is that TEM requires thin samples, in the order of 100 nm [25].

2.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a technique that allows a much lower magnification (from 12 to 500 thousands) than transmission electron microscopy (that reach 10 millions) and with a lower resolution. But, unlike TEM, it can be used to analyze metal particles over bulk surfaces, which is the main limitation of the transmission microscopy technique [25]. Due to larger depth of focus it is an ideal technique for the investigation of highly corrugated surfaces, like those found in most heterogeneous catalysts [24]. Another distinct difference with TEM is the pre-treatment of the sample prior to the analysis, in case of morphology studies, for instance materials comprising metal oxides only. For SEM analysis the surface must be a conductor [26], therefore if the sample is not a metal, a metal coating is needed, and this is usually carried out using gold deposition. For SEM machines that can operate at low vacuum the coating is not necessary.

SEM can be equipped with EDX detectors like TEM. The principle of the energy dispersive X-ray spectroscopy relies on the analysis of the kinetic energy of electrons which are inelastically scattered from the sample [24]. Kinetic energy of these electrons is a function of the atomic number Z, and this allows to carry out a chemical analysis of the composition of the sample. This is particularly useful for the mapping of metal nanoparticles over metal oxides or carbons, which are difficult to mineralise and to analyse using atomic absorption spectroscopy, and they often require X-ray fluorescence to be quantified [27].

A schematic of a SEM equipment to compare with TEM, is reported below in Fig. 2.6.

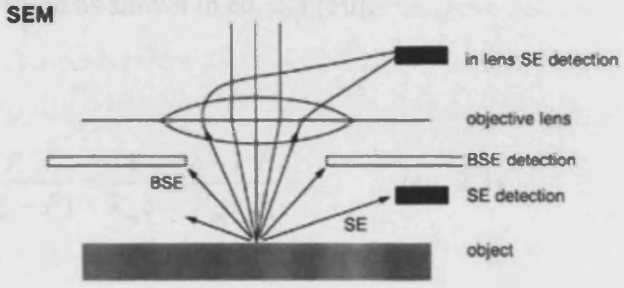

Figure 2.6. SEM detection. Please note that in comparison with TEM, the electron beam does not cross the sample, but the signal is collected from back scattered electrons [24].

SEM-EDX was used to characterize some of the catalysts prepared using a Carl Zeiss Evo-40 SEM instrument, equipped with Oxford instruments energy dispersive X-ray elemental microanalysis.

2.3.4 Surface area determination, the Brunauer, Emmett and Teller method (BET)

The vast majority of the surface area determinations in catalysis make use of the Brunauer, Emmett and Teller (BET) model [28] which is considered an extension of the Langmuir adsorption theory [29]. Such methodologies rely on the formation of layers of an adsorbate species to determine the surface area of a solid. In case of the Langmuir

isotherms the layer of adsorbate is only one layer. In practice the formation of multilayers of adsorbate is possible, and this is taken into account by the BET model by assuming that the heat of adsorption for all the layers is equal to the heat of condensation of the adsorbate, with the only exception of the first layer. Therefore, knowing the surface area of the adsorbed molecule and the total volume of the probe gas used for the determination adsorbed over the catalyst, it is possible to determine the surface area of the solid.

Usually the adsorbed molecule is nitrogen, and therefore measurements are carried out close to the liquid nitrogen temperature of 77K. In these conditions the adsorption isotherm of the volume of adsorbate V versus the relative equilibrium pressure P/P_0, can be written as shown in eq. 2.3 [30].

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\frac{P}{P_0} \qquad \text{(eq. 2.3)}$$

Where V_m is the volume of the monolayer, P_0 the standard pressure of the adsorbate and c is a constant that correlated with the adsorption/desorption equilibrium of the adsorbate over the surface, and therefore with the enthalpy, ΔH, of the adsorption process.

It is then possible to plot a linear correlation of $\frac{P}{V(P_0 - P)}$ versus $\frac{P}{P_0}$, and because P_0, P and V are experimental data, from the intercept and the slope of this straight line to calculate V_m.

In the present work, surface area determination were carried out using a Micromeritics ASAP 2000 instrument operating with liquid nitrogen. Samples were outgassed in nitrogen atmosphere at 120 °C for 4 h to eliminate adsorbed water.

2.3.5 Atomic Absorption Spectroscopy (AAS)

Atomic absorption is used for the analysis of trace metals in a variety of samples, from inorganic materials to biological samples, where the sample is converted from a solid or most commonly a liquid form, to an atomic gas [31]. There exist two general methods of converting: electrothermal atomization and flame atomization, the latter being used in the present work using an acetylene/air flame. The most common way to introduce a sample into a flame atomizer is a continuous aspiration, in which sample is continuously passed through the burner while monitoring changes in the absorbance of an incident UV radiation through the flame. The UV radiation is obtained by means of a hollow cathode lamp made of the same metal to be analysed, and the amount of metal is obtained from absorbance data compared with the absorbance of standard solutions.

A schematic of the flame atomizer and the aspiration system is reported below (Fig. 2.7).

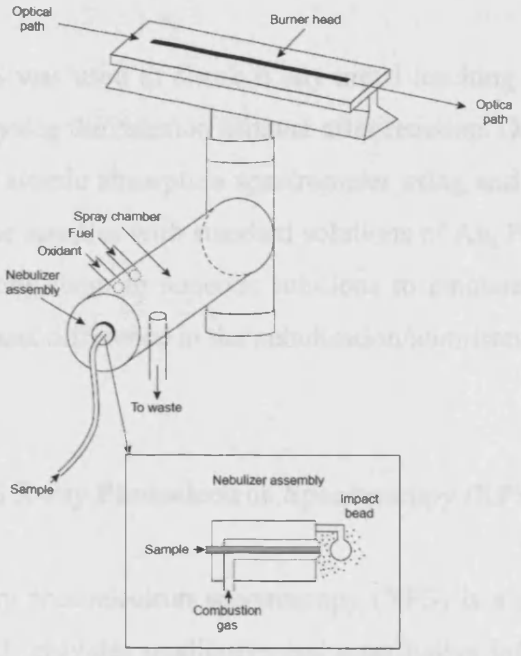

Figure 2.7. Diagram of the flame burner and aspiration system for an atomic absorption spectrometer [32].

The main advantage of this technique is the reproducibility with which the sample is introduced for further analysis (continuous aspiration and subsequent nebulisation to an aerosol), whereas the main disadvantage is poor efficiency of atomization [33] due to the low temperature that can be reached to carry out this process, usually in the range of 2300 °C for an air/acetylene flame, and ca. 2700 °C for a N_2O/acetylene flame. Moreover, if the aerosol droplets are too large the sample may be diluted by a large volume of combustion gases, which can introduce further sources of errors.

Another aspect that needs to be carefully evaluated when performing AAS is the possible presence of systematic errors in the amount determination induced by differences in viscosity and acidity of standard solutions and samples to be analysed. This may influence the aerosol formation process, and in turn the amount of metal through the burner versus time [34]. Additionally, there exists an interference phenomenon when more metals are present on the same catalyst, and this should be taken into account when calculating the values of metal concentration.

AAS was used to check if any metal leaching was present after reproducibility tests, by analysing the reaction mixture after reaction. Determinations were carried out using a AA 55B atomic absorption spectrometer using and air/acetylene flame, comparing the signal of the samples with standard solutions of Au, Pd and Pt (Aldrich, 1000 ppm, in 1M HCl), diluting them in aqueous solutions to emulate the reaction media in order to take into account difference in the nebulisation/atomisation processes.

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique [35,36] which provides qualitative and quantitative information of the atoms present on the top layers of a solid substance. It can be used to determine the surface atomic composition of a solid including the oxidation state of the atoms and therefore allows to gain information on the chemical environment in which the atoms are confined [37]. This is particularly

useful in catalysis, where metal active species may exist in different oxidation states, or may be oxidized or reduced during the reaction, therefore allowing more accurate insight in the catalyst behaviour and in the identification of the active species [38]. The samples are analysed in ultra high vacuum conditions, typically 10^{-10} Torr, and usually at room temperature.

The inner principle of the XPS is the photoelectric effect, which is induced by incident X-ray radiation (and hence the name of this method). In the photoelectric effect, an atom absorbs a photon of energy $h\nu$ and a core or valence electron specific for that atom and its oxidation state, is ejected with kinetic energy E_k, in agreement with the equation reported below (eq. 2.4) [39].

$$E_k = h\nu - E_B - \phi \qquad \text{(eq. 2.4)}$$

Where E_B is the binding energy of the electron and ϕ is defined as the 'work function', *i.e.* the difference between the vacuum energy level of that electron and the 'Fermi energy', which, is the energy of an electron in the highest occupied molecular orbital in the valence band at absolute zero temperature (Fig. 2.8).

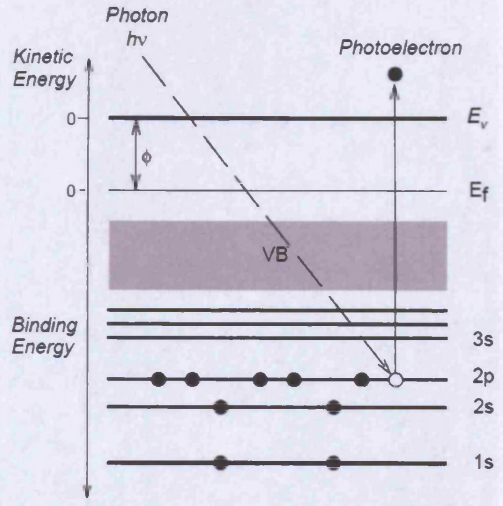

Figure 2.8. Photoemission process from a surface; the symbols used means: E_v, energy of the vacuum level, E_f, Fermi energy, and ϕ work function.

In other words, the excited electron propagates from the solid to the surface and further emits to the vacuum. It is worth mentioning that this is possible only when the electron has a kinetic energy contribution which is higher than that needed to reach the surface. This relates to the mean free path of the electron [40], which is in the range of few nanometres, or few atoms layers. That is why XPS is a surface technique. Electrons in the bulk of the solid are expelled from the atoms, whereas the electrons close to the surface of the solid have a distance which is shorter than their mean free path, and therefore they can be expelled and detected.

The binding energy of the photo-emitted electrons gives qualitative information on the atomic composition (and oxidation state), while the number of counted electrons gives information on the amount of species on the surface.

In this thesis, XPS was used to determine both the surface composition of the catalysts and the oxidation states of the metal nanoparticles deposited over the titania and carbon support. The spectra were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic AlK_{α} X-ray source (120 W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples were mounted using double-sided adhesive tape and binding energies referenced to the C(1s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV

2.4 Catalyst testing

2.4.1 Types of reactors used

In order to evaluate catalyst activity, different types of reactors have been used. A round bottom flask reactor with condenser was used for testing at atmospheric pressure, Radley's glass reactor was used for the experiments at low pressures (0.5-3 bar) and experiments at higher pressures were obtained in HEL autoclave.

2.4.1.1 Radley's low pressure glass reactor

Alkali metal bases (2, 1, 0.5 or 0.25 eq. to alcohol) in the form of powder for LiOH, NaOH and KOH and commercially available solutions of RbOH and CsOH were dissolved in C_3- or C_4- diol (20mL, 0.6M aqueous) in a Radley's reactor flask. Catalyst was added to the solution (substrate to metal molar ratio, s:m=2000-8000). The round bottom flask was charged with oxygen (3, 2 or 1 bar), raised to the required temperature (40°C - 115°C), stirring constantly using magnetic stirrer bar. The solution was heated at the appropriate temperature for 4-24 hours. The reactor flasks were cooled down to the room temperature, the system was depressurised and the reaction mixture was then filtered off and further analysed.

2.4.1.2 High pressure autoclave reactor

Reactions were carried out using a 100ml HEL autoclave reactor system with anchor magnetic stirring. Catalyst was added to 40 ml of 0.6M aqueous solution of 1,2-propanediol (s:m=2000-8000) in the vessel. The vessel was charged with oxygen to the desired pressure (3 or 10 bar), raised to the required temperature (40-100 °C) and upon reaching the required temperature stirring was started. The solution was heated at the appropriate temperature for the desired amount of time (4-24 hours). Sampling was carried out hourly at the beginning of the experiments and then occasionally in the middle and close to the end, i.e. 1 h, 2 h, 3 h, 4 h, 8 h, 24 h and 72 h.

Pressure and temperature values were chosen to explore mild reaction conditions and to satisfy safety requirements of the equipment used.

2.4.1.3 Round bottom flask glass reactor

The setup for experiments at atmospheric pressure consists of a three-neck round bottom flask with thermometer, reflux condenser (water-jacketed) and a heating source (oil bath

and hotplate). The whole setup was connected to an oxygen gas line. Catalyst (s:m=2000) was added to the solution of 1,2-propanediol (20mL, 0.6M aqueous). Oxygen was bubbled in to the reaction mixture at atmospheric pressure (with the rate of 100 ml/min) for 24 hours after the system was heated up to 100 °C. The losses of reaction mixture volume were evaluated using measuring cylinder by substracting the volume of reaction solution after the experiment is over from the initial volume (normally 20 ml).

Reactions in the absence of base were carried out as described above except the addition of base was omitted.

2.4.2 Characterization of products

Nuclear magnetic resonance and high-performance liquid chromatography were carried out for the characterization of reaction products. Also the description of the techniques and examples of conversion and selectivity calculations are reported.

2.4.2.1 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is extensively used to characterize organic products. The physical principle of this analytical tool is the resonant absorption of radio frequency radiation by nuclei exposed to a magnetic field [41], which can be summarised in figure 7, where the case of a ^1H nucleus which has spin number I=1/2 is considered.

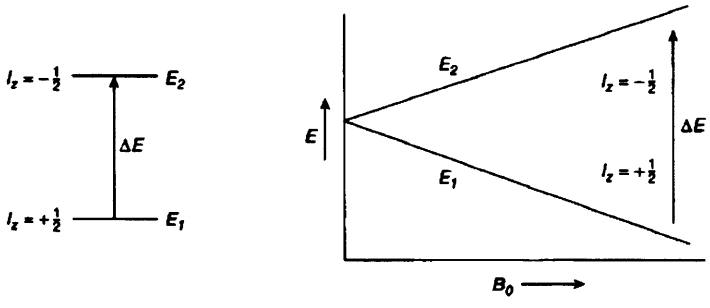

Figure 2.8. Energy difference between spin states as a function of the external magnetic field B_o at resonance condition [42].

If a magnetic field B_o is applied, a splitting of the energy levels is observed, with separation of the population of nuclei with angular momentum I_z +1/2 and I_z -1/2 [43]. This is described by the equation 2.5:

$$\Delta E = \frac{h\gamma}{2\pi} B_o \qquad \text{(eq. 2.5)}$$

Where ΔE is the energy level separation, h the Plank constant, γ the magnetogyric ratio and B_o the intensity of the magnetic field. The resonance condition, is reached when the energy separation of the levels α and β is equal to the energy of the photons in the electromagnetic field as expressed by the equation 2.4.

$$\Delta E = h\nu = \frac{h\gamma}{2\pi} B_0 = h\nu_L \qquad \text{(eq. 2.6)}$$

where ν_L, Larmor frequency, is the frequency at which the nucleus resonates, and ν, the frequency of the applied magnetic field.

An interesting property of the resonance condition is that nuclear magnetic moments can interact with the local magnetic field due to the nucleus environment. This effect is known as 'shielding constant' and allows identification of protons bonded to different functional groups, because they will resonate at slightly different frequencies, *i.e.* different chemical shifts, therefore allowing qualitative determination of a compound.

It should be underlined that not all the nuclei are NMR active, but only those which have a spin angular momentum number $I \neq 0$. This is the case, for instance of ^{1}H, which has I=1/2 as well as ^{13}C, ^{19}F, ^{31}P; and nuclei such as ^{14}N and ^{2}H, which has I=1. In contrast, nuclei like ^{12}C and ^{16}O cannot be NMR active because they have I=0 [37].

The nuclei most widely used in NMR are ^{1}H and ^{13}C and for several reasons: i) they are the most abundant in organic compounds, and ii) they possess a high magnetogyric ratio γ ($267 \cdot 10^6$ and $67 \cdot 10^6$ rad s^{-1} T^{-1} respectively) which reflects in analysis with high

sensitivity [39].

It is also useful to note that ^{2}H, despite having a I=1, and a magnetogyric ratio of *ca.* $41 \cdot 10^{6}$ rad s^{-1} T^{-1} is not detected at the frequency used to collect ^{1}H-NMR spectra, making it 'NMR silent', this is a very functional property and that is why NMR solvents are deuterated.

Finally, coupling among nuclei is also possible, leading to further energy level splitting known as 'coupling constants', J, which can be a further useful diagnostic tool for the qualitative identification of organic compounds.

For the analysis of the reaction mixtures, ^{1}H-NMR spectra were acquired using a Bruker 400 MHz DPX system equipped with a 5mm auto tune broadband probe over a 16 scan period. All samples were prepared for NMR analysis using D_2O as a solvent. Sample NMR spectrum of reaction mixture in the end of the reaction is given in Appendix A.

2.4.2.2 High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) is a method of separation and analysis of mixtures. It involves a sample (or sample extract) being dissolved in a liquid mobile phase. The mobile phase is then forced through an immobile, immiscible stationary phase, at a pressure of *ca.* 100 bar [31]. The phases are chosen so that components of the mixture have differing solubilities, or affinity, or polarity in each phase.

A component which displays affinity to the stationary phase will take longer to travel through it than a component which does not. As a result of these differences in affinity among components, these components will become separated from each other as they travel for a sufficient length through the stationary phase. A schematic diagram of a typical HPLC instrument is shown in Figure 2.9.

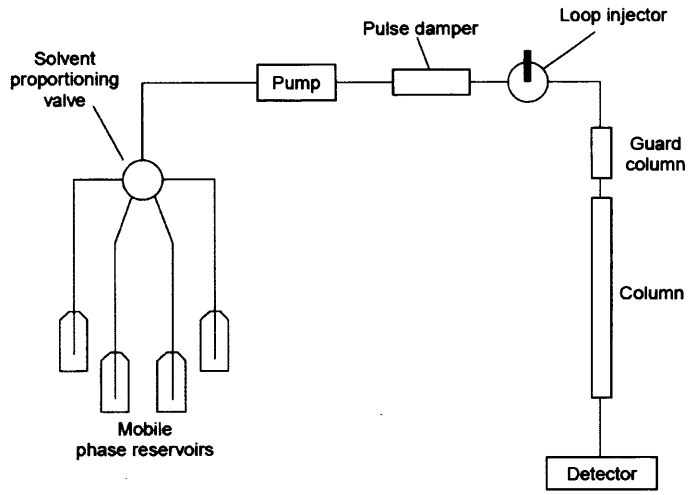

Figure 2.9. Schematic diagram of a high-performance liquid chromatograph equipped for solvent gradient mixtures [32].

In this thesis reverse-phase chromatography has been used, where the stationary phase is non-polar and the mobile phase is polar (H_3PO_4 in H_2O). Modifier is used for controlling pH and suppression of analyte's ionisation, which results in a better peaks shape [44].

In detail, HPLC analysis was carried out using a Varian 920-LC liquid chromatograph 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) with a flow of 0.3 ml min^{-1}. Samples of the reaction mixture (0.5 ml) were diluted using the eluent (4.5 ml) prior to injection to a 20 μL sample loop. Products were identified by comparison of the retention times with standard samples. Product stability was confirmed by analysing the same calibration standards at regular interval (monthly). Sample chromatogram is given in Appendix A.

2.4.2.3 Conversion and selectivity calculations

The data obtained from NMR and/or HPLC analysis were used to calculate conversion *C*, and selectivity *s* values according to the eq 2.7 and 2.8 below:

Conversion equals:

$$C = \frac{\Sigma c_i}{\Sigma c_i + c_{sm}} \qquad \text{(eq. 2.7)}$$

In turn, selectivity can be calculated in the following way:

$$S = \frac{c_i}{\Sigma c_i} \qquad \text{(eq.2.8)}$$

Where c_i is the concentration (from peak area) of products formed and c_{sm} is the concentration (from peak area) of the starting material left at the end of the reaction.

The procedure of quantifying the amount of products formed and of the consumption of the starting material using HPLC technique is described below. Firstly, calibration curves were plotted using the values of peak areas for calibration standards (all substances that may be found in the reaction mixture) against given (known) concentrations. Secondly, response factors for each substance were calculated (as the slopes of the calibration curves). Finally, the concentrations of products in the reaction mixture were the result of multiplication of a peak area and a response factor of each substance. These data were further used to calculate conversion and selectivities according to the eq. 2.7 and 2.8.

Quantification of products from NMR spectra is much more straightforward. Integration values of every component found in the reaction mixture were used directly in the eq. 2.7 and 2.8. instead of concentration (taking into account the number of protons, *i.e.* signal from –CH group is 3 times less that that of $-CH_3$ group).

Closed carbon mass balance could be estimated from NMR data within 5% error. However, an accurate estimation of the mass balance (including also CO and CO_2) was not possible due to problems with sampling of gaseous products (see paragraph 3.3.1)

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Chapter 3: OXIDATION OF 1,2-PROPANEDIOL IN BASIC MEDIA

3.1 Introduction

In this chapter, the results of 1,2-propanediol oxidation under basic conditions will be described, with the aim to drive the selectivity to lactic acid formation. Initially, a range of precious metal catalysts known for their activity in the oxidation of alcohols will be tested. After choosing the most suitable support, the alloying metal will be chosen and the metal ratio (in case of bimetallic catalysts) will be optimized. Once the most efficient catalyst is found, such factors as pressure influence and type of base will be tested. Furthermore, characterization of the catalysts used will be undertaken as well as testing for reproducibility. Finally, the results of recycling tests and tests for catalyst poisoning will be described.

3.2 Experimental

A range of different precious metal supported on different metal oxides or activated charcoal and graphite based catalysts were tested to oxidize 1,2-propanediol to lactic acid. Details of catalyst preparation are described in Chapter 2.

Catalytic activity measurements were carried out using several types of reactor varying from glass reactors to parallel multi-reactor systems. Details of these reactors are given in sections 3.2.1 and 3.2.2.

3.2.1 Studies in a glass reactor

Alkali metal bases (2, 1, 0.5 or 0.25 eq. to alcohol) were dissolved in 1,2-propanediol (20 mL, 0.6 M aqueous solution) in a round bottom flask. The catalyst was added to the solution (with substrate to metal ratio s:m=2000-8000). The round bottom flask was charged with oxygen (3, 2 or 1 bar) and the reaction mixture raised to the

required temperature (40°C - 80°C), under constant stirring. The solution was heated at the appropriate temperature for 4-24 hours.

3.2.2 Autoclave studies

Reactions were carried out using a 100 ml HEL autoclave reactor system with magnetic stirring. The catalyst was added to the solution (s:m=2000-8000) in the vessel, which was charged with oxygen to the desired pressure (3 or 10 bar), the reaction mixture heated to the required temperature (40-100 °C); upon reaching the required temperature, stirring was started. The solution was maintained at the appropriate temperature for the desired amount of time (4-24 hours) then cooled to room temperature.

3.3 Results and discussion

3.3.1 Investigation of reactor type

Catalyst performance was evaluated in several different reactor vessels, ranging from simple glass vessels to a high pressure autoclave.

The Radley's glass reactor is a simple instrument for catalytic investigation which allows operation at low pressures that do not exceed 5 bar above atmospheric; however, due to safety restrictions, it was recommended to work with no more than 3 bar pressures. It consists of a multi-pot base for 5 round-bottom flasks and a hotplate with the latter connected to a thermocouple to control temperature, and a gas plunger for delivering the desired gas inside of the glass reactors. The control unit on the hotplate panel allows control of both stirrer speed (a small or medium magnetic bar is usually used for this purpose) and temperature. Despite being easy to operate, this reactor has one major disadvantage: the possibility of taking samples is restricted, because of the need to depressurize the whole system before taking these. Therefore, classical sampling techniques like using a glass tap/suba seal arrangements and a small syringe with a long needle were not possible to apply. This may influence the

results, as once the reactor is repressurized again, at best more gas may fill the volume of a flask, at worst a change in the equilibrium is present by depressurizing not only the gas used as an oxidizer/reducer but also any other gases formed during the reaction.

The HEL high pressure autoclave reactor is a much more complex device which consists of eight independently controlled zones, offering both high and low pressure solutions and working volumes up to 500 ml. It has the advantage to mix and match up to eight different reactors of different sizes. It is constructed in a way that allows for independent temperature control and monitoring of each reactor at any time. Stirring is provided by means of an anchor bottom magnetic stirrer. Unlike the Radley's reactor, HEL autoclave allows the removal of samples at any time during an experiment without significant disruption. A further significant difference, when compared with the Radley's reactor, is the larger volume of reaction mixture (up to 500 mL) needed to carry out experiments.

A specially designed glass reactor at Imperial College London was also used for determination of mass transfer limitations and for checking the possibility of using air as an oxidant instead of oxygen. Details of this apparatus are given in section 3.3.3.8.

3.3.2 Oxidation of 1,2-propanediol over metal oxide supported catalysts

Precious metal nanoparticles are widely used as oxidation catalysts [1-3]. Thus, nanocrystalline gold catalysts can provide tuneable, active catalysts for the oxidation of hydrocarbons [4-6], the oxidation of carbon monoxide in the presence of hydrogen [7-9] and the partial oxidation of oxygen-containing molecules [10,11] *etc.* After careful screening the previous findings on alcohol oxidation it was decided to select Au, Pd and Pt supported on different oxides as these showed intrinsic activity as catalytic systems under basic conditions [12,13]. All catalytic tests have been carried out in a low pressure Radley's glass reactor. Table 3.1 shows the results of testing the variety of catalysts on different metal oxides supports.

Table 3.1. Conversion and selectivity in the 1,2-propanediol oxidation over metal oxide supported Au-Pd catalysts.

	5%Pd/ SiO_2 [a]	1%Au/ Al_2O_3 [b]	2%Au/ CeO_2 [b]	2.5%Pd+ 2.5%Au/ CeO_2 [a]	2.5%Au+ 2.5%Pd/ TiO_2 [a]	1%AuPd/ C[b]	5%Pt/ TiO_2 [c]
Conversion,%	0.6	9	11	10	25	15	0.4
Selectivity Lactic Acid,%	98	90	97	99.8	97	99	100
Selectivity Acetic Acid,%	0	7	2	0.2	1	1	0
Selectivity Formic Acid,%	3	3	1	0	2	0	0

Reaction conditions: 1,2-propanediol concentration=0.6 M, pressure=3 bar, NaOH=2 eq, T=60 °C, stirrer speed=1000 rpm, time=4 h.

[a] Catalysts prepared via impregnation (Impr) method.

[b] Catalysts prepared via sol immobilization (SI) method.

[c] Catalysts prepared via deposition precipitation (DP) method.

The results reported in Table 3.1 illustrate that reasonably high conversions and product selectivities can be reached by varying the support, the types of metal and the preparation method. Particularly, while all catalysts were capable of selectivities to lactate > 90%, the supports that showed higher conversions were TiO_2 and carbon, giving 15% and 25% conversion respectively, both including Au and Pd bimetallic catalysts.

3.3.2.1 Effect of the amount of base and metal ratio.

In view of the results reported in section 3.3.2, the best catalyst in terms of conversion is Au-Pd/TiO_2. To further investigate the impact of each metal, it was decided to prepare and test the whole range of Au-Pd/TiO_2 catalysts with variations from monometallic Au to monometallic Pd. Also it would be of interest to evaluate the influence of the amounts of NaOH used for this reaction; therefore tests using 1 and 2 eq of base were also carried out. The results are given in Fig. 3.1 A.

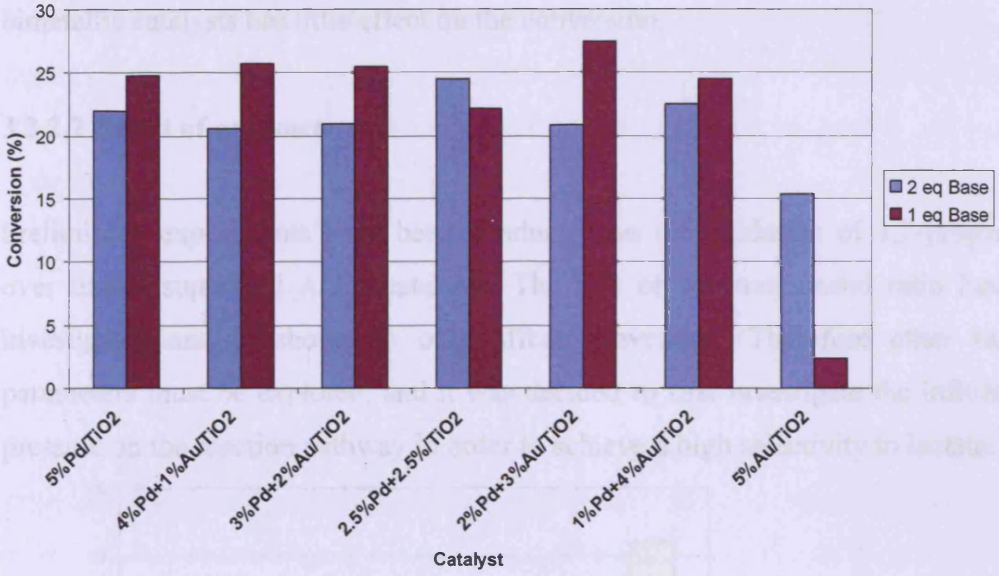
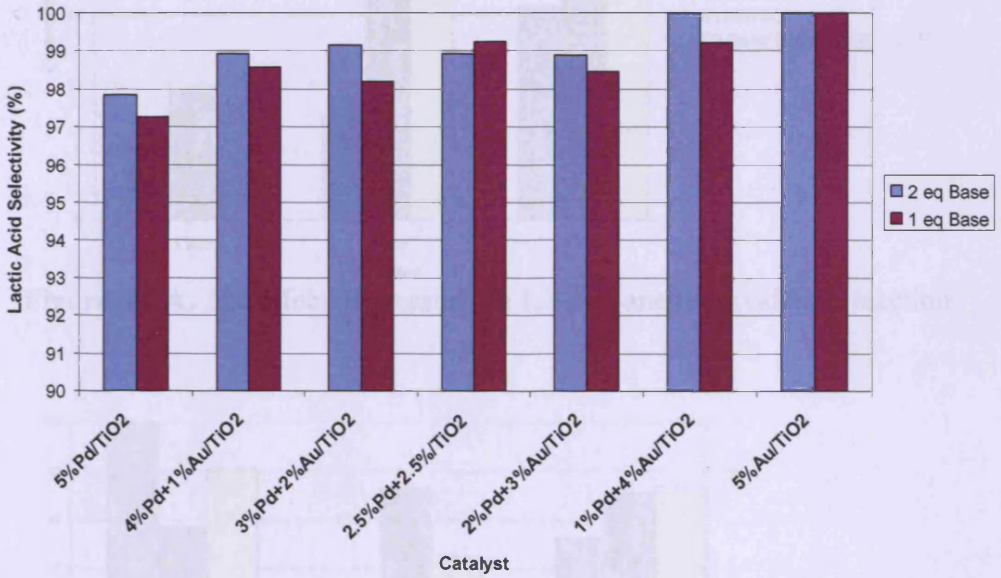


Figure 3.1 A. Test of catalysts with different Au-Pd ratio at 1 and 2 eq of NaOH



Reaction conditions: 1,2-propanediol concentration=0.6 M, pressure=3 bar, Base/1,2-propanediol molar ratio = 2 or 1, T=60 °C, stirrer speed=1000 rpm, time=4 h.

Figure 3.1 B. Selectivity values for tests of catalysts with different Au-Pd ratio at 1 and 2 eq of NaOH

After a reaction time of 4 hours, all bimetallic catalysts showed a higher conversion than monometallic Au/TiO_2 and Pd/TiO_2, but it is worth noting that 100% selectivity was reached only for monometallic gold catalyst and bimetallic $Au\text{-}Pd/TiO_2$ (4:1 molar ratio) catalyst (Fig.3.1 B). As can be also seen, the substrate metal ratio for

bimetallic catalysts has little effect on the conversion.

3.3.2.2 Effect of pressure

Preliminary experiments have been conducted on the oxidation of 1,2-propanediol over titania supported AuPd catalysts. The role of substrate metal ratio has been investigated and is shown to only affect conversion. Therefore other reaction parameters must be explored, and it was decided to first investigate the influence of pressure on the reaction pathway in order to achieve a high selectivity to lactate.

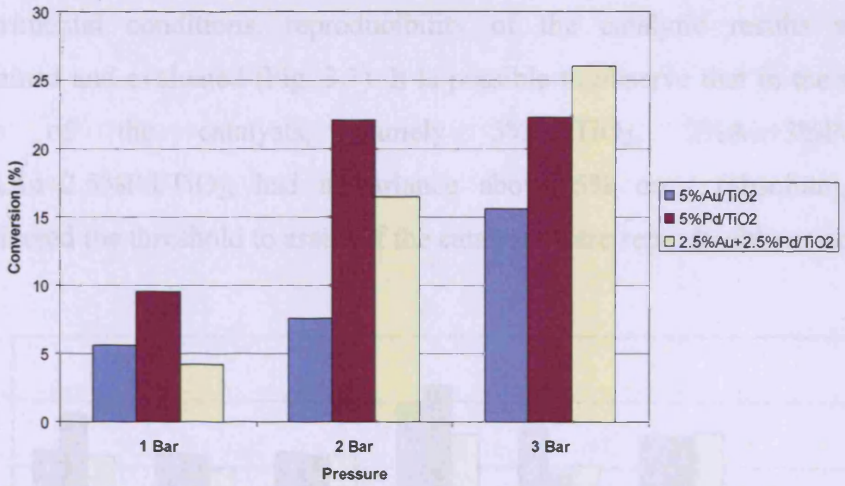
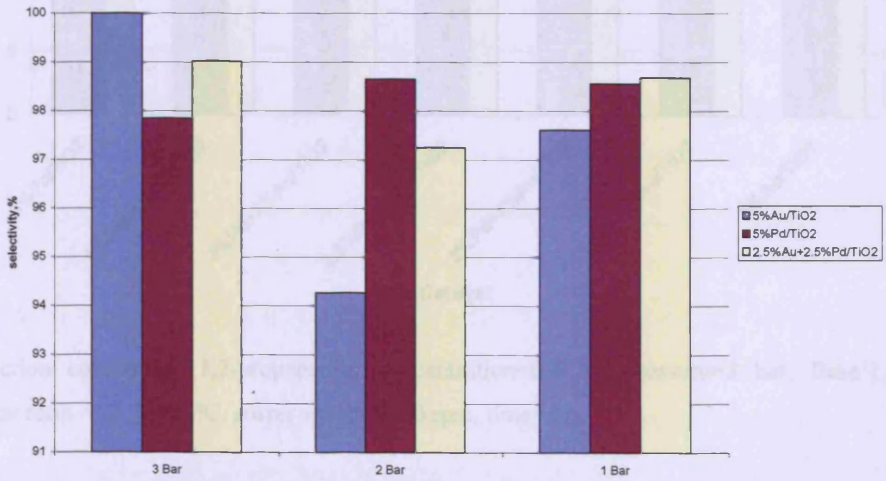


Figure 3.2 A. The effect of pressure on 1,2-propanediol oxidation reaction



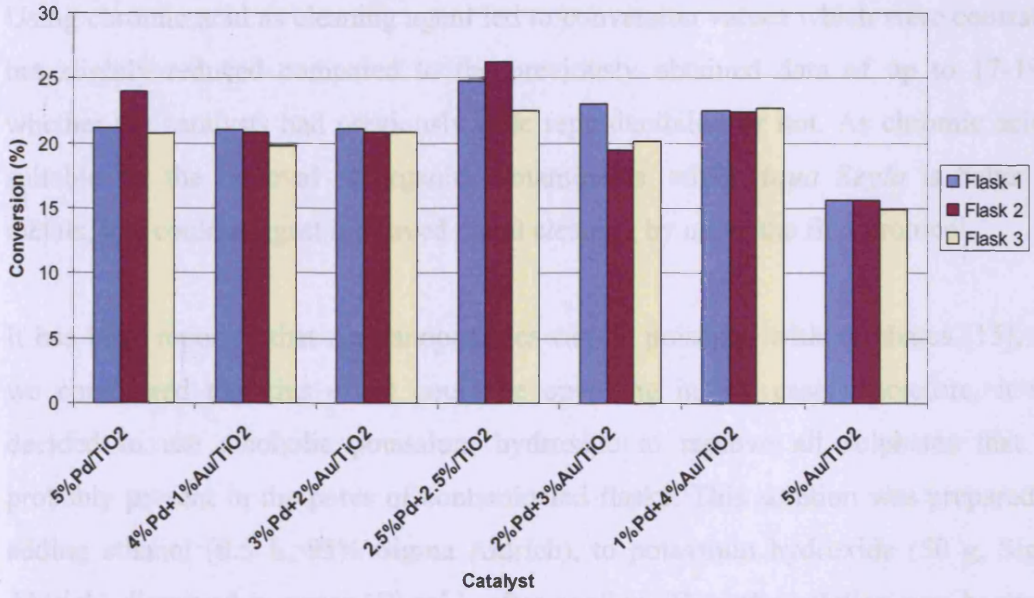
Reaction conditions: 1,2-propanediol concentration=0.6M, pressure=3, 2 or 1 bar, Base/1,2-propanediol molar ratio = 2, T=60°C, stirrer speed=1000 rpm, time=4 hours

Figure 3.2 B. Selectivity to lactic acid at different pressures

As shown on Fig. 3.2 A using higher pressures significantly increases the conversion (up to 25%), but 100% selectivity to lactic acid is obtained only for 5%Au/C catalyst (Fig. 3.2 B), whereas for the monometallic Pd and bimetallic Au-Pd catalysts, the selectivity varies from 94% to 98%.

