PhD Thesis

School of Chemistry

Cardiff University

The direct synthesis of hydrogen peroxide using bimetallic gold and palladium supported catalysts

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Thesis submitted in accordance with the requirements of the University of Cardiff for the degree of doctor in philosophy by:

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2015

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Dedicated to my family.

To my mum and brothers who made this possible.

To my beloved "Abbaji" and "Bibiji" (R.I.P).

Abstract

In this thesis the direct synthesis of hydrogen peroxide (H_2O_2) from hydrogen and oxygen using gold-palladium supported catalysts was investigated. The direct route represents a greener and sustainable alternative to the current industrial manufacturing process. The main objective of this study was to achieve the industrial requirements of H_2O_2 yields and selectivity, which would make the direct process industrially viable. In order to reach the required target, two innovative approaches for the direct synthesis of H_2O_2 were examined.

The first part of this thesis was dedicated to the development of a biphasic solvent system comprising an organic alcohol and water. The advantages of this system was highlighted and the effect of reaction variables (such as solvent composition, pressure, reagent ratio, temperature and reaction time) were evaluated using two different catalysts. The identification of two optimum conditions resulted in an important enhancement in the H_2O_2 yield for the two catalysts examined. By finely tuning the reaction conditions and using two different solvent systems ((i) decan-1-ol-water (ii) diisobutyl carbinol-water) H_2O_2 concentrations between ~ 0.30 and 28 wt. % were achieved.

The second part of this thesis was dedicated to studying the direct gas phase synthesis of H_2O_2 in a continuous gas flow reactor. Two lab scale flow reactors were designed and built *in situ:* The first was for studying the direct gas phase synthesis of H_2O_2 at atmospheric pressure and the second for studying the reaction at pressures above atmospheric. The results demonstrate the direct gas phase synthesis of H_2O_2 was challenging and the absence of solvent seriously compromises the stability of the H_2O_2. Despite this, the results demonstrate by using gold-palladium nanoparticles and a mixture of hydrogen and oxygen it is possible to not only oxidise organic molecules in the gas phase but the synthesis rates were high enough to detect H_2O_2 as a product in a fixed bed gas phase reactor and a temporal analysis of products (TAP) reactor. This observation opens up the possibility of synthesising H_2O_2 directly in a gas phase reaction.

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Introduction

1

1.1 Catalyst and Catalysis

The term catalysis was first published by Swedish scientist Jons Jakob Berzelius in 1836[1] and was described as a "catalytic power" that can be added to a chemical reaction and accelerate its rate without itself being consumed. Berzelius stated[1]:

> *"Many bodies have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, is common both in organic and inorganic nature; I shall call it catalytic power. I shall also call Catalysis the decomposition of bodies by this force."*

Today catalysis is better defined as the acceleration of a chemical reaction due to the presence of a catalyst. A catalyst works by providing an alternative reaction mechanism comprising a different transition state characterized by a lower activation energy (E_a). Consequently more molecules possess sufficient energy to reach the transition state and overcome the energy activation barrier, allowing them to react and be transformed into products (Figure 1.1). This process can be described by the Boltzmann distribution equation (equation 1.1).

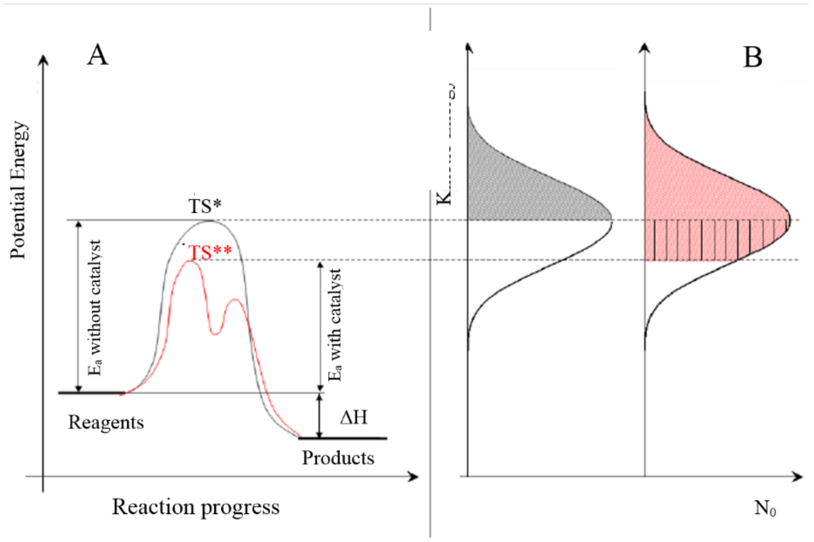


Figure 1.1 Reaction potential energy profile for an uncatalysed reaction (black line) and a catalysed reaction (red line), showing a decrease in the activation energy barrier of the latter. The highest energy peak represents the transition state (T.S) for a given reaction. B) Boltzmann distribution of reagent energies. Black area represents the number of molecules having sufficient energy to form the transition state for the uncatalysed reaction whereas the red area refers to the catalysed reaction which has a lower transition state energy.

This process is described by the Boltzmann distribution equation (Equation 1.1)

$$\frac{N_i}{N_j} = e^{\left(-\frac{Ei - Ej}{kT}\right)} \qquad \text{Equation 1.1}$$

$N_{i,\,j}$ = number of particular related to energy states E*i*,*j*

$E_{i,\,j}$ = energy states

K = Boltzmann constant

T = temperature

It can also be explained in terms of the Arrhenius law (equation 1.2) where lower activation energies will result in higher rate kinetic constants and therefore lead to faster reactions.

$$k = Ae^{(-\frac{E_a}{RT})}$$ Equation 1.2

k = rate contant

A = pre-exponential factor

E_a = activation energy

R = molar gas constant

T = absolute temperature

Today catalysis lies at the heart of many chemical processes and represents a vital component in everyday living and the economy. Approximately 90% of chemicals produced require a catalyst during one or more stages of their production. The fuel industry employs catalysts for the ‘cracking’ and ‘reforming’ of oil into diesel and petrol. The food industry requires catalysts for the hydrogenation of unsaturated oils and finally polymerisation processes require catalysts for the production of plastics. In 2005 catalytic processes generated almost $900 billion in products worldwide and this figure is increasing year by year. By understanding and careful use of catalysis many processes can be made faster, cleaner and more sustainable.

1.2 Classes of Catalysis

Catalysis can be divided into three main classes’ namely Biological catalysis, Homogeneous catalysis and Heterogeneous catalysis. Biological catalysts are better known as enzymes and these naturally occur in living organisms. The reactant in an enzyme catalysed reaction is called a substrate and an enzyme converts this to a different molecule resulting in the desired product. Most enzymes are proteins and these enzymes catalyse more than 5,000 biochemical reaction types. Table 1.1 highlights some important reactions that occur with enzymes.

Table 1.1 Important reactions that employ enzymes.

Application	**Enzyme**	**Use**
Digestive system	Proteases, amylase, lipase	Used to digest protein, carbohydrates and fats.
Molecular biology	Nucleases, DNA ligase, polymerase	Used in restriction digestion and the polymerase chain reaction to create recombinant DNA.
Biological Detergent	Proteases, Amylases, Lipase	Remove protein, starch, fat and oil stains from laundry and dishware.
Dairy Industry	Rennin	Hydrolyse protein in the manufacture of cheese.

In homogeneous catalysis the catalyst is in the same phase as the reactants. Usually everything will be present as a gas or contained in a liquid phase. A number of commercially viable processes have been developed in recent years which employ homogeneous catalysts (Table 1.2).

Table 1.2 Important chemical reactions that employ homogeneous catalysts.

Commercial Process	**Catalyst**	**Application**
Hydroformylation	Rh/PR_3 Complexes	Production of aldehydes
Adiponitrile process	Ni/PR_3 Complexes	Production of nylon
Olefin polymerization	$(RC_5H_5)_2ZrCl_2$	Production of high-density polyethylene

Many of these homogeneous catalysts are expensive transition metal compounds, and recovering these catalysts from solution has been a major challenge. In addition to this problem many homogeneous catalysts can only be used at relatively low temperatures and even then they tend to decompose slowly in solution.

In heterogeneous catalysis the catalyst is in a different phase from the reactants. Figure 1.2 illustrates a simplified energetics diagram showing the steps involved in a heterogeneous reaction and Table 1.3 highlights important catalytic reactions which employ heterogeneous catalysts. Typically in heterogeneous catalysis, the catalyst is a solid and the reactants are either a liquid or gas. The reactant will interact with the surface of the catalyst via a physical process known as adsorption wherein the chemical bond of the reactant (A) weakens and breaks. Next, reactant (B) adsorbs to the catalyst surface. Reactant (B) reacts with adsorbed reactant (A) atoms on the surface of a catalyst via a step wise process after which the product desorbs from the catalyst surface.

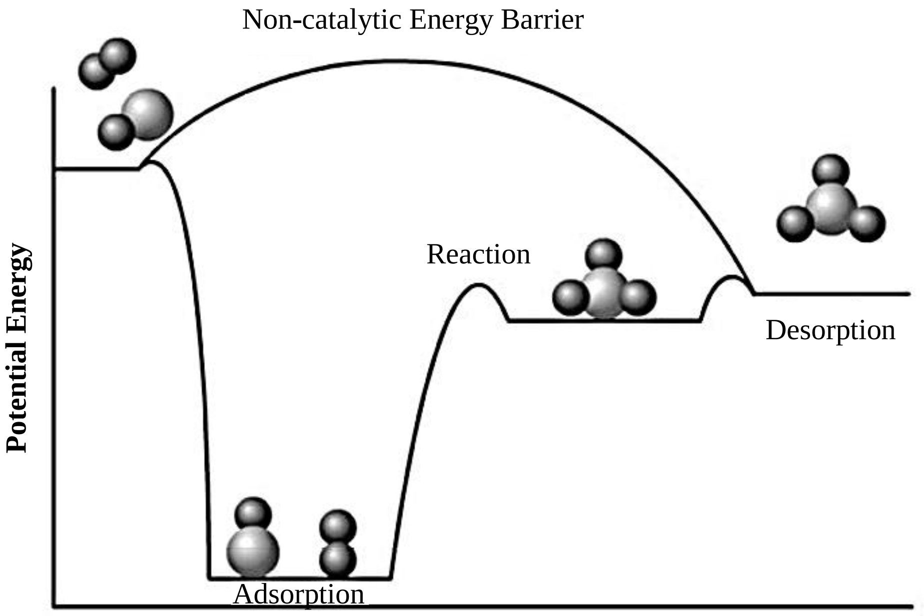


Figure 1.2 Simplified energetics diagram showing the steps involved in a heterogeneous reaction.[2]

Table 1.3 Important catalytic reactions which employ heterogeneous catalysts.

Commercial Process	**Catalyst**	**Final Commercial Product**
Contact process	V_2O_5 or Pt	Sulphuric acid
Haber process	Fe, K_2O, Al_2O_3	Ammonia
Ostwald process	Pt and Rh	Nitric Acid
Water–gas shift reaction	Fe,Cr_2O_3 or Cu	H_2 for Ammonia, methanol and other fuels
Catalytic hydrogenation	Ni, Pd or Pt	Partially hydrogenated oils for margarine

This thesis focuses on the synthesis of hydrogen peroxide directly from H_2 and O_2, by the use of supported heterogeneous catalysts with a view to making its production 'greener' and as a result increasing its contribution to 'Green Chemistry'.

1.3 Green Chemistry

Over the years different principles have been proposed that can be used when thinking about the design, development and implementation of chemical products and processes. These principles enable scientists and engineers to protect and benefit the economy, people and the planet by finding creative and innovative ways to reduce waste, conserve energy, and discover replacements for hazardous substances.

1.3.1 The Principles of green chemistry

The 12 principles of green chemistry were developed in 1998 by Paul Anastas and John Warner[3] and are outlined below.

1 **Prevention -** It is better to prevent waste than to treat or clean up waste after it has been created.

2 **Atom economy -** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3 **Less Hazardous Chemical Synthesis -** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4 **Designing Safer Chemicals -** Chemical products should be designed to affect their desired function while minimizing their toxicity.

5 **Safer Solvents and Auxiliaries -** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6 **Design for Energy Efficiency -** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7 **Use of Renewable Feedstock's -** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8 **Reduce Derivatives -** Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9 **Catalysis -** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10 **Design and Degradation -** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11 **Real – Time analysis for Pollution Prevention -** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12 **Inherently Safer Chemistry for Accident Prevention -** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Ryoji Noyori, a nobel laureate in chemistry identified three important developments in green chemistry.[4] The first was to solve a solvent problem by the use of supercritical CO_2, the second was ‘‘Green’’ oxidation with aqueous hydrogen peroxide and finally the last was the use of hydrogen in asymmetric synthesis. This thesis will focus on the synthesis of hydrogen peroxide via a greener cleaner route in the presence of heterogeneous catalysts. The aim is to produce hydrogen peroxide directly from H_2 and O_2 keeping in mind the 12 principles of green chemistry. This thesis will focus on promoting the design and manufacture of hydrogen peroxide which will prevent waste, reduce unnecessary derivatives and avoid the use of auxiliary substances. Furthermore it will focus on making the synthesis of hydrogen peroxide more atom and energy efficient, less hazardous and promote safe chemistry for accident prevention.

The next few sections will focus on the properties, applications and production of hydrogen peroxide.

1.4 Hydrogen Peroxide

Hydrogen peroxide is a chemical compound with the formula H_2O_2. This chemical is a clear colourless liquid which is completely miscible with water. H_2O_2 and water do not form azeotropic mixtures and therefore can be completely separated by distillation to obtain a pure 100% m/m solution. Pure 100% m/m H_2O_2 can be obtained by fractional distillation however it is usually of academic interest only and not produced on an industrial scale. Indeed some niche uses may require the use of pure H_2O_2 for example NASA are interested in employing pure H_2O_2 for the propulsion of rockets as the handling of pure H_2O_2 is inherently safer than the use of liquid oxygen. H_2O_2 can undergo a range of reactions and the heats of formation and decomposition of H_2O_2 are given in figure 1.3.

$$\begin{array}{llll}
H_2\,(g) + O_2\,(g) & \longrightarrow & H_2O_2\,(g) & -136.2\text{ KJ mol}^{-1} \\
H_2\,(g) + O_2\,(g) & \longrightarrow & H_2O_2\,(l) & -187.9\text{ KJ mol}^{-1} \\
H_2O_2\,(g) & \longrightarrow & H_2O\,(g) + 0.5\,O_2\,(g) & -105.8\text{ KJ mol}^{-1} \\
H_2O_2\,(l) & \longrightarrow & H_2O\,(l) + 0.5\,O_2\,(g) & -98.3\text{ KJ mol}^{-1}
\end{array}$$

Figure 1.3 Heats of formation and decomposition of H_2O_2

H_2O_2 can decompose to give water, gaseous oxygen and the evolution of heat (100.4 KJ mol^{-1}). The decomposition rate increases with temperature at about 2.3 times per 10 °C rise [5] however several other factors can also effect the rate of H_2O_2 decomposition these include the pH, concentration of H_2O_2 and the presence of stabilisers or impurities. H_2O_2 decomposes in the presence of many substances, including most of the transition metals and their compounds as well as certain organic compounds.

Decomposition of H_2O_2 $2H_2O_2 \longrightarrow 2H_2O + O_2$

H_2O_2 is a very active chemical and a versatile oxidant which can oxidise and react with a range of organic and inorganic substrates under mild reaction conditions. H_2O_2 can react over the whole pH range with high oxidation potentials $E_0 = 1.763$ V at pH 0, $E_0 = 0.878$ V at pH 14.[6]

Oxidation by H_2O_2 $H_2O_2 + M \longrightarrow MO + H_2O$

H_2O_2 is a strong reducing agent and has the ability to reduce other strong oxidising compounds such as $Ce(SO_4)_2$, $KMNO_4$, NaClO and Cl_2.[6] $KMNO_4$ and $Ce(SO_4)_2$ are commonly used as standards for volumetric determination of H_2O_2 as later discussed in Chapter 2.5.1.

Reduction by H_2O_2 $H_2O_2 + R \longrightarrow RH_2 + O_2$

H_2O_2 can also undergo substitution reactions with organic reagents to produce a variety of peroxide compounds that are widely used in organics synthesis and numerous applications.

Substitution reaction by H_2O_2 $H_2O_2 + RX \longrightarrow ROOH + HX$

In the liquid phase H_2O_2 can also bind molecularly to metal peroxides, oxoacids, salts, percarbonates, nitrogen compounds and urea (to form urea-hydrogen peroxide (UHP) which is widely used in dental applications for the whitening of teeth).

Addition reactions with H_2O_2 $H_2O_2 + A \longrightarrow AH_2O_2$

1.4.1 Applications

H_2O_2 was first discovered in 1818 by Louis-Jacques Thenard.[7] Since then its applications have increased immensely (Figure 1.4) and today H_2O_2 is one of the world's important commodity chemical within the fine chemical industry and the home. The synthesis of H_2O_2 is vital as it has applications in bleaching, disinfectants, waste water treatment and as a green oxidant for the production of numerous valuable compounds.[8] Currently over three million metric tonnes of H_2O_2 are produced annually, around 80% of this is used for the fine chemical synthesis and in the paper and textile bleaching industries.[9]

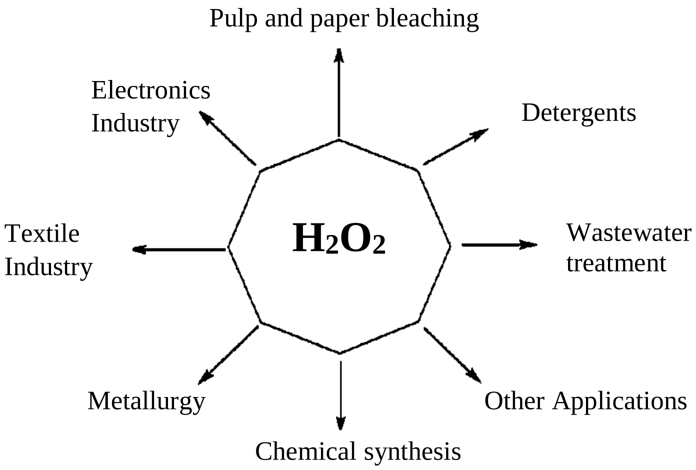


Figure 1.4 Principle uses of H_2O_2.[6]

H_2O_2 is currently presented as an attractive alternative to the industrial use of oxidants such as tBuOOH, N_2O, NaClO, chromate or permanganate.[10] These stoichiometric oxidants produce large amounts of waste by-products requiring additional purification and separation steps. In contrast, H_2O_2 is a highly active and selective oxidation agent for many oxidation reactions, it has a high active oxygen content (47 wt. %) producing only water as a CO-product.[11-12]

Until very recently there was limited use of H_2O_2 as an oxidising agent however an important breakthrough in this field took place since the discovery of titanium silicate (TS-1).[13] (TS-1) is a ZSM-5 type molecular sieve and has an outstanding ability to catalyse various oxidation reactions with aqueous H_2O_2 as the primary oxidant. In 2008 the commercialisation of the Hydrogen peroxide-Propelene Oxide (HPPO) process took place which involves the epoxidation of propylene with H_2O_2 to obtain propylene oxide using TS-1 as a catalyst. The use of H_2O_2 for oxidation reactions is highly favourable as the only by-product of the reaction is water. It is therefore considered as an alternative green oxidant and its demands have increased immensely especially due to the increasing demand for propylene oxide. The forecast demand for H_2O_2 was predicted to exceed 4.3 million metric tonnes in 2015.[9]

1.4.2 Manufacturing

Since the discovery of H_2O_2 in 1818[7] the manufacturing of H_2O_2 has gone through three main industrial processes. From 1818 to the beginning of the 20th century H_2O_2 was produced via a wet chemical process,[7] following this most of the world's H_2O_2 was produced by the electrolysis of ammonium sulphate[14] and today virtually all production of H_2O_2 is based on the Anthraquinone auto-oxidation process.[15]

1.4.2.1 Wet chemical process

The industrial manufacture of H_2O_2 can be tracked down to its isolation in 1818 by L.J. Thenard.[7] Thenard treated barium peroxide with nitric acid which produced low concentrations of aqueous H_2O_2. This process was significantly improved by the use of hydrochloric acid which yielded hydrogen peroxide in conjunction with barium chloride, both of which are water soluble. The barium chloride was removed by precipitation with sulphuric acid. Figure 1.5 shows the steps involved in the chemical wetness of H_2O_2 and this resulted in the first commercial manufacture of H_2O_2.

$$\begin{array}{lcl} BaO_2 + 2HCl & \longrightarrow & BaCl_2 + H_2O_2 \\ BaCl_2 + H_2SO_4 & \longrightarrow & BaSO_4 + 2HCl \\ \hline BaO_2 + H_2SO_4 & \longrightarrow & BaSO_4 + H_2O_2 \end{array}$$

Figure 1.5 Thenard's route to aqueous hydrogen peroxide.

Although Thenard's route was still operating until the mid 20th century and approximately 2000 metric tonnes of H_2O_2 were produced using this process there were some major drawbacks. The concentration of H_2O_2 produced was a 3 wt. % aqueous solution and it only had a limited market because the production costs were extremely high. Furthermore, the stability of H_2O_2 formed was poor due to the high levels of impurities present in the isolated H_2O_2. This process was later replaced by the electrochemical process.

1.4.2.2 Electrochemical manufacture of aqueous H_2O_2

In 1853, Meidenger[13] discovered that H_2O_2 can be formed electrolytically from aqueous sulphuric acid. Berthtot[14] later proposed a reaction scheme (figure 1.6) for this process and showed that the reaction proceeded via a peroxodisulfuric intermediate which was hydrolysed to form H_2O_2 and sulphuric acid. In 1908 the first pilot plant was based on the electrochemical technology.

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + H_2$$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

$$2H_2O \longrightarrow H_2O_2 + H_2$$

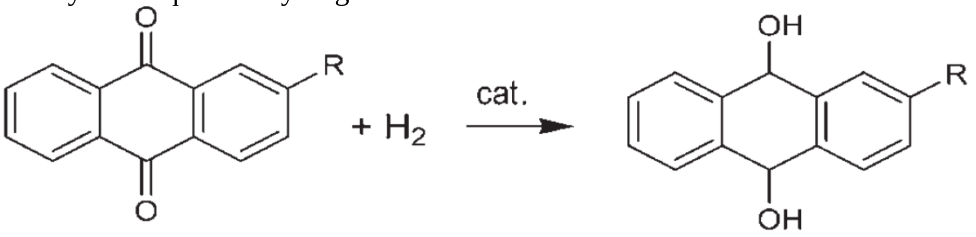
Figure 1.6 Electrochemical manufacture of aqueous hydrogen peroxide.

This process was later improved by replacing sulphuric acid with ammonium sulfate, and the resulting ammonium peroxodisulfate was hydrolysed to H_2O_2. As a result the hydrogen peroxide production as 100% m/m rose to approximately 35 x 10^3 tonnes per annum.[18]

1.4.2.3 Anthraquinone Auto Oxidation Process (AO)

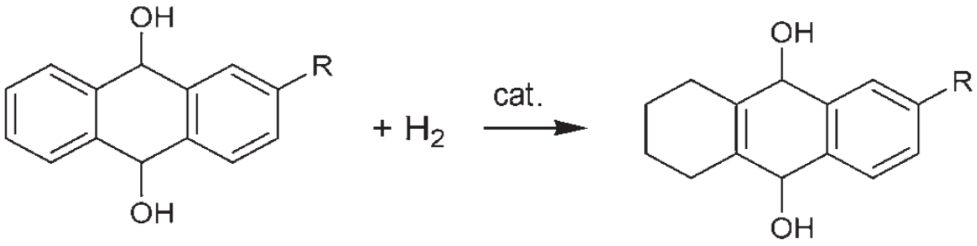
Currently H_2O_2 is commercially produced by an anthraquinone auto oxidation process (AO process) which was developed by Hans-Joachium Riedl and George Pfleiderer of BASF in 1939.[19-22] The process is illustrated in Figure 1.7 and a typical autoxidation plant schematic is summarised in Figure 1.8.

a) Alkylanthraquinone hydrogenation



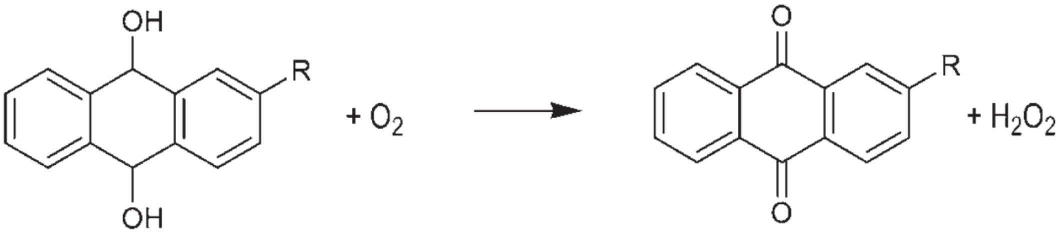
2-alkylanthraquinone (AQ) 2-alkylanthrahydroquinone (AHQ)

b) Ring hydrogenation



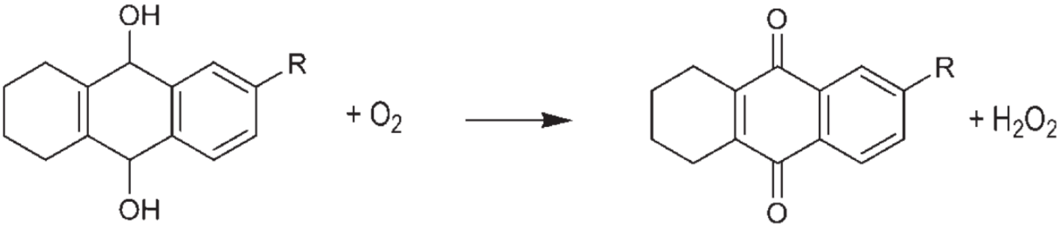
AHQ 5, 6, 7, 8-tetrahydroanthrahydroquinone (THAHQ)

c) Hydrogen peroxide formation



AHQ AQ

d) Hydrogen peroxide formation



THAHQ THAQ

Figure 1.7 Anthraquinone auto-oxidation reactions.[6]

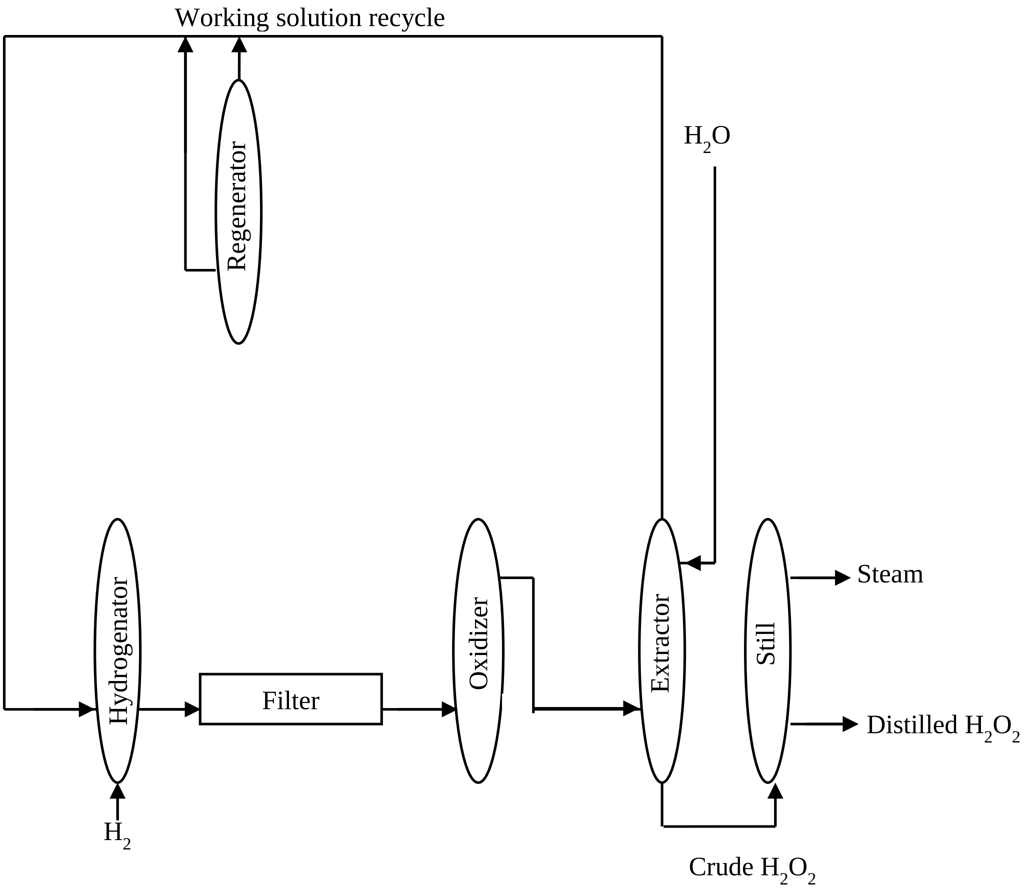


Figure 1.8 Schematic Diagram of the AO process.[5]

In the AO process a 2-alkylanthraquinone (AQ, usually 2-ethylanthraquinone) is dissolved in an appropriate solvent or a mixture of solvents, this is catalytically hydrogenated to the corresponding alkyl hydroanthraquinone (AHQ) at temperatures of 40-50 ºC, under H_2 partial pressure up to 4 bar. The solution containing the AHQ is separated from the hydrogenation catalyst and then oxidised with air (at 30-60 ºC, near atmospheric pressure) to reform the alkylanthraquinone and simultaneously form equimolar amounts of H_2O_2. The H_2O_2 is then stripped from the organic working solution by demineralised water to produce a solution that is usually 30 % by wt H_2O_2. The aqueous extract is then distilled to remove impurities and increase the concentration to as high as 70 wt. %, and the solvent/anthraquinone mixture is recycled.

Figure 1.7 is an oversimplification of the reactions involved in the AO process. A series of side reactions occur in the AO process which lead to the net consumption of anthraquinone. The alkylhydroanthraquinone (A) when in contact with the catalyst will undergo a small amount of catalytic reduction, initially on the unsubstitued ring to yield 5, 6, 7, 8 tetrahydroanthrahydroquinone (B). (Figure 1.9).

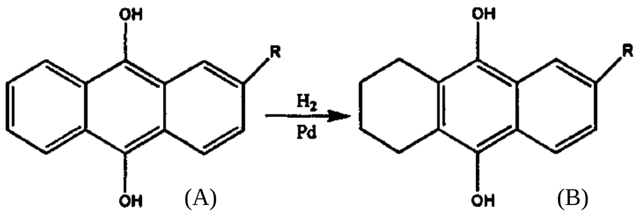


Figure 1.9 Side reactions in the anthraquinone process.

The 2-anthraquinone can tautomerise to yield hydroxyanthrones (D, E) which can further reduce to anthrones (G. H Figure 1.10)

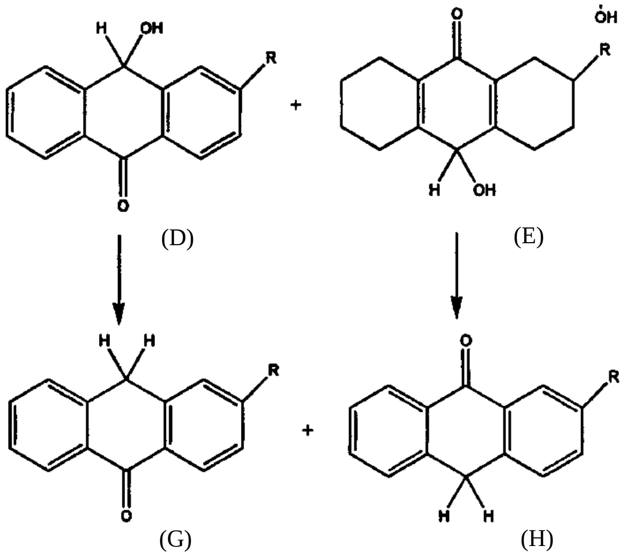


Figure 1.10 Side reactions in the anthraquinone process

The tetrahydroalkylanthraquinone can further reduce or oxide to an octa-product (C) or epoxide (F) respectively. Once the former is produced it remains until purged due to its very low rate of oxidation. The latter does not participate in the formation of H_2O_2 and leads to the loss of active quinone. Developments have therefore been made for regenerating the tetrahydro compound from the epoxide; however this results in an increase in cost.[23]

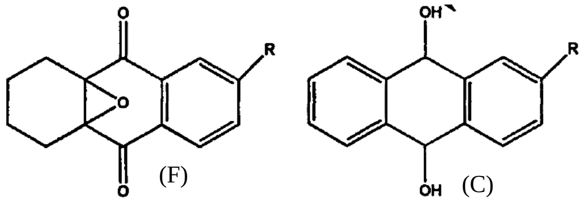


Figure 1.11 Side reactions in the anthraquinone process.

Although the AO process has been used in industry for several decades and accounts for 95% of the world H_2O_2 production[6, 24] it has several drawbacks as it involves many non-green aspects.[25] These include the periodic replacement of costly quinone-derivative due to non selective hydrogenation, use of complex and toxic solvent system, deactivation of hydrogenation catalyst and the requirements of energy intensive process steps to remove organic impurities. Furthermore the process is only economically viable on a large scale production (> 40 x 10^3 tons per annum) and produces H_2O_2 in concentrated forms (70 wt. %). However, most uses of H_2O_2 generally require concentrations between 2 and 8 wt. % and on a much smaller scale. Thus this makes the indirect process expensive as a high amount of energy is used on an incompatible process and still the desired low concentration product is not formed. The concentrated solutions of H_2O_2 has to be transported to the point of use which isn't favourable as the storage and transport of high concentrations of H_2O_2 can be hazardous and explosive if it violently decomposes.[26] The process of transportation requires further energy, time and capital costs. These issues have fascinated engineers and scientists for several years to develop a more cost effective and cleaner process for manufacturing H_2O_2.

1.5 Different approaches to the direct synthesis of H_2O_2

Due to the problems associated with the AO process many researchers have been trying to develop new methods for producing H_2O_2. Different synthetic routes have been studied however none of them have been implemented on an industrial scale yet. Some of the most important routes are summarised hereunder.

1.5.1 Fuel cells

A promising alternative is the synthesis of H_2O_2 with fuel cells.[27-31] Several methods have been proposed for the direct and continuous production of H_2O_2 in fuel cells. The simplest design consists of a fuel cell divided by an electrolyte membrane (nafion 117). The anodic face of this membrane (where H_2 is oxidized) is deposited with Pt, and the cathode face (where O_2 is reduced to hydrogen peroxide) is covered with graphite or an Au mesh.[32] The fuel cell process is based on the reduction of O_2 to H_2O_2 which takes place at the three phase boundary (solid cathode, aqueous electrolyte and gases O_2).

There are two advantages of fuel cell systems over the catalytic direct synthesis of H_2O_2. Firstly, the explosion hazards related with the direct mixing of O_2 and H_2 is eradicated because the reagent gases are fed separately due to the electrolyte membrane. Secondly due to the fuel cell setup electric power is generated along with the formation of H_2O_2.

Yamanka and co-workers[29] have shown that H_2O_2 could be produced with selectivity of 93% using a fuel cell system. Due to the higher cost of Pt recent efforts have been made to develop non precious metal based fuel cells systems.[30-31] Indeed the direct synthesis of H_2O_2 in a fuel cell system is considered as a green process for H_2O_2 production; however the process is still far from commercial exploitations.[14]

1.5.2 Plasma

According to early literature H_2/O_2 can be converted into H_2O_2 and H_2O under atmospheric pressure if they are activated into a non-equilibrium plasma by silent electric discharge. [33-35] In comparison to other known methods, the plasma method has several advantages the plasma method is unique because it does not involve any other chemicals except the H_2/O_2 feed, it is performed in the gas-phase, while the stoichiometry of H_2/O_2 providing the best selectivity for H_2O_2 meets the non-explosive regime of H_2–O_2 mixtures.[35] Furthermore, the plasma method doesn't have the problem of diffusivity limits, it is a safe and green process[36] which is suitable for the direct synthesis of a pure H_2O_2 aqueous solution. However, until very recently, the actual H_2O_2 yields reported with previous plasmas was very low (ca. less than 5%).[33] More recently Zhou *et al* [37] have demonstrated that under ambient conditions H_2O_2 could be synthesised with high selectivity (56.25%) and a moderate yield (32.51%) via the gas phase reaction of H_2/O_2

non equilibrium plasma.[37] The process is based on using a dielectric barrier discharge reactor (DBD) to produce non equilibrium plasma from a mixture of H_2/O_2 and to generate H_2O_2 and H_2O. The use of a plasma method has shown great potential in producing H_2O_2 via the direct synthesis and recently it has been shown that propene epoxidation can be carried out with *in-situ* H_2O_2 generated from the reaction of H_2/O_2 non equilibrium plasma.[38] However there are issues concerning this method which are related to the configuration of the reactor and its electric energy utilisation. In order for this process to be successful on a large scale work must be conducted to increase the electric energy utilization by optimizing the discharge conditions and the structure of the discharge reactor.[37-38]

1.5.3 Supercritical CO_2

The synthesis of H_2O_2 from H_2 and O_2 using supercritical CO_2 has been investigated using both homogeneous[39-41] and heterogeneous Pd based catalysts. [42-43]When compared to other organic solvents the use of a supercritical CO_2 as the reaction medium is more favourable since it is non-flammable, less toxic, naturally abundant and it does not react with any of the products formed. Additionally it exists as a 2 phase fluid-solid system as O_2 and H_2 are miscible with CO_2 above 31 ºC.[44] This is favourable as it reduces or even eliminates the mass transfer resistance observed in the three phase (gas-liquid-solid) direct liquid synthesis of H_2O_2. Landon *et al*.[45-46] evaluated 5 wt. % Au, Pd and AuPd catalysts supported on ZnO for the synthesis of H_2O_2 using supercritical CO_2. They found that Pd only catalyst were inactive for the production of H_2O_2 as only water was generated as the product. On the contrary the Au/ZnO and Au-Pd/ZnO catalysts did display activity for H_2O_2 synthesis; however the rates obtained were low. The literature [45-46] demonstrates that although H_2O_2 can be produced using supercritical CO_2 as a reaction medium the rate of H_2O_2 decomposition is too rapid at temperatures above the critical temperature (31.1 ºC) for this reaction medium to be beneficial.

1.5.4 Direct synthesis of H_2O_2 using Pd based catalysts

The first patent on the direct synthesis of H_2O_2 was granted to Henkel and Weber in 1914.[47] The patent described the use of palladium (Pd) catalysts to catalyse the direct synthesis of H_2O_2 from its elements. Hence the majority of the early work was focussed on the direct synthesis of H_2O_2 using Pd catalysts[47-81] and high concentrations of H_2O_2 (> 35 wt. %) were achieved using elevated pressures and H_2/O_2 mixtures in the explosive region. However such studies carried out in the explosive region are extremely dangerous.

Although the direct synthesis of H_2O_2 has been studied for over a century there is still no industrial process based on the direct synthesis of H_2O_2 and the reasons for this are two. First, H_2/O_2 gas mixtures are explosive over a wide range of concentrations (5-95 v/v% for H_2 in O_2). Hence in order to operate the reaction below the lower explosive limit the ratio of H_2 to O_2 has to be carefully controlled or the reactant gases have to be diluted in inert gases such as N_2, Ar, or CO_2. [82-96] The second reason is related to catalyst design, catalysts that are active for the direct synthesis reaction are also active for the parallel combustion reaction and the consecutive hydrogenation and decomposition reactions (all of which are thermodynamically more favoured than the synthesis reaction to form water). A key requirement for the direct synthesis to be considered on an industrial level is high H_2 selectivity (> 95 %) and the catalyst must have minimal or no activity for the unwanted side reactions.

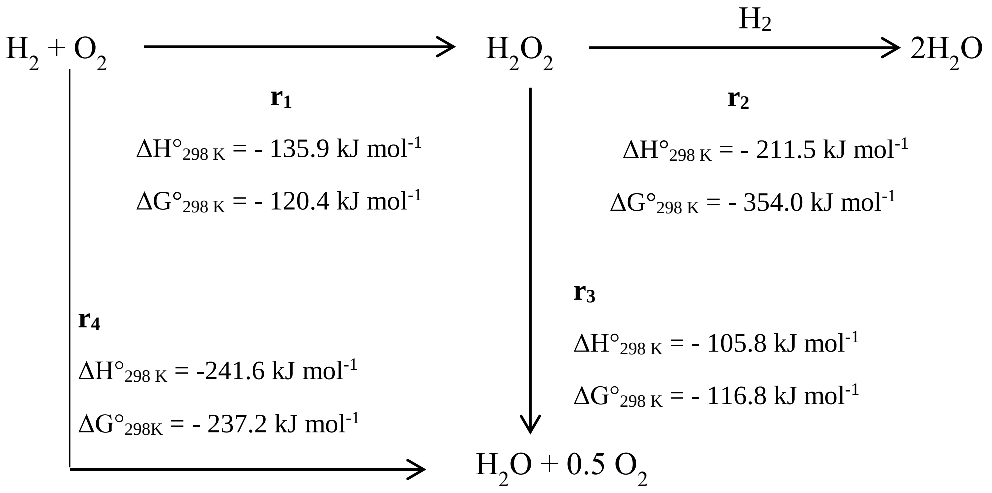


Figure 1.12 Reactions involved in the direct production of H_2O_2.

