Oxidation catalysis using supported gold nanocrystals

Thesis submitted in accordance with the regulations of the

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Doctor of Philosophy

By

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Declaration

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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To my parents

To my wife

To my children Basil, Danh and Hatem

Publications

1- **Hamed Alshammari**, Peter J. Miedziak, Salam Bawaked, David W. Knight and Graham J. Hutchings, Solvent-free Liquid-phase Oxidation of 1-Hexene using Supported Gold Catalysts,ChemCatChem,2012,4,1565-1572.

2- **Hamed Alshammari**, Peter J. Miedziak, David W. Knight and Graham J. Hutchings, Control of the Selectivity in multi-functional group molecules using supported gold–palladium nanoparticles, Green chemistry, **DOI**: 10.1039/c3gc36828a.

3- **Hamed Alshammari**, Peter J. Miedziak, David W. Knight, David J. Willock and Graham J. Hutchings, The effect of ring size on the selective oxidation of cycloalkenes using supported metal catalysts, Catalysis Science and Technology, **DOI:** 10.1039/C3CY20864H.

4- **Hamed Alshammari**, Peter J. Miedziak, David W. Knight, David J. Willock and Graham J. Hutchings, Initiator-free hydrocarbon oxidation using carbon-supported gold nanoparticles, Angewandte chemie, submitted.

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Abstract

Oxidation is a key process for commercial applications, in the production of chemical intermediates, high tonnage commodity chemicals, high value fine chemicals, agrochemicals and pharmaceuticals. These oxidations often use stoichiometric oxygen donors such as chromate or permanganate, oxygen donors that give rise to pollutants of considerable environmental concern. Free solvent oxidation of 1-hexene with air using supported gold catalysts with a catalytic amount of *tert*-butyl hydroperoxide (TBHP) as initiator has been conducted in the liquid phase. Reaction conditions such as radical initiator concentration and reaction temperature were varied to obtain optimum conditions. The gold supported on graphite is an effective catalyst for such oxidations and that graphite was the best of the supports studied. Preparation of catalysts using modified sol-immobilisation including washing under reflux resulted in enhanced catalyst activity by a solvent treatment prior to the reaction.

Gold, palladium and gold-palladium catalysts supported on TiO_2 has been used for oxidation of *trans*-2-hexen-1-ol and 1-hexene-3-ol with air at 50 ˚C. The effect of the preparation method, catalyst mass, support, gold: palladium ratio and temperature have been investigated. The main aim was to determine if either the alcohol or alkene functional group can be oxidised selectively. However, based on the reaction products observed *trans*-2-hexen-1-ol forms *trans*-2-hexene, hexanal, *trans*-2-hexenal, *trans*-3-hexen-1-ol, 4-hexen-1-ol and *trans*-2-hexanoic acid. 1-hexen-3-ol forms 1-hexene, 3-hexanone, 1hexen-3-one and 3-hexenol), the main pathway in these reactions is isomerisation and, in addition, significant yields of the products are due to a disproportionation reaction. Controlling the selectivity in molecules with multiple function groups by manipulating the catalyst composition and reaction conditions can promote or hinder the various reaction pathways, thereby increasing the selectivity to the desired oxidation products.

Oxidations of cyclic alkenes were carried out using supported gold nanoparticles under mild solvent-free conditions. The influences of support, preparation method and choice of metal have been investigated. The selectivity to the epoxide is dependent on the size of the cyclic alkene ring. In particular, the epoxide selectivity is very low for $< C_7$, and the origins of this effect are discussed. The influence of the removing stabiliser form cycloalkene has been demonstrated that cycloalkene can be oxidized in the absence of radical initiators when cycloalkene is free of stabilisers.

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Chapter one

Introduction

1. Introduction

1.1. History of catalysis

One of the earliest descriptions of systematic catalysis was made in 1836 by Berzeliues[1]. He explained the impact of porous platinum on the combustion of hydrogen and oxygen at ambient temperatures. The first note that demonstrates the reason for the increase in the rate of reaction was made by Faraday in 1813 when he studied the influence of platinum on oxidation reactions[2]. Fulhame (1794) was the first to explore the principle of catalysis, and generated results suggesting that a small amount of water was necessary for the oxidation of carbon monoxide. Nevertheless, the water involved was unaffected by the chemical reaction[3, 4]. The Deacon process, which using a clay brick impregnated with copper (II) salts as a catalyst to convert hydrochloric acid to chlorine, was the first industrial catalytic process[5]. Thereafter, many discoveries were made, which contributed to the improvement of catalysis as an industrial process. Further important milestones in the history of heterogeneous catalysis are summarised in Table 1.1.

Currently, the use of catalysts is important in both academic and industrial research. Between 85–90% of the products of the chemical industry products are produced with the use of catalysts. However, regardless of their importance in industry, catalysts play an essential role in many human processes such as the development of energy sources and control of pollution[6-8].

Table 1.1: Important milestones in heterogeneous catalysis[9]

Year	Investigator	Phenomenon
1831	Phillips	Oxidation of sulphur dioxide on platinum.
1869	Van Hoffman	Oxidation of methanol to formaldehyde on silver.
1880	Humphrey Davy	Use of platinum in catalysis.
1905	Sabatier & Sanderens	Hydrogenation of unsaturated hydrocarbons on nickel.
1915	Langmuir	Theory of adsorption.

1.2. Catalysts defined

Catalysts can be broadly and simply defined as any substance that will alter the rate of a chemical reaction without being used up in the reaction. However, a catalyst will not change the equilibrium position because the effect of the catalyst will take place in both the forward and reverse reactions (i.e. increasing the rate constant of the reaction, K_1 and K_2)[10], as shown here:

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

The rate constant, k, can be further defined by the Arrhenius equation:

$$k = A \cdot \exp^{(-Ea/RT)}$$

Equation 1.1: Arrhenius equation

where A is the collision frequency, Ea is the activation energy (KJ mol^{-1}), R is the gas constant (8.314 JK^{-1} mol^{-1}) and T is the temperature (K).

The effect of a catalyst on the pathway of reaction is to decrease the activation energy barrier as shown in Figure 1.1. As can be clearly seen (Figure 1.1), the reaction pathway in the presence of a catalyst is that of lower activation energy than the reaction pathway in the absence of a catalyst.

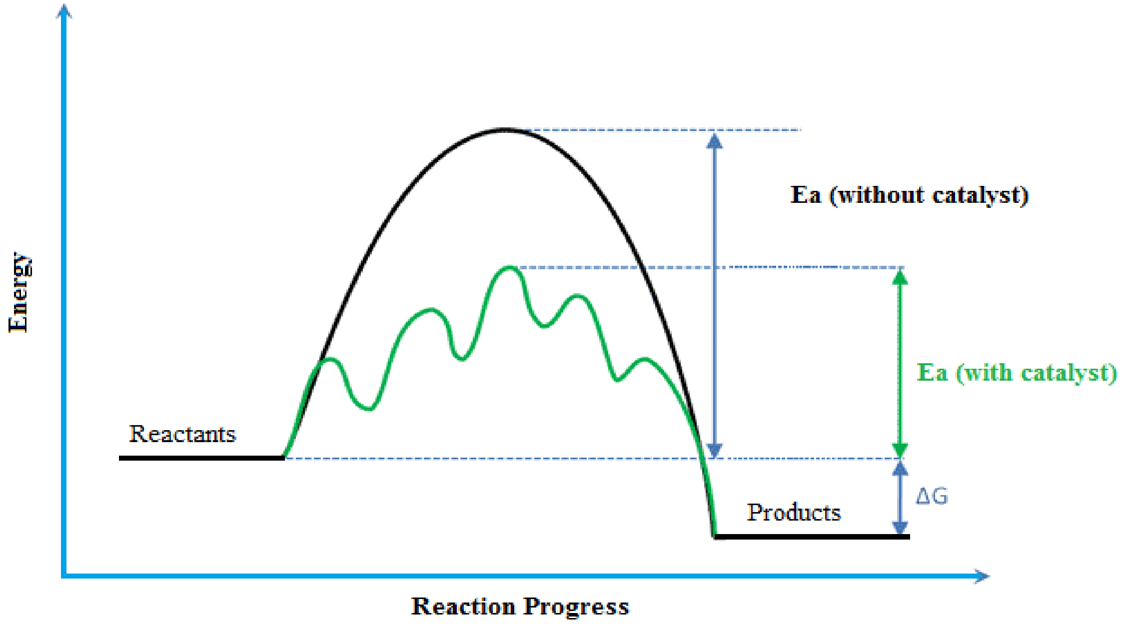


Figure 1.1: Activation energy barriers of a catalysed/uncatalysed reaction

1.3. Types of catalysis

Catalysis can generally be classified into three types: bio-catalysis, homogeneous catalysis and heterogeneous catalysis. The first type, bio-catalysis, takes place with natural catalysts. The second type, homogeneous catalysis, involves mixing the catalyst and reaction in the same, usually liquid, phase. In heterogeneous catalysis, the catalyst and reaction mixture are in different phases; most industrial chemical processes use processes of heterogeneous catalysis.

1.3.1. Bio-catalysis

Enzyme catalysis (bio-catalysis) is a natural process, which all living processes depend on. The enzyme in the catalysis consists of protein and the active site in enzyme catalysis contains amino acids, which are linked together by an amide bond and this bond establishes the enzyme’s structure. The active site of an enzyme is usually a cleft surrounded by an array of amino acid residues. An enzyme is bound to the substrate by some of the residues (Figure 1.2), which takes place as a result of four kinds of interactions: electronic interactions, hydrogen bonding, van der Waals interactions and hydrophobic interactions[11].

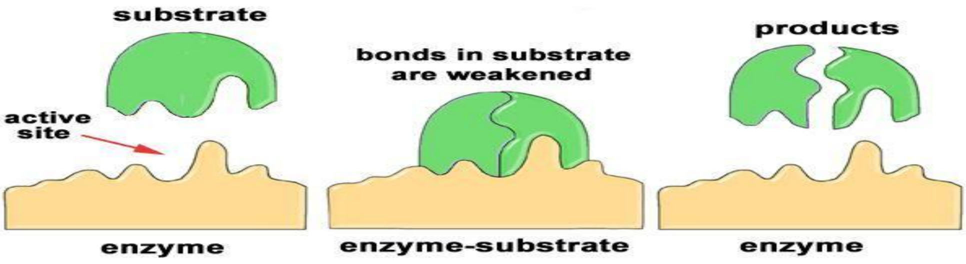


Figure 1.2: Enzyme-substrate binding

Enzyme catalysis have been used widely to provide catalysts for industrial processes in recent times. The advantage for enzyme catalysis is that the process is more selective than other kinds of catalysis. However, heating might destroy an enzyme catalysis by breaking the weak bonds that hold the active site in its correct configuration[9].