3.3.2.3 Reproducibility tests

Because of the large number of catalysts to compare under a wide range of different experimental conditions, reproducibility of the catalytic results was carefully examined and evaluated (Fig. 3.3). It is possible to observe that in the set under test, three of the catalysts, namely 5%Pd/TiO_2, 2%Au+3%Pd/TiO_2 and 2.5%Au+2.5%Pd/TiO_2, had a variance above 5% error (absolute), which was considered the threshold to assess if the catalysts were reproducible or not.



Reaction conditions: 1,2-propanediol concentration=0.6 M, pressure=3 bar, Base/1,2-propanediol molar ratio = 2, T=60 °C, stirrer speed=1000 rpm, time=4 h.

Figure 3.3. Reproducibility tests on different Au and Pd catalysts supported on TiO_2 in the oxidation of 1,2-propanediol.

It was initially assumed that this lack of reproducibility for some of the catalysts could be due to ineffective cleaning of the reaction flasks after each experiment. *Aqua Regia* has been used earlier as a cleaning solution due to presence of gold residues in the reaction mixture. However, after 3 months of use, a thin, opaque coat at the bottom of every flask appeared, as well as small but visible scratches, diagnostic of ineffective removal of contaminants.

On this basis, it was decided to substitute *Aqua Regia* by chromic acid. The chromic acid solution was prepared using the following protocol [14]: technical grade potassium dichromate (Sigma Aldrich, 45 g) was placed in a beaker (2 L), and sulphuric acid (1.5 L, Aldrich, assay 98%) was slowly added under constant stirring until full dissolution of all the dichromate. The solution was left overnight to release any gases (sulphur oxides) and then placed into a desiccator and kept in a fume cupboard.

Using chromic acid as cleaning agent led to conversion values which were consistent but slightly reduced compared to the previously obtained data of up to 17-19%, whether the catalysts had previously little reproducibility or not. As chromic acid is suitable for the removal of organic contaminants, while *Aqua Regia* is better for metals, this could suggest improved metal cleaning by using the first protocol.

It has been reported that Au nanoparticles can be poisoned with sulphates [15], and we considered that this effect could be operating in our case. Therefore, it was decided to use alcoholic potassium hydroxide to remove all sulphates that are probably present in the pores of contaminated flasks. This solution was prepared by adding ethanol (0.5 L, 95% Sigma Aldrich), to potassium hydroxide (50 g, Sigma Aldrich) dissolved in water (50 mL), after cooling. Then the solution was heated to 65°C, and the glassware immersed for a maximum of 10 minutes. It is well known that even at ambient temperature, glass can be attacked by alkaline solutions of such strength, making glass surfaces translucent or opaque.

Using this procedure, a series of experiments with 2.5%Au+2.5%Pd/TiO_2 catalyst was carried out and the results were at an acceptable level of consistency (*ca* 23% conversion to lactate) and very close to the data obtained in the original set.

In view of this, the glassware cleaning procedure described has been used as a standard protocol throughout all the subsequent studies reported in this project. This also shows the importance that traces amount of contaminants can have in the assessment of the final catalytic performances, which is unsurprising, given the relatively small amounts of catalyst routinely employed. This has been further confirmed by a large number of studies in catalysis [16,17].

3.3.3 Oxidation of 1,2-propanediol over activated carbon supported catalysts

After having tested titania-supported catalysts and having evaluated their activity for 1,2-propanediol oxidation, our attention turned to the activated carbon supported catalysts, as such supports also showed an excellent performance in this reaction. It has been previously reported that carbon-supported transition metals can be used for liquid phase alcohol oxidation [18-21]. Moreover, extensive literature reports show that the addition of Au to Pd and Pt catalysts improves the catalytic activity and selectivity to the desired product [22-24].

3.3.3.1 The choice of alloying metal

The purpose of this section is to try to clarify which of the metals (or which combination of metals) is optimal for the oxidation of 1,2-propanediol. Therefore a range of Au, Pd and Pt catalysts comprising different metal amounts and their bi- and trimetallic combinations will be tested and the results obtained will be used hopefully to define an optimum catalyst constitution.

The oxidation experiments were carried out in a Radley's glass reactor using oxygen at 3 bar and a temperature of 40 °C. The amount of base, NaOH, was varied from 1 to 2 equivalents to starting diol to evaluate its influence on the catalytic properties of the supported metals. The data obtained as a result of these experiments are collected in a Table 3.2.

Table 3.2. Catalytic tests of mono-, bi- and trimetallic Au, Pd and Pt supported on activated carbon (KB-B) at different amount of NaOH

Entry	Catalyst	Amount of base	Conv. (%)	Selectivity, %					TOF (h^{-1})
				Lactate	Formate	Acetate	Hydroxy acetone	Pyruvate	
1	Au	2 eq	46	67	4	29	0	0	460
2		1 eq	30	62	3	35	0	0	300
3	Pd	2/1 eq	0	0	0	0	0	0	0
4	Pt	2/1 eq	0	0	0	0	0	0	0
5	Au-Pt	2 eq	50	92	2	6	0	0	500
6		1 eq	78	86	3	11	0	0	780
7	Au-Pd	2 eq	61	87	1	12	0	0	610
8		1 eq	52	81	2	17	0	0	520
9	Pd-Pt	2 eq	33	94	1	4	0	0	330
10		1 eq	22	96	4	0	0	0	220
11	Au-Pd-Pt	2 eq	72	91	1	8	0	0	720
12		1 eq	56	89	1	10	0	0	560

Reaction conditions: 0.6 M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, Base/1,2-propanediol molar ratio = 2 or 1, T = 40 °C, p = 3 bar, time = 4h

It is important to underline that, under these experimental conditions, the catalyst containing monometallic gold (table 3.2, entries 1 and 2) shows less than 50% conversion both at 1 and 2 equivalents of base. This is in contrast with literature results by Prati and Rossi [25] who reported that Au is the most active and selective for alcohols oxidation reactions. In addition, Pd and Pt supported catalysts are not active at all (entries 3 and 4). On the contrary, the activities of bimetallic catalysts and a trimetallic preparation show clear enhancements in both activity and selectivity to lactate, compared to monometallic gold. This indicates that the activity of bimetallic catalyst is enhanced by the presence of the second metal (either Au or Pd or Pt) and that a synergistic effect is present. The presence of base also influences catalytic activity for all catalysts except bimetallic 0.5%Au+0.5%Pt/C (entries 5 and 6). Bimetallic AuPt/C catalyst appeared to be the most active in terms of yield/conversion, and the anomalous effect of the amount of base on the reaction (i.e conversion at 1 eq of NaOH is nearly 20% higher than at 2 eq) is observed only for the AuPt system. It is an interesting phenomenon, unique to this particular catalyst

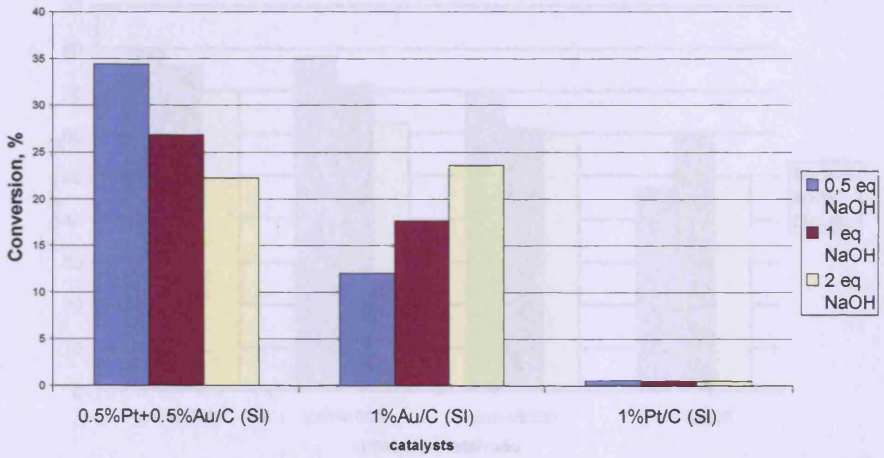
only, that the presence of a higher amount of base seems to inhibit the reaction probably by deactivating active sites of the catalysts. These results were repeated for reproducibility and the same trend was observed systematically from every test.

On testing different catalysts for 1,2-propanediol oxidation, we were able to demonstrate the effect of metal on the selectivity of the reaction. The selectivity towards the desired product – lactic acid – can be increased by introducing the second metal into the catalytic system, while the monometallic counterpart could not be necessarily active for the investigated reaction.

0.5%Au+0.5%Pt/C bimetallic catalyst seems to be the material that shows the highest activity and in view of this AuPt catalysts were further chosen for catalytic tests.

3.3.3.2 Effect of support

Several carbon matrixes with different surface areas, pore volume and pH, have been tested as supports for the preparation of catalysts for 1,2-propanediol oxidation. The first support to be tested was graphite powder (Sigma-Aldrich). This support has a very low surface area (*ca.* 10 m^2/g) and a particle size around 45 μm. Catalysts were prepared by a sol immobilization method [26,27] with Au and Pt used as active species. The results of testing these catalysts are show on the Fig. 3.4.



Reaction conditions: Radley's glass reactor, 1,2-propanediol concentration=0.6 M, pressure=3 bar, NaOH=2, 1 or 0.5 eq, T=60 °C, stirrer speed=1000 rpm, time=4 h.

Figure 3.4. Catalytic tests for graphite supported AuPt catalysts for the 1,2-propanediol oxidation

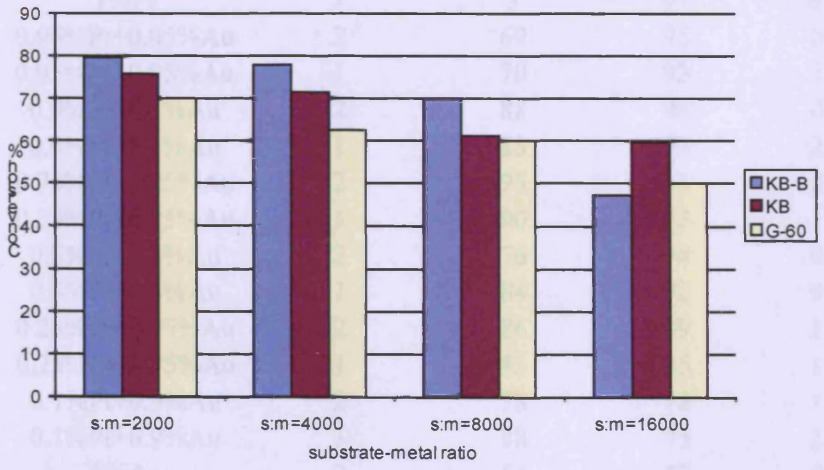
All of the graphite supported catalysts showed little activity with the conversions no higher than 35% but, like in the case of activated charcoal (KB-B) supported catalysts, synergistic effect can be detected.

Other carbon supports which were tested included Darco Sigma-Aldrich activated charcoals. These supports differ from one another by surface area, porosity, pH of water extracts and the amounts of iron and phosphates present. The data from Sigma-Aldrich specification sheets are given in a Table 3.3.

Table 3.3. Surface area, pore volume and pH of Darco Sigma-Aldrich supports.

Carbon	Surface area, m^2/g	Pore volume, ml/g	pH	Fe, ppm	Phosphates
G-60	600	0.95	6-8	200	-
KB	1500	2	5	-	0.5
KB-B	1500	2	5	100	0.5

Generally, it can be expected that catalysts prepared with use of the support of higher surface area and pore volume will be more active. To prove or disprove this assumption, a series of tests have been carried out using Au and Pt as supported metals due to their high catalytic activity in previous tests. Conversion data are depicted in Fig.3.5 below.



Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-16000, NaOH/1,2-propanediol molar ratio = 1, temperature = 40 °C, time = 4h, stirrer speed = 1000 rpm.

Figure 3.5. Comparison of bimetallic AuPt catalysts supported on activated carbons: G60, KB and KB-B.

Figure 3.5 shows that catalysts supported on all activated charcoal supports, in direct contrast to graphite, are extremely active and that the conversion decreases with the increase of substrate to metal ratio (while using catalysts with constant metal loading across the experiments), thus proving that the higher the surface area the better the conversion, with the only exception being the KB supported catalyst at s:m=16000. It should be noted, however, that surface area is not the only factor that may influence the catalyst activity and such factors as pH, trace amounts of metals or moisture should be taken into consideration when evaluating the activity.

3.3.3.3 Metal loading optimisation

While it has been shown that the support plays a crucial part in catalytic activity, it is not the only factor. The amount of metal loaded can influence the activity as well. The results of experiments aimed at assessing this factor are presented in the following Tables (3.4-3.6)

Table 3.4. Tests of AuPt bimetallic catalysts with different metal loading using KB-B as support.

Entry	Catalyst	NaOH/S[a]	Conversion (%)	Selectivity, %			TOF (h^{-1})
				Lactate	Formate	Acetate	
1	1%Pt	2	6	96	0	4	30
2	1%Pt	1	3	97	0	3	15
3	0.95%Pt+0.05%Au	2	69	95	0	5	345
4	0.95%Pt+0.05%Au	1	70	93	1	6	350
5	0.9%Pt+0.1%Au	2	88	96	0	4	440
6	0.9%Pt+0.1%Au	1	85	93	2	5	425
7	0.75%Pt+0.25%Au	2	95	96	0	4	475
8	0.75%Pt+0.25%Au	1	90	93	1	6	450
9	0.5%Pt+0.5%Au	2	76	94	0	4	380
10	0.5%Pt+0.5%Au	1	84	92	0	8	420
11	0.25%Pt+0.75%Au	2	86	89	1	10	430
12	0.25%Pt+0.75%Au	1	83	85	1	14	415
13	0.1%Pt+0.9%Au	2	78	78	1	21	390
14	0.1%Pt+0.9%Au	1	88	75	2	23	440
15	1%Au	2	54	67	5	28	270
16	1%Au	1	36	62	6	32	180

Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, NaOH/1,2-propanediol molar ratio = 1, temperature = 60 °C, time = 4h, TOF calculated at 4h on the basis of total metal loading. Stirrer speed = 1000 rpm.

[a] NaOH : substrate molar ratio.

Table 3.5. Effect of AuPt bimetallic catalysts with different metal loading on the oxidation of 1,2 propanediol at 30°C

Entry	Catalyst	NaOH/S[a]	Conversion (%)	Selectivity, %			TOF (h^{-1})
				Lactate	Formate	Acetate	
1	1%Pt	2	<1	-	-	-	-
2	1%Pt	1	<1	-	-	-	-
3	0.95%Pt+0.05%Au	2	24	96	0	4	120
4	0.95%Pt+0.05%Au	1	30	93	1	6	150
5	0.9%Pt+0.1%Au	2	55	93	2	5	275
6	0.9%Pt+0.1%Au	1	60	90	2	8	300
7	0.75%Pt+0.25%Au	2	58	93	2	5	290
8	0.75%Pt+0.25%Au	1	65	89	2	9	325
9	0.5%Pt+0.5%Au	2	69	92	2	6	345
10	0.5%Pt+0.5%Au	1	73	83	3	14	365
11	0.25%Pt+0.75%Au	2	59	80	2	18	295
12	0.25%Pt+0.75%Au	1	66	71	4	25	330
13	0.1%Pt+0.9%Au	2	48	62	2	36	240
14	0.1%Pt+0.9%Au	1	61	60	3	37	305
15	0.05%Pt+0.95%Au	2	35	56	5	39	175
16	0.05%Pt+0.95%Au	1	24	48	5	47	120
17	1%Au	2	30	50	5	45	150
18	1%Au	1	18	49	4	47	90

Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, NaOH/1,2-propanediol molar ratio = 1, T = 30 °C, time = 4h, TOF calculated at 4h on the basis of total metal loading. Stirrer speed = 1000 rpm.
[a] NaOH : substrate molar ratio.

Table 3.6. Tests of AuPt bimetallic catalysts with different metal loading using carbon G-60 as support.

	Catalyst	Conversion (%)	NaOH/S[a]	Selectivity, %			TOF (h^{-1})
				Lactate	Formate	Acetate	
1	0.75%Pt+0.25%Au	57	2	94	0	6	285
2	0.75%Pt+0.25%Au	69	1	88	2	10	345
3	0.5%Pt+0.5%Au	61	2	97	0	3	305
4	0.5%Pt+0.5%Au	71	1	92	1	7	355
5	0.25%Pt+0.75%Au	57	2	97	0	3	285
6	0.25%Pt+0.75%Au	67	1	94	0	6	335

Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, NaOH/1,2-propanediol molar ratio = 1, T = 60 °C, time = 4h, TOF calculated at 4h on the basis of total metal loading. Stirrer speed = 1000 rpm. [a] NaOH : substrate molar ratio.

Tables 3.4-3.6 show catalytic data for 1,2-propanediol oxidation at 30-60 °C for AuPt/C catalysts with different metal loading, varying from Au-only catalyst to Pt doped with a small amount of gold (0.05wt%) for KB-B support and with 1:3 and 3:1 weight ratios for G-60 supported catalysts. As can be seen from these tables, the highest conversions can be achieved for 3:1 Pt-Au ratio at 60 °C (Table 3.4, entries 7-8) and when using equal amounts of two metals for KB-B support at 30 °C (Table 3.1, entries 9-10). The G-60 activated charcoal showed lower conversions compared with KB-B for all metal to metal ratios, which correlates with the data described in section 3.3.3.2. It is also worth mentioning that the selectivity to lactic acid drastically changes when moving to a higher loading of gold (Table 3.5, entries 13-18), and this trend is obtained just for KB-B support. As the only variable between these two types of catalyst is the support, it is likely that the interaction between the support and metal particles causes the difference in both activity and selectivity. This could directly affect the interface metal/carbon and in turn the activity of sites present there, or to induce different particle size because of a different nucleation process at the carbon surface.

To rule out any role of the support in converting the substrate to the desired product lactic acid, a few blank tests have been carried out using only supports as catalysts under the standard conditions used for catalytic 1,2-propanediol oxidation (40 °C and 3 bar O_2); unsurprisingly, these resulted in no conversion. This is important because carbon matrixes always contain traces of metals [28], such as Fe, K, and Cu, thus showing that these do not affect our results.

Further control tests were carried out with the supports treated with PVA and $NaBH_4$ and dried at 110 °C in air to emulate catalyst preparation but excluding the step of adding metals. These materials were then tested to evaluate if any of the components used during preparation may influence the conversion, but this also resulted in no oxidation of the starting material.

It should be noted that the solution containing products after the experiment was slightly yellowish when KB and KB-B support were used, whereas it was not coloured after using G-60 support. UV-vis spectroscopy was used to assess the origin of this colouring, but no absorption bands were observed at 400-450 nm

(corresponding to a yellow colour). It was concluded that the colouration arises from extremely small quantities, perhaps of metal phosphate complexes, that can be found in traces amounts on carbon (Appendix B) which can be present in different concentrations in KB and KB-B supports, and absent in G-60.

3.3.3.4. Physical mixtures of catalysts

It has been previously shown (Table 3.5, section 3.3.3.3) that different metals show different activity in the oxidation of 1,2-propanediol. The AuPt/C catalyst was of the highest activity, whereas monometallic gold catalyst gave half the values of conversion and monometallic platinum was totally inactive. In view of these experiments, the behaviour of physical mixtures of these two metals was investigated to evaluate if Au and Pt were operating as independent metal clusters or not, and to evaluate the impact of each metal in the catalytic activity singularly in order to ascertain the presence of synergistic effects, when the metals were alloyed. The results of these experiments are given in a Table 3.7.

Table 3.7. Catalytic tests using Au and Pt containing carbon supported catalysts alloyed and as physical mixture

				Selectivity, %				
Entry	Catalyst	s:m ratio	Weight of cat in grams	Conversion(%)	Lactate	Formate	Acetate	TOF (h^{-1})
1	0.5%Au+0.5%Pt/C **bimetallic**	4000	0.06	78	86	3	11	780
			Metal loading effect					
2	1%Au/C + 1%Pt/C * **(physical mixture)**	total 4000 (8000+8000)	0.03 + 0.03	66 / 70	72 / 74	7 / 5	21 / 21	660 / 700
3	1%Au/C *	4000	0.06	28 / 29	60 / 57	4 / 8	36 / 35	280 / 290
4	1%Pt/C *	4000	0.06	<1 / <1	-	-	-	-
			Metal dispersion effect					
5	0.5%Au/C + 0.5%Pt/C **(physical mixture)**	total 1000 (2000+2000)	0.12 + 0.12	62	74	4	22	620
6	0.5%Au/C + 0.5%Pt/C **(physical mixture)**	total 2000 (4000+4000)	0.06 + 0.06	51	78	2	20	510
7	0.5%Au/C	2000	0.12	22	63	6	31	220
8	0.5%Au/C	4000	0.06	28	56	7	38	280
9	0.5%Pt/C	2000	0.12	<1	-	-	-	-
10	0.5%Pt/C	4000	0.06	<1	-	-	-	-
			Low metal loading					
11	0.25%Au+0.25%Pt/C **(bimetallic)**	1000	0.24	91	87	2	11	910
12	0.25%Au+0.25%Pt/C **(bimetallic)**	2000	0.12	79	87	2	12	790
13	0.25%Au+0.25%Pt/C **(bimetallic)**	4000	0.06	67	86	2	12	670
14	0.25%Au+0.25%Pt/C **(bimetallic)**	8000	0.03	52	85	4	11	520

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 1000-8000, Base/1,2-propanediol molar ratio = 1, T = 40 °C, p = 3 bar, time = 4h

3.3.3.4.1 Effect of metal loading

As can be seen from the Table 3.7, entry 1 shows the data on conversion and selectivity of a bimetallic AuPt/C catalyst and this was chosen as a basis for comparison with the other catalysts. Entries 2, 3 and 4, reveal the effect of metal loading which was emulated by using half as much of each monometallic catalyst in comparison with the amount of bimetallic 0.5%Au+0.5%Pt/C catalyst used. Surprisingly, using a physical mixture led to results which were very close, in terms of conversion, to those of the bimetallic material. However, changes in the selectivities towards all the products were detected. If for a bimetallic catalyst the selectivity to a major product reaches 86% with the rest for by-products (entry 1), for a mixture of monometallic catalyst the selectivities resemble that of a gold-only catalyst with an increased selectivity towards a by-product, namely acetic acid. These sets of data strongly suggest that a synergistic affect is present when using physical mixtures of two monometallic catalysts in the amounts analogous to the amounts of metals of a bimetallic example.

3.3.3.4.2 Effect of metal dispersion

To further investigate the target of enhancing the activity by using physical mixtures, another set of experiments has been carried out to emulate the dispersion of the metals in the bimetallic AuPt/C catalyst. Two more monometallic catalysts have been prepared by sol immobilization method and tested, with half the amounts of Au and Pt. The idea behind this test is that by halving the amount of metals will lead to twice as much dispersed catalyst. The data obtained by using these mixtures are given in entries 5-10 (Table 3.7), where this can be compared with entry 1 for a bimetallic one, highlighted in red. The results show that the presence of platinum enhances the activity of gold giving twice as high conversions but leading to lower selectivities compared with a bimetallic catalyst. These results also indicate the presence of a synergistic effect when using more dispersed physical mixtures of catalysts.

3.3.3.4.3 Low metal loading for bimetallic AuPt/C catalyst

The next step was to investigate the influence of the amount of metal immobilized on the carbon surface on the overall activity of a catalyst. In view of this a bimetallic catalyst with half the quantity of metal was prepared and tested (Table 3.7, entries 11-14). The results unambiguously prove that even by decreasing the amounts of metals, it is possible to reach high conversions while also keeping the selectivity to lactate at the same high level. This has a clear economical advantage for the catalyst preparation on a larger scale.

3.3.3.5 24h time experiments

In order to reach total conversion, the timescale of the experiment has been increased from 4 to 24 hours. Simultaneously, the amount of catalyst loaded was decreased from s:m=2000 to 16000 and even 24000 (Table 3.8). Increasing the reaction time increases the conversion up to 99%; this could also be achieved by drastically reducing the amount of catalyst as far as a substrate to metal ratio of 16000. It is intriguing that the results for a reaction time of 24h showed the same activity for using different amounts of NaOH, a phenomenon which needs further investigation.

Table 3.8. 24 h time experiments, bimetallic 0.5%Au+0.5%Pt/C (KB-B) catalyst.

			Selectivity, %				
s:m ratio	NaOH/S [a]	Conversion (%)	Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
16000	2	99	92	2	6	0	0
16000	1	94	90	1	9	0	0
24000	2	96	93	2	6	0	0
24000	1	81	85	3	12	0	0

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, Base/1,2-propanediol molar ratio = 2 or 1, T = 40 °C, p = 3 bar, time = 24h
[a] NaOH : substrate molar ratio

3.3.3.6 Comparison of different inorganic bases tested for the oxidation reaction of 1,2-propanediol

Traditionally, alcohol oxidation requires the addition of an inorganic base to assist in proton dissociation from the hydroxyl group, with subsequent alkoxide formation [29-31]. Therefore a range of different inorganic bases, namely LiOH, NaOH, KOH, RbOH and CsOH, have been tested with different substrate to base ratios using 0.5%Au+0.5%Pt/C as a bimetallic catalyst (Table 3.9). Across the alkali metal bases, lithium hydroxide gave the highest conversion (*ca.* 80%). This trend was observed independently from the amount of base used. Therefore the general trend is the following: the bigger is the atomic radius of the cation, the higher is the basicity, and the lower is the conversion. With the decrease of the amount of any base, the selectivity changes to the formation of hydroxyacetone although it has been reported that this is unstable under alkaline conditions and is rapidly converted to lactic acid, presumably by an isomerisation-oxidation mechanism [10]. At the same time using higher amount of base resulted in an increase of selectivity to lactate and mostly prevents formation of over-oxidation products such as pyruvic acid. In view of this, it could be of interest to study other classes of bases, such as carbonates or phosphates.

Surprisingly, when using NaOH as the base, it has been observed that equimolar amounts of hydroxide gives higher conversion relative to the use of two equivalents; this trend is observed only for NaOH and it appeared to be systematic.

A similar trend is observed for 0.5%Au+0.5%Pt/C catalysts with different metal loading (see Tables 3.4-3.5). It is worth noting that in the experiments at 30°C using an equimolar amount of sodium hydroxide gives much higher conversions compared to two equivalents (75% and 84%), whereas the conversions at 60 °C are very similar when using different amounts of base for different metal loadings. The same trend is observed for using G-60 supported Au-Pt catalysts (Table 3.6).

Table 3.9. Effect of base on the oxidation of 1,2-propanediol using 0.5%Au+0.5%Pt/C

Base	base/S[a]	Conversion (%)	Selectivity, %					TOF (H^{-1})
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone	
LiOH	2	78	91	3	6	0	0	780
LiOH	1	80	85	4	11	0	0	800
LiOH	0.5	62	66	3	17	3	11	620
LiOH	0.25	42	50	0	12	6	32	420
NaOH	2	50	92	2	6	0	0	500
NaOH	1	78	86	3	11	0	0	780
NaOH	0.5	44	62	2	4	4	13	440
NaOH	0.25	29	51	0	14	6	29	290
KOH	2	70	92	2	6	0	0	700
KOH	1	69	85	3	12	0	0	690
KOH	0.5	47	69	2	14	7	8	470
KOH	0.25	28	54	0	9	8	29	280
RbOH	2	69	93	2	5	0	0	690
RbOH	1	66	88	3	9	0	0	660
RbOH	0.5	40	68	3	15	7	7	400
RbOH	0.25	29	56	0	8	8	28	290
CsOH	2	49	94	2	4	0	0	490
CsOH	1	53	89	3	8	0	0	530
CsOH	0.5	56	87	3	10	0	0	560
CsOH	0.25	37	66	2	17	8	7	370

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, Base/1,2-propanediol molar ratio = 2; 1; 0.5 or 0.25, T = 40 °C, p = 3 bar, time = 4h
[a] NaOH : substrate molar ratio

A furhter aspect that need to be considerd is the possible generation of CO_2 in the system and its repercussion on the conversion and the selectivity of the reaction. In fact, CO_2 promply interacts with bases (OH^-) to lead to the formation of carbonates. As long as carbonates are formed, base is consumed, but the base is exactly what is needed to trigger the reaction by breaking the bond in hydroxylic functional group and forming alcoxide, which will take part in further transformations. Therefore, less alcohol will react and the conversion will decrease. Another factor that can be influenced by the carbon dioxide formation is selectivity. The results of catalytic tests indicate that the less base present in the reaction mixture the more is the shift to the formation of another product, namely hydroxyacetone. Therefore, if the base is

consumed due to the reaction with CO_2, the selectivity to the target molecule -lactic acid, will decrease and the formation of unwanted by-products will increase.

It should be noted that because of peculiarities of the reactor system (see. paragraph 3.3.1) it was not possible to analyse gaseous products and therefore to determine the carbon mass balance. However, its estimation from the pressure of the reaction system at the end of the reaction and amount of products as determined by NMR, allow to assume a maximium CO_2 formation of *ca.* 5%. Therefore effects on conversion and selectivity are possible, but these should not considered dramatic for the reaction systems in presence of 1 or 2 moles of base in the reaction mixture.

3.3.3.7 Pressure influence

Previous studies reported that 1,2-propanediol oxidation occurs at high pressures [32]. In order to check whether it is possible to operate at lower pressures, a series of experiments have been carried out using different types of reactor.

Table 3.10. Effect of pressures variation to the oxidation of 1,2 propanediol by using different reactors.

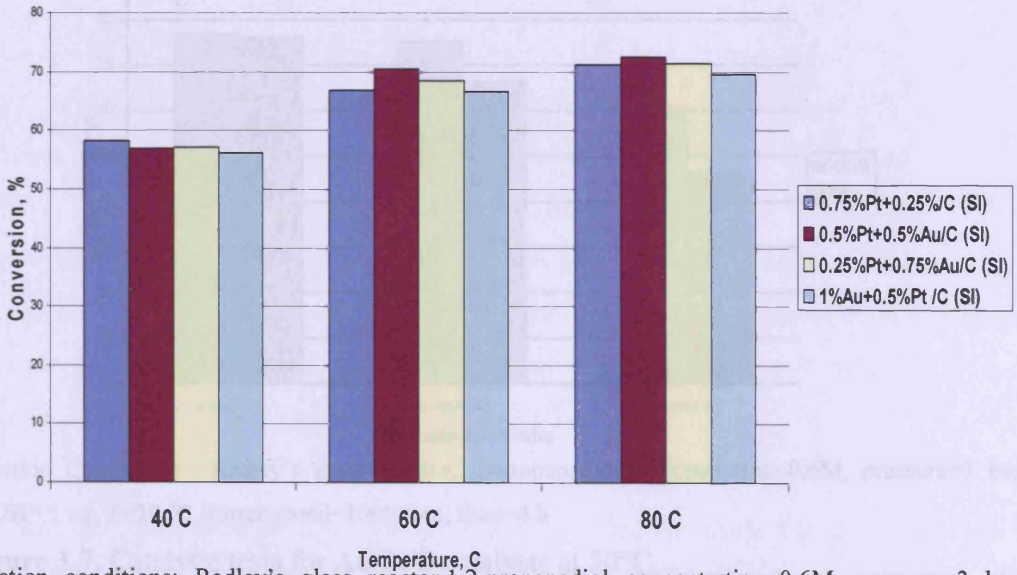
Catalyst	Radley's glass reactor[a] (P = 3 bar)	HEL autoclave reactor[b] (P = 10 bar)
Au	30	32
Pd	-	-
Pt	-	-
Au-Pt	78	79
Au-Pd	52	43
Pd-Pt	22	35
Au-Pd-Pt	56	61

Reaction conditions: Radley's glass reactor,1,2-propanediol concentration=0.6M, pressure=3 bar (for Radley's glass reactor) or 10 bar (for HEL autoclave), NaOH= 1 eq, T=40°C, stirrer speed=1000 rpm, time = 4 h.

Table 3.10 clearly shows that there is no difference in conversion values when the pressure was increased (except Au-Pd and Pd-Pt catalysts for which the conversion variations were around 10%). The same trend was observed for the tests carried out at pressures lower than 3 bar using Radley's glass reactor (going down to 1 bar pressure above atmospheric), thus showing that this reaction proceeds independently of oxygen pressure, at least within the range 1 to 10 bar.

3.3.3.8 Oxidation at ambient temperature

High temperature is known to promote high conversions in alcohol oxidation to the corresponding aldehydes or acids. However, increasing the temperature may give a rise to unwanted side reactions such as C-C bond cleavage [33] as well as possibly switching the reaction to a diffusion control regime. Therefore, the range of temperatures which are suitable for a highly selective diol oxidation should be carefully optimized depending on a type of catalytic system used.



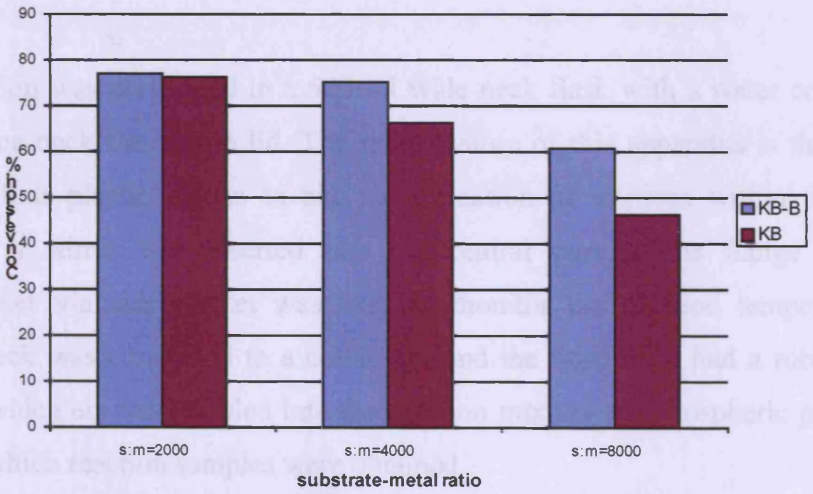
Reaction conditions: Radley's glass reactor,1,2-propanediol concentration=0.6M, pressure=3 bar, NaOH= 1 eq, T=40-60-80°C, stirrer speed=1000 rpm, time=4 h.