Several patents and papers have revealed the beneficial effect of acid and halide promoters in promoting the direct synthesis of H_2O_2 over Pd-based catalysts.[97-113] In the early 1960's Pospelova[114-116] demonstrated that the addition of acid (HCl, HNO_3) to supported Pd catalysts was essential to achieve high H_2O_2 yield. These findings were extended by Choudhary *et al.*[117] who investigated the effect of acids and halides on H_2O_2 decomposition activity using a 5% Pd/Carbon catalyst in an aqueous reaction medium. The studies revealed that the acids can be classified into two groups Oxyacids (acetic acid, phosphoric acid, nitric acid, sulphuric acid and perchloric acid) and halide acids (hydrochloric acid, hydrobromic acid and hydroiodic acid). The former group have the ability to reduce the H_2O_2 decomposition activity however the production of H_2O_2 was very little or none via the direct synthesis pathway. Whereas the latter group, which were strong suppressing acids, largely improve the selectivity for H_2O_2 formation.

Choudhary *et al.*[117] identified that low concentrations of phosphoric acid (0.03 M) was a suitable acid additive to the reaction medium as it caused negligible leaching of Pd into the reaction medium. The role of the phosphate ions was to stabilise the H_2O_2 produced as well as reduce the base catalysed H_2O_2 decomposition.[118]

The effect of halide addition to the catalyst structure (incorporated via pre-treatment or addition to the reaction medium) on H_2O_2 yield has been highlighted in many studies and bromide is found to be the most active among the halide ions. [14, 102, 117-125] Lunsford and Choudhary have demonstrated that among the halide ions, in particular Cl and Br, is effective in blocking active sites responsible for H_2O_2 decomposition reactions. [117, 125-132]These halide ions are believed to inhibit the cleavage of molecular oxygen to give water.

Lunsford and Dissanayake [98, 104-105, 109-110, 133-136] have shown that colloidal palladium is an active phase for the direct synthesis of H_2O_2. In their studies they used concentrated HCl (1.0 M) solution as the reaction medium and Pd/SiO_2 as the catalyst. The addition of HCl to $PdCl_2$ resulted in oxidation of Pd^0 to form $PdCl_4^{2-}$ ions in solution, which subsequently reduced back to metallic Pd by H_2, thus leaving some metal present as colloid establishing a Pd^0/Pd^{2+} steady state. Although the use of a colloidal system is interesting at a fundamental level it is not appropriate for an industrial process since the palladium system can be considered as a homogeneous catalytic system and the management and recovery of this system would be a difficult task.

The key issue with the direct synthesis of H_2O_2 using monometallic Pd catalysts is the catalysts active for the synthesis of H_2O_2 are also active for its degradation leading to water formation. The addition of high quantities of acid into the reaction medium is undesirable because these additives: i) have to be subsequently removed (ii) can present operational safety concerns associated with the corrosion of reactor materials (iii) may cause dissolution of the metal active phase of the catalyst into the reaction medium and consequently result in instability of the catalyst as well as the H_2O_2 produced. Therefore a new catalytic system has to be developed that would improve the efficiency of the Pd catalysts.

1.6 Gold Catalysis

The selective oxidation of substrates is a key synthetic process for the production of a broad range of intermediates and products within the pharmaceutical and fine chemical industry. However, on a commercial scale many of these reactions are conducted using stoichiometric oxygen donors (e.g. manganates) or activated forms of O_2 (e.g. H_2O_2.) In contrast to selective oxidation reactions catalytic hydrogenation processes utilise molecular hydrogen as a reagent. The key difference for the use of hydrogen and dioxygen as reagent is in their activity. Hydrogen, to be effective in hydrogenation requires activation on the surface of a heterogeneous catalyst. As a result, non-catalysed hydrogenations do not compete with the catalysed process and this leads to great control over the reaction selectivity. However this is not the case for selective oxidation processes, dioxygen in its ground state is a di-radical so homogeneous non-catalysed oxidations can compete readily with the catalysed process, especially at elevated temperatures.

This is a key reason why small scale oxidations using dioxygen or air have not been exploited, as control of selectivity presents a major experimental problem. This emphasizes the importance of development in the design of selective oxidation catalysts which can be used alongside molecular oxygen. Indeed supported gold catalysts have shown to be active catalysts for oxidation reactions and Au nanoparticles have been found to be active for the selective oxidation of carbon monoxide, epoxidation of alkenes and oxidation of alcohols.

For several years gold was considered as an inert metal which was only valued for its high value and beauty in the jewellery industry. Thus gold was never used in chemical processes and catalysis. Although Bond *et al.*[137] reported the use of nanoparticle gold to catalyse the hydrogenation of dienes, gold catalysts were less effective than the palladium or platinum catalysts and as these catalysts were well established gold was not seen as a viable alternative.

During the last few decades there has been a huge transformation in the field of gold chemistry. The extremely popular and well established principle that gold was an unreactive metal with very limited chemistry has been overturned. In the 1980's two great discoveries were made with regards to utilizing gold in chemical reactions. Haruta and Hutchings[138] reported the use of nanoparticle gold as heterogeneous catalysts. Haruta reported the use of gold in low temperature CO oxidation[139] and Hutchings predicted and later verified gold as the best catalyst for acetylene hydrochlorination.[140-145] Although these findings were reported in the 1980's real interest in catalysis by gold arose in the late 1990's.[146] Since then gold catalysis has become a hot topic where the number of reports and patents published in this area is growing exponentially (Figure 1.13).

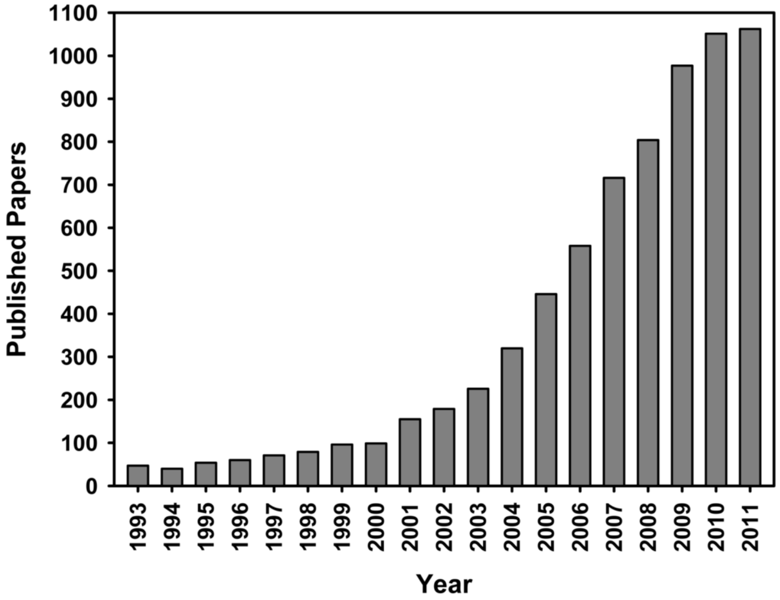


Figure 1.13 Published papers on the topic of 'Gold catalysis' (sourced from Scifinder)

When gold is finely divided, consisting of nanoparticles made up of just several hundreds of atoms it displays remarkable activity either as a homogeneous or heterogeneous catalyst and indeed in certain cases is the catalyst of choice surpassing the catalytic properties of the Group VIII metals.[146] Nanoparticulate gold is seen as an effective material for catalysing a wide range of reactions including selective oxidation reactions such as CO oxidation, the oxidation of alcohols and the direct synthesis for H_2O_2.[140-152] In the following sections some of the most important applications where Au nanoparticles are successfully employed are reviewed.

1.6.1 Carbon Monoxide Oxidation

CO emissions within exhaust gases of petrol/diesel engine vehicles and industrial processes is a huge burden to the environment and human health and for this reason the control of CO emissions is significantly important. Haruta *et al.*[139] demonstrated that supported Au nano-crystals (< 5 nm) can be highly effective catalysts for the oxidation of CO at very low temperatures (< 0 ºC). Catalytic materials prepared by precipitation methods resulted in more active catalysts when compared to catalysts prepared by impregnation methods. It was shown that the nature of the support and catalyst preparation method can have a significant effect on the catalyst activity and selectivity and as a result this may vary the active site for heterogeneous catalysts. Majority of the active catalysts for CO oxidation consist small crystallites with a diameter of 2-4 nm of Au supported on an oxide.

There has been much debate concerning the nature of the active site for these catalysts. Bond and Thomspon[146] proposed a model where Au atoms at the interface between the Au particle and the oxide are the active oxidation sites. A great deal of research has been carried out on the role of Au^0 and Au^{3+} however it still remains unclear what is the active gold component in the catalytic reaction.[147-151] Goodman *et al*.[147] have shown that the small size (3-5 nm) Au particles are most active for CO oxidation and the reaction can be attributed to quantum size effects. Whereas Boyen *et al.*[148] demonstrate that Au^{55} could be the active site for CO oxidation and Au particles containing 5 atoms with a diameter of 1.4 nm are most active and stable. Furthermore Norskion[149] show that the most energetically favoured path for CO oxidation occurs on Au particles with 10 atoms. On the contrary other groups have focussed on the role of Au^{3+}. Baker *et al.*[150] reported mechanistic proposal in agreement with Bond and Thomson who stated that the peripheral effects of the small Au nanoparticles contribute to the high catalytic activity. Finally Hutchings *et al*. also showed that Au^{3+} in Au/FeO_3 was the important component for CO oxidation.[151]

1.6.2 Hydrochlorination of acetylene

One of the methods to produce vinyl chloride was based on the hydrochlorination of acetylene with mercuric chloride supported on carbon. Although this was one of the main routes to produce vinyl chloride in the early 1980's the active component in the catalyst sublimed which resulted in catalyst deactivation. There was therefore an increased desire to find a more stable catalyst for this reaction. The hydrochlorination of acetylene was one of the early studies that showed cationic gold can be an effective heterogeneous catalyst. Shinoda *et al.*[152] investigated a range of metal chlorides supported on carbon which were active for this reaction however the activity was correlated with the standard electrode potential and gold, more importantly Au^{3+} was predicted to be the best catalyst for this reaction.[142, 144, 153] Further research by Hutchings[154] verified this prediction as gold was a more stable catalyst in comparison to the mercuric chloride catalyst however with time these new catalysts deactivated. It was observed that the rate of deactivation was dependent on temperature and at temperatures of ca. 100 ºC lowest deactivation was observed. However at this temperature the catalyst was not sufficiently active and temperatures of ca. 180 ºC are preferred.[154] At temperatures below 100 °C the deactivation was attributed to the deposition of polymeric carbonaceous materials whereas at higher temperatures the deactivation occurred due to the reduction of Au^{3+} to Au^0.[155] The deactivation was inhibited by *in-situ* reactivation by cofeeding dilute NO in with the reactor feedstock. This did not affect the selectivity of the catalyst however, did stop deactivation.[155]

1.6.3 Alkene epoxidation

The oxidation of propene to propylene oxide (PO) is a major research target as PO is an important commodity chemical used in the manufacture of polyols as well as polyurethane. PO is also used to produce solvents, chemical intermediates, synthetic lubricants, flame retardants, chemicals for oil drilling and textile surfactants. The present global production of PO is approximately 3.5 million tonnes per annum, producing a market of US $7 billion a year. Currently the commercial process by which PO is manufactured involves a 2 staged chemical reaction using Cl_2 or organic peroxides yielding by-products stoichiometrically.

The direct gas-phase synthesis of propene oxide, by the use of molecular oxygen, has long been desired. Indeed the commercial process for the epoxidation of ethene with dioxygen is currently operating with selectivities greater than 90% using a supported Ag catalyst.[156] Nevertheless the oxidation of propene has proved to be much more challenging.[157] One of the major problems associated with the vapour phase oxidation of propene to PO using molecular oxygen is low reaction selectivity. The formation of the epoxides requires the electrophilic addition of an oxygen intermediate to the carbon–carbon double bond however propene can be easily activated via the formation of allylic species which leads to non-selective oxidation. While Lambert *et al.* have shown that in the absence of a sacrificial reductant, using supported catalysts selectivities of ~ 50% and conversions of 0.25% can be achieved, the selectivity rapidly declines with increasing conversion.[158]

Since a commercial process for the direct oxidation of propene with dioxygen has proved to be difficult many research groups have advanced in designing a promising alternative process for the epoxidation of propene.[159-164] The Hydrogen peroxide-Propene Oxide (HPPO) process allows production of PO via a direct reaction between propene and hydrogen peroxide over a titanium silicalite (TS-1) catalyst. It was predicted that due to the HPPO process and the increasing demand for PO, the demand for H_2O_2 production would exceed 4.3 million tonnes by 2015.[165]

However due to the relatively high and steady changing costs of H_2O_2 a process based on molecular oxygen is far more preferable. For economic reasons, attempts were made to replace H_2O_2 by employing a mixture of O_2 and H_2 that generates H_2O_2 *in-situ*. Haruta and co-workers[166-167] were the first to demonstrate that highly dispersed Au/TiO_2 catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (> 99 %), using a combination of H_2 and O_2 as oxidant. H_2 aided as a sacrificial reductant which permits the activation of dioxygen at relatively low temperatures (303-393 K) and therefore allowing selective oxidation of propene to propene oxide. Haruta found that when gold is deposited on TiO_2 by a deposition–precipitation technique as hemispherical particles with diameters smaller than 4.0 nm it produces propylene oxide with selectivities higher than 90% and conversions of 1–2% at temperatures of 303–393 K.[166-167] Since this discovery the catalytic properties of Au/TiO_2 and related systems have attracted chemical industries[168] and academia. Extended studies using Au/TiO_2 for the oxidation of propylene revealed that among single metal oxides, TiO_2 in its anatase form only makes Au selective for the reaction.[169]

A range of titanium silicates and Ti deposited on SiO_2, have been tested as a support for Au particles and it was found that when these Ti/SiO_2 support materials are used, Au is selective to epoxidation up to 473 K, resulting in improved conversion upto two folds (~5%) [167, 169-170] Several materials were screened for the reaction including titanosilicates TS-1, Ti-zeolite, Ti-MCM41, Ti-MCM48, all materials were found to have different sizes and structures of pores and Ti-MCM48 demonstrated the best catalytic performance.[170] Additional studies by Haruta and co-workers[171] revealed drawbacks of the Au/TiO_2 catalyst including poor H_2 utilisation. Poor H_2 utilisation was tackled by using mesoporous titanosilicates as the support and as a result reasonable H_2 efficiency (40 %), propene conversions (7 %) and high propene oxide yields ((93 g (h^{-1}kgcat^{-1}) at 160 ºC) and selectivities (49 %) were attained.

Since TS-1 proved to be a selective support for the epoxidation of propene with H_2O_2 as the oxidising species[172, 159-164] the majority of the early studies used this as a support. Haruta and co-workers[174] found the Au supported on TS-1 produced more propanal than propene oxide whereas Moulijn and co-workers[175] demonstrated that Au/ TS-1 catalysts were very stable and could be very selective to the formation of propene oxide. Mechanistic studies showed the important role of the gold nanoparticles involved in establishing a bidentate propoxy species as an intermediate.[176]Further studies by Haruta *et al.* [177] demonstrated that carefully tuning of the gold loading is important to achieve high selectivities and the active species in these catalysts are gold species with diameters smaller than 2 nm. Furthermore trimethylamine was identified as a gas phase promoter for the epoxidation of propene with supported gold catalysts.[178]

1.6.4 Alcohol Oxidation

The selective oxidation of alcohols is of paramount importance in the fine chemical industry where a large number of substrates are oxidised to alcohols and ketones. Rossi, Prati and co-workers[179-181] were the first to demonstrate in their seminal studies that gold nanoparticles can be very effective for the selective oxidation of alcohols, including diols such as 1, 2 propane diol. Gold catalysts display higher activity and selectivity (> 98 %) in comparison to other noble metals. In these studies bimetallic Au-Pd and Au-Pt were investigated and a synergistic effect was reported. The resistance to poisoning was proved by recycling experiments done under pressure and the bimetallic catalysts showed increased activity and selectivity with respect to their monometallic counterparts.[182-183]

These studies were extended by several groups and supported Au nanoparticles were effective for a range of substrates including glucose and glycerol.[145] Glycerol is a highly functionalised molecule which is readily available from biosustainable sources such as the by-product of the utilisation of sunflower crops and rapeseed oils. More importantly glycerol is the main by-product in the synthesis of biodiesel and its production has increased significantly in the last decade. Carettin *et al*.[184-185] have shown that glycerol can be oxidised to glycerate with > 99 % selectivity using Au supported on graphite and molecular oxygen under relatively mild conditions.

Furthermore Taaring, Gorbanev and co-workers[186-187] have studied the oxidation of hydroxymethyl furfural (HMF) using Au nanoparticles supported on TiO_2. HMF is a dehydration product of sugars and can be selectively oxidised to 2, 5 –furandicarboxylic acid (FDCA) or its ester depending on the reaction conditions employed. FDCA has been reported to have a large potential as a replacement of terephthalic acid a component widely used in various polyesters. Corma *et al.*[188] also studied this reaction and reported selective conversions of 5-HMF to 5-FDCA with 99 mol % yield in water and under mild conditions (65-130 ºC, 10 bar, air). They demonstrated that gold nanoparticles supported on nanoparticulate Ceria (Au/CeO_2) and on TiO_2 (Au/TiO_2) were extremely active and selective for this reaction.

1.6.5 Direct synthesis of H_2O_2

Ishihara *et al.*[189] were the first to show that monometallic Au catalysts are active for the direct synthesis of H_2O_2. In their studies they tested 1 wt. % Au/SiO_2 catalysts in the absence of halide promoters which showed promising H_2O_2 activity, with 30% H_2 selectivity. When monometallic Pt, Pd and Ag supported on SiO_2 were evaluated no H_2O_2 activity was observed under identical reaction conditions. The rates for synthesis and subsequent side reactions were compared for the monometallic Au catalysts with a range of supports. It was reported that Au/SiO_2 performed the best whereas basic supports such as MgO and ZnO were unfavourable supports as they catalysed the undesired reactions and only produced water. The addition of 1 wt. % Pd to Au supported on SiO_2 increased H_2O_2 synthesis rates and a maximum yield of H_2O_2 was observed using a Pd: Au weight ratio of 82:18.

Following this Hutchings *et al*.[190-191] investigated the direct synthesis of H_2O_2 using Au catalysts. Latter Hutchings they reported[192-205] reported that AuPd bimetallic catalysts significantly increased both rates and selectivity of H_2O_2 in comparison to Au-only and Pd-only catalysts. The promotional effects of Au to Pd catalysts for the direct synthesis of H_2O_2 has been extensively studied by Hutchings *et al.*[192-205] for over a decade and this key finding was observed for numerous AuPd supported catalysts. Initial experiments were performed in a stainless steel sealed autoclave at 37.5 bar, using 5% H_2/CO_2 and 25% O_2/CO_2 (1:2 molar) and water-methanol as the solvent. The optimum conditions for the synthesis of H_2O_2 were reported by Edwards *et al.*[201] Short reaction times were preferred in order to prevent the build-up of H_2O_2 which can favour the unwanted hydrogenation and decomposition reaction. It was found that the reactions carried out at 2 °C for 30 minutes in the presence of a methanol-water solvent mixture (80:20) gave highest activities and thus was ideal for the reaction.[201, 204] A wide range of AuPd catalysts of various wt. % were analysed and it was found that the optimum formulation for catalysts prepared by impregnation was 2.5 wt. % Au and 2.5 wt. % Pd.[203]

As showed by Edwards *et al.*[194] if CO_2 and the correct experimental conditions are used the addition of promoters such as halides or acids isn't required to AuPd catalysts. The CO_2 diluent acts as an *in-situ* promoter by forming carbonic acid and acting as a stabilizer. It was reported that the addition of halide and acid promoters to bimetallic catalysts can be deleterious. A major advantage of employing AuPd catalysts for the direct synthesis of H_2O_2 over monometallic Pd catalysts is the reaction medium is free from acid and halide promoters. This represents a crucial difference and advantage for the bimetallic catalysts, as it makes the process green, saves the reactor from corroding and if these bimetallic AuPd catalysts would be used commercially no purification of H_2O_2 would be required. To date the best H_2 selectivity reported for the direct synthesis of H_2O_2 using Pd supported catalysts is ~80%[136] Edwards *et al.*[203] have shown that alloying Au with Pd markedly enhance the catalyst activity and selectivity and in the absence of halide and acid promoters a selectivity greater than 95% was achieved with AuPd supported catalysts.

Edwards *et al.*[208] reported the effect of heat treatment can influence the activity of catalysts employed for the direct synthesis of H_2O_2. The findings showed higher yields of H_2O_2 can be obtained with the uncalcined materials in comparison to the catalysts calcined in static air at 400 ºC. Nevertheless the uncalcined catalysts had a low stability when they were employed for second use and a large amount of the total metal content was lost therefore reducing overall activity. [208] However when the catalysts were calcined in static air, the catalysts showed increased stability as they were used numerous times.[205, 211] Hence suggesting calcined catalysts will be most appropriate for industrial application.

The nature of the alloy in the bimetallic catalysts prepared by impregnation has been studied in detail by Hutchings and coworkers.[199, 203, 211,]X-ray photoelectron spectroscopy (XPS) indicated the development of a core shell structure (Pd rich shell and Au rich core) for the AuPd particles supported on TiO_2, Fe_2O_3 and Al_2O_3 when the catalyst had been calcined in static air. A high Pd/Au ratio was observed with a dramatic decrease in Au signal after calcination at 400 ºC. Scanning transmission electron microscopy (STEM) images showed a bimodal distribution of small (2-10 nm) and large (35-80 nm) nanoparticles. There was a size dependent effect on the composition of the nanoparticles.[88] The larger nanoparticles comprise mainly gold whereas the small nanoparticles comprise mainly Pd. When the structure of the calcined AuPd carbon supported catalysts was analysed via XPS it was reported as random AuPd alloys.

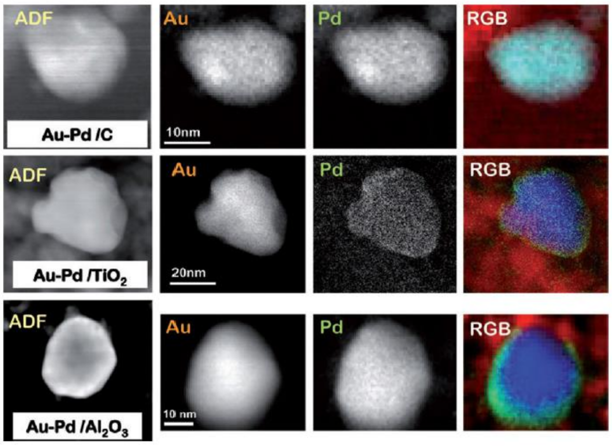


Figure 1.14 Montage of HAADF image: Au, Pd and RGB reconstructed overlay map (Au blue, Pd green) for calcined catalysts on three different supports.

Previous work carried out by Ishihara *et al.* [191] suggested the activity of the catalyst was dependent on the support used. As apparent from figure 1.12 there are three possible pathways for loss of yield and selectivity of H_2O_2. The hydrogenation and decomposition reactions are known to be the most common competing reactions. In order to investigate and further understand these competing reactions a range of bare supports and supported monometallic catalysts were analysed.[206] In comparison to the bare supports, higher rates of decomposition and hydrogenation were observed with the Pd supported catalyst. These results coincide with the early studies[104, 109-110, 133-136,136] which concluded that Pd catalysed synthesis of H_2O_2 is challenging and can only be effective in the presence of halide and acid promoters which control the competing reactions.

When Au-supported catalysts were analysed, certain catalysts showed decreased rates of hydrogenation and decomposition in comparison to the bare supports, thus suggesting that the active sites for the direct synthesis of H_2O_2 and the competing reactions may differ. These findings also suggested that gold nanoparticles may play an important role in blocking the sites for the competing decomposition and hydrogenation reactions. These suggestions were confirmed by Ishihara *et al.*[207] who carried out DFT studies to investigate the direct synthesis of H_2O_2. It was reported that the formation of the undesired water via the dissociation reaction took place on the Pd (111) surface. The role of the gold nanoparticles was to block the dissociation sites and increase the selectivity of H_2O_2.

Ntainjua *et al.*[205] showed the rates of AuPd carbon supported catalysts were almost a factor of two higher than the corresponding TiO_2-supported catalysts and almost an order of magnitude greater than the Al_2O_3-supported catalysts. These results demonstrated that the nature of the support plays a key role in the direct synthesis of H_2O_2. Further investigation showed the role of the support in particular the acidity and isoelectric point had an effect on H_2O_2 yields, selectivities and stabilisation of H_2O_2.[205] A wide range of supports such as SiO_2, TiO_2, Al_2O_3, Fe_2O_3 and carbon were analysed. More acidic supports, with low isoelectric points (e.g. carbon and silica) were reported to be better than the less acidic supports which have higher isoelectric points (e.g. Al_2O_3 and MgO). The basic supports catalysed undesirable reactions (decomposition and hydrogenation) which reduced the rate of H_2O_2.

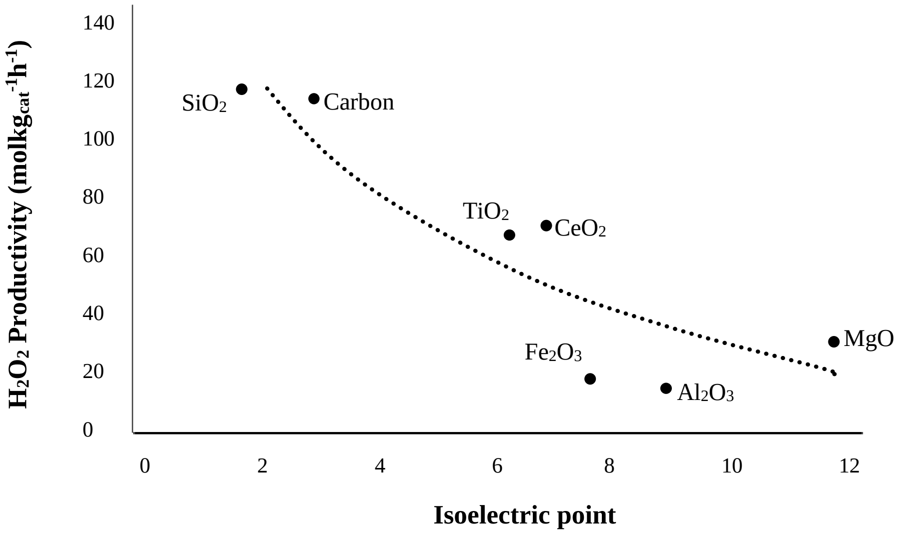


Figure 1.13 H_2O_2 productivity over Au-Pd catalysts as a function of the isoelectric point.[205]

Each support has a different surface charge under reaction conditions which is controlled by the isoelectric point. The approximate isoelectric points for the common Pd supports were reported by Toebes *et al.*[209] and are listed below:

SiO_2 (1.0-2.0) < MnO_2 (3.9-4.5) <SnO_2 (5.5) < TiO_2 (6.0) < ZrO_2 (6.7) < CeO_2 (6.8) <

a, y-Al_2O_3 (7.0-9.0) < ZnO (8.7-9.7) < MgO (12.1-12.7)

The isoelectric point for raw carbon black was reported to be 6.7 however this value can be substantially modified from 1.3-3.0 to 7.5-8.8 via acid or base treatment respectively. [210]

Acid pre-treatment of the support has been reported to have significant effect on the productivity of H_2O_2 for AuPd catalysts. Edwards and co-workers[204] showed that acid pre-treatment of an activated carbon support prior to Au and Pd impregnation resulted in a catalyst with exceptionally high H_2 selectivities (> 95 %). The AuPd alloy catalyst did not hydrogenate or decompose H_2O_2 in the presence of high H_2O_2 concentrations and 30 bar 5% H_2/CO_2. The activity of this material was attributed to increase in number of smaller (2-6 nm) Pd rich nanoparticles which presumably decorated and inhibited the decomposition reaction. The group expanded on their initial studies on this material and demonstrated that the oxidation state of the Pd in the AuPd alloys plays an important role in the overall activity of this catalyst.[211] The calcination temperature affects both the hydrogenation activity and reusability of the catalyst. Detailed characterisation using XPS and aberration-corrected scanning transmission electron microscopy showed that the greater activity is associated with a higher surface concentration of Pd in the acid pretreated catalysts which is primarily present as $Pd^{2+.}$ Calcination of the catalysts at 400 °C is required to achieve re-usable and stable catalysts, and this is associated with the morphology and dispersion of the metal nanoparticles. The calcination stage of the catalyst preparation is vital to oxidise the surface Pd, as Edwards *et al.*[211] have reported Pd^0 is considered to catalyse H_2O_2 hydrogenation and decomposition pathway.

Furthermore the surface ratio of Pd^0/Pd^{2+} was found to be an essential factor in controlling the hydrogenation activity of H_2O_2 and a series of controlled reduction and re oxidations of a sample show how the Pd^0/Pd^{2+} surface ratio can influence the relative rates of H_2O_2 synthesis and hydrogenation. When the acid pre-treated catalyst was analysed almost all of the Pd was present in the 2+ state across all drying and calcination regimes. On the other hand the untreated AuPd catalyst showed an increase in metallic Pd under all drying and calcination regimes. The switching off in H_2O_2 hydrogenation is solely observed in the acid treated catalyst calcined at 400 ºC which suggests a stable, un-leachable form of Pd^{2+} is a crucial feature in highly selective AuPd catalysts.

The disadvantages of using acidic medium in the direct synthesis of H_2O_2 have been discussed previously (page 22). However recently studies have shown some of the drawbacks associated with the use of an aqueous acidic medium can be overcome. Lee and co-workers[212] recently reported the development of Pd core-SiO_2 shell structure; these materials would provide a means of preventing metal leaching when an acidic reaction medium is used. These new materials showed enhanced activities in comparison to analogous SiO_2 supported catalysts. The enhance activity of these materials was attributed to the increased dispersion of Pd within the SiO_2 shell as well as stabilisation of less highly coordinated Pd crystals in the SiO_2 shell.

Indeed the addition of acids to the direct synthesis of H_2O_2 can be very beneficial for stabilising H_2O_2 and increasing H_2O_2 selectivity and yields. Similar effects to this can be introduced to the reaction via other means such as the use of super acidic supports, e.g. heteropolyacids a brief comparison of AuPd catalysts supported on acidic supports is shown in table 1.4.

Table 1.4 A comparison of productivities for catalysts reported in literature.

Catalyst	**Temp (K)**	**Pressure (Bar)**	**Solvent**	**Reaction Time (h)**	**Productivity ($mol_{H2O2}kg_{cat}^{-1}$ h^{-1})**
2.5% Au/2.5% Pd/C (2% HNO_3) (0.01 g)	275	40	H_2O + MeOH	0.5	160
1% Pd/0.19% Au/Al-SBA15 (0.15 g)	283	17.5	MeOH	0.25	90
$Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$ (1 g)	301	10	MeOH + H_3PO_4 + NaBr	6	5.9
$Cs_{2.5}H_{0.2}PW_{12}O_{40}$/Pd/MCF (1 g)	301	10	MeOH + H_3PO_4 + NaBr	6	6.8
0.9% Pd/N-CNT (0.03 g)	298	10	MeOH + H_3SO_4	1.5	12.8
1.5% Pd/SiO_2 (0.0135 g)	293	1.0	MeOH + H_3SO4	5	11.4
2.5%Au/2.5% Pd/TiO_2 (2% HNO_3) (0.01 g)	275	40	H_2O + MeOH	0.5	110
2.5%Au/2.5%Pd/SiO_2 (2% HNO_3) (0.01 g)	275	40	H_2O + MeOH	0.5	83
2.5% Au/2.5% Pd/C (0.01 g)	275	40	H_2O + MeOH	0.5	110
2.5% Au/2.5% Pd/TiO_2 (0.01 g)	275	40	H_2O + MeOH	0.5	64

Mixed metal oxide for example SiO_2-Al_2O_3 and SiO_2-ZrO_2 have a higher surface area and larger surface acidity in comparison to pure metal oxides. Park *et al.*[213] studied TiO_2-ZrO_2 as a support for the direct synthesis of H_2O_2 and concluded the role of the support acidity was key in producing effective catalysts for the direct synthesis of H_2O_2. A range of catalysts were prepared with varying ZrO_2 content and the catalyst that exhibited the greatest surface area and total surface acidity had the highest yield of H_2O_2.

Gemo *et al.*[214] investigated doped mesoporous SBA 15 catalysts and showed higher productivity and selectivity were achieved when Al was incorporated into SBA 15 framework. The enhanced performance observed was attributed to the increased number of Bronsted acid sites in the support framework. Patents have been published which show that use of acidic supports such as Niobium oxide[215] and Zirconium oxide[216] provide improved selectivity and activity for the direct synthesis of H_2O_2.

Furthermore Park and co-workers[217] investigated Pd catalysts supported on HZSM-5 with a variation of Si/Al ratio. They evaluated these catalysts for the direct synthesis of H_2O_2 and reported the yield of H_2O_2 increased with increasing Bronsted:Lewis ratio. Park, Sun and coworkers[218-220] prepared Pd containing insoluble HPA catalysts by an ion exchange method using various alkaline metal ions (K^+, Rb^+, Cs^+) Sun *et al.*[218] demonstrated that a Keggin-type herteropolyacid, tungstophosphoric acid, can be utilised as a support for Pd (after precipitation with $Cs^{+)}$. The Pd supported herteropolyacid catalysts showed greater selectivity towards H_2O_2 in comparison to the more conventional Pd catalysts supported on TiO_2, SiO_2, ZrO_2, XC72, graphite and HZSM-5. Park and co-workers [219-220] investigated Pd only exchanged heteropolyacids using varying contents of alkaline metal ions (Rb, Cs, K). They showed greater rates of conversion and H_2O_2 yields were obtained with the Cs incorporated catalyst to those catalysts that incorporated Rb and K.

Following on from these studies Ntainjua *et al.*[221] investigated and evaluated Au-Pd exchange and supported Cs containing heteropolyacid catalysts for the direct synthesis of H_2O_2. When compared to the most active catalyst (2.5% Au-2.5% Pd/Acid washed Carbon) both the AuPd exchanged and Cs containing HPA catalysts were more active at economically favourable ambient reaction conditions.

Abate and co-workers[222] have shown that supported Pd on N-doped nanocarbon can improve specific activity of Pd particles due to increased dispersion and stabilisation of Pd particles. It was also postulated that the introduction of nitrogen functional groups resulted in an increase in support acidity and as a result led to stabilisation of H_2O_2.

The catalyst preparation technique has a huge effect on the synthesis rate, morphology, particle size and composition. As discussed previously Hutchings and co-workers have extensively studied the direct synthesis of H_2O_2 using AuPd catalyst prepared by impregnation. Although the catalysts prepared by the impregnation method produce highly selective catalysts and display appreciable activity the nanoparticles are present as large particle size distribution. However it is logical that only a small proportion of the nanostructures that are present are active for catalysis. Hutchings and co workers[223] hypothesised the small nanoparticles could well be the active species for the direct synthesis of H_2O_2. They therefore decided to tailor make these structures via a method known as sol immobilisation which was previously shown to produce highly active Au supported nanoparticles for the oxidation of alcohols.[224]

The sol immobilisation method involves the dissolution of $HAuCl_4$ and $PdCl_2$ in a dilute solution of polyvinyl alcohol (PVA). The role of the PVA is to coat the nanoparticles in order to resist them from sintering during subsequent synthesis steps. A reducing agent is then added to forms a sol of homogeneous AuPd nanoparticles which can then be readily supported onto the supports.[225-226] This method can be tailored to produce Au core or Pd core structures by initially forming either the Au or Pd nanoparticles first then using these as a template to second metal.

Analysis of the sol immobilised materials show that this method produces particles with a narrow particle size distribution as typically the particle size was in the range of 3 nm. However, in the sol immobilisation catalyst, the small nanoparticles comprise mainly Au and the larger nanoparticles comprise mainly Pd; this is totally the opposite trend to that observed for the impregnation catalysts as discussed previously.
The activity of these sol immobilised catalysts were observed to be 10 times more active than the catalysts prepared by impregnation. Although high synthesis activities were observed with these catalysts, the selectivities were extremely low as the rate of hydrogenation/decomposition is roughly three times higher than that of the synthesis reaction. These results suggest that the small nanoparticle structures facilitated by the sol immobilization technique are not highly selective species that are present in the materials prepared by impregnation that demonstrate much higher selectivities

The main problem with both sol immobilisation and impregnation catalysts is the variation in the composition of the nanoparticles as the particle size increases. In the impregnation technique method the small nanoparticles are comprised of Pd whereas the Au is mainly deposited as large nanoparticles. This suggest that these methods do not lead to effective dispersion of the Au metal. This is not observed for the sol immobilisation technique where the Au is more effectively and highly dispersed in comparison to the Pd.

In order to improve the dispersion of the Au in the catalysts prepared by impregnation very recently Sankar *et al.*[227] investigated an excess anion method in which additional halide was added to the impregnation solution. In this method aqueous HCl was used to dissolve the $HAuCl_4$ and $PdCl_2$. This solution was then used to impregnate the support (TiO_2) and then dried. In order to remove the halide from the material a reduction treatment with H_2 was conducted.

These new materials were almost four times more active than the impregnation and sol immobilisation catalysts and the catalyst was fully reusable. The high activity was attributed to the addition of excess halide which results in increased dispersion of the gold. In the absence of the excess halide (impregnation preparation) SEM detected over 95% of the Au as large micrometer sized particles.[230]When the excess halide is incorporated to the impregnation (modified impregnation technique) the larger particles are absent therefore the role of halide is to aid dispersion of gold in the impregnation method.

The modified impregnation materials were analysed using STEM-XEDS after the reduction step at 400 ºC in 5% H_2/Ar and it was found that the materials show 5-10 nm particles which have a distinct Au rich core and Pd rich shell morphology. Furthermore unlike the catalysts prepared by impregnation (where the Pd rich clusters and atomically dispersed species are remained on the TiO_2) all the clusters and atomically dispersed species were efficiently submersed into the larger random alloy particles. There was a distinct difference in the particle size distribution between the 1% AuPd/TiO_2 reduced catalyst prepared by impregnation and modified impregnation. The former had a particle size distribution with mean values of 4.7 whereas the latter had a mean value of 2.9 nm. The reduction step in the modified impregnation method therefore allows the preparation of random alloys supported on TiO_2 with the absence of very small nanostructures.

1.7 Summary, Aims and objectives

As discussed in the literature review since its discovery in 1818, a great deal of research has been carried out on the manufacture of H_2O_2. Many advances have been made towards a feasible process for the direct synthesis of H_2O_2 however, the problem of low selectivities because of subsequent hydrogenation and decomposition reactions remain a major obstacle. This suggests there is room for an improved technology for the direct synthesis which will limit the subsequent reactions and increase the overall yield and selectivity of H_2O_2. Research into new approaches for the direct synthesis of H_2O_2 and investigating optimum reaction conditions in different reactor configurations may provide further developments that could help the commercialisation of the process.

By far the most common method for testing catalysts for the direct synthesis of H_2O_2 is a batch autoclave system in which the catalyst is in close contact with the H_2O_2 produced for an extended period of time. An important reaction parameter to consider when dealing with a process which has subsequent and competing reactions is the time the reaction product is in contact with the catalyst. By carefully tuning the time that the reactants are in contact with the catalyst it is possible to control and suppress the subsequent decomposition and hydrogenation reactions. One method to achieve this in a batch autoclave system is by using a biphasic solvent system which consists of a hydrophobic solvent (which contains the catalyst and produces H_2O_2) and a hydrophilic aqueous solvent (which extracts H_2O_2 *in situ*). Examples in the patent literature report the use of a biphasic solvent system to produce H_2O_2 however low concentrations of H_2O_2 are produced.

Furthermore it has been shown that by using a fixed bed reactor it is possible to control the residence time over the catalyst. Examples in the patent literature report the direct combination of H_2 and O_2 in the gas phase at elevated pressures and temperature, however, these studies include the presence of acid and halides in the gas phase as stabilisers. There are numerous potential advantages for the synthesis of H_2O_2 in the gas phase over the current approaches using combined liquid and gas phase reactants. A convenient gas phase process allows small-scale applications, and this permits simpler process design if the H_2O_2 is used in a subsequent oxidation reaction. In contrast the liquid phase suffers from the disadvantage of low concentrations of O_2 and H_2 which limits the rate of reaction; in addition there is the potential for leaching of catalyst components. Moreover, using a gas phase reaction permits more facile fundamental research.

The main aim of this research is to produce H_2O_2 directly from H_2 and O_2 by heterogeneous catalysis. This research has been conducted in collaboration with Solvay® who have specified the parameters required ($[H_2O_2]$ = 3-8 wt. %, H_2 selectivity > 90 %), for the direct synthesis of H_2O_2 to be industrially viable. This thesis will focus on minimising the contact time between the catalyst and H_2O_2 formed via studying two different reactor systems. The objectives to reach this aim are as follows:

1. Development of a biphasic solvent system, in order to investigate its potential for the direct synthesis of H_2O_2 and produce high H_2O_2 concentrations via studying the effect of reaction parameters (solvent composition, temperature, reaction time, catalyst mass, pressure and reagent ratio).

2. Design and development of a lab scale continuous gas flow reactor to prove the feasibility of producing H_2O_2 in the gas phase directly from H_2 and O_2 at atmospheric pressure.