1.3.2. Homogeneous catalysis

Homogeneous catalysis involves a catalyst and reaction mixture in the same phase, which is most often liquid. In homogeneous catalysis, a ligand plays an important role in adjusting the selectivity of the catalyst. Thus, choosing the right metal and the right ligand can improve the catalytic activity and selectivity[12]. An example is the styrene dimerisation reaction (Figure 1.3)[13].

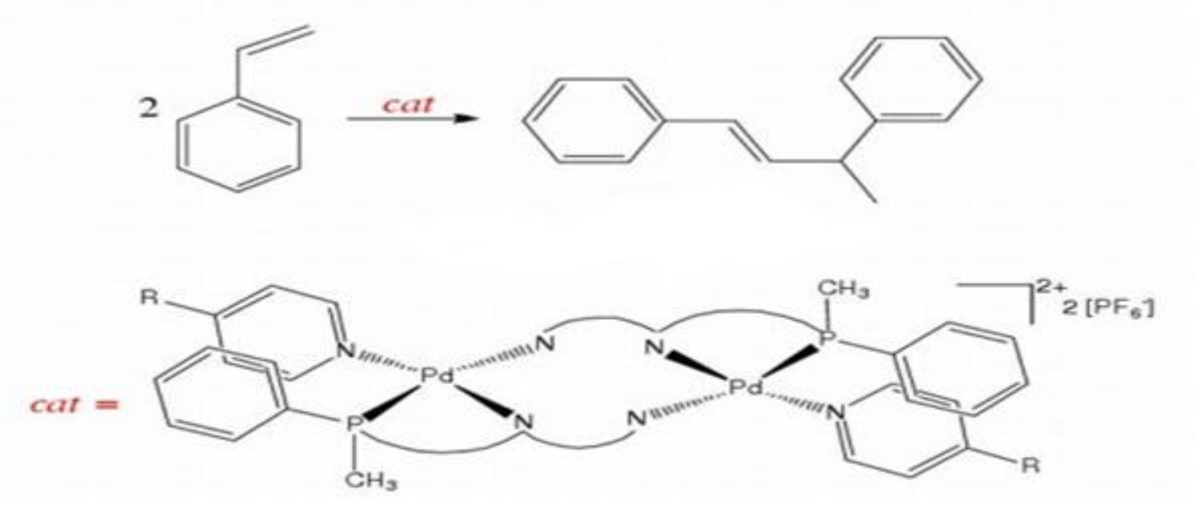


Figure 1.3: Styrene dimerisation reaction using a homogeneous catalyst

An increasing number of industrial applications use homogeneous catalysis. The advantages for homogenous catalysis are its high selectivity, the ease of studying the reaction mechanism by spectroscopic methods and the improvements that are found in this stage, which are often quicker and simpler. However, difficulties of the recovery and separation of the catalyst are major disadvantages in homogenous catalysis.

1.3.3. Heterogeneous catalysis

Heterogeneous catalysis occurs at a different phase from the reaction mixture. Heterogeneous catalytic reactions involve the steps as shown in Figure 1.4[11]. In the first stage of the cycle of heterogeneous catalysis, the reaction is adsorbed on the catalyst surface at the active site. The next stage on the cycle of heterogeneous catalysis is the attachment of the reactant molecules to the surface, these attached molecules are hit by the other molecules that are moving freely in the gas or liquid. In the last stage, the product molecules are desorbed and then the active site will be available for new molecules to attach and react.

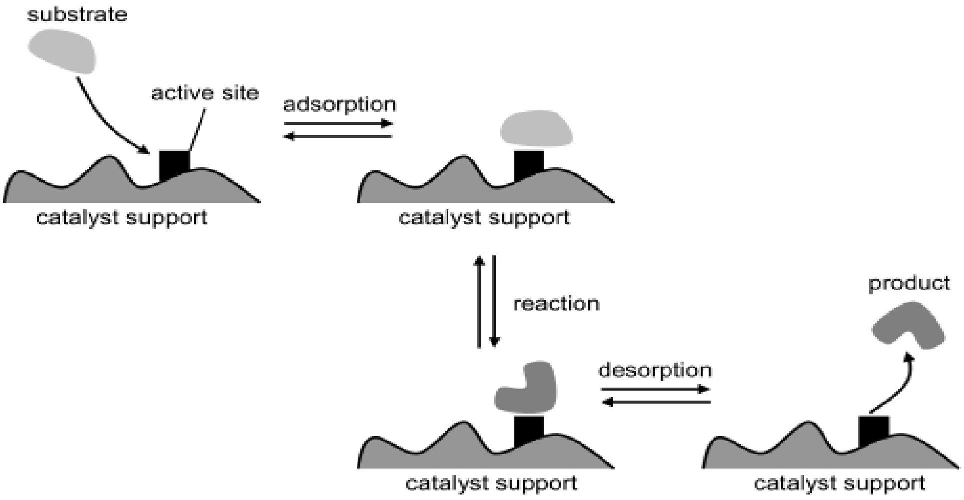


Figure 1.4: The reaction on a catalyst surface

Heterogeneous catalysis has several advantages over homogenous catalysis. Table (1-2) shows the difference between heterogeneous catalyst and homogenous catalyst.

Table 1.2: Comparison between heterogeneous and homogenous catalyst[14]

	Heterogeneous	Homogenous
Catalyst phase	Usually solid	Metal complex
Selectivity	variable	High
Recyclability	Easy	Difficult
Solvent	Usually not required	Usually required
Stability at high temperature	Stable	Decomposed
Application	wide	Limited

There are many industrial applications that use heterogeneous catalysis, such as are found in the chemical, pharmaceutical and petrochemical industries [5, 8, 15-17]. Moreover, heterogeneous catalysis has been used for new applications such as are generated by green chemistry[18, 19], fuel cells[20, 21] and biotechnology[22-25]. Table 1.3 shows some major industrial processes using heterogeneous catalysis.

Table 1.3: Important processes based on heterogeneous catalysts[8, 26]

Process	Catalyst
Haber-Bosch NH_3 synthesis	Magnetite (Fe)
Methanol synthesis	$Cu/ZnO/Al_2O_3$
Polymerisation of ethylene	Cr, $TiCl_x/MgCl_2$
Alkylation	Solid acide
Isomerisation of (xylenes, toluene)	HZSM-5 zeolites
Hydrogenation of vegetable oil	Ni
Dehydrogenation of alkanes	Pt/Al_2O_3
Oxidation of xylenes	Vanadium oxide
Ethylene epoxidation	Ag
Oxidative dehydrogenation of propane	Fe_2O_3, Cr_2O_3

1.4. Oxidation catalysis

Oxidation is a very important reaction industry. There are a number of valuable products that are produced for useful organic chemicals and intermediates as well as for environmental clean-up and pollution abatement by oxidation processes [27]. Oxidation processes can be divided into two types, total oxidation and selective oxidation. In total oxidation, the CO_2 and water are the thermodynamically stable products. Total oxidation is used in energy production as well as in environmental removal of the pollutants. In the selective oxidation kinetic control must be employed as the desirable products are not thermodynamically stable [28]. The common oxidation reaction and their catalysts are summarized in table 1.4.

Table 1.4. Common oxidation processes and their catalysts[27]

	Reaction	Catalysts
Total oxidation	Oxidation of carbon monoxide to carbon dioxide	CuMnO4, Au/MOx at 25 ˚C, Pt/MOx > 200 ˚C
	Oxidation of sulphur dioxide to sulphur trioxide	Pt, V2O5
	Oxidation of volatile organic compounds (VOCs) to CO2 and water	Pt, Pd/Al2O3
Selective oxidation	Oxidation of butane to maleic anhydride	Vanadium phosphate
	Oxidation of propene to acrolein	$MoOBi_2O$, US_3O_{10},$FeSbO_4$
	Oxidation of propene to acrylonitrile	$MoBi_2O_6$, US_3O_{10},$FeSbO_4$
	Oxidation of o-xylene to phthalic anhydride	V_2O_5
	Oxidation of methanol to formaldehyde	Iron molybdate, Ag
	Oxidation of ethane to ethylene oxide	Ag
	Oxidation of ethyl benzene to styrene	V_2O_5/TiO_2

Selective oxidation of hydrocarbons such as alkenes, alcohol, aldehydes and acids is a key process for commercial applications, in the production of chemical intermediates, high tonnage commodity chemicals, high value fine chemicals, agrochemicals and pharmaceuticals. These oxidations often use stoichiometric oxygen donors such as chromate or permanganate, oxygen donors that give rise to pollutants of considerable environmental concern [29]. Accordingly, research to find green alternatives is now attracting considerable interest, as replacement production processes are crucial to providing cleaner routes to important oxidation products. The ultimate goal is to employ dioxygen with an efficient oxidation catalyst. Many metals and metal oxides have been used as heterogeneous catalysts for the oxidation reaction. Metal oxides catalysts have been used in several industrial processes such as oxidation of H_2S to sulphur element over supported Fe_2O_3/SiO_2 and MnO_x/SiO_2 catalysts[30]. Metal catalysts are widely used in the chemical industries. Gold is one of these metals which have shown promising results. Gold catalysts have been shown to be effective for several types of oxidation reactions, particularly the oxidation of alcohols[31], oxidative esterification of alcohols[32], the direct synthesis of hydrogen peroxide[33] and the oxidation of alkenes[34].

1.5. Catalysis by gold

Gold, together with silver and copper, constitutes the eleventh group of the periodic table. The atomic configuration of gold is [Xe] $4f^{14}5d^{10}6s^{1}$. In comparison with other elements of group 11, gold has unique and special qualities, such as being resistant to corrosion and oxidation. Table 1.5 shows the comparison of some physical properties of the elements of group 11[35]. The range of the oxidation state of gold is from -1 to +5. The less common oxidation states of gold in its compound forms are Au (-1), Au (II) and Au (V). However, Au (0), Au (I) and Au (III) are the most common oxidation states of gold.

Table 1.5: Physical properties of group 11 in periodic table

Property	Copper	Silver	Gold
Atomic number	29	47	79
Atomic weight	63.55	107.86	196.97
Electronic configuration	$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$	$[Xe]4f^{14}5d^{10}6s^1$
Structure	Fcc	Fcc	Fcc
MP (˚C)	1083	961	1064
BP (˚C)	2570	2155	2808
Density (g/ml)	8.95	10.49	19.32
Electrical resistivity(μohm-cm)	1.673	1.59	2.35
Electronegativity	1.9	1.9	2.4
Electron infinity (kJ mol^{-1})	87	97	193
First ionization energy (kJ mol^{-1})	745	731	890
Metal radius in (12-coordination)/pm	128	144	144
Number of natural isotopes	2	2	1

Historically, gold has been considered to be catalytically inactive, as the d-orbitals in the Au atom are filled[36]. The first use of gold as a catalyst was achieved in the 1970s by Bond and co-workers when they prepared Au/SiO_2 by impregnation, which has found usage in the hydrogenation of alkenes [37].

Catalysis by gold has become an exciting topic in chemistry after two significant reports in the 1980s that completely changed the understanding and highlighted the special attributes of gold as a heterogeneous catalyst. These observations are as follows:

1- Haruta reported that gold nanoparticles are very active for CO oxidation at low temperatures[38].
2- Hutchings showed that gold is the best catalyst for ethyne hydrochorination[39].