Figure 3.6. Catalytic tests at different temperatures for oxidation of 1,2-propanediol over AuPt/carbon catalysts, support G-60

Temperatures of 40, 60 and 80 °C have been tested to evaluate the corresponding

catalyst activities and the results are presented in Fig. 3.6. By plotting 1,2-propanediol conversion against temperatures used to oxidise the substrate for the different metal loadings, it is possible to see that most catalysts follow a very similar path for any metal loading and there is no large enhancement in conversion by increasing the temperature from 40 to 80 °C.

As was previously presented in Table 3.4, the conversions may reach 85% when operating at higher temperatures (*i.e.* 60 °C). The results obtained for another support, G-60, also at 60 °C (Fig. 3.6), displayed similarly high conversions, but the results clearly do not differ one from another. This may be explained by the external mass transfer control which can be overcome by moving the reaction to a kinetic region [34]. Therefore it is important to investigate the behaviour of the most active catalyst at lower temperatures, in our case below 40 °C, in order to fully evaluate effects induced by mass transfer limitations. The results of a series of such experiments are displayed in Fig. 3.7.



Reaction Conditions: Radley's glass reactor,1,2-propanediol concentration=0.6M, pressure=3 bar, NaOH= 1 eq, T=30 °C, stirrer speed=1000 rpm, time=4 h.

Figure 3.7. Catalytic tests for Au-Pt/C catalysts at 30°C.

The results obtained show that the reaction is really switched to the uncontrolled diffusion regime at higher temperature; and at higher s:m ratio comes under kinetic control as the conversion becomes more proportional to the amount of catalyst. This effect is particularly marked for the less active catalysts, KB supported, compared with the KB-B supported examples.

To further prove the presence of a mass transfer limitation, several experiments have been carried out at Imperial College's laboratories using specially designed reactor shown in Fig. 3.8.

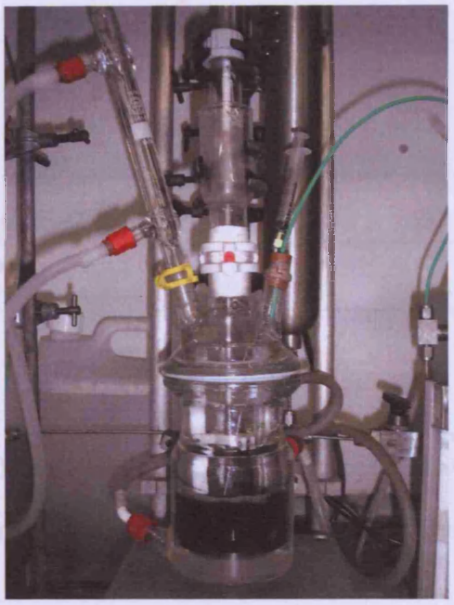
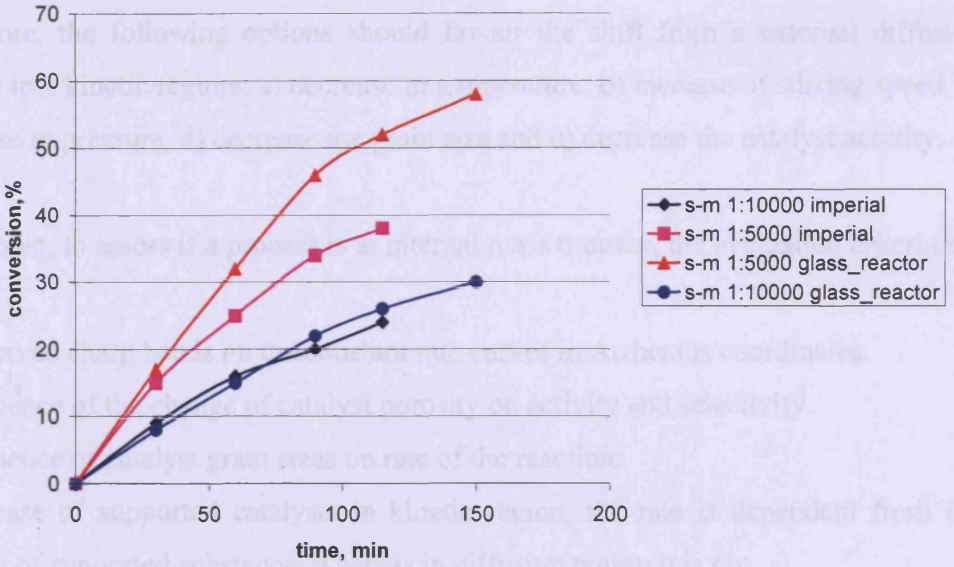


Figure 3.8. Glass reactor used at Imperial College, London.

The reaction was performed in a 500 ml wide neck flask with a water cooled jacket and a three neck flat flange lid. The main feature of this apparatus is that the flask contains four plastic inserts to aid the formation of vortices within the reaction mixture. A stirrer was inserted into the central port of the flange lid, and a thermometer via side pocket was used to monitor the reaction temperature. The second neck was connected to a condenser and the third neck had a rubber stopper through which air was bubbled into the reaction mixture at atmospheric pressure and through which reaction samples were obtained.

The catalyst (s:m ratio = 5000 or 10000) was added to the solution of 0.6M 1,2-propanediol at 25°C and samples were collected at 30 min intervals, when the reaction is still under kinetic control. The samples were then passed through a 0.22μm syringe filter to remove the catalyst and the filtrate was analysed by HPLC.

The results obtained were compared with those obtained using a Radley's glass reactor to evaluate if air can be used instead of oxygen for efficient 1,2-propanediol oxidation (Fig. 3.9).



Reaction conditions: 1,2-propanediol concentration=0.6M, pressure= 3 bar (or bubbling air at atmospheric pressure), NaOH= 1 eq, T=25 °C, stirrer speed=1000 rpm (for Radley's), time=30 min to 1 h.

Figure 3.9. Oxidation of 1,2-propanediol – Radley's vs Imperial's reactors

As can be seen from this figure, appropriate conversions may be achieved even using air at ambient temperature given the reactor is specially designed to provide a more accurate temperature control and, especially, more efficient stirring. As this reactor type provides better stirring regime and allows the taking of samples during the experiment, it was used to assess if the reaction is mass transfer limited.

There exist several criteria to determine if a process is in external mass transfer regions [35], particularly:

1) low temperature coefficient of the reaction rate.

2) dependence of the process speed on stirring speed (for liquid phase), or the linear velocity of a gas stream (for gas phase reactions).

3) observed 1st order of the reaction.

4) proportionality of the observed rate of reaction to the surface of catalyst grain, whereas in the kinetic regime it is proportional to the (grain) volume.

5) in case of exothermic reaction there is significant difference in temperature between the catalyst and reaction mixture, with subsequent heating up of the catalyst.

6) absence (up to some limit) of influence on the rate of the reaction by changes in catalyst activity.

Therefore, the following options should favour the shift from a external diffusion control to a kinetic regime: a) decrease in temperature, b) increase of stirring speed, c) decrease in pressure, d) decrease the grain size and e) decrease the catalyst activity.

In contrast, to assess if a process is at internal mass transfer, the evaluation criteria are [35] :

1) observed sharp bends on the constant rate curves in Arrhenius coordinates.
2) influence of the change of catalyst porosity on activity and selectivity.
3) influence of catalyst grain sizes on rate of the reaction.
4) in case of supported catalysts in kinetic region, the rate is dependent from the amount of supported substance, whereas in diffusion region it is not.

In view of this, feasible ways to move from internal diffusion region could be to decrease the temperature and/or to decrease the catalyst porosity.

To further investigate if mass transfer limitations are present, The Method of Initial Rates was applied [36]. This procedure involves measuring the rate of reaction, r, at the beginning of the reaction at such short times from its start that no significant changes in concentration have yet occurred. The following mathematical formulae were applied:

The rate of the reaction is:

$$r = k_{ef} \cdot c \qquad \text{(eq. 3.1)}$$

Where k_{ef} is effective rate constant and c the concentration of substrate.

k_{ef} is defined like:

$$k_{ef} = \frac{1}{\frac{1}{k_d} + \frac{1}{k_x}} \qquad \text{(eq. 3.2)}$$

Where k_d is the mass transfer constant and k_x is kinetic rate constant

Therefore, substituting eq. 3.2 in eq. 3.1:

$$r = \frac{c}{\frac{1}{k_d} + \frac{1}{k_x}} \qquad \text{(eq. 3.3)}$$

whereas the inverse rate equals to:

$$\frac{1}{r} = \frac{\frac{1}{k_d} + \frac{1}{k_x}}{c} \quad \text{or} \quad \frac{1}{r} = \frac{c}{k_d} + \frac{c}{k_x} \qquad \text{(eq. 3.4)}$$

The mass transfer coefficient k_d is defined like:

$$k_d = \frac{D}{\delta} \qquad \text{(eq. 3.5)}$$

where D is the diffusion constant and δ is the thickness of boundary layer

while k_x is defined like:

$$k_x = k \cdot c_{cat} \qquad \text{(eq. 3.6)}$$

Inserting eq. 3.5 and eq. 3.6 into eq. 3.4 we get:

$$\frac{1}{r} = \frac{\delta \cdot c}{D} + \frac{c}{k \cdot c_{cat}} \qquad \text{(eq. 3.7)}$$

The plot of $\frac{1}{r}$ versus $\frac{1}{c_{cat}}$ gives a straight line with a positive slope that equals $\frac{c}{k}$, and the intersection with Y axis equals to $\frac{\delta \cdot c}{D}$

Therefore, when building a plot of the reciprocal reaction rate versus the reciprocal catalyst concentration (mass) [37], a straight line that intersects the Y-axis is obtained, which is a proof that the reaction is mass transfer limited. (Fig. 3.10).

Using the set of coordinates described above, a kinetic regime would lead to a straight line that intercepts the X and Y axis at the origin.

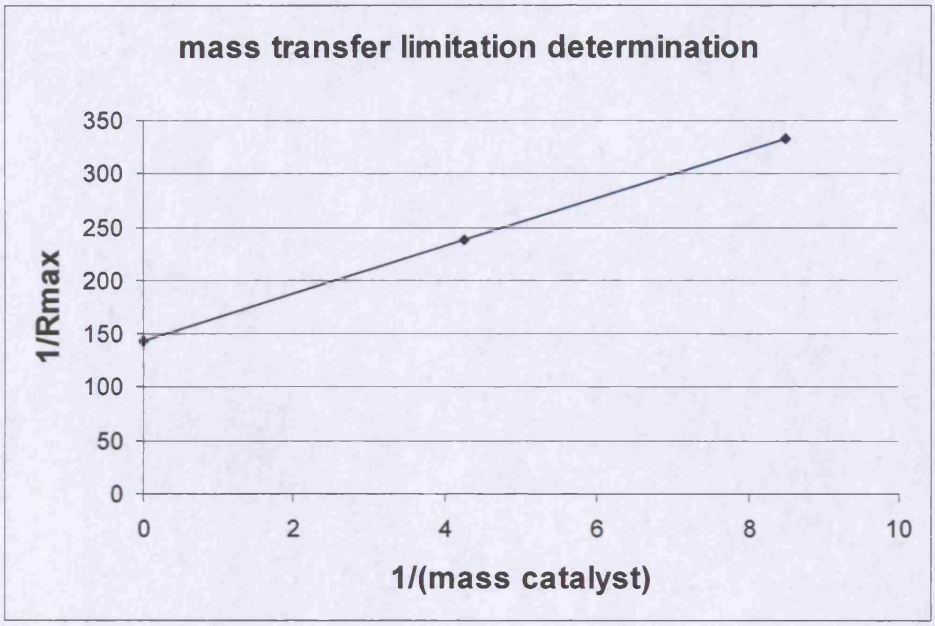


Figure 3.10. Mass transfer limitation determination for reaction of 1,2-propanediol oxidation catalyzed by 0.5%Au+0.5%Pt/C catalyst, 1/Rmax - [L·min/mol], 1/mass catalyst – [g^{-1}]

By carrying out experiments with different catalyst concentrations and building a plot in the coordinates described above, we may see that the reaction of 1,2-propanediol oxidation is mass transfer limited when using 0.5%Au+0.5%Pt/C catalyst. In view of the mathematical tools used above, to move this reaction from a region of external diffusion to a kinetic regime the following parameters may be changed: a) decrease δ, or decrease in catalyst activity (by using less porous catalyst or a catalyst with less supported metal), b) increase D, or intensification of stirring regime, c) increase *k*, or decreasing temperature.

3.3.3.9 Time on-line studies

In order to understand the detailed reaction profile of selective oxidation of 1,2-propanediol, time-on-line studies have been carried out by taking samples every hour and more frequently during the initial reaction period to investigate how the reaction propagates with time. The Radley's glass reactor was used for these purposes.

Table 3.11. Time-on-line data for bimetallic 0.5%Au+0.5%Pt/C catalyst.

	15 min	30 min	1 h	2 h	3 h	4 h
Conversion (%)	5	12	20	43	67	75
Selectivity to lactate (%)	89	88	89	87	86	87
Selectivity to acetate (%)	11	12	11	11	12	11
Selectivity to formate (%)*	0	0	0	2	2	2

Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, NaOH/1,2-propanediol molar ratio = 1, T = 40 °C, stirrer speed = 1000 rpm
(*) – the detection limit for formate was 0.5%

As can be seen from Table 3.11, the selectivities to lactic and acetic acid remain constant for the whole experiment where the formation of formate starts in the middle of the reaction. Most probably formate and/or acetate production occurs due to C-C bond cleavage in any of the molecules present in the reaction mixture, forming carbon oxides as gaseous by-products. However, due to the design of the reactor (see section 3.3.1) it was not possible to carry out direct sampling in the gas phase, so this assumption could be neither proven nor disproven.

Moreover, comparing the result after 4 hours of reaction time in this experiment with other 4 hour experiments with the same s:m ratio, it is clear that although the conversion is still high, it has reduced from the expected 90% to around 75%. This can possibly be explained by the peculiarities of the sampling (changing the equilibrium when depressurizing the system). Yet, the general trend is the following: the relative amount of lactic acid, as well as the acetic acid, remains invariable, and another by-product, formic acid, is produced later, presumably due to the C-C bond cleavage.

In order to investigate the kinetics of this reaction, the data obtained earlier were analysed to determine the rate law and the activation energy.

One of the methods to determine the order of the reaction is to build a table based on the data of time-dependant conversions [38]. For these purposes, reactant

consumption with time is calculated, and then the experimental data are used for calculation of the rate constants.

The expressions of k_i from 0th to 3rd order are reported below:

0th order:

$$k_i = \frac{c_0 - c}{t_i} \qquad \text{(eq. 3.8)}$$

1st order:

$$k_i = \frac{1}{t_i} \ln \frac{c_0}{c} \qquad \text{(eq. 3.9)}$$

2nd order:

$$k_i = \frac{1}{t_i}\left(\frac{1}{c} - \frac{1}{c_0}\right) \qquad \text{(eq. 3.10)}$$

3rd order:

$$k_i = \frac{1}{2t_i}\left(\frac{1}{c^2} - \frac{1}{c_0^2}\right) \qquad \text{(eq. 3.11)}$$

The results of these calculations are given in a Table 3.12.

Table 3.12. Kinetic data for 1,2-propanediol oxidation at 40°C.

time, min	0	15	30	60	120	180	240
conversion	0	0.05	0.12	0.20	0.43	0.67	0.75
concentration	0.6	0.57	0.53	0.48	0.34	0.20	0.15
k_0, zeroth order	**0**	**0.00200**	**0.00240**	**0.00200**	**0.00215**	**0.00223**	**0.00188**
k_1, first order	0	0.00341	0.00426	0.00371	0.00468	0.00615	0.00577
k_2, second order	0	0.22807	0.11868	0.06250	0.03825	0.03731	0.03472
k_3, third order	0	2.25069	12.1384	46.8750	346.311	2045.68	5000.00

It can be seen from this Table that the rate constants remain unchanged for zero-order

calculations. The only exception is represented by the values at 240 min but this was possibly due to the sampling problems described above.

Another similar test for a given integrated rate law is to make a plot of the data that should show a straight line. For this purposes the graphs, in coordinates: [A] - t, ln[A] – t, and 1/[A] – t were plotted (Fig. 3.11) with the former giving a straight line proving that the investigated reaction has the zero order in 1,2-propanediol.

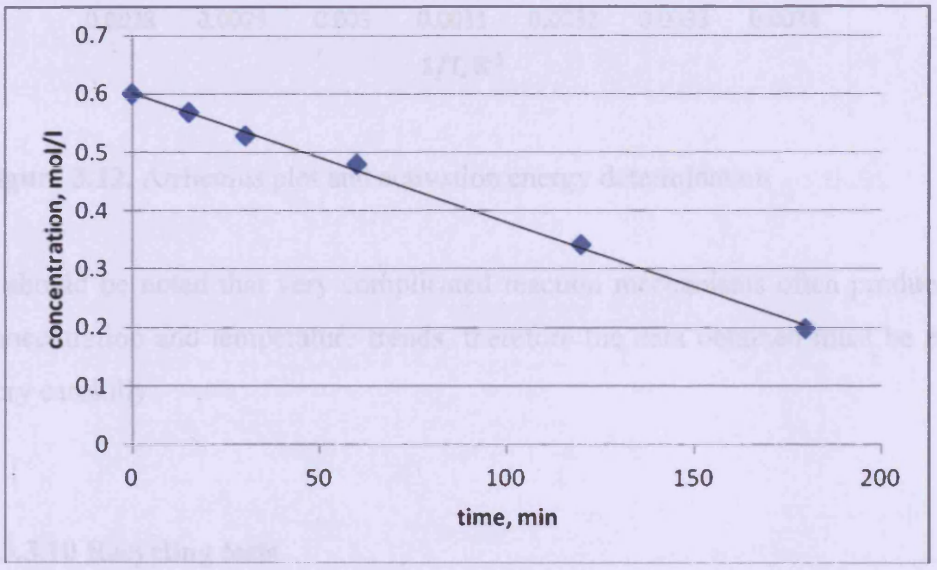


Figure. 3.11 Reaction order determination for the reaction of 1,2-propanediol oxidation over 0.5%Au+0.5%Pt/C catalyst

The next step was to calculate activation energy, given that the rate constants at different temperatures are known. These rate constants were calculated based on the data obtained from earlier experiments (Fig. 3.6 and Table 3.7). The values of ln k were then plotted against the inverse temperatures giving a straight line (R^2 = 0.91) where the gradient of the line was equal to $-E_a/R$ (Fig. 3.12). Then the activation energy was calculated, giving the value of 43 kJ/mol. It should be noted that the low R^2 value could be due to the poor reactor temperature control of the setup used for these experiments.

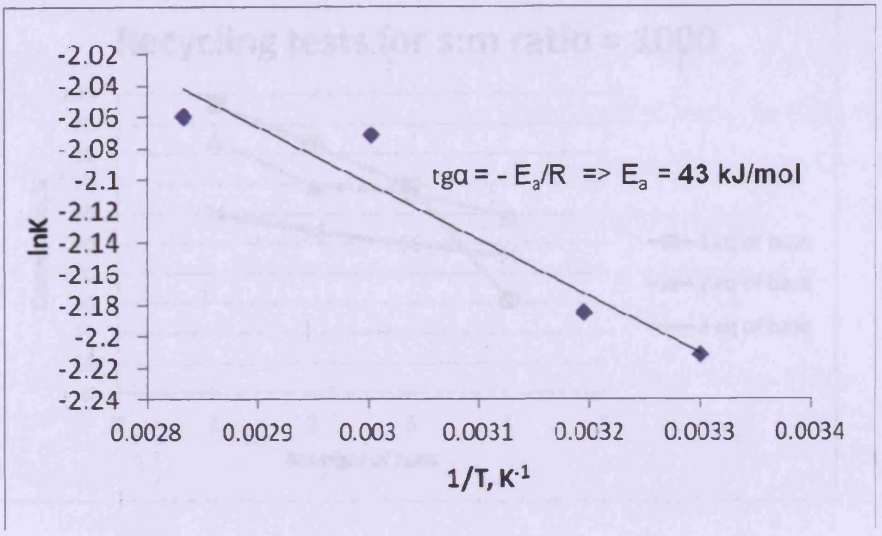


Figure 3.12. Arrhenius plot and activation energy determination

It should be noted that very complicated reaction mechanisms often produce simple concentration and temperature trends, therefore the data obtained must be evaluated very carefully.

3.3.3.10 Recycling tests

Extensive reusability studies have been carried out in the following way. Initially, several sets of experiments at s:m ratios of 1000 and 2000 have been run to obtain enough catalyst for further recycling. After obtaining sufficient amounts of catalysts (s:m 1000 and 2000, separately from one another), three more subsequent runs have been carried out to assess the reusability of the 0.5%Au+0.5%Pt/C (KB-B) catalyst by varying the NaOH/substrate molar ratio in the range from 1 to 3 eq. The results are presented in Figs. 3.13-3.14. At low NaOH/1,2-propanediol ratios, the experiments showed a significant decrease in conversion after the third use (from 99% to 30%). In contrast, by increasing the base concentration to two eq, the reusability was improved, while by using three equivalent of NaOH, the conversion decreased from 60 to 46% after four uses. These data indicate that improved reusability of the catalyst at higher alkaline concentrations is related to the lower deactivation effect in the presence of base. Since the presence of base will facilitate desorption of by-products, it minimises the poisoning effects of these and therefore preserves catalytic activity.

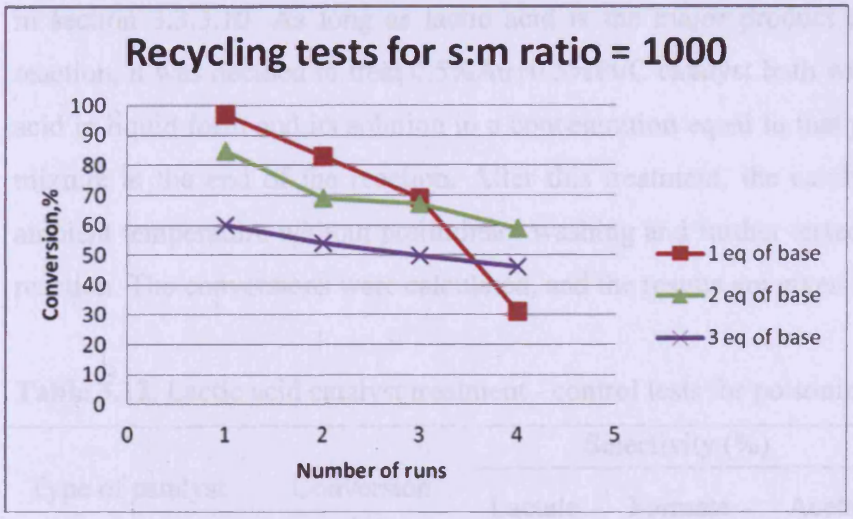
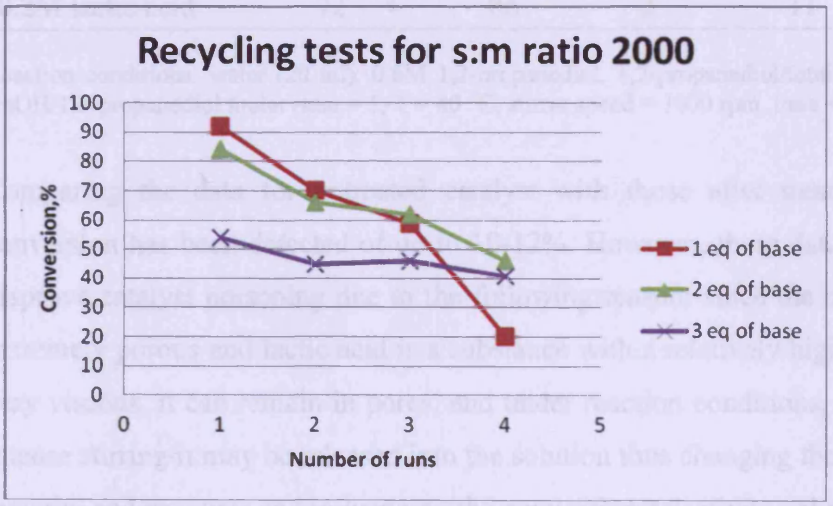


Figure 3.13. The results of reusability tests for AuPt/C (KB-B) catalyst, substrate to metal ratio 1000.



Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 1000 or 2000, Base/1,2-propanediol molar ratio = 1-3, T = 40 °C, p = 3 bar, time = 4h.

Figure 3.14. The results of reusability tests for AuPt/C (KB-B) catalyst, substrate to metal ratio 2000.

3.3.3.11 Tests for poisoning by reaction products

The possibility of poisoning by any of the reaction products have been investigated taking into account the significant drop in conversion (up to 30%) previously reported

in section 3.3.3.10. As long as lactic acid is the major product formed during the reaction, it was decided to treat 0.5%Au+0.5%Pt/C catalyst both with undiluted lactic acid in liquid form and its solution in a concentration equal to that present in reaction mixture at the end of the reaction. After this treatment, the catalysts were dried at ambient temperature without preliminary washing and further tested for the oxidation reaction. The conversions were calculated, and the results are given in a table 3.12.

Table 3.12. Lactic acid catalyst treatment - control tests for poisoning

Type of catalyst treatment	Conversion (%)	Selectivity (%)			TOF (h^{-1})
		Lactate	Formate	Acetate	
None	84	88	2	10	460
Lactic acid	66	86	2	12	330
0.2M lactic acid	72	86	3	11	360

Reaction conditions: water (20 ml), 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, NaOH/1,2-propanediol molar ratio = 1, T = 40 °C, stirrer speed = 1000 rpm, time = 4h.

Comparing the data for untreated catalyst with those after treatment, a drop in conversion has been detected of up to 10-12%. However, these data cannot prove or disprove catalyst poisoning due to the following reason: since the catalyst surface is extremely porous and lactic acid is a substance with a relatively high molar mass and very viscous, it can remain in pores, and under reaction conditions, after heating and intense stirring it may be released into the solution thus changing the ratios of starting material and products and influencing the conversion/selectivity values.

Initial studies on catalyst poisoning revealed no meaningful results, therefore it was decided to further investigate this problem. The idea was to add each of the intermediates formed at the beginning of the reaction in the amounts that 1) mimic the concentrations of these intermediates that are obtained when the reaction is finished and 2) significantly exceed the amounts that may be formed. The results of these experiments are shown in a Table 3.13.

Table 3.13. Intermediates treatment: control tests for poisoning

product	Concentration	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
---	0.3M	92	93	2	5	0	0
Lactic acid	0.3M	90	88	1	11	0	0
	0.03M	95	92	1	7	0	0
Acetic acid	0.3M	95	75	0	25	0	0
	0.03M	94	93	0	7	0	0
Formic acid	0.3M	94	93	-*	7	0	0
	0.03M	94	94	-*	6	0	0

Reaction conditions: 0.3M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, Base/1,2-propanediol molar ratio = 4, T = 40 °C, p = 3 bar, time = 4 h.

* the intermediate added is consumed during the reaction

After careful analysis of the data obtained and comparison of these with the data for diol oxidation, it can be seen that there is no change in catalytic activity when adding any of the intermediates.

To further prove that there is no catalyst poisoning, it was decided to carry out additional experiments by taking samples during the reaction, to find if there is any change in selectivity both at the initial period and at the end of the reaction. These results are given in a Table 3.14.

Table 3.14. Time-on-line data for oxidation of 1,2-propanediol (addition of 0.3M lactic acid)

time	Conversion(%)	Selectivity, %				
		Lactate	Formate	Acetate	Pyruvate	Hydroxyacetone
30 min	10	92	0	8	0	0
1 h	32	90	0	10	0	0
2 h	49	92	0	8	0	0
3 h	67	91	0	9	0	0
4 h	90	88	1	11	0	0

Reaction conditions: 0.3M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, Base/1,2-propanediol molar ratio = 4 (1.2M), T = 40 °C, p = 3 bar.

The results shown above suggest that the selectivity remains unchanged during the whole reaction period.

This is indicative that neither small amounts of any of the intermediates, nor their presence in large excess, are able to change catalytic activity, which suggests that the problem of catalyst deactivation can be due to the changes in surface morphology or rearrangements or in metal exposure/distribution [40,41] or CO_2 poisoning [42].

3.3.4 Characterisation of fresh and used catalysts

An essential part of any catalysis study is the characterization of the materials used and linking it to the reactivity observed. A vast array of catalysts has been tested in this study and they were characterized using different techniques to identify properties such as: surface and elemental composition, bulk structure, surface physical properties.

3.3.4.1 TGA analysis

Thermogravimetric analysis and differential scanning calorimetry were conducted on carbon supported catalysts to measure the losses and the rate of change in the weight of spent catalysts, under temperature ramps, in order to determine the amount of possible adsorbed species over the catalyst surface. A fresh unused catalyst and a untreated support were used as references to eliminate weight losses due to the moisture present in the support and residues of PVA left after catalyst preparation.

The TGA profile of the carbon catalyst in nitrogen is shown in Fig. 3.15 with weight normalized to 1 for direct comparative purposes. In the temperature range of 40–110 °C, the TGA profile of the all catalysts displays a rapid weight loss due to the presence of water (*ca.* 17%) (Table 3.15). There is then is a light weight loss for the fresh catalyst and quite a significant loss for both washed (using water as a solvent) and unwashed used catalysts up to 250 °C, in the range of *ca.* 3 and 6% respectively,

indicating the presence of PVA molecules. With a further increase in temperature, the mass evenly decreased which can be due to the decarboxylation processes of the carbon matrixes that occur at high temperatures. These results clearly indicate that there is no meaningful difference between washed and unwashed catalysts after the effects of moisture and PVA originating from the preparation procedure have been eliminated, as verified by the trend of the support only.

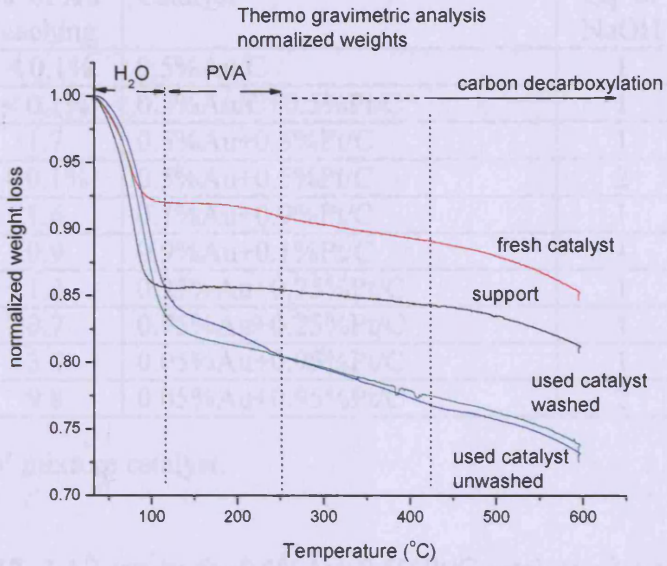


Figure 3.15. TGA results for activated carbon supported catalysts before and after treatment with lactic acid.

Table 3.15. Weight loss calculations for activated carbon supported catalysts

	Weight loss, %		
	water	PVA	decarboxylation
support only	15.7		3
fresh catalyst	8	2.9	3.6
used catalyst washed	18.1	4.5	3.5
used catalyst unwashed	16.7	6.7	3.2

3.3.4.2 AAS analysis

AAS analysis was carried out for a range of catalysts to determine if any metal leaching occurred. To analyze if any gold was released into a solution, a series of reaction mixtures were filtered off from catalysts and were used directly for atomic

absorption analysis to determine if gold was present. Tables 3.16 and 3.17 below show the results of the AA analysis performed on gold and platinum containing catalysts.

Table 3.16. AAS results for different carbon-based catalysts after 1 use (test for metal leaching)

N	% of **Au** leaching	Catalyst	Eq. of NaOH	T (° C)
1	< 0.1%	0.5%Au/C	1	40
2	< 0.1%	0.5%Au/C+0.5%Pt/C*	1	40
3	1.7	0.5%Au+0.5%Pt/C	1	60
4	< 0.1%	0.5%Au+0.5%Pt/C	2	60
5	1.6	0.1%Au+0.9%Pt/C	1	60
6	0.9	0.9%Au+0.1%Pt/C	1	60
7	1.2	0.25%Au+0.75%Pt/C	1	60
8	0.7	0.75%Au+0.25%Pt/C	1	60
9	3.4	0.05%Au+0.95%Pt/C	1	60
10	9.8	0.05%Au+0.95%Pt/C	2	60

* Physical mixture catalyst.

Table 3.17. AAS results for 0.5%Au+0.5%Pt/C catalyst after reusability tests.

N	% of **Au** leaching	Catalyst	Eq of NaOH	T (° C)	Number of cycles
1	0.7	0.5%Au+0.5%Pt/C	1	40	1
2	0.4	0.5%Au+0.5%Pt/C	1	40	2
3	0.7	0.5%Au+0.5%Pt/C	1	40	3
4	0.6	0.5%Au+0.5%Pt/C	1	40	4

What is immediately apparent from these tables, is that there is no or minor (<1%) Au leaching for:

- catalysts used for the recycling tests (up to the 4th run)
- catalysts with 0.1%; 0.25%; 0.5%; 0.75% and 0.9% Au loading
- the monometallic Au/C catalyst
- a physical mixture of Au/C and Pt/C catalyst

There is significant leaching for 0.05%Au+0.95%Pt bimetallic catalyst (Table 3.16,

entry 9) which can be possibly explained by weak alloying of these metals at a given metal ratio [39]. (Please note that it was not possible to analyse Pt due to a permanent instrument failure in the AA spectrophotometer).

3.3.4.3 SEM studies

The detailed information on surface morphology of all the supports used for 1,2-propanediol oxidation was obtained from the SEM images. Moreover, it was possible to determine particle size of different supports. Besides generating high-resolution images of the surfaces, an approach of qualitatively and semi-quantitatively determining chemical compositions was applied using integrated EDS.

SEM micrographs of the catalysts supported on metal different oxides and activated carbon (Sigma-Aldrich Darco KB-B) are presented in Fig. 3.16-3.19 showing clear difference in the morphology and the support particles size.

Fig. 3.16 $1\%_{wt}$(Au-Pt)/TiO_2

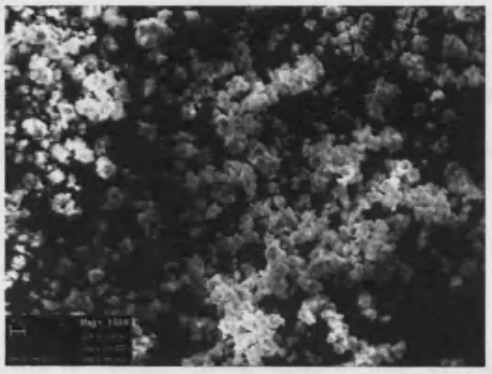


Fig. 3.17 $1\%_{wt}$(Au-Pt)/MgO

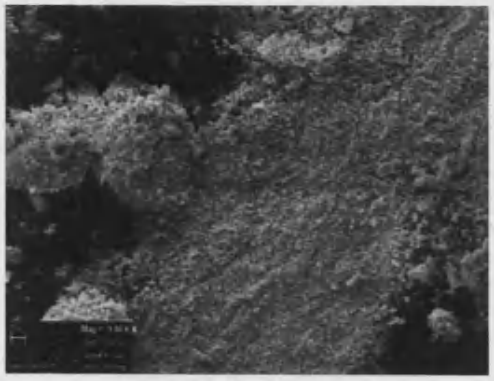


Fig. 3.18 $1\%_{wt}$(Au-Pt)/ZnO

Fig. 3.19 $1\%_{wt}$(Au-Pt)/C

A gold on titania catalyst has been further analysed using the backscatter detector. As it can be seen from Fig 3.20-3.21, impregnation of gold on titanium oxide leads to the appearance of some submicron-size metal particles, these gold clusters are detected on the TiO_2 surface having a size of ca. 200-300 nm and evenly covering the support surface.