This thesis will focus on setting up and understanding the maximum potential of these two different system using heterogeneous catalysts that have been previously employed for the direct synthesis of H_2O_2. As discussed in the literature review the addition of Au to Pd can enhance H_2O_2 synthesis rates by suppressing the subsequent hydrogenation and decomposition reactions. A range of Au-Pd supported catalyst will be prepared and evaluated for the direct synthesis of H_2O_2 in the absence of acid and halide promoters. These AuPd supported catalysts have previously been employed for the direct synthesis of H_2O_2 and have also been fully characterised. The characteristics of these AuPd supported catalysts have been discussed in Chapter 1 and will also be will be discussed throughout this thesis in relation to their H_2O_2 synthesis, hydrogenation and decomposition activity.

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Experimental

2

2.1 Introduction

A range of bimetallic AuPd supported catalysts were prepared, characterised and evaluated for the direct synthesis of hydrogen peroxide. In this chapter, catalyst precursors, preparation techniques, evaluation set up and characterisation techniques are discussed.

2.2 Materials

2.2.1 Catalyst precursors (supplied by Johnson Matthey)

Palladium Chloride, $PdCl_2$ (99.99% trace metals basis), Hydrogen Tetrachloroauric acid, $HAuCl_4.3H_2O$ (Au assay: 41.21%).

2.2.2 Reagents

Methanol (HPLC, Aldrich), Water (HPLC Chromasolve, Aldrich), Decan-1-ol (Aldrich), Stabilised 50 wt. % H_2O_2 in water (Aldrich). Diisobutyl Carbinol (Solvay), Sextate (Solvay), Solvesso (Solvay).

2.2.3 Support materials

TiO_2 (Degussa P-25), Carbon (Darco G-60), Carbon (CABOT Vulcan XC-72), Carbon (Norit), Nuclear grade Carbon (BNFL), SiO_2 (Johnson Matthey), CeO_2 (Aldrich), ZrO_2 (Aldrich), BN (Aldrich), $CsNO_3$ (Aldrich) $H_3PW_{12}O_{40}$ (Aldrich).

2.2.4 Gases

All gases were obtained from BOC Gases. Purity of gases listed below as: 25 % O_2/CO_2 (99.99 %), 5 % H_2/CO_2 (99.99 %), 2 % H_2/Air (99.99 %), Industrial Grade Air (99.99 %), 25 % O_2/N_2 (99.99 %), 5 % H_2/N_2 (99.99 %)

2.3 Catalyst Preparation

2.3.1 Preparation of AuPd supported catalysts by wet impregnation

AuPd bimetallic catalysts were prepared *via* wet impregnation of various supports (see section 2.2.3). The standard preparation of 2.5 wt. % Au-2.5 wt.% Pd supported catalyst is described as follows (all quantities stated are per 1 g of finished catalyst). $PdCl_2$ (0.0417 g) was added to $HAuCl_4.3H_2O$ (2.040 ml, 12.25 g Au in 1000 ml). The solution was stirred and heated (80 °C) until the $PdCl_2$ dissolved completely to form a homogeneous solution. The appropriate support (0.95 g) was added to the solution and stirred until a paste was formed. The resultant material was dried in an oven (110 ˚C, 16 h) before being calcined in static air (400 °C, 3h, 20 ºC min^{-1}).

2.3.2 Preparation of AuPd supported catalysts by sol immobilisation

AuPd colloidal materials were prepared via sol impregnation. The standard preparation of 0.5 wt. % Au-0.5 wt. %Pd nanoparticles supported on carbon is described as follows. A colloid was formed by adding polyvinyl alcohol (1 wt. %) to an aqueous solution (400 ml) of $PdCl_2$ (0.5 ml of 10mg/mL solution) and $HAuCl_4$ (0.408 mL of 12.25 mg/mL solution). The metals were then reduced using $NaBH_4$ (2.539 mL of 0.1M aqueous solution). The solution was left to equilibrate (30 minutes) before adding the carbon support (0.99 g) and acidifying to pH 1 using sulfuric acid (0.1 M). After stirring (1 h), the solution was filtered and the catalyst was washed thoroughly with distilled water (neutral mother liquors). The resultant material was dried in an oven (110 °C, 16 h).

2.4 Support preparation

2.4.1 Preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

$CsNO_3$ (0.152 g) and $H_3PW_{12}O_{40}$ (0.897 g) were dissolved separately in deionised water while heating (80 ºC) and stirring (5 minutes). The $CsNO_3$ was added dropwise to an aqueous solution of $H_3PW_{12}O_{40}$ the solution was continuously stirred while heating (80 ºC) to obtain a paste. The resulting material was dried (110 ºC, 16 h) and calcined (300 ºC, 2 h) before being used for the catalyst preparation.

2.4.2 Preparation of acid washed carbon

AuPd supported catalysts were prepared using wet impregnation, where the support was pre-treated with acid prior to impregnation of the metals onto the support. During the acid pre-treatment step the support (5 g) was suspended in aqueous nitric acid (150 ml, 2 wt. %) for 3 hours whilst stirring at ambient temperature. Following this the support was filtered, thoroughly washed (until the washings were neutral) and dried before being used for the catalyst preparation.

2.5 Catalyst evaluation

2.5.1 Catalyst evaluation in a batch system

Catalyst testing was performed using a Parr Instruments stainless steel autoclave (figure 2.1) which had a nominal volume of 100 ml and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0-2000 rpm) and provision for measurement of temperature and pressure. The temperature of the reaction was maintained with a cooling jacket. Pre-mixed gas cylinders were connected to the autoclaves.

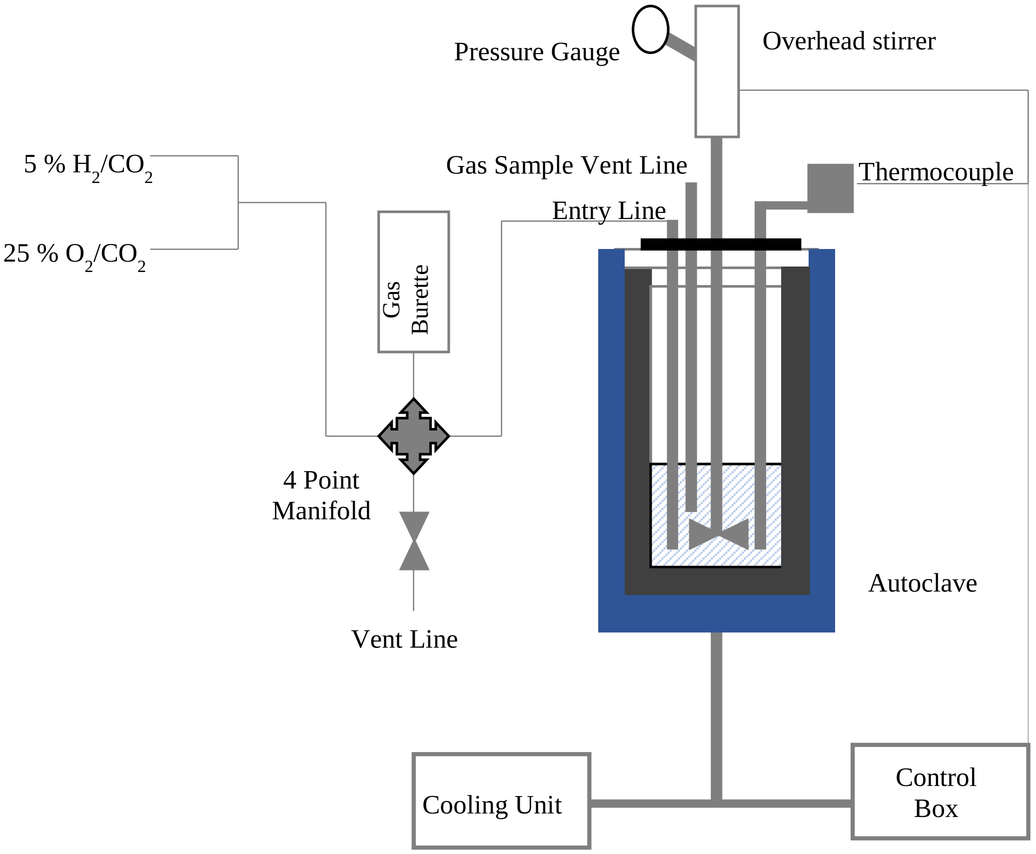

Figure 2.1 Schematic of the batch autoclave system.

In the next section the standard reaction conditions are described. However as described later in the thesis these conditions were varied to investigate the effect of reaction parameters on H_2O_2 concentrations.

2.5.1 Standard direct H_2O_2 synthesis conditions for organic solvents in a batch system

In Chapter 3 the direct synthesis of H_2O_2 was studied using high chain alcohols and hydrophobic solvents. The reaction conditions are stated below. All reactions for decan-1-ol were run at 25 °C or 10°C to prevent the reaction medium from freezing.

To test the direct synthesis of H_2O_2, the autoclave was charged with catalyst (0.01 g) and solvent (0.33 g H_2O and 8.17 g organic solvent). The charged autoclave was purged three times with 5 % H_2/CO_2 (100 psi) and then filled with 5% H_2/CO_2 (420 psi) and 25% O_2/CO_2 (160 psi) to give a hydrogen oxygen ratio 1:2 and a total working pressure of 580 psi. The reaction mixture was allowed to cool to the desired temperature (10 and 25 ^{o}C) after which stirring commenced (1200 rpm) and experiments were carried out for 30 minutes. H_2O_2 yield was determined by titrating aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ (1.18×10^{-2} mol L^{-1}). The $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2Fe(SO_4)_2.6H_2O$ using ferroin as an indicator.

In chapter 3 the amount of hydrogen peroxide produced was primarily discussed in terms of the concentration (wt. % H_2O_2) required to reach the industrial target (3-8 wt. % H_2O_2). The H_2O_2 concentration in chapter 3 was expressed as wt. % using equation 2.1 and the value obtained represents a theoretical H_2O_2 concentration in water assuming no water or H_2O_2 is soluble in the organic solvent.

$$H_2O_2\ (\text{wt. \%}) = \frac{\text{g } H_2O_2 \text{ produced } (H_2O + \text{organic solvent})}{\text{g } H_2O_2} \times 100 \qquad \text{Equation 2.1}$$

To compare the performance of the catalysts over the reaction time the average rate of H_2O_2 production was calculated and normalised to catalyst mass to give a productivity value which is presented as $mol_{H2O2}kg_{cat}^{-1}h^{-1}$. The number of moles of H_2O_2 produced and rates ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$) were determined for each reaction using the following calculations:

$$\text{Volume Ce(SO}_4)_2 \text{ to titrate whole reaction solution} = \frac{\text{Titre x Solvent mass}}{\text{Sample mass}}$$

$$\text{Moles Ce(SO}_4)_2 = \frac{\text{Vol. Ce(SO}_4)_2 \text{ to titrate reaction solution x [Ce(SO}_4)_2]}{1000}$$

$$\text{Moles } H_2O_2 = \frac{\text{Moles Ce(SO}_4)_2}{2}$$

$$\text{Productivity} = \frac{\text{Moles } H_2O_2}{\text{Catalyst mass (kg) x Reaction Time (h)}}$$

$$\text{Wt. \% } H_2O_2 = \frac{\text{Moles } H_2O_2 \text{ x Mr } H_2O_2}{\text{Solvent mass}} \text{ x 100}$$

2.5.2 Standard H_2O_2 hydrogenation and decomposition conditions

To test the H_2O_2 hydrogenation the autoclave was charged with the catalyst (0.01 g) and an organic solvent-water solution containing 4 wt.% H_2O_2 (0.33 g 4 wt. % H_2O_2, 8.17 organic solvent). The charged autoclave was then purged three times with 5 % H_2/CO_2 (100 psi) and then filled with 5 % H_2/CO_2 (420 psi). The temperature was allowed to cool to 25 °C or 10 ^oC followed by stirring (1200 rpm) of the reaction mixture for 30 minutes. The amount of hydrogenated H_2O_2 was determined before and after by titrating aliquots with acidified Ce $(SO_4)_2$ (1.18 x 10^{-2} mol L^{-1}). $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2Fe(SO_4)_26H_2O$ using ferroin as indicator.

The hydrogenation reaction described measures the catalysts activity towards H_2O_2 hydrogenation and decomposition. In order to evaluate the catalysts activity towards H_2O_2 decomposition only, 5 % H_2/CO_2 is omitted and 25 % O_2/CO_2 is utilised.

For the hydrogenation experiments the results were expressed in terms of both % of H_2O_2 destroyed over 30 minutes and rate of H_2O_2 hydrogenated ($molkg_{cat}^{-1}h^{-1}$).

Since the addition of acids have shown to suppress the hydrogenation/decomposition activity of AuPd supported catalysts[1-2] experiments were conducted where the water content was replaced with aqueous solutions of various acids.

2.5.3 Determination of H_2O_2 concentration in a biphasic solvent system

For most experiments in chapter 3 the organic solvent was either saturated with water or had very small amounts of water present in the organic solvent–water mixture. The separation of water from the organic solvent was therefore very complicated and time consuming. Hence in all the experiments in chapter 3 the overall concentration of H_2O_2 was determined by titration of the whole emulsion (organic solvent-water) with acidified $Ce(SO_4)_2$ solution (1.18×10^{-2} mol L^{-1}), using ferroin as indicator.

In order to evaluate the error when using this method compared to separating the individual phases and titrating the water phase, experiments were run with increasing masses of decan-1-ol and water. After each experiment the H_2O_2 concentration was determined via i) a direct titration of the whole emulsion and using equation .2.1 and ii) a titration of the separated water phase, the results are given in figure 2.2.

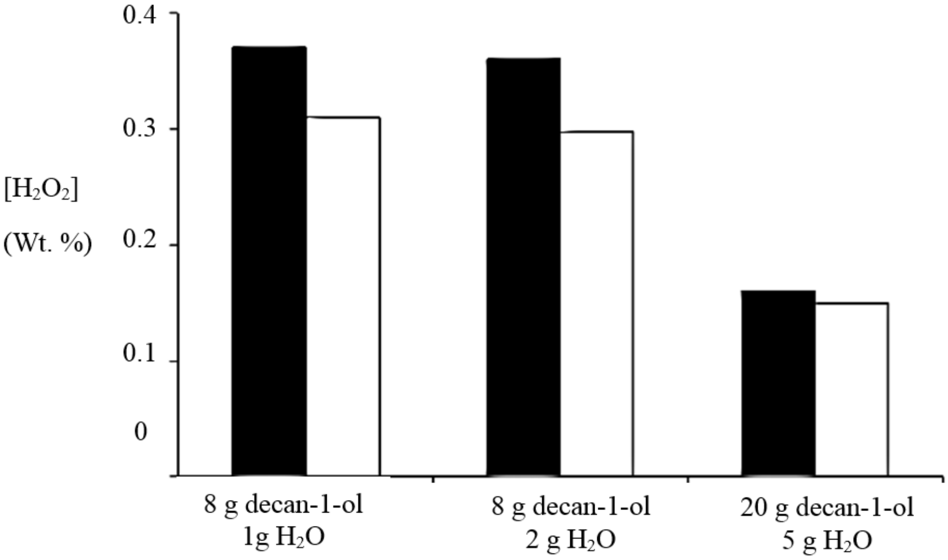

Figure 2.2 Evaluation of the error of H_2O_2 determination: ■ H_2O_2 concentration calculated from titration of whole emulsion. ☐ H_2O_2 concentration determined from water phase separation

Reaction conditions AuPd/C (10 mg), 5% H_2/CO_2 (420 psi), 25 % O_2/CO_2 (160 psi), X g solvent, 1200 rpm, 25 °C, 30 minutes.

The results show when less water was added to the experiments (8g decan-1-ol, 1 g H_2O and 8 g decan-1-ol, 2 g H_2O) the error is ~20% between the H_2O_2 calculated from the whole emulsion and the H_2O_2 determined from water phase after separation. When a larger amount of water was added (20 g decan-1-ol, 5 g H_2O) the error is ~ 6%. This error may be due to inefficient separation of the 2 phases when less water is added to the decanol-water system.

Indeed a more accurate method of determining the H_2O_2 concentration would be by determining the content of H_2O_2 present in the water phase only. As more water is added to the system (20 g decan-1-ol, 5 g H_2O) the error in discrepancy decreases, however the amount of H_2O_2 obtained becomes less concentrated. Since the separation of water from the organic solvent proved to be very complicated and time consuming the H_2O_2 concentration in chapter 3 was determined by titrating the whole emulsion and using equation 2.1.

2. 5.4 Reliability of results

In order to determine accurate and reliable results the activity of the catalysts were verified by performing a minimum of two repeat experiments. Furthermore the autoclave was cleaned frequently with hot water and aqua *regia* in order to prevent contamination as well as confirm the absence of any possible background activity. Blank tests were performed regularly, in the absence of a catalyst and at the standard operating conditions: a productivity of 0 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$was achieved at all times.

2.6 Characterisation techniques

2.6.1 UV-Visible Spectroscopy (UV-Vis)

2.6.1.1 Background

Spectroscopy is a fundamental technique that allows quantifying the amount of radiation absorbed, emitted or scattered by a sample. Many types of radiations can be used to study different properties of a materials. In this particular case ultraviolet (200-400 nm) and visible light (400-750 nm) radiation was used. A spectrometer is an instrument that detects the characteristics of light scattered, emitted or absorbed by atoms or molecules. Figure 2.2 shows the schematic of a UV-visible spectrometer. Two different lamps are used to generate both the ultraviolet and the visible radiation. The beam is directed to a monochromator that selects one single wavelength. In the sample compartment choppers allow the beam (P_0) to pass through the sample and reference cell Absorption takes place and the beam of radiation leaving the sample is defined as P. The detector is synchronized with the reference and sample cell so that the relative absorption can be determined. There are two different methods of describing the amount of radiation absorbed by a sample:[3-4]

Transmittance (T) is defined as the fraction of initial radiation that crosses through the sample

$$T = \frac{P}{P_0}$$ Equation 2.2

Where P is the irradiance, energy per second per unit of light beam.

Absorbance (A), is defined as the logarithm (base 10) of the reciprocal of the transmittance

$$A = -\log T = \log \frac{P_0}{P}$$ Equation 2.3

Absorbance and transmittance are two different ways of describing the amount of radiation absorbed by a sample, however the former is most used because it is directly proportional to the concentration, c, of the light absorbing species present in the sample as stated by the Beer-Lambert Law (equation 2.4)

$$A = \varepsilon bc$$ Equation 2.4

Where c is the concentration of the sample, b is the path length and ε is the molar absorptivity (also known as the extinction coefficient) a constant for a particular compound at a chosen wavelength.

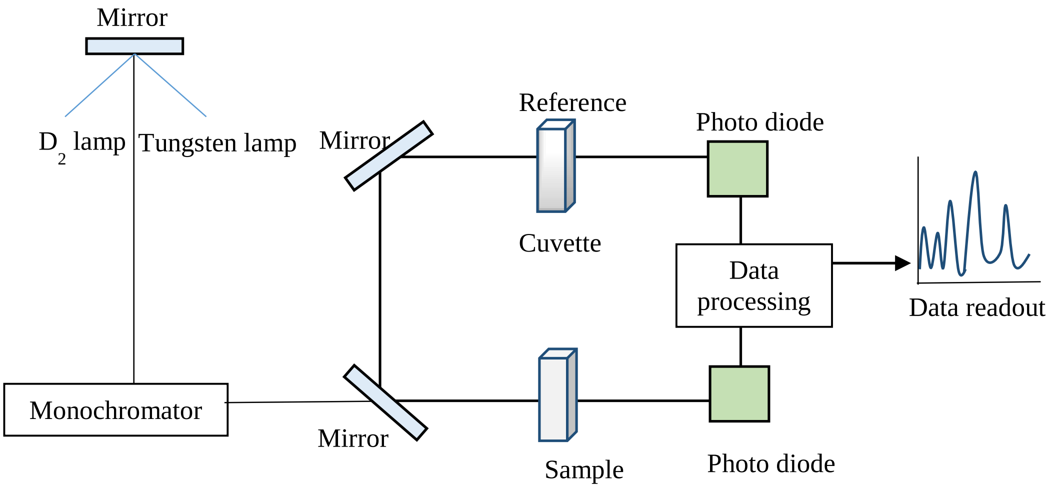

Figure 2.2 Schematic of UV-Visible spectrometer

2.6.1.2 Experimental

2.6.1.2.1 Determination of hydrogen peroxide using UV-vis

The sample solution was diluted in a volumetric flask (100 ml) using water and 50 ml of Ti^{4+} solution (The titanium solution (1g/l in sulphuric acid) was prepared by dissolving 7.39 g of potassium titanium oxyoxalate ($C_4K_2O_9Ti.2H_2O$) in 1 litre of sulphuric acid 2N. A few drops of diluted H_2O_2 (1g/L) were added in order to prevent the reduction of Ti^{4+} to Ti^{3+}).[5] Analysis was carried out using a JASCO UV/VIS/NIR V-570 spectrophotometer. The absorbance was measured at a wavelength of 410 nm against a reagent blank and compared with a calibration curve.

2.6.2 Temporal Analysis of Products

2.6.2.1 Background

Temporal Analysis of Products (TAP) is an experimental technique that allows the study of interactions between gases and solid materials such as heterogeneous catalysts. The technique is based on short pulse-response experiments at low background pressure (10^{-6}-10^{2} Pa), which are used to probe different steps on the surface of the catalytic material. These include diffusion, adsorption, surface reactions, and desorption. The TAP system consists of a heated microreactor situated on a high vacuum source containing a quadrapole mass spectrometer (QMS). A fast-acting "pulse valve" is situated on top of the reactor which enables small pulses of a test gas to enter the evacuated microreactor. While the injected gas molecules cross the microreactor, they encounter the catalyst on which they may undergo chemical transformations. Unconverted and newly formed gas molecules eventually reach the reactor's outlet and escape into an adjacent vacuum chamber, where they are detected with millisecond time resolution by the QMS. The exit flow rates of reactants, products and inert molecules recorded by the QMS can be used to quantify catalytic properties and deduce reaction mechanisms.

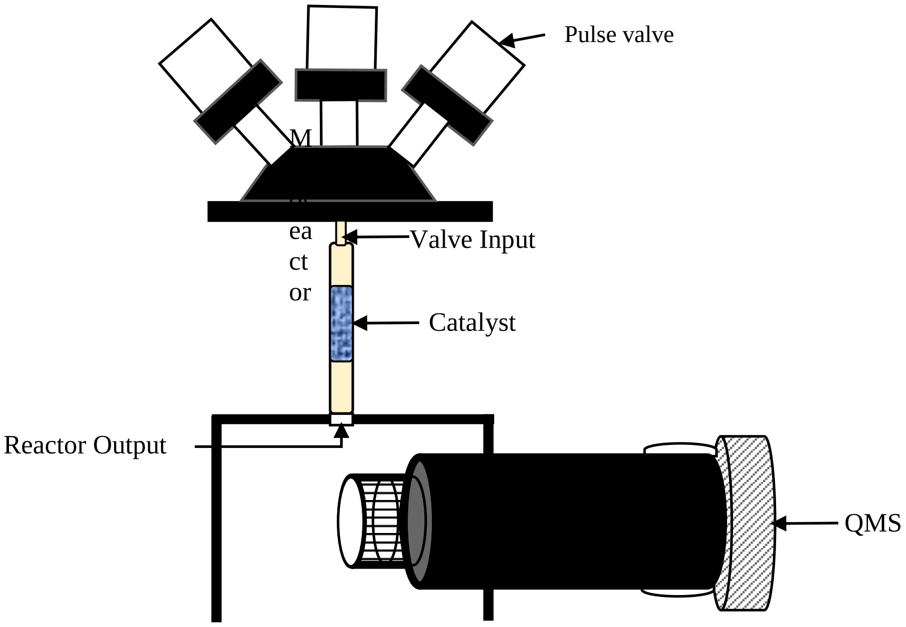

Figure 2.4 Schematic of TAP

2.6.2.2 Experimental

The TAP experiments were performed using a TAP-2 system.[6] A gas mixture containing 2% H_2 in air was pulsed over the catalyst from a reservoir at a pressure of 0.6 bar. The reactor was packed with 0.045 g of powdered catalyst held in place with SiC inert packing. The gas exiting the reactor bed was detected via quadrupole mass spectrometer. The response for mass 34 (H_2O_2) and mass 2 (H_2) was monitored over a time of 2 s for each pulse, giving a curve of intensity against time. The experiment was carried out at 60 °C with a train of 20 pulses averaged per experiment.

2.6.3 Karl Fischer Experiments

2.6.3.1 Background

The amount of water present in a chemical reaction can affect the reactivity and selectivity of a chemical reaction immensely and this is highlighted in detail in chapter 3. Karl Fischer titration is a classic titration method in analytical chemistry that uses coulometric or volumetric titration to determine trace amounts of water in a sample.

The general reactions behind Karl Fischer titration are shown in equations 2.5 and 2.6.[7]

$CH_3\,OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3$ Equation 2.5

$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4\,CH_3 + 2\ [RNH]I$ Equation 2.6

(RN = Base)

This reaction consumes water and iodine in a 1:1 ratio. In 1979 Scholz improved the Karl Fischer titration by replacing noxious pyridine with imidazole. This innovation resulted in foundation of HYDRANAL® - the world's leading pyridine-free reagents for Karl Fischer titration.

Karl Fischer volumetry is a convenient and easy method for determining the water content in samples. In this method an iodine-containing solution serves as titrating agent. The water content of the sample is calculated using titration volume of the titrating agent.

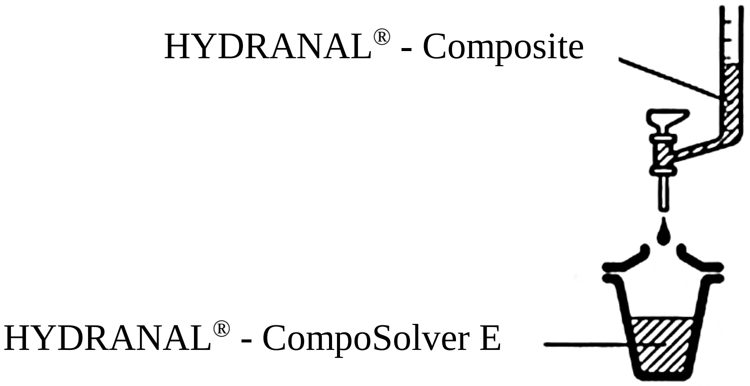

Figure 2.5 Volumetric one-component titration with HYDRANAL®-Composite.[7]

2.6.3.2 Experimental

In chapter 3 Karl Fischer titrations were conducted to determine the saturation point in a range of organic solvents. The volumetric Karl Fischer method was performed using a TitroLine KF where the titrating agent was accurately added through a piston burette. The standard procedure for each titration was as follows. The burette was filled with the titrating agent (Hydranal®-Composite 5). The working medium (Hydranal®-CompoSolver E) was added to the titration vessel, which was titrated to dryness with the titrating agent. The organic solvent sample was added (between 0.1 – 1 g depending on expected water concentration). The sample was titrated with the titrating agent to determine the water concentration.

2.8 References

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Organic solvents for the direct synthesis of H_2O_2

3

3.1 Introduction

H_2O_2 was first discovered by Thenard in 1818[1] and since then the reaction has been carried out in a wide range of reaction medium including water based solvents.[2-11] Indeed water is a desired solvent for any reaction due to its availability, non-toxicity, and it is low priced in comparison to other chemical solvents. Moreover using water as a solvent for the direct synthesis of H_2O_2 can be highly useful as aqueous H_2O_2 can be used directly for a number of growing applications; in particularly as a substitute for chlorine or chlorine containing oxides in the paper/pulp and bleaching industry.[12]

Although there are several advantages of using water as a solvent for the direct synthesis of H_2O_2 it is not the most ideal solvent for this reaction. This is because the reactant gases, H_2 and O_2, have a low solubility in water (1.62 mg/L and 40 mg/L respectively) which leads to low H_2O_2 synthesis rates. [5-6] To overcome the gas solubility limitations a great deal of research has been carried out on other solvents for the direct synthesis of H_2O_2 these include, supercritical CO_2,[13-18] fluorinated and halogenated solvents[19-21] as well as low chain alcohols.[2-4, 22-23]

The use of a biphasic solvent mixture containing water, fluorinated solvents [19-20] and halogenated hydrocarbon compounds [21] has been investigated by Moseley[19] and Kawakami *et al.* [21] whereby the volume ratio of the water to the organic solvent in the reaction medium ranges from 5:95-95:5. The process involves the production of H_2O_2 through catalytic reaction of H_2 and O_2 in the presence of platinum and palladium group metal catalyst. However when these systems are employed low concentrations of H_2O_2 (0.78 – 4.7 wt. %) are obtained.

Supercritical CO_2 is becoming a more desired commercial and industrial solvent due to its low toxicity and environmental impact. It can be particularly beneficial for the direct synthesis of H_2O_2 since both H_2 and O_2 are miscible with CO_2 above 31ºC.[25] Hence the gas-liquid-solid three phase reaction system is simplified to a fluid-solid two phase system, and this can dramatically reduce/eliminate mass transfer resistance. However Landon *et al.*[13-14] have shown that extremely poor yields of H_2O_2 are obtained when supercritical CO_2 is used as the reaction medium. The cause of this was found to be the rapid decomposition of H_2O_2 above 31 ºC.

3.2 Alcohols for the direct synthesis of H_2O_2

It has been reported that the rate of H_2O_2 production in low chain alcohols is much higher than that in aqueous media.[2-4, 7, 22-24]This is due to the higher solubility of the reactant gases in the alcohols than water. The solubility of H_2 in low chain alcohols has been reported to be 4-5 times higher than in water whereas that of O_2 may increase up to eightfold. [5] Although the solubility of H_2 and O_2 is high in low chain alcohols, these solvents are highly miscible with H_2O_2. This can be a major problem because the final H_2O_2-alcohol mixture will be in close contact with the reactant gases and catalyst; as a result this will lead to low synthesis rates because catalysts active for the direct synthesis of H_2O_2 are also active for its subsequent decomposition/hydrogenation reactions.

One method to overcome this problem is to use a biphasic solvent system which consists of a hydrophobic organic solvent and water. As depicted in figure 3.1, ideally the catalyst and gases will be held in the organic phase where H_2O_2 will be produced. As soon as the H_2O_2 is produced it will be extracted *in-situ* into the aqueous phase due to the higher solubility of H_2O_2 in water than the organic solvent. The use of a biphasic solvent system for producing H_2O_2 from its elements can be very beneficial, since the contact time between the catalyst and reactant gases with H_2O_2 will be minimal. This will diminish the contribution from the subsequent reactions resulting in higher concentrations of H_2O_2.

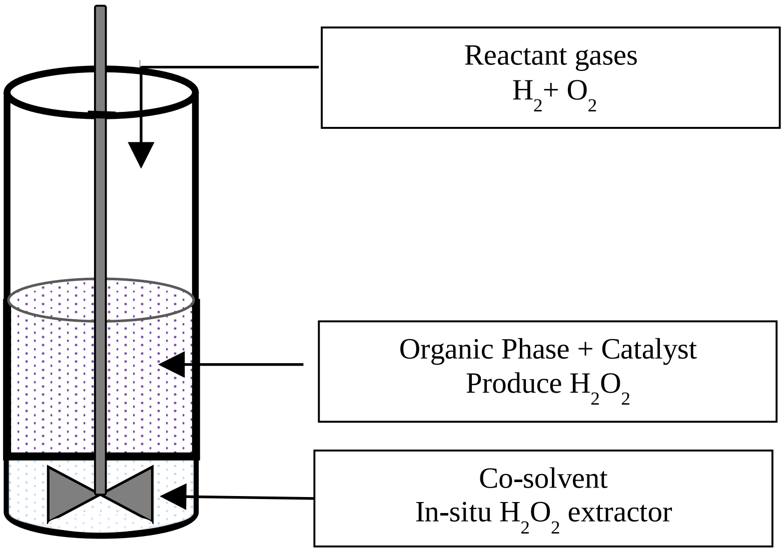

Figure 3.1 A schematic highlighting the key features of the biphasic solvent system

In this chapter the direct synthesis of H_2O_2 based on a biphasic water-alcohol solvent system has been investigated in detail. This work was conducted under the guidance of Solvay® with a goal of producing a H_2O_2 concentration of 3-8 wt. % which would be required for the direct synthesis of H_2O_2 to be industrially viable.

3.3 Choice of Solvents

For this study to be successful two different solvents are required; an organic solvent and an aqueous co-solvent. Water was selected as the co-solvent because it is readily available, has a low solubility of the reactant gases and H_2O_2 is readily soluble in water. Since H_2 and O_2 are more soluble in alcohols in comparison to water, initially only alcohols have been considered for the organic solvent. Primary alcohols have been successfully used as a reaction medium for the direct synthesis of H_2O_2[2-4, 7-8, 22-24] hence in order to narrow down the search for a suitable organic solvent initially only primary alcohols were used for this investigation. However, in future further investigation into the solvent will be required and preliminary studies were reported in section 3.12.

Au, Pd and Au-Pd catalysts supported on a range of metal supports have proved to be excellent catalysts for the direct synthesis of H_2O_2.[2-4, 15, 22, 27-33] When compared with monometallic Au supported or Pd supported catalysts, bimetallic Au-Pd supported catalysts show enhanced activity, with extremely high H_2 selectivity. The work of Edwards *et al.* showed that a 2.5 wt. % Au–2.5 wt. % Pd catalyst supported on carbon has high activity for the direct synthesis of H_2O_2.[22] This catalyst was therefore prepared by wet impregnation and the direct synthesis of H_2O_2 from H_2 and O_2 was studied in a high pressure stirred autoclave using this catalyst. Different alcohols were evaluated for H_2O_2 synthesis using reaction conditions stated in chapter 2.5.1 (580 psi total pressure, H_2:O_2 (0.525), 1200 rpm, 30 min, 25 ºC, solvent loading (8.5 g alcohol), catalyst loading (10 mg)). The results are shown in Figure 3.2.

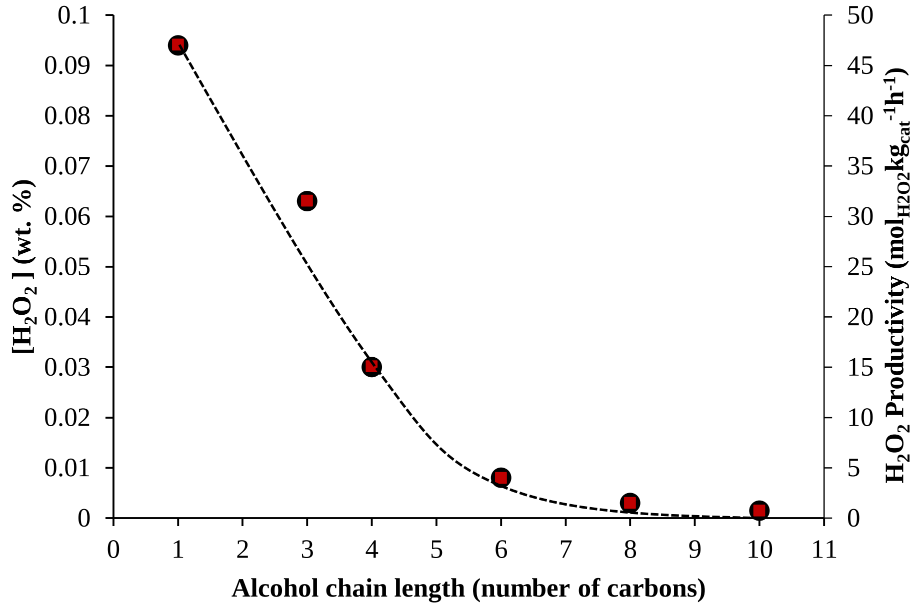

Figure 3.2 H₂O₂ concentration (●) and productivity (■) as a function of alcohol chain length.

Reaction conditions 2.5 wt. % Au-2.5 wt. %Pd/C (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 ºC, 30 min.

Figure 3.2 shows as the alcohol carbon chain length increases the productivity and concentration of H_2O_2 produced in the organic solvent decreases. The highest concentration of H_2O_2 was produced in methanol and lowest in decanol. Although the highest concentration of H_2O_2 was achieved with methanol whilst choosing the organic solvent for this new biphasic system 3 important points have to be considered:

1) The direct production of H_2O_2 must be possible in the presence of the organic solvent
2) The organic solvent must have a low water solubility in order to form a two phase system

3) And finally the solvent must be hydrophobic so the concentration of alcohol in the final H_2O-H_2O_2 solution is minimal to decrease industrial costs related to separation and purification.

In order to narrow the search down even further the water solubility of each alcohol was analysed using Karl Fischer apparatus and the results are given in Table 3.1. The water solubility of methanol, propan-1-ol and butan-1-ol was not determined as these alcohols are completely miscible with water.

Table 3.1 Solubility of water in high chain alcohols.

Solvent	**Water solubility (g H_2O dm^{-3})**
Methanol	n.d
Propan-1-ol	n.d
Butan-1-ol	n.d
Hexan-1-ol	77
Octan-1-ol	44
Decan-1-ol	39

As the carbon chain length of the primary alcohol increases from 6 to 10 carbon the water solubility also decreases, with decan-1-ol having the lowest saturation point. These results suggest it would be more favourable to employ a high chain alcohol such as decan-1-ol for the new biphasic system explained.

Francesconi *et al.*[34] and Wainright *et al.*[35] have shown that the H_2 solubility in C1-4 n-primary alcohols increases with increasing carbon chain length. Hence it is reasonable to expect that as the chain length increases the solubility of H_2 also increases and decan-1-ol will have higher H_2 solubility in comparison to methanol. However as apparent from figure 3.2 the productivity of H_2O_2 decreases with increasing chain length this may be attributed to the increased hydrophobic properties of the alcohol with increased chain length which results in increased mass transfer limitation.

The direct synthesis of H_2O_2 in the liquid phase occurs in a three phase system and thus the concentration of H_2O_2 is strongly dependant on the overall rate of mass transfer. As depicted in figure 3.3 there are three key stages which contribute to the process. Firstly the transfer of reactant gases from the gas phase into the liquid phase, secondly the transfer of gases from the liquid phase to the catalytic surface and finally the transfer of product from the catalytic surface into the liquid phase.

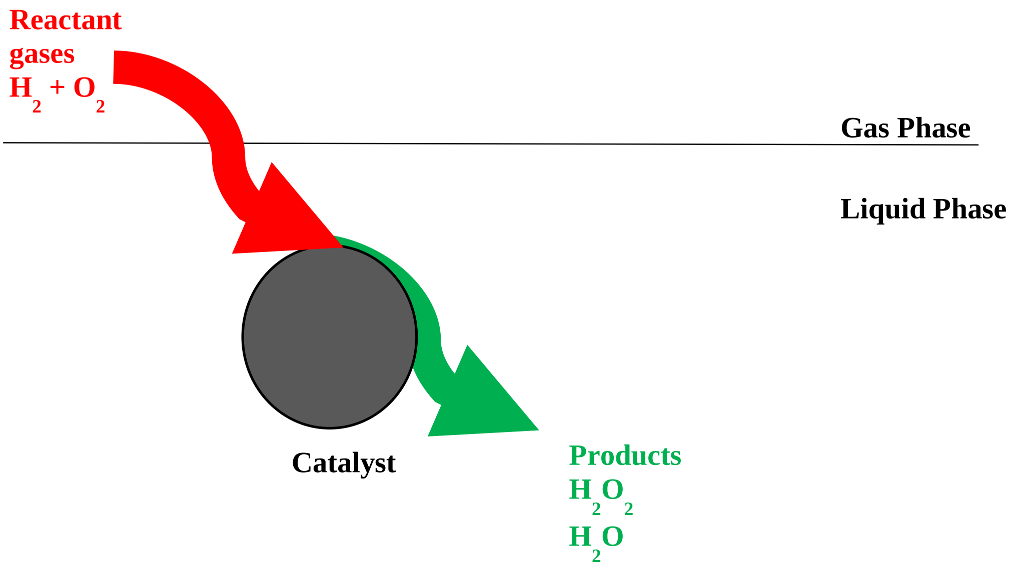

Figure 3.3 A schematic highlighting the pathway of reactants and products in the direct synthesis of H_2O_2.

Several factors can influence the overall rate of mass transfer as well as increase it, some of these include (i) using solvents which have higher gas solubility (ii) increasing the solubility of the reactant gases by increasing the pressure as well as the stirrer speed (iii) using solvents with lower viscosity and surface tension.

For this biphasic system to work at its best it is essential to employ an organic solvent which is hydrophobic and has low solubility in water. Therefore due to its low water solubility and high hydrophobic properties, decan-1-ol was selected as the organic solvent for this study.

3.4 Stability of decan-1-ol

In order to ascertain the stability of the decan-1-ol used in this investigation to the reaction conditions, the solvent was tested under the direct synthesis reaction conditions (580 psi total pressure, H_2/O_2 (0.525), 1200 rpm, 30 min, 25 °C, decan-1-ol (8.5 g)) with the catalyst (5%AuPd/Carbon, 10 mg) and in the absence of the catalyst. The working solution was filtered after the reaction and then analysed by ^{1}H NMR.

Spectra were recorded at room temperature on a Bruker DPX 500 MHZ ultra-shield NMR spectrometer (^{1}H 500.13 MHz) and compared to the reference spectra of decan-1-ol. No differences were observed indicating decan-1-ol is stable towards the reaction conditions employed.

3.5 Choice of a suitable support and catalyst

In order to select the ideal support for the catalyst to be used in this study, a series of supports were evaluated for H_2O_2 hydrogenation. In these experiments the reactor was charged with the support, decan-1-ol, 4 wt. % H_2O_2 solution and 5% H_2 /CO_2 (420 psi). The temperature was allowed to cool to 25 °C followed by stirring (1200 rpm) of the reaction mixture for 30 minutes. The results are shown in Table 3.2.