As a result of the development of gold catalysis that followed in the wake of these two reports, the number of publications and patents has been on the increase (Figure 1.5)[40, 41]. There are many applications for gold as a catalyst such as in chemical industrial processes, environmental control and fuel cells. The single most important industrial application for the use of gold catalysis is CO oxidation at low temperatures, which could be used in fuel cell and car exhaust gas purification systems[42-45]. Further significant applications of the use of gold as a catalyst are in the production of hydrogen peroxide, oxidation of alcohol, oxidation of hydrocarbon and hydrogenation of alkynes[46].

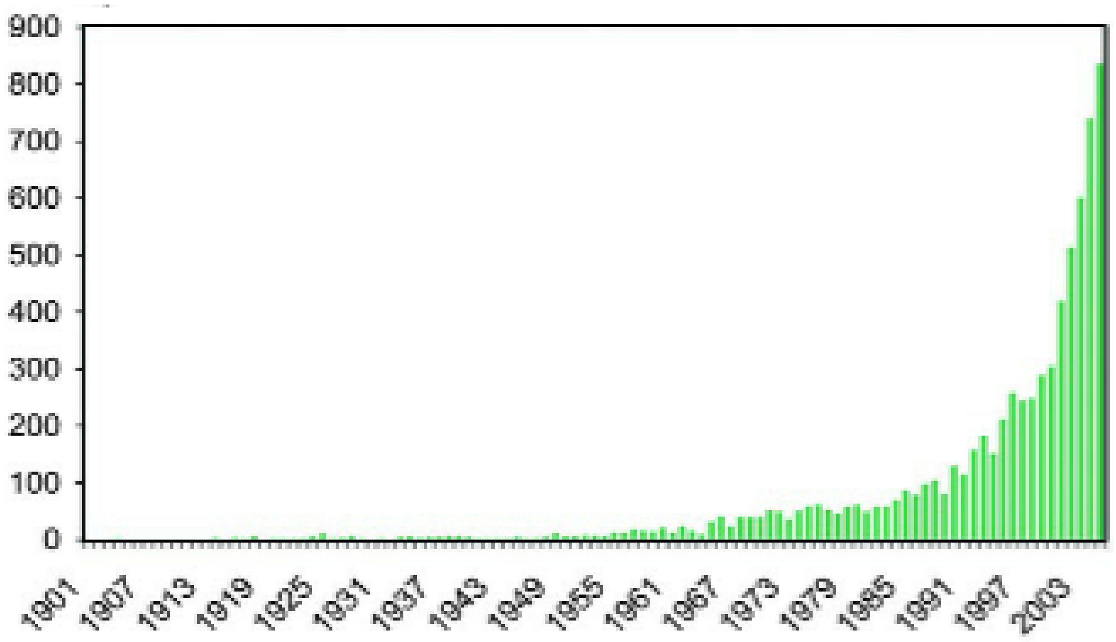


Figure 1.5: Number of Publications on gold catalysis

1.6. Principles of the preparation method of supported gold catalysts

There are some factors that could have an effect on the catalyst activity such as the preparation method and the choice of support. The size of gold particles is a very important parameter in obtaining active catalysts. The preparation method strongly influences the particle size [35]. The introduction of gold precursors on the support by impregnation, deposition – precipitation and sol-immobilisation is the first main step for the preparation method followed by drying and calcinations.

1.6.1. Impregnation

The impregnation method is a simple method and can be applied with any support. The impregnation can be obtained by the adsorption of the active phase from a gold solution by adding support to the aqueous solution of gold precursors. The chloroauric acid

($HAuCl_4$) and gold chloride ($AuCl_3$) are most often used as gold precursors. The gold particles by impregnation method are large (10-30 nm) duo to chloride ion which promotes mobility and agglomeration of gold species during thermal treatment [35].

1.6.2. Deposition – precipitation (DP)

The DP method is widely used for preparing the small gold particles support on metal oxides. In this method the support is added to an aqueous solution of $HAuCl_4$ and then the pH of the mixture is increased to a fixed value by adding sodium hydroxide or carbonate. Usually, the pH 7 or 8 is the optimal condition duo to correspond to the best compromise between the gold particle size and gold loading. The suspension is heated to a certain temperature with stirring for 1h. Deposition – precipitation contains washing steps which help remove as much chlorine as possible. The product is then dried and calcined in air at a higher temperature. The DP method can be used with support having a point of zero charge (PZC) greater than five such as magnesia, titania and alumina, but it is not suitable for support such as silica (PZC ~ 2) and tungsta (PZC ~ 1)[35].

1.6.3. Sol-immobilisation

The gold particles are immobilised on support by adding the support to a colloidal suspension. A stabiliser such as poly vinyl alcohol (PVA) is added to the aqueous solution of gold precursors. The most important role of the stabilising polymer is to protect the nanoparticles from aggregation. However, recent work has shown that, when PVA is used as a stabilising ligand, it can be removed after the nanoparticles have been supported by extraction with water. The support is added to the aqueous solution of gold precursors and then the catalyst is washed and dried. A sol-immobilisation method gives a higher dispersion of gold with a much smaller nanoparticle size distribution (2-5 nm) [35, 47].

1.7. Selective oxidation of hydrocarbons by gold

Selective oxidation of hydrocarbons to produce oxygen-containing organic compounds is a task of key importance for modern chemical processes. Gold catalysis has been found to be effective for the oxidation of hydrocarbons such as alkenes and alcohols under green chemistry conditions by using more environmentally friendly and cheaper oxidants such as oxygen.

1.7.1. Selective oxidation of alkenes

The selective oxidation of hydrocarbons is an essential step in transformations for the pharmaceuticals industry, even though this remains difficult to achieve whilst observing the tenets of green chemistry. There is therefore a pressing need to identify environmentally friendly approaches for the design of new oxidation catalysts that can operate with molecular oxygen.

1.7.1.1. Oxidation of α- alkenes

Epoxidation of propene to propene oxide (PO) is one of the very important topics in industrial processes. The earliest study of the use of supported gold for the epoxidation of alkenes was by Haruta[48]. These researchers investigated the possibility that gold catalysts can be used for the epoxidation of propene in the presence of hydrogen as a sacrificial reductant. Haruta *et al.* [49] reported that 1% conversion with 99% selectivity to propene oxide was achieved when using gold supported on TiO_2 in the presence of hydrogen and oxygen. Propene oxidation can be used in the production of several kinds of products depending on the catalyst and reaction conditions used[50] (Figure 1.6).

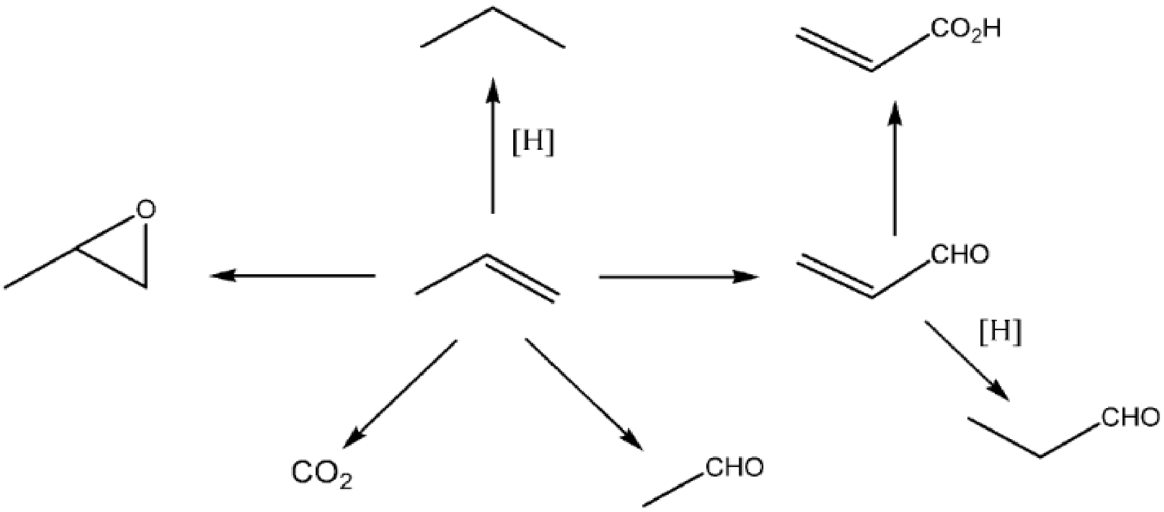


Figure 1.6: The possible products of the oxidation of propene

Nijhuis and co-workers [51] investigated that gold provides a peroxide species, which subsequently epoxidises propene on the support sites. In their work, they propose the following reaction mechanism. Propene reacts with TiO_2 to form an adsorbed bidentate peroxy species which subsequently is catalysed by Au/TiO_2. The peroxide species, which is produced from the reaction of H_2 and O_2 on a gold surface, aids in the desorption of the bidentate peroxy species from the catalyst, producing propene oxide and water. Mul *et al* [52] used the IR spectra to show that bidentate peroxy species is present on the surface of the catalyst and it is oxidised to formate and acetate species on

TiO_2, while the bidentate peroxy species could not be oxidised on Au/TiO_2/SiO_2. The use of gold on titania including Ti-MCM-41, Ti-MCM-48 and TS-1 has been reported in the literature [51, 53-59]. Haruta and co-workers demonstrated that by using an Au/Ti-MCM-41 catalyst at 100 ˚C, 2% conversion with 95% selectivity to PO was achieved. Delgass *et al*. [60] further demonstrated that the pretreatment of Au/TS-1 with NH_4NO_3 improved the catalytic activity (5%) with 83 % selectivity to PO at 200˚C. Makkee and co-workers [53] used Au/TiO_2-based catalyst for the epoxidation of propene. It was demonstrated that low PO yield over catalyst duo to non-langmuir adsorption noting that an increase in catalyst loading does not lead to improving the yield of PO. The authors suggest that consecutive reaction over Ti---O---Ti containing units might be the reason for low PO yield over Au/TiO_2-based catalyst. Haruta *et al.* [61] used gold on titanosilicate (TiO-SiO) as a catalyst prepared by a modified Sol gel method. In their investigations, they determined that a conversion of 4.5% was obtained with 79 % selectivity to PO when using 0.6% of gold on support in the presence of hydrogen.

Another example of the oxidation of α-alkenes by using a supported gold catalyst is 1-octene. Corma *et al.* [62] have shown that the use of Au/CeO_2 was active for the oxidation of 1-octene in the presence of 2,2-Azoisobutyronitrile (AIBN) as the radical initiator. It has been found that very low conversion was observed after 5 h of reaction in the absence of AIBN. However, in the presence of the radical initiator, the conversion increased up to 5% with 45% selectivity to 1,2-octane oxide. In another significant result, a conversion of 40% with 90% selectivity to 1,2-octane oxide was achieved for

1-octene oxidation over Au/CeO_2–Ti-MCM-41 in the presence of 3-methyl-pentane. According to these authors, 1-octene can be oxidised to several possible products, which are shown in Figure 1.7.