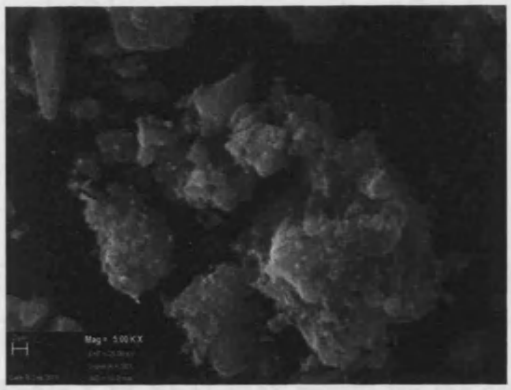


Fig. 3.20 5%Au/TiO_2

Fig. 3.21 5%Au/TiO_2 (BSE)

The next target was to quantify the chemical composition of the variety of catalysts that have been used for 1,2-propanediol oxidation. The results are given in tables 3.18-3.20.

Table 3.18. SEM-EDX results for the composition of metal oxides supported catalysts

	Supported metals		
catalyst	% Au	% Pd	% Pt
5%Pd/TiO_2 Impr		2.62	
1% wt (Au-Pt)/MgO SI	-		0.41
1% wt (Au-Pt)/TiO_2 SI	0.15		0.77
1% wt (Au-Pt)/ZnO SI	-		1.63
1% wt (Au-Pt)/Al_2O_3 SI	-		0.40
5%Au/TiO_2 Impr	2.55		

Table 3.19. SEM-EDX results for the composition of activated carbon supported catalysts

catalyst	% Au	% Pd	% Pt	% C	% Na	% O	% Cl
1%Au	-			80.40	0.14	19.62	
1%Pd		0.7		88.02	0.14	11.04	0.1
1%Pt			0.75	79.94	0.12	18.89	0.3
1% wt (Au-Pd)	-	0.83		88.89	0.12	10.06	0.10
1% wt (Pd-Pt)		0.35	1.43	85.86	0.18	11.95	0.21
1% wt (Au-Pt)	-		1.10	81.75	0.06	16.96	0.13
1% wt (Au-Pd-Pt)	-	0.04	0.09	87.50	0.18	12.11	0.08

Table 3.20. SEM-EDX results for the composition for $1\%_{wt}$(Au-Pt)/C KB-B catalyst after reusability tests (2 and 1 eq of NaOH)

N of cycles	Base	% Au	% Pt	% C	% Na	% O
1	1	-	0.64	78.65	1.71	19.00
3	1	-	0.17	78.38	2.01	19.44
4	1	-	0.09	78.12	2.12	19.67
1	2	-	0.55	79.38	1.42	18.65
4	2	-	0.12	78.00	1.84	20.04

Interestingly, gold was not detected for any catalysts but for those supported on titania where metal loading was significantly higher compared to other catalysts. This can be due to the equipment limitations for detection of the elements (which is 0.1wt %).

It is worth noting that the SEM analysis performed on the spent catalysts after a series of recycling tests (Table 3.20) showed that both fresh and used catalysts appear to have similar carbon particle size with no clear change in morphology seen. In addition, the amount of platinum decreases with the increasing number of runs which correlates with the results obtained by XPS (see section 3.3.4.5). As it was previously demonstrated (paragraph 3.3.4.2) that gold leaching was not responsible for the decrease in activity, this could be due to platinum leaching.

SEM analysis also showed (Table 3.20) a small but consistent rise in Na content, which could also contribute in the explanation of the catalytic trend observed [42].

3.3.4.4 XRD studies

The aim of this section is to obtain information on the size of metal particles and also to, possibly, find indirect evidence for the formation of an alloy in the case of bimetallic catalysts. In fact, the XRD technique allows particle sizes to be estimated by the analysis of the reflection via Scherrer equation [43] as long as they are in the range of *ca.* 4 nm to 100 nm. If two metals are alloyed this can also be detected by changes in the lattice parameters of the unit cell of these metals.
In view of this, X-ray powder diffraction (XRPD), was carried out on both the catalysts comprising carbon and TiO_2 as support.

On the one hand, for the carbon supported catalysts (Fig. 3.22) it was possible to observe a diffraction pattern for the catalysts comprising Pt only and in monometallic form, by the reflections [44]. On the other hand, for the Au and Pd catalysts no reflection arising from the metals can be detected.

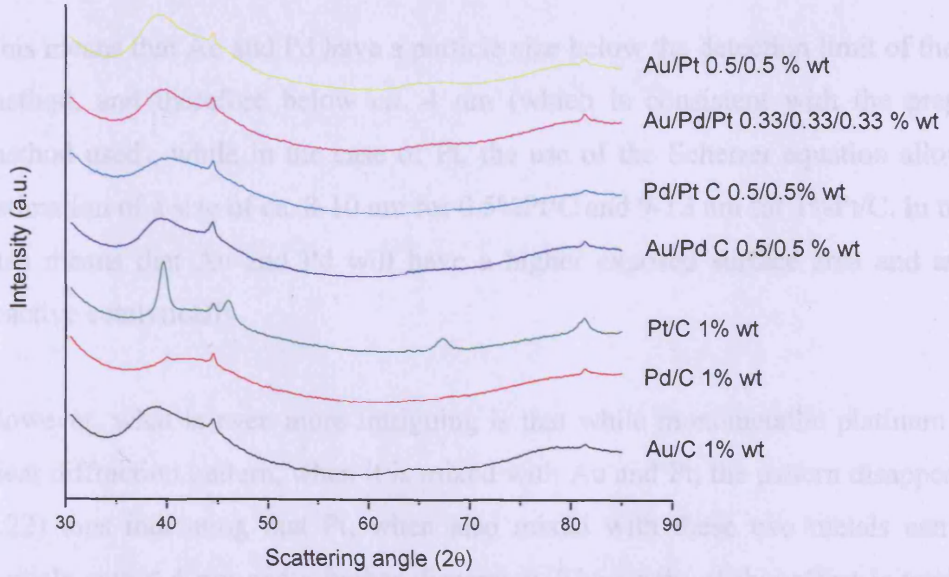


Figure 3.22. XRD patterns for activated carbon supported catalysts using a metal sample holder

Control tests carried out using a silicon and a stainless steel sample holder ascertained that, in the case of Pd and Pt, the reflections detected at ca 44 ^{o} 2θ, are actually arising from the Fe of the sample holder to the transparency effect (Figure 3.23). Even the analysis time > 2h using amorphous silicon holders did not reveal any reflection associated with gold metal.

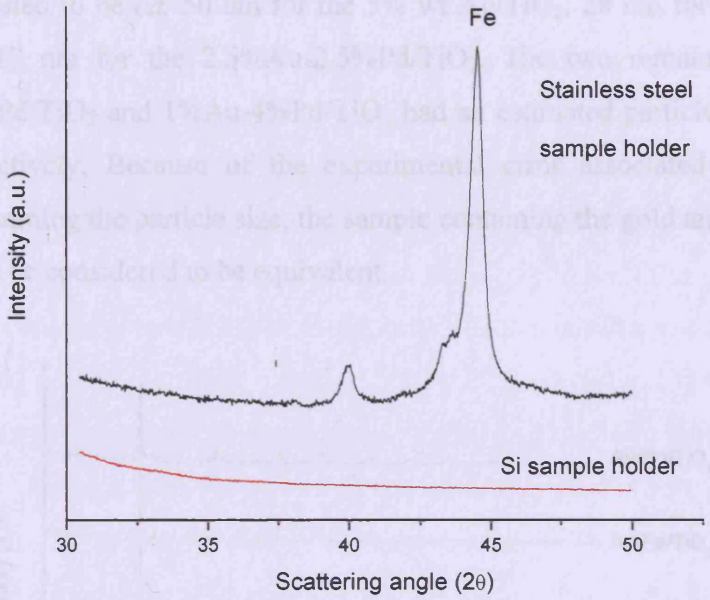


Figure 3.23. Comparison of background patterns form amorphous silicon and stainless steel sample holders.

This means that Au and Pd have a particle size below the detection limit of the XRPD method, and therefore below *ca.* 4 nm (which is consistent with the preparation method used), while in the case of Pt, the use of the Scherrer equation allowed the estimation of a size of ca. 8-10 nm for 0.5%Pt/C and 9-12 nm for 1%Pt/C. In turn, this also means that Au and Pd will have a higher exposed surface area and are more reactive catalytically.

However, what is even more intriguing is that while monometallic platinum gives a clear diffraction pattern, when it is mixed with Au and Pt, the pattern disappears (Fig. 3.22) thus indicating that Pt, when also mixed with these two metals can have a particle size < 4 nm and a higher dispersion. The origin of this effect is unclear and could either be due to a competitive nucleation process over the carbon surface [45] or segregation, and therefore a dispersion, effect.

Unlike the case of carbon used as support, catalysts supported on TiO_2 Au were clearly detected for Au and AuPd (Figure 3.24) and it is possible to observe how the intensities of the diagnostic reflections (111) and (200) at 38.2 and 44.4 ° 2θ respectively [46] are decreasing, moving from a 5% wt composition to a 1% wt composition. This allowed the particle size for gold to be determined, which was estimated to be *ca.* 50 nm for the 5% wt Au/TiO_2, 28 nm for the 4%Au-1%Pd/TiO_2 and 17 nm for the 2.5%Au-2.5%Pd/TiO_2. The two remaining samples 2.5%Au-2.5%Pd/TiO_2 and 1%Au-4%Pd/TiO_2 had an estimated particle size of 20 and 18 nm respectively. Because of the experimental error associated with the method for determining the particle size, the sample containing the gold amount from 2.5% to 1% could be considered to be equivalent.

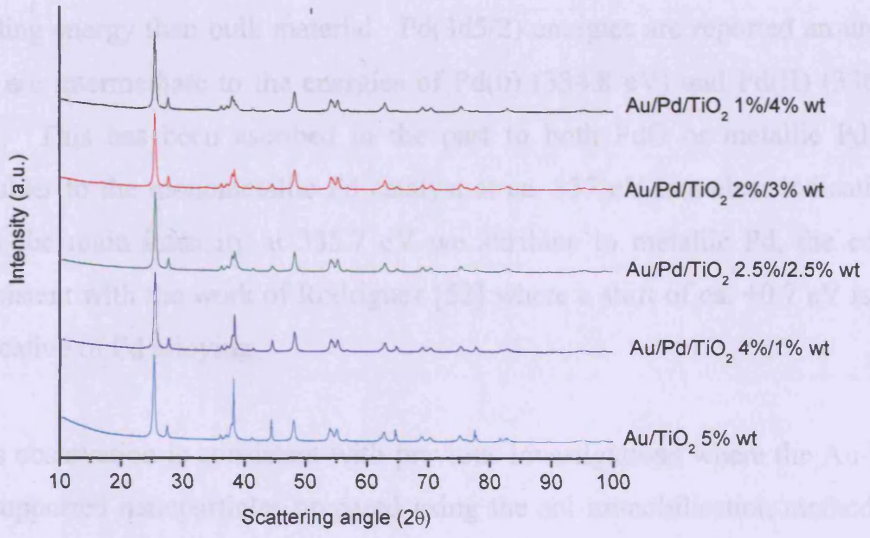


Figure 3.24. XRPD patterns for Au and Pd catalysts supported on TiO_2

Interestingly, no palladium could be detected for the diagnostic reflections (111) and (200) at 40.2 and 46.7 ° 2θ [47]. This could either mean dispersed palladium particles below 4 nm, or the formation of core-shell structures [48], with gold core and a palladium shell, a structure that would allow gold detection but not palladium detection. The latter structure is possible also when the metals are deposited from mixed metal solution, like in our case.

Finally, the XRPD pattern of TiO_2 reveals the presence of both anatase [49] and rutile

[50] with the diagnostic (100) reflections at 25.3 and 27.4 ° 2θ respectively, as expected for the P25 titania used in the current study.

3.3.4.5 XPS studies

Results of the XPS characterisation of the carbon supported nanoparticles (Table 3.21) indicate all Au species are present in the metallic state as inferred by a Au(4f7/2) binding energy of ca. 84eV, irrespective of whether they are present in the mono or bimetallic systems. Similarly, the reported Pt(4f7/2) energies (ca. 71.5 eV) are slightly higher than expected for metallic Pt (71.1 eV), but this is evidence for the nanoparticulate nature of the metal, with final state effects giving an apparent higher binding energy than bulk material. Pd(3d5/2) energies are reported around 335.7 eV and are intermediate to the energies of Pd(0) (334.8 eV) and Pd(II) (336.8 in PdO) [51]. This has been ascribed in the past to both PdO or metallic Pd, a definite shoulder to the monometallic Pd catalyst at ca. 337 eV is a clear indication of PdO, with the main intensity at 335.7 eV we attribute to metallic Pd, the energy being consistent with the work of Rodriguez [52] where a shift of ca. +0.7 eV is considered indicative of Pd alloying.

This observation is consistent with previous investigations where the Au-Pd and Au-Pt supported nanoparticles prepared using the sol-immobilisation method have been extensively characterised by STEM-HAADF analysis, and it has been reported that the particle size is in the range of 2-5 nm with a narrow particle size distribution and the Au-Pd and Au-Pt nanoparticles are random alloys [53,54]. No evidence for PdO is observed for the bimetallic catalysts.

Molar ratios for the Pt/Au and Pd/Au supported on the KB-B carbon are found to be 1.25 (expected 1/1) and 1.25 (1.85 expected); entries 1 and 3 respectively. For KB support the Pt/Au ratio is 1.68 which is higher than expected (entry 8).

A 1/1 ratio is observed only for the set of G-60 supported catalysts at 0.5%Au+0.5%Pt catalyst (entry 9), the rest have deviations from their expected

values; increasing with increase of gold content (entries 10-12).

Monometallic graphite-supported catalysts showed lower metal loading compared with expected values whereas bimetallic 0.5Au+0.5%Pt/C was close to 1/1 predicted molar ratio (entries 13-15).

Table 3.21. XPS analysis of Au, Pd, Pt, Au-Pd and Au-Pt supported nanoparticles

	Sample ID	BE Au $4f_{7/2}$	BE Pt $4f_{7/2}$	BE Pd $3d_{5/2}$	At% Au	At% Pt	At% Pd
1	0.5Au+0.5Pt KB-B	84.1	71.5	0	1.03	1.31	0
2	0.5Pd+0.5Pt KB-B	0	71.7	335.7	0	1.50	0.77
3	0.5Au+0.5Pd KB-B	84.0	0	335.7	1.07	0	1.34
4	0.33Au+0.33Pt+0.33Pd KB-B	84.2	71.7	335.7	0.5	0.7	1.36
5	1Au KB-B	84.2	0	0	2.29	0	0
6	1Pd KB-B	0	0	335.6	0	0	1.39
7	1Pt KB-B	0	71.4	0	0	0.31	0
8	0.5Au+0.5Pt KB	84.1	71.8	0	0.82	1.38	0
9	0.5Au+0.5Pt G-60	84.1	71.5	0	0.73	0.73	0
10	0.25Au+0.75Pt G-60	84.2	71.8	0	0.34	0.71	0
11	0.75Au+0.25Pt G-60	84.2	71.7	0	1.04	0.78	0
12	1Au+0.5Pt G-60	84.3	71.8	0	1.35	1.19	0
13	1Au graphite	84.2	0	0	0.6	0	0
14	1Pt graphite	0	71.7	0	0	0.56	0
15	0.5Au+0.5Pt graphite	84.1	71.5	0	0.57	0.66	0

Further XPS characterisation has been done for catalysts after reusability tests to evaluate the correlation between surface composition and the conversion values. The results are given in Fig. 3.25 showing a clear dependence of the catalytic activity and decreasing metal exposure for experiments carried out using both 2 and 1 equivalents of NaOH.

Sample ID	At% Au	At% Pt
fresh	1.140	1.430
2 eq NaOH		
1st run	0.378	0.573
2nd run	0.173	0.290
3rd run	0.078	0.116
4th run	0.052	0.080
1 eq NaOH		
1st run	0.315	0.584
2nd run	0.137	0.221
3rd run	0.051	0.084
4th run	0.035	0.040

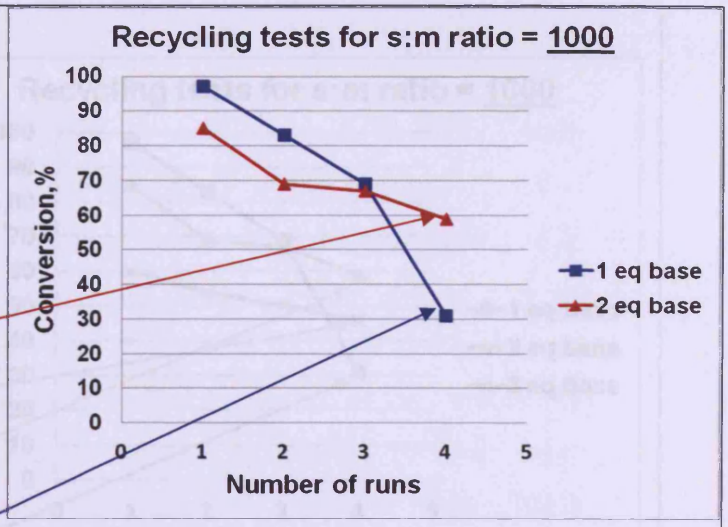


Figure 3.25. Surface atomic composition, as determined by XPS, for the 0.5%Au+0.5%Pt/C catalysts used in reusability tests compared with the catalytic activity.

3.3.4.6 BET studies

In order to verify if the trend in the decrease of the conversion observed for reusability tests could be a surface area function, the catalysts before and after the experiments were analysed using the 48 points (full isotherm) BET method. By studying the surface morphology it was hoped it would be possible to identify the reasons for poor reusability. The figure presented below gives the full correlation picture between surface area and a drop in catalytic activity.

Sample ID	Surface area, m^2/g	Pore volume, ml/g
KB-B (data from Aldrich)	1500	2
KB-B (measured value)	1097	0.69
AuPt/C fresh	1319	0.90
3 eq, 1st run	1105	0.73
3 eq, 4th run	994	0.64
2 eq, 1st run	978	0.63
2 eq, 4th run	883	0.54
1 eq, 1st run	910	0.56
1 eq, 4th run	*628*	*0.38*

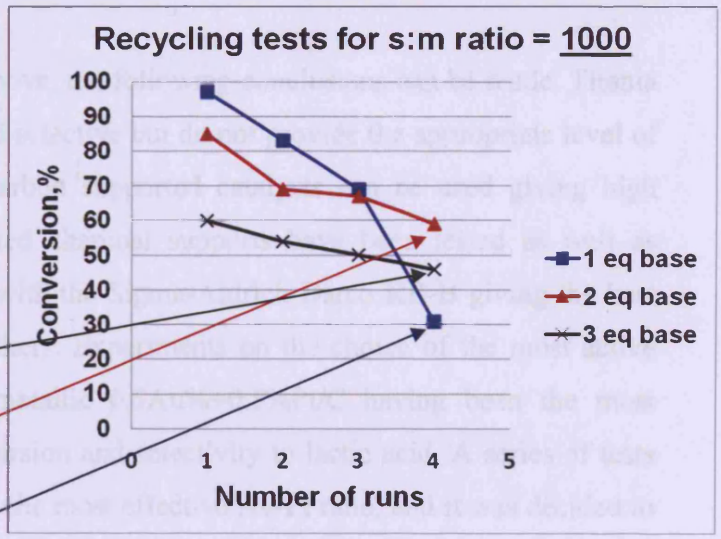


Figure 3.26. Correlation between surface area measured by BET method and the conversion of 1,2-propanediol oxidation.

The BET results show a clear decrease in the catalyst surface area at nearly 50% for the catalyst after the 4th run at 1 eq of NaOH and 25-30% at 2 and 3 eq of base compared with the fresh unused catalyst, which may be due to a certain decrease in porosity as the pore volume decreases accordingly, thus preventing diffusion of reagents to the catalyst active sites. This decrease could be due to the formation of carbonaceous deposit inside the carbon pores. The data obtained by BET is in a good correlation with XPS results where the metal exposure drastically decreases after each catalyst cycle (see section 3.3.4.5, Fig. 3.25) and with SEM-EDX measurements (section 3.3.4.3, Table 3.20) where the surface metal (platinum) composition also changes to the smaller values compared with unused catalyst.

3.4 Conclusions

Based on the results described above, the following conclusions can be made. Titania supported catalysts are active and selective but do not provide the appropriate level of conversion. Instead, activated carbon supported catalysts can be used giving high conversions. A range of activated charcoal supports have been tested as well as examples with graphite support with the Sigma-Aldrich Darco KB-B giving the best results when compared to the others. Experiments on the choice of the most active metal were conducted with bimetallic 0.5Au%+0.5%Pt/C having been the most efficiency both in terms of conversion and selectivity to lactic acid. A series of tests have been carried out to evaluate the most effective Au-Pt ratio, and it was decided to further use the 1:1 wt ratio, *i.e.* 0.5%Au+0.5%Pt/C (KB-B) catalysts, for further experiments. Different parameters have been varied, such as pressure and temperature, which led to the assumption that there existed a mass transfer limitation. The presence of external diffusion limitation factor was proven by using a specially designed reactor with enhanced stirring (Imperial College) and confirmed by means of mathematical analysis. A series of experiments up to 24h have been carried out showing that full conversion might be achieved even at high substrate to metal ratios. Physical mixtures of monometallic Au/C and Pt/C have been tested to verify that the synergistic effect is present when adding one metal to other, both in terms of dispersion and metal loading. Tests with lower metal ratios have also been conducted to show that decreasing the amounts of metals does not lead to drastic changes in conversions, thus proving that efficient oxidation can be carried out using catalysts with small amounts of metals immobilised on the support. Finally, a series of reusability tests showed that there is the decrease in conversion. This has been extensively investigated using a range of analytical techniques and control tests for catalyst poisoning. It appeared that catalyst deactivation occurred due to a decrease in porosity of the activated carbon support.

3.5 References

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Chapter 4: BASE-FREE OXIDATION OF 1,2-PROPANEDIOL

4.1 Introduction

The aim of this chapter is to investigate the reaction profile of 1,2-propanediol oxidation under base-free conditions. Firstly, a range of different supports will be screened, and after choosing the most efficient, a variety of combinations of Au, Pd and Pt supported nanoparticles will be tested to find the most effective catalyst composition. The influence of pressure and temperature will also be investigated in detail.

Several attempts of lactaldehyde synthesis will be carried out in order to identify the reaction mechanism of lactic acid formation, as well as the oxidation of all possible intermediates under standard reaction conditions. For this reason, also 1-propanol and 2-propanol will be oxidized as model compounds for competitive alcohol group oxidation.

Finally, reusability tests will be conducted to understand the causes of decrease in conversions as well as to evaluate the possibility of catalyst poisoning and/or catalyst deactivation.

4.2 Experimental

A range of catalysts used for base-free 1,2-propanediol oxidation has been prepared by sol immobilization method (for a detailed description of this procedure, see section 2.2.2.1). The catalytic tests described in this chapter, have been carried out in a low-pressure glass reactor and in a high-pressure autoclave, as described in a section 3.2, with the exception that the addition of base step was omitted.

4.3 Results and discussion

It's well known that 1,2-propanediol and other polyols can be selectively oxidized to corresponding acids under basic conditions [1-4]. However, these routes are not considered green as the presence of base in high concentrations causes the problem of contaminated waste water. It could be interesting from environmental and economical point of view to carry out the oxidation processes in aqueous media. Therefore a new way of oxidizing these substrates is required, ideally without using base as a promoter or significantly reducing its amount. It has been reported that it is possible to oxidize polyols in aqueous media [5-8]. Thus, non-activated alcohols can be oxidized using colloidal nanoparticles [9] and glycerol can be selectively oxidized under base-free conditions over MgO-supported nanoparticles [10]. The aim of this chapter is to extend previous findings on non-basic alcohol oxidation in aqueous media over heterogeneous reusable catalysts and to possibly identify the mechanism of the 1,2-propanol oxidation to lactic acid.

4.3.1 Preliminary experiments in presence of base and at non-basic conditions

At the initial stage of this study it was decided to test catalysts that proved themselves efficient for the 1,2-propanol oxidation (sections 3.3.2 and 3.3.3). An explorative series of tests has been carried out in a Radley's low pressure glass reactor using AuPt catalysts supported on titania, magnesia and activated carbon under base and base-free conditions. The results of these preliminary experiments are given in Table 4.1.

Table 4.1 Tests of different AuPt catalysts supported on TiO_2, MgO and activated carbon for the 1,2-propanediol oxidation, in presence and absence of base.

				Selectivity, %				
Entry	Catalyst	NaOH/S	Conversion (%)	Lactate	Formate	Acetate	Pyruvate	Hydroxyacetone
1	0.5Au+0.5Pt/TiO_2	1	20	96	4	0	0	0
2	0.5Au+0.5Pt/TiO_2	0	0	0	0	0	0	0
3	0.5Au+0.5Pt/MgO	1	22	85	5	10	0	0
4	0.5Au+0.5Pt/MgO	0	40	32	0	3	0	65
5	0.5Au+0.5Pt/C	1	78	86	3	11	0	0
6	0.5Au+0.5Pt/C	0	4	40	0	0	0	60

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, Base/1,2-propanediol molar ratio (NaOH/S) = 1 or 0, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm

As can be seen from this table, magnesia and activated carbon supported catalysts showed activity under base-free conditions with the former being extremely active (entries 3 and 4), with conversion values of ~20 and 40%, whereas titania supported catalyst could oxidise the diol only in the presence of base (entry 1). On that basis, the MgO-supported catalyst was chosen for further studies. Interestingly, when moving from basic conditions to aqueous media, another product is formed, namely hydroxyacetone (entries 4 and 6) in quantities larger than the desired lactic acid. It has been previously reported [11] that in basic media hydroxyacetone is unstable and is converted into condensed products, therefore its formation in the absence of base is expected.

To investigate the ways of increasing conversion values and shifting the equilibrium to the production of lactic acid, it was decided to try different reactor systems and to carry out experiments at elevated pressures. An experiment in high pressure autoclave has been conducted at 10 bar pressure to evaluate its influence on lactic acid formation, and its result is reported in Table 4.2.

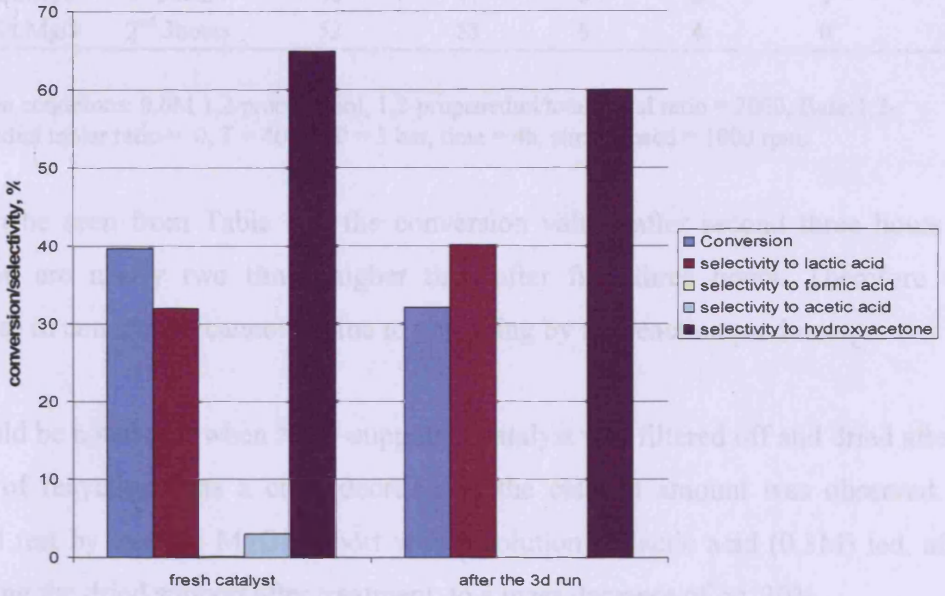
Table 4.2 Oxidation of 1,2-propanediol at basic and base-free conditions in HEL autoclave

Catalyst	NaOH/ S	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/MgO	0	28	49	0	3	0	48

Reaction conditions: 1,2-propanediol concentration=0.6M, P=10 bar, T=40°C, stirrer speed=1000rpm, time=4 hours, temperature 40 °C, s:m = 1:4000

What is immediately obvious when comparing the result obtained in autoclave (Table 4.2) and entry 4 from Table 4.1, is that high pressure is favourable to increase the selectivity to lactic acid, though it clearly decreases the overall conversion. After calculating the yield of the reaction at 3 and 10 bar pressure, which appeared to be the same, it was decided to operate at less demanding lower pressures.

As 0.5%Au+0.5%Pt/MgO catalyst proved to be active in the absence of base, reusability tests were further carried out in Radley's glass reactor to evaluate the behaviour of MgO-supported catalyst after several cycles (Fig. 4.1). Straightforward comparison of the results obtained after the first and the third runs clearly shows the decrease in conversion (proved by reproducibility tests), therefore tests for investigating the reasons of catalyst deactivation were required.



Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm

Figure 4.1 Reusability tests for MgO supported catalyst

Catalyst deactivation is a complex phenomenon and it which may occur for a number of reasons: sintering, coke formation, change of metal oxidation state, blocking or poisoning of active sites by products formed or even by starting material *etc* [12]. It was decided to start with experiments on catalyst poisoning. These tests were carried out in the following way: a standard amount of catalyst (0.1176 g) was used for the oxidation reaction for the first 3 hours, and then a sample was taken to measure the conversion and selectivity. However, before repressurizing the system a fresh catalyst was added into the reactor, and the reaction continued for further 3 hours. Before the catalyst is added, products will already be forming and so this procedure will check if reaction products lead to catalyst poisoning. In fact, if they are, the conversion should

drop down when comparing the data obtained after first and second 3 hours.

Table 4.3. Control test for catalyst poisoning for no-base 1,2-propanediol oxidation

Catalyst	time	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/MgO	1st 3hours	30	47	6	2	1	45
0.5Au+0.5Pt/MgO	2nd 3hours	52	53	6	4	0	37

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, Base/1,2-propanediol molar ratio = 0, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm.

As can be seen from Table 4.3, the conversion values after second three hours of reaction are nearly two times higher than after first three hours. Therefore the decrease in conversion cannot be due to poisoning by the reaction products.

It should be noted that when MgO-supported catalyst was filtered off and dried after a series of recycling tests a clear decrease in the catalyst amount was observed. A control test by treating MgO-support with a solution of lactic acid (0.3M) led, after weighing the dried support after treatment, to a mass decrease of *ca.* 30%.

The conclusion that was made is that lactic acid which is formed in along the reaction is strong enough (pK_a = 3.86) to dissolve the basic magnesia oxide, and therefore MgO supported catalysts are not suitable for the reaction when strong acids are being formed. In fact upon loss of the MgO support, gold particles can agglomerate. This explains also the activity of MgO-supported catalyst in base: NaOH added at the beginning of the reaction neutralizes lactic acid by forming lactate and therefore prevents the support from being dissolved.

4.3.2 Test of Au, Pd and Pt nanoparticles supported on activated carbon

As it has been reported in Chapter 3, precious metal catalysts supported on activated carbon showed intrinsic activity in 1,2-propanediol oxidation at basic conditions. Preliminary tests of AuPt/C catalyst conducted in the absence of base (Table 4.1 entry

6) displayed some activity under no-base conditions.

A selected range of carbon-supported catalysts were tested and the results are shown in Table 4.4. As 0.5%Au+0.5%Pt/C previously was tested at 4 hours and gave only 4% conversion, so it was decided to increase the reaction time up to 24 hours in order to obtain higher conversion values.

Table 4.4. Test of different mono- and bi-metallic catalysts at 40 °C, support – activated carbon (KB-B), in Radley's glass reactor

Entry	Catalyst	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
1	1Au	0	0	0	0	0
2	1Pd	0	0	0	0	0
3	1Pt	2	40	0	0	60
4	0.5Au+0.5Pt	33	39	0	0	60
5	0.5Au+0.5Pd	4	14	0	0	86
6	0.5Pd+0.5Pt	13	44	0	0	56
7	0.3Au+0.3Pd+0.3Pt	15	32	2	1	65

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, T = 40 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Surprisingly, monometallic Au/C catalyst appeared to be inactive in the absence of base (entry 1) while it is known to be active under basic conditions (Chapter 3, Table 3.2). Pd/C catalyst is totally inactive under both basic and base-free conditions (entry 2), whereas Pt/C appears to oxidize 1,2-propanediol as well as bi- and tri-metallic combinations of these three metals (entries 3-7). The highest conversion and lactic acid selectivity values were achieved when using 0.5%Au+0.5%Pt/C catalyst (entry 4). Interestingly, 0.5%Au+0.5%Pd/C catalyst shifts the reaction pathway to the formation of hydroxyacetone and lower yields to lactic acid, whereas the combination of Au with Pt results is close to 1:1 product ratio.

For further improvements in conversions it was decided to increase the temperature at which the experiments are carried out to 100 °C and to test the full range of Au-Pd-Pt catalysts. The data are summarized in Table 4.5.

Table 4.5 Test of different mono- and bi-metallic catalysts at 100 °C, support – activated carbon (KB-B), in Radley's glass reactor, for 1,2-propanediol oxidation.

Entry	Catalyst	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
1	1Au	9	13	6	0	81
2	1Pd	6	17	8	0	75
3	1Pt	31	45	9	5	41
4	0.5Au+0.5Pt	75	40	20	2	38
5	0.5Au+0.5Pd	35	14	15	2	69
6	0.5Pd+0.5Pt	61	48	11	2	39
7	0.3Au+0.3Pd+0.3Pt	48	26	19	53	2

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000 T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Under these more vigorous reaction conditions the conversions are considerably higher. Thus, monometallic Au/C and Pd/C oxidized 1,2-propanediol at the level of *ca.* 10% (entries 1 and 2) with the tendency to form large amounts of hydroxyacetone, and the same trend was observed for bimetallic combination of those metals. The trend in activity observed for bi- and tri-metallic catalysts was AuPd < AuPdPt < PdPt < AuPt with 0.5%Au+0.5%Pt/C being the most active. The trend mentioned above is not followed for selectivities to the desired product, lactic acid, and it appeared that 0.5%Pd+0.5%Pt/C works more selectively over the whole range.

It is important to note that lactaldehyde was detected by NMR when using monometallic Pt/C catalyst, though its amount was close to the accuracy limit of NMR integration, therefore its quantitative integration was not possible. For practical purposes NMR was the only technique that was possible to use as thsi substance is commercially unavailable due to instability and therefore cannot be used as calibration standard for GC. It has been reported that the probable mechanism of the reaction of 1,2-propanediol oxidation includes aldehyde formation [13], which would be quickly transformed to lactic acid. During our studies in the presence of base, it was not possible to detect this intermediate.

To further investigate the formation of lactaldehyde and its transformation to lactic acid an experiment with sequential sampling was performed. As long as the amount of

lactaldehyde is very small and cannot be calculated in relation to starting material or lactic acid, a specially designed sealed glass insert, containing tetramethylsilane (TMS) dissolved in $CDCl_3$ was used as as an internal standard for NMR analysis [14] to calibrate and to evaluate the amount of lactaldehyde and dynamics of its formation/transformation. The results of these time-on-line experiments are given in Table 4.6. with two platinum containing catalysts with different metal loading being tested.