Table 3.2 H_2O_2 decomposed by hydrogenation in the new solvent system using a range of potential catalyst supports materials.

Entry	**Support**	**H_2O_2 Hydrogenated (%)**	**H_2O_2 hydrogenation rate ($molkg_{cat}^{-1}h^{-1}$)**
1	Carbon	13	10
2	Ceria	7	5
3	Magnesium Oxide	72	56
4	Titania	8	6
5	Silica	19	15
6	Boron Nitride	23	18
7	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	9	7

Reaction Conditions	Support (10 mg), total pressure (5% H_2/CO_2 420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol), 25 ºC, 30 min.

All of the supports evaluated hydrogenated the H_2O_2, however ceria, titania, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (heteropolyacid (HPA)) and carbon hydrogenated the least H_2O_2. Previously these supports, following the addition of Au and Pd, have been shown to produce H_2O_2 in the standard methanol-water system as described in Chapter 1.6.5.[2-4, 32-33, 36]

3.5.1 Direct synthesis of H_2O_2 activity

As published by Edwards *et al.* the optimum metal loading for the direct synthesis of H_2O_2 is 2.5 wt. % Au-2.5 wt. % Pd.[36] Following these studies a series of 2.5 wt. % Au-2.5 wt. % Pd supported catalysts were prepared by impregnation. In order to see if the catalysts were active in the new system they were tested for the direct synthesis of H_2O_2 as described in chapter 2.5.1. The results are shown in figure 3.5.

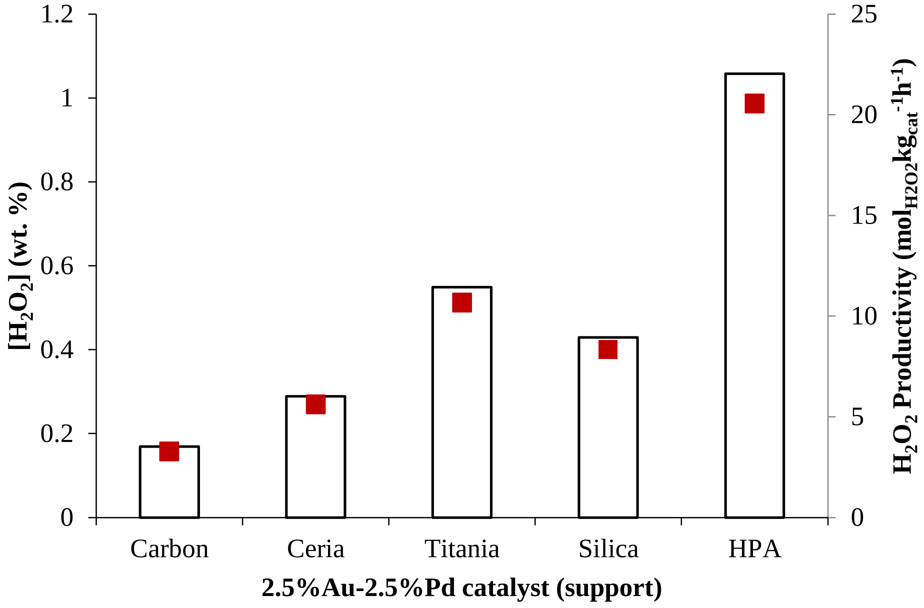

Figure 3.5 H_2O_2 concentration (□) and productivity (■) produced in the new solvent system using AuPd supported catalysts prepared by impregnation.

Reaction conditions Catalyst (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33g H_2O, 8.17 g decan-1-ol,), 25 °C, 30 min.

AuPd supported materials that have been previously used for H_2O_2 synthesis were screened for the direct synthesis of H_2O_2 in the new solvent system. Figure 3.5 shows the 5%AuPd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst displayed the highest concentration in comparison to the other supported catalysts, with carbon having the lowest H_2O_2 concentration. Bimetallic AuPd/heteropolyacid catalysts are extremely efficient for the direct synthesis of H_2O_2 as Ntainjua *et al.* have reported previously that in 30 minutes H_2O_2 productivity of 236 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$ can be achieved in a methanol-water solvent system.[32] However the fact that carbon had the lowest activity in the decan-1-ol -water system and out of all the oxide supports TiO_2 had the highest was surprising. These results are in contrast to the observed activity in the methanol-water system, where carbon has the highest productivity (110 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) and TiO_2 the lowest (64 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$).[31]The different catalytic activity observed in the new decan-1-ol-water system can presumably be due to the varying interaction between the catalyst and the water phase.

3.5.2 Hydrogenation Activity

In order to understand the new system better and see if H_2O_2 hydrogenation plays a role when using decan-1-ol-water as the solvent system, the catalysts were evaluated for the hydrogenation activity as previously described in chapter 2.5.2. The results are shown in figure 3.6.

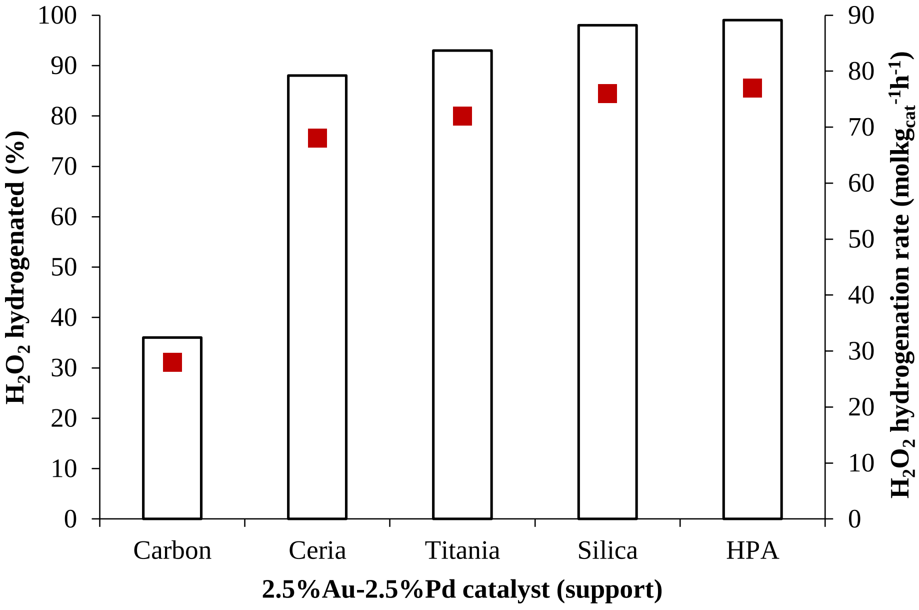

Figure 3.6 H_2O_2 destroyed by hydrogenation in the new solvent system using AuPd supported catalysts prepared by impregnation. % H_2O_2 destroyed (□) H_2O_2 hydrogenation rate (■)

Reaction conditions	Catalyst (10 mg), total pressure (5% H_2/CO_2 420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol), 25 ºC, 30 min.

All the catalysts hydrogenated H_2O_2, however, the carbon supported AuPd catalyst hydrogenated the least. When AuPd was supported on CeO_2, TiO_2, SiO_2 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ almost all of the H_2O_2 present in the reaction medium was hydrogenated. These results were unexpected as they contradicted the hypothesis illustrated in figure 3.1 which proposed that the new biphasic system would be a method of preventing or completely diminishing the rate of hydrogenation. In order to ascertain the reactor itself did not catalyse the degradation of H_2O_2, blank decomposition and hydrogenation experiments were conducted in the absence of a catalyst. The experiments were conducted using the standard operating conditions for H_2O_2 decomposition (25% O_2/CO_2 (420 psi), solvent (8.5 g), 25 °C, 1200 rpm, 30 minutes) and hydrogenation (5% H_2/CO_2 (420 psi), solvent (8.5 g), 25 °C, 1200 rpm, 30 minutes). The results are given in table 3.3.

Table 3.3 H_2O_2 decomposition, hydrogenation and direct synthesis experiments in the absence of a catalyst.

Solvent	**% H_2O_2 decomposed**	**% H_2O_2 hydrogenated**	**Amount of H_2O_2 produced**
Water	0	0	0
Decan-1-ol	0	0	0
Water-Decan-1-ol	0	0	0

The results in table 3.3 show when the H_2O_2 decomposition and hydrogenation experiments were carried out in the absence of a catalyst there was no loss in H_2O_2. This indicates the reactor itself does not catalyse the decomposition or hydrogenation of H_2O_2 and the solvents used are free from impurities which could possibly degrade the H_2O_2.

In order to ascertain the reactor itself did not catalyse the direct synthesis of H_2O_2, blank direct synthesis experiments were carried out using water, decan-1-ol and decan-1-ol-water as the solvent. The experiments were conducted using 5%H_2/CO_2 (420 psi) and 25% O_2/CO_2 (160 psi) at 25 °C, whilst stirring (1200 rpm) for 30 minutes. No

H_2O_2 was detected after these blank direct synthesis experiments. These blank experiments indicate the activity for the direct synthesis and H_2O_2 hydrogenation observed in figure 3.5 and 3.6 was solely due to the AuPd supported catalysts employed. It was clear from the results obtained that an important factor was contributing to the high hydrogenation rates.

For the biphasic system to be effective it is essential to select a support/catalyst which will be retained in the decan-1-ol phase only. If the catalyst is far from the water phase, which acts as the in situ H_2O_2 extractor, the possibility of destroying H_2O_2 due to subsequent hydrogenation reactions will be minimal. In order to see which phase the catalyst resides in, a simple vial test was carried out. The various supported AuPd catalysts were added to separate vials which contained a mixture of decan-1-ol and water. The results are tabulated in Table 3.4 with a selection of pictures in Figure 3.7.

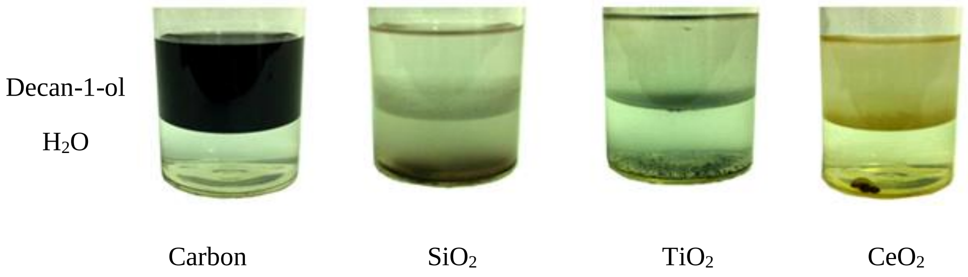

Figure 3.7 Simple vial experiments to indicate which phase the catalyst resides

Table 3.4 Indication of which phase the catalyst resides

Entry	**5%AuPd supported catalyst**	**Catalyst Phase**
1	Carbon	Decan-1-ol
2	Ceria	Both
3	Titania	Both
4	Silica	Water
5	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Interphase

The vial tests indicated that the 5%AuPd/carbon was the only catalyst which resides in decan-1-ol phase completely. 5%AuPd/Silica resides in the water phase only, the 5%AuPd/herteropolyacid catalyst resides on the interphase and finally both CeO_2 and TiO_2 catalysts resides in both phases.

The results obtained from the vial tests were extremely useful and they explained the high hydrogenation activity observed in Figure 3.6. It was clear that supports which reside in the decan-1-ol phase only, in this case carbon, lead to lower hydrogenation activities in comparison to supports which reside partially or completely in the water phase. This indicates that the decan-1-ol-water solvent system has potential to work as first hypothesised in section 3.1.

3.6 AuPd/ Carbon catalyst for the direct synthesis of H_2O_2 using decan-1-ol-water solvent system

Since the 2.5 wt.% Au-2.5 wt. %Pd/carbon catalyst resides in the decan-1-ol phase only and shows the lowest hydrogenation activity, the effect of reaction parameters using this catalyst was investigated in collaboration with a colleague, Greg Shaw and the optimum reaction conditions are highlighted in table 3.5.

Table 3.5 Optimum reaction conditions using the 5%AuPd/Carbon catalyst.[37]

Conditions	**AuPd/C**
Solvent decan-1-ol (wt% H_2O)	0.39
Solvent mass (g)	4
Catalyst loading (mg)	>20
Time (min)	30-60
Stirring speed (rpm)	1200
Total pressure (psi)	700

After investigating a range of reaction parameters (table 3.5) a maximum H_2O_2 concentration of 0.8 wt. % was produced in the aqueous phase using the 5%AuPd/carbon catalyst.[37] Previously acid washing the support prior to impregnating with Au and Pd has shown to decrease the final materials activity towards H_2O_2 hydrogenation. In the case of 2.5 wt. %Au–2.5 wt. %Pd/acid washed carbon the path can be switched off completely in the methanol-water system.[29-30] Edwards *et al.*[29] have previously reported the highest concentration achieved in the methanol-water solvent system is *ca.* 0.7 wt. % using a 2.5 wt. % Au–2.5 wt. %Pd/acid washed carbon supported catalyst. Although 0.8 wt. % H_2O_2 was obtained in the decan-1-ol-water system using the 2.5 wt. % Au–2.5 wt. % Pd/carbon catalyst and the initial result highlights the potential of using a biphasic solvent system unfortunately the required target of 3-8 wt. % H_2O_2 was unreachable using this catalyst and the optimum reaction conditions stated in table 3.5.

3.7 Further Development of Carbon as a Support in the biphasic system

From the work done thus far all the experiments suggest that the new biphasic system may be a good alternative method for producing H_2O_2. Carbon supported catalysts were found to be the best candidate as it was the only catalyst which completely resides in the decan-1-ol phase, it had the lowest hydrogenation activity and after optimising the reaction conditions a H_2O_2 concentration of 0.8 wt. % was obtained in the aqueous phase. There are numerous carbon supports which can be purchased from a range of suppliers and each carbon support has different surface properties as well as hydrophobicity. In an attempt to search for a more active and selective carbon based support to reach the required target of 3-8 wt. % H_2O_2, a range of 2.5 wt. % Au-2.5 wt. % Pd carbon supported catalysts were prepared and tested in the decan-1-ol-water system. The direct synthesis and hydrogenation results are shown in Table 3.6.

Table 3.6 H_2O_2 concentration, productivity and hydrogenation using various 5 wt. % AuPd supported catalysts and indication of which phase the catalyst resides in

Entry	**5%AuPd/ Support**	**Phase**	**$[H_2O]^a$ (Wt.%)^a**	**H_2O_2 Productivity^a ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**	**Hydrogenation (%)^b**	**H_2O_2 Hydrogenation rate^b ($molkg_{cat}^{-1}h^{-1}$)**
1	G60 Carbon	Decan-1-ol	0.17	3	37	29
2	Acid washed G60	Decan-1-ol	0.29	3	24	19
3	Graphite	Decan-1-ol	0.15	6	99	77
4	Cabot VXC72	Decan-1-ol	0.19	3	99	77
5	Carbon Norit	Water	0.20	4	99	77
6	Graphite BNFL	Interphase	0.13	4	36	28

Reaction conditions [a] Catalyst (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33g of H_2O, 8.17 g decan-1-ol,), 25 ºC, 30 min.

[b] Catalyst (10 mg), total pressure (5% H_2/CO_2 420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol), 25 ºC, 30 min.

2.5 wt. % Au–2.5 wt. % Pd/ Carbon Norit (table 3.6, entry 5) was the only catalyst which resides in the water phase and as a result, it had a very high hydrogenation activity. However, it was interesting to observe how the 2.5 wt. % Au–2.5 wt. % Pd supported on graphite and carbon VXC72 (table 3.6, entries 3-4), which reside in the decan-1-ol phase, also hydrogenated majority of the H_2O_2 present in the reaction medium. The reason for this may be due to the presence of impurities in the carbon as carbon supports are known to have a variety of impurities which can affect the reactivity of a chemical reaction. As apparent from table 3.6 two different types of graphite supports were used. The 2.5 wt. % Au–2.5 wt. % Pd supported on BNFL graphite (table 3.6, entry 6), however, did not have a high hydrogenation activity. This is an extremely pure form of nuclear grade graphite which is pre-treated to remove any impurities from the material. This may explain the low hydrogenation activity in comparison to the graphite purchased from Sigma Aldrich (table 3.6, entry 3).

In 2009 Edwards *et al.*[29] reported an alternative method to produce AuPd carbon supported catalysts which resulted in a promotion in activity and selectivity towards H_2O_2 synthesis, exhibiting zero hydrogenation activity. The method involved pre-treating the carbon support with a dilute acid. The beneficial effect of this treatment is it enhances the gold dispersion in the bimetallic alloy particles by generating smaller AuPd nanoparticles, and these presumably decorate sites on the support that are otherwise active for the subsequent side reaction of H_2O_2.When the 2.5 wt. % Au–2.5 wt. % Pd/ acid washed G60 catalyst (Table 3.6, entry 2) was screened in the new decanol-water system it exhibited the lowest hydrogenation activity and a higher activity for the direct synthesis of H_2O_2 in comparison to the parent catalyst (table 3.6, entry 1). Based on table 3.6 and the discussion stated it was decided to investigate the effect of reaction variables using the 2.5% Au-2.5% Pd /acid washed carbon catalyst in the decan-1-ol-water system.

NB from this point on 2.5 wt. % Au–2.5 wt. % Pd/acid washed G60 will be referred to as 5%AuPd/A.W. Carbon.

3.7.1 The effect of decan-1-ol-water ratio

Firstly the ratio between decan-1ol and water was investigated keeping the total amount of solvent constant at 8.5 g (Figure 3.8).

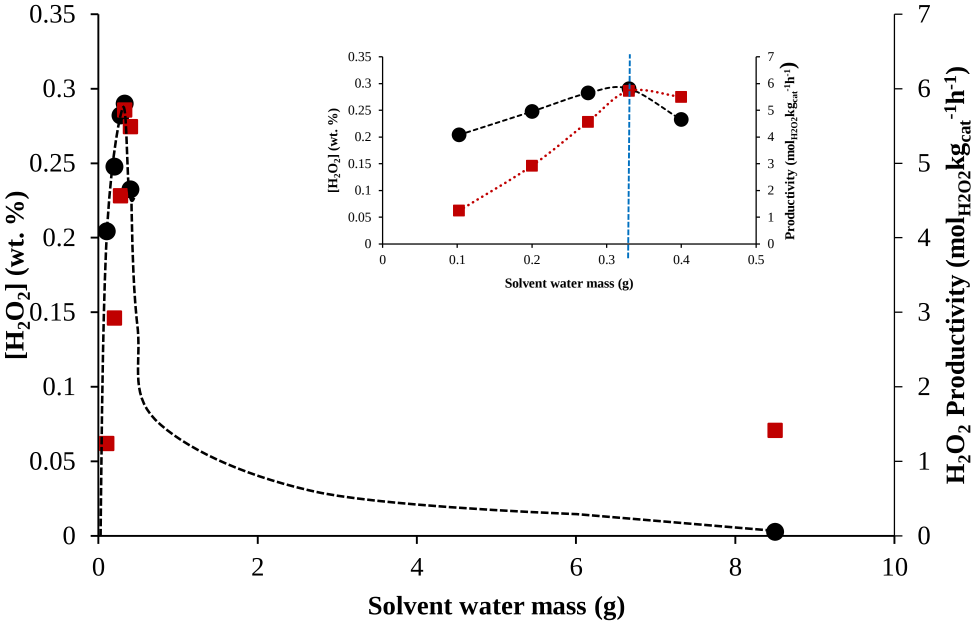

Figure 3.8 H_2O_2 concentration (●) and productivity (■) as an effect of water content.

Reaction Conditions 5%AuPd/A.W Carbon (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 °C, 30 min.

The results in figure 3.8 show variation of this parameter has a major effect on the H_2O_2 concentration and productivity. As shown in figure 3.8 the addition of ~ 0.1 g water to pure decan-1-ol is essential to produce high concentrations of H_2O_2. The water solubility in decan-1-ol was experimentally determined by Karl Fischer titrations and is indicated by the blue line on figure 3.8. To the left of this line the reaction occurs in a single phase whilst to the right of this line the decan-1-ol is oversaturated with water and is present in the reaction in two phases. It was interesting to observe that the optimum decan-1-ol-water ratio is the saturation point of decan-1-ol. The results show the reaction is sensitive to the amount of water added to the reaction medium as varying the water content above or below the optimum point leads to a decrease in the concentration of H_2O_2. The AuPd/A.W. Carbon catalyst prepared by impregnation showed lower activity for H_2O_2 synthesis using H_2O as the solvent rather than decanol water. This is expected as the solubility of the reactant gases is lower in water than in alcohols. In the absence of water the overall H_2O_2 concentration drops massively. This result indicates that the presence of small amounts of H_2O is essential for producing enhanced concentrations of H_2O_2. Since the highest concentration of H_2O_2 is observed using 0.33 g water and 8.17 g decan-1-ol, all experiments from this point were carried out using this decan-1-ol-water ratio.

3.7.2 The effect of solvent mass and catalyst mass

The effects of solvent mass and catalyst mass were investigated in order to produce the highest H_2O_2 concentration with the 5% AuPd/A.W carbon catalyst. Firstly, the mass of solvent was decreased whilst keeping the catalyst loading at 10 mg; the results are shown in Table 3.7

Table 3.7 H_2O_2 concentration and productivity as a function of total solvent mass.

Entry	**Solvent mass (g)**	**[H_2O_2] (Wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kgcat^{-1}h^{-1}$)**
1	4.25	0.44	4
2	6.00	0.41	6
3	8.50	0.29	6

Reaction Conditions	5%AuPd/A.W. Carbon (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (4.25-8.50 g), 25 ºC, 30 min.

The results in table 3.7 show as the mass of solvent is increased the concentration of H_2O_2 decreases and a maximum concentration of 0.45 wt. % is obtained using a total solvent mass of 4.25 g. These results were expected because if the total amount of solvent in the reaction mixture is reduced the amount of water present will also decrease hence a more concentrated solution of H_2O_2 will be obtained.

Next, experiments were conducted to investigate the effect of catalyst mass.

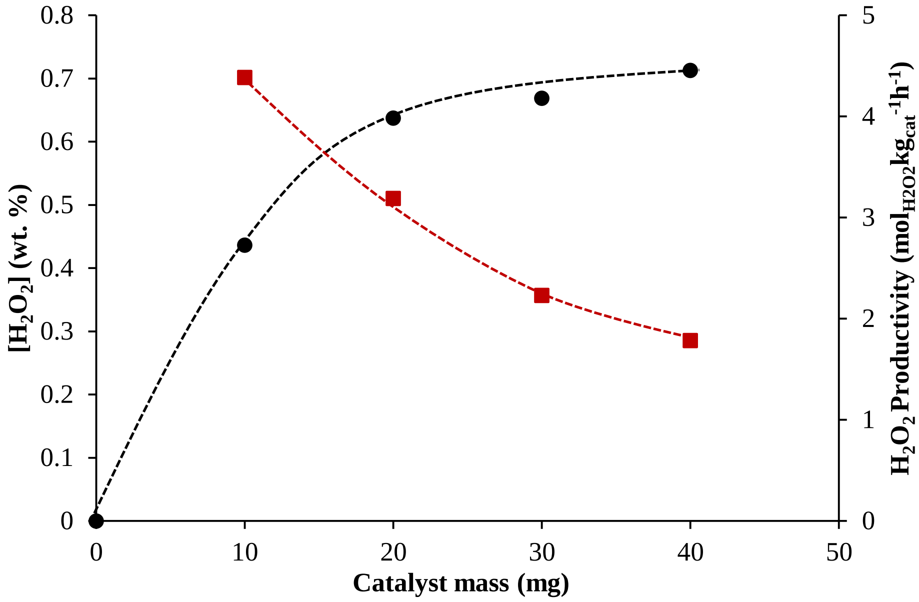

Figure 3.10 H_2O_2 concentration (●) and productivity (■) as a function of catalyst loading.

Reaction conditions 5%AuPd/A.W Carbon (0-40 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (4.25 g), 25 ºC, 30 min

The results shown in figure 3.10 clearly illustrate that the reaction is diffusion limited at higher catalyst mass. Indeed by increasing the catalyst loading from 10 mg to 40 mg it was possible to increase the H_2O_2 concentration from 0.43 wt. % to 0.71 wt. %. However the H_2O_2 concentration only increases until 20 mg of catalyst, after which it remains fairly constant corresponding to a decrease in the H_2O_2 productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$). This suggests that when a higher mass of catalyst is used the reaction becomes predominantly mass transfer limited.

3.7.3 The effect of reaction time

The effect of reaction time was investigated keeping the total solvent mass constant at 8.5 g and using 10 mg 5%AuPd/A.W Carbon.

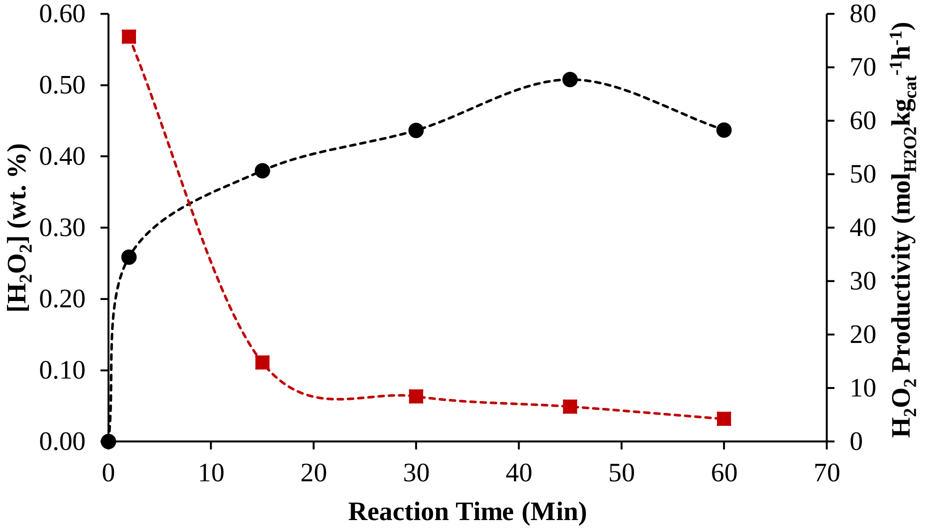

Figure 3.11 H_2O_2 concentration (●) and productivity (■) as a function of time.

Reaction conditions 5% AuPd/A.W Carbon (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 °C, time (0-60 min).

Figure 3.11 shows as the reaction time increases so does the concentration of H_2O_2 until a maximum H_2O_2 concentration of 0.51 wt. % is obtained after 45 minutes. Longer reaction time results in a decrease in H_2O_2 concentration and this can be attributed to two factors: i) at higher residence times the concentration of H_2 and O_2 in the reaction mixture decreases, as reaction is in a batch system this will lead to low synthesis rates (ii) at higher residence times the contribution of H_2O_2 hydrogenation/decomposition rates increases which will result in an overall decrease in H_2O_2 concentration.

3.7.4 The effect of pressure

Finally the effect of pressure was investigated. As discussed previously in section 3.3 one method to overcome mass transfer limitation is to increase the solubility of reactant gases by increasing the pressure. According to Henry's Law (equation 1) "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$P = k_{\mathrm{H}}c \qquad \text{(Equation 3.1)}$$

Where P = the partial pressure of the gases solute above the solution

C = concentration of the dissolved gas

k_H is a constant with the dimensions of pressure divided by concentration

Since the gases used are diluted in CO_2 the highest possible pressure to conduct direct synthesis experiments is 700 psi, above this point the CO_2 can liquefy. In order to increase the H_2O_2 concentration even further the overall pressure was increased to 700 psi whilst maintaining the H_2/O_2 ratio as 0.525. The effects are shown in figure 3.12.

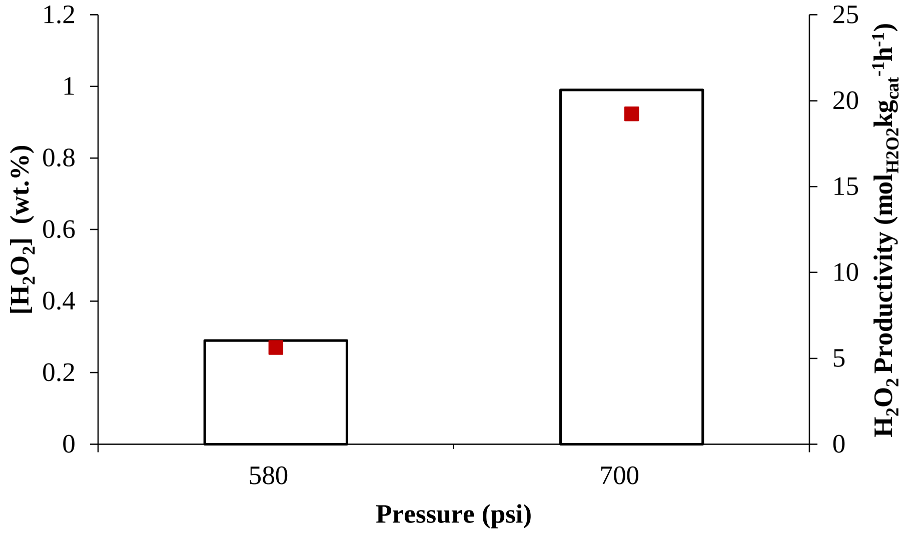

Figure 3.12	H_2O_2 concentration (□) and productivity (🟥) as a function of total pressure.
Reaction conditions	5% AuPd/A.W. Carbon (10 mg), total pressure (580-700 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 ºC, 30 min.

As expected there was an enhancement in H_2O_2 concentration and productivity as the pressure was increased. A H_2O_2 concentration of 0.99 wt. % was achieved using a total pressure of 700 psi. Indeed higher pressures can lead to a higher gas solubility and this can have a positive effect on mass transfer limitations for the direct synthesis of H_2O_2 leading to higher concentrations of H_2O_2.

3.7.5 Optimum reaction conditions using the 5%AuPd/A.W Carbon Catalyst

Based on the set of reactions carried out it is possible to define a new set of reaction parameters, required to produce the maximum number of H_2O_2 moles (2.53 x 10^{-5}) after optimisation of reaction parameters using a 5 % AuPd/A.W Carbon catalyst. It should be noted the theoretical maximum H_2O_2 produced in the water phase, assuming 100% H_2 conversion with 100% selectivity to H_2O_2 is 34 wt. % and 3.37 x 10^{-3} moles. The optimum reaction conditions using the 5% AuPd/A.W. Carbon catalyst are listed in table 3.8.

Table 3.8 Optimum reaction conditions using the 5%AuPd/A.W Carbon catalyst.

Conditions	**5%Au-Pd/A.W Carbon**
Solvent decan-1-ol (wt% H_2O)	0.39
Solvent mass (g)	4.25
Catalyst loading (mg)	>20
Time (min)	30-60
Stirring speed (rpm)	1200
Total pressure (psi)	700

3.8 Revisiting the 2.5 % Au-2.5 %Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Although there was a significant increase in H_2O_2 concentration after optimising the reaction parameters the concentration of H_2O_2 obtained with the 5 % AuPd/A.W.Carbon catalyst was still lower than the most active catalyst screened in the new solvent system (2.5 wt. % Au-2.5 wt. % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$) (figure 3.13)

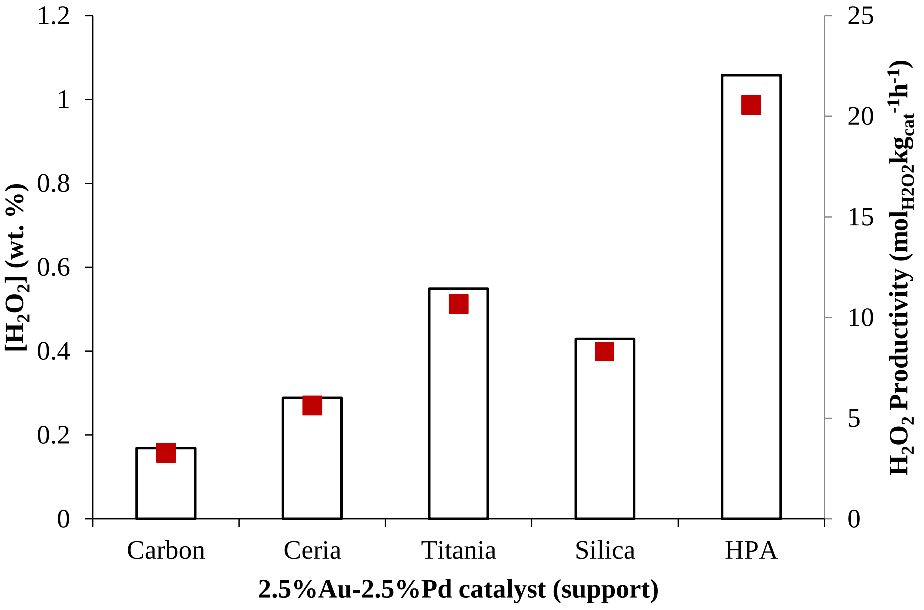

Figure 3.13 H_2O_2 concentration (□) and productivity (■) as a function of catalyst.

Even though 2.5 wt. % Au-2.5 wt.% Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ hydrogenated the most H_2O_2 in the decan-1-ol-water system, it was the most active for the direct synthesis pathway giving the highest H_2O_2 concentration (1.06 wt. %) under the initial reaction conditions (580 psi total pressure, H_2/O_2 (0.525), 1200 rpm, 30 min, 25 °C and solvent loading 8.5 g (0.33 g H_2O, 8.17 g decan-1-ol), 10 mg catalyst). Previously the 2.5 wt. % Au-2.5 wt. % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts have been reported to be extremely active catalysts for the direct synthesis of H_2O_2 in the methanol-water system. At standard reaction conditions (580 psi total pressure, H_2/O_2 (0.525), 1200 rpm, 30 min, 2 °C and solvent loading 8.5 g (2.9 g H_2O, 5.6 g methanol), 10 mg catalyst), in the methanol-water system these catalysts display productivities more than two folds higher than other 5% AuPd supported catalysts prepared by standard impregnation. [32]

It must not be forgotten that the results obtained for the 2.5 % Au-2.5 % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst thus far were carried out using the standard reaction conditions for the decan-1-ol-water system (Chapter 2.5.1) and the optimum reaction conditions for each catalyst are unique. Hence this prompted us to evaluate the effect of the reaction conditions on the synthesis of H_2O_2 using the 2.5 % Au-2.5 % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the decan-1-ol-water system. At this stage it was thought that the high hydrogenation activity observed for the 2.5 wt. % Au-2.5 wt. % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst may be observed due to the high stirring speed (1200 rpm) of the reaction. This can cause higher dissolution of hydrogen resulting in increased H_2O_2 degradation rates and/or causing the catalyst to be pushed into the water phase.

As already described in Figure 3.1, it was thought that the new solvent system will reduce/eliminate the subsequent hydrogenation and decomposition reactions. An advantage of using a solvent system containing an organic alcohol and water is it would provide *in situ* extraction of H_2O_2 from the organic phase due to the higher solubility of H_2O_2 in water than the organic solvent. Furthermore if the catalyst is held in the organic phase this would lead to better shielding of H_2O_2 from the consecutive reactions and as a result this will lead to an enhancement in H_2O_2 concentrations in the aqueous phase. In an attempt to further understand the direct synthesis and hydrogenation activity in the reaction system the effect of reaction variables using 2.5 wt. %Au-2.5 wt. % Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was studied.

3.8.1 Effect of reaction variables using 2.5%Au-2.5%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

In this section the effect of reaction parameters on H_2O_2 concentration will be investigated using the 2.5 wt. % Au-2.5 wt. % Pd /$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst. The aim is to produce a H_2O_2 concentration of 3-8 wt. %, so that the direct synthesis of H_2O_2 may be industrially viable.

NB. Hereafter the abbreviation 5%AuPd/HPA will always be used for referring to 2.5wt. % Au - 2.5 wt. % Pd / $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

3.8.1.1 The effect of decan-1-ol-water ratio

Firstly the effect of solvent composition was investigated whilst keeping the solvent mass constant at 8.5g.

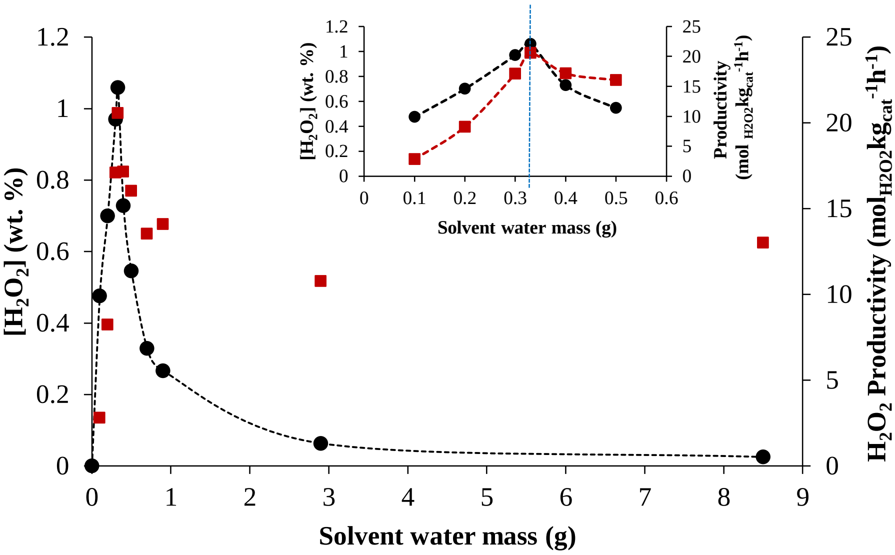

Figure 3.14 H_2O_2 concentration (●) and productivity (■) as an effect of water content.

Reaction Conditions 5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 °C, 30 min.

Figure 3.14 shows the decanol-water ratio has a major effect on the concentration of H_2O_2 produced. The highest concentration of H_2O_2 (1.06 wt. %) and productivity (21 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) is obtained with 0.33g of H_2O and 8.17g of decan-1-ol. Three interesting features are observed in figure 3.14: Firstly the rate of H_2O_2 synthesis and concentration is very sensitive around its optimal point. The second is that the total absence of water leads to very low concentrations of H_2O_2 being observed and finally the use of pure water still leads to an effective rate for the production of H_2O_2. This final observation was also reported by Freakley *et al.*[35] who showed AuPd heteropolyacid catalyst show relatively higher activity in water as solvent when compared to other standard impregnation catalysts.

The results in figure 3.14 show the rate of H_2O_2 synthesis remains fairly constant between 0.40 g and 8.5 g solvent water mass. Although the rate of H_2O_2 synthesis stay fairly constant after the optimal decanol-water ratio, there is a dramatic decrease in the concentration of H_2O_2 produced. The decrease in H_2O_2 concentration between 0.40 g and 8.50 g solvent mass can be attributed to the H_2O_2 being dissolved in a larger amount of water. Since the highest concentration of H_2O_2 is observed using 8.17 g decanol and 0.33 g water, all experiments from this point were carried out using this decanol-water ratio.

3.8.1.2 The effect of reagent reloading

In 30 minutes, under the initial reaction conditions (chapter 2.5.2) a H_2O_2 concentration of 1.06 wt. % was produced using the 5%AuPd/HPA catalyst. In order to increase the H_2O_2 concentration even further top-up experiments were carried out (figure 3.15). Top up experiments consist of the subsequent refilling of the autoclave with reagent gases for a given number of times. The reaction was refilled with 5%H_2/CO_2 (420 psi) and 25%O_2/CO_2 (160 psi) every 30 minutes as shown in figure 3.15.

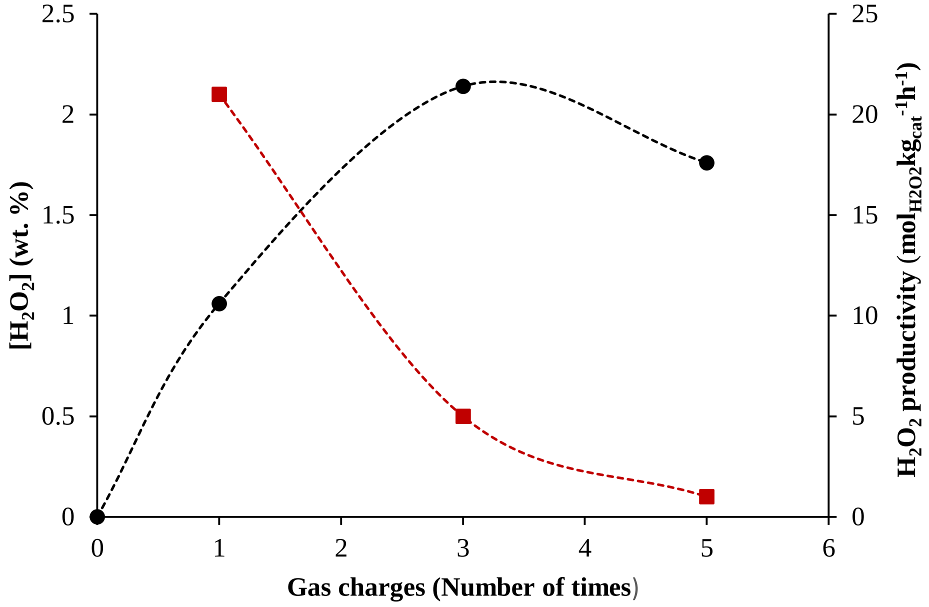

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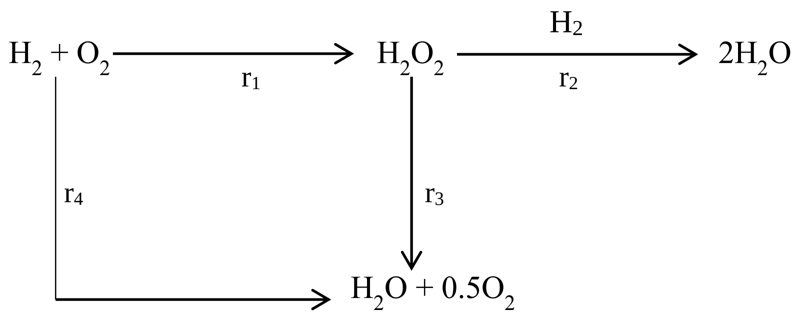
Figure 3.15 The effect of sequential experiments using gas top-up on H_2O_2 concentration (●) and productivity (🟥)

Reaction conditions Each gas charge, total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol), 25 °C, 30 min. 5%AuPd/HPA (10 mg for 1 gas charge, 30 mg for 3 gas charges and 50 mg for 5 gas charges).