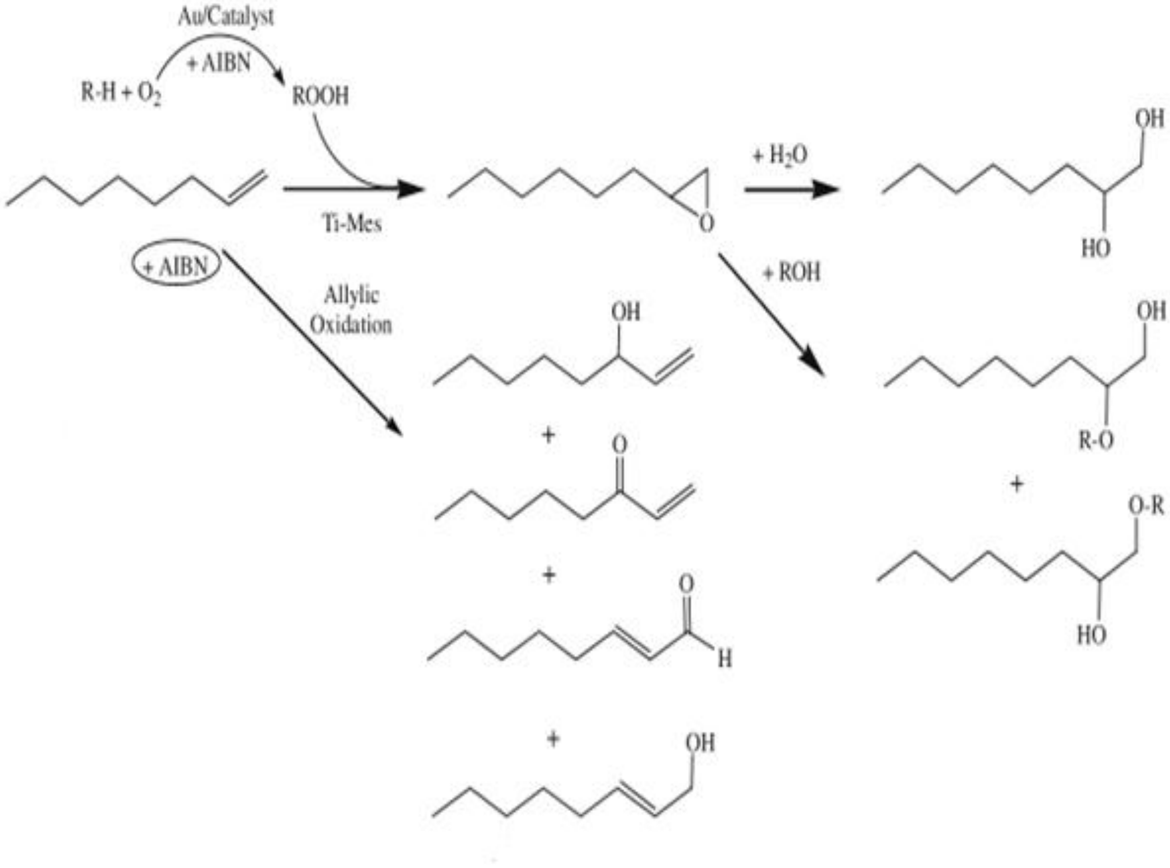
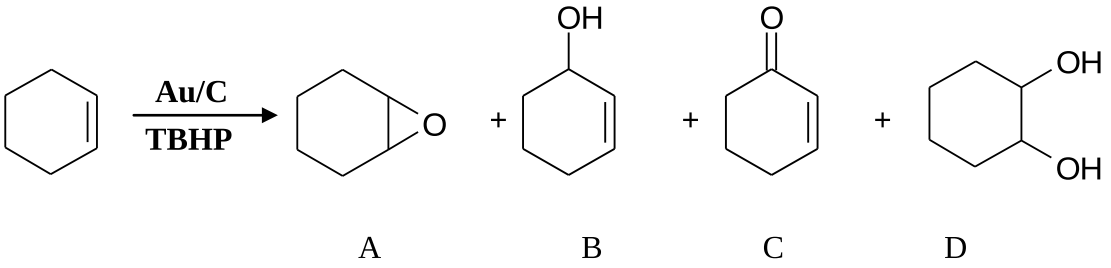


Figure 1.7: Reaction network of 1-octene aerobic epoxidation

1.7.1.2. Oxidation of cycloalkenes

Hutchings' groups[34] have found that Au/C as a catalyst is effective for the oxidation of cyclohexene at 60 ˚C in the presence of an initiator (either H_2O_2 or TBHP). It has been demonstrated that the oxidation of cyclohexene is dependent on the choice of solvent. For instance, 100% conversion with no C_6 products was achieved in the presence of water as solvent. However, the selectivity to C_6 products was increased to 76% (50% cyclohexane oxide and 26% 2-cyclohexen-1-one) with a conversion of 30% when using 1,2,3,5-tetramethylbenzene as the solvent. Greater selectivity to C_6 products (97%) was obtained when the Au/C catalyst was added by the addition of Bi to the catalyst. The possible products of allylic oxidation of cyclohexene are 2-cyclohexen-1-ol (B) plus possible further oxidation to 2-cyclohexen-1-one (C). In addition, the possible product of the epoxidation of cyclohexene is cyclohexane oxide (A), followed by ring-opening to cyclohexane-1,2-diol (D) (Scheme 1.1)



Scheme 1.1: The possible products of the oxidation of cyclohexene. Cyclohexane oxide (A), 2-cyclohexen-1-ol (B), 2-cyclohexen-1-one (C) and cyclohexane-1,2-diol (D)

Oxidation of cyclohexene can be carried out by using other radical initiators. Corma and co-workers[63] demonstrated that the AIBN can be used as a radical initiator for cyclohexene oxidation at 60 ˚C using Au/CeO_2 as the catalyst. 20% selectivity to cyclohexane oxide and 15% to 2-cyclohexen-1-ol was achieved. However, in the absence of AIBN, a negligible conversion was observed. Tsang *et al.* [64] showed that by using gold nanoparticles supported on Si nanowires (SiNWs), a high rate of conversion (92%) with 75% selectivity to 2-cyclohexen-1-ol was observed in the presence of Tertbutylhydroperoxide (TBHP). In addition, selectivity to cyclohexane oxide was very low in solvent-free conditions. According to the authors, the reason for the high activity of this catalyst is the high surface area of SiNWs. Gold nanoparticles supported on multi-walled carbon nanotubes (Au/CNTs) was used for cyclohexene oxidation by Li *et al.*[65]. It was demonstrated that Au/CNTs were very active for cyclohexene oxidation in the presence of CH_3CN as the solvent and TBHP as the radical initiator. The product distribution of cyclohexene was 51% cyclohexane oxide, 7.5% 2-cyclohexen-1-one and 9% 2-cyclohexen-1-ol at 85% conversion.

Supported gold has been used as a catalyst for the epoxidation of cyclooctene. Hutchings *et al.* [34] have shown that graphite-supported gold nanoparticles are active for cyclooctene epoxidation in the presence of TBHP as the radical initiator. 28% conversion with 94% selectivity to cyclooctane oxide was observed in the presence of 1,2,3,5-trimethylbenzene as solvent. In solvent-free conditions, a conversion of 8% with 81% selectivity toward cyclooctane oxide was achieved. Li and co-workers[65] reported that 1% gold supported on carbon nanotubes (CNTs) can be used as the catalyst to convert cyclooctene to cyclooctane oxide. It was demonstrated that 54% conversion and 44% selectivity to cyclooctane oxide were obtained when using CH_3CN as the solvent in the presence of TBHP. Subsequently, Hutchings and co-workers [66, 67] have shown that the activity of gold on different supports for cyclooctene oxidation was as follows: graphite ≈ SiC > Al_2O_3 ≈ SiO_2 > TiO_2, and different supports were effective on the selectivity to cyclooctane oxide as follows: graphite ≈ SiO_2 ≈ TiO_2 > SiC > Al_2O_3. The work also tested the influence of preparation methods on cyclooctene epoxidation. One percent Au/graphite was prepared using the deposition precipitation, sol-immobilisation and impregnation methods. The catalyst prepared by the sol-immobilisation method was more active than others with respect to epoxidation. It was proposed that the small particle size (2–3 nm) for a catalyst prepared by sol-immobilisation methods was the reason for the high activity. In contrast, the particle size distribution of the 1% Au/graphite catalyst prepared by deposition precipitation and impregnation method is 10–30 nm, which also gave very similar activities (Table 1.6).

Table 1.6: The influence of preparation methods on cyclooctene epoxidation

Preparation method	Conversion (%)	Selectivity to epoxide
Deposition precipitation	4	78
Sol-immobilisation	7.7	81
Impregnation	4.2	71

Tsang *et al.* [64]demonstrated that nanoparticles of gold supported on Si nanowires (SiNWs) were active for cyclooctene epoxidation. A conversion of 38% with 90% selectivity to cyclooctane oxide was achieved in the presence of TBHP at mild conditions. The authors suggest that the high activity of the catalyst is due to the high loading of gold and the high surface area of support. More recently, Hutchings *et al.* [68] have carried out studies into the influence of the Au:Pd ratio on cyclooctene activity using a range of graphite-supported Au-Pd catalysts (Figure 1.8). This study demonstrated the maximum in activity observed with an Au:Pd molar ratio of 0.35:0.65 and the minimum in activity at Au:Pd = (0.74:0.26 and 0.09:0.91). However, in the case of monometallic Au and Pd, the catalysts were more active than the bimetallic Au-Pd = 0.35:0.65. Moreover, the Au:Pd molar ratio had no effect on selectivity to epoxide, alcohol and ketone.