Table 4.6 Time-on-line experiments – lactaldehyde formation over monometallic Pt/C catalyst, in Radley's glass reactor

	Lactaldehyde signal (*)			
Catalyst	1 hour	4 hours	8 hours	24 hours
1%Pt/C	0.052	0.099	0.087	0.087
0.5%Pt/C	0.060	0.073	0.075	0.075

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000 T = 100 °C, P = 3 bar, time = 1 - 24h, stirrer speed = 1000 rpm.
(*)obtained direct integration values imposing the peak of TMS as "1".

As can be seen from this table, in case of 1%Pt/C the formation of lactaldehyde is detected already at 1 hour after the reaction start, its amount is doubled after 4 hours of reaction and it is slowly consumed, presumably to form lactic acid, in an interval between 4 and 8 hours staying unchanged up to the reaction is finished. For 0.5%Pt/C the pattern is slightly different. Lactaldehyde is formed during the first hour of the reaction, and it increases in the next 3 hours and stays at the same level up to 24 hours time. The difference in the way lactaldehyde is formed and consumed is probably correlated with the amount of supported metal. Further attempts to study the formation of lactaldehyde will be described in section 4.3.8.

4.3.3 Results obtained using Radley's glass reactor and HEL autoclave

Two activated carbon-supported catalysts have been chosen for further studies considering the results reported in Table 4.5, they are: 0.5%Au+0.5%Pt/C which gave

the highest conversion values, and 0.5%Pd+0.5%Pt/C which was the most selective towards lactic acid.

It was decided to evaluate the activity of these catalysts using different reactor systems under different pressures and with different types of stirring. The results of these comparative studies are given in Table 4.7.

Table 4.7 Comparison of the results for Radley's glass reactor and HEL autoclave at 100 °C and 3 bar pressure

Entry	Catalyst	Reactor type	Pressure, bar	Conversion (%)	Selectivity, %			
					Lactate	Acetate	Pyruvate	Hydroxy acetone
1	0.5Au+0.5Pt/C	Radley's	3	54	39	3	1	57
2	0.5Au+0.5Pt/C	HEL	3	56	42	20	3	35
3	0.5Au+0.5Pt/C	HEL	10	67	34	12	1	52
4	0.5Pd+0.5Pt/C	Radley's	3	30	43	3	1	53
5	0.5Pd+0.5Pt/C	HEL	3	36	31	27	3	39
6	0.5Pd+0.5Pt/C	HEL	10	20	30	14	2	53

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, T = 100 °C, P = 3 or 10 bar, time = 24 h, stirrer speed = 1000 rpm.

The first step is to compare the results obtained under the same pressure (3 bar) in glass reactor and autoclave in order to evaluate how the type of stirring influences the reaction pathways. Comparing between entries 1-2 and 4-5 in Table 4.7, it can be seen that experiments in autoclave favour the formation of high amounts of the unwanted by-product, acetic acid, up to 27%, whereas in glass reactor only 3% of acetic acid is formed. The selectivity to lactic acid remains nearly the same for 0.5%Au+0.5%Pt/C catalyst, and 0.5%Pd+0.5%Pt/C becomes less selective toward the desired product.

The second step is the comparison of the behaviour of a catalytic system in the same reactor but under different pressures. Increasing the pressure from 3 to 10 bar leads to higher conversion for AuPt/C catalyst and to the suppression of by-products formation (entries 2-3), though their amount is still higher than that of experiments in low pressure glass reactor. The same trend of lower values for acetic and pyruvic acid selectivities was observed for 0.5%Pd+0.5%Pt/C catalyst (entries 5-6), but surprisingly the conversion drastically decreased which suggests that higher pressures are not needed when using PdPt catalysts.

Another parameter that may influence the conversion and/or selectivity is the temperature. A series of experiments have been conducted at elevated temperature (115 °C) for both 0.5%Au+0.5%Pt/C and 0.5%Pd+0.5%Pt/C catalysts at different substrate to metal ratios to detect any possible enhancements, Table 4.8.

Table 4.8 Testing of Au-Pt/C and Pd-Pt/C (KB-B) catalyst under glass reactor conditions at 115 °C

Entry	Catalyst	S:M ratio	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	0.5Au+0.5Pt/C	2000	83	44	29	2	25
2	0.5Au+0.5Pt/C	4000	77	39	29	2	30
3	0.5Pd+0.5Pt/C	2000	73	50	23	3	24
4	0.5Pd+0.5Pt/C	4000	67	47	16	4	33

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio (S:M) = 2000-4000, T = 115 °C, p = 3 bar, time = 24 h, stirrer speed = 1000 rpm.

The results given in Table 4.8 clearly show that elevated temperatures lead to higher conversions (*ca.* 83%). At the same time, the tendency to form unwanted by-products is also observed when using both catalysts, which is explained by overoxidation to pyruvic acid and further C-C bond scission which results in forming C_2 by-product, namely acetic acid.

To further understand the mechanism of by-products formation it was decided to run the experiment at a shorter time over 0.5%Au+0.5%Pt/C catalyst to evaluate the distribution of products at the beginning of the reaction (Table 4.9).

Table 4.9 Testing of Au-Pt/C (KB-B) catalyst under glass reactor conditions at 115 °C at a shorter time (4 hours)

Catalyst	S:M ratio	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/C	2000	48	40	0	7	2	51

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 115 °C, p = 3 bar, time = 4 h, stirrer speed = 1000 rpm.

The conversion value is expectedly lower than after 24 hours (*ca.* 48%), but the ratio

between two major products is still close to 1:1 with small amounts of by-products formed. This indicates that the formation of pyruvic and acetic acids occurs after longer times therefore the time-on-line experiments are needed to better understand the overall process of 1,2-propanediol oxidation.

4.3.4 Time online studies for 1,2-propanediol oxidation over AuPt/C and PdPt/C catalysts

A series of time-on-line experiments have been carried out in HEL autoclave reactor as it allows sampling without depressurizing the system and therefore without shifting the reaction equilibrium. The reactions were conducted using both 0.5%Au+0.5%Pt/C and 0.5%Pd+0.5%Pt/C catalysts to also evaluate the differences in reaction pathways. The results of these tests are given in Tables 4.10 and 4.11.

Table 4.10 Testing of Au-Pt/C (KB-B) catalyst at 115 °C under autoclave conditions

Time, hours	S:M ratio	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
4	4000	58	35	18	2	44
8	4000	69	29	42	4	25
24	4000	82	24	66	5	5
24	2000	93	35	52	7	6

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio (S:M) = 2000-4000, T = 115 °C, P = 10 bar, time = 4h, 8h and 24 h, stirrer speed = 1000 rpm.

Table 4.11 Testing of Pd-Pt/C (KB-B) catalyst at 115 °C under autoclave conditions

Time, hours	S:M ratio	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
4	4000	49	36	15	3	46
8	4000	55	34	29	4	33
24	4000	64	30	60	3	7
24	2000	71	47	41	4	7

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 115 °C, P = 10 bar, time = 4h, 8h and 24 h, stirrer speed = 1000 rpm.

Expectedly, conversions gradually increase with time, but the changes in selectivities

are not straightforward. The selectivity to lactic acid decreases negligibly while using both catalysts, whereas the selectivity to hydroxyacetone drastically decreases with time from 46% at 4 hours to 7% at 24 hours. In contrast, the formation of acetic acid under these conditions is substantial (up to 60%), though the amounts of pyruvic acid remain constant (*ca.* 4%).

Surprisingly, increasing the substrate to metal ratio from 2000 to 4000 and thus decreasing the amount of catalyst used, leads to a decrease in acetic acid formation (60% against 41%) thus shifting the equilibrium towards the formation of the desired product – lactic acid. This trend is observed for both AuPt and PdPt catalysts, with the latter showing higher selectivity to lactic acid even under such vigorous conditions.

4.3.5 Lower pressures and lower temperatures effect on the reaction

Previously it has been shown (section 4.3.4) that high pressure and temperature shift the reaction pathway to the formation of degradation by-products. To evaluate how the decrease in these parameters will influence the reaction of 1,2-propanediol oxidation, it was decided to conduct experiments at 100 and 70 °C, and at the same time, reducing the pressure. It was also decided to carry out the experiments at different substrate to metal ratios, spanning from 2000 to 4000. This is because studies at elevated temperatures (~115 °C) revealed a dependence between the amount of catalyst used and the selectivity toward lactic acid. The results are presented in Tables 4.12 – 4.15.

Table 4.12 Testing of Au-Pt catalyst in Radley's glass reactor (3, 2 and 1 bar) at 100 °C

Entry	S:M ratio	Pressure (bar)	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	2000	3	72	44	16	2	37
2	2000	2	73	43	14	2	41
3	2000	1	65	38	18	2	42
4	4000	3	59	44	12	2	42
5	4000	2	64	43	11	2	44
6	4000	1	68	41	12	2	45

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 100 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Table 4.13 Testing of Pd-Pt catalyst in Radley's glass reactor (3, 2, 1 bar) at 100 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	2000	3	65	50	11	2	37
2	2000	2	66	47	11	3	39
3	2000	1	58	42	13	3	42
4	4000	3	52	47	8	2	43
5	4000	2	55	46	9	3	42
6	4000	1	54	44	9	3	44

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 100 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

What is evident from both tables is that there is no drastic drop in conversion when decreasing the pressure to 1 bar above atmospheric. Using higher amounts of catalyst (entries 1-3 in both tables) results in higher selectivities towards lactic acid but at the same time the amount of acetic acid is high as well. At an increased substrate to metal ratio of 4000, the conversion values are generally slightly lower (entries 4-6) compared to the ones at s:m=2000 but the amount of degradation products obtained is lower as well.

When operating at lower temperatures (Tables 4.14-4.15) the same trend for conversions and selectivities, as expected, is observed: the more the amount of catalyst, the higher the conversion. It is worth noting that the trend to higher selectivities to lactic acid, which was described in a previous section for experiments at 100 °C, is now diminished, giving nearly the same ratios between lactic acid and hydroxyacetone and much less acetic and pyruvic acids formed.

Table 4.14 Testing of Au-Pt catalyst in Radley's glass reactor (3, 2, 1 bar) at 70 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxyacetone
1	2000	3	50	38	4	2	56
2	2000	2	50	37	3	1	59
3	2000	1	52	36	4	1	59
4	4000	3	39	37	3	2	60
5	4000	2	40	38	2	2	60
6	4000	1	42	38	3	1	60

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 70 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Table 4.15 Testing of Pd-Pt catalyst in Radley's glass reactor (3, 2 and 1 bar) at 70 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxyacetone
1	2000	3	36	48	3	1	48
2	2000	2	36	47	2	2	49
3	2000	1	35	47	3	1	49
4	4000	3	24	44	2	2	52
5	4000	2	20	44	0	0	56
6	4000	1	23	43	2	2	53

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 70 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Finally, considering the results described above, it should be highlighted that no clear influence of pressure on the conversion of 1,2-propanediol was detected, meaning that this reaction can be conducted under milder conditions and consuming less oxygen for the oxidation process.

4.3.6. Physical mixtures of catalysts

Previous studies have shown that, in the presence of base, a physical mixture of monometallic Au/C and Pt/C presented a clear synergistic effect with increase of the conversion up to 70%. This effect was proven in terms of both metal loading and metal dispersion when compared with the bimetallic 0.5%Au+0.5%Pt/C. Also the possibility of reducing the total amount of metals was investigated proving that a catalyst with two times less amount of both metals can be used without significant loss in conversion (section 3.3.3.4). In view of these experimental evidences and the results in absence of base so far described, it was decided to carry out control tests for physical mixtures in absence of base.

Chapter 4: BASE-FREE OXIDATION OF 1,2-PROPANEDIOL

4.1 Introduction

The aim of this chapter is to investigate the reaction profile of 1,2-propanediol oxidation under base-free conditions. Firstly, a range of different supports will be screened, and after choosing the most efficient, a variety of combinations of Au, Pd and Pt supported nanoparticles will be tested to find the most effective catalyst composition. The influence of pressure and temperature will also be investigated in detail.

Several attempts of lactaldehyde synthesis will be carried out in order to identify the reaction mechanism of lactic acid formation, as well as the oxidation of all possible intermediates under standard reaction conditions. For this reason, also 1-propanol and 2-propanol will be oxidized as model compounds for competitive alcohol group oxidation.

Finally, reusability tests will be conducted to understand the causes of decrease in conversions as well as to evaluate the possibility of catalyst poisoning and/or catalyst deactivation.

4.2 Experimental

A range of catalysts used for base-free 1,2-propanediol oxidation has been prepared by sol immobilization method (for a detailed description of this procedure, see section 2.2.2.1). The catalytic tests described in this chapter, have been carried out in a low-pressure glass reactor and in a high-pressure autoclave, as described in a section 3.2, with the exception that the addition of base step was omitted.

4.3 Results and discussion

It's well known that 1,2-propanediol and other polyols can be selectively oxidized to corresponding acids under basic conditions [1-4]. However, these routes are not considered green as the presence of base in high concentrations causes the problem of contaminated waste water. It could be interesting from environmental and economical point of view to carry out the oxidation processes in aqueous media. Therefore a new way of oxidizing these substrates is required, ideally without using base as a promoter or significantly reducing its amount. It has been reported that it is possible to oxidize polyols in aqueous media [5-8]. Thus, non-activated alcohols can be oxidized using colloidal nanoparticles [9] and glycerol can be selectively oxidized under base-free conditions over MgO-supported nanoparticles [10]. The aim of this chapter is to extend previous findings on non-basic alcohol oxidation in aqueous media over heterogeneous reusable catalysts and to possibly identify the mechanism of the 1,2-propanol oxidation to lactic acid.

4.3.1 Preliminary experiments in presence of base and at non-basic conditions

At the initial stage of this study it was decided to test catalysts that proved themselves efficient for the 1,2-propanol oxidation (sections 3.3.2 and 3.3.3). An explorative series of tests has been carried out in a Radley's low pressure glass reactor using AuPt catalysts supported on titania, magnesia and activated carbon under base and base-free conditions. The results of these preliminary experiments are given in Table 4.1.

Table 4.1 Tests of different AuPt catalysts supported on TiO_2, MgO and activated carbon for the 1,2-propanediol oxidation, in presence and absence of base.

				Selectivity, %				
Entry	Catalyst	NaOH/S	Conversion (%)	Lactate	Formate	Acetate	Pyruvate	Hydroxyacetone
1	0.5Au+0.5Pt/TiO_2	1	20	96	4	0	0	0
2	0.5Au+0.5Pt/TiO_2	0	0	0	0	0	0	0
3	0.5Au+0.5Pt/MgO	1	22	85	5	10	0	0
4	0.5Au+0.5Pt/MgO	0	40	32	0	3	0	65
5	0.5Au+0.5Pt/C	1	78	86	3	11	0	0
6	0.5Au+0.5Pt/C	0	4	40	0	0	0	60

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, Base/1,2-propanediol molar ratio (NaOH/S) = 1 or 0, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm

As can be seen from this table, magnesia and activated carbon supported catalysts showed activity under base-free conditions with the former being extremely active (entries 3 and 4), with conversion values of ~20 and 40%, whereas titania supported catalyst could oxidise the diol only in the presence of base (entry 1). On that basis, the MgO-supported catalyst was chosen for further studies. Interestingly, when moving from basic conditions to aqueous media, another product is formed, namely hydroxyacetone (entries 4 and 6) in quantities larger than the desired lactic acid. It has been previously reported [11] that in basic media hydroxyacetone is unstable and is converted into condensed products, therefore its formation in the absence of base is expected.

To investigate the ways of increasing conversion values and shifting the equilibrium to the production of lactic acid, it was decided to try different reactor systems and to carry out experiments at elevated pressures. An experiment in high pressure autoclave has been conducted at 10 bar pressure to evaluate its influence on lactic acid formation, and its result is reported in Table 4.2.

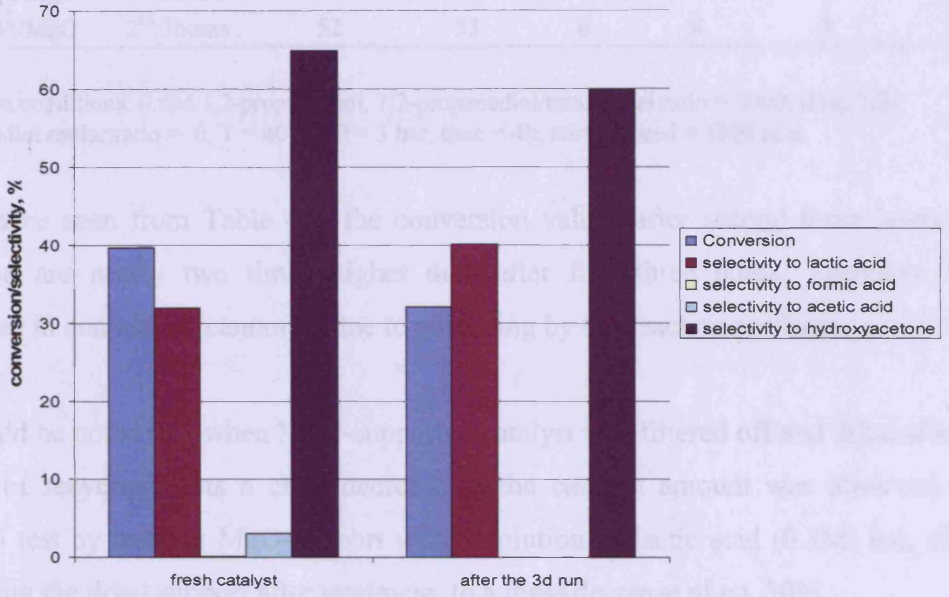
Table 4.2 Oxidation of 1,2-propanediol at basic and base-free conditions in HEL autoclave

Catalyst	NaOH/ S	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/MgO	0	28	49	0	3	0	48

Reaction conditions: 1,2-propanediol concentration=0.6M, P=10 bar, T=40°C, stirrer speed=1000rpm, time=4 hours, temperature 40 °C, s:m = 1:4000

What is immediately obvious when comparing the result obtained in autoclave (Table 4.2) and entry 4 from Table 4.1, is that high pressure is favourable to increase the selectivity to lactic acid, though it clearly decreases the overall conversion. After calculating the yield of the reaction at 3 and 10 bar pressure, which appeared to be the same, it was decided to operate at less demanding lower pressures.

As 0.5%Au+0.5%Pt/MgO catalyst proved to be active in the absence of base, reusability tests were further carried out in Radley's glass reactor to evaluate the behaviour of MgO-supported catalyst after several cycles (Fig. 4.1). Straightforward comparison of the results obtained after the first and the third runs clearly shows the decrease in conversion (proved by reproducibility tests), therefore tests for investigating the reasons of catalyst deactivation were required.



Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm

Figure 4.1 Reusability tests for MgO supported catalyst

Catalyst deactivation is a complex phenomenon and it which may occur for a number of reasons: sintering, coke formation, change of metal oxidation state, blocking or poisoning of active sites by products formed or even by starting material *etc* [12]. It was decided to start with experiments on catalyst poisoning. These tests were carried out in the following way: a standard amount of catalyst (0.1176 g) was used for the oxidation reaction for the first 3 hours, and then a sample was taken to measure the conversion and selectivity. However, before repressurizing the system a fresh catalyst was added into the reactor, and the reaction continued for further 3 hours. Before the catalyst is added, products will already be forming and so this procedure will check if reaction products lead to catalyst poisoning. In fact, if they are, the conversion should

drop down when comparing the data obtained after first and second 3 hours.

Table 4.3. Control test for catalyst poisoning for no-base 1,2-propanediol oxidation

Catalyst	time	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/MgO	1st 3hours	30	47	6	2	1	45
0.5Au+0.5Pt/MgO	2nd 3hours	52	53	6	4	0	37

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, Base/1,2-propanediol molar ratio = 0, T = 40 °C, P = 3 bar, time = 4h, stirrer speed = 1000 rpm.

As can be seen from Table 4.3, the conversion values after second three hours of reaction are nearly two times higher than after first three hours. Therefore the decrease in conversion cannot be due to poisoning by the reaction products.

It should be noted that when MgO-supported catalyst was filtered off and dried after a series of recycling tests a clear decrease in the catalyst amount was observed. A control test by treating MgO-support with a solution of lactic acid (0.3M) led, after weighing the dried support after treatment, to a mass decrease of *ca.* 30%.

The conclusion that was made is that lactic acid which is formed in along the reaction is strong enough (pK_a = 3.86) to dissolve the basic magnesia oxide, and therefore MgO supported catalysts are not suitable for the reaction when strong acids are being formed. In fact upon loss of the MgO support, gold particles can agglomerate. This explains also the activity of MgO-supported catalyst in base: NaOH added at the beginning of the reaction neutralizes lactic acid by forming lactate and therefore prevents the support from being dissolved.

4.3.2 Test of Au, Pd and Pt nanoparticles supported on activated carbon

As it has been reported in Chapter 3, precious metal catalysts supported on activated carbon showed intrinsic activity in 1,2-propanediol oxidation at basic conditions. Preliminary tests of AuPt/C catalyst conducted in the absence of base (Table 4.1 entry

6) displayed some activity under no-base conditions.

A selected range of carbon-supported catalysts were tested and the results are shown in Table 4.4. As 0.5%Au+0.5%Pt/C previously was tested at 4 hours and gave only 4% conversion, so it was decided to increase the reaction time up to 24 hours in order to obtain higher conversion values.

Table 4.4. Test of different mono- and bi-metallic catalysts at 40 °C, support – activated carbon (KB-B), in Radley's glass reactor

Entry	Catalyst	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
1	1Au	0	0	0	0	0
2	1Pd	0	0	0	0	0
3	1Pt	2	40	0	0	60
4	0.5Au+0.5Pt	33	39	0	0	60
5	0.5Au+0.5Pd	4	14	0	0	86
6	0.5Pd+0.5Pt	13	44	0	0	56
7	0.3Au+0.3Pd+0.3Pt	15	32	2	1	65

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, T = 40 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Surprisingly, monometallic Au/C catalyst appeared to be inactive in the absence of base (entry 1) while it is known to be active under basic conditions (Chapter 3, Table 3.2). Pd/C catalyst is totally inactive under both basic and base-free conditions (entry 2), whereas Pt/C appears to oxidize 1,2-propanediol as well as bi- and tri-metallic combinations of these three metals (entries 3-7). The highest conversion and lactic acid selectivity values were achieved when using 0.5%Au+0.5%Pt/C catalyst (entry 4). Interestingly, 0.5%Au+0.5%Pd/C catalyst shifts the reaction pathway to the formation of hydroxyacetone and lower yields to lactic acid, whereas the combination of Au with Pt results is close to 1:1 product ratio.

For further improvements in conversions it was decided to increase the temperature at which the experiments are carried out to 100 °C and to test the full range of Au-Pd-Pt catalysts. The data are summarized in Table 4.5.

Table 4.5 Test of different mono- and bi-metallic catalysts at 100 °C, support – activated carbon (KB-B), in Radley's glass reactor, for 1,2-propanediol oxidation.

Entry	Catalyst	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
1	1Au	9	13	6	0	81
2	1Pd	6	17	8	0	75
3	1Pt	31	45	9	5	41
4	0.5Au+0.5Pt	75	40	20	2	38
5	0.5Au+0.5Pd	35	14	15	2	69
6	0.5Pd+0.5Pt	61	48	11	2	39
7	0.3Au+0.3Pd+0.3Pt	48	26	19	53	2

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000 T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Under these more vigorous reaction conditions the conversions are considerably higher. Thus, monometallic Au/C and Pd/C oxidized 1,2-propanediol at the level of *ca.* 10% (entries 1 and 2) with the tendency to form large amounts of hydroxyacetone, and the same trend was observed for bimetallic combination of those metals. The trend in activity observed for bi- and tri-metallic catalysts was AuPd < AuPdPt < PdPt < AuPt with 0.5%Au+0.5%Pt/C being the most active. The trend mentioned above is not followed for selectivities to the desired product, lactic acid, and it appeared that 0.5%Pd+0.5%Pt/C works more selectively over the whole range.

It is important to note that lactaldehyde was detected by NMR when using monometallic Pt/C catalyst, though its amount was close to the accuracy limit of NMR integration, therefore its quantitative integration was not possible. For practical purposes NMR was the only technique that was possible to use as thsi substance is commercially unavailable due to instability and therefore cannot be used as calibration standard for GC. It has been reported that the probable mechanism of the reaction of 1,2-propanediol oxidation includes aldehyde formation [13], which would be quickly transformed to lactic acid. During our studies in the presence of base, it was not possible to detect this intermediate.

To further investigate the formation of lactaldehyde and its transformation to lactic acid an experiment with sequential sampling was performed. As long as the amount of

lactaldehyde is very small and cannot be calculated in relation to starting material or lactic acid, a specially designed sealed glass insert, containing tetramethylsilane (TMS) dissolved in $CDCl_3$ was used as as an internal standard for NMR analysis [14] to calibrate and to evaluate the amount of lactaldehyde and dynamics of its formation/transformation. The results of these time-on-line experiments are given in Table 4.6. with two platinum containing catalysts with different metal loading being tested.

Table 4.6 Time-on-line experiments – lactaldehyde formation over monometallic Pt/C catalyst, in Radley's glass reactor

	Lactaldehyde signal (*)			
Catalyst	1 hour	4 hours	8 hours	24 hours
1%Pt/C	0.052	0.099	0.087	0.087
0.5%Pt/C	0.060	0.073	0.075	0.075

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000 T = 100 °C, P = 3 bar, time = 1 - 24h, stirrer speed = 1000 rpm.
(*)obtained direct integration values imposing the peak of TMS as "1".

As can be seen from this table, in case of 1%Pt/C the formation of lactaldehyde is detected already at 1 hour after the reaction start, its amount is doubled after 4 hours of reaction and it is slowly consumed, presumably to form lactic acid, in an interval between 4 and 8 hours staying unchanged up to the reaction is finished. For 0.5%Pt/C the pattern is slightly different. Lactaldehyde is formed during the first hour of the reaction, and it increases in the next 3 hours and stays at the same level up to 24 hours time. The difference in the way lactaldehyde is formed and consumed is probably correlated with the amount of supported metal. Further attempts to study the formation of lactaldehyde will be described in section 4.3.8.

4.3.3 Results obtained using Radley's glass reactor and HEL autoclave

Two activated carbon-supported catalysts have been chosen for further studies considering the results reported in Table 4.5, they are: 0.5%Au+0.5%Pt/C which gave

the highest conversion values, and 0.5%Pd+0.5%Pt/C which was the most selective towards lactic acid.

It was decided to evaluate the activity of these catalysts using different reactor systems under different pressures and with different types of stirring. The results of these comparative studies are given in Table 4.7.

Table 4.7 Comparison of the results for Radley's glass reactor and HEL autoclave at 100 °C and 3 bar pressure

Entry	Catalyst	Reactor type	Pressure, bar	Conversion (%)	Selectivity, %			
					Lactate	Acetate	Pyruvate	Hydroxy acetone
1	0.5Au+0.5Pt/C	Radley's	3	54	39	3	1	57
2	0.5Au+0.5Pt/C	HEL	3	56	42	20	3	35
3	0.5Au+0.5Pt/C	HEL	10	67	34	12	1	52
4	0.5Pd+0.5Pt/C	Radley's	3	30	43	3	1	53
5	0.5Pd+0.5Pt/C	HEL	3	36	31	27	3	39
6	0.5Pd+0.5Pt/C	HEL	10	20	30	14	2	53

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 4000, T = 100 °C, P = 3 or 10 bar, time = 24 h, stirrer speed = 1000 rpm.

The first step is to compare the results obtained under the same pressure (3 bar) in glass reactor and autoclave in order to evaluate how the type of stirring influences the reaction pathways. Comparing between entries 1-2 and 4-5 in Table 4.7, it can be seen that experiments in autoclave favour the formation of high amounts of the unwanted by-product, acetic acid, up to 27%, whereas in glass reactor only 3% of acetic acid is formed. The selectivity to lactic acid remains nearly the same for 0.5%Au+0.5%Pt/C catalyst, and 0.5%Pd+0.5%Pt/C becomes less selective toward the desired product.

The second step is the comparison of the behaviour of a catalytic system in the same reactor but under different pressures. Increasing the pressure from 3 to 10 bar leads to higher conversion for AuPt/C catalyst and to the suppression of by-products formation (entries 2-3), though their amount is still higher than that of experiments in low pressure glass reactor. The same trend of lower values for acetic and pyruvic acid selectivities was observed for 0.5%Pd+0.5%Pt/C catalyst (entries 5-6), but surprisingly the conversion drastically decreased which suggests that higher pressures are not needed when using PdPt catalysts.

Another parameter that may influence the conversion and/or selectivity is the temperature. A series of experiments have been conducted at elevated temperature (115 °C) for both 0.5%Au+0.5%Pt/C and 0.5%Pd+0.5%Pt/C catalysts at different substrate to metal ratios to detect any possible enhancements, Table 4.8.

Table 4.8 Testing of Au-Pt/C and Pd-Pt/C (KB-B) catalyst under glass reactor conditions at 115 °C

Entry	Catalyst	S:M ratio	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	0.5Au+0.5Pt/C	2000	83	44	29	2	25
2	0.5Au+0.5Pt/C	4000	77	39	29	2	30
3	0.5Pd+0.5Pt/C	2000	73	50	23	3	24
4	0.5Pd+0.5Pt/C	4000	67	47	16	4	33

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio (S:M) = 2000-4000, T = 115 °C, p = 3 bar, time = 24 h, stirrer speed = 1000 rpm.

The results given in Table 4.8 clearly show that elevated temperatures lead to higher conversions (*ca.* 83%). At the same time, the tendency to form unwanted by-products is also observed when using both catalysts, which is explained by overoxidation to pyruvic acid and further C-C bond scission which results in forming C_2 by-product, namely acetic acid.

To further understand the mechanism of by-products formation it was decided to run the experiment at a shorter time over 0.5%Au+0.5%Pt/C catalyst to evaluate the distribution of products at the beginning of the reaction (Table 4.9).

Table 4.9 Testing of Au-Pt/C (KB-B) catalyst under glass reactor conditions at 115 °C at a shorter time (4 hours)

Catalyst	S:M ratio	Conversion (%)	Selectivity, %				
			Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
0.5Au+0.5Pt/C	2000	48	40	0	7	2	51

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 115 °C, p = 3 bar, time = 4 h, stirrer speed = 1000 rpm.

The conversion value is expectedly lower than after 24 hours (*ca.* 48%), but the ratio

between two major products is still close to 1:1 with small amounts of by-products formed. This indicates that the formation of pyruvic and acetic acids occurs after longer times therefore the time-on-line experiments are needed to better understand the overall process of 1,2-propanediol oxidation.

4.3.4 Time online studies for 1,2-propanediol oxidation over AuPt/C and PdPt/C catalysts

A series of time-on-line experiments have been carried out in HEL autoclave reactor as it allows sampling without depressurizing the system and therefore without shifting the reaction equilibrium. The reactions were conducted using both 0.5%Au+0.5%Pt/C and 0.5%Pd+0.5%Pt/C catalysts to also evaluate the differences in reaction pathways. The results of these tests are given in Tables 4.10 and 4.11.

Table 4.10 Testing of Au-Pt/C (KB-B) catalyst at 115 °C under autoclave conditions

Time, hours	S:M ratio	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
4	4000	58	35	18	2	44
8	4000	69	29	42	4	25
24	4000	82	24	66	5	5
24	2000	93	35	52	7	6

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio (S:M) = 2000-4000, T = 115 °C, P = 10 bar, time = 4h, 8h and 24 h, stirrer speed = 1000 rpm.

Table 4.11 Testing of Pd-Pt/C (KB-B) catalyst at 115 °C under autoclave conditions

Time, hours	S:M ratio	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
4	4000	49	36	15	3	46
8	4000	55	34	29	4	33
24	4000	64	30	60	3	7
24	2000	71	47	41	4	7

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 115 °C, P = 10 bar, time = 4h, 8h and 24 h, stirrer speed = 1000 rpm.

Expectedly, conversions gradually increase with time, but the changes in selectivities

are not straightforward. The selectivity to lactic acid decreases negligibly while using both catalysts, whereas the selectivity to hydroxyacetone drastically decreases with time from 46% at 4 hours to 7% at 24 hours. In contrast, the formation of acetic acid under these conditions is substantial (up to 60%), though the amounts of pyruvic acid remain constant (*ca.* 4%).

Surprisingly, increasing the substrate to metal ratio from 2000 to 4000 and thus decreasing the amount of catalyst used, leads to a decrease in acetic acid formation (60% against 41%) thus shifting the equilibrium towards the formation of the desired product – lactic acid. This trend is observed for both AuPt and PdPt catalysts, with the latter showing higher selectivity to lactic acid even under such vigorous conditions.

4.3.5 Lower pressures and lower temperatures effect on the reaction

Previously it has been shown (section 4.3.4) that high pressure and temperature shift the reaction pathway to the formation of degradation by-products. To evaluate how the decrease in these parameters will influence the reaction of 1,2-propanediol oxidation, it was decided to conduct experiments at 100 and 70 °C, and at the same time, reducing the pressure. It was also decided to carry out the experiments at different substrate to metal ratios, spanning from 2000 to 4000. This is because studies at elevated temperatures (~115 °C) revealed a dependence between the amount of catalyst used and the selectivity toward lactic acid. The results are presented in Tables 4.12 – 4.15.

Table 4.12 Testing of Au-Pt catalyst in Radley's glass reactor (3, 2 and 1 bar) at 100 °C

Entry	S:M ratio	Pressure (bar)	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	2000	3	72	44	16	2	37
2	2000	2	73	43	14	2	41
3	2000	1	65	38	18	2	42
4	4000	3	59	44	12	2	42
5	4000	2	64	43	11	2	44
6	4000	1	68	41	12	2	45

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 100 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Table 4.13 Testing of Pd-Pt catalyst in Radley's glass reactor (3, 2, 1 bar) at 100 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	2000	3	65	50	11	2	37
2	2000	2	66	47	11	3	39
3	2000	1	58	42	13	3	42
4	4000	3	52	47	8	2	43
5	4000	2	55	46	9	3	42
6	4000	1	54	44	9	3	44

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 100 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

What is evident from both tables is that there is no drastic drop in conversion when decreasing the pressure to 1 bar above atmospheric. Using higher amounts of catalyst (entries 1-3 in both tables) results in higher selectivities towards lactic acid but at the same time the amount of acetic acid is high as well. At an increased substrate to metal ratio of 4000, the conversion values are generally slightly lower (entries 4-6) compared to the ones at s:m=2000 but the amount of degradation products obtained is lower as well.

When operating at lower temperatures (Tables 4.14-4.15) the same trend for conversions and selectivities, as expected, is observed: the more the amount of catalyst, the higher the conversion. It is worth noting that the trend to higher selectivities to lactic acid, which was described in a previous section for experiments at 100 °C, is now diminished, giving nearly the same ratios between lactic acid and hydroxyacetone and much less acetic and pyruvic acids formed.

Table 4.14 Testing of Au-Pt catalyst in Radley's glass reactor (3, 2, 1 bar) at 70 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxyacetone
1	2000	3	50	38	4	2	56
2	2000	2	50	37	3	1	59
3	2000	1	52	36	4	1	59
4	4000	3	39	37	3	2	60
5	4000	2	40	38	2	2	60
6	4000	1	42	38	3	1	60

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 70 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Table 4.15 Testing of Pd-Pt catalyst in Radley's glass reactor (3, 2 and 1 bar) at 70 °C

Entry	S:M ratio	Pressure, bar	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxyacetone
1	2000	3	36	48	3	1	48
2	2000	2	36	47	2	2	49
3	2000	1	35	47	3	1	49
4	4000	3	24	44	2	2	52
5	4000	2	20	44	0	0	56
6	4000	1	23	43	2	2	53

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000-4000, T = 70 °C, P = 3, 2 or 1 bar, time = 24 h, stirrer speed = 1000 rpm.

Finally, considering the results described above, it should be highlighted that no clear influence of pressure on the conversion of 1,2-propanediol was detected, meaning that this reaction can be conducted under milder conditions and consuming less oxygen for the oxidation process.