Interestingly after three gas charges (90 minutes) a H_2O_2 concentration of 2.14 wt. % is achieved using 30 mg of catalyst. However after 5 gas charges (150 minutes) the H_2O_2 concentration drops to 1.76 wt. %. The results obtained from these experiments can be explained in terms of the hypothetical kinetic model for the direct synthesis of H_2O_2 (Figure 3.16). At higher residence times the concentration of H_2O_2 begins to build up, but as soon as more gases are charged into the reaction vessel the hydrogenation rate becomes faster than the synthesis rate. This therefore results in an overall consumption of the H_2O_2 and limits the maximum H_2O_2 concentration obtainable in this system. These experiments give an understanding of the reaction limits of the direct synthesis of H_2O_2 and suggest the formation of H_2O_2 may be favoured at short residence times.



$r_1 = k_1 [H_2]^a [O_2]^b$ — H_2O_2 synthesis

$r_2 = k_2 [H_2]^c [H_2O_2]^d$ — H_2O_2 hydrogenation

$r_3 = k_3 [H_2O_2]^e$ — H_2O_2 decomposition

$r_4 = k_4 [H_2]^f [O_2]^g$ — H_2 combustion

Figure 3.16 Hypothetical model of the kinetics involved in the direct H_2O_2 synthesis and its side reactions

3.8.1.3 The effect of reaction time and reagent loading

A series of short reactions and top-up experiments were carried out and the results are given in table 3.9 and 3.10 respectively. When compared to a standard 30 minute reaction (H_2O_2 concentration of 1.06 wt. %) a higher concentration of H_2O_2 (1.54 wt. %) and productivity (359 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) was achieved in 2.5 min. The highest concentration of H_2O_2, 1.87 wt. % was observed after a 10 minute reaction.

Table 3.9 H_2O_2 concentration and productivity as a function of reaction time.

Entry	**Time (min)**	**$[H_2O_2]$ (Wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
1	2.5	1.54	359
2	10	1.87	109
3	20	1.46	43
4	30	1.06	21

Reaction conditions 5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol)), 25 °C, 30 min.

Filling the reaction mixture with gases after a shorter period of time also proved to be successful for producing higher concentrations of H_2O_2. The highest concentration of H_2O_2 (2.12 wt. %) was observed when the reaction vessel was re-filled with gases after 5 minutes had relapsed in a total reaction time of 10 minutes. (Table 3.10, entry 2).

Table 3.10 H_2O_2 concentration and productivity as a function of reagent gas charges.

Entry	**Number of Gas Charges**	**$[H_2O_2]$ (Wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
1	3 in 30 min (after 10 min)	1.99	39
2	2 in 10 min (after 5 min)	2.12	124
3	4 in 10 min (after 2.5 min)	1.98	115
4	2 in 5 min (after 2.5 min)	1.84	214

Reaction conditions Catalyst (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol)), 25 °C, 30 min

These results suggest shorter reactions are more favourable for the direct synthesis of H_2O_2. At lower residence times there is very little contact time between the catalyst and H_2O_2 thus this will restrain the H_2O_2 from reacting further with the reagent gases to produce the unwanted by-product, water. At higher residence times the concentration of H_2O_2 builds up and the contact between the catalyst and H_2O_2 leads to H_2O_2 degradation. One thing to note here is that the 5%AuPd/HPA catalyst behaves differently to the 5%AuPd/A.W Carbon catalyst. Although the H_2O_2 concentration produced by the 5% AuPd/A.W. Carbon catalyst is much lower, the concentration of H_2O_2 does not drop dramatically after 10 minutes (Figure 3.11). This shows that the 5%AuPd/A.W.carbon has the ability to hydrogenate less and the H_2O_2 concentration only begins to drop after 45 minutes because the concentration of reagent gases decrease over time.

In order to see whether H_2O_2 destruction played a greater role at longer residence times the activity of 5%AuPd/HPA was evaluated for the hydrogenation of H_2O_2 at different reaction times. The results are given in figure 3.17.

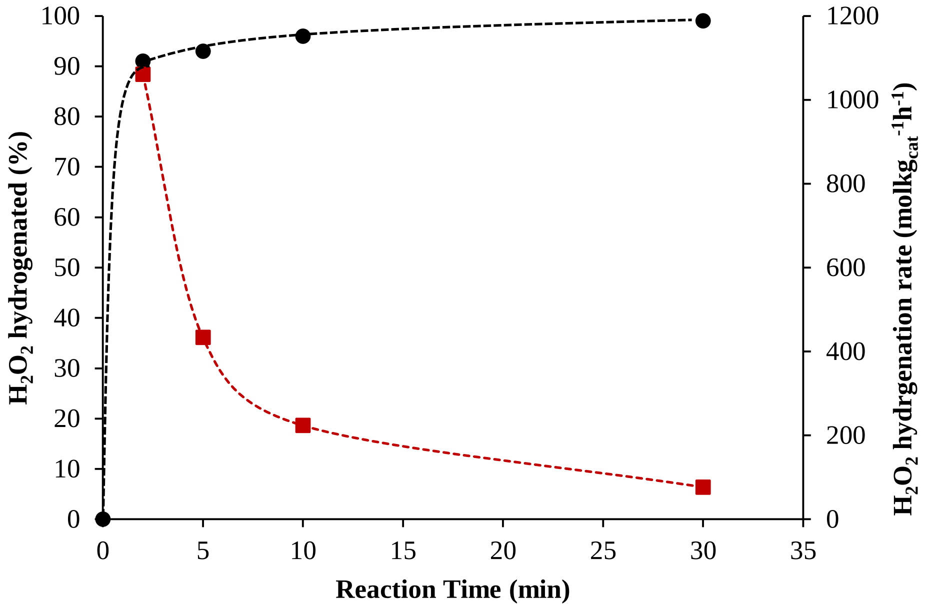


Figure 3.17	H_2O_2 hydrogenation as a function of reaction time. % H_2O_2 hydrogenated (●) H_2O_2 hydrogenation rate (🟥)
Reaction Conditions	5%AuPd/HPA (10 mg), total pressure (5% H_2/CO_2, 420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 25 °C, 30 min**.**

When a blank hydrogenation reaction was conducted in the absence of a catalyst there was no loss in H_2O_2 however when H_2O_2 hydrogenation experiments were conducted with the 5%AuPd/HPA catalyst more than 90 % of H_2O_2 present in the reaction medium hydrogenated. Surprisingly both short and long residence times gave extremely high hydrogenation activities. This was not expected for short residence times which suggests three possibilities: (i) the reaction temperature (room temperature) is high which is causing the H_2O_2 to decompose quickly; (ii) the amount of H_2 in the reaction system may be too high thus the hydrogenation rate is faster than the rate of H_2O_2 synthesis leading to a net consumption of the H_2O_2 and finally (iii) the catalyst used is extremely active for both synthesis and hydrogenation reactions and the H_2O_2 formed is quickly degraded to water.

3.8.1.4 The effect of temperature

The effect of temperature on the direct synthesis rate was further investigated. Several papers have described that H_2O_2 formation rate decreases with increasing temperature due to an enhancement of the decomposition and hydrogenation reaction on H_2O_2 production.[3, 8,10,13,38] Since decan-1-ol freezes at 6.4 °C up to this point all the experiments have been carried out at room temperature. In order to decrease the H_2O_2 degradation activity the reaction temperature was lowered to 10 °C.

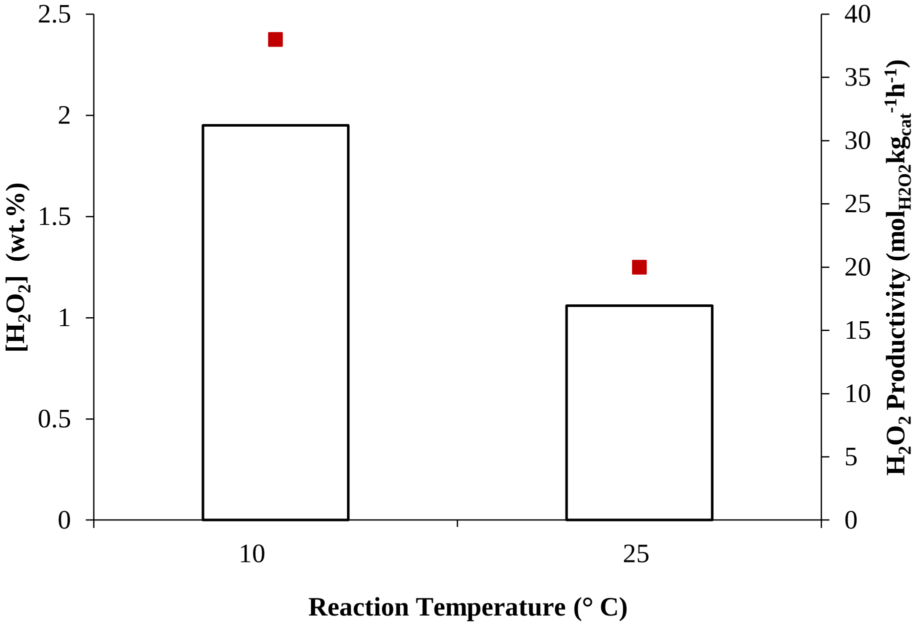


Figure 3.18 H_2O_2 concentration (□) and productivity (■) as a function of temperature.

Reaction conditions	5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol), temperature (10 and 25 ºC), 30 min

Figure 3.18 shows the results for when the catalyst was screened for the direct synthesis of H_2O_2 at 10 ºC whist keeping all other reaction conditions constant. Operating at a lower temperature significantly increased the H_2O_2 concentration and synthesis rate. The H_2O_2 concentration increased from 1.06 wt. % (25 ºC) to 1.95 wt. % (10 ºC). These results coincide with literature studies which show that at higher reaction temperatures there is enhanced hydrogenation and decomposition of H_2O_2 which lead to decreased rates of H_2O_2 production.

3.8.1.5 The effect of H_2:O_2 ratio

The effect of H_2:O_2 ratio on H_2O_2 concentration and productivity was investigated at 25 ºC whilst keeping the total partial pressure constant at 580 psi. The results are given in table 3.11.

Table 3.11 H_2O_2 concentration and productivity as a function of H_2:O_2 ratio

H_2/O_2 Ratio	$5\%H_2/CO_2$ (psi)	$25\%O_2/CO_2$ (psi)	$[H_2O_2]$ (Wt. %)	H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)
0	0	0	0	0
0.0442	105	475	1.13	22
0.113	210	370	2.17	43
0.151	250	330	1.92	37
0.214	300	280	1.78	35
0.525	420	160	1.06	21

Reaction conditions	5%AuPd/HPA (10 mg), total pressure (580 psi), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol), 25 ºC, 30 min.

A number of reactions were conducted varying the H_2:O_2 ratio. A maximum H_2O_2 concentration (2.17 wt. %) and productivity (43 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) was produced when a 0.113 H_2:O_2 ratio was used. At H_2:O_2 ratios above this point it seems there is an excess of H_2 in the system which is causing the H_2O_2 to degrade more readily. Therefore, at higher residence time the hydrogenation rate is faster than the H_2O_2 synthesis rate leading to a net consumption of the H_2O_2. For H_2:O_2 ratios lower than the optimum the H_2O_2 concentration and productivity is much lower which suggests H_2 is the limiting reagent in these experiments, as the reaction time increases the amount of H_2 in the reaction mixture decreases leading to slower H_2O_2 synthesis rates.

Since the highest concentration of H_2O_2 is achieved when a lower partial pressure of 5% H_2/CO_2 is used, the effect of temperature was investigated using the optimum H_2/O_2 ratio (0.113). The results are given in table 3.12.

Table 3.12 Evaluation of 5%AuPd/HPA towards H_2O_2 synthesis at different temperatures using a H_2:O_2 ratio of 0.113.

Temp (ºC)	**5% H_2/CO_2 (psi)**	**25% O_2/CO_2 (psi)**	**[H_2O_2] (wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
25	210	370	2.17	43
10	210	370	2.75	53

Reaction conditions	Catalyst (10 mg), total pressure (580 psi), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol)), 30 min.

Changing the H_2:O_2 ratio (0.113) and lowering the reaction temperature to 10 ºC had a significant effect on the H_2O_2 concentration and productivity. The H_2O_2 concentration increased from 2.17 wt. % (25 ºC) to 2.75 wt. % (10 ºC). Once again these results show at a lower temperature and H_2:O_2 ratio there is a decrease in H_2O_2 degradation which is counteracted by an increase in H_2O_2 production rate.

3.8.1.6 The effect of temperature and H_2:O_2 ratio at short residence times

The effect of lower temperature and H_2:O_2 ratio was investigated for a shorter reaction time and the results are shown in figure 3.20.

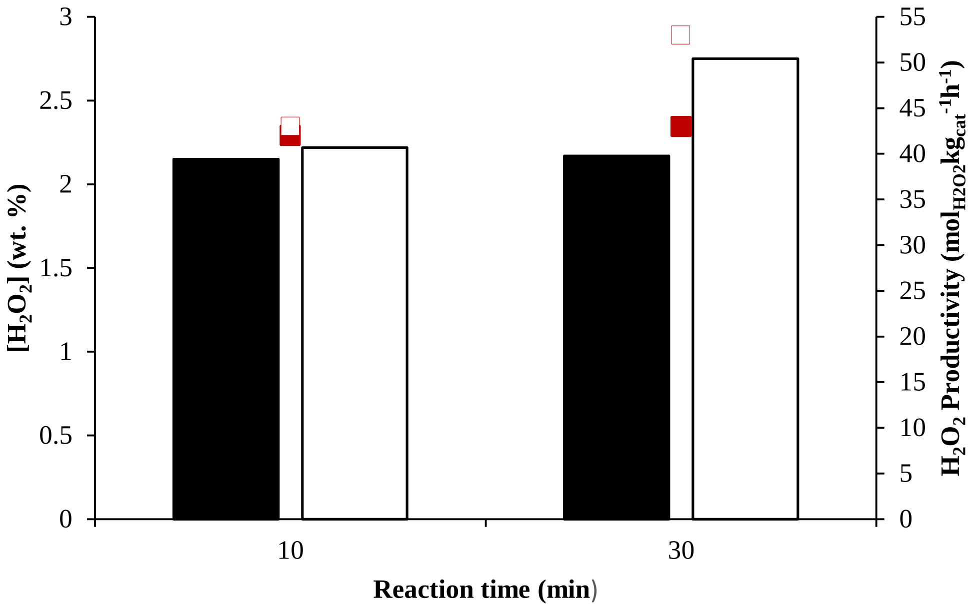


Figure 3.20	H_2O_2 concentration and productivity as a function of time and temperature at lower H_2:O_2 (0.113) ratios. ■ H_2O_2 concentration, 25 °C, □ H_2O_2 concentration, 10 °C, 🟥 H_2O_2 productivity, 25 °C, □ H_2O_2 concentration 10 °C.
Reaction conditions	5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.113), 1200 rpm, solvent loading (8.5 g (0.33 g H_2O, 8.17 g decan-1-ol)), temperature (10 and 25 °C), time (10 and 30 min).

The effect of lowering the temperature and H_2:O_2 ratio as a function of time was investigated. The results show these factors combined together did not enhance the H_2O_2 concentration and productivity as significantly for the reaction carried out at lower residence time. The importance of lowering the reaction temperature has been highlighted in previous studies[3, 8, 10, 13, 38] and as an effect the rates of H_2O_2 synthesis have increased immensely. However this effect, was not observed in this study at a lower residence time (10 min). It was thought that due to the viscosity of the liquid at shorter residence times there is diffusion limitation of the reactants into the solvent. Hence, there isn't enough time to produce increased concentrations of H_2O_2. However at higher residence times there is enough time for the reactants to diffuse into the solvent and therefore enhance the H_2O_2 concentration and productivity.

3.8.1.7 The effect of solvent mass and catalyst loading

One of the simplest ways to increase the concentration of H_2O_2 is by reducing the total amount of solvent in the reaction mixture. Figure 3.21 shows the concentration and productivity obtained using different volumes of solvent at different residence times.

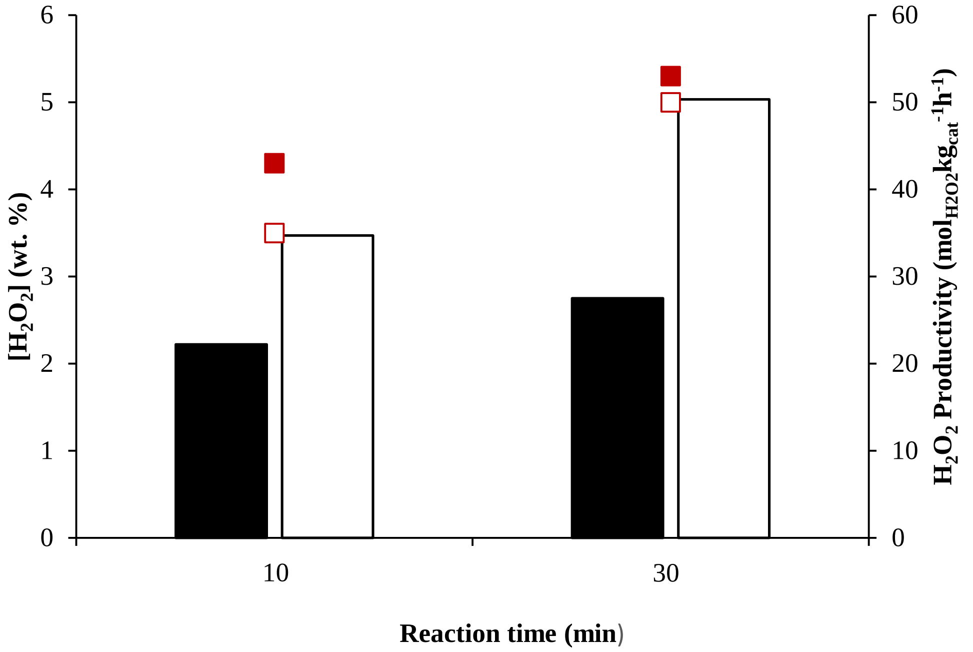


Figure 3.21 H_2O_2 concentration and productivity as a function of solvent mass.

■ H_2O_2 concentration, 8.5 g, solvent 10 °C,

□ H_2O_2 concentration, 4.25 g, solvent 10 °C,

🟥 H_2O_2 productivity, 8.5 g solvent, 10 °C,

□ H_2O_2 productivity, 4.25 g, solvent 10 °C.

Reaction conditions 5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.113), 1200 rpm, solvent loading (4.25 g and 8.50 g), 10 ºC, time (10 and 30 min).

Figure 3.21 shows how it is possible to enhance the concentration of H_2O_2 by decreasing the solvent mass. This was expected as the H_2O_2 is dissolved in a lower mass of H_2O hence the H_2O_2 solution will be more concentrated as the solvent mass is decreased. Since the greatest effect of temperature and H_2:O_2 was observed at higher residence times (30 minutes) from this point all experiments were carried out for 30 minutes.

Next the effect of catalyst loading was varied whilst keeping the solvent mass constant at 4.25 g.

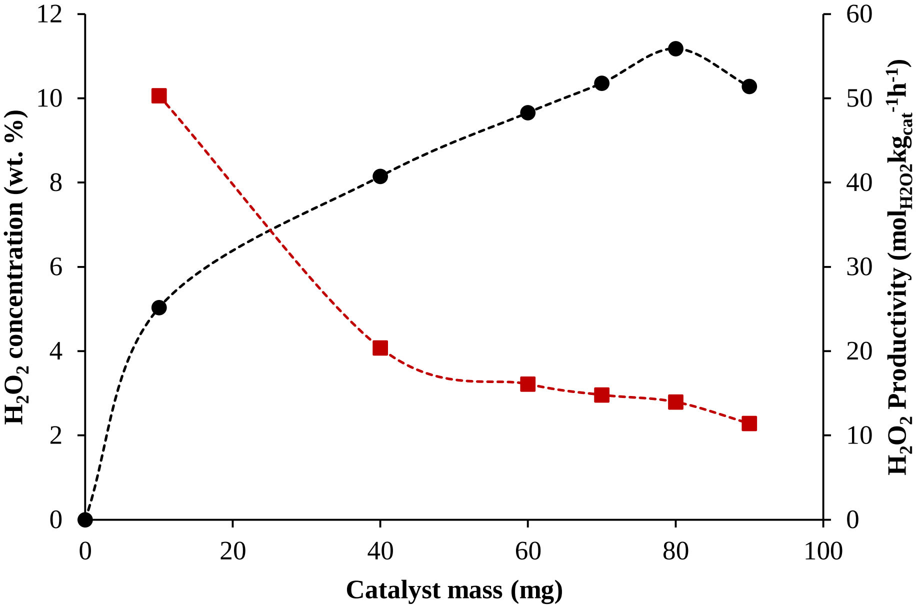


Figure 3.22 H_2O_2 concentration (●) and productivity (■) as a function of catalyst loading.

Reaction conditions 5%AuPd/HPA (0-90 mg), total pressure (580 psi), H_2/O_2 (0.113), 1200 rpm, solvent loading (4.25 g (0.17 g H_2O, 4.08 g decan-1-ol), 10 °C, 30 min.

Figure 3.22 shows as the catalyst loading is increased the concentration of H_2O_2 also increases. A maximum concentration of 11.18 wt. % is produced when 80 mg of catalyst is used. There is a decrease in H_2O_2 productivity with an increase in catalyst mass which could be due to two reasons; (i) there is not enough reagent gases being provided to the catalyst surface for it to work at maximum efficiency; (ii) the decan-1-ol is not able to retain the catalyst forcing a higher concentration of catalyst into the water phase, thus increasing the hydrogenation contribution.

3.8.1.9 Optimum Reaction conditions for 5%AuPd/HPA in the decan-1-ol - water system

Based on the set of reactions carried out it is possible to define a new set of reaction parameters, required to produce the highest possible H_2O_2 concentration (11.18 wt. %) after optimisation of reaction parameters using a 5%AuPd/HPA catalyst.

Table 3.13 Optimum reaction conditions for 5%AuPd/HPA catalyst.

Conditions	**AuPd/HPA**
Solvent decan-1-ol (wt.% H_2O)	0.39
Solvent mass (g)	4.25
Catalyst loading (mg)	80
Time (min)	30
Stirring speed (rpm)	1200
Total pressure (psi)	580
Conversion (%)	54
H_2 Selectivity (%)	55

3.9 Separation Experiments

Since all experiments were conducted using saturated decan-1-ol, the H_2O_2/H_2O phase was in close contact with decan-1-ol phase. In order to see how much water is required to physically separate and extract the H_2O_2/H_2O phase from the decan-1-ol phase, excess water was added to saturated decan-1-ol which contained a known concentration (24 wt. %) of H_2O_2 ((4.08 g decan-1-ol, 0.17 g 24 wt. % H_2O_2)). Three individual experiments were carried out where increasing masses of water (0.17 g, 0.33 g and 0.85 g) were added to the saturated decanol-H_2O_2 mixture. After each experiment the H_2O_2 concentration in the water phase was determined via titration of the separated water phase. This value was compared to the actual amount of H_2O_2 present in the water calculated using the dilution equation (equation 3.2).

$$C_1 \times V_1 = C_2 \times V_2 \qquad \text{Equation 3.2}$$

where:

C_1 = Initial concentration or molarity.

V_1 = Initial volume.

C_2 = Final concentration or molarity.

V_2 = Final volume

The results are given in figure 3.23.

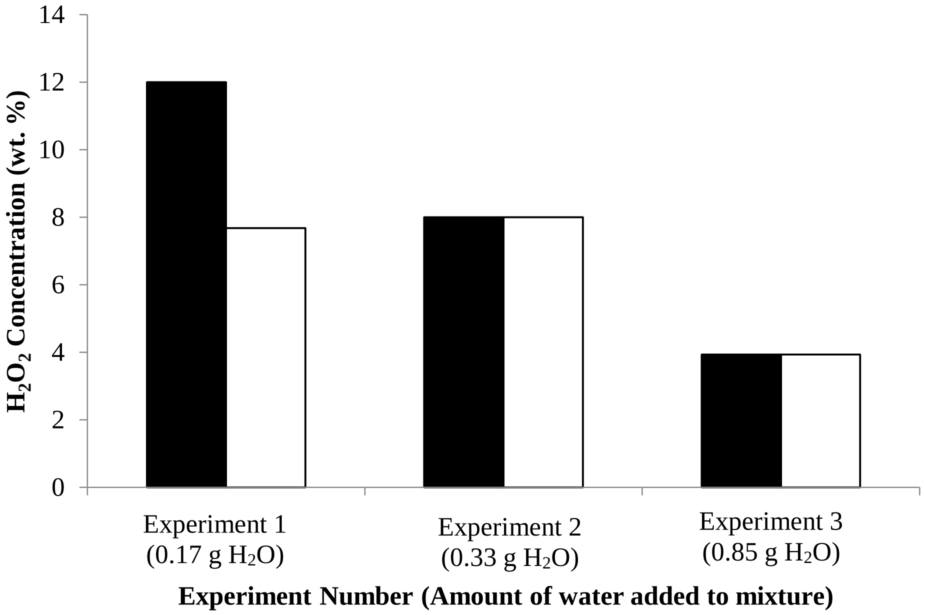


Figure 3.23 H_2O_2 extraction experiments. Effect of water addition on the amount of H_2O_2 extraction. ■ H_2O_2 concentration calculated using equation 3.2 and □ H_2O_2 concentration in water phase determined through Ce $(SO_4)_2$ titration on a separated aqueous sample.

Depending on the amount of water added to the saturated decan-1-ol-H_2O_2 mixture the final H_2O_2 concentration determined after extraction varied. For the first experiment (0.17 g of water was added to saturated decan-1-ol-H_2O_2 solution) a 36% of discrepancy was observed from the calculated value whereas for the second and third experiments 0% discrepancy was observed. Figure 3.23 shows that when 0.33

g of water is added to saturated decan-1-ol (experiment 2) it was possible to separate and extract all of the H_2O_2. The maximum concentration of H_2O_2 which can be extracted after these separation experiments is 8 wt. %. The addition of more water in experiment 3 (0.85 g H_2O) provides easier separation of water/H_2O_2 from the decan-1-ol phase but it also led to less concentrated H_2O_2 solutions (3.94 wt. %).

3.10 Factors influencing the hydrogenation activity

Although a maximum concentration of 11.18 wt. % was achieved using the 5%AuPd/HPA catalyst, the high hydrogenation activity observed by this catalyst is a major problem for the biphasic system and will be addressed in the next part of this chapter.

3.10.1 The effect of stirring speed

All reactions up in until now were conducted at a stirring speed of 1200 rpm. The high stirring speeds could be responsible for forcing the catalyst into the aqueous phase and thus increasing the H_2O_2 degradation rate whilst decreasing the synthesis rate. The effect of stirring speed with temperature as well as the addition of acid were investigated in an attempt to lower the H_2O_2 degradation activity in the new system.

3.10.1.1 The effect of stirring speed and temperature

The effect of stirring speed on the hydrogenation activity was evaluated at room temperature and 10 ºC. The results are shown in figure 3.24

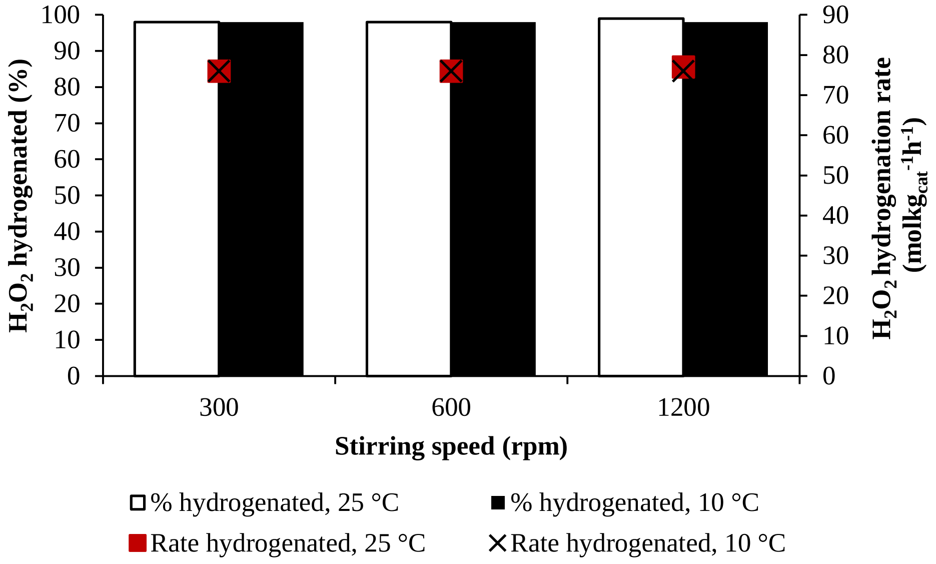
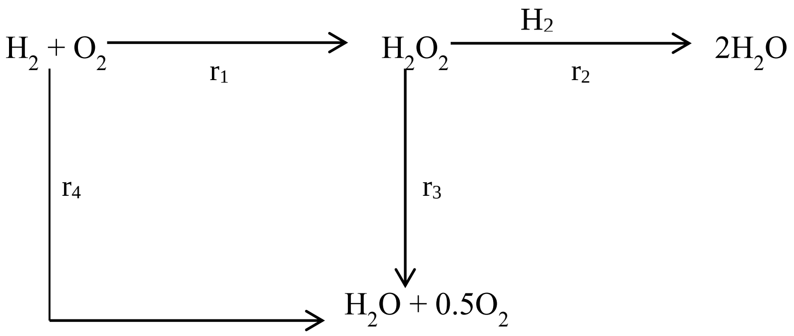


Figure 3.24	H_2O_2 hydrogenated at different stirring speeds and reaction temperatures.
Reaction Conditions	5%AuPd/HPA (10 mg), total pressure (5% H_2/CO_2 420 psi), stirring speed (300-1200 rpm), solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 10-25 ºC, 30 min.

Figure 3.24 shows that conducting reactions at a lower temperature and stirring speed did not influence the hydrogenation activity and the hydrogenation activity was still equal to or greater than 98%; so the effect of acid was evaluated next.

3.10.1.2 The effect of acid

One of the serious problems associated with the direct synthesis of H_2O_2 is that the catalysts used for this reaction have an unwanted catalytic activity for H_2 oxidation to water (r_4), decomposition (r_3) and hydrogenation (r_2) of H_2O_2.



This ability can be inhibited by adding acid and halide promoters to the reaction medium. [8,15,16,23-24,39-53]. Studies have shown how the addition of halides/acids is beneficial for lowering the rate of H_2O_2 degradation in the direct synthesis of H_2O_2 and in particularly most of the early studies on the direct synthesis of H_2O_2 were focussed on the addition of acid to the reaction media. [8,15,16,23-24,39-53,] Keeping this in mind the hydrogenation and decomposition activity was evaluated in the presence of acids.

Table 3.14 % H_2O_2 degraded in the presence of acids.

Acid	**Reaction**	**No Acid**	**0.1M**	**0.5M**	**1M**
Nitric Acid	Hydrogenation	98^b	97^b	97^b	98^b
	Decomposition	11^a 11^b		4^b	
Phosphoric Acid	Hydrogenation	98^b	97^b	97^b	97^b

Reaction Conditions 5%AuPd/HPA (10 mg), total pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 30 min 25 ºC,^{a}10 ºC ^{b}.

The results show that adding acids to the reaction media did not lower the hydrogenation activity however it did have a subtle effect on the decomposition activity. It has been demonstrated in several papers and patents that the presence of oxoacids drastically reduce the H_2O_2 decomposition activity[53] as the role of the H^+ ions is reported to reduce the base catalysed H_2O_2 decomposition [54-68] Previously the use of low concentration acidic/halide mediums have led to subtle effects in lowering the activity of the subsequent reactions however with re-use of the catalyst the promotion observed due to the addition of the halide/acid is not retained [9, 46] When this is coupled with the increasing desire to avoid the use of harmful and toxic additives that can require costly removal from the reaction medium, as well as lead to reactor corrosion and active metal leaching, it is clear that the use of such materials should be avoided and a more greener alternative route should be considered.

The results from table 3.14 show the rate of H_2O_2 decomposition is slower than the rate of hydrogenation. Since all the H_2O_2 is hydrogenated in the reaction medium the results suggest the reaction is mass transfer limited due to not enough reactant, H_2O_2 in this case, present in the reaction. In order to investigate further the effect H_2O_2 concentration on the rate of H_2O_2 hydrogenation was studied.

3.10.2 The effect of H_2O_2 concentration on hydrogenation activity

Up to this point all experiments were conducted with 4 wt. % H_2O_2, it was thought that if small amounts of H_2O_2 are present in the reaction system it is possible that all the H_2O_2 present in the reaction medium will degrade in 30 minutes. Therefore in order to see the effect of H_2O_2 hydrogenation on high concentrations of H_2O_2, the effect of H_2O_2 hydrogenation was investigated as a function of H_2O_2 concentration. The reactor was charged with 5%AuPd/HPA (10 mg) and decan-1-ol-water (8.5 g) containing various concentrations of H_2O_2 (1-20 wt. %). The reactor was pressurised with 5% H_2/CO_2 (420 psi) and the rate of H_2O_2 hydrogenation was studied in 30 minutes. The results are given in figure 3.25.

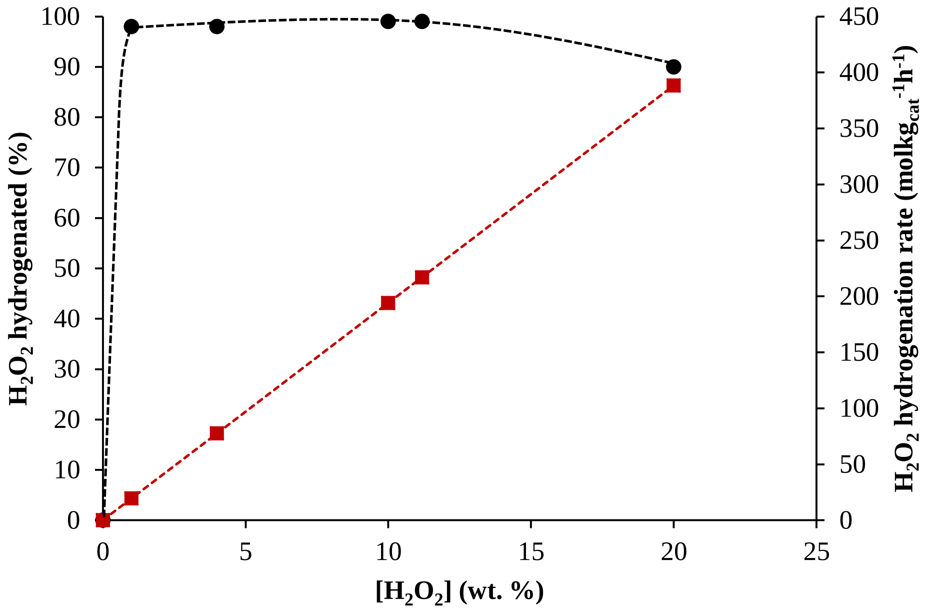


Figure 3.25 H_2O_2 hydrogenated as a function of H_2O_2 concentration.

% H_2O_2 hydrogenated (●) H_2O_2 hydrogenation rate (■)

Reaction conditions 5%AuPd/HPA (10mg), total 5 % H_2/CO_2 pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 1-20 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 30 min.

It is well known that as the concentration of H_2O_2 increases the rates of H_2O_2 hydrogenation also increase and the results in figure 3.25 also illustrate this. Figure 3.25 also show the % H_2O_2 hydrogenated as a function of H_2O_2 concentration. When lower H_2O_2 concentrations (1-11.18 wt. %) were added to the hydrogenation experiments, the amount of H_2O_2 hydrogenated in the reaction was greater than 96 %. However when a higher concentration of H_2O_2 (20 wt. %) was added to the reaction medium there was a marginal drop in the overall amount of H_2O_2 hydrogenated to 90%. Since there is a greater amount of H_2O_2 present in the latter experiment there is a possibility that a small amount of it will survive at the end of the 30 minute reaction, hence the lower hydrogenation activity of 90%. Even though there was a marginal drop in the amount of H_2O_2 hydrogenated the results show the 5%AuPd/HPA catalyst is extremely active for the hydrogenation reaction.

3.10.3 Consecutive direct synthesis-hydrogenation reaction

Figure 3.22 (page 100) shows that thus far the maximum amount of H_2O_2 produced in the decan-1-ol-water system is 11.18 wt. %. However figure 3.25 (page 106) shows that when 11.18 wt. % H_2O_2 is added to the reaction mixture to conduct a hydrogenation experiment all the H_2O_2 in the system degrades. Since standard hydrogenations are carried out with commercially synthesised H_2O_2 an experiment was performed where a direct synthesis experiments was carried out using the optimum H_2O_2 conditions to produce 11.18 wt. %. As soon as the direct synthesis reaction was finished after 30 minutes, the gases were vented and the reaction vessel was filled with 5%H_2/CO_2 (420psi) to conduct a standard H_2O_2 hydrogenation experiment. After 30 minutes it was found that all the H_2O_2 in the system had been destroyed. This suggests that the rate of direct synthesis is faster than the rate of hydrogenation.

3.10.4 Comparing the hydrogenation reaction conditions used in the methanol-water and decan-1-ol water system

All experiments in this report prove that the biphasic system may be feasible towards the finding of a new H_2O_2 synthesis pathway that could overtake the current indirect process. The 5 %AuPd/HPA catalyst was found to be the best candidate for the direct synthesis pathway and a concentration of 11.18 wt. % H_2O_2 was obtained after optimisation of reaction conditions.

Although high concentrations of H_2O_2 were obtained with the 5%AuPd/HPA catalyst the hydrogenation activity is extremely high. Despite trying several methods to lower the hydrogenation activity the catalyst still destroyed almost all H_2O_2 in the reaction medium. Both 5% AuPd/A.W carbon and 5% AuPd/HPA hydrogenated H_2O_2 in the new system. This was a surprising results for the former since this catalyst is known to have zero hydrogenation in the methanol-water system. A few suggestions to why the hydrogenation activity may be much lower in the methanol-water system than the decan-1-ol-water system are listed below

i) Methanol is known to stabilise H_2O_2 as Melada *et al*.[50] have reported that formation of surface formate species in methanol can block the most reactive Pd sites responsible for HO-OH bond breaking

ii) The solubility of the reactant gases maybe different in the methanol-water and Decan-1-ol-water solvent system and this may result in different direct synthesis and hydrogenation activity in both systems.

iii) The reaction conditions are different in both methanol-water and decan-1-ol-water systems.

In order to get a better understanding of the rates of H_2O_2 hydrogenation in the decan-1-ol-water system, the reaction conditions used were compared to those of the methanol-water system. The difference in reaction conditions are illustrated in figure 3.26.

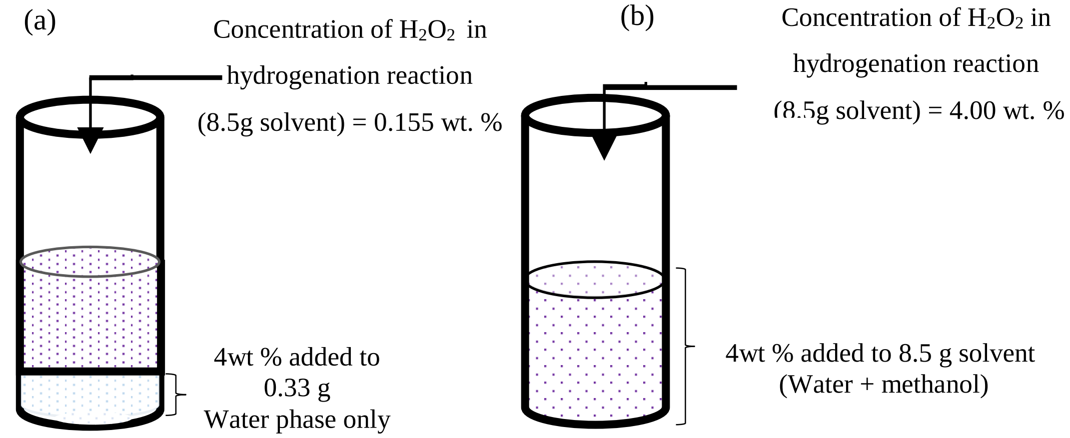


Figure 3.26 A schematic comparing the hydrogenation reaction conditions used in the a) decan-1-ol water system and b) methanol-water system

As apparent from figure 3.26 a greater amount of H_2O_2 is added in methanol-water experiments than the decan-1-ol-water experiments (4wt. % vs. 0.155 wt. % respectively). In order to investigate further, hydrogenation experiments were conducted in the methanol-water system using the decanol-water hydrogenation conditions (i.e. 0.155 wt. % H_2O_2 in the hydrogenation reaction), the results are show in table 3.15.