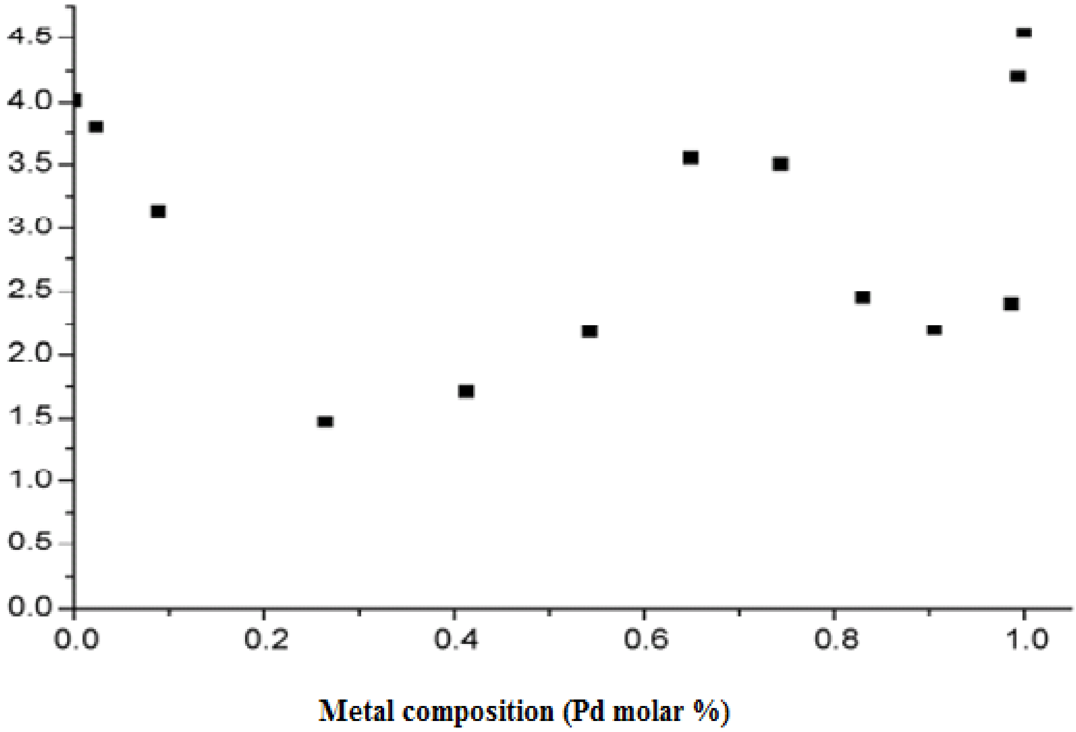
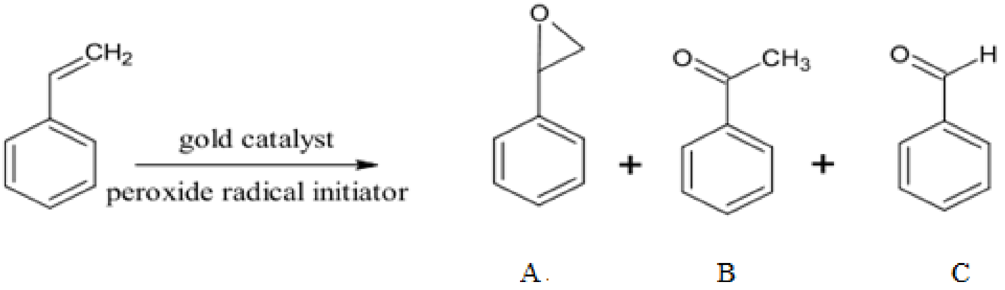


Figure 1.8: Effect of metal composition on *cis*-cyclooctene conversion

Oxidation of styrene can be performed by using supported gold catalysts in the presence of a radical initiator (Scheme 1.2). Yin *et al.* [69] have been using gold on mesoporous alumina and TBHP as oxidant for the epoxidation of styrene. A selectivity of 74% to epoxide and benzyaldehyde as by products was observed at 82 ˚C with 68% conversion. The authors tested different types of mesoporous alumina, which have different surface basicity. In this study, by increasing the surface basicity, the activity of the catalyst was increased.



Scheme 1.2: The possible products of the oxidation of styrene. Styrene epoxide (A), acetophenone (B) and benzaldehyde (C)

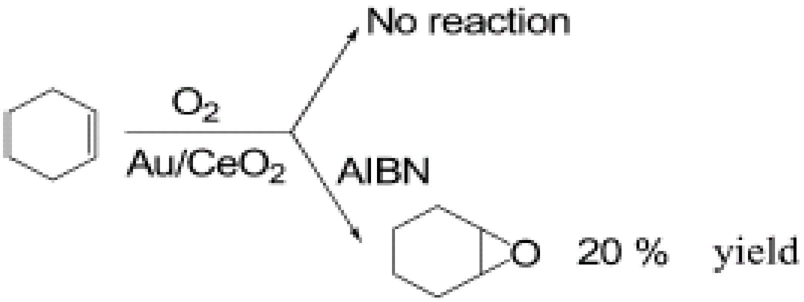
Lambert and a co-workers[70] studied the possibility that very small Au_{55} nanocrystals supported on carbon were very active for styrene oxidation with oxygen in the absence of a radical initiator, but benzaldehyde was the major product. The influence of support on the activity of styrene was strong. Coudhary *et al.*[71, 72] used the supports TiO_2 and CeO_2 for the oxidation of styrene. It was found that TiO_2 shows the highest activity with respect to styrene oxide in the presence of TBHP. Other supports were tested by the same author[73], namely TiO_2,Cr_2O_3, MnO_2, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, Y_2O_3, ZrO_2, La_2O_3 and U_3O_8. It was found that TiO_2 and CuO were the best support among the other oxide supports for the oxidation of styrene when using TBHP as the oxidant. The gold supported on Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3 were tested as well on styrene oxidation[74]. The activity of gold on different supports was as follows: $Au/Al_2O_3 < Au/Ga_2O_3 < Au/In_2O_3 < Au/Tl_2O_3$. Hutchings and co-workers[34] reported that by using Au/C and hexaflurobenzene as solvent, 46% selectivity to benzyladhyde together with 29% epoxide and 11% acetophenone selectivity were obtained at a conversion of 8% in the presence of TBHP as the oxidant. Wang and co-workers[75] reported that gold nanoparticles supported on carbon nanotubes were very active for styrene in the presence of TBHP. A conversion of 95% with 78% selectivity to epoxide was achieved after 22 h of reaction in the presence of CH_3CN as solvent.

Peroxide plays an important role in the oxidation of alkenes. The use of peroxide as reaction initiator (catalytic amounts) and gold as the catalyst for the oxidation of alkenes has been reported in the literature [69, 76-79]. Hutchings and co-workers have demonstrated the use of TBHP as an initiator for cyclohexene oxidation. It was demonstrated that in the absence of TBHP, no conversion was observed. Bodong *et al.* [65] have shown the influence of the TBHP amount on cyclooctene oxidation. It was found that by increasing the concentration of TBHP (1.25 to 5 % mol based on cyclooctene), the activity increased from 25% to 54%. However, the increased concentration of TBHP greater than 5% mol based on cyclooctene was not effective on the activity of reaction. The authors suggest that the action of TBHP concentration in reducing the rate-determining step seems to be the formation of oxygen free radicals, but if the concentration of TBHP is high, the rate control could turn to the transfer of oxygen free radical species. Subsequently, Hutchings and co-workers [66, 67] have tested other radical initiators on cyclooctene oxidation such as cumene hydroperoxide (CHP), di-tert-butyl peroxide (DTBP), dibenzoyl peroxide (DBP) and azobisisobutyronitrile (AIBN) in the absence and the presence of a catalyst (Table 1.7). It was found that CHP, DBP and AIBN were active in the absence of a catalyst and the activity was very poor when DTBP was used as a radical with or without a catalyst. However, TBHP only showed enhancement in activity when a catalyst is present (Table 1.7). In addition, by increasing the concentration of the initiator, the activity was increased whether with or without a catalyst. Wang *et al*. [75] reported that the reaction activity of styrene increases with an increase in the TBHP amount.

Table 1.7: Cyclooctene epoxidation using five different radical initiators in the absence and in the presence of catalyst

Peroxide initiator (0.0103×10^{-2} mol)	Without catalyst		With catalyst	
	Conversion %	Selectivity to epoxide %	Conversion %	Selectivity to epoxide %
TBHP	0.02	0	4.0	78.2
CHP	1.3	64.1	2.9	79.3
DTBP	0.04	0	0.04	0
AIBN	4.1	82.4	4.1	80.7
DBP	5.6	83.5	3.3	79.4

Coundhary and a co-worker [71-74, 80] have been using many supports for the oxidation of styrene in the presence of TBHP as a radical initiator. Caps and a co-worker[81] used TBHP and DTBP as the radical initiator for stilbene epoxidation. These researchers found that TBHP led to a high yield for the epoxidation pathway. Corma *et al.* [63] have used AIBN as a radical initiator for the oxidation of cyclohexene. Their studies demonstrated that no cyclohexene conversion was obtained in the absence of AIBN. However, a significant increase in activity was observed when a small amount of AIBN was added (Scheme 1.3).



Scheme 1.3: Oxidation of cyclohexene using Au/CeO_2 in the absence and in the presence of AIBN

Corma and a co-worker[62] have also used the radical initiator (AIBN) for 1-octene oxidation. In these efforts, they demonstrated that catalytic amounts of these initiators are required. Other radical initiators were tested as shown in Table 1.8.

Table 1.8: Effect of the type of radical initiator on 1-octene oxidation

Initiator	Conversion %	Selectivity %	
		Epoxide	Allyl. oxide products[a]
AIBN	5.3	88.4	9.6
Benzoyl peroxide	0.6	74.8	23.1
CHP	0.4	71.5	27.4
TBHP	0.6	68.3	28.2
TBPB[b]	0.4	64.8	32.2

A = allyl oxide products (1-octen-3-ol, 1-octen-3-one, 2-octen-1-ol, and 2-octenal), b = tert-butyl-peroxybenzoate(TBPB)

Recently, Hutchings *et al.* [67] have proposed a mechanism for cyclooctene oxidation using Au/graphite as the catalyst and TBHP as a radical initiator (Figure 1.9). It was demonstrated that the pathway depends on radical initiator concentration. As the first step in the presence of gold, TBHP may decompose to $(CH_3)COO^{\cdot}$ or $(CH_3)CO^{\cdot}$, which is more likely. The formed radical abstracts a hydrogen atom from cyclooctene and produces an allylic radical (1), which, through the oxygen adduct (2), produces cyclooctene hydroperoxide (3). This step could explain the induction period, after which the concentration of cyclooctene hydroperoxide is sufficient to support the oxidation of cyclooctene on the surface of the gold catalyst. In this case, the authors make the assumption that to carry out the transformation of (3) into cycloocteneyloxy radical (4), the catalyst cycle must be completed by abstraction of allylic hydrogen from a further molecule of cyclooctene or attachment to the double bond of cyclooctene, therewith forming a radical (5) that generates a cyclooctane oxide and the allylic radical.