4.3.6. Physical mixtures of catalysts

Previous studies have shown that, in the presence of base, a physical mixture of monometallic Au/C and Pt/C presented a clear synergistic effect with increase of the conversion up to 70%. This effect was proven in terms of both metal loading and metal dispersion when compared with the bimetallic 0.5%Au+0.5%Pt/C. Also the possibility of reducing the total amount of metals was investigated proving that a catalyst with two times less amount of both metals can be used without significant loss in conversion (section 3.3.3.4). In view of these experimental evidences and the results in absence of base so far described, it was decided to carry out control tests for physical mixtures in absence of base.

Table 4.16. Catalytic tests using Au and Pt containing carbon supported catalysts alloyed and as physical mixture

		Selectivity, %							
	Catalyst	s:m ratio	Weight of catalyst (g)	Conversion (%)	Lactate	Formate	Acetate	Hydroxy-acetone	Pyruvate
1	0.5%Au+0.5%Pt/C **bimetallic**	4000	0.06	62	43	0	12	43	2
		Metal loading effect							
2	1%Au/C + 1%Pt/C **(physical mixture)**	total 4000 (8000+8000)	0.03 + 0.03	37	49	0	9	40	2
3	1%Au/C	4000	0.06	6	10	0	0	90	0
4	1%Pt/C	4000	0.06	32	46	0	6	44	4
		Metal dispersion effect							
5	0.5%Au/C + 0.5%Pt/C **(physical mixture)**	total 1000 (2000+2000)	0.12 + 0.12	38	57	0	9	33	1
6	0.5%Au/C	2000	0.12	6	18	0	9	73	0
7	0.5%Pt/C	2000	0.12	27	41	0	9	45	5
8	0.5%Au/C + 0.5%Pt/C **(physical mixture)**	total 2000 (4000+4000)	0.06 + 0.06	26	57	0	7	34	2
9	0.5%Au/C	4000	0.06	3	20	0	0	80	0
10	0.5%Pt/C	4000	0.06	18	38	0	6	50	6
		Low metal loading							
11	0.25%Au+0.25%Pt/C **(bimetallic)**	1000	0.24	64	38	0	18	43	1
12	0.25%Au+0.25%Pt/C **(bimetallic)**	2000	0.12	51	39	0	14	45	2
13	0.25%Au+0.25%Pt/C **(bimetallic)**	4000	0.06	40	42	0	10	46	2
14	0.25%Au+0.25%Pt/C **(bimetallic)**	8000	0.03	31	41	0	6	51	2

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 1000-8000, T = 100 °C, P = 3 bar, time = 24h

A series of experiments have been carried out in the absence of base at 100 °C and 24 hours to evaluate if there is any tendency to enhance the conversion when using physical mixtures of Au/C and Pt/C catalysts. The results of these tests are reported in Table 4.16. Entry 1 of this table shows the results of using bimetallic 0.5%Au+0.5%Pt/C catalyst and will be further used for a comparison. Entries 2 and 8 show the results of mixing monometallic Au/C and Pt/C and testing them in amounts calculated to emulate the effect of the same metal loading, or the same metal dispersion, of the bimetallic 0.5%Au+0.5%Pt/C catalyst. Entries 3-4, 6-7 and 9-10 indicate the results of testing monometallic catalysts for further comparison with the tests on physical mixtures in attempts to prove or disprove the presence of a synergistic effect.

Interestingly, unlike in the presence of base, where Au/C when mixed with inactive Pt/C gave conversion values compared to those of bimetallic catalysts, at non-basic condition the situation is different in several aspects. Firstly, in absence of base the activity is nearly the opposite to that in the presence of base: Au/C has very low activity (*ca.* 6%), whereas Pt/C converts up to 32% of 1,2-propanediol. Secondly, comparing the results of testing a bimetallic catalyst (entry 1) with a physical mixture taken in the amount that mimics total metal loading of the bimetallic one (entry 2), no significant synergistic effect is observed and the conversion value is about 37% (against 67% for a bimetallic catalyst). Thirdly, using the catalysts for imitating the metal dispersion does not result in the same conversions as when using the bimetallic 0.5%Au+0.5%Pt/C.

Finally, reducing the amount of metals does not give the expected high conversion values, which means the optimal metal loading is 1 wt %. It should be noted that, like in the case of basic oxidation over physical mixtures, in the absence of base Au/C is less selective to lactic acid than Pt/C, which contradicts the results obtained by Prati and Rossi [15] having reported that Au/C is extremely active and selective for 1,2-propanediol oxidation. This could be due to the difference in the nature of the activated carbon support used.

4.3.7 Use of air as an oxidant at atmospheric pressure

Previous studies under different pressures (section 4.3.5) showed that the amount of oxygen needed to carry out the reaction can be significantly reduced without noticable losses in conversions. Therefore studies were carried out using oxygen bubbled through the reaction mixture to evaluate the reaction behaviour under atmospheric pressure. To further decrease the environmental impact of this reaction, studies were carried out using air as oxidant in place of pure oxygen (for a detailed description of the reactor used for oxidation at atmospheric pressure, see section 2.4.1.3)

Table 4.17 Comparison of testing Au-Pt catalyst in Radley's glass reactor (3, 2 and 1 bar) and 3 neck round bottom flask reactor (O_2 bubbling)

Entry	Oxygen pressure	Reactor type	Conversion (%)	Selectivity, %			
				Lactate	Acetate	Pyruvate	Hydroxy acetone
1	3 bar	Radley's	72	44	16	2	37
2	2 bar	Radley's	73	43	14	2	41
3	1 bar	Radley's	65	38	18	2	42
4	100 ml/min flow	flask+condenser	59	19	44	4	33
5	Air at atm. pressure	flask+condenser	-	-	-	-	-

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, T = 100 °C, p = 3,2,1 bar (for Radley's); 100 ml/min bubbling or stirring at atmospheric pressure (for round bottom flask) or static air, time = 24 h, stirrer speed = 1000 rpm.

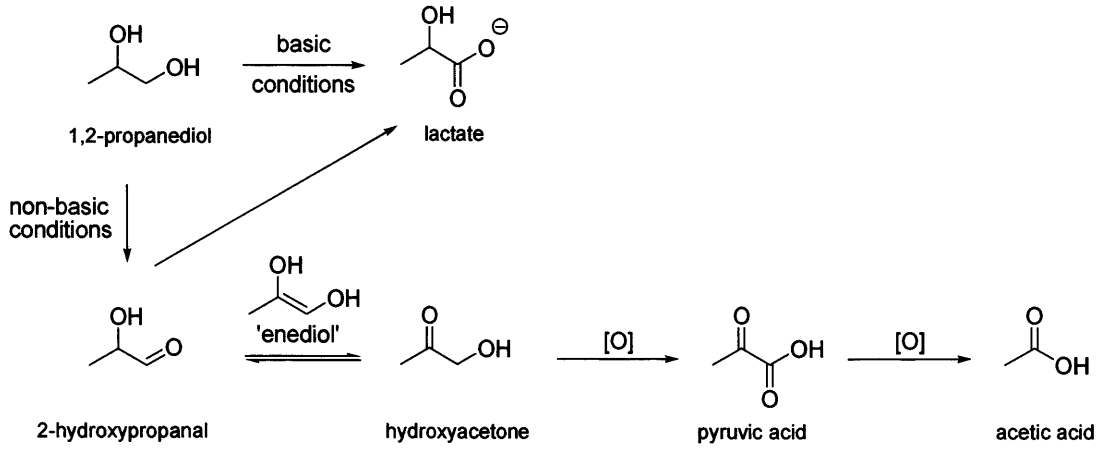
The results obtained after a series of experiments are given in a Table 4.17 and clearly show that oxygen supply is necessary for the successful transformation of 1,2-propanediol, as carrying out experiments using air resulted in no conversion (entry 5).

Interestingly, using oxygen as an oxidant source, but bubbling it through the aqueous 1,2-propanediol, changed the reaction profile to the formation of acetic acid and a drastic decrease in selectivity to lactic acid. This indicates that, though oxidation can be done at atmospheric pressure, pressurizing the system is vital to drive the lactic acid selectivity to higher values and to decrease the formation of degradation products.

4.3.8 Lactaldehyde synthesis and possible mechanism for no-base oxidation

Mechanistic considerations of the 1,2-propanediol oxidation in the absence of base can be made by taking into account all the results obtained at different reaction conditions and described in previous sections.

A possible explanation for the observed outcomes of these reactions is presented in Scheme 4.1. In the presence of base, the oxidation follows a well-established pattern of highly selective oxidation of the primary alcohol group, to the exclusion of any reaction at the secondary hydroxy site [11]. This is in agreement with the relative acidity of the two hydroxyl groups, because the primary hydroxyl is about ten times more acidic than the secondary hydroxyl group [16] and hence deprotonation of the primary hydroxyl group is an important step facilitating oxidation. Therefore, it can be expected that in basic conditions the primary hydroxyl group will be more reactive to oxidation. In this case, the initial product should be 2-hydroxypropanal (see Scheme 4.1); however, it is assumed that it is either very rapidly oxidized to lactate or that it is never released from the catalyst surface prior to the second oxidation step.



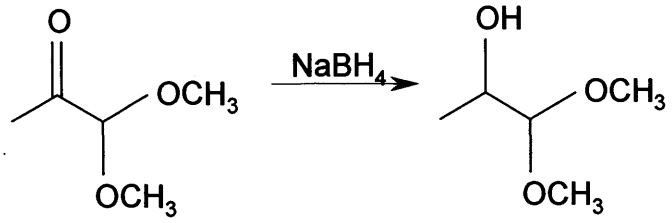
Scheme 4.1. Possible oxidative pathways to the observed products

Suprisingly, hydroxyacetone was formed as a major product during the base-free reactions. As a product of a single oxidation, it is perhaps obvious that it originates from selective oxidation at the secondary alcohol site of the propanediol. Such a substantial loss of regioselectivity has not been observed before in this type of

catalysed oxidation [17,18]. An alternative explanation is that the initial 2-hydroxypropanal rearranges to the observed hydroxyacetone *via* an enediol intermediate. This interchange has been inferred previously [19,20]; and this rearrangement can easily be triggered by an acid but also by a base – but this is exactly the reagent that is missing when the unexpected hydroxyacetone formation takes place. It would therefore seem that the equilibration must be triggered on the catalyst surface.

In order to prove or disprove these assumptions it was decided to oxidize all possible intermediates formed during the reaction. The only compound being not commercially available due to instability was 2-hydroxypropanal, or lactaldehyde, therefore a syntetic route was attempted.

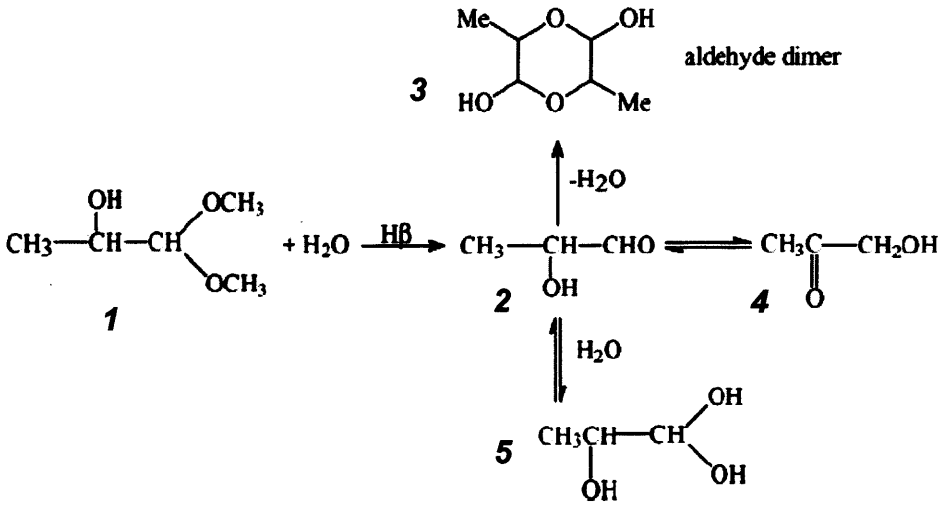
Lactaldehyde synthesis was carried out in 2 sequential steps.



The first step was conducted according to the following procedure [21]. To a solution of pyruvic aldehyde dimethyl acetal (11.81 g, 100 mmol) in MeOH/THF (50 mL/50 mL) was added $NaBH_4$ (3.783 g, 100 mmol, 1.0 equiv) in portions over 10 min at 0 °C. The mixture was then allowed to warm to room temperature and was stirred for 30 minutes. The mixture was then poured into saturated aqueous NH_4Cl solution (50 mL) and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were concentrated by rotary evaporation to give a pale yellow residue. The residue was dissolved in CH_2Cl_2 (150 mL) which was washed with brine (50 mL) and then was dried (Na_2SO_4), and filtered. The solvent was removed by rotary evaporation to give the crude product, which was purified by Kugelrohr distillation to afford 10.09 g (84% yield) of a colourless liquid.

This first stage was successful with yield 50% (though the reported value from literature was 84% probably due to losses when purifying and evaporating solvents), with ^{1}H and ^{13}C NMR spectra that fully match the description given in literature.

The second step of lactaldehyde synthesis was carried out using three different approaches [22-24], in a three neck round bottom flask with heating control and stirring. The Scheme 4.2 depicts all possible isomers that may exist in equilibrium with lactaldehyde.



Scheme 4.2. Transformation of 2-hydroxypropanal to possible isomers [22].

Route 1: – use of zeolites H-ZSM-5 or H-β as catalysts.

Reaction conditions:

- molar water/substrate ratio=20/1
- catalyst 5 wt.%,
- T = 90 °C,
- reaction time = 5 hours.

H-Zeolite-β was reported to be the best catalyst, with 100% conversion and transformation to lactaldehyde and hydroxyacetone and selectivity depending on the reaction times. But after reproducing this synthesis, the conversion appeared to be ca. 80%, and mainly to dimer - dioxane based structures **3** (54%), hydroxyacetone **4** (43%) and only traces of free aldehyde **2** (~2%); for H-ZSM-5, which was reported to be the the second most effective catalyst, the conversion is negligible (less than < 1%). Farther synthesis could involve higher dilutions and lower temperatures.

Route 2: use of pyridinium *p*-toluenesulfonate (PPTS) and EtOH as solvent.

Reaction conditions:

- molar substrate/PPTS ratio = 10:1
- weight EtOH/substrate ratio = 10:1
- T = 55 °C,
- reaction time = 3 hours.

Conversion value for this second route was 22%, and the selectivity to corresponding diethylacetal 70%; 8% to products **2**, **3** and **4** overall (with traces only of free aldehyde); and the remaining 22% in selectivity is for an unknown product.

Route 3: use of pyridinium *p*-toluenesulfonate (PPTS) and H_2O as solvent.
Reaction conditions:
- molar substrate/PPTS ratio=10:1
- weight H_2O /substrate ration =10:1
- T = 90 °C,
- Reaction time = 5 hours.

In this case, the reaction is almost quantitative with a conversion above 95%, with selectivity to product **3** of *ca.* 75% and the remaining 25% unidentified dimer dioxane based structures (All corresponding NMR spectra are given in Appendix C).

Despite reports in literature which claim that it is possible to synthesise lactaldehyde, in our case the preferential product was always dimer **3**, therefore it appears to be difficult to isolate the aldehyde in free form. A further, possible route could be to modify Route 3, which was the most efficient, in terms of conversion, by decreasing the water/substrate ratio.

In view of this, a series of experiments on oxidation of all possible intermediates (except lactaldehyde) have been carried out both in absence and presence of base to understand the mechanism of 1,2-propanediol oxidation and the formation of undesired by-products. The results of these tests are presented in Table 4.18.

Table 4.18. Mechanistic studies of 1,2-propanediol oxidation under basic and base-free conditions.

Substance	basic conditions, catalyst 0.5%Au+0.5%Pt/C 100°C, 3 bar O_2, 24 hours	basic conditions, **no catalyst** 100°C, 3 bar O_2, 24 hours	no base catalyst 0.5%Au+0.5%Pt/C 100°C, 3 bar O_2, 24 hours	no base **no catalyst** 100°C, 3 bar O_2, 24 hours
Lactic acid	Conversion **6%** Acetic acid (**100%**)	-	Acetic acid (traces~**2%**)	-
Pyruvic acid	Conversion **100%** Acetic acid (**83%**) Formic acid (**17%**)	Conversion **100%** Acetic acid (**93%**) Formic acid (**7%**)	Conversion **38%** Acetic acid (**100%**)	Conversion **5%** Acetic acid (**100%**)
Hydroxy-acetone	Conversion **100%** Lactic acid (**52%**) Acetic acid (**37 %**) Formic acid (**11%**) Unknown (**4%**)	Conversion **100%** Lactic acid (**41%**) Acetic acid (**36%**) Formic acid (**17%**) Unknown (**6%**)	- Acetic acid (traces ~ **1%**)	-
Methyl glyoxal	Conversion **100%** Lactic acid (**80%**) Acetic acid (**15%**) Pyruvic acid (**5%**)	Conversion **96%** Lactic acid (**80%**) Acetic acid (**11%**) Formic acid (**9%**)	Conversion **71%** Acetic acid (**100%**)	Conversion **14%** Acetic acid (**62%**) Formic acid (**38%**)

*Values in brackets represent selectivities to a corresponding product, amount of NaOH used (when used) – 1 eq to corresponding substance

As long as it was not possible to prove or disprove the transformation of lactaldehyde into hydroxyacetone, our attention has been paid to the formation of all other reaction products.

Under basic conditions lactic acid is stable and can be hardly oxidized to acetic acid. Pyruvic acid is selectively oxidized, and what is interesting – transformed, to acetic acid, in the presence of base giving formate as the second product. Methyl glyoxal under basic conditions selectively rearranges to lactic acid even with no catalyst present (intramolecular Canizzaro reaction), though without base it is transformed to acetic acid. The most interesting behaviour is that of hydroxyacetone. Just after treatment with sodium hydroxide it appears to be unstable [11] - NMR after 5 min shows lots of aldol products, after 1 hour – no clearly defined peaks detected (see Appendix C). In case of heating, oxygen supply and in the presence of base, it is converted to lactic acid, giving acetic and formic acid as by-products. Control tests showed the stability of all other products under basic conditions.

What is clear from these results is that acetic acid most likely derives from cleavage of pyruvic acid and/or methyl glyoxal (despite methyl glyoxal was detected only in small amounts, it was also oxidized as possible intermediate). Formic acid appears to be produced only if triggered by the presence of base with the exception of small amounts formed after methyl glyoxal C-C bond cleavage. The nature of pyruvic acid formation is still unclear as both lactic acid and hydroxyacetone (major products observed at no base oxidation) are very stable under these reaction conditions.

However, despite the accuracy and the number of tests carried out, the final mechanism of no base oxidation is still unclear. In fact, it is still hard to tell whether hydroxyacetone always arises by isomerisation of lactaldehyde or if there is a separate reaction pathway in the absence of base that favours oxidation at the secondary hydroxyl group of the diol. As a support is weakly acidic, it can also catalyse the isomerisation of hydroxyacetone to lactic acid.

It should be noted that in the absence of base the hydroxyacetone is un-reactive. This means that once this product is generated it does not react further and so is observed. The earlier observations (Tables 4.10 - 4.11) showed that hydroxyacetone decreases

with reaction time indicating that other products must have an effect, for instance due to changing the reaction pH.

Presumably, the overall mechanism of 1,2-propanediol oxidation, and the formation of pyruvic acid, depends on the formation of other products in the reaction media that may change the pH and compete for catalyst active sites, therefore it is hard to evaluate the contribution of each substance previously tested. Also it could be helpful to conduct CO/CO_2 measurements for a better understanding of the reaction profile, to ascertain/rule out decarboxylation.

4.3.9 Oxidation of 1-propanol and 2-propanol as model studies

A series of experiments for the oxidation of 1-propanol and 2-propanol have been carried out in order to understand the competitive oxidation of primary and secondary hydroxyl groups in 1,2-propanol molecule. The results of these time-on-line tests in the absence of base and their comparison with data on 1,2-propanediol oxidation are reported in Tables 4.19-4.20.

Table 4.19. Time on line data for oxidation of **1,2-propanediol** using 0.5%Au+0.5%Pt/C, in the absence of base at 70° C

		Selectivity, %				
Time	Conversion (%)	Lactate	Formate	Acetate	Pyruvate	Hydroxyacetone
1 hour	16	33	0	0	1	66
2 hours	22	34	0	0	2	64
3 hours	25	37	0	0	2	61
6 hours	31	36	0	1	3	60
24 hours	44	43	0	2	1	54

Reaction conditions: 1,2-propanediol (0.6 mol), 1,2-propanediol/total metal ratio = 4000, P oxygen = 3 bar, 1-24h, stirrer speed = 1000 rpm.

Table 4.20 Time on line data for oxidation of **1-propanol** using 0.5%Au+0.5%Pt/C, in the absence of base at 70 ° C

		Selectivity, %		
Time	Conversion (%)	Propionic aldehyde	propionic acid	Acetic acid
1 hour	5	67	33	0
2 hours	8	60	40	0
3 hours	9	55	45	0
6 hours	12	40	60	0
24 hours	43	6	92	2

Reaction conditions: 1-propanol (0.6 mol), alcohol/total metal ratio = 4000, P oxygen 3 bar, 1-24h, stirrer speed = 1000 rpm.

The diol oxidation starts rather more rapidly than 1-propanol probably because the secondary OH-group has a small acidifying effect on the primary OH-group and this could contribute to the faster rate, but inhibition seems to appear after a few hours on line. 1-propanol seems to be oxidized as well, with the conversion roughly linear with time and the aldehyde yield peaking after ca. 5 hours, and proceeding to give propionic acid. In turn, 2-propanol was fully oxidized to acetone with 100% selectivity.

It should be noted that, in the case of 2-propanol studies, it was not possible to take samples because the boiling point of acetone is lower than the operating temperature, but it should be stressed that 2-propanol was fully oxidised to the corresponding ketone.

Another set of experiments have been carried out in the presence of base (Tables 4.21-4.22).

Table 4.21 Time on line data for oxidation of **1-propanol** using 0.5%Au+0.5%Pt/C, in the presence of base at 40° C

		Selectivity, %			
Time	Conversion (%)	Propionic aldehyde	Propionate	Acetate	Formiate
1 hour	9	0	91	9	0
2 hours	15	0	75	16	9
3 hours	19	0	75	17	8
6 hours	30	0	74	17	9
24 hours	68	0	82	9	9

Reaction conditions: 1-propanol (0.6 mol), alcohol/total metal ratio = 4000, P oxygen 3 bar, 1-24h, 1,2-propanediol/NaOH = 1, stirrer speed = 1000 rpm.

Table 4.22 Oxidation of **2-propanol** using 0.5%Au+0.5%Pt/C, in the presence of base at 40° C

Time	Conversion (%)	Selectivity, % acetone
1 hour	23	100
2 hours	29	100
3 hours	39	100
6 hours	46	100
24 hours	70	100

Reaction conditions: 2-propanol (0.6 mol), alcohol/total metal ratio = 4000, oxygen 3 bar, 1-24h, 1,2-propanediol/NaOH = 1, stirrer speed = 1000 rpm.

In the presence of NaOH the reaction profile is different from those of diol oxidation. 1-propanol seems to be oxidized at higher rates without any traces of aldehyde detected which is in good correlation with the results of basic oxidation of 1,2-propanediol; the formation of by-products occurs at the same level. Surprisingly, propionaldehyde wasnot detected when the base is present. Its absence could be explained by Canizzaro reaction. Surprisingly, 2-propanol was selectively oxidized to acetone while in case of diol no secondary alcohol group oxidation is observed under basic conditions.

Model studies at base-free conditions very well correlate with the data obtained on base-free 1,2-propanediol oxidation. The major product – hydroxyacetone – is a result of a secondary hydroxy-group oxidation and 2-propanol seems to be oxidized more rapidly than 1-propanol. Small amounts of propionaldehyde were observed, as well as it was possible to detect lactaldehyde but in much smaller amounts. Acetic acid was also detected as a by-product like in the case of diol oxidation. The studies in the presence of base were surprising as it was expected to observe a much slower the rate of oxidation of secondary OH-group than that of a primary one in 1-propanol.

It is important to underline that the presence of both hydroxylic groups in 1,2-propanediol does not only slightly increase the pH, but also changes the geometry of the molecule and the explanation of activity based only on the acidic properties of OH-groups is insufficient, therefore the data obtained from model studies should be interpreted very carefully.

4.3.10 Reusability tests

Finally, it was decided to carry out reusability tests as despite 0.5%Au+0.5%Pt/C catalyst was extremely active for basic oxidation of 1,2-propanediol, it appeared to lose its activity after several runs (see section 3.3.3.10).

A series of reusability tests were run to evaluate the overall catalytic activity of bimetallic 0.5%Au+0.5Pt/C. The methodology of conducting these tests was similar to those of oxidation under basic conditions. Firstly, an excess amount of the catalyst at s:m ratio 1000 was prepared, to obtain sufficient amount of catalysts for further reusing. Then this amount of catalyst was further used for three consecutive experiments. The results of this set of reusability tests are reported in Table 4.23.

Table 4.23. Reusability tests for bimetallic 0.5%Au+0.5%Pt/C (KB-B) catalyst (Radley's glass reactor)

Number of cycles	Conversion(%)	Selectivity, %				
		Lactate	Formate	Acetate	Pyruvate	Hydroxyacetone
1st	88	39	0	27	3	31
2nd	85	42	0	29	3	26
3rd	66	40	0	19	3	37
4th	51	30	0	14	3	53

Reaction conditions: 0.6M 1,2-propanediol, 1,2-propanediol/total metal ratio = 1000, T = 100 °C, P = 3 bar, time = 24h.

Unfortunately, a significant decrease in conversion (up to 51 %) is observed after four cycles, but what is interesting is that the selectivities change too, with a decrease to lactic acid formation, an increase to hydroxyacetone and acetic acid, up to 30% and 53% respectively, whereas the amount of pyruvic acid remains constant (*ca.* 3%). Nevertheless, the catalyst is definitely much less deactivated compared with those after reusability tests conducted at basic conditions (51% conversion after the 4^{th} cycle in the absence of base against 20% under basic conditions).

4.3.11 Tests for poisoning by reaction products

In order to evaluate the possibility of catalyst poisoning by the presence of reaction products, several tests have been carried out to prove or disprove this assumption.

Lactic, acetic and formic acids were added at the beginning of the reaction to a solution of 1,2-propanediol in equimolar and in 1/10 molar amount.
Formic acid was also tested, though it has not been previously detected in the reaction mixture. In fact, this does not rule out the possibility to be formed and further degraded to gaseous products over Pt catalyst. The results of the series of independent experiments are given in a Table 4.24.

Table 4.24 Control tests for poisoning - addition of lactic, acetic and formic acid.

			Selectivity, %				
Product added	Concentration	Conversion (%)	Lactate	Formate	Acetate	Pyruvate	Hydroxy acetone
No product	0.3M	61	42	0	11	3	44
Lactic acid	0.3M	51	65	0	8	2	25
	0.03M	62	42	0	12	3	43
Sodium lactate	0.3M	-*	-	-	-	-	-
	0.03M	56	35	0	10	10	45
Acetic acid	0.3M	63	44	0	10	2	44
	0.03M	67	44	0	14	2	40
Formic acid	0.3M	60	31	0	14	3	52
	0.03M	67	42	0	13	3	43

Reaction conditions: 0.3M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, T = 100 °C, p = 3 bar, time = 24h.
* the intermediate added is consumed during the reaction, yet starting material is consumed as well

As can be seen from Table 4.25, the addition of acetic or formic acid does not change the reaction profile. Formic acid was consumed during the reaction presumably forming carbon oxides which could not be detected using Radley's reactor system.

There are two interesting points in these experiments. First, addition of equimolar amount of lactic acid shifts the reaction to the formation of more lactic acid, whereas adding of less amount of this compound seems not to play any significant role in the final product distribution. And secondly, after replacing lactic acid with sodium lactate it was not possible to work out the conversion values. From the NMR spectra it was clear that the starting material was consumed as its amount decreases after 24 hour reaction time, but the amount of sodium lactate was reduced as well.

A detailed description of these experiments is the following: for evaluating conversion/selectivity values a sealed glass insert filled with TMS/$CDCl_3$ was used (see section 4.3.2). At the beginning of the reaction when an intermediate was added, the reaction mixture was analysed by ^1H NMR being taken in the amount of 400 μL plus 100 μL of D_2O. This volume of (400 + 100) μL was kept constant for all future measurements. The signal from glass insert (at 0.00 ppm) was considered as integration standard value of "1" and the amounts of 1,2-propanediol and intermediates were worked out according to this normalization. After completion of the reaction, 400 μL of the reaction mixture were sampled and, after mixing with D_2O, further analysed. The peak signals are obtained in the same way, by comparing with the standard TMS/$CDCl_3$ signal. As long as the volume of the reaction mixture to be analysed was always kept constant from measurement to measurement and a glass insert with the same TMS concentration was used for NMR analysis, it is possible to work out:

- how much starting material being consumed by subtracting the value of peak signal after the reaction from the initial peak signal;

- how much intermediate being formed (in case it was formed) by subtracting the initial peak signal value from the peak signal obtained after the reaction is finished.
Other products were worked out independently from the peak signals of starting material and added intermediate.

Considering how the conversion/selectivities were calculated, it is clear that both starting material and an intermediate are consumed during the reaction. At the same time nothing can be said whether this intermediate was produced. It's not possible to evaluate how much intermediate was consumed if it was really produced at the beginning of the reaction; therefore continuous sampling rather than batch analysis would be needed.

To further prove the shift of the equilibrium to the formation of lactic acid when lactic acid was added, or the consumption of lactate after being added to the reaction mixture in equimolar amounts, further reproducibility tests were carried out. The results are given in Table 4.25.

Table 4.25 Reproducibility tests - addition of lactic acid / sodium lactate.

Product added	Concentration	Conversion (%)	Selectivity, %			
			Lactate	Acetate	Pyruvate	Hydroxy acetone
No product	0.3M	61	42	11	3	44
Lactic acid	0.3M	51	65	8	2	25
	0.3M	49	59	10	5	26
	0.3M	51	63	10	1	26
	0.03M	62	42	12	3	43
	0.03M	60	41	12	2	45
	0.03M	60	44	15	2	39
Sodium lactate	0.3M	-*	-	-	-	-
	0.3M	-	-	-	-	-
	0.3M	-	-	-	-	-
	0.03M	56	35	10	10	45
	0.03M	56	32	10	9	50
	0.03M	52	36	10	8	46

Reaction conditions: 0.3M 1,2-propanediol, 1,2-propanediol/total metal ratio = 2000, Base/1,2-propanediol molar ratio = 0, T = 100 °C, P = 3 bar, time = 24 h

* the intermediate added is consumed during the reaction, yet starting material is consumed as well

It is quite evident from this table that the addition of an excess amount of lactic acid favours the formation of more acid, though after the addition of smaller amounts, the ratio between hydroxyacid and hydroxyketone remains nearly 1:1. Calculations after the addition of sodium lactate were not possible to work out again, demonstrating difficulties in interpretation of the results, although the trend observed is systematic.

It was assumed that a Na^+ cation may play a role in such dramatic change in the reaction profile, on this basis it was decided to carry out an experiment with crown ether [25] with the aim to eliminate the ion influence. An equimolar amount of 15-crown-5 was added before the start of the reaction to capture Na^+ ions and to evaluate how it will change the reaction profile. Unfortunately, despite it has been reported that 15-crown-5 was miscible in water after the reaction was completed it seemed that the exterior hydrophobic ring coordinated the organic components of the reaction

mixture, thus preventing the reaction to occur. Therefore the data obtained from NMR analysis were not reliable. However, it should be noted that despite the conversion values were significantly lower, the ratio between products remain similar to those obtained at standard conditions.

Another assumption that can be made is the influence of the pH of the reaction mixture as sodium lactate is more basic than lactic acid itself, and more experiments need to be conducted to understand the change in the reaction profile after the addition of acid and its salt at the beginning of the reaction.

4.4 Characterisation of fresh and used catalysts

A detailed characterization of the catalysts used for base-free 1,2-propanediol oxidation, by means of an array of characterization tools, is given in section 3.3.4 as the same catalysts were used for oxidation in the presence of base.

In addition to these previous results, BET analysis was carried out for the fresh and spent 0.5%Au+0.5%Pt/C catalyst that was used in reusability tests. The same trend was observed, as in case of basic oxidation: the surface area and the pore volume dropped down with each cycle.

Table 4.26 BET results for fresh and spent catalyst after reusability tests

Sample ID	Surface area, m^2/g	Pore volume, ml/g
Fresh unused catalyst	1319	0.90
Spent catalyst, after 1st run	1286	0.81
Spent catalyst, after 4th run	1031	0.65

However, it should be noted that both conversion and surface area decreased to a lesser extent compared with the oxidation at 1 equivalent of NaOH where the observed decrease in conversion (3 times less) correlated with drastic decrease in surface area (2 times less). This indicates that the most probable reason of loss of catalytic activity is the decrease in the catalyst surface area, which could be caused by organic species deposit, although in principle metal dispersion changes should not be ruled out.

4.5 Conclusions

Screening of the variety of precious metal based catalysts on different supports at both basic and non-basic conditions revealed the possibility of 1,2-propanediol oxidation in the absence of base. Preliminary tests of MgO-supported catalysts displayed high activity, but due to reusability problems, such as a decrease of the amount of catalyst left after each cycle, it was further proven that MgO support is not suitable for this particular reaction, as the acid formed gradually dissolves magnesium oxide.

Further experiments with activated carbon supported catalysts proved that it was feasible to operate under base-free conditions and by varying such parameters as temperature, pressure and the amount of catalyst it was possible to achieve reasonably high levels of conversion (*ca.* 70-75%). Surprisingly, in the absence of base, hydroxyacetone – a result of a secondary alcohol group oxidation – was the major product formed during the reaction. Therefore, it was proposed that it was formed *via* enediol rearrangement of 2-hydroxypropanal, and it was further decided to investigate the reaction mechanism firstly by carrying out time-on-line studies and secondly by oxidation of all possible intermediates produced in this reaction.

Several attempts of synthesising lactaldehyde, one of the expected intermediates, have been conducted but with little success, and a new refined synthesis protocol will be needed. On the other hand, the results obtained after carrying out tests on intermediates oxidation do not provide final proof of our assumption on the formation of the products but are still helpful in understanding the formation of acetic and formic acid.

Further model studies on 1-propanol and 2-propanol oxidation in the absence of base confirmed the preferential formation of secondary OH-group oxidation product whereas the studies in the presence of NaOH require more experiments for clearer understanding of the mechanism of primary and secondary OH-group activation. A series of reusability tests have been carried out revealing the drop in conversion, though it was less significant (51% against 20%) than at basic conditions.

Tests for poisoning proved no catalyst deactivation by any of the by-products formed.

In contrast, these tests revealed an interesting influence of sodium lactate added to the reaction mixture at the beginning of the reaction instead of lactic acid. Attempts to isolate the sodium cation have been conducted using crown ether but due to its hydrophobic nature the results obtained should not be considered as reliable. Finally, BET analysis has been carried out and the results were supportive of the assumption of drop in conversion due to decrease in catalyst surface area. The assumption of CO_2 poisoning cannot be applied in the current context due to the absence of base in the reaction mixture.

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Chapter 5: OXIDATION OF BUTANEDIOLS AND HIGHER HOMOLOGUES OVER ACTIVATED CARBON SUPPORTED GOLD, PALLADIUM AND PLATINUM CATALYSTS

5.1 Introduction

The aim of this chapter is to test the most promising catalysts for 1,2-propanediol oxidation towards the range of butanediols and higher 1,2-diols. Initially, C_4-diols will be oxidized over monometallic activated carbon supported Au, Pd and Pt catalysts, as well as their bimetallic combinations. A more detailed investigation of 2,3-butanediol oxidation will be carried out, as this reaction can be of an interest due to mild oxidation conditions. Finally, mechanistic studies using C_3-C_5 1,2-diols will be conducted to evaluate the dependence between the starting material carbon chain length and the formation of the by-products.