Table 3.15 H_2O_2 hydrogenated in methanol-water and decan-1-ol-water system

H_2O_2 hydrogenated	**methanol-water system**	**decanol-water system**
%	99	99
$molkg_{cat}^{-1}h^{-1}$	77	77

Reaction conditions	5%AuPd/HPA (10 mg), 5%H_2/CO_2 (420 psi), solvent loading (8.5 g (0.33 g of 4 wt. % H_2O_2 in aqueous, 8.17 g alcohol)), 1200 rpm, 25 °C, 30 min.

When the hydrogenation conditions for the decan-1-ol-water system were used in the methanol-water system it was found that the 5%AuPd/HPA catalysts hydrogenated all the H_2O_2 in the system. However one thing to note is the H_2O_2 hydrogenation activity in the methanol-water and decan-1-ol-water system cannot be compared if all the H_2O_2 in both systems is being destroyed. In order to find a condition where hydrogenation was not 100%, the effect of catalyst mass and reaction time were investigated.

3.10.4.1 The effect of catalyst mass and reaction time on H_2O_2 hydrogenation

In order to find a condition where the system wasn't over hydrogenating the effect of catalyst mass on the rate of H_2O_2 hydrogenation was investigated and the results are given in figure 3.27.

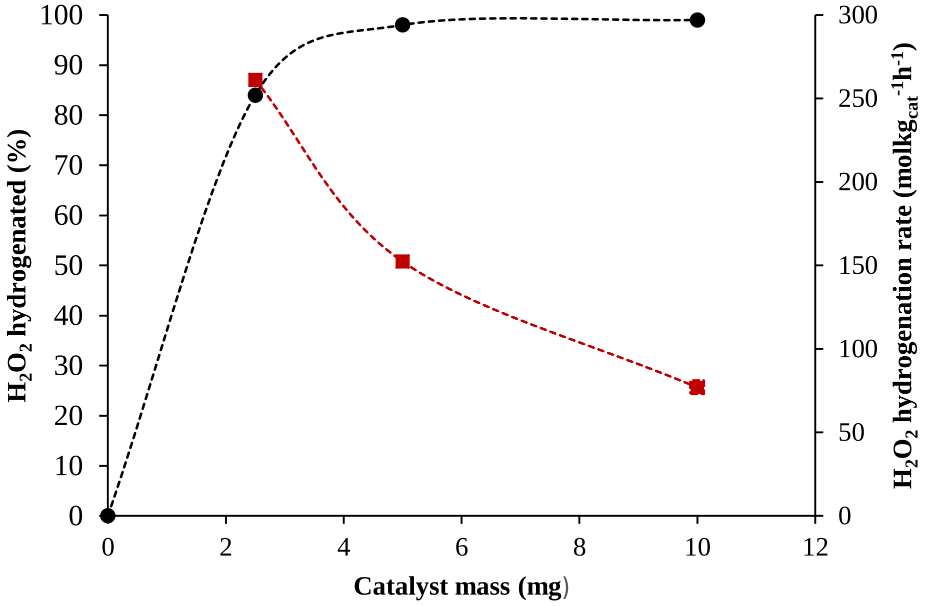


Fig 3.27 Effect of catalyst mass on H_2O_2 hydrogenation

% H_2O_2 hydrogenated (●) H_2O_2 hydrogenation rate (■)

Reaction Conditions 5%AuPd/HPA (0-10 mg), total 5% H_2/CO_2 pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol), 25 °C, 30 min.

Figure 3.27 shows as the catalyst mass increases the overall rate of H_2O_2 hydrogenation decreases. These results suggest the amount of H_2O_2 present in the system is limiting the catalysts activity. Figure 3.27 also illustrates the effect of catalyst mass on the % H_2O_2 hydrogenated. Up to this point all hydrogenation experiments have been conducted using 10 mg of catalyst. When 10 mg of catalyst was used 99 % of the H_2O_2 present in the reaction medium was destroyed. Figure 3.27 shows when the catalyst mass is reduced to 5 mg the amount of H_2O_2 hydrogenated still remains very high (93%). However when the catalyst mass is reduced to 2.5 mg the amount of H_2O_2 hydrogenated in the reaction medium lowers to 85%. The effect of reaction time on the rate and % of H_2O_2 hydrogenation was therefore investigated using 2.5 mg of catalyst, the results are given in figure 3.28.

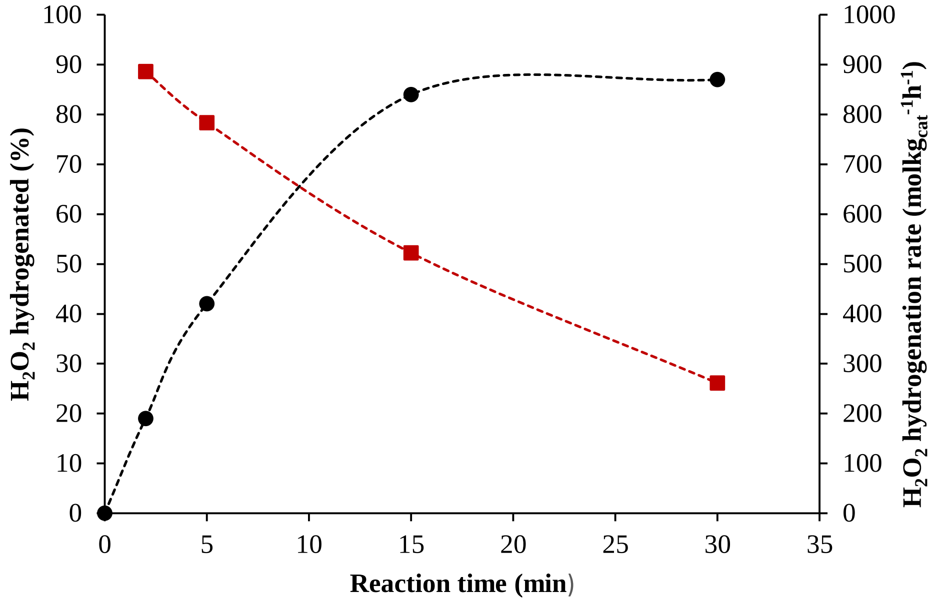


Figure 3.28 Effect of reaction time on H_2O_2 hydrogenation using 2.5 mg catalyst. % H_2O_2 hydrogenated (●) H_2O_2 hydrogenation rate (🟥)

Reaction Conditions 5%AuPd/HPA (2.5 mg), total H_2/CO_2 pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 25 ºC, 0-30 min.

Figure 3.28 shows as the reaction time increases the rate of H_2O_2 hydrogenation decreases. This is due to the overall concentration of H_2O_2 decreasing in the system as illustrated previously in figure 3.25. Furthermore figure 3.28 also shows the effect of reaction time on % H_2O_2 hydrogenated. At higher reaction times (15-30 minutes) ~85 % of the H_2O_2 in the reaction medium is hydrogenated. However as the reaction time is lowered (2-5 minutes), the amount of H_2O_2 hydrogenated decreases. Conducting hydrogenation experiments for 2 minutes using 2.5 mg of catalyst can lower the amount of H_2O_2 hydrogenated to 19%.

3.10.4.2 Comparison of H_2O_2 hydrogenation in the decan-1-ol-water and methanol-water system

Once a suitable condition (5%AuPd/HPA (2.5 mg), total 5% H_2/CO_2 pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g decan-1-ol,), 25 ºC, 2 minutes) was found where the hydrogenation wasn't ~100%, the rate of hydrogenation in both methanol-water and decan-1-ol-water system was compared. The results are shown in figure 3.29

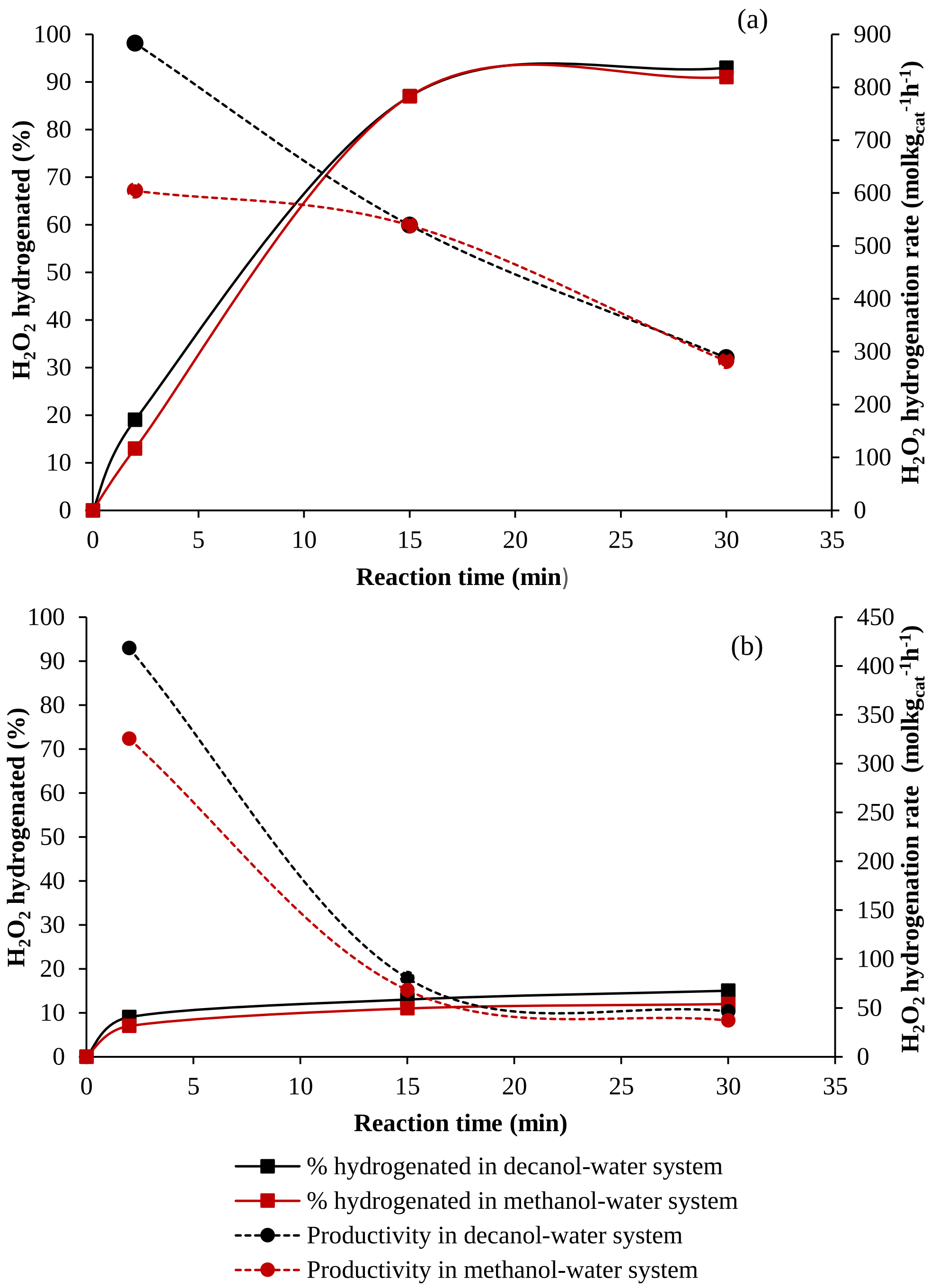


Figure 3.29 Evaluation of H_2O_2 hydrogenation in the methanol water and decan-1-ol-water system (a) 5%AuPd / HPA (b) 5 AuPd/ A.W. Carbon.

Reaction Conditions Catalyst (2.5 mg), total 5% H_2/CO_2 pressure (420 psi), 1200 rpm, solvent loading (8.5 g (0.33g of 4 wt. % H_2O_2 in aqueous, 8.17 g alcohol), 25 ºC

As the reaction time increased from 2 – 30 minutes the rates of H_2O_2 hydrogenation decreased for both catalysts. This suggests that H_2 and/or H_2O_2 maybe a limiting reagent in the system at higher residence times, therefore resulting in a dramatic drop in the overall rate of H_2O_2 hydrogenation. At shorter residence times the rates of H_2O_2 hydrogenation were higher in the decanol-water system than the methanol water system with both catalysts. This can be attributed to the higher solubility of H_2 in higher chain alcohols[35-36] which suggest at shorter reaction times H_2 is more soluble and less mass transfer limited in the decanol-water system than the methanol-water system. This can possibly lead to marginally higher rates of H_2O_2 hydrogenation in the former system.

When the % H_2O_2 hydrogenated for both 5 % AuPd/A.W.Carbon and 5 % AuPd/HPA were compared in the methanol-water and decan-1-ol-water system very similar hydrogenation values were observed in both systems. It therefore can be concluded the high hydrogenation activities observed in the first part of this chapter were due to their only being very small amounts of H_2O_2 present at the beginning of the reaction. As a result all the H_2O_2 was hydrogenated by the 10 mg of catalyst within 30 minutes. Higher rates of hydrogenation were observed with the 5%AuPd/HPA catalyst in comparison to the 5%AuPd/A.W. Carbon catalyst, these results are consistent with those reported previously in literature.[31-33]

3.11 The effect of diluent

Up until this point all previous experiments were conducted using 5 % H_2/CO_2 and 25% O_2/CO_2 as the reagent mixtures. However from an industrial point of view using N_2 as the diluent would be more beneficial as it would decrease the overall costs by ~ 37%. Therefore experiments were performed using N_2 as the diluent and the results are shown in table 3.16.

Table 3.16 Experimental results for 5%AuPd/HPA and 5%AuPd/A.W.Carbon using different reagent gases.

Entry	**Reagent sources**	**Total Pressure (psi)**	**H_2:O_2**	**H_2O loading (g)**	**Decan-1-ol loading (g)**	**Catalyst loading (mg)**	**Time (min)**	**[H_2O_2] (Wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
	5%AuPd/HPA								
1	5%H_2/CO_2 -25%O_2/CO_2	580	0.525	0.33	8.17	10	30	1.05	21
2	5%H_2/N_2 - 25%O_2/N_2	580	0.525	0.33	8.17	10	30	0.57	11
3	5%H_2/CO_2 - 25%O_2/CO_2	580	0.113	0.17	4.08	80	30	11.18	14
4	5%H_2/N_2 - 25%O_2/N_2	580	0.113	0.17	4.08	80	30	3.51	4
	5%AuPd/A.W.Carbon								
5	5%H_2/CO_2 -5%O_2/CO_2	580	0.525	0.33	8.17	10	30	0.29	6
6	5%H_2/N_2 - 25%O_2/N_2	580	0.525	0.33	8.17	10	30	0.22	4
7	5%H_2/CO_2 -25%O_2/CO_2	700	0.525	0.33	8.17	10	30	0.99	19
8	5%H_2/N_2 - 25%O_2/N_2	700	0.525	0.33	8.17	10	30	0.41	8

Under the standard reaction conditions using N_2 instead of CO_2 (table 3.16, entries 2 and 6) resulted in a significant decrease in H_2O_2 concentration. For the 5%AuPd/HPA and 5%AuPd/ A.W Carbon the H_2O_2 concentration dropped from 1.05 wt. % to 0.57 wt. % and 0.29 wt. % to 0.22 wt. % respectively. It is well known that acidic solutions are added to direct synthesis reaction media to both stabilise and enhance H_2O_2 in the direct synthesis. However Edwards *et al*.[69] have shown that if CO_2 is used as the diluent the addition of promoters such as halides or acids isn't required to AuPd catalysts since the CO_2 diluent acts as an *in-situ* promoter by forming carbonic acid and acting as a stabilizer. This can explain the higher H_2O_2 activities observed when using CO_2 as the diluent. In order to investigate further, the optimum reaction conditions for 5%AuPd/HPA (table 3.16, entry 3-4) and 5%AuPd.A.W.Carbon (table 3.16, entry 7-8) were employed. Once again a dramatic decrease in H_2O_2 concentration was observed when N_2 was used as the diluent. These results further support the important role of CO_2 in stabilising and enhancing H_2O_2 in the direct synthesis reaction.

3.12 Industrial solvents for the biphasic solvent system

A number of solvents which are used for the synthesis of H_2O_2 in the current AO process were provided by Solvay® and these were screened using 5%AuPd/HPA catalyst. The reactivity of these solvents was evaluated against the decan-1-ol system and the results are given in Table 3.17.

Table 3.17 Catalytic activity 5%AuPd.HPA catalyst using different industrial solvents

Entry	**Solvent**	**$[H_2O_2]$ (Wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
1	Solvesso	0.0158	8
2	Sextate	0.0094	5
3	Diisobutyl Carbinol	0.0291	15
4	Decan-1-ol	0.0295	15
5	Saturated Decan-1-ol	1.06	21

Reaction conditions Catalyst (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 ºC, 30 min.

When industrial solvents Sextate and Solvesso (Table 3.17, entries 1-2) were used for the synthesis of H_2O_2 extremely low results were obtained. However when diisobutyl carbinol (DBC) was used very similar results to decan-1-ol were achieved. As previously shown in Section 3.7.1 and 3.8.1.1 it is possible to further increase the H_2O_2 concentration by varying the decan-1-ol-water ratio. In order to see if the addition of water and its ratio had an effect on H_2O_2 concentration the ratio of DBC-water was investigated whilst keeping the total solvent mass constant at 8.5 g. The results are shown in figure 3.30.

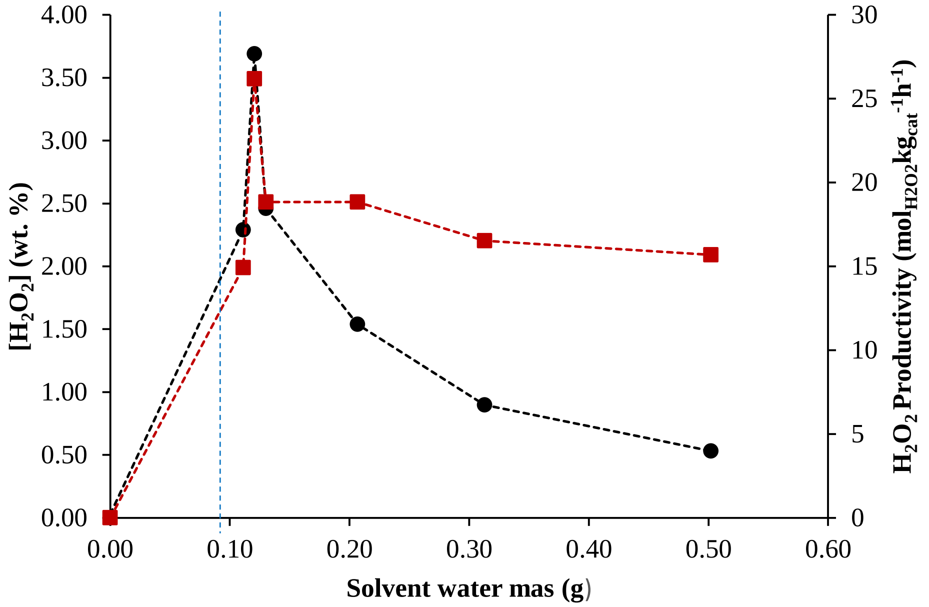


Figure 3.30 H_2O_2 concentration (●) and productivity (■) as an effect of solvent water mass.

Reaction conditions 5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (8.5 g), 25 °C, 30 min.

The results in figure 3.30 clearly show that the DBC-water ratio is indeed an important parameter and the optimal ratio is 8.38 g DBC and 0.12 g water. By using the optimum DBC-water ratio it is possible to produce a H_2O_2 concentration and synthesis rate of 3.69 wt. % and 26 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$ respectively. The H_2O_2 synthesis rate appears to be very sensitive around the optimal point. Increasing the water concentration above the optimal value leads to a decrease in the rate of H_2O_2 synthesis. After which the rate of H_2O_2 synthesis remains fairly constant between 0.13 g and 0.50 g solvent water mass. Equally a dramatic decrease in H_2O_2 concentration is observed above the optimal DBC-water ratio. Although the rates of H_2O_2 synthesis are fairly constant between 0.13 g and 0.50 g solvent water mass, the H_2O_2 concentration drops dramatically between these points and this can be attributed to H_2O_2 being dissolved in a larger amount of water.

Karl Fischer titrations were conducted to determine the water content in saturated DBC. The saturation point is highlighted by the dotted blue line at 0.095 g in figure 3.30. The saturation point of DBC was found to be below the optimum DBC-water ratio which means that the optimum DBC-water ratio is truly a biphase system. Unlike the decan-1-ol-water system (section 3.9) an excess of water is not required to physically separate the organic phase from the aqueous phase in the DBC-water system.

3.12.1 Screening DBC using the optimum reaction conditions

The optimum decan-1-ol-water reaction conditions for 5%AuPd/HPA and 5%AuPd/A.W Carbon are highlighted in table 3.7 and Table 3.8 respectively. These conditions were used along with the optimum DBC-water ratio (0.12 g H_2O and 8.38 g DBC) to study the direct synthesis of H_2O_2 with the 5%AuPd/HPA and 5%AuPd/A.W. Carbon catalysts. The results are given in Table 3.18.

Table 3.18 Direct synthesis activity using the optimum DBC-water ratio

Catalyst	**Decanol**	**water system**	**DBC**	**Water system**
	$[H_2O_2]$ (wt. %)	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**	**$[H_2O_2]$ (wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
5%AuPd/AWC[a]	0.71	2	1.39	1
5%AuPd/HPA[b]	11.18	14	23.37	10

Reaction Conditions [a] 5%AuPd/A.W. Carbon (40 mg), total pressure (580 psi), H_2/O_2 (0.525), 1200 rpm, solvent loading (4.25 g), 25 ºC, 30 min.

[b] 5%AuPd/HPA (10 mg), total pressure (580 psi), H_2/O_2 (0.133), 1200 rpm, solvent loading (4.25 g), 10 ºC, 30 min.

The results show that the concentration of H_2O_2 can be increased by ~ 2 folds if decan-1-ol-water is replaced with DBC-water. Remarkably a significantly high H_2O_2 concentration of 23.37 wt. % was obtained with the 5%AuPd/HPA catalyst in the DBC-water system. Of course the optimal conditions for DBC-water will vary from decan-1-ol-water for both catalysts and so it can be reasonably anticipated that at the optimal conditions for DBC-water much higher concentrations of H_2O_2 will be attained.

3.12.3 Further investigation using the 5%AuPd/HPA catalyst

3.12.3.1 The effect of reaction temperature using 5%AuPd/HPA

Since decan-1-ol freezes at 6.4 ºC the lowest temperature at which reactions were conducted were 10 ºC. However the freezing point of DBC is below 0 ºC. In order to see how much further the H_2O_2 concentration can be increased using 5%AuPd/HPA, the effect of reaction temperature using 5%AuPd/HPA and DBC-water was investigated. The results are given in Table 3.19.

Table 3.19 H_2O_2 concentration and productivity as a function of reaction temperature

Temperature (ºC)	**H_2O_2 Concentration (wt. %)**	**H_2O_2 Productivity ($mol_{H2O2}kg_{cat}^{-1}h^{-1}$)**
23	19.00	8
10	23.37	10
2	28.92	13

Reaction conditions 5%AuPd/HPA (80 mg), total pressure (580 psi), H_2/O_2 (0.113), 1200 rpm, solvent loading (4.25 g), 2-23 ºC, 30 min.

The results in table 3.19 show the H_2O_2 productivity and concentration increase with a decrease in temperature and a phenomenal H_2O_2 concentration of 28.92 wt. % is achieved at 2 ºC. These results show that the biphasic DBC-water system is extremely promising as high H_2O_2 concentrations can be obtained. The initial studies conducted in this chapter are extremely promising confirming the important role that the direct synthesis may have in the near future.

3.13 Discussions

In this chapter the direct synthesis of H_2O_2 has been studied in a biphasic solvent system using decan-1-ol-water and DBC-water as the solvent mixtures. The results obtained showed that much higher (~ 2 folds) concentrations of H_2O_2 are obtained in the DBC-water solvent system in comparison to the decan-1-ol-water system. It is likely that the differences in H_2O_2 concentrations observed in the two systems occur due to the following factors:

i) *A difference in overall rate of mass transfer in the two systems.* As depicted in figure 3.3 (page 71), the overall rate of mass transfer in the direct synthesis of H_2O_2 is dependent on 3 crucial steps. Firstly the transfer of reactant gases from the gas phase to the liquid phase, secondly the transfer of gases from the liquid phase to the catalytic surface and finally the transfer of product from the catalytic surface into the liquid phase.

ii) *Varying amount of interaction between the catalyst and aqueous phase in the two systems.*

Although the exact solubility of the reactant gases is unknown in the reaction mixtures, Francesconi *et al.*[34] and Wainright *et al.*[35] have shown that the H_2 solubility in C1-C4 alcohols increases with increasing carbon chain length therefore it is reasonable to assume the solubility of H_2 would increase with increasing chain length of alcohol. The structures of decan-1-ol and diisobutyl carbinol are shown in figure 3.32.

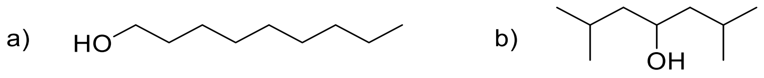


Figure 3.32 a) Structure of Decan-1-ol b) Structure of Diisobutyl Carbinol

Decan-1-ol ($C_{10}H_{21}OH$) is a straight chain fatty alcohol with ten carbon atoms whereas Diisobutyl carbinol ($C_9H_{19}OH$) which is also referenced as 2, 6, dimethyl-4- heptanol is a 7 carbon chain alcohol containing 2 methyl groups. Keeping in mind Francesconi[34] and Wainright's[35] work it would be reasonable to say that the solubility of the reactant gases would be greater in decan-1-ol than DBC. Nevertheless it is well known that the direct synthesis of H_2O_2 is strongly influenced by the rate of mass transfer which can be affected by several factors including: pressure, solubility of the gases and viscosity of the solvent system. Table 3.20 shows the comparison between DBC-water system and the decan-1ol-water system using the 5%AuPd/HPA and 5%AuPd/A.W. Carbon catalyst.

Table 3.20 Comparison of H_2O_2 concentrations in decan-1-ol-water and DBC-water using 5%AuPd/HPA and 5%AuPd/A.W. Carbon prepared by impregnation

Entry	**Catalyst**	**[H_2O_2] (wt. %) in Decan-1-ol-H_2O**	**[H_2O_2] (wt. %) in DBC-H_2O**
1	5% AuPd/A.W Carbon [a]	0.71	1.39
2	5%AuPd/HPA[b]	11.18	23.37

The experiments were conducted at the same pressures and reaction conditions for both solvent systems, therefore this factor is not contributing to the difference in activity. Though DBC is less viscous than decan-1-ol, therefore there is a possibility that the transfer of the reactants from the gas phase to the liquid phase/catalyst surface and the transfer of products from the catalyst surface to the liquid phase will be faster in the DBC-water system than the decan-1-ol-water system. If the direct synthesis of H_2O_2 is being conducted in a solvent system where the rate of mass transfer is faster it is more likely to produce increased concentrations of H_2O_2 in this system and the results shown in table 3.20 support this.

Furthermore the higher H_2O_2 concentration observed in the DBC-water system can also be attributed to the optimum alcohol-water ratio. In section 3.71 and 3.8.1.1 the optimum alcohol-water ratio for decan-1-ol-water system was 0.33g water and 8.17 g decan-1-ol; Karl Fischer titrations showed that this was the saturation point of decan-1-ol. On the other hand when similar experiments were conducted for the DBC-water system in section 3.12 the optimum ratio was found to be above the saturation point of DBC. This means the DBC-water system was present as a true biphase system, as required and hypothesised in figure 3.1.

As discussed previously the 5%AuPd/A.W. Carbon catalyst resides in the organic phase whereas the 5%AuPd/HPA catalyst resides on the interphase between the organic and aqueous phase. Since the DBC-water system was present as a biphase system the catalyst wouldn’t be in extreme contact with the aqueous phase hence as hypothesised in figure 3.1 the contact time between the catalyst and reactant gases with H_2O_2 will be minimal. This will diminish the contribution from the subsequent reactions resulting in higher concentrations of H_2O_2 as observed in the DBC-water system (table 3.20).

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Direct gas phase synthesis of H_2O_2 using a continuous gas flow reactor

4

4.1 Introduction

As already discussed in chapter 1, a great deal of research has been carried out to find alternative methods to produce H_2O_2 via the direct synthesis. However to date, the requirements for industrial scale plants of high H_2O_2 concentrations (5 wt. %) and high H_2 selectivity (> 90 %) have not yet been achieved.

Although the direct synthesis of H_2O_2 from H_2 and O_2 could be a viable alternative to replace the current anthraquinone process there are two major drawbacks. The first is safety, H_2/O_2 gas mixtures are explosive over a wide range of concentrations (5-95 v/v% for H_2 in O_2) and the explosive range is further widened with increasing pressure. In order to operate safely below the lower explosive limit H_2 and O_2 have to be diluted in inert gases such as CO_2 and N_2 which reduces the reaction rate and maximum possible concentration that can be formed. The second drawback is that catalysts active for the direct synthesis of H_2O_2 (figure 4.1, r_1) can also be active for the parallel combustion reaction (figure 4.1, r_4) as well as the subsequent hydrogenation and decomposition reactions (figure 4.1, r_2, r_3). All of these reactions are thermodynamically more favoured than the direct synthesis reaction, therefore leading to low H_2 selectivities.

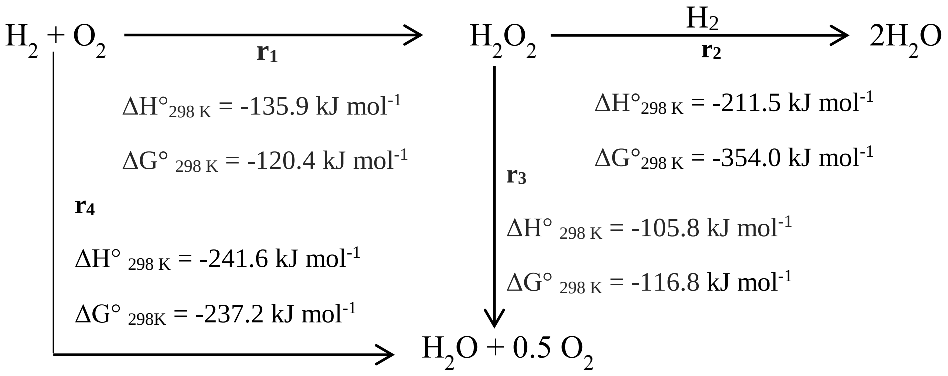

Figure 4.1 Schematic for the direct H_2O_2 synthesis (r_1) and its parallel (r_4) and consecutive (r_2, r_3) reactions.

To date the direct synthesis of H_2O_2 has been studied extensively in batch reactors such as high pressure autoclaves. In batch systems, the catalyst remains in close contact with the dissolved reagent gases and H_2O_2. As a result this can lead to increased decomposition and hydrogenation rates as higher concentrations of H_2O_2 are produced during the reaction. A key necessity for the direct synthesis of H_2O_2 to meet industrial requirements is high H_2 selectivity and the catalysts used in the reaction must have minimal or no activity for the side reactions.

These issues related to the direct synthesis of H_2O_2 can be resolved by designing catalysts which suppress the subsequent decomposition/hydrogenation activity leading to increased selectivity. An alternative approach to overcome this problem is to use a continuous flow reactor to produce H_2O_2. Using a continuous reactor the residence time can be controlled carefully which can minimize the contribution from the subsequent decomposition and hydrogenation reactions, resulting in higher productivities of H_2O_2. As illustrated in the hypothetic theoretical model in figure 4.2, an important reaction parameter which strongly influences the rates of H_2O_2 synthesis as well the non-selective side reactions is the residence time.

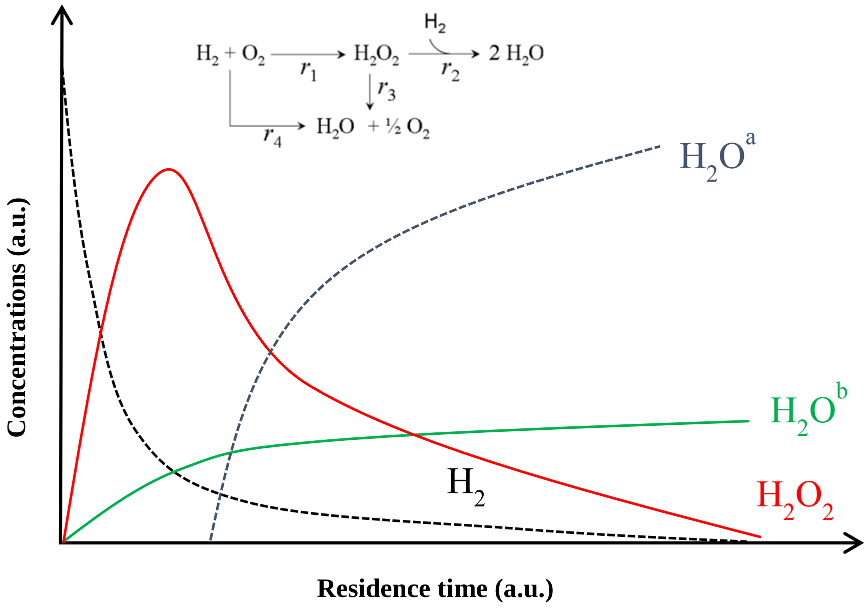

Figure 4.2 Effect of residence time on the concentration of H_2O_2 reactants and its products. Hypothetic theoretical model of the kinetics involved in the direct synthesis based on equation 4.1-4.4. Legend H_2O^a water formed during the subsequent hydrogenation of H_2O_2 and H_2O_2 decomposition, H_2O^b water formed during H_2 combustion.

$r_1 = k_1 [H_2]^a [O_2]^b$ Equation 4.1

$r_2 = k_2 [H_2]^c [H_2O_2]^d$ Equation 4.2

$r_3 = k_3 [H_2O_2]^e$ Equation 4.3

$r_4 = k_4 [H_2]^f [O_2]^g$ Equation 4.4

If we carefully tune the contact time between the reactants and catalyst we can control and suppress the competing subsequent reactions. Figure 4.2 shows the effect of residence time on the concentration of reactants and products. At short residence times the conversion of H_2 is low however the main product of reaction is H_2O_2 which results in high H_2 selectivities. Although there is no contribution from the consecutive reactions at short residence times, small amounts of water are produced via the direct combustion of H_2 because the combustion of H_2 is dependent on the H_2 and O_2 concentration (equation 4.4).

At higher residence times the concentration of H_2O_2 starts to build up and the contribution from these subsequent reactions becomes more pronounced. This is because the consecutive hydrogenation (equation 4.2) and decomposition (equation 4.3) reactions are dependent on H_2O_2 concentrations. As the subsequent reactions become more prominent with increasing residence times the rate of H_2O_2 consumption becomes greater than the rate of H_2O_2 formation this will result in an overall decrease in H_2O_2 concentration and selectivity at higher residence times. As apparent from figure 4.2 the control of the residence time is key in achieving high yields and selectivities of H_2O_2.

Small scale fixed bed reactors[1-5] have been employed to study the direct synthesis of H_2O_2 in a continuous mode using 3 phase systems, however the selectivities and conversion obtained thus far are below the targets industrially required. If the direct synthesis of H_2O_2 is studied in a continuous mode in the gas phase only, the issues related to mass transfer limitations of the gas-liquid-solid interfaces, observed in a 3 phase reaction system can be avoided as the products and reactants will all be in the same phase.

Although majority of the work carried out on the direct synthesis of H_2O_2 has been conducted in a 3 phase system a great deal of research has been carried on the oxidation of propene to propene oxide (PO) in the gas phase.[6-17] The oxidation of propene to PO is highly desired as PO is an important commodity chemical used in the manufacture of polyols as well as polyurethane. The direct gas-phase synthesis of PO using molecular O_2 has long been desired. However, one of the major problems associated with the vapour phase oxidation of propene to PO using molecular O_2 is low reaction selectivity. Since a commercial process for the direct oxidation of propene with dioxygen has proved to be challenging many research groups have advanced in designing a promising alternative process for the epoxidation of propene. The Hydrogen Peroxide Propene Oxide (HPPO) process allows production of PO via a direct reaction between propene and H_2O_2 over a titanium silicate (TS-1) catalyst. Attempts have been made to replace H_2O_2 by employing a mixture of O_2 and H_2 that generate H_2O_2 *in situ*. Haruta and co-workers[6-7] were the first to demonstrate that highly dispersed Au/TiO_2 catalysts show an extraordinary selectivity in the oxidation of propene to the corresponding epoxide (> 99 %), using a combination of H_2 and O_2 as oxidant. H_2 aided as a sacrificial reductant which permits the activation of molecular O_2 at relatively low temperatures (303-393 K) and therefore allowing selective oxidation of propene to PO.

An alternative method to produce H_2O_2 is via the partial oxidation of a primary or secondly alcohol, which produces an aldehyde or ketone as a coproduct. From 1957 to 1980 Shell Chemicals used this method to produce H_2O_2.[18-20] This liquid-phase process was based on the autoxidation of propan-2-ol (Figure 4.3).

Figure 4.3 H_2O_2 synthesis by the oxidation of a secondary alcohol.

The propan-2-ol/water azeotrope was oxidized by an oxygen-enriched gas stream (80–90 % O_2) at moderate temperatures (90–140 ºC) under pressure (10–20 bar). Indeed Shell and several other research groups [6-24] have shown that H_2O_2 can be produced by a range of methods. H_2O_2 can also be produced *in situ* via the oxidation of a substrate [21] however the direct gas phase synthesis of H_2O_2 has not been studied extensively. Currently no papers have been found on the direct gas phase synthesis of H_2O_2 at atmospheric pressure using a continuous gas flow reactor; and to the best of our knowledge this is the first attempt to produce H_2O_2 in the gas phase at atmospheric pressure. The advantage of studying the direct synthesis of H_2O_2 at atmospheric pressure is that it is a safe and potentially a low pressure energy efficient process. Furthermore costs related to compressing gases will be avoided.

The aim of the study is to set up and operate a gas flow system to investigate the direct gas phase synthesis of H_2O_2 using AuPd catalysts. The aim is to show that H_2O_2 can be produced and captured directly in the gas phase at ambient pressure. Once this is done the effect of reaction parameters (temperature, gas flow rate and pressure) will be investigated under flow conditions.

4.2 Gas Flow Continuous reactor

The schematic of the lab scale rig is shown in figure 4.4

4.2.1 Reactor set up

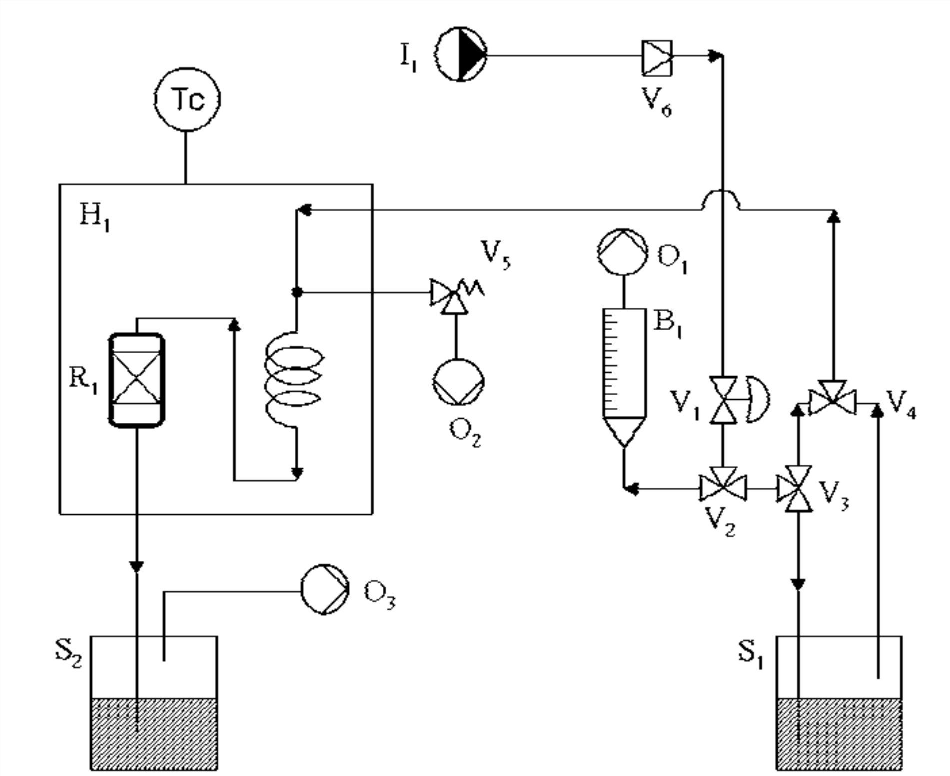

Figure 4.4 Schematic for gas flow packed reactor for the direct synthesis of H_2O_2.

Legend

B_1	Bubble flow meter
H_1	Oven
I_1	Inlet gases: 2% H_2/air for hydrogenation and direct synthesis experiments. Industrial grade air for decomposition experiments
O_{1-3}	Outlet gases – vent line
R_1	Reactor
T_c	Temperature controller
S_1	Gas saturator
S_2	H_2O_2 water trap
V_1	Millimetric valve
V_{2-4}	Three way valves
V_5	Safety release valve (spring valve)
V_6	One-way valve

4.2.2 Safety and working condition

When carrying out the direct synthesis of H_2O_2 from H_2 and O_2 it is very important to carry out reactions safely and avoid contact between concentrated H_2 and O_2 mixtures. This can be achieved by working below the lower explosive limit of H_2, 5% in air at room temperature.[4] To ensure reactions were conducted safely intrinsically safe reaction mixtures, 2% H_2/air were used to study the direct synthesis of H_2O_2.