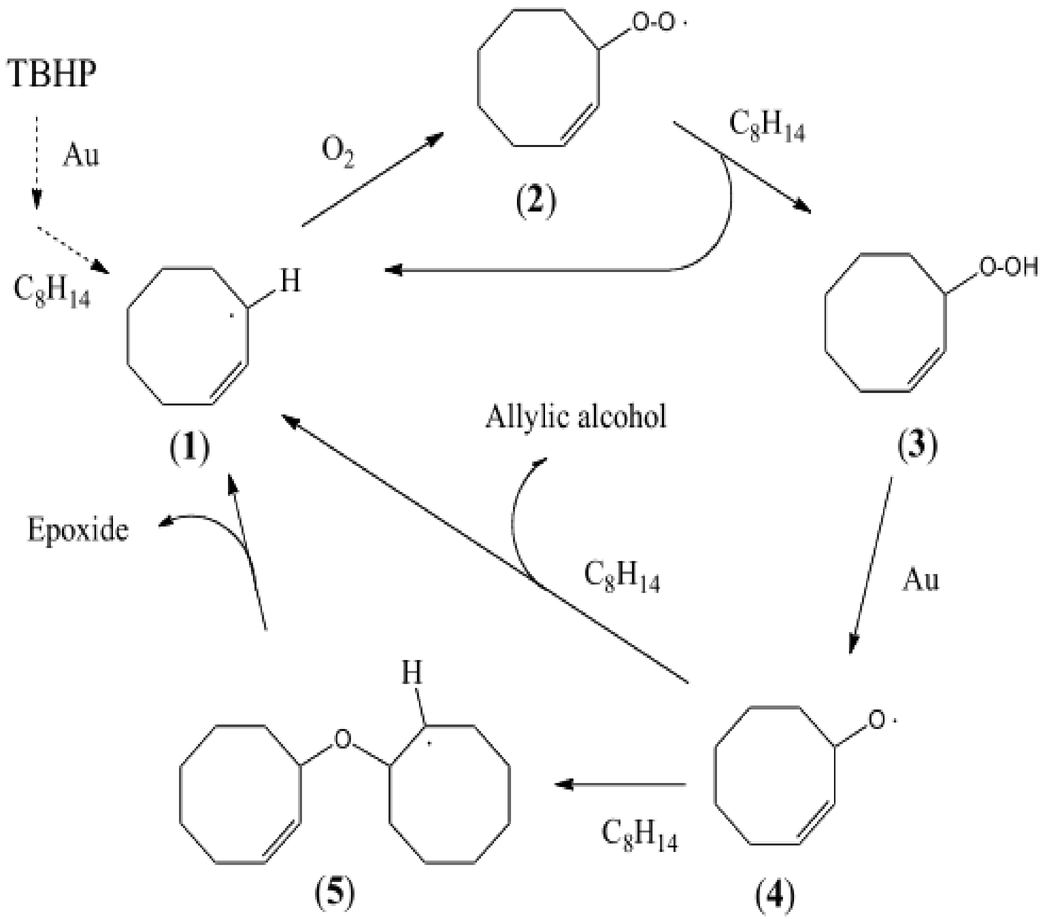


Figure 1.9: Proposed mechanism for *cis*-cyclooctene oxidation using 1% Au/graphite as catalyst in presence of TBHP

1.7.2 Oxidation of alcohol

The selective oxidation of alcohols to aldehydes or ketones is one of the most important and useful transformations[82]. There are many reports that the oxidation of alcohols has been obtained under solvent- and/or base-free conditions, but these tend to have a lower activity than the reaction with a solvent and/or base[83]. Catalytic reactions using oxygen from air are preferred in accordance with the principles of green chemistry.

Oxidation of 2-buten-1-ol can be carried out by using a supported gold catalyst. According to a report of Kawanami *et al.*[84], an Au/TiO_2 catalyst was active for 2-buten-1-ol oxidation when using O_2 as oxidant. A conversion of 57% with 94% selectivity toward aldehyde was achieved after 5 h of reaction at 70 ˚C. More recently, Hutchings and co-workers[68] reported that gold can oxidise 2-buten-1-ol to several products using air as the oxidant (Figure 1.10). It was demonstrated that TBHP was not effective for activity or selectivity. A weight of 1% of gold-graphite supported catalyst prepared by sol-immobilisation achieved a conversion of 3.3% with 47% selectivity to cortonaldehyde in a solvent-free condition. However, the activity increases significantly when using bimetallic Au-Pd catalyst, of which the ratio is 1:1 by weight. This process obtained 18% conversion and 3-buten-1-ol was one of the major products.

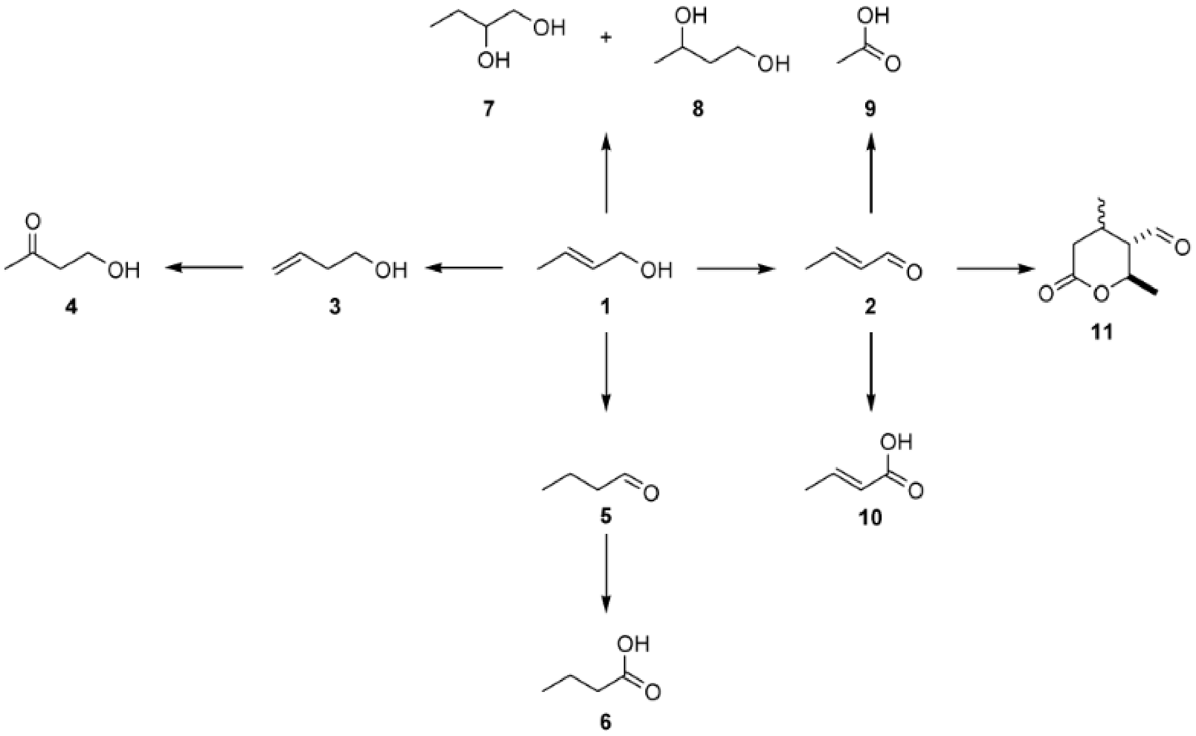
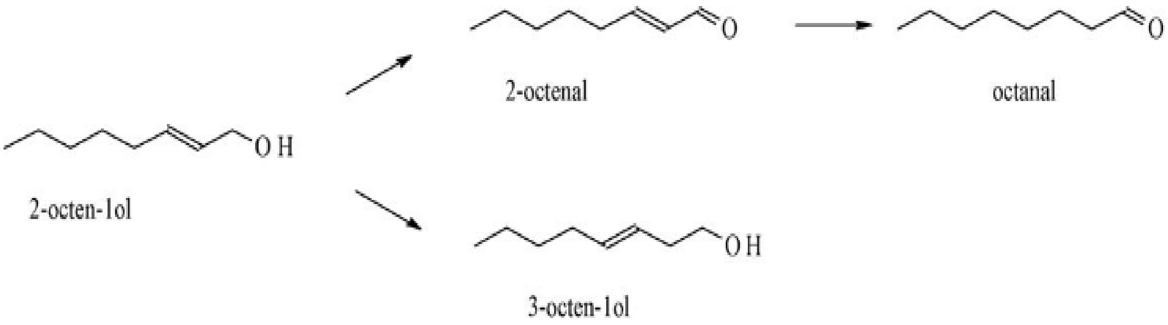


Figure 1.10: Crotyl alcohol (1) oxidation and isomerisation products. 2-butenal (2), 3-buten-1ol (3), 4-hydroxybutan-2-one (4), butanal (5), butanoic acid (6), butane-1,3-diol (7), butane-1,2-diol (8), acetic acid (9), 2-butenoic acid (10), lactons (11)

Supported gold has been used as a catalyst for the oxidation of 2-octen-1-ol. Corma *et al.* were the first to use a form of gold supported on a ceria catalyst. In their research, it was demonstrated that the gold supported on ceria was active for oxidation of 2-octen-1-ol under solvent-free condition using O_2 as oxidant at 120 ˚C. Under these conditions, 56% conversion with 72% selectivity to 2-octen-1-al was achieved. The reaction was repeated in the presence of toluene as solvent and the results show that the activities for Au/CeO_2 and Au-Pd/CeO_2 were comparable (90% and 95% respectively). However, the selectivity to 2-octen-1-al was different (91% and 73% respectively). Another support

(TiO_2) was tested and bimetallic gold-palladium on TiO_2 displayed low activity (17%) with 60% selectivity toward 2-octen-1-al[82]. The influence of bimetallic gold-palladium on 2-octen-1-ol oxidation was studied by Prati and co-workers[85]. A synergistic effect was obtained after 2 h of reaction at 50 ˚C with 3 bar O_2. Under these conditions, monometallic gold catalyst leads to a trace of conversion and when using the monometallic palladium catalyst, 3% conversion was achieved. However, bimetallic gold-palladium on carbon was a more active catalyst for 2-octen-1-ol oxidation with a conversion of 97% and 58% selectivity to 3-octen-1-ol with 2-octenal and octanal as by products (Scheme 1.4).



Scheme 1.4: The possible products of the oxidation of 2-octen-1-ol

Corma and co-workers[86] showed that gold on ceria nanoparticles (npCeO_2) was a very active catalyst for 2-octen-1-ol oxidation. 90% conversion with 91% selectivity toward 2-octenal was observed at 90 ˚C and toluene is present as the solvent. According to the authors, ceria acts as an oxygen "pump" to guarantee the oxidation of metal hydrides into water.

Another example of alcohol oxidation is 1-octen-3-ol. Hutchings *et al.* [87] were able to illustrate the efficiency of a 2.5%Au-2.5%Pd/TiO_2 catalyst to selectively oxidise a range of alcohols at 160 ˚C using molecular oxygen as the oxidant. Under the previous conditions, 1-octen-3-ol was oxidised and a turnover frequency (TOF) of 12600 h^{-1} was obtained after half an hour of reaction. Corma *et al.* [82] reported that by using Au/CeO_2 and Au-Pd/ CeO_2 as the catalyst for 1-octen-3-ol oxidation under solvent-free conditions, 99% conversion was achieved. However, the selectivity to 1-octen-3-one was very high when using the monometallic catalyst (90%) compared with 23% when using a bimetallic catalyst. The selectivity products from C-C double bond isomerisation and C-C double bond hydrogenation increase when Pd is present (Figure 1.11). According to the authors, the stability of Pd-H and Au-H plays an important role in the reaction pathway if the reaction proceeds through the oxidation route or hydrogenation route. The stability and therefore steady state concentration of Au-H and Pd-H on the metal surface during the reaction had been proposed as the reason for the high selectivity of gold compared to palladium. They subsequently demonstrated that by using Pd/CeO_2 as the catalyst, a conversion of 99% with 58% selectivity to 1-octen-3-one was consistently achieved.