5.2 Experimental

A range of Au, Pd and Pt catalysts supported on activated carbon and their bimetallic combinations were prepared by Sol Immobilization method. Details of catalyst preparation technique are described in Chapter 2. Catalytic tests have been conducted using a low-pressure Radley's glass reactor, as described in section 3.2, but omitting the use of base.

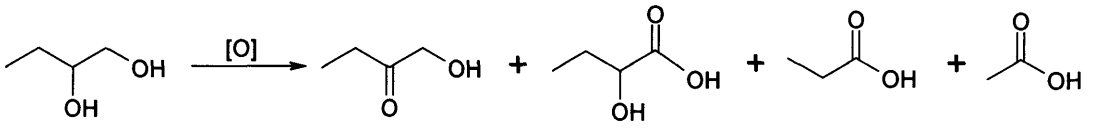
5.3 Results and discussion

Butanediols can be oxidized selectively to corresponding hydroxyacids and hydroxyketones by a wide range of methods, including: electrooxidation [1-3], homogeneous catalysis [4], oxidation in gas phase [5], bacterial oxidation [6]. There are several reports claiming to have simultaneously achieved high conversion and selectivity values, but these reports have disadvantages compared to the procedure

that has been followed in this work. For instance, harsh oxidants (H_2O_2, dimethyldioxirane, pyridinium bromochromate) are used [7,8], as well as severe reaction conditions and non-aqueous systems (acetone, alkaline or acidic media) are applied [9-12], or the reaction is homogeneously catalyzed [13]. These disadvantages can be overcome by developing a new approach of heterogeneously catalyzed oxidation reaction under mild, solvent-free conditions using oxygen at low pressures. The feasibility and applicability of all these requirements will be evaluated in this chapter.

5.3.1 Oxidation of 1,2-butanediol

Under base-free conditions 1,2-butanediol can be oxidized mainly to 2-hydroxybutyric acid and 1-hydroxy-2-butanone (see Scheme 5.1). These reaction products are of great interest as they are used in biological studies and as flavour and fragrance agents [14, 15].



Scheme 5.1 General scheme of 1,2-butanediol oxidation.

The oxidation of 1,2-butanediol was carried out in the absence of base over mono- and bimetallic Au, Pd and Pt catalysts supported on activated carbon (Sigma Aldrich KB-B). Interestingly, the reaction scheme suggested in this work differs from those reported in the literature. Catalytic oxidation over ceria supported AuPd catalysts resulted in formation of hydroxyaldehyde at high selectivities [16], whereas electrooxidation in basic media leads to the formation of both hydroxyketone and hydroxyaldehyde [17]. Comparing with the results from literature and the products reported in Scheme 5.1 it is clear that the reaction pathways are different when using carbon supported nanoparticles as oxidation proceeds further to hydroxyacids. It is

worth noting that 2-hydroxybutyric acid is normally produced by bacterial oxidation [18].

The pressure influence on the formation of reaction products has been evaluated varying its value from 1 to 3 bar above atmospheric. The results are reported in Tables 5.1 and 5.2.

Table 5.1 Tests of different monometallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,2-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %			
				2-hydroxy butyric acid	1-hydroxy-2-butanone	Propionic acid	Acetic acid
1	1%Pd	3	16	52	43	3	3
2	1%Pd	2	10	60	40	0	0
3	1%Pd	1	11	50	50	0	0
4	1%Pt	3	25	53	42	2	4
5	1%Pt	2	24	55	41	0	4
6	1%Pt	1	30	52	42	3	4
7	1%Au	3	19	55	45	0	0
8	1%Au	2	18	54	46	0	0
9	1%Au	1	17	52	48	0	0

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Table 5.2 Tests of different bimetallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,2-butanediol

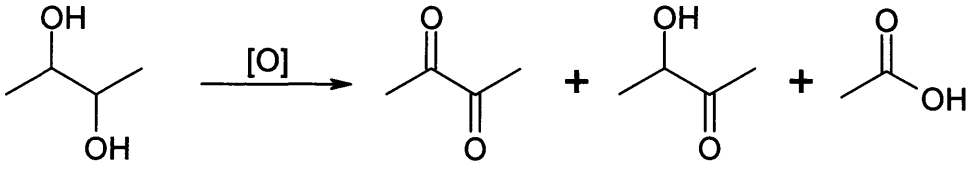
Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %			
				2-hydroxy butyric acid	1-hydroxy-2-butanone	Propionic acid	Acetic acid
1	0.5%Au+0/5%Pt	3	75	45	42	5	8
2	0.5%Au+0/5%Pt	2	48	47	38	9	6
3	0.5%Au+0/5%Pt	1	42	46	40	11	3
4	0.5%Pd+0/5%Pt	3	31	54	28	11	7
5	0.5%Pd+0/5%Pt	2	31	47	41	7	5
6	0.5%Pd+0/5%Pt	1	31	49	41	8	2
7	0.5%Au+0/5%Pd	3	33	44	45	6	4
8	0.5%Au+0/5%Pd	2	28	52	35	6	7
9	0.5%Au+0/5%Pd	1	27	46	43	7	4

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

As can be seen from these tables, 2-hydroxybutyric acid and 1-hydroxy-2-butanone are formed in nearly equal amounts (with 1:1 ratio). The formation of these products was expected as 1,2-propanediol was oxidized to give the same types of products with a similar ratio. Interestingly, decreasing pressure decreases the conversion values only for bimetallic catalysts, whereas for monometallic catalysts no significant drop in conversion is observed when reducing pressure from 3 to 1 bar. Regarding the distribution of by-products, clearly monometallic Pt (Table 5.1 entries 4-6) and Pt-containing bimetallic catalysts (Table 5.2, entries 1-3 and 4-6) produce more acetic acid, whereas monometallic Au was the most selective towards the hydroxyacid and the hydroxyketone, without acetic acid being formed and with small amount of propionate produced only at 3 bar pressure (Table 5.1 entry 7). It should be noted that bimetallic catalysts were in general more efficient than monometallic ones due to a synergistic effect present when introducing the second metal. The highest conversion value (*ca.* 75%) was reached when using bimetallic 0.5%Au+0.5%Pt/C catalyst, which correlates with the data on 1,2-propanediol oxidation where this catalyst was the most active both with and without base added.

5.3.2 Oxidation of 2,3-butanediol

After evaluating the activity of activated carbon supported catalysts for the oxidation of 1,2-butanediol it was decided to test other C_4-diol isomers. The next isomer chosen was 2,3-butanediol, its oxidation follows the scheme given below. The reaction products formed, namely butanedione and 3-hydroxy-2-butanone, are used as flavouring agents in food industry [19,20].



Scheme 5.2 General scheme of 2,3-butanediol oxidation.

Au, Pd and Pt and their bimetallic combinations supported on activated carbon were tested to oxidize 2,3-butanediol at 3, 2 and 1 bar pressure. The results of these tests

are given in Tables 5.3 and 5.4.

Table 5.3 Tests of different monometallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 2,3-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %		
				butanedione	3-hydroxy-2-butanone	Acetic acid
1	1%Pd	3	13	4	92	4
2	1%Pd	2	10	0	100	0
3	1%Pd	1	11	0	96	4
4	1%Pt	3	10	6	94	0
5	1%Pt	2	14	0	96	4
6	1%Pt	1	14	0	96	4
7	1%Au	3	12	4	88	8
8	1%Au	2	14	0	96	4
9	1%Au	1	14	0	96	4

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

Table 5.4 Tests of different bimetallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 2,3-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %		
				butanedione	3-hydroxy-2-butanone	Acetic acid
1	0.5%Au+0/5%Pt	3	62	4	84	12
2	0.5%Au+0/5%Pt	2	63	6	86	8
3	0.5%Au+0/5%Pt	1	72	6	83	11
4	0.5%Pd+0/5%Pt	3	37	4	89	7
5	0.5%Pd+0/5%Pt	2	47	4	87	9
6	0.5%Pd+0/5%Pt	1	51	3	88	9
7	0.5%Au+0/5%Pd	3	54	6	86	8
8	0.5%Au+0/5%Pd	2	53	6	87	7
9	0.5%Au+0/5%Pd	1	48	6	88	6

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

The equilibrium is shifted mostly to the formation of 3-hydroxy-2-butanone, though small amounts of butanedione were observed as well. Acetic acid was also detected as the only by-product, its formation (of *ca.* 12%) was the highest for 0.5%Au+0.5%Pt/C catalyst (Table 5.4, entries 1-3). This catalyst was also the most

active in terms of conversion, giving *ca.* 72% value at 1 bar pressure (Table 5.2, entry 3). All combinations of bimetallic catalysts were more active than monometallic, with the same trend observed for oxidation of 1,2-butanediol (section 5.3.1) due to synergistic effect. Interestingly, the highest selectivities to the hydroxyketone were detected when using monometallic Au/C and Pd/C, with the best result of 100% selectivity to 3-hydroxy-2-butanone when using Pd/C at 2 bar pressure, though the conversion did not exceed 10%.

5.3.2.1 Reproducibility tests

It was decided further to carry out reproducibility tests for Pd/C catalyst at 2 bar pressure. It was reported [21] that 2,3-butanediol can be catalytically oxidized to butanedione (diketone) at severe reaction conditions (Cu chromite catalyst, ~290 °C, white mineral oil as a solvent). In turn, 3-hydroxy-2-butanone is usually produced by fermentation processes [22]. Therefore it was assumed that partial oxidation of 2,3-butanediol to hydroxyketone in aqueous media over heterogeneous catalyst can be advantageous. The results of the test are given in Table 5.5.

Table 5.5 Reproducibility tests for Pd/C catalyst (KB-B), for oxidation of 2,3-butanediol at 2 bar pressure

Conversion (%)	Selectivity, %		
	butanedione	3-hydroxy-2-butanone	Acetic acid
8	0	100	0
10	0	100	0
9	0	100	0

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 2 bar, time = 24h, stirrer speed = 1000 rpm.

It can be seen that despite low conversion values (*ca.* 10%), the selectivity towards hydroxyketone remains constant (100%), therefore this reaction may need further investigation to understand the mechanism of oxidation of each hydroxyl group and to optimise the conditions to reach higher conversions possibly without losing high selectivities.

5.3.2.2 72 hours experiments and influence of temperature

Reaction time was the first parameter to change in order to find optimal conditions for 2,3-butanediol oxidation. A series of experiments have been carried out for 72 hours (against 24 hours standard experiment time) varying pressure and also the substrate to metal ratios to evaluate the influence of the amount of catalyst on the conversion/selectivity changes. The results are reported in Table 5.6.

Table 5.6 Experiments on oxidation of 2,3-butanediol over Pd/C at 100 °C and 72 hours

Entry	s:m ratio	Pressure (bar)	Conversion (%)	Selectivity, %		
				butanedione	3-hydroxy-2-butanone	Acetic acid
1	1000	2	18	7	85	8
2	1500	2	18	6	86	8
3	2000	2	18	8	84	8
4	4000	2	11	5	90	5
5	1000	1	22	6	84	10
6	1500	1	21	6	85	9
7	2000	1	19	5	90	5
8	4000	1	14	5	91	4

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-4000, T = 100 °C, P = 2 or 1 bar, time = 72h, stirrer speed = 1000 rpm

From the data shown in above, it can be seen that at 72 hours conversion values are nearly two times higher than at 24 hours, reaching the maximum of 22% (entry 5), but none of the experiments gave 100% selectivity to 3-hydroxy-2-butanone. Expectedly, the more catalyst was used, the lower was the selectivity to the major product. The formation of unwanted by-product - acetic acid – was also dependent on the amount of catalyst used increasing with increase of the substrate to metal ratio. Interestingly, at 1 bar pressure the conversion is slightly higher than at 2 bar, which possibly indicates that high pressures are not needed for this particular oxidation reaction.

The next step was to investigate the reaction profile at the reduced temperature (80 °C) but varying the reaction time and the amount of catalyst used. It was also decided to test monometallic Au/C catalyst as it showed the second highest selectivity to the

hydroxyketone in the series of initial experiments (Table 5.1, entries 8-9). The results of experiments using Pd/C catalyst are given in Tables 5.7 and 5.8.

Table 5.7 Experiments on oxidation of 2,3-butanediol over Pd/C at 80 °C and 24 hours

Entry	s:m ratio	Conversion (%)	Selectivity, %		
			butanedione	3-hydroxy-2-butanone	Acetic acid
1	1000	6	0	100	0
2	1500	3	0	100	0
3	2000	3	0	100	0
4	4000	4	0	100	0

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-4000, T = 80 °C, P = 2 bar, time = 24h, stirrer speed = 1000 rpm.

Table 5.8 Experiments on oxidation of 2,3-butanediol over Pd/C at 80 °C and 72 hours

Entry	s:m ratio	Conversion (%)	Selectivity, %		
			butanedione	3-hydroxy-2-butanone	Acetic acid
1	1000	10	0	95	5
2	1500	9	0	100	0
3	2000	8	0	100	0
4	4000	4	0	100	0

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-4000, T = 80 °C, P = 2 bar, time = 72h, stirrer speed = 1000 rpm.

It can be seen from these tables that reducing the temperature favours the increase in selectivity towards desired product, though the conversion slightly decreases (3-6%). This can be overcome by increasing time of the reaction up to 72 hours, in this case the conversion is around 10%, with 100% selectivity to hydroxyketone. It should be noted that at low substrate to metal ratio (1000) the formation of acetic acid as a by-product is observed (Table 5.8, entry 1).

With Au/C catalyst the situation is different. As reported in Tables 5.9 and 5.10, the conversion values at 24 hours and 80 °C are lower than that of Pd/C though 100% selectivity to 3-hydroxy-2-butanone is still preserved. When increasing time of the

experiment up to 72 hours the conversion values are higher when compared to Pd/C, but the selectivity to the major product decreases and more by-product is formed at any substrate to metal ratio (Table 5.10).

Table 5.9 Experiments on oxidation of 2,3-butanediol over Au/C at 80 °C and 24 hours

Entry	s:m ratio	Conversion (%)	Selectivity, %		
			butanedione	3-hydroxy-2-butanone	Acetic acid
1	1000	3	0	100	0
2	1500	4	0	100	0
3	2000	3	0	100	0
4	4000	4	0	100	0

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-4000, T = 80 °C, P = 2 bar, time = 24h, stirrer speed = 1000 rpm

Table 5.10 Experiments on oxidation of 2,3-butanediol over Au/C at 80 °C and 72 hours

Entry	s:m ratio	Conversion (%)	Selectivity, %		
			butanedione	3-hydroxy-2-butanone	Acetic acid
1	1000	14	0	89	11
2	1500	11	0	91	9
3	2000	9	0	94	6
4	4000	4	0	100	0

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-4000, T = 80 °C, P = 2 bar, time = 72h, stirrer speed = 1000 rpm

To further investigate the reaction profile under different conditions, it was decided to run the time-on-line experiments at maximum possible temperature of 110 °C (for an aqueous solution at 2 bar pressure) for both Pd/C and Au/C catalysts, varying also s:m ratios. The results are reported in Tables 5.11 and 5.12.

Table 5.11 Experiments on oxidation of 2,3-butanediol over Pd/C at 110 °C and 72 hours

Entry	Time, hours	s:m ratio	Conversion (%)	Selectivity, %		
				butanedione	3-hydroxy-2-butanone	Acetic acid
1	4	1000	4	0	100	0
2	8	1000	9	0	100	0
3	24	1000	15	7	90	3
4	72	1000	23	14	69	17
5	4	2000	2	0	100	0
6	8	2000	7	0	100	0
7	24	2000	15	7	90	3
8	72	2000	22	11	79	10

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-2000, T = 110 °C, P = 2 bar, time = 72h, stirrer speed = 1000 rpm.

At elevated temperatures (110 °C) and up to 8 hours of reaction time, no by-products were detected when using Pd/C catalyst (entries 1-2 and 5-6). The conversion at substrate to metal ratio 1000 is slightly higher than at 2000, but increasing the s:m ratio leads to the formation of acetic acid and diketone at the times of 24 and 72 hours (entries 3-4 and 7-8). The highest conversion value was 23% at 72 hours and s:m=1000 but the selectivity to 3-hydroxy-2-butanone drastically decreased to 69%.

Table 5.11 Experiments on oxidation of 2,3-butanediol over Au/C at 110 °C and 72 hours

Entry	Time, hours	s:m ratio	Conversion (%)	Selectivity, %		
				butanedione	3-hydroxy-2-butanone	Acetic acid
1	4	1000	4	0	100	0
2	8	1000	9	0	94	6
3	24	1000	17	0	91	9
4	72	1000	35	4	71	25
5	4	2000	3	0	100	0
6	8	2000	5	0	100	0
7	24	2000	11	0	95	5
8	72	2000	23	2	78	20

Reaction conditions: 0.6M 2,3-butanediol, butanediol/total metal ratio = 1000-2000, T = 110 °C, pP = 2 bar, time = 72h, stirrer speed = 1000 rpm

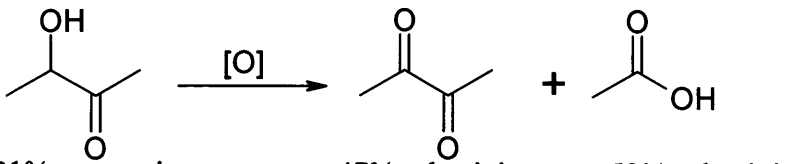
Over the initial period of time the Au/C catalyst's behaviour is similar to Pd/C, *i.e.* 3-hydroxy-2-butanone was the only product observed, except the result at 8 hours for

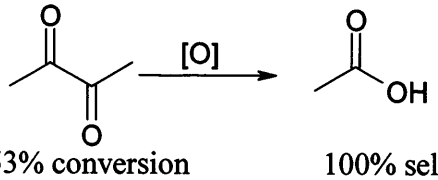
s:m ratio 1000 (entry 3) when acetic acid already started to form. With time at high substrate to metal ratio it was possible to reach conversion of *ca.* 35%, though the selectivity dropped down to ca. 71% (entry 4) due to the formation of large amounts of acetic acid and butanedione.

Despite the fact that it was possible to reach a maximum of 35% conversion, it is clear high temperatures favour the C-C bond cleavage to form acetic acid and the overoxidation of 3-hydroxy-2-butanone to corresponding diketone, therefore the significant loss of selectivity was observed at longer reaction times. Similar trend was observed for 1,2-propanediol oxidation in the absence of base, when at elevated temperatures (115 °C) the selectivity to a by-product - acetic acid - increased from 4% to 29% compared with the results obtained at 100 and 80 °C (Chapter 4, paragraph 4.3.3).

5.3.2.3 Mechanistic studies of 2,3-butanediol oxidation

Considering the results of the experiments described above, it can be assumed that the reaction of 2,3-butanediol oxidation is sequential. Evidence of sequential oxidation has been reported in literature [17], but in these cases, the oxidation was carried out in basic media and over Au electrodes. Therefore, it was decided to evaluate the possibility of the consecutive oxidation of 3-hydroxy-2-butanone into butanedione and to understand the nature of acetic acid formation. A series of experiments were conducted at 24 and 72 hours under 100 °C and 2 bar pressure to oxidize separately both 3-hydroxy-2-butanone and butanedione. The results of the experiments on oxidation of intermediates after 24 hours are reported in Scheme 5.3.

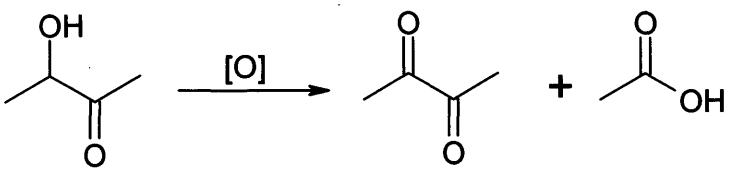




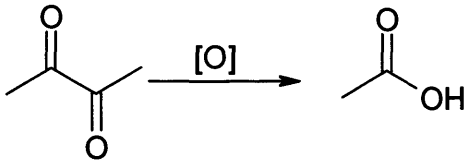
Scheme 5.3 Mechanistic studies of 2,3-butanediol intermediates oxidation at 24 hours

From this scheme it is clear that under the conditions usually used for 2,3-butanediol oxidation, 3-hydroxy-2-butanone can be oxidized to butanedione at 21% conversion, giving both butanedione and acetic acid with selectivities of 47% and 53% accordingly. When oxidizing butanedione, it was transformed into acetic acid with 100% selectivity and 53% conversion, thus suggesting that acetic acid formation arises from diketone oxidation.

The results of intermediates oxidation at 72 hours are reported in Scheme 5.4.



33% conversion 36% selectivity 64% selectivity



73% conversion 100% selectivity

Scheme 5.4 Mechanistic studies of 2,3-butanediol intermediates oxidation at 72 hours

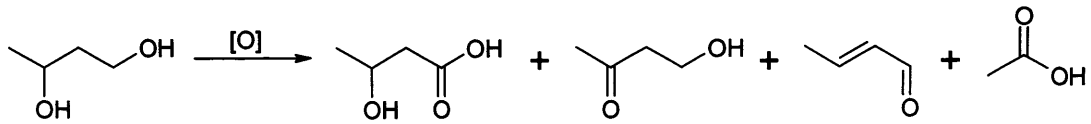
Increasing the time of the experiment clearly leads to the formation of more products. Thus, 3-hydroxy-2-butanone is now oxidized at the level of 33% with selectivity shifted to the formation of acetic acid rather than diketone. This shift can be proven by oxidation of butanedione, which gives acetic acid at 73% conversion.

The data described above indicate that the possible reaction mechanism is the following: initially, only one OH-group of 2,3-butanediol is oxidized to form 3-hydroxy-2-butanone, this compound in turn is further oxidized to butanedione. The diketone formed is then further oxidized and, coupling with C-C bond cleavage, gives finally acetic acid as a by-product. Thus, the results reported above favour the assumption that the reaction of 2,3-butanediol oxidation over carbon supported catalysts in aqueous media can be considered sequential with the following rates:

2,3-butanedione >> 3-hydroxy-2-butanone > 2,3-butanediol

5.3.3 Oxidation of 1,3-butanediol

Another isomer to be tested is 1,3-butanediol. This compound is oxidized according to the scheme given below.



Scheme 5.5 General scheme of 1,3-butanediol oxidation

The major products formed are 3-hydroxybutyric acid and 4-hydroxy-2-butanone; the former is used for production of biodegradable plastic, such as poly(3-hydroxybutyrate) [23], the latter – in organic synthetic chemistry [24,25] and as a precursor for synthesis of β-hydroxylactones [26].

Catalytic oxidation of 1,3-butanediol has already been reported [8] using the tungsten-containing mesoporous silica catalysts in the presence of o-hydroxyl phenol as an auxiliary additive over a temperature range from 35 to 80 °C under for 1–16 h. Interestingly, the products detected only partially correspond to those reported in Scheme 5.5. They are 4-hydroxy-2-butanone, 2-hydroxy-4-butyl aldehyde, acetic acid and formic acid. As in the case of 1,2-butanediol (see paragraph 5.3.1), hydroxyaldehydes in both case seem not to be present due to their further oxidation to corresponding acids under given conditions.

The same set of catalysts, previously tested for oxidation of 1,2- and 2,3-butanediols, was used for evaluating the activity in 1,3-butanediol oxidation. The results of these catalytic tests at different pressures (1-3 bar) are given in Tables 5.12 and 5.13.

Table 5.12 Tests of different monometallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,3-butanediol.

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %			
				3-hydroxy butyric acid	4-hydroxy-2-butanone	2-butenal	Acetic acid
1	1%Pd	3	9	47	53	0	0
2	1%Pd	2	9	47	53	0	0
3	1%Pd	1	8	40	60	0	0
4	1%Pt	3	35	42	10	47	1
5	1%Pt	2	33	48	10	42	0
6	1%Pt	1	38	43	10	46	1
7	1%Au	3	7	0	100	0	0
8	1%Au	2	6	0	100	0	0
9	1%Au	1	5	0	100	0	0

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm

Table 5.13 Tests of different bimetallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,3-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %			
				3-hydroxy butyric acid	4-hydroxy-2-butanone	2-butenal	Acetic acid
1	0.5%Au+0/5%Pt	3	67	56	39	3	2
2	0.5%Au+0/5%Pt	2	69	55	40	2	3
3	0.5%Au+0/5%Pt	1	55	60	35	3	2
4	0.5%Pd+0/5%Pt	3	54	54	23	18	5
5	0.5%Pd+0/5%Pt	2	44	52	24	20	4
6	0.5%Pd+0/5%Pt	1	39	55	25	17	3
7	0.5%Au+0/5%Pd	3	34	35	63	0	3
8	0.5%Au+0/5%Pd	2	29	32	67	0	2
9	0.5%Au+0/5%Pd	1	27	37	62	0	1

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

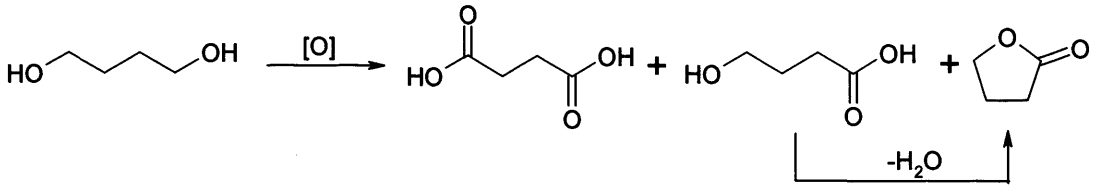
It is immediately evident that bimetallic catalysts are more active than monometallic ones, with the most active 0.5%Au+0.5%Pt/C giving *ca.* 69% conversion as highest value. In addition, the pressure change from 1 to 3 bar seems not to influence significantly the conversion values. In terms of selectivity, 1%Au/C appeared to be the most selective (Table 5.12, entries 7-9) with 100% selectivity to the hydroxyketone. Oxidation of 1,3-butanediol over 1%Pd/C (Table 5.12, entries 1-3) gave the 1:1 distribution between both 4-hydroxy-2-butanone and 3-hydroxybutyric acid. Interestingly, no by-products were formed while using these catalysts, though it

should be noted that conversions were no higher than 9%.

Surprisingly, monometallic 1%Pt/C, being quite active for 1,3-butanediol oxidation, gave an unsaturated aldehyde 2-butenal (crotonaldehyde) as a by-product (Table 5.12, entries 4-6), which can probably be the result of dehydration of 3-hydroxybutyric acid to crotonic acid. Interestingly, the formation of crotonaldehyde is observed only for Pt-containing catalysts, with the selectivity to 2-butenal decreasing with the trend Pt > PdPt > AuPt (Table 5.12, entries 4-6 and Table 5.13, entries 1-6).

5.3.4 Oxidation of 1,4-butanediol

The last isomer to be tested for oxidation over mono and bimetallic Au, Pd and Pt carbon supported catalysts was 1,4-butanediol. The general reaction profile under given conditions is displayed in Scheme 5.6. This reaction can be of interest as the products formed find many different applications. For instance, succinic acid is produced by fermentation [27] and can be used in both food industry as a flavouring agent [28] and non food applications for production of dyes, perfumes, lacquers etc. In turn, 4-hydroxybutyric acid is used for medical purposes [29], and γ-butyrolactone, besides medical applications, is used as a chemical intermediate in agrochemicals, pharmaceuticals and dyes [30, 31].



Scheme 5.6 General scheme of 1,4-butanediol oxidation

Tables 5.14 and 5.15 summarize the results of experiments on 1,4-butanediol oxidation over carbon supported catalysts.

Table 5.14 Tests of different monometallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,4-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %		
				Succinic acid	4-hydroxy-butytic acid	γ-butyrolactone
1	1%Pd	3	11	4	31	65
2	1%Pd	2	9	6	29	65
3	1%Pd	1	8	7	27	66
4	1%Pt	3	16	6	18	76
5	1%Pt	2	12	8	25	67
6	1%Pt	1	10	6	17	77
7	1%Au	3	4	0	29	71
8	1%Au	2	3	0	17	83
9	1%Au	1	3	0	20	80

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm

Table 5.15 Tests of different monometallic Au, Pd and Pt catalysts supported on activated carbon (KB-B), for oxidation of 1,4-butanediol

Entry	Catalyst	Pressure (bar)	Conversion (%)	Selectivity, %		
				Succinic acid	4-hydroxy-butytic acid	γ-butyrolactone
1	0.5%Au+0/5%Pt	3	100	16	21	63
2	0.5%Au+0/5%Pt	2	99	16	22	62
3	0.5%Au+0/5%Pt	1	69	5	23	72
4	0.5%Pd+0/5%Pt	3	73	11	23	66
5	0.5%Pd+0/5%Pt	2	59	9	23	68
6	0.5%Pd+0/5%Pt	1	50	7	31	62
7	0.5%Au+0/5%Pd	3	54	9	22	69
8	0.5%Au+0/5%Pd	2	50	8	22	70
9	0.5%Au+0/5%Pd	1	40	6	22	72

Reaction conditions: 0.6M 1,2-butanediol, butanediol/total metal ratio = 2000, T = 100 °C, P = 3 bar, time = 24h, stirrer speed = 1000 rpm.

As can be seen from both tables, γ-butyrolactone is the major product formed in this reaction independently from the catalyst used. Its formation can be explained by the dehydration and further cyclization of 4-hydroxybutyric acid. Another possible pathway could involve formation of γ-butyrolactone from aldehyde *via* cyclic hemiacetal and then oxidised. Remarkably, 0.5%Au+0.5%Pt/C catalyst fully converted 1,4-butanediol with selectivity to succinic acid of *ca.* 16%, to 4-hydroxybutytic acid of *ca.* 21% and to γ-butyrolactone of *ca.* 63% (Table 5.15, entry

1). 0.5%Pd+0.5%Pt/C was the second active catalyst (Table 5.15, entries 4-6), giving *ca.* 73% conversion with 11% selectivity to succinic acid. Monometallic 1%Au/C catalyst was most selective to lactone, but giving no succinic acid and resulting in low conversion values (Table 5.14, entries 7-9). Pressure influence was noticeable, but seemed to be insignificant when decreasing from 3 to 2 bar and did not exceed 4% for monometallic and 15% for bimetallic catalysts, though when it was decreased further to 1 bar some meaningful changes were observed (up to 25% decrease compared to those obtained at 3 bar).

5.3.5 Oxidation of C_5 1,2-diol and studies on by-product formation

Previous studies on C_3 and C_4 1,2-diols oxidation revealed high activity of activated carbon supported Au, Pd and Pt catalysts under base-free conditions. Moreover, an interesting trend was observed on the by-product formation. Thus, oxidation of 1,2-propanediol in the absence of base led to the formation of acetic acid, whereas oxidation of 1,2-butanediol resulted in producing also propanoic acid as a by-product. It could be of an interest to test the activity of previously used catalysts towards the oxidation of higher 1,2-diols and to evaluate if the same reaction mechanism will be followed and if the longer chain by-products would be formed.

To prove or disprove this assumption, an experiment on the oxidation 1,2-pentanediol was carried out under the same conditions as for 1,2-propanediol and 1,2-butanediol oxidation (i.e. 0.5%Au+0.5%Pt/C catalyst with s:m=2000, 3 bar pressure, 100 °C and 24 hours in Radley's glass reactor). NMR analysis of the reaction mixture at the end of the experiment displayed the presence of 2-hydroxypentanoic acid, 1-hydroxypentanone and 3 by-products, namely: acetic, propanoic and butanoic acid thus showing that the longer chained product was formed from a longer chained diol. In view of this formic acid would also be expected but it is probably decomposed uder experimental conditions.

Further to this work it would be interesting to study the oxidation of C_6 and longer chain 1,2-diols to check if the same trend in activity and by-product formation will be

observed when the chain length (and geometry) of the starting material is changed. As long as C_6 and higher diols are not water soluble/miscible, and appropriate adjustments of the reaction conditions, and particularly choice of solvent, should be made.

5.4 Conclusions

1,2-butanediol appeared to behave similarly to 1,2-propanediol, resulting in the same 1:1 distribution between hydroxyacid and hydroxyketone. Bimetallic 0.5%Au+0.5%Pt/C catalyst was the most active in terms of conversion (*ca.* 75%), though it should be noted that only monometallic 1%Au/C did not lead to the formation of any of the undesired by-products (propionic and acetic acids) but at low conversion values (*ca.* 19%).

It was possible to oxidize 2,3-butanediol with 100% selectivity to 3-hydroxy-2-butanone over monometallic Pd/C and Au/C catalysts, but the conversions did not exceed 10-11%. As long as oxidation over heterogeneous catalyst in aqueous media and using oxygen as an oxidant was considered to be "green" compared to existing routes of 3-hydroxy-2-butanone production by fermentation, it was decided to carry out more detailed studies on 2,3-butanediol oxidation. Thus, the influence of pressure, temperature and the duration of the reaction were investigated, showing that the best results (of 10-12%) are at 8 hours and 110°C and 24 hours and 100°C, at 80°C selectivity is still 100% after 72 hours. The mechanistic studies conducted revealed the the oxidation of 2,3-butanediol is a sequential process that firstly lead to hydroxyketone 3-hydroxy-2-butanone, then to diketone butanedione and finally C-C bond scission to form acetic acid.

1,3-butanediol was oxidized to the corresponding 3-hydroxybutyric acid and 4-hydroxy-2-butanone at quite high conversions (*ca.* 69%) with 0.5%Au+0.5%Pt/C being the most active catalyst. Surprisingly, the formation of unsaturated aldehyde was detected when using Pt-containing catalysts, which can be possibly explained by dehydration of hydroxyacid and a further transformation to form unsaturated crotonaldehyde.

The last isomer to be tested was 1,4-butanediol, with γ-butyrolactone being the major product formed. Its formation under given conditions can be explained by dehydration of hydroxyaldehyde. It also was possible to produce succinic acid with a maximum of 16% selectivity. The most active catalyst was 0.5%Au+0.5%Pt/C allowing to fully convert 1,4-butanediol to corresponding acids and lactone.

Testing the range of 1,2-diols (C_3-C_5) helped to evaluate the activity of 0.5%Au+0.5%Pt/C catalyst for the oxidation of longer chain diols and it was detected that longer chain by-products are formed when oxidizing longer chain 1,2-diol. These preliminary results could be worth investigating further, to test this assumption.

5.5 References

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Chapter 6: CONCLUSIONS AND FUTURE WORK

6.1 General conclusions

In this thesis, heterogeneous catalytic oxidation of 1,2-propanediol and a range of butanediols over Au, Pd and Pt nanoparticles have been investigated. Summarizing the results, the following main conclusions can be drawn:

1) In the presence of base, 1,2-propanediol can be successfully oxidized to lactic acid under mild conditions, *i.e.*: ambient temperature, low oxygen pressure (1-3 bar) or even air at atmospheric pressure, low loading of catalyst used (s:m ratios up to 24000) and short reaction times (4 hours).

2) Base-free oxidation proved to be also possible at high conversion (of *ca.* 75%), though it should be noted that in the absence of the base the reaction profile changes towards the formation of both hydroxyacetone and lactic acid as major products [1].

3) Catalysts used for oxidation of 1,2-propanediol are also active for the oxidation of the range of C_4-diol isomers to the corresponding hydroxyacids and hydroxyketones.

A more detailed description of the results obtained and possible future research lines are given in the paragraphs below.

6.1.1 Selective oxidation of 1,2-propanediol in basic media

Initial studies of 1,2-propanediol oxidation in basic media over titania supported AuPd nanoparticles displayed that no meaningful level of conversion can be achieved, therefore attention has been paid to activated carbons as a support [2]. After careful screening of the available activated charcoal and graphite supports coupled with experiments to choose the alloying metal, it was shown that 0.5%Au+0.5%Pt/C (KB-B, Sigma Aldrich) catalyst was the most active in terms of both conversion and selectivity to the major product – lactic acid.