4.2.3 Evaluation of background activity

Before a reaction was carried out, blank tests were carried out to understand the contribution of the rig itself to the decomposition and hydrogenation of H_2O_2. In order to measure the hydrogenation and decomposition rates, it is important to compare the H_2O_2 lost to known values; hence H_2O_2 vaporisation has to be understood first.

4.2.3.1 Determination of the H_2O_2 vaporisation calibration curve

A calibration curve was determined which showed the relationship between the amounts of H_2O_2 vaporized as a function of gas carrier flow rate. To determine the calibration curve the reactor system was bypassed, the gas saturator (S_1) was filled with 50 wt. % H_2O_2 solution and connected straight after the H_2O_2 water trap (S_2).

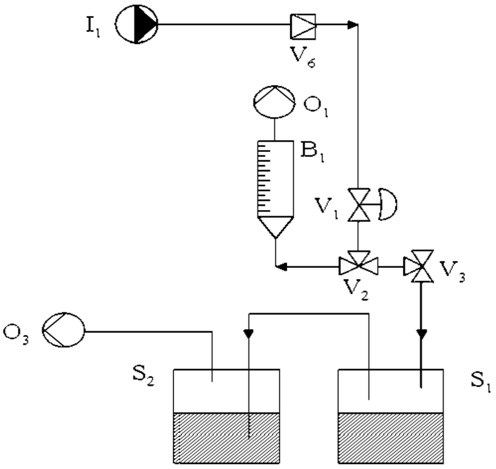

Figure 4.5 Schematic for the calibration curve determination set up (S_1 filled with a 50 wt. % H_2O_2 solution and S_2 filled with water).

The results for the calibration curve are shown in Figure 4.6.

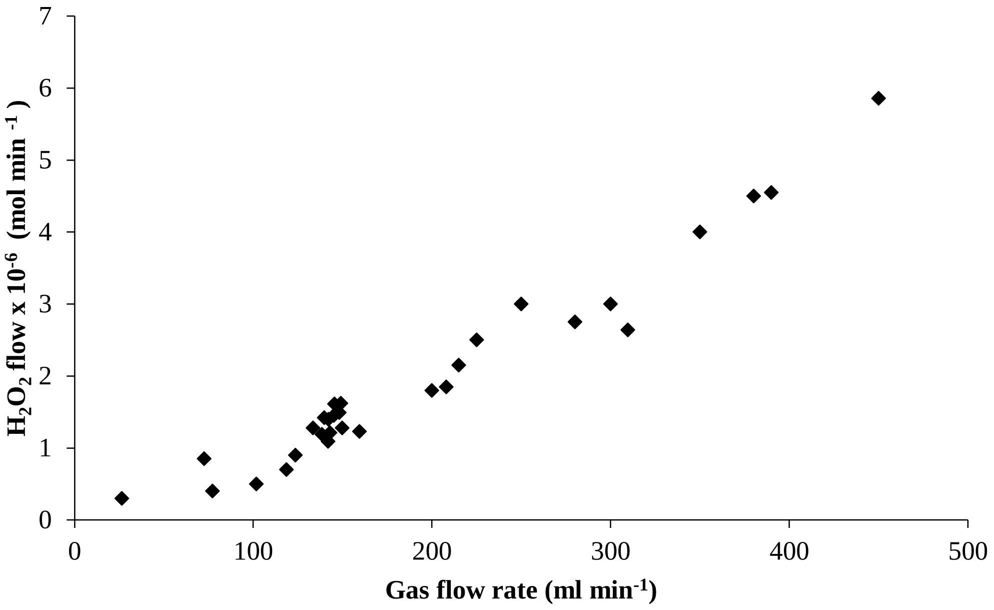

Figure 4.6 Calibration curve showing the concentration of H_2O_2 in the gas phase as a function of gas carrier flow rate.

Reaction conditions Gas source (Industrial grade air), 25 ºC.

4.2 3.2 Screening of suitable materials for the reactor

After the determination of a suitable calibration curve, potential reactor materials were screened. In order to evaluate the reactor background, the potential reactor materials were inserted between the H_2O_2 saturator (S_1) and H_2O_2-water trap (S_2). The gas mixture was bubbled through the H_2O_2 saturator (S_1) which was subsequently re-collected in the water trap (S_2). By calculating the amount of H_2O_2 lost, rates of decomposition and hydrogenation could be determined.

The first material to be evaluated was “1/8” stainless steel AISI 316 tube from Swagelok (●). As shown in figure 4.8 a loss of ca. 90 % in H_2O_2 was observed for this material. It was clear that stainless steel is not a suitable material for the gas phase reactor. Hence in order to decrease the reactor activity poly-difluoroethylene (PTFE) was evaluated. When a PTFE tube was used the number of moles of H_2O_2 carried through the tube in the gas phase matched the calibration curve in both synthetic air (●) and 2% H_2 in air. (■) The lack of any loss in H_2O_2 makes PTFE a suitable material for the reactor. In order to avoid decomposition of H_2O_2 at this stage all the reactor and its lines were replaced with PTFE. All future experiments were carried out with a PTFE reaction tube.

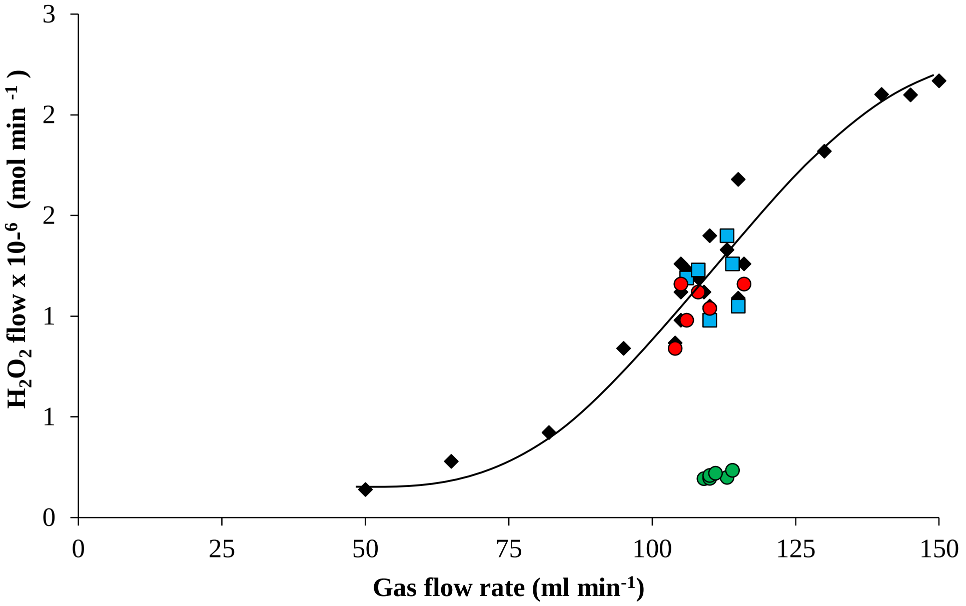

Figure 4.7 Evaluation of the reactor background activity. H_2O_2 calibration curve (◆) and results for 1/8” AISI 316 Swagelok using industrial grade air (●) 1/4” PTFE tube using industrial air (●) and 2% H_2/air (■).

Reaction conditions 25 °C.

4.3 Catalytic tests

Once the H_2O_2 vaporisation and blank tests were carried out an attempt was made to produce H_2O_2 in the gas phase. Pritchard *et al.*[25] previously prepared a series of catalysts by sol immobilisation and evaluated their activity for the direct synthesis of H_2O_2 in the autoclave system.[25] The catalysts prepared using the sol immobilisation technique were extremely active and showed 50% higher activity when compared with the catalyst prepared by impregnation.[25] Furthermore the rate of H_2O_2 hydrogenation/decomposition was roughly three times that of the synthesis reaction. Indeed the sol immobilisation catalysts exhibit high hydrogenation activities in the liquid phase in comparison to catalysts prepared by impregnation. However the high H_2O_2 productivities make these catalysts attractive candidates to study in a continuous gas flow reactor. As the low residence times in the flow reactor should mitigate the influence of subsequent hydrogenation and decomposition reactions as already described in the introduction (Chapter 4.1).

Several gas phase reactions were carried out using 0.5 wt. % Au - 0.5 wt. % Pd / Carbon catalysts prepared by sol immobilisation and the initial results are shown in table 4.1.

Table 4.1 Catalytic results for 0.5 wt. % Au - 0.5 wt. % Pd / Carbon prepared using sol-immobilisation technique using the H_2O_2–water trap

Reaction time (h)	**H_2O_2 observed (g)**
0.5, 1, 2, 4, 6, 8, 12, 24, 48, 76	0

Reaction conditions Atmospheric pressure, 2% H_2/air (50 ml min^{-1}) catalyst (50 mg) Residence time: (1.98 s), Reaction time (X h).

Determination of H_2O_2 carried out by titrating the final solution with acidified $Ce(SO_4)_2$ solution.

The direct synthesis of H_2O_2 was studied at a range of reaction times. However even after 76 hours no H_2O_2 was observed. It was thought that the current H_2O_2 water trap was not sufficient for low concentrations of H_2O_2. If H_2O_2 is formed via the direct synthesis it is likely to be in low concentrations. Thus trapping it efficiently using the water trap may not be possible and/or the H_2O_2 may be stripping from the water trap into the vent line. In order to avoid H_2O_2 stripping from the trap and allow efficient trapping of the H_2O_2 formed, the water trap was replaced with an acidic solution containing potassium titanium oxalate (chapter 2.6.1.2.1). This solution is used by Solvay® to trap H_2O_2 in industrial reactions. The Ti (IV) ions react immediately with H_2O_2 to form a [Ti-H_2O_2] complex that is yellow-orange in colour and can be quantified using a UV-Vis spectrophotometer at 410 nm.[26]

When the H_2O_2 water trap was replaced with the Ti^{4+} solution, direct synthesis experiments were conducted with the sol immobilised catalyst. The results are shown in table 4.2.

Table 4.2 Catalytic results for 0.5 wt. % Au - 0.5 wt. % Pd / Carbon prepared using sol-immobilisation technique and the Ti^{4+} trap.

Reaction Time (h)	**H_2O_2 observed (g)**
0.5, 1, 2, 4, 6, 12 ,24, 48, 76	0

Reaction conditions Atmospheric pressure, 2% H_2/air (50 ml min^{-1}) catalyst (50 mg) Residence time: (1.98 s), Reaction time (X hours).

Determination of H_2O_2 carried out using spectroscopy analysis.

Several direct synthesis reactions were conducted using the 0.5 wt. % Au - 0.5 wt. % Pd / Carbon prepared by sol immobilisation and the production of H_2O_2 was not observed (table 4.2). There is a possibility that these reaction conditions were not ideal for the catalysts being tested. In order to investigate further the effect of flow rate on H_2O_2 production was investigated.

4.3.1. The effect of flow rate

The effect of flow rate was investigated by changing the carrier gas flow rate, and consequently the effect residence time on the product yield was also studied. Experiments were carried out at room temperature over a range of carrier gas flow rates of 25 ml min^{-1} to 100 ml min^{-1}, using a 0.5 wt. % Au - 0.5 wt. % Pd/C catalyst prepared by sol immobilisation. The effect of carrier gas flow rate on product yield is shown in table 4.3.

Table 4.3 Catalytic results for 0.5 wt. % Au - 0.5 wt. % Pd / C using the Ti^{4+}-H_2O_2-trap

Entry	**Flow rate (ml min^{-1})**	**Residence time (s)**	**H_2O_2 produced (g)**
1	25	3.94	0
2	50	1.97	0
3	75	1.31	0
4	100	0.98	0

Reaction conditions	Atmospheric pressure, 2% H_2/air (X ml min^{-1}) catalyst (50 mg) Residence time: (X s), Reaction time (80 h). ^{a}Determination of H_2O_2 carried out using spectroscopy analysis.

The direct synthesis of H_2O_2 was studied at various gas flow rates using the sol immobilised catalysts however the direct gas phase synthesis of H_2O_2 was not detected under these conditions. Hence it was apparent that the hypothesis that these materials would be extremely active for the direct gas phase synthesis of H_2O_2 in a continuous gas flow reactor was not substantiated. The inactivity of the catalysts could be attributed to the synthesis method. The sol immobilisation method involves the dissolution of $HAuCl_4$ and $PdCl_2$ in a dilute solution of a stabilising ligand, in this case polyvinyl alcohol (PVA). The role of the PVA is to coat the nanoparticles in order to prevent them from sintering during subsequent synthesis steps. A reducing agent is then added to form a colloidal solution of homogeneous AuPd nanoparticles which can then be readily supported onto the supports.

When the immobilised nanoparticles are formed in the preparation they remain coated with the stabilising ligand. For most applications, once the metal nanoparticles have been immobilised onto the solid support the stabilising ligand is no longer needed. The stabilising molecule can interfere with catalysis and recently it was reported as a major problem for gas phase reactions.[27, 28] This can explain the lack of activity observed for the direct gas phase synthesis of H_2O_2 using the sol immobilisation catalyst. The PVA does not allow access to the active metal sites on the supported nanoparticles which inhibit the catalysts activity for the direct gas phase synthesis of H_2O_2.

4.3.2 The effect of catalyst

The catalyst preparation procedure has a huge influence on the structure, activity, particle size distribution and dispersion of Au-Pd supported catalysts. Over recent years the effect of preparation methods on the direct synthesis of H_2O_2 has been studied extensively. Pritchard *et al.* [25] have found that catalysts prepared by the sol immobilisation are more active than a catalyst prepared by conventional impregnation. Sankar *et al.*[29] have shown that by modifying the conventional impregnation method slightly, the dispersion of the gold can be increased and as a result this leads to an in increase in H_2O_2 productivity. In this modified impregnation method, aqueous HCl is added to the water used to dissolve the $HAuCl_4$ and $PdCl_2$. This solution is then used to impregnate the support until it is dried completely. In order to remove the halide from the material a reduction treatment with H_2 is employed. Furthermore Kondrat *et al.*[30] have reported the preparation of supported AuPd bimetallic catalysts by the physical mixing of the acetate salts of the metals followed by a heat treatment under He. These chloride free catalysts are more active than equivalent catalysts prepared by the impregnation route for some redox processes such as benzyl alcohol oxidation.

In the previous chapter AuPd catalysts supported on heteropolyacids[31] have also shown exceptionally high activities for the direct synthesis of H_2O_2 in the liquid phase. Different AuPd supported catalysts prepared by the synthesis techniques discussed above were employed for the direct gas phase synthesis of H_2O_2 and the results are given in table 4.4.

Table 4.4 Activity for different catalysts for the direct gas phase synthesis of H_2O_2 in continuous gas flow reactor.

Catalyst	**Preparation Method**	**H_2O_2 observed (g)**
0.5 wt. % Au - 0.5 wt. % Pd /Carbon	Sol immobilisation	0
2.5 wt. % - 2.5% wt. % $Cs_{2.5}H_{0.5}PW_{12}o_{40}$	Impregnation	0
0.5 wt. % Au - 0.5 wt.% Pd / TiO_2	Modified Impregnation	0
2.5 wt % - 2.5% wt% Pd/Carbon	Physical grinding	0

Reaction conditions Atmospheric pressure, 2% H_2/air (50 ml min^{-1}), catalyst (50 mg) Residence time: (1.98 s), Reaction time (80 h). Determination of H_2O_2 carried out using spectroscopy analysis.

Table 4.4 shows that the effect of catalyst preparation method did not have an influence on the rate of H_2O_2 production in the gas phase. Catalysts which are extremely active in the liquid phase direct synthesis of H_2O_2 were evaluated for the direct gas phase synthesis of H_2O_2 but the formation of H_2O_2 in the gas phase was not observed. The lack of production may possibly be attributed to the catalyst which can be decomposing the H_2O_2 before it reaches the H_2O_2-trap.

4.4 Evaluating the catalyst and support activity towards H_2O_2 degradation

In order to evaluate the catalytic activity towards H_2O_2 decomposition, the catalyst was inserted into the reactor as shown in figure 4.8 and screened for H_2O_2 degradation.

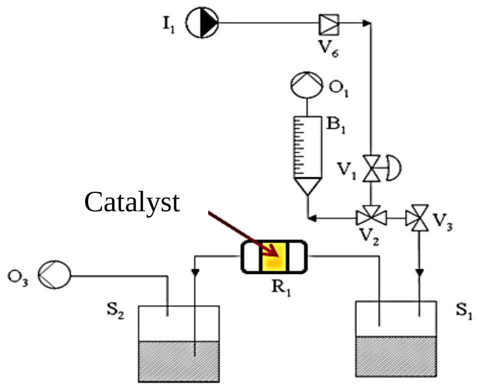

Figure 4.8 Schematic for evaluating the catalyst activity towards H_2O_2 degradation.

For the decomposition tests the catalyst (0.01 g) was placed in the reactor and supported with quartz wool after the catalyst bed to hold the catalysts in position. The catalysts were evaluated for H_2O_2 decomposition and the results obtained from these decomposition reactions were compared to the calibration curve (Figure 4.6) obtained from the vaporisation experiments. The results from these decomposition experiments are given in table 4.4.

Table 4.4 Decomposition of H_2O_2 in the gas phase over various materials.

Entry	**Material**	**H_2O_2 Decomposition (%)**
1	0.5 wt. % Au – 0.5 wt.% Pd/Carbon[a]	75
2	2.5 wt. % Au - 2.5% wt. % Pd/ $Cs_{2.5}H_{0.5}PW_{12}o_{40}$[b]	89
3	2.5 wt % - 2.5% wt% Pd/TiO_2[c]	89
4	2.5 wt % - 2.5% wt% Pd/Carbon[d]	73
5	Quartz Wool	0

Reaction conditions Gas source (industrial grade air). Catalyst (0.01g), 25 °C. Determination of H_2O_2 carried out by titrating the H_2O_2-water solution with acidified Ce $(SO_4)_2$.

a) Catalyst prepared using sol immobilisation technique[25]
b) Catalyst prepared using wetness Impregnation. [31]
c) Catalyst prepared using modified impregnation technique [29]
d) Catalyst prepared using physical grinding technique[30]

A loss of ca. 75-90 % in H_2O_2 was observed with all catalysts. Quartz wool was also evaluated for H_2O_2 decomposition; there was no loss of H_2O_2. This indicates the quartz wool and the reactor itself were inert to H_2O_2 decomposition and it must be the catalysts that are solely responsible for decomposing H_2O_2.

Since the AuPd supported catalysts were decomposing ca. 75-90 % H_2O_2, different supports were evaluated for H_2O_2 degradation. To do this the support was placed in the reactor, then inserted between the water trap (S_2) and H_2O_2 saturators (S_1) where it was screened for H_2O_2 degradation. The objective of this study was to find a support which will not decompose H_2O_2 greatly. This support would be used to make a AuPd supported catalyst which would be employed for the direct gas phase synthesis of H_2O_2. A range of supports were evaluated and the results are given in figure 4.9.

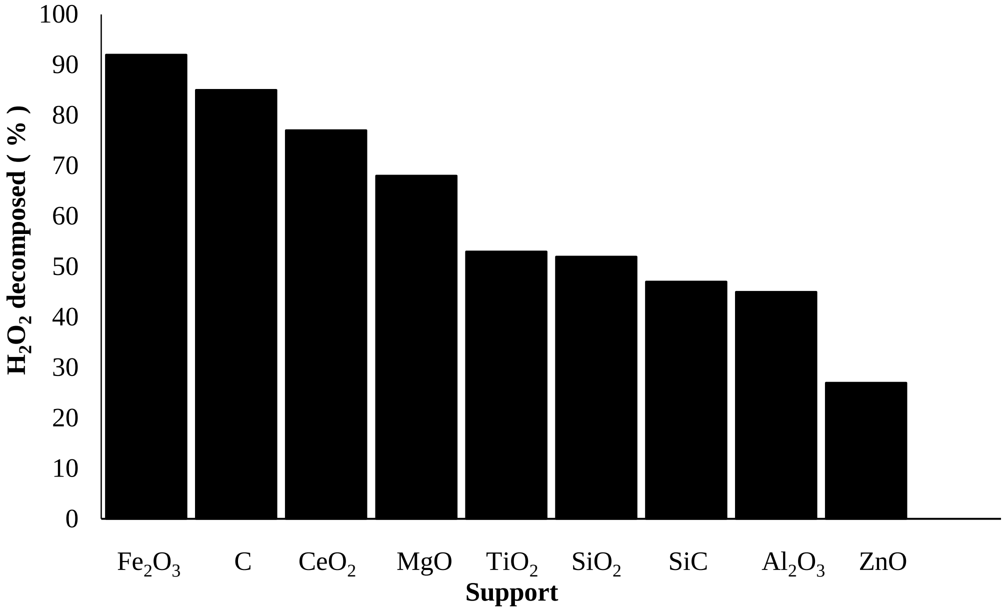

Figure 4.9	Decomposition of H_2O_2 in the gas phase over various catalyst support materials.
Reaction conditions	Support (0.01g), 25 °C, 145 ml min^{-1}, Reaction time (30 min). Determination of H_2O_2 carried out by titrating the H_2O_2-water solution with acidified Ce $(SO_4)_2$.

Various support materials that have previously been used to support Au, Pd and AuPd nanoparticles for heterogeneous catalysts were screened for H_2O_2 decomposition activity in the gas phase reactor. Figure 4.9 shows that almost all supports tested showed significant H_2O_2 decomposition. These results were in contrast to observed decomposition activity in the liquid phase. This can be attributed to the high surface concentrations of H_2O_2 passing over the catalyst without the protection of solvation that is available in the liquid phase.

4.5 Detection of H_2O_2

4.5.1 Oxidation of Alcohols

As discussed previously in section 4.1 H_2O_2 can be produced *in situ* during oxidation reactions. Moreover the liquid phase oxidation of propan-2-ol to acetone was carried out by Shell Chemicals for over 2 decades to produce H_2O_2. The oxidation of propan-2-ol to acetone using 2 % H_2/air as the reactant gas (Figure 4.16) was therefore investigated to probe the presence of oxidative species formed by the catalyst. The aim was to produce H_2O_2 *in-situ* with 2% H_2/air in the presence of a heterogeneous catalyst, the H_2O_2 formed would then oxidise the alcohol to the corresponding ketone and give water as a coproduct (Figure 4.16).

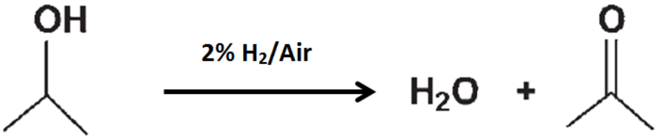

Figure 4.10 Oxidation of a secondary alcohol with H_2O_2 produced in situ.

Shell and coworkers[20] oxidised propan-2-ol/water azeotrope mixtures using oxygen enriched gas stream (80-90 % O_2) at high temperatures (90-140 ºC) under pressure (10-20 bar). The gas phase oxidation of propan-2-ol using Au catalysts and oxygen has also been studied previously by Biella and Rossi [32] at 393 K, who showed that propan-2-ol can be oxidised by air to the corresponding carbonyl derivatives with high selectivity. Further studies by Holz *et al.* have shown that in the presence of oxygen, Au/TiO_2 catalysts are active for the reaction with light off curves beginning at 350 – 400 K.[33] Therefore in order to avoid any reaction with oxygen alone the gas phase oxidation reactions were conducted at 60 °C. Initial experiments were carried out using 2.5 wt. % Au / 2.5 wt. % Pd / TiO_2 (5%AuPd/TiO_2) prepared by conventional impregnation and calcined at 400 °C / 4 h with a ramp rate of 20 °C min^{-1}.[34] Despite the high decomposition rate of the catalyst support material this catalyst was chosen because it has been studied extensively in the batch system and its known for its non-leaching, reusable properties.

The oxidation of propan-2-ol was carried out in a fixed bed vertical PTFE reactor carrying the catalyst (0.05 g) and was contained in an oven which allowed heating (60 ºC) of the catalyst bed as well as the starting material propan-2-ol. The gas mixture (2%H_2/air or Industrial grade air (50 ml min^{-1})) was controlled by a needle valve and the alcohol was placed in a saturator (S_1). When the gas was bubbled through the alcohol (S_1) liquid vaporisation occurred on the reactor wall prior to the catalytic bed. The condensable reaction products were collected by bubbling the effluent into a solvent free cold trap. The products were analysed via ^{1}H NMR (Figure 4.11-4.12) and the results are given in table 4.5. ^{1}H NMR spectra were referenced to TMS ($\delta = 0$ ppm) using a 1 wt. % TMS/$CDCl_3$ external standard.

Table 4.5 Catalytic tests for the direct gas phase oxidation of propan-2-ol to acetone

Entry	**Catalyst**	**Gas Mixture**	**Oxidation to Acetone**
1	None	Industrial Grade air	No
2	None	2 % H_2/air	No
3	TiO_2	Industrial Grade air	No
4	TiO_2	2 % H_2/air	No
5	5%AuPd/TiO_2	Industrial Grade air	No
6	5%AuPd/TiO_2	2 % H_2/air	Yes

Reaction Conditions Catalyst mass (50 mg) Temperature (60 °C), Flow rate (50 ml min^{-1}), reaction time (7 h).

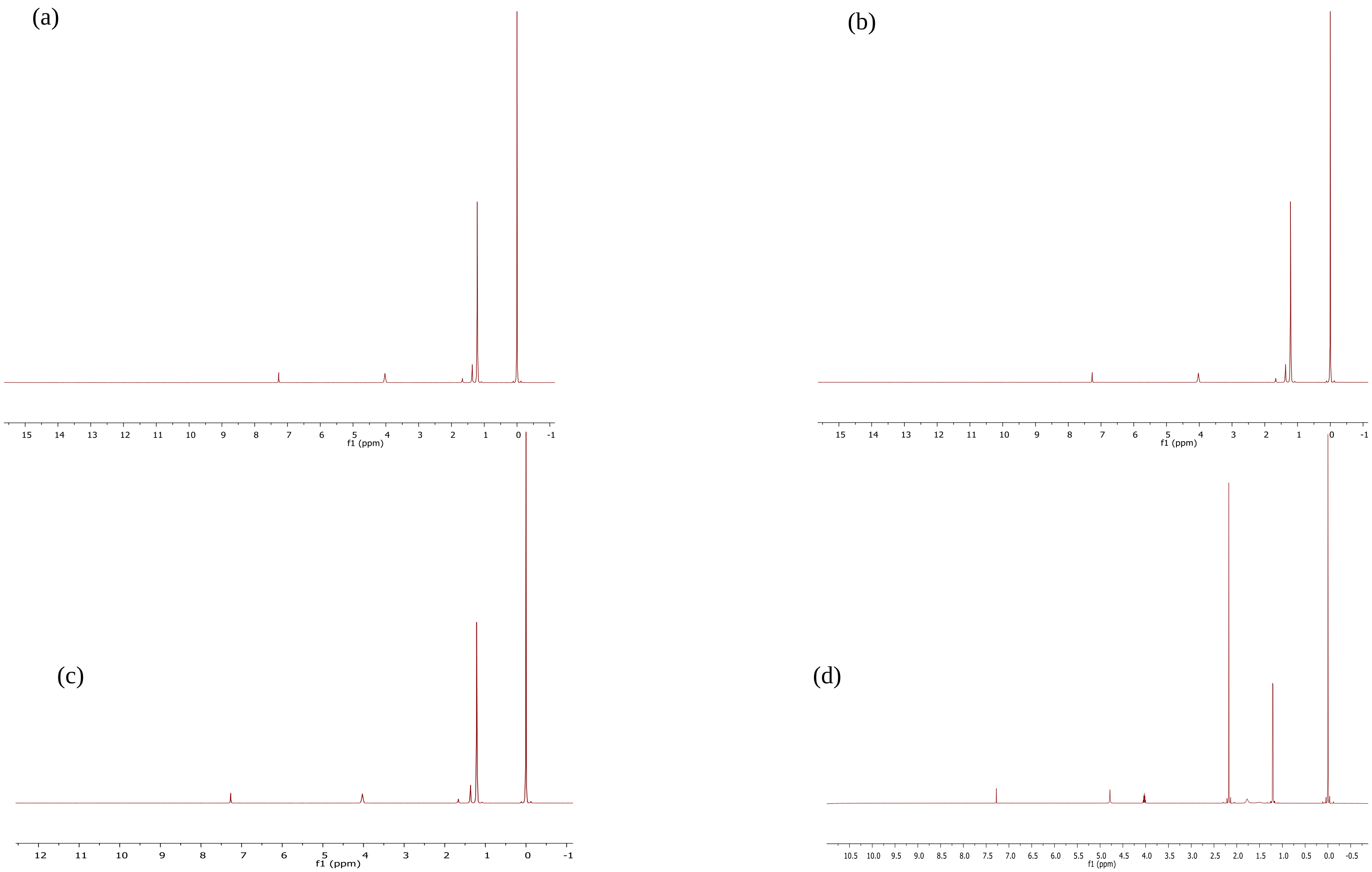

Figure 4.11 ^{1}H NMR spectra for experiments conducted with 5%AuPd/TiO_2 (a) blank reaction in the absence of a catalyst using industrial grade air, (b) reaction with catalyst and Industrial Grade air, (c) blank reaction in the absence of a catalyst using 2% H_2/air, (d) reaction with catalyst using 2 % H_2/air.

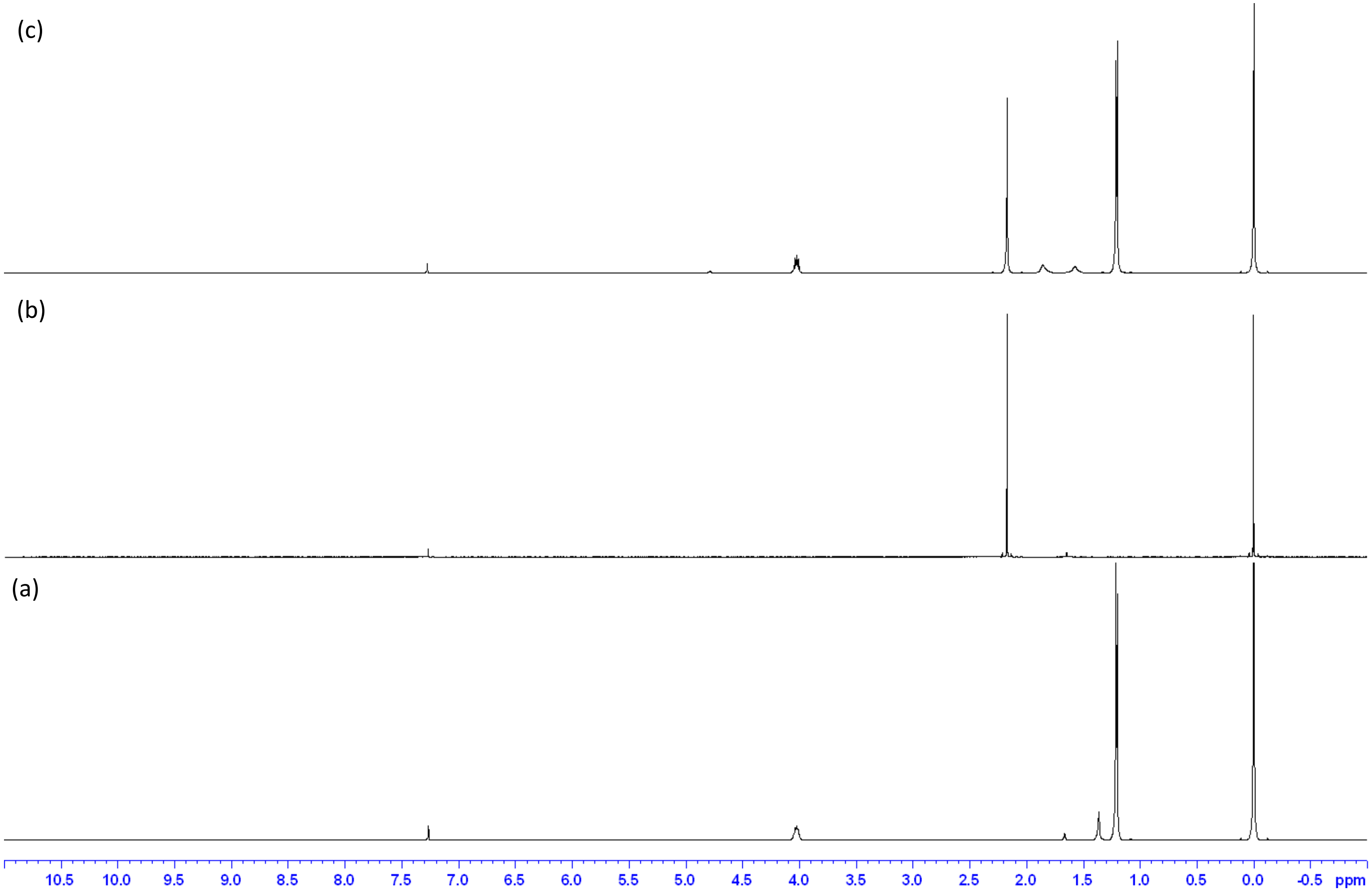

Figure 4.12 ^{1}H NMR spectra for (a) Propan-2-ol standard, (b) Acetone standard, (c) Reaction with 2 % H_2 / air using 5% AuPd/TiO_2.

Experiments were carried out at 60 ºC without the presence of a catalyst with industrial grade air and 2%H_2/air, in both these experiments no oxidation products were detected by

NMR. Moreover when the catalyst was present with propan-2-ol and industrial grade air no oxidation products were detected. However, when reactions were conducted in the presence of 50 mg catalyst using 2%H_2/air NMR analysis (Figure 4.11- 4.12) confirmed the presence of acetone in the reaction solutions. This indicates that at 60 ºC the AuPd particles can activate oxygen in the presence of H_2 to oxidise organic molecules. This temperature is lower than reported for oxidation reactions that use oxygen alone, therefore suggesting that it is the H_2 that initiates the oxidation at lower temperatures via the formation of a bound-hydroperoxy intermediate or through the formation of free H_2O_2 which is further activated to conduct the oxidation. These low temperature oxidation results coincide with those of Haruta *et al.*[6-7] who have also shown that supported Au catalysts are extremely active and selective in the oxidation of propene to the corresponding epoxide with molecular H_2 and O_2. Haruta suggested that the active oxygen species are produced by the reductive activation of molecular O_2 with molecular H_2 at the perimeter boundary between the Au particles and the TiO_2 support. H_2 aids as a sacrificial reductant which permits the activation of dioxygen at relatively low temperatures (303-393 K). In order to ascertain if the selective oxidation reaction was conducted via bound peroxy species or free H_2O_2, Temporal Analysis of Products was carried out on the 5%AuPd/TiO_2 catalyst.

4.5.2 Temporal Analysis of Products

Temporal Analysis of Products (TAP) can be conducted to detect short-lived substances that are released by the catalyst surface into the gas phase and then reveal information about various elementary steps of the complex catalytic reaction. TAP was conducted to investigate whether H_2O_2 is formed and is able to desorb from the 5%AuPd/TiO_2 catalyst. TAP experiments were carried out at 60 ºC by pulsing 2% H_2/air over the catalyst bed under vacuum. These experiments revealed significant information on the behaviour of this catalyst in the direct gas phase synthesis of H_2O_2. The results are given in Figure 4.13.

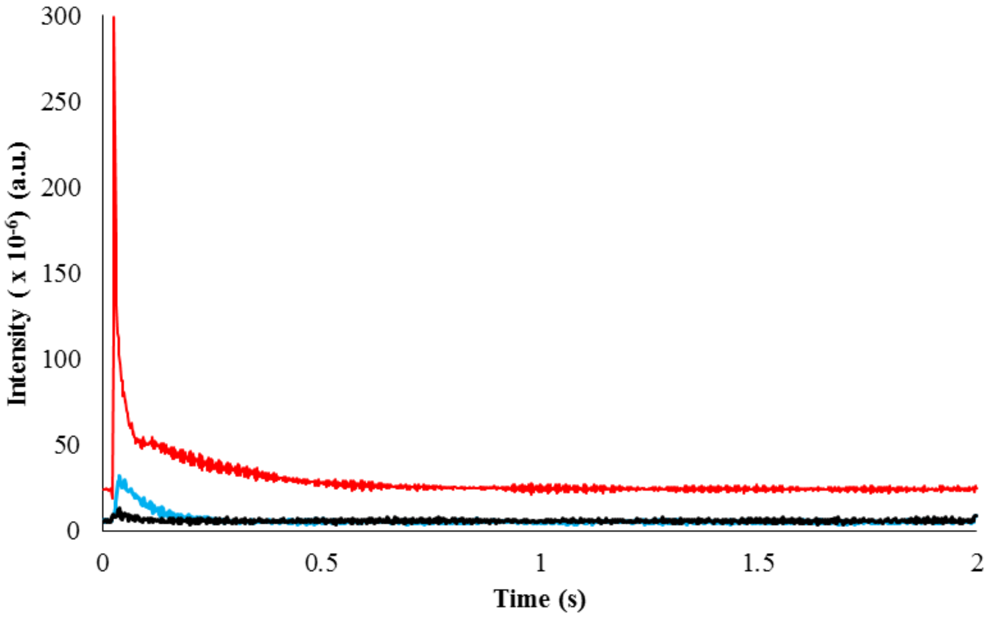

Figure 4.13 Temporal Analysis of Products of reaction between 2% H_2 in air over 5%AuPd/TiO_2.

Reaction Conditions Temperature 60 °C, pulse of 2% H_2 in air over 5%AuPd/TiO_2

Red line – mass spec signal at mass 2 (H_2) at 60 °C

Blue line – mass spec signal at mass 34 (H_2O_2) at 60 °C

Black line (blank).

Figure 4.13 shows the observed response when the 2%H_2/Air was scanned over mass 34 (H_2O_2) at 60 ºC compared to the response for the baseline of the TAP reactor. When 2%H_2/Air was scanned over mass 34, H_2O_2 was observed consistently. Small amounts of responses were observed due to the low concentration of H_2 used and the very small pulse size of the TAP. The results show that it is possible to generate H_2O_2 in the gas phase under the vacuum of the TAP reactor and more importantly it is possible to desorb H_2O_2 from the surface of the catalyst and detect it further downstream.

4.6 Revisiting the direct synthesis of H_2O_2

Having found that H_2O_2 can be detected in the gas phase via TAP and propan-2-ol can be oxidised successfully by using a combination of H_2 and O_2 as the oxidant the direct synthesis of H_2O_2 was revisited using conditions analogous to the oxidation experiments. The set up used for the direct gas phase synthesis of H_2O_2 is shown in figure 4.14 and the reaction conditions are listed in table 4. 6. There was a key difference between these H_2O_2 reactions carried out below and the direct synthesis reactions previously reported (Chapter 4.3). The reactions below were conducted at 60 ºC. A large ice bath was used for the sample cold trap, and the entire H_2O_2 collection vessel (S_2) was placed in this new cold trap. This meant the collection vessel (S_2) was completely covered in ice which would allow full condensation of products. Furthermore the amount of H_2O_2 produced was detected via titrating the final product solution with dilute $Ce(SO_4)_2$ solution.

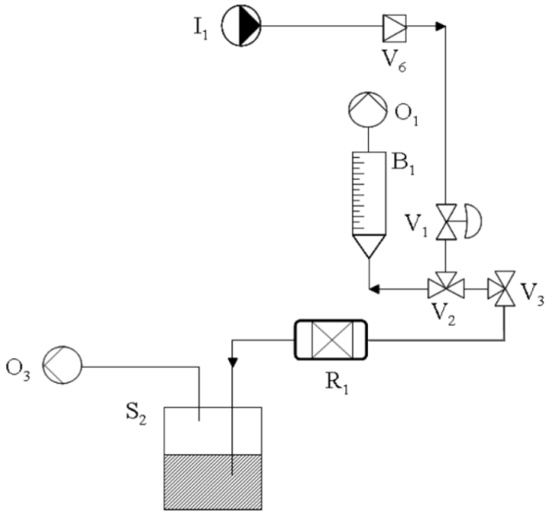

Figure 4.14 Schematic for the set up used for the reactions carried out at high temperatures (R_1 placed in an oven, S_2 placed in an ice bath which acted as a sample cold trap).

Table 4.6 Reaction Conditions for revisiting the direct gas phase synthesis of H_2O_2

Gas Mixture	2 % H_2/air
Flow Rate	50 ml min^{-1}
Temperature	60 ºC
Catalyst	50 mg
Product collection method	Condense in ice bath (cold trap)

A range of H_2O_2 direct synthesis were conducted and the results are given in table 4.7.

Table 4.7 Catalytic tests for the direct gas phase synthesis of H_2O_2

Entry	Catalyst	Gas Mixture	Condensate (g)	Concentration H_2O_2 (ppm)[a]
1	None	Industrial Grade air	0	0
2	None	2 % H_2/air	0	0
3	TiO_2	Industrial Grade air	0	0
4	TiO_2	2 % H_2/air	0	0
5	2.5%Au-2.5%Pd/TiO_2	Industrial grade air	0	0
6	2.5%Au-2.5%Pd/TiO_2	2 % H_2/air	0.63	53

Reaction Conditions As stated in table 4.16.

[a] Amount of H_2O_2 produced was determined by titrating the final solution with dilute acidified $Ce(SO_4)_2$ solution.