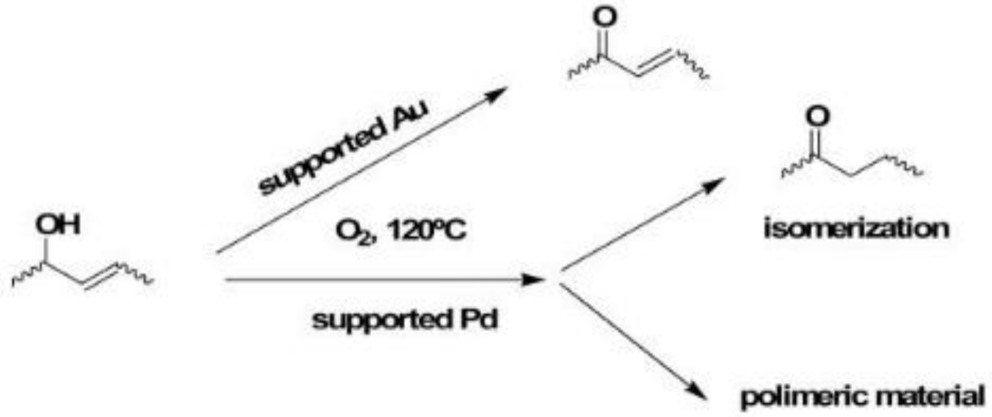


Figure 1.11: Aerobic oxidation of allylic alcohols under solvent-free conditions in the presence of gold and palladium catalysts

Corma and co-workers [88] have demonstrated that gold-supported nanocrystalline ceria can be used to convert 1-octen-3-ol into a corresponding ketone. Under solvent-free conditions at 80 ˚C with O_2 at atmospheric pressure, 80% conversion with 99% selectivity was obtained after 3.5 h of reaction. Gold supported on nanoparticle ceria oxide was tested for the oxidation of 1-octen-3-ol using toluene as the solvent and atmospheric air as the oxidant. In their work, 99% of 1-octen-3-ol was converted to 1-octen-3-one (90%) after 6 h [86]. This was the proposed mechanism for oxidation of alcohol when using air as the oxidant and gold as the catalyst (Figure 1.12). According to the authors, the first step is the formation of a metal-alcoholate species. In this step, the free alcoholate would be in equilibrium with the metal-alcoholate. The second (rate-determining) step is one in which the metal-alcoholate species would undergo a metal-hydride shift giving rise to the carbonylic product and a metal-hydride intermediate. The third step is re-oxidation of the metal-hydride by oxidation, giving rise to the initial metallic site and water.

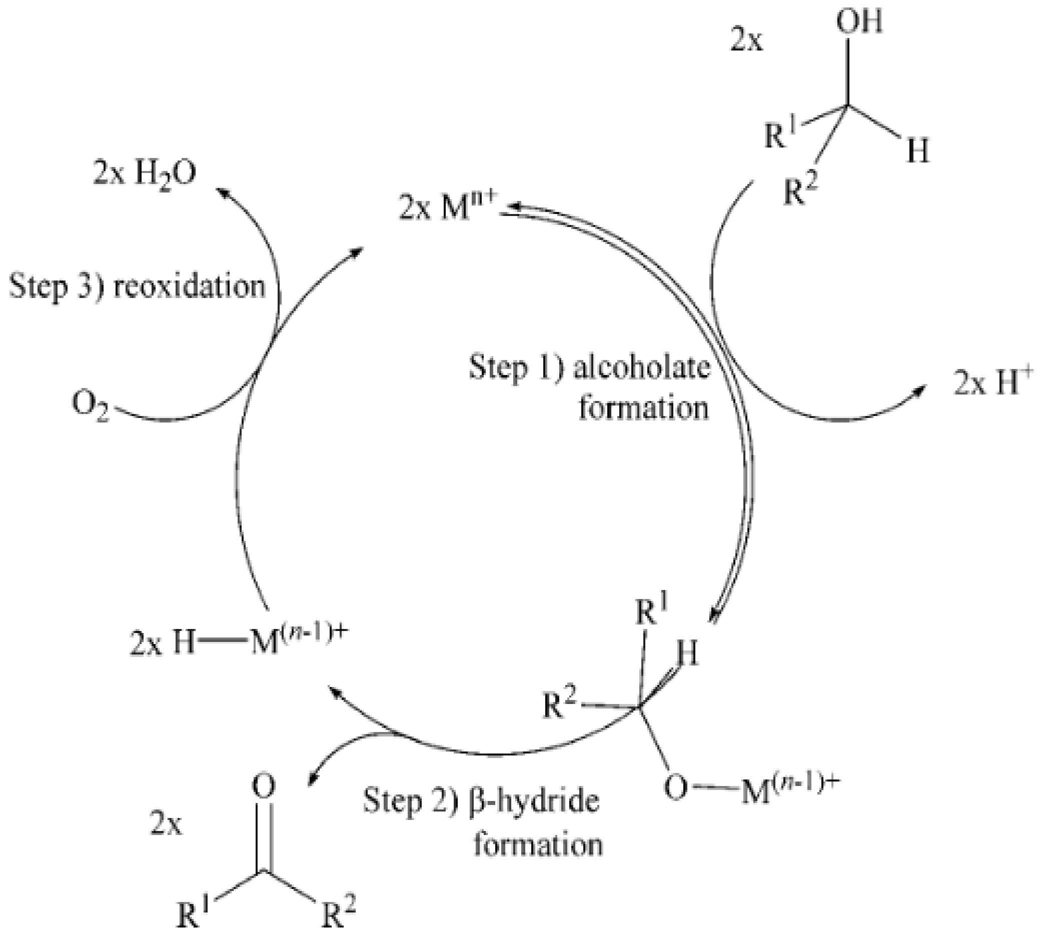


Figure 1.12: Proposed mechanism for the Au/npCeO$_2$ catalysed aerobic oxidation of alcohols

The possible products of aerobic oxidation by using gold or palladium nanoparticles as a catalyst are shown in Figure 1.13[89].

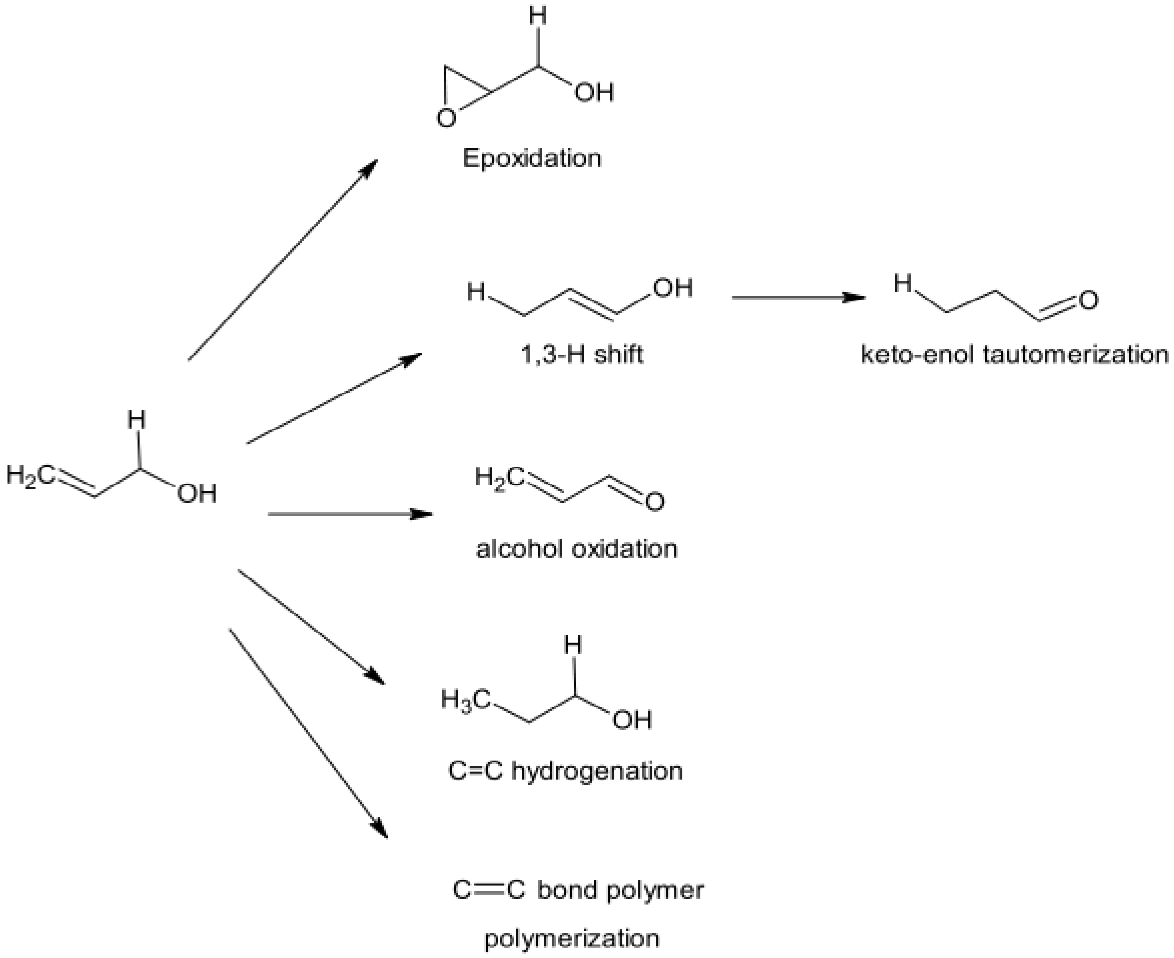


Figure 1.13: Possible competing reactions in allylic alcohols oxidation

1.8. Aim of the study

The selective oxidation of alkenes and alcohols are a promising and challenging topic in heterogeneous gold catalysis. The oxidation of alkenes and alcohols will be studied using supported gold catalysts under a green oxidation system.

Objective

1- Demonstrate the use of a supported gold nanoparticulate catalyst for selective, solvent-free oxidation of 1-hexene under green conditions and optimisation of the reaction conditions, namely the support, catalyst preparation method and choice of metal.

2- Demonstrate if either the alcohol or alkene functional group can be oxidise in *trans*-2-hexen-1-ol and 3-hexen-1-ol and also investigate the influence of the bimetallic system, namely gold-palladium, on the oxidation of alcohols, namely 1-hexen-3-ol and trans-2-hexen-1-ol under green conditions and study the effect of the metallic ratio and observe the effect of temperature, support, the choice of metal and the preparation method.

3- Study the effect of the length of the cyclic alkenes ring on the selectivity of epoxide products and observe the effect of temperature, support, the choice of metal and the preparation method and also study the effect of remove stabiliser from cycloalkene on reaction.