Changing the ratio of Au and Pt in bimetallic catalysts allowed the influence of the second metal on both conversion and selectivity to be evaluated. Monometallic 1%Pt/C showed little activity, but when introducing Au into the catalytic system as 0.95%Pt+0.05%Au/C, the conversion increased nearly ten times from 6% to 70%. It is worth noting that further increasing the amount of gold and decreasing Pt led to a drop in selectivity to lactate from 96% to 67%. Monometallic 1%Au/C was also less active than bimetallic catalyst 0.1%Pt+0.9%Au/C with the drop in conversion from 86% to 54% clearly indicating that synergistic effect is present when using these two metals.

Tests on the physical mixtures of monometallic gold and platinum catalysts also proved the presence of a synergistic effect by emulating both metal loading and metal dispersion. In addition, tests on lower total metal loadings showed no drastic decrease in conversions with clear economical advantage in the possibility to use lower amount of precious metal in the final material. Carrying out the 24 hour tests with lower amounts of catalyst (substrate to metal ratios 16000 and 24000) showed full conversion of 1,2-propanediol at high level of selectivity to lactate of *ca.* 92%.

After careful analysis of the results obtained over AuPt activated carbon supported catalysts, an assumption has been made that this reaction is mass transfer limited. This was proven by means of a series of targeted tests using a specially designed reactor at Imperial College London in order to improve the stirring of the solution. Also, the activation energy and reaction order were determined, giving the value of 43kJ/mol and zero reaction order, thus indicating saturation of the catalyst active sites by the reactant.

Reusability experiments displayed a decrease in conversion after 4 cycles therefore a series of tests have been carried out to reveal possible reasons. Thus, AAS analysis proved there was no Au leaching, and tests on introducing all possible intermediates into the reaction mixture before it starts showed no catalyst poisoning. Finally, BET analysis was carried out revealing a drastic decrease in surface area and pore volume, which could be a possible explanation of the catalytic activity drop because of the decreased diffusion of the substrate to the catalyst surface.

6.1.2 Selective oxidation of 1,2-propanediol under base-free conditions

A series of activated carbon supported catalysts that showed the intrinsic activity for 1,2-propanediol oxidation in the presence of base were also tested under base-free conditions. It was possible to oxidize the diol but surprisingly the major product of this reaction was hydroxyacetone, though lactic acid was observed in high amounts.

Two most efficient catalysts for base-free oxidation were 0.5%Au+0.5%Pt/C in terms of conversion values (up to 75%) and 0.5%Pd+0.5%Pt/C in terms of selectivity towards the desired product, namely lactic acid (up to 50%), and these catalysts were chosen for further experiments. The influence of pressure and temperature was investigated, as well as tests by using air instead of oxygen as oxidizing agent, revealing that increased temperatures promoted C-C bond cleavage and formation of more by-products (such as acetic acid). High pressures were also found to favour C-C bond scission. Yet pressurizing the system is still necessary, as bubbling oxygen experiments resulted in high amounts of acetic acid and formation of only little amounts of lactic acid (with selectivities of 44% and 19% respectively).

Physical mixtures of monometallic gold and platinum were also tested, but unlike in the presence of the base, under base-free conditions no significant synergistic effect was detected. Moreover, using lower metal loadings resulted in significant decrease in conversion, though in the presence of base lower amounts of metals could be used without meaningful losses in activity.

Reusability tests were conducted and despite promising results, it appears that the catalysts could support only up to *ca.* 4 repeated cycles under experimental conditions. Tests on catalyst poisoning showed that no catalyst reactivation occurred due to any intermediate formed during the reaction. It seems possible to conclude, by using BET and porosimetry for these materials, that the deactivation per repeated runs should be ascribed to a decrease in surface area and pore volume like in the case of basic oxidation of 1,2-propanediol.

6.1.3 Possible reaction mechanism of 1,2-propanediol oxidation

It was initially assumed that lactic acid was formed *via* the enediol rearrangement of 2-hydroxypropanal. In order to prove this hypothesis, mechanistic studies were carried out.

Firstly, it was noted that lactaldehyde, possible intermediate in the reaction of 1,2-propanediol oxidation, was detected in very small amounts when using Pt/C catalyst. Therefore, several attempts of synthesising lactaldehyde were conducted [3] but with little success as the material rapidly dimerises.

In view of this, all possible intermediates (lactic, pyruvic and acetic acids, hydroxyacetone and methyl glyoxal) were oxidized separately under standard reaction conditions to understand the formation of by-products. The results obtained did not support the original assumption that lactic acid was formed *via* enediol rearrangement of 2-hydroxypropanal. Yet, the following conclusions were possible: formic acid is produced only in the presence of a base (as the free acid appears to decompose in the presence of platinum metal group catalysts), whereas hydroxyacetone is unstable under basic conditions. In addition, pyruvic acid seems to be the major source of acetic acid production under both basic and base-free conditions, although the nature of formation of pyruvic acid itself is still unclear.

This prompted us to understand the competitive mechanism of primary and secondary alcohol oxidation using a set of experiments with 1-propanol and 2-propanol in the presence and in the absence of base. Some similarities with 1,2-propanediol oxidation under base-free conditions were found, namely: oxidation of 2-propanol was more rapid than 1-propanol, which correlates with the formation of more hydroxyacetone than lactic acid; acetic acid was detected as a by-product; small amounts of propionaldehyde in the case of 1-propanol were detected as well as lactaldehyde in the case of 1,2-propanediol.

In the presence of base, a much higher rate of oxidation of secondary OH-group in 2-propanol was observed than that of a primary one in 1-propanol which needs further investigations.

6.1.4 Oxidation of butanediols

In order to evaluate the activity of the most promising catalysts for the oxidation of higher diols, a series of experiments on the oxidation of the full range of C_4-diols were carried out. For the whole spectrum of diols the 0.5%Au+0.5%Pt/C catalyst appeared to be the most active in terms of conversion.

1,2-butanediol seemed to behave very similar to 1,2-propanediol giving the same distribution of hydroxyketone and hydroxyacid. When oxidizing 1,3-butanol, the unsaturated crotonaldehyde was detected in significant amounts but only when using Pt-containing catalysts. In contrast, 1,4-butanediol was oxidized mostly to γ-butyrolactone at high conversion values, also succinic acid was detected at selectivities of *ca.* 16% when using bimetallic 0.5%Au+0.5%Pt/C catalyst.

An enhanced 2,3-butanediol oxidation was carried out as Pd/C and Au/C catalyst oxidized this molecule to hydroxyketone at 100% selectivity, though the conversion was not very high (*ca.* 10-12%). Several tests were conducted to understand the reaction mechanism, and the results seem to prove that the reaction of 2,3-butanediol oxidation is sequential, forming hydroxyketone first, then diketone which is further oxidized to form acetic acid, with products which appear to be oxidised more rapidly than the starting diol.

6.2 Concluding remarks

The systematic approach used in this work proves that the presence of base in the reaction media is an essential requirement to achieve high conversion and selectivity towards lactic acid. On the other hand, the lack of a base surprisingly led to relatively high conversion values, but at the cost of a diminished selectivity to the desired product, namely lactic acid.

The best catalyst for any substrate was proved to be a 0.5%Au+0.5%Pt/C regardless the presence or the absence of base. This was quite a surprising result, because when these two metals were present as monometallic catalysts, the base triggered gold

activity but quenched that of platinum, while the reverse was observed when the base was not present. These could also explain why 1:1 ratio of these two metals gave the best catalyst.

The effect of temperature was found to be negligible due to mass transfer limitations in the presence of the base. In contrast, under the base free conditions increasing temperature led, as expected, to higher conversion but lower selectivity to lactic acid due to C-C bond cleavage.

The tests on pressure and choice of oxidant showed that under the base-free conditions high pressures were not needed to reach high conversions, yet pressurizing the system with oxygen was still needed. In the presence of base a similar situation was observed, though the air could also be used as an oxidant source in a specially designed reactor.

These results show that the overall activity is the sum of several factors (basicity of the reaction media, alloying of the metals, temperature and pressure) with a final effect difficult to predict *a priori*. Therefore future work will strongly rely on empirical methods to assess the final activity of these materials.

6.3 Future work

The results reported above, represent a good starting ground for additional investigations aimed at further improving catalyst activity and selectivity towards the desired products and to understand the reaction mechanisms. In view of this, the following studies are proposed to supplement the work described in this thesis:

- First of all it could be worth trying other preparation methods as in this work the main attention was concentrated on the sol immobilization technique. Varying preparation methods, such as deposition precipitation, or impregnation, will help to achieve different metal particle sizes, which, despite the broader particles size, distribution compared to sol immobilization, can also lead to different metal/support interface and different metals distribution. This, in turn may influence the conversion

values as well as the selectivity.

- Further metal and metal precursors could be used as dopants or promoters. The choice of metal(s) should be made based on careful screening of existing literature of similar oxidation reactions such as Bi, Sn or Te [4,5]. Other supports can be also chosen to evaluate their activity like iron oxide or alumina.

- The effect of the amount of base definitely deserves attention, as the nature of higher conversions at 1 eq. of NaOH rather then at 2 or 3 equivalents, despite being systematic, is still unclear. This could be coupled with tests on the use of air as an oxidant instead of oxygen; this combined approach could have considerable benefits with respect to green chemistry.

- Further evaluation of the possibility of shifting the reaction from external mass transfer region to a kinetic regime. This could be achieved by testing the catalysts at low temperatures combined with intensified stirring rates or implemented reactor design.

- The catalyst characterization could be further extended in order to acquire information of the catalyst morphology, particles sizes and composition. TEM and XRF can be appropriate tools for particles size and composition [6] respectively. The overall morphology is also important because it was proven in this work that catalyst deactivation does not occur due to poisoning, but rather due to a decrease in pore volume, likely due to carbonaceous product deposition in the presence of base. Therefore it is worth analysing fresh and spent catalysts to test for coke formation carrying out thermal desorption test.

- Despite the level of mechanistic information acquired in this work, further mechanistic tests could be carried out. For instance, it could be helpful to conduct CO/CO_2 measurements for a better understanding of the reaction profile, to ascertain the presence of, or to rule out, decarboxylation. The influence of Na^+ cation at non-basic conditions is unclear and can be worth evaluating, as it can help to understand the shifting of reaction profile when introducing the excess of sodium lactate into the reaction mixture before the reaction starts. The studies on 1-propanol and 2-propanol

could be further extended due to unexpected activity of 2-propanol, to understand the reasons of competitive oxidation of primary and secondary hydroxylic groups.

- Finally, mechanistic studies on 2,3-butanediol oxidation are worthy to be extended. The formation of crotonaldehyde when oxidizing 1,3-butanediol over Pt-containing catalysts can be further investigated to understand the reaction mechanism. Adjusting conditions of 1,4-butanediol oxidation can be of interest to reach higher conversions to succinic acid as this compound at present is produced by fermentation process. The activity of higher 1,2-diols in oxidation reactions would be interesting to further investigate , therefore an appropriate solvent and reaction conditions should be chosen due to the weak water solubility of higher alcohols.

6.2 References

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Appendix A. SAMPLE CHROMATOGRAM AND SAMPLE NMR SPECTRUM FOR THE REACTION OF 1,2-PROPANEDIOL OXIDATION OVER METAL SUPPORTED NANOPARTICLES

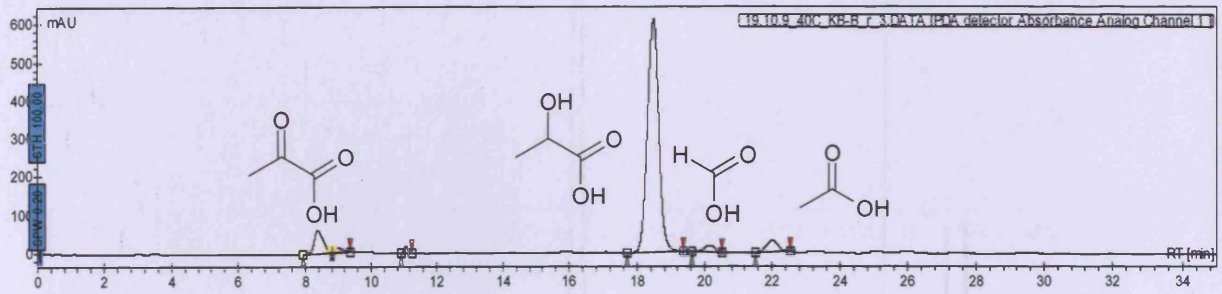

Figure A.1 Chromatogram of reaction mixture of 1,2-propanediol oxidation in the presence of base (signal from UV detector)

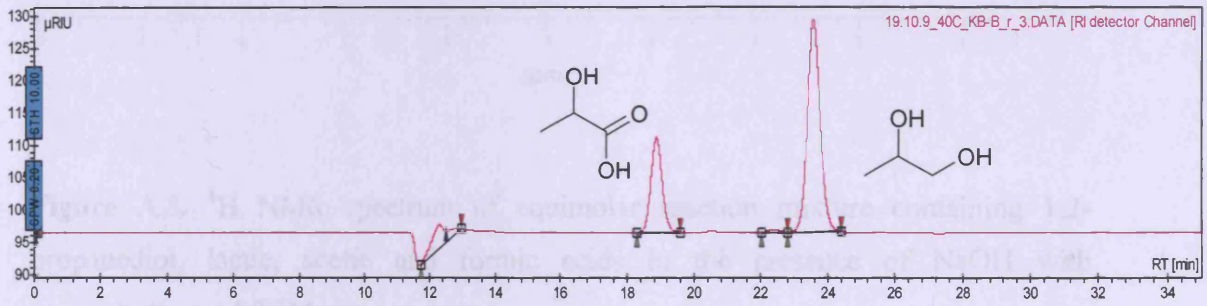

Figure A.2. Chromatogram of reaction mixture of 1,2-propanediol oxidation in the presence of base (signal from RI detector)

Retention times for the products obtained are given in the Table A.1 below

Table A.1. Retention times for different detector types

Product	Retention time, min	
	UV detector	RI detector
1.2-propanediol	-	23.6
Lactic acid	18.5	18.4
Acetic acid	22.0	-
Formic acid	20.3	-
Pyruvic acid	8.4	-

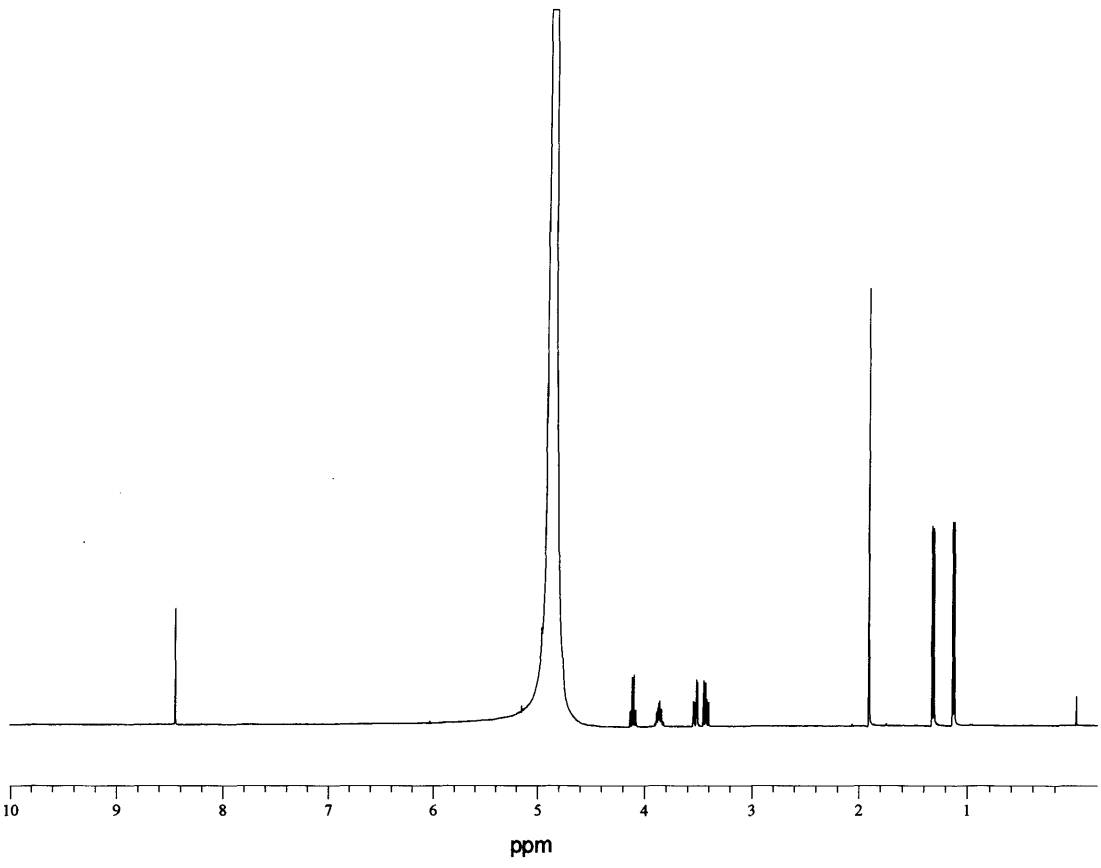

Figure A.3. ^{1}H NMR spectrum of equimolar reaction mixture containing 1,2-propanediol, lactic, acetic and formic acids in the presence of NaOH with concentrations of 0.3M

The signal at 0 ppm is generated from the protons of TMS (used as a standard), signals at 1.22 (CH_3-), 3.48 (-CH_2-) and 3.83 ppm (-CH-) arise from starting material 1,2-propanediol, lactic acid is detected at 1.30 (CH_3-) and 4.10 ppm (-CH-), by-products acetic acid and formic acid are detected at 1.91 (CH_3-) and 8.42 ppm (CH_3-) respectively.

Appendix B. SPECIFICATIONS FOR ACTIVATED CARBONS DARCO G-60, KB AND KB-B (SIGMA-ALDRICH)

Table B.1. Comparison between different Darco activated carbon supports from Sigma-Aldich

Type	**G-60**	**KB**	**KB-B**
Description	High-purity powder	Wet powder	Wet powder
Particle size (mesh)	100-325	100-325	100-325
Surface area (m^2/g, approx.)	600	1500	1500
Pore volume (ml/g, dry basis)	0.95	2	2
Moisture (%, max.)	12	33	33
pH (water extract, approx.)	6-8	5	5
Ash (%)	3.5	3	3
Water solubles (%, max.)	0.5	1.5	1.5
Tamped bulk density (lb/cu ft)	25	28	28
Fe (ppm, max.)	200	-	100
Phosphates (%, extractable)	-	0.5	0.5

Appendix C. NMR SPECTRA FOR MECHANISTIC STUDIES OF THE REACTION OF 1,2-PROPANEDIOL OXIDATION

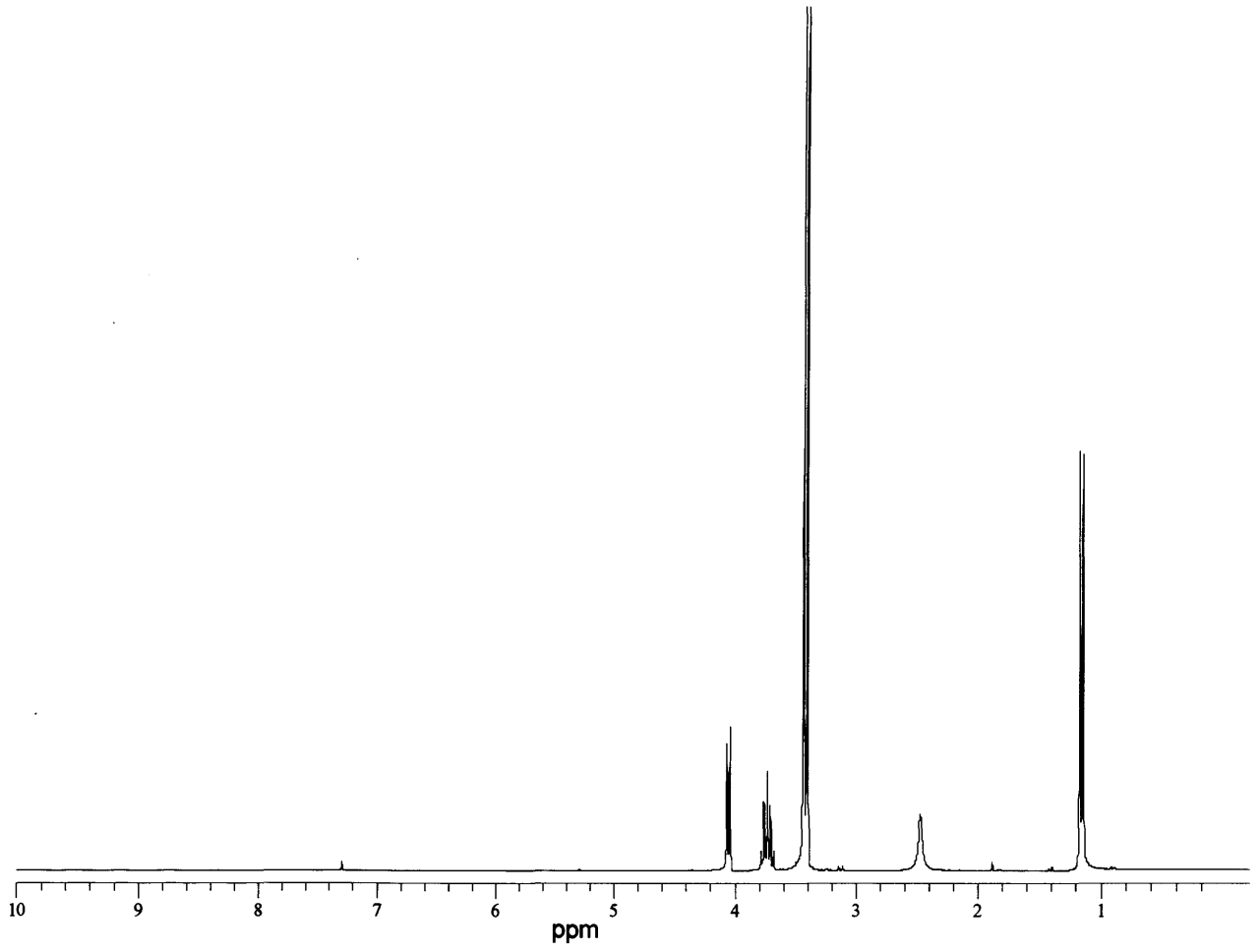

Figure C.1. ^{1}H NMR spectrum of 1,1-dimethoxy-2-propanol in $CDCl_3$

The signals of 1,1-dimethoxy-2-propanol were detected at 1 at 1.16 (CH_3-), 2.47 (-CH-), 3.40 (CH_3-), 3.75 (-CH-) and 4.05 ppm (CH-). $CDCl_3$ signal was detected at 7.28 ppm (-CH-). No starting material left.

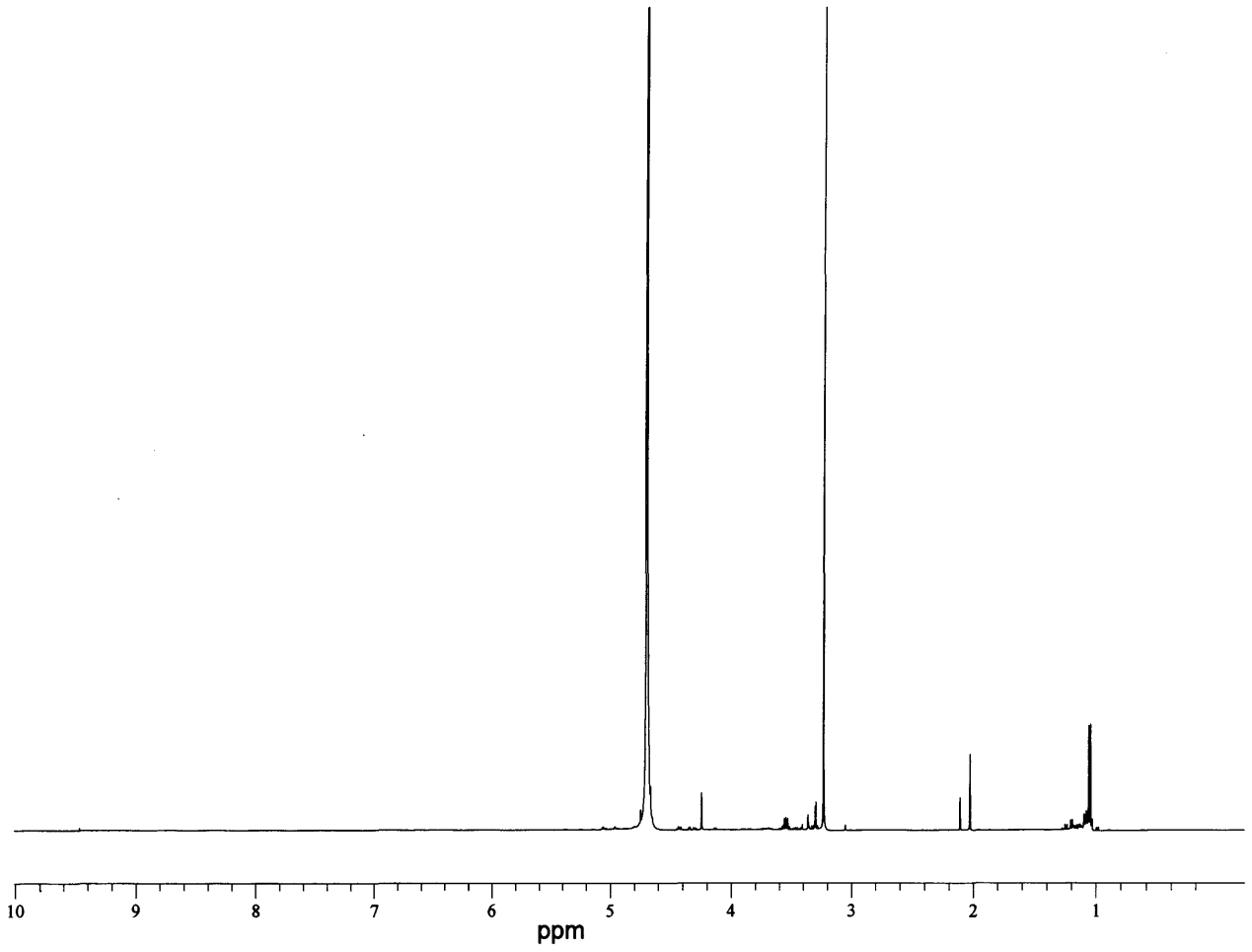

Figure C.2. ^{1}H NMR spectrum of the reaction mixture of lactaldehyde synthesis (using H-zeolite-β) in D_2O

Starting material 1,1-dimethoxy-2-propanol still can be observed at 1.16 (CH_3-), 2.47 (-CH-), 3.40 (CH_3-), 3.75 (-CH-) and 4.05 ppm (CH-), dioxane based structures were detected mostly around 1.05 (CH_3-, -CH-) and 4.2 ppm (O-CH-), hydroxyacetone was detected at 2.03 and 4.24 ppm, acetone was also detected at 2.11 ppm (CH_3-), dimethyl ether – at 3.22 ppm (CH_3-), and finally clear evidence of lactaldehyde presence was detected at 9.46 ppm (-COH) (signal for carbonyl group).

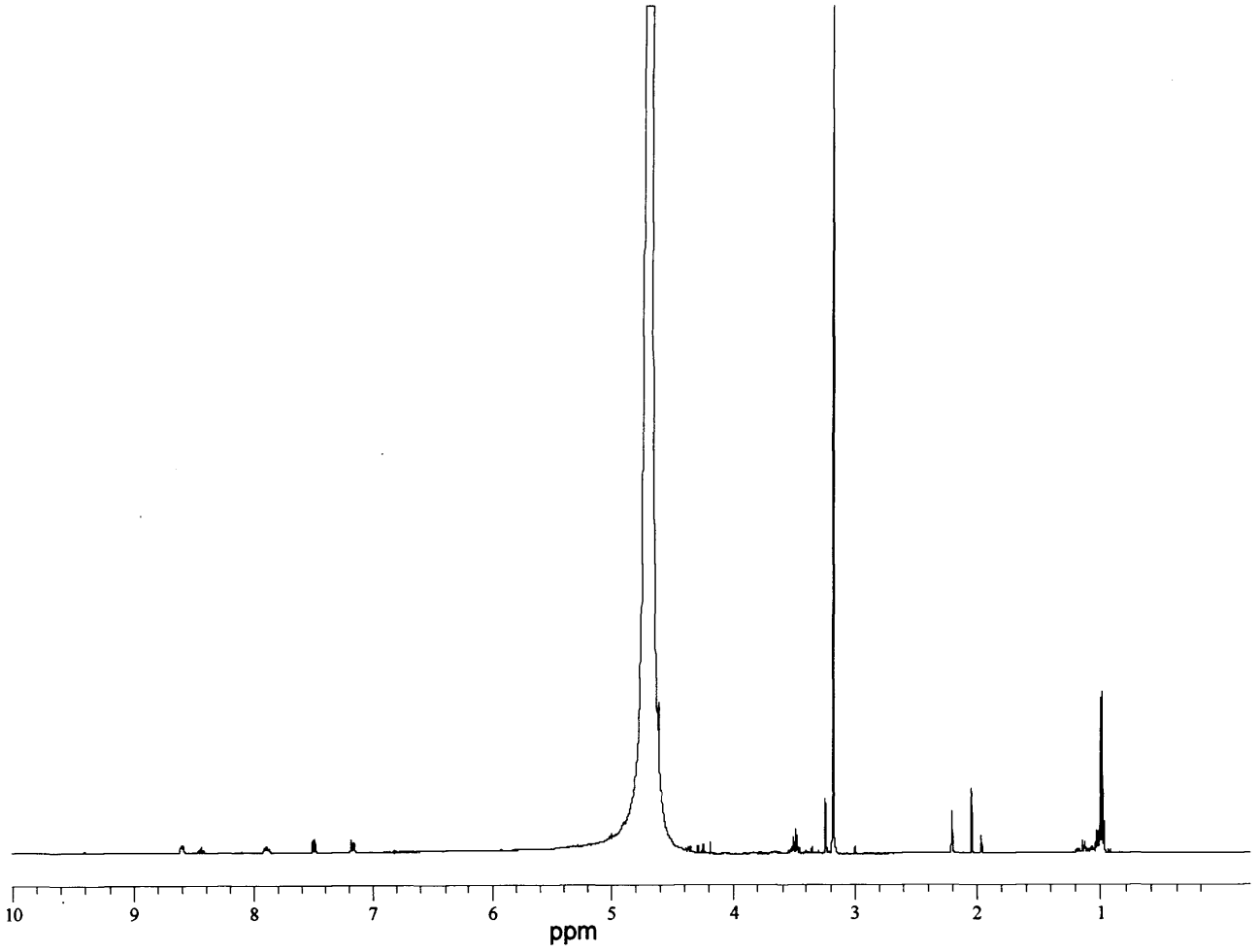

Figure C.3. ^{1}H NMR spectrum of the reaction mixture of lactaldehyde synthesis (using PPTS and H_2O as solvent) in D_2O

No starting material 1,1-dimethoxy-2-propanol can be detected, dioxane based structures were detected between 0.95 (CH_3-) and 1.25 (-CH-) ppm and 4.22 (O-CH-) ppm; hydroxyacetone was detected in small amounts at 2.03 (CH_3-) and 4.24 ppm (-CH_2-) as well as acetone at 2.11 ppm (CH_3-); dimethyl ether – at 3.22 ppm (CH_3-); catalyst PPTS (*p*-toluenesulfonate) was observed at 2.31 (CH_3-), 7.17 (-Ph-H), 7.49 (-Ph-H), 7.90 (-Ph-H pyr), 8.43 (-Ph-H pyr) and 8.61 ppm (-Ph-H pyr); and free form of lactaldehyde was detected at 9.46 ppm (-COH) (signal for carbonyl group).

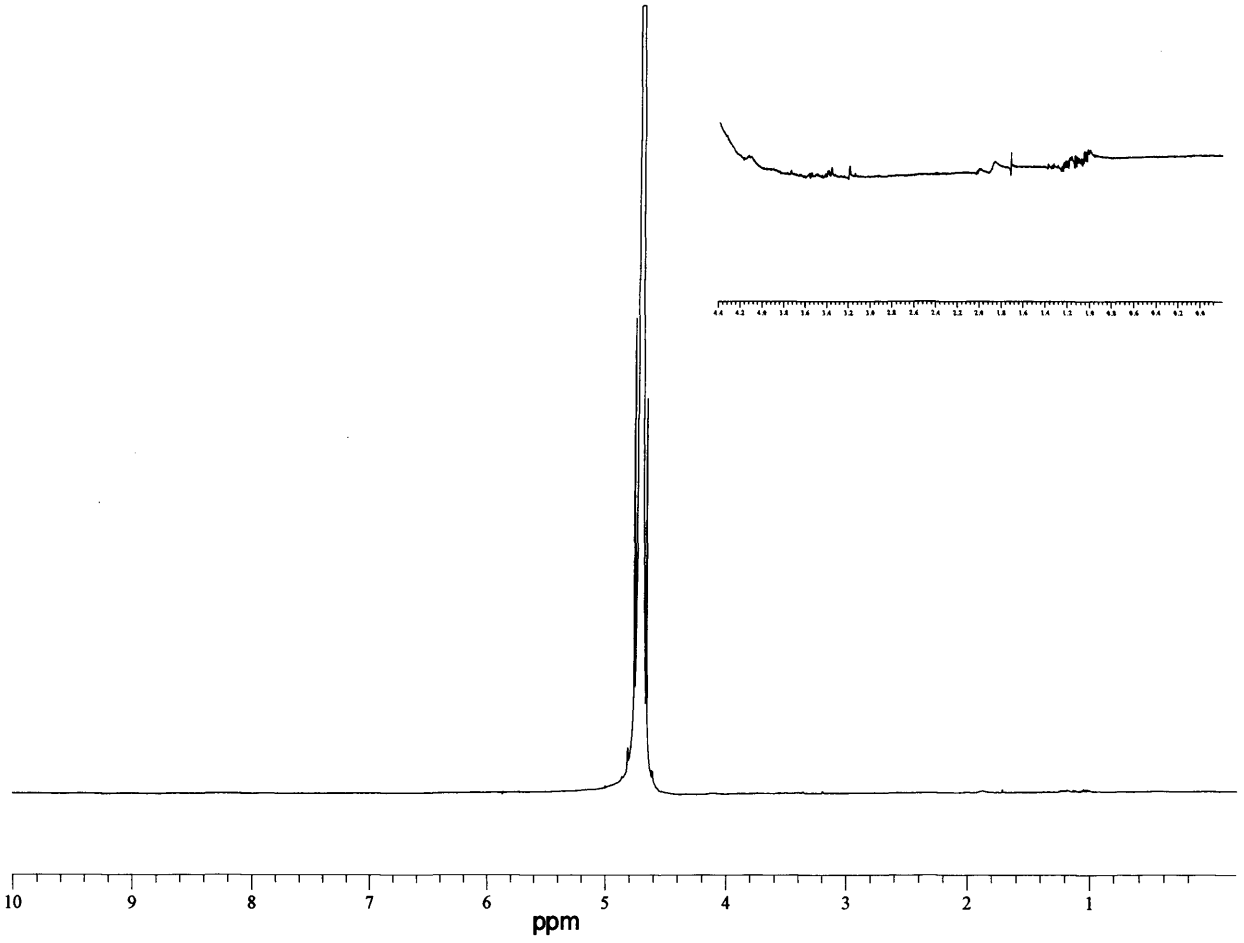

Figure C.4. ^{1}H NMR spectrum of hydroxyacetone (stability test in NaOH after 1 hour time)

No clearly defined peaks detected after 1 hour in basic solution.