At 60 ºC when no catalyst was present with industrial grade air or 2% H_2/air no condensate was observed in the cold trap (Table 4.7, entries 1-2). This indicated there was no detectable moisture in the gas feeds. Furthermore when experiments were conducted in the presence of the support (TiO_2) only, no condensate was present in the cold trap (Table 4.7, entries 3-4). When the direct gas phase synthesis of H_2O_2 was conducted in the presence of 50 mg catalyst with industrial grade air no condensate was observed in the cold trap. However when 2% H_2/air was used as the reactant gas (table 4.7, entry 6) liquid condensate was detected in the cold trap. This revealed that at 60 ºC AuPd nanoparticles were capable of reacting the H_2 and O_2 in the gas phase to produce H_2O_2. On titration of the final product solution 53 ppm of H_2O_2 was detected. As no condensate was observed without the presence of the catalyst it can be concluded the H_2O_2 formed is through the combination of H_2 and O_2 over the AuPd catalyst.

4.6.1 Direct Synthesis of H_2O_2 using 5% AuPd/TiO_2

5%AuPd/TiO_2 has been studied extensively in the batch system and has been shown to be reusable in this system. In order to try and avoid any metal leaching during the gas flow experiments this catalyst was selected for further studies to investigate the effect of reaction variables (temperature, flow rate and pressure).

4.6.1.1 The effect of reaction temperature on H_2O_2 synthesis

The effect of reaction temperature was investigated to determine the optimum temperature at which to carry out further reactions. Experiments were conducted at different temperatures while keeping the catalyst mass and all other reaction conditions constant. The results are shown in figure 4.15.

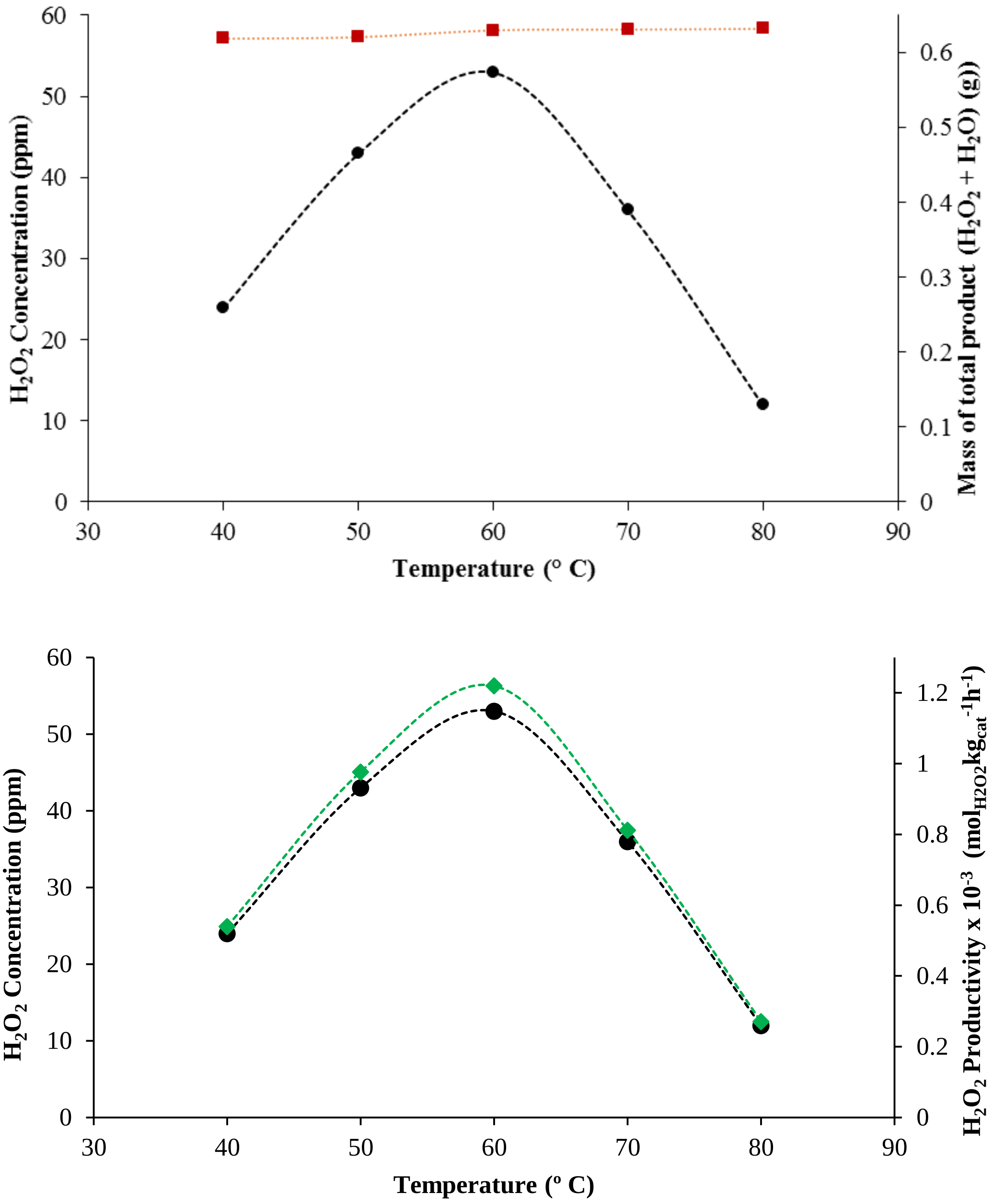

Figure 4.15	Effect of reaction temperature on the synthesis of H_2O_2 in the gas phase. H_2O_2 concentration (●), mass of condensate (■), productivity of H_2O_2 (◆) obtained at various temperatures.
Reaction conditions	Atmospheric pressure, temperature (40–60 °C), 2% H_2/air (50 ml min^{-1}), 5%AuPd/TiO_2 (50 mg).

Figure 4.15 shows the effect of increasing the reaction temperature from 40-80 °C. As the temperature increased the amount of product condensed in the cold trap after 16 hours remained constant. Since full conversion of the H_2 in the gas stream was observed between 40 and 80 °C, this can explain why there is no increase in reaction product with increasing temperature. Figure 4.15 also shows that the temperature has an effect on the formation of H_2O_2 in the gas phase. The rates of H_2O_2 synthesis increased from 2.7×10^{-4} at 40 °C to 1.22×10^{-3} at 60 °C before decreasing at temperatures above 60 °C. This indicates that there is a balance between the synthesis / desorption and stability of H_2O_2 through the catalyst bed. H_2O_2 synthesis rates over the duration of the experiments were approximately 1×10^{-3} $mol_{H2O2}kg_{cat}^{-1}h^{-1}$, these rates are significantly lower than reported rates in the liquid phase at elevated pressure under optimum conditions (30 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$). The observation that it is possible to detect H_2O_2 at all suggests that the water produced could be the result of a H_2O_2 decomposition pathway rather than combustion.

A volcano shape curve with a maximum in H_2O_2 concentration of 53 ppm at 60 °C was observed. Increasing the reaction temperature greater than 60 °C results in a drop in H_2O_2 concentration. This volcano type effect may be attributed to the increase in H_2O_2 degradation at higher temperature as the H_2O_2 produced is not capable of surviving under harsh temperatures.[35-38] These high temperature results are consistent with several other studies.[22-24, 39-41] Nystrom[22] and Benggtsson[23] studied the direct gas phase synthesis of H_2O_2 in a flow system in the presence of halides and acids using high temperatures (70-130 °C) and pressures (20 bar). The studies specified that unless the reaction temperature is sufficiently high, only very low concentrations of H_2O_2 can be dissolved in the gas stream. Nystrom *et al.* reported the selectivity was fully satisfactory at temperatures between 110-130 °C and pressures of 13-17 bar. Whereas Bertsch[24] and Benggtsson[23] reported the preferred reaction temperatures were between 20-70 °C and 20-80 °C respectively. Furthermore Blanca-Brieva[39] and Morena *et al.*[41] observed higher productions of H_2O_2 with an increase in temperature in a semi-continuous reactor system. Pashkova *et al.*[40] studied the direct synthesis of H_2O_2 using a 5 %Pd/TiO_2 catalyst and found an increase in productivity and conversion with temperature. This trend was different from the one they observed under batch conditions. The batch results coincided with those of Hutchings *et al*.[36-38] who reported that high rates of H_2O_2 synthesis were observed at 2 ºC in an autoclave reactor system.

As reviewed by Serna *et al.*[42] the reaction temperatures for the direct synthesis of H_2O_2 have been evaluated between -10 °C to 60 °C and patented in a wider range. Several groups have reported the beneficial effects of working below 35 ºC however this is not recommended from an industrial perspective since it would be difficult to remove the heat produced in the reaction, because low temperature utility is expensive. Therefore, operations between 40 and 60 °C is reported to be affordable for the direct synthesis of H_2O_2.[42]

4.6.1.2 The effect of gas flow rate on H_2O_2 synthesis

The effect of total gas flow rate was investigated whilst conducting the reactions at 60 °C and keeping the catalyst mass constant at 50 mg. The results are shown in figure 4.16.

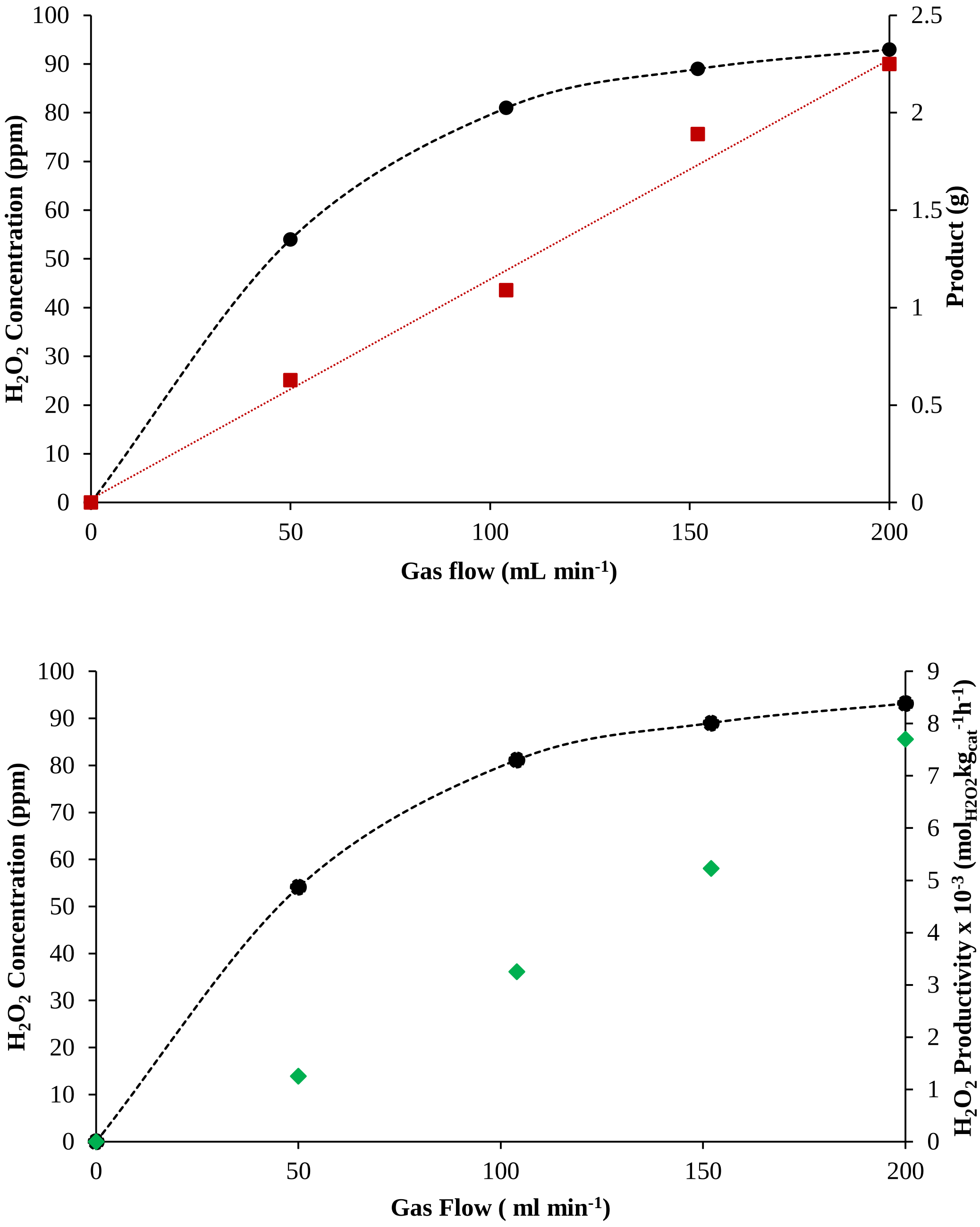

Figure 4.16 Effect of gas flow rates on the synthesis of H_2O_2 in the gas phase. H_2O_2 concentration (●), mass of condensate (🟥) and productivity (◆) obtained at various gas flow.

Reaction conditions atmospheric pressure; 60 ºC; 2% H_2/air (50-200 ml min^{-1}) 5% AuPd/TiO_2 (50 mg).

The influence of gas flow rates was investigated with the 5%AuPd/TiO_2 catalyst and the results are given in figure 4.16. As the gas flow increased, the concentration of H_2O_2 also increased to a maximum concentration of 93 ppm at 200 ml min^{-1}. Figure 4.16 shows that as the total gas flow was increased the H_2O_2 synthesis rates (mol$_{H2O2}$kg$_{cat}$$^{-1}$h^{-1}) increased from 1.25 x 10^{-3} at 50 ml min^{-1} to 7.7 x 10^{-3} at 200 ml min^{-1}. The increase in H_2O_2 concentration and productivity with an increase in gas flow rate can be attributed to shorter residence times and the faster flow rates stripping the H_2O_2 from the catalyst bed.

H_2, O_2 and air have a certain ability to dissolve water vapour and H_2O_2 vapour.[23] The limit of solubility is defined as the dew point. If a larger flow of dry gas mixture is passed to the reactor, it is possible to get the formed H_2O_2 and water to vaporise and to dissolve in the gas mixture as soon as they are formed on the surface of the catalyst. The time the H_2O_2 remains on the catalyst surface will therefore be very short which means that the undesired decomposition of H_2O_2 to water and oxygen gas will be very small. After the reaction with the catalyst, the gas mixture can be cooled which means that the dew point for H_2O_2 and water is exceeded and these compounds can be isolated as a liquid in the cold trap.

Figure 4.16 also shows with increasing gas flow the total amount of liquid product (H_2O + H_2O_2) observed increases linearly. These results are in agreement with the complete conversion of H_2 passing over the catalyst. The plateau observed for the H_2O_2 concentration at higher gas flow rates may be attributed to two possible factors: (i) the build-up of H_2O_2 in the product collection vessel over the 16 hour reaction which results in H_2O_2 decomposition to water (ii) the rate of total products (H_2O + H_2O_2) is faster than the rate of H_2O_2 formation which results in weaker concentrations of H_2O_2 at higher flow rates.

4.7 Direct Gas Phase synthesis of H_2O_2 at High Pressures

In the first part of this thesis chapter it has been shown that H_2O_2 can be synthesised directly in the gas phase using 2% H_2/air. Although the feasibility of producing H_2O_2 in the gas phase has been demonstrated at atmospheric pressure the H_2O_2 yields obtained thus far are too low and the study presented represents only a starting point. One of the easiest methods to increase the yield of H_2O_2 is to operate reactions at higher working pressures. Several patents and papers have revealed the beneficial effect of pressure in promoting the overall rate of H_2O_2 formation.[4, 22-24, 43] Furthermore some patents have detailed the formation of H_2O_2 in the gas phase at high working pressures and temperatures. Bengtsson *et al.* [23]

claimed that in the presence of acids using pressures up to 20 bar and temperatures up to 100 ºC H_2O_2 can be produced in the gas phase without the presence of any solvent. Furthermore Nystrom *et al* [22] invented a process of continuously producing H_2O_2 using H_2 and O_2 directly at an absolute pressure of 20 bar. In the presence of an aqueous acidic bath containing H_2SO_4 and NaBr, 4.4mg of H_2O_2 was produced at a temperature of 80-100 °C.

4.7.1 Reactor Set up

In an attempt to increase the H_2O_2 concentration even further a high pressure gas flow reactor was designed and built *in-situ* to investigate the direct synthesis of H_2O_2 at pressures above atmospheric. A schematic of the rig is given in Figure 4.17.

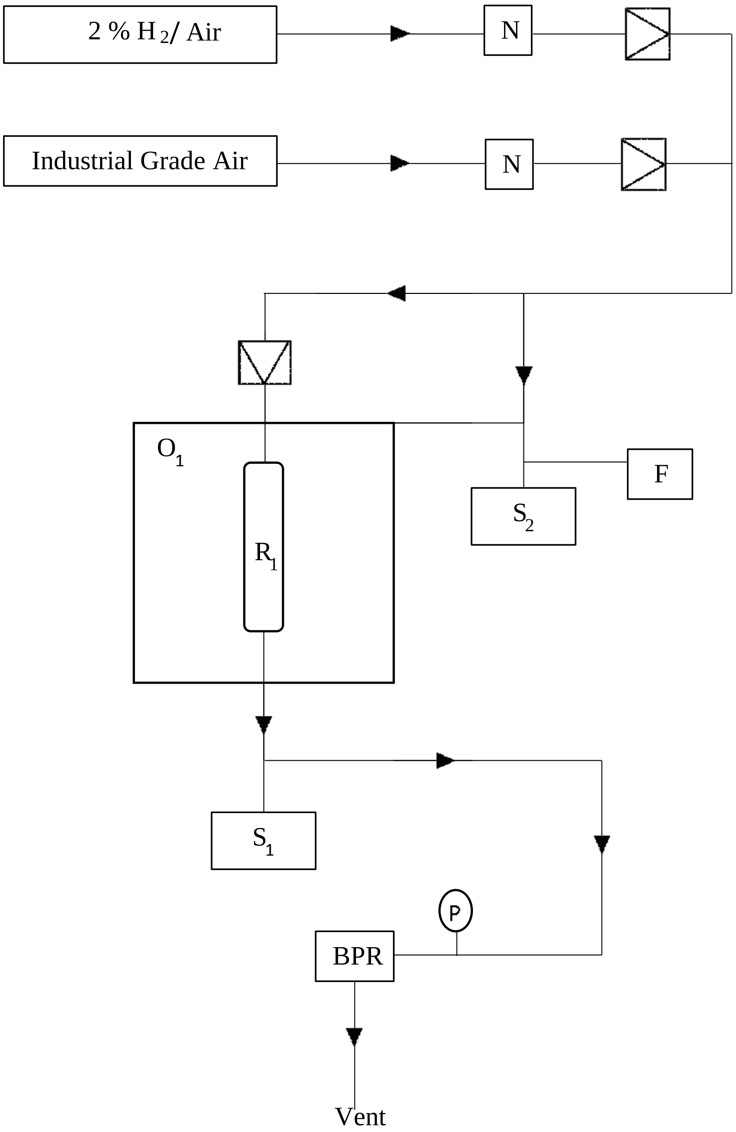

Figure 4.17 Schematic for the high pressure continuous gas flow reactor for the direct synthesis of H_2O_2.

Legend:

BPR	Back pressure regulator
F	H_2O_2 filling tube
N	Needle valve
O_1	Oven
P_1	Pressure gauge
R_1	Reactor
S_1	Sample bomb - H_2O_2 Collection Vessel
S_2	H_2O_2 vessel

A high pressure gas flow reactor was designed to allow testing of catalysts for the direct gas phase synthesis of H_2O_2 in a continuous flow system, the schematic of which is shown in figure 4.17. The reactor was constructed using Swagelok which had an internal diameter of ¼ inch. The gas flow was controlled using a simple needle valve (N) and the pressure was maintained using a back pressure regulator (BPR) at the end of the system.

The glass dreschel bottles (S_1 and S_2) which were used as H_2O_2 saturators and traps in the previous rig were placed with stainless steel bombs (S_1 and S_2). Since stainless steel decomposes H_2O_2, the catalyst bed and the product collection vessel were lined with PTFE.

One way valves were placed after the needle valves and just before the reactor bed (R_1) to prevent any backflow of gases. Pressure gauges (P) were placed after the catalyst bed to monitor the pressure as well as point out any sudden drop in pressure.

Samples of the product were collected via opening the valve at the bottom of the sample bomb (S_1). Although it was not used in this study another sample bomb (S_2) was placed to the left of the reactor (R_1). This was to allow the possibility of studying the effect of hydrogenation and decomposition.

4.7.2 Safety and working conditions

As described previously H_2/O_2 mixtures can be explosive and it is extremely essential that all parts of the gas phase rig are far from the explosive region. In order to ensure this intrinsically safe gas mixture, 2%H_2/air was used.

After conducting a thorough risk assessment it was concluded that the risk of an explosion is virtually zero however the rapid increase of pressure due to a blockage in the system can lead to failure in one of the reactor joints. Hence in order to avoid such a scenario safety pressure relief valves were placed before and after the catalyst bed.

4.7.3 Initial Synthesis Reactions using 5%AuPd/TiO_2

Once the rig was designed and built the catalytic activity for 5%AuPd/TiO_2 was studied and the initial results are shown in Figure 4.18.

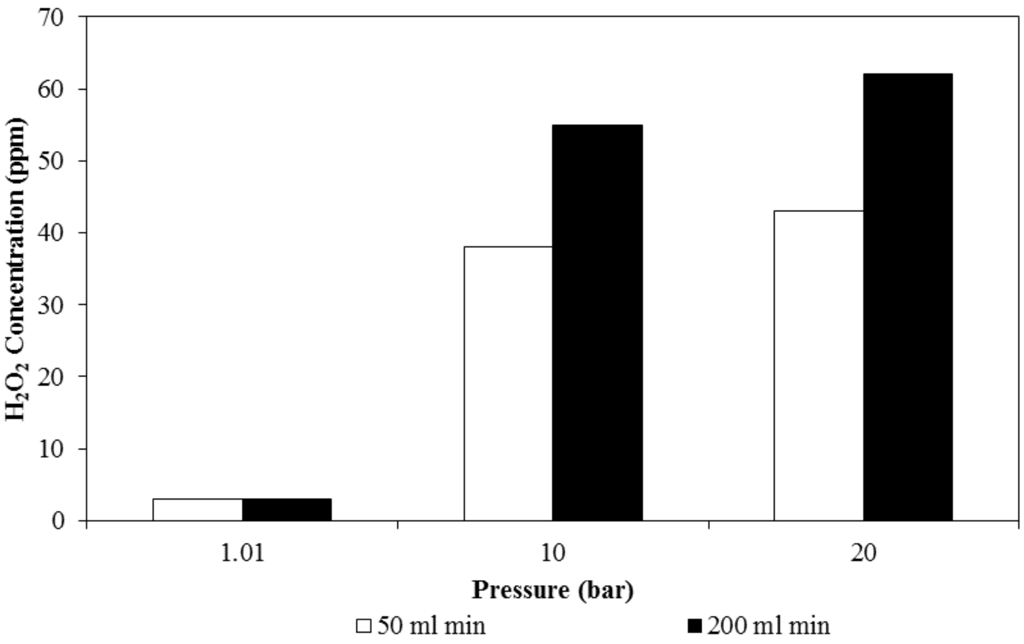

Figure 4.18	Catalytic results for 5% AuPd/TiO_2 at high pressure.
Reaction Conditions	5% AuPd/TiO_2 (50 mg), 2 % H_2/air, pressure (1.01 – 20 bar), flow rate (50 ml min^{-1} and 200 ml min^{-1}), 16 hours, 60 °C.

The use of high pressures resulted in an increase in H_2O_2 concentration going from 3 ppm at atmospheric pressure to 62 ppm at 20 bar. As demonstrated previously in section 4.6.1.2 increasing the flow rate from 50 ml min^{-1} to 200 ml min^{-1} showed an increase in H_2O_2 concentrations at both 10 and 20 bar pressures.

Initial results showed that an increase in pressure has a positive effect on the formation of H_2O_2. However lower rates of H_2O_2 were observed in comparison to the analogous experiments conducted in the atmospheric rig. Results given in figure 4.18 show very little (3 ppm) H_2O_2 is produced at atmospheric pressure in the new high pressure rig in comparison to that produced in the previous atmospheric rig (53 and 93 ppm at 50 ml min^{-1} and 200 ml min^{-1} respectively). However as the pressure is increased in the new rig the concentration of H_2O_2 increases and a maximum concentration of 62 ppm is produced at 20 bar using a flow rate of 200 ml min^{-1}.

Although the catalyst bed and sample bomb (S_1) were lined with PTFE the piping used to connect these two parts was made out of a stainless steel. This may be the reasons for the lower concentration of H_2O_2 observed in the new rig. H_2O_2 degradation might be occurring in the stainless steel piping once it is travelling from the catalyst bed to the sample bomb (S_1). As shown in section 4.2.3.2 and previously reported by industrial companies[20] the decomposition of H_2O_2 in stainless steel reactors is a serious problem. In order to avoid the decomposition of H_2O_2 formed Shell Chemicals constructed reaction vessels with enamel-lined steel or passivated steel.[20] This problem associated with H_2O_2 decomposition in the high pressure rig wasn’t resolved, however future experiments will address this as discussed in the final chapter of this thesis.

4.8 Conclusions

The aim of this study was to prove the feasibility of producing H_2O_2 in the gas phase directly from H_2 and O_2 at atmospheric pressure in a continuous gas flow reactor. The synthesis of H_2O_2 from H_2 and O_2 in the gas phase is postulated to be a key reaction step in the gas phase epoxidation of propene using Au/TS1 catalysts. During this process H_2O_2 is not typically observed as a reaction product instead it is consumed in a secondary step to oxidise propene to propene oxide which is an important commodity chemical used in the manufacture of polyols and polyurethane.

It is clear from the early work outlined in this chapter that the direct gas phase synthesis of H_2O_2 from H_2 and O_2 using supported Au-Pd catalyst is a complex one. Therefore the oxidation of propan-2-ol to acetone was studied using 2%H_2/air to probe the presence of oxidative species formed by a 5%AuPd/TiO_2 catalyst, which is known to have high H_2O_2 synthesis rates in the liquid phase. Moreover TAP experiments were conducted to see whether free H_2O_2 can be formed in the gas phase and desorbed from the surface of the catalyst. The results show it was possible to not only detect free H_2O_2 in the TAP system but also oxidise organic molecules in the gas phase using H_2 and O_2. When the direct synthesis of H_2O_2 was studied with the 5%AuPd/TiO_2, H_2O_2 was detected in the gas phase and not only H_2O as a liquid reaction product. After optimisation of reaction temperature and gas flow rate up to 93 ppm of H_2O_2 were produced in the gas phase using the AuPd/TiO_2 catalyst. The results show the H_2O_2 produced in the gas phase is unstable under a range of conditions. Thus preventing the subsequent hydrogenation and decomposition of H_2O_2 through the catalyst bed and in the cold trap remains a challenge. Since no liquid condensate is detected from the gas phase without the presence of the catalyst it can be concluded that the water and H_2O_2 formed in the presence of a catalyst is through the combination of H_2 and O_2 over the catalyst bed This result is of paramount importance and opens up the possibility of synthesising H_2O_2 directly from H_2 and O_2 in a gas phase reaction.

4.9 References

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Conclusions and Future Work

5

5.1 Introduction

As previously discussed in Chapter 1, the current worldwide production of H_2O_2 is based on the anthraquinone auto-oxidation (AO) process. This process has been successfully operated on a large scale for over 60 years and has been optimised to give high H_2 selectivity and high H_2O_2 concentrations. Despite this, there are various disadvantages of the AO process, most notably the continuous requirement to refill organic solvents. Furthermore the AO process is only economically viable on a large scale. This means that H_2O_2 production has to be centralised with the product being distributed in a highly concentrated form before being diluted with water prior to use.

The current concern for environmental issues and energy costs, has caused an increased desire to design a process which is capable of producing specific concentrations of H_2O_2 at the point of use. This has inspired many researchers to look for alternative routes for the production of H_2O_2.The direct synthesis of H_2O_2 from H_2 and O_2 is an ideal candidate for such a process as it provides a more atom efficient route compared to the current commercial AO process. The quest to find suitable catalysts and reaction conditions for the direct synthesis of H_2O_2 has remained a challenge for over a century. Although industrial specifications (H_2O_2 concentrations >3-8 wt. %, H_2 selectivity > 90 %), for starting a scale up process have not yet been achieved, many important developments have been achieved in the recent years.

In this work, the direct synthesis of H_2O_2 was extensively studied in collaboration with Solvay®, the largest manufacturer of H_2O_2 using the AO process. The main objective of this study was to produce high H_2O_2 concentrations via carefully tuning the reaction parameters and minimising the contact time between the catalyst and H_2O_2/reagent gases. This was done by investigating the direct synthesis of H_2O_2 in 2 different systems; a biphasic solvent system (Chapter 3) and a continuous gas flow system (Chapter 4). The results obtained from this study have been extremely promising confirming the important role that the direct synthesis may have in the near future.

5.2 The direct synthesis of H_2O_2 in a biphasic solvent system

For the direct synthesis of H_2O_2 to be considered on an industrial scale the required H_2 selectivities (> 90 %) and H_2O_2 concentrations (> 3-8 wt. %) have to be achieved. The benefit of the direct process is that it will permit local synthesis on a small scale as and when required thereby ensuring that H_2O_2 no longer needs to be stored and transported, both of which are potentially hazardous. Indeed, methanol-water systems are the most studied solvent system for the direct synthesis of H_2O_2. Although methanol-water systems are most studied for the direct synthesis of H_2O_2, the H_2O_2 is completely miscible with the methanol-water solution. This can lead to the formation of water via the subsequent reactions once H_2O_2 is formed. An approach based on the use of a biphasic solvent system (organic solvent and water) was extensively investigated in chapter 3. An advantage of using a biphasic solvent system is that it would provide *in-situ* extraction of H_2O_2 from the organic phase due to higher solubility of H_2O_2 in water than the organic solvent. This would provide better shielding for H_2O_2 from consecutive hydrogenation/decomposition reactions and as a result lead to an enhancement in H_2O_2 concentration in the water phase.

The results from chapter 3 show that by finely tuning and optimising the reaction conditions H_2O_2 concentrations between 0.29 -28.92 wt.% can be obtained on a small scale as required for the direct synthesis of H_2O_2. Two different catalysts were used for identifying the reaction parameters which resulted in the highest H_2O_2 concentration. Under the optimum reaction conditions it was possible to significantly increase the H_2O_2 concentration in comparison to the catalyst performance under the “standard” reaction conditions (described in Chapter 2.5.1). The H_2O_2 concentration increased from 0.29 wt. % to 0.71 wt.% for the 5%AuPd/A.W.Carbon catalyst and 1.06 wt. % to 11.18 wt. % for the 5%AuPd/HPA catalyst. Experiments were conducted where H_2O_2 hydrogenation was compared between the methanol-water and decan-1-ol-water system. Decan-1-ol-water system shows similar hydrogenation activity to the methanol-water system.

Various solvents investigated in the AO process were screened for the biphasic solvent system and in particularly the DBC-water system gave very promising results. Here it was possible to further increase the overall H_2O_2 concentrations to 1.39 wt. % and 28.92 wt. % for the 5%AuPd/A.W. Carbon and 5%AuPd/HPA catalyst respectively.

5.2.1 Future work

The results obtained in chapter 3 are extremely promising and if future work focusses on further understanding and improving the biphasic system it has great potential for being an ideal candidate for the direct synthesis of H_2O_2. Future work will focus on:

- Optimising the DBC-water system - When the 5%AuPd/HPA catalyst was evaluated for the direct synthesis of H_2O_2 in the DBC-water system, up to 28.92 wt. % was obtained under the optimum reaction conditions for the decan-1-ol-water system. As mentioned previously in chapter 3 the optimal conditions for DBC-water vary from decan-1-ol-water and so it can be reasonably anticipated that at the optimal conditions for DBC-water much higher concentrations of H_2O_2 will be attained. The effect of reaction parameters (such as temperature, reaction time, pressure, solvent loading and catalyst mass) for the DBC-water system will therefore be investigated in order to maximise the efficiency of this system.

- Full characterisation of catalyst after use and investigation of catalyst stability and reuse - In this study the direct synthesis of H_2O_2 was carried out using 5%AuPd/HPA and 5%AuPd/A. W. Carbon catalysts prepared by impregnation. These materials have been fully characterised previously and studied in the methanol-water system.[1-3] Future work will focus on fully characterising these catalysts after a direct synthesis reaction in the biphasic solvent system. This will provide an in depth understanding of how the catalyst behaves in the biphasic system. Furthermore to establish the stability of the catalyst, reusability tests will be carried out, where the catalyst will be tested under the standard conditions, recovered and retested under the standard conditions.

- Catalyst design and screening of highly active catalysts - In this study the direct synthesis of H_2O_2 was studied with catalysts which had a 1:1 Au:Pd ratio prepared by impregnation. Hutchings *et al.* have shown that these catalysts are extremely active in the methanol-water system.[1-7] Furthermore they have demonstrated that the addition of a 3rd metal (Pt) to these Au-Pd catalysts could specifically improve the H_2O_2 synthesis activity, without increasing the rate of subsequent H_2O_2 hydrogenation over the catalyst.[8] The addition of Pt to Au, Pd and Au-Pd provides evidence of a synergistic effect induced by Pt in the bimetallic and trimetallic catalysts. Therefore, further investigation into the preparation and use of these trimetallic catalysts and their preparation methods can give greater understanding of catalytic activity in the biphasic system. Modified impregnation catalysts prepared by Sankar *et al.*[9] have also shown superior activities in the direct synthesis of H_2O_2 in the liquid phase in comparison to catalysts prepared by standard impregnation. These materials will also be evaluated in the biphasic system since they should produce substantially high concentrations of H_2O_2.

- <u>Hydrophilicity of the catalyst</u> - As mentioned in section 3.5 if the catalyst is more hydrophobic, the catalyst will mainly remain in the organic phase during the course of the reaction. This will decrease interaction between H_2O_2-catalyst therefore minimising the rates of H_2O_2 consecutive reactions. Further work will focus on detailed investigations and screening of hydrophobic catalysts for the biphasic solvent system.

- <u>Reactor design</u> - The effect of reagent loading was studied in Chapter 3.8.1.3 and proved to be beneficial for increasing H_2O_2 concentrations. Further investigation into reactor design may be useful for increasing H_2O_2 concentrations. As reagent reloading in the batch system has proved to increase H_2O_2 concentrations, continuously flowing reagent gases in a semi continuous flow system should also lead to an increase in activity. Since the rate of H_2O_2 synthesis is dependent on the H_2 concentration (equation 5.1) H_2 can become the limiting reagent in a reaction.

$$r_1 = k_1\,[H_2]^{a}\,[O_2]^{b} \qquad \text{Equation 5.1}$$

Figure 5.1 highlights the difference in H_2 concentration under semi-continuous flow conditions and reagent reloading in the batch reactor.

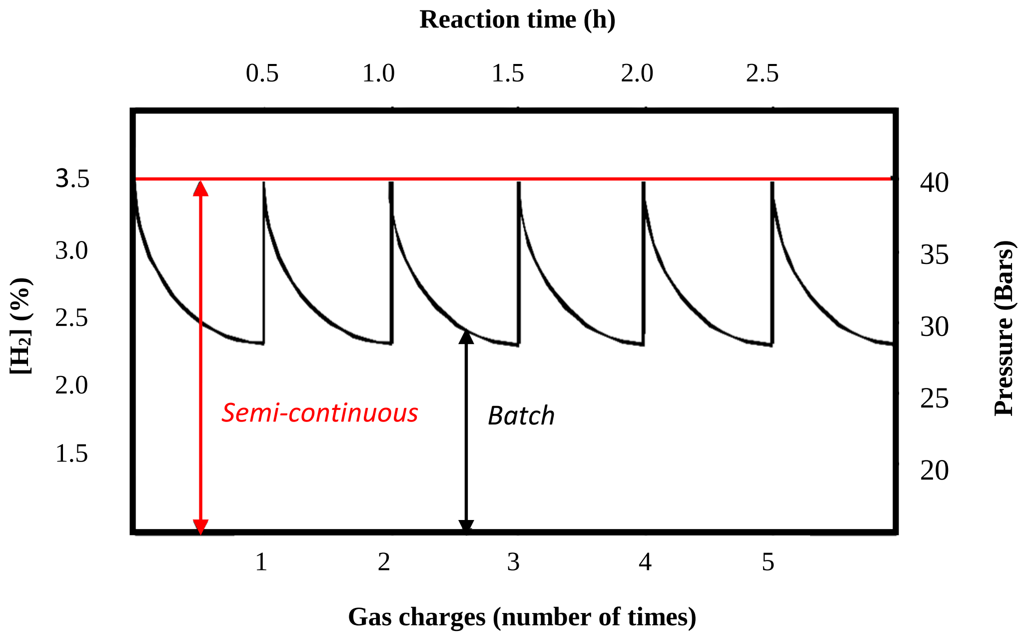

Figure 5.1 Difference between reagent reloading in batch and semi-continuous flow conditions.

The use of a semi continuous flow reactor may be beneficial for increasing H_2O_2 concentrations because as shown in figure 5.1, the concentration of the reagent gases can be maintained throughout the reaction. Furthermore the constant flow of reagent gas can also enable constant pressure in the reaction system which can also contribute to increasing H_2O_2 concentrations.

5.3 The direct synthesis of H_2O_2 in a continuous gas flow reactor

In Chapter 4 the possibility of carrying out the direct synthesis of H_2O_2 in a continuous gas flow reactor was investigated. The first part of chapter 4 was dedicated to studying the direct synthesis of H_2O_2 in the gas phase at atmospheric pressure. The initial aim of this study was to prove the feasibility that H_2O_2 can be produced in the gas phase at atmospheric pressure and then be trapped immediately for analysis. H_2O_2 is known to decompose over various metals and stainless steel,[9] therefore PTFE was selected as a suitable inert material for the atmospheric pressure rig. Several direct synthesis experiments were conducted with a range of reaction conditions but the process found to be extremely difficult and complicated. Despite these difficulties H_2O_2 was synthesised using a 5%AuPd/TiO_2 catalyst at 60 °C under atmospheric pressure. The direct synthesis of H_2O_2 in the gas phase was confirmed by TAP experiments and oxidation reactions. The effect of temperature and gas flow rate was investigated in the gas flow rig and a maximum H_2O_2 concentration of 93 ppm was achieved under optimum reaction conditions (atmospheric pressure, 2%H_2/air, (200 ml min^{-1}), 60 °C, 5%AuPd/TiO_2 catalyst (50 mg).

Recent patents have detailed the formation of H_2O_2 at high temperatures and pressures.[10-11] Therefore a high pressure lab scale flow reactor was designed and built *in-situ* to study the synthesis of H_2O_2 in the gas phase. In agreement with the patents, the use of pressure increased the H_2O_2 concentration in the high pressure reactor and initial tests showed there was a 20 times increase in H_2O_2 concentrations when experiments were conducted at high pressures.

5.3.1 Future work

Although greater H_2O_2 concentrations were produced at higher pressure, the results obtained from the atmospheric experiments in the high pressure rig were much lower than analogous experiments conducted in the atmospheric rig. (3 ppm vs 53 ppm). It was thought that this may be due to H_2O_2 decomposition occurring in the reactor. Future work will focus on resolving this problem as well as further investigating and improving the gas phase system. Future work is discussed in the points below.

- Evaluation of high pressure reactor background to H_2O_2 decomposition – In order to ensure no decomposition occurs in the high pressure rig, all stainless steel piping within the rig will be lined with PTFE. Following this, the reactor background activity towards H_2O_2 decomposition will be evaluated. Once the reactor is proved to be not active towards the H_2O_2 degradation, the catalytic activity for 5%AuPd/TiO_2 catalyst will be evaluated at atmospheric pressure to ensure the same results can be achieved as shown in Chapter 4.6.1.

- Further investigation of 5%AuPd/TiO_2 catalyst - The catalytic activity for 5%AuPd/TiO_2 should be studied at atmospheric pressure and high pressures. Future work will intensively study the effect of reaction variables (temperature, residence time, catalyst loading, pressure, H_2:O_2 ratio etc.) on the direct gas phase synthesis of H_2O_2.

- Effect of active metal loading - Initial experiments have shown that high H_2 conversion is observed at all temperatures, in order avoid this the catalyst can be prepared with lower active metal loadings. Future work will focus on a detailed investigation to study the effect of active metal loading on the H_2 conversion.

- Investigation of conversion and selectivity - A gas chromatograph will be used to analyse the gas composition and determine the H_2 selectivity and conversions; this will allow a deeper understanding of the direct synthesis reaction and its side reactions.

- Use of stabiliser to trap H_2O_2 - Although the synthesis of H_2O_2 was observed over a range of reaction conditions, the H_2O_2 concentration plateaued at higher flow rates. This may be attributed to the build-up of H_2O_2 in the sample cold trap over the reaction period which can result in decomposition of H_2O_2 therefore resulting in lower concentrations of H_2O_2. In order to avoid this, future studies will use an acidic trap which will stabilise the H_2O_2 as soon as it reaches the sample cold trap.

- Screening of highly active catalysts for the direct synthesis of H_2O_2 - As mentioned previously, the modified impregnation catalyst prepared by Sankar *et al.*[9] has superior activities in the liquid phase in comparison to catalyst prepared by impregnation. In order to increase activities of H_2O_2 production in the gas phase reactor more active catalyst will be screened for this reaction.

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