1.9. References

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Chapter two

Experimental

2. Experimental

2.1. Introduction

This chapter provides detailed information on catalyst preparation methods, the basic principle of characterisation used in catalysis research and catalytic testing. The reaction of alkenes and alcohols will be performed in glass reactors at atmospheric pressure using different supported gold catalysts.

2.2. Catalyst preparation

All catalyst metal percentages are percentage metal by weight of support

2.2.1. Sol immobilisation

1% Au, Pd and Au–Pd bimetallic catalysts were prepared using the sol-immobilisation method. For example, a 1 wt% Au-Pd/support catalyst with Au-Pd molar ratio of 1:1 was prepared as follows: An aqueous solutions of $PdCl_2$ (Johnson Matthey, 6 mg in 1 ml) and $HAuCl_4.3H_2O$ (Johnson Matthey, 12.25 g in 1000 ml) were prepared. Polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, Mw=10000, 80% hydrolyzed) was added (PVA/metal (wt/wt) =0.65) to an aqueous solutions of $PdCl_2$ and $HAuCl_4.3H_2O$ with stirred for 15 min. 0.1M of $NaBH_4$ [Aldrich, $NaBH_4$/(Au+Pd) (mol/mol=5)] was freshly prepared and then added to form a dark brown sol. The mixture was stirred for 30 min and adjusted to pH = 1 by the dropwise addition of sulphuric acid. Support (1.98 g) was added to the mixture. The slurry was then stirred for 1 h; following this, the catalyst was recovered by filtration, washed with 2 L distilled water and dried at 110 ºC overnight[1].

2.2.2. Reflux sol immobilisation method

A 1g batch of catalyst that was prepared by the sol-immobilisation method, placed in a round bottom flask and a desired volume of water (250 ml) was added into the flask. The round bottom flask was connected to a reflux condenser and placed in an oil bath, which was heated at 90 ºC under vigorous stirring. The solution was left to reflux at 90 ºC for 1 h. Afterwards, the catalyst was recovered by filtration, washed with 2 L distilled water, and dried at 110 ºC overnight[2].

2.2.3. Impregnation method

A 1 g, 1% Au/support catalyst was prepared as follows: A solution of $HAuCl_4.3H_2O$ (0.816 ml, which is pipette out from the stock solution containing 12.25 mg/ml Au) was added to support (0.99 g). The mixture was stirred until a paste was formed; this paste was dried at 110 ºC for 16 h. The resulting powder was ground and calcined in static air at 400 ºC for 3 h at a ramp rate of 20 ºC min^{-1}. The preparation of 1 g of the 1 wt% Au-Pd/support catalyst with Au-Pd molar ratio of 1:1 was used an aqueous solutions of $PdCl_2$ (0.584 ml, which is pipette out from the stock solution containing 6 mg/ml Pd) and $HAuCl_4.3H_2O$ (0,53 ml, which is pipette out from the stock solution containing 12.25 mg/ml Au). The resultant solution was added to the support (0.99 g) and then the mixture was stirred until a paste was formed. The resulting slurry was dried at 110 ^oC

for 16 h. The resulting powder was ground and calcined in static air at 400 °C for 3 h at a ramp rate of 20 °C min^{-1}[3].

2.2.4. Deposition precipitation

A 1% Au/support catalyst was prepared as follows: support (0.99 g) was mixed with 150 ml distilled water and stirred at 60 ºC. Subsequently, a solution of sodium carbonate (1M) was added dropwise to the mixture to maintain an overall pH of 9. To this, a solution of $HAuCl_4{\cdot}3H_2O$ (0.816 ml, which is pipette out from the stock solution containing 12.25 mg/ml Au) was added with a simultaneous addition of sodium carbonate solution to maintain an overall pH of 9. After 1.5 h, the solution was filtered and the solid was washed with 1 L distilled water. The catalyst was dried at 110 ºC for 16 h. The resulting powder was ground and calcined in static air at 400 ºC for 3 h at a ramp rate of 20 ºC min^{-1}. In a similar way, 1 g of the 1 wt% Au-Pd/support catalyst with Au-Pd molar ratio of 1:1 was also prepared by deposition precipitation using required amount of a solutions of $PdCl_2$ (0.584 ml, which is pipette out from the stock solution containing 6 mg/ml Pd) and $HAuCl_4.3H_2O$ (0,53 ml, which is pipette out from the stock solution containing 12.25 mg/ml Au) [4].

2.3. Catalyst evaluation

2.3.1. Oxidation of alkenes: Standard reaction conditions

Oxidation of alkenes using oxygen from air was carried out in a glass reactor consisting of a 50 ml round-bottomed flask fitted with a reflux condenser (Figure 2.1). Typically a supported gold catalyst (0.12 g) was suspended in the alkene (10 ml) at a range of temperatures followed by the addition of a small amount of radical initiator TBHP (0.1ml, 70% in H_2O) under solvent-free conditions. The reaction mixture was stirred for 24 h at atmospheric pressure. A sample of the reaction was analysed after the reaction was completed. The analysis was conducted using gas chromatography (GC) (Varian Star CP-3800) with a CP-Wax 52 column and a flame ionization detector (FID).

2.3.2. Oxidation of alcohols: Standard reaction conditions

Oxidation of alcohols using oxygen from air was carried out in a glass reactor consisting of a 50 ml round-bottomed flask fitted with a reflux condenser (Figure 2.1). Typically a supported gold catalyst (0.06 g) was suspended in the alcohol (5 ml) at a range of temperatures under solvent-free conditions. The reaction mixture was stirred for 24 h at atmospheric pressure. A sample of the reaction was taken for analysis after the reaction was completed. Analysis was carried out using gas chromatography (Varian star CP-3800) with CP-wax 52 column and a flame ionization detector.

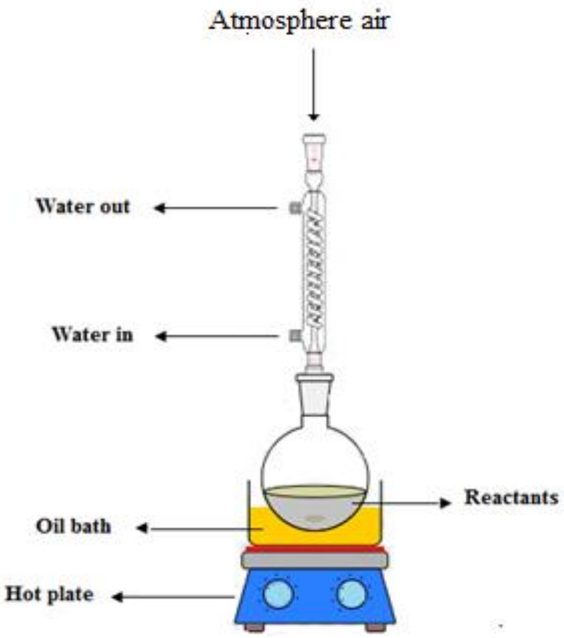

Figure 2.1: Schematic diagram of the glass reactor.

2.3.3. Treatment method to remove stabiliser from cycloalkene

The inhibitors of free radicals reduce the rate of auto-oxidation, the irganox 1076 [3-Octadecyl-(3,5-di-t-butyl-4-hydroxyphenyl)-propaoate] are typically added to some commercial alkenes as stabilisers to prevent auto-oxidation during storage. For example, *cis*-cyclooctene (alfa Aeaser) stabilised with 100-200 ppm irganox 1076. In this study, it will be shown that selective cyclic alkene oxidation can be achieved under solvent-free conditions without the addition of a radical initiator when these stabilisers are removed from cycloalkene by pre-treatment of washing with aqueous potassium hydroxide and subsequent distillation as follows: Typically, 20 ml of aqueous potassium hydroxide (3M) was added to 20 ml of cycloalkene under vigorous stirring for 10 min at room temperature. The two layers were separated and then a farther 20 ml of aqueous potassium hydroxide (3M) was added to the cycloalkene layer under vigorous stirring. The cycloalkene layer was separated and then washed thoroughly with distilled water (20 ml) two times under vigorous stirring for 10 min at room temperature. The cycloalkene layer was separated and then dried over magnesium sulfate and filtered. The resultant cycloalkene was distilled.

Oxidation of of cycloalkene after treatment (cycloalkene inhibitor-free) using oxygen from air was carried out in a glass reactor consisting of a 50 ml round-bottomed flask fitted with a reflux condenser (Figure 2.1). Typically a supported gold catalyst (0.12 g) was suspended in the cycloalkene (10 ml) at a range of temperatures. The reaction mixture was stirred for 24 h at atmospheric pressure under solvent-free conditions.

2.4. Catalyst characterisation

2.4.1. BET

2.4.1.1. Background

Surface area measurement is widespread in characterising porous materials. Surface area frequently plays an essential role in the reactivity of catalysts. The Brunauer–Emmett–Teller (BET) method is one of the most commonly used techniques in determining the surface area. The concept of the BET method determines the surface area based on the amount of gas adsorbed. The adsorptive gas in BET is normally N_2 at a cryogenic temperature (77 K). The amount of gas adsorbed at a given pressure can be used to calculate the number of adsorbed gas molecules that would be required to form a monolayer on the surface. Based on the known size of the gas molecule adsorbed, the surface area can be easily calculated.

The theory is based on the BET equation [5]:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_o}$$

Equation 2.1: BET isotherm equation.

where V is the volume of the adsorbed gas, V_m is the volume of the monolayer of the adsorbed gas, P is the equilibrium gas pressure, P_0 is the saturation pressure of the adsorbate, and C is the BET constant.

2.4.1.2. Experimental

Samples were prepared for BET analysis by degassing at 120 ºC for 1 hour then connecting to a Micromeritices Gemini 2360 Analyser automatic multi point surface area analyser. The samples were immersed in liquid nitrogen during the analysis.

2.4.2. Scanning electron microscopy

2.4.2.1. Background

Zworykin *et al.* described the first modern scanning electron microscope (SEM) [6]. SEM uses electrons as an alternative to light to form an image[7]. The electron beam is produced from an electron gun fitted with tungsten filament, which works as a cathode and allows it to be heated for electron emission. The electron beam follows a vertical path through the column of the microscope, and it is focussed through a series of lenses and directed towards the sample (Figure 2.2). As the electron beam hits the sample, two types of electrons are produced, namely, secondary and backscattered electrons. Secondary electrons are produced when the high-energy electron beam displaces loosely held surface electrons that are recorded using a secondary electron detector to produce an image of the surface (Figure 2.3). Secondary electrons depend on the surface in the specific area of intersection of the beam and therefore refer to topographic features. Backscattered electrons consist of high-energy electrons from electron beams that are reflected off the sample by the atomic nuclei (Figure 2.4). These electrons provide information about the topography of the surface and the average atomic number in the scanned area. The higher atomic number elements appear brighter than the lower atomic number elements.

Secondary and backscattered electrons are collected by a detector that converts them into a signal and then sends them to a viewing screen to create the image of the sample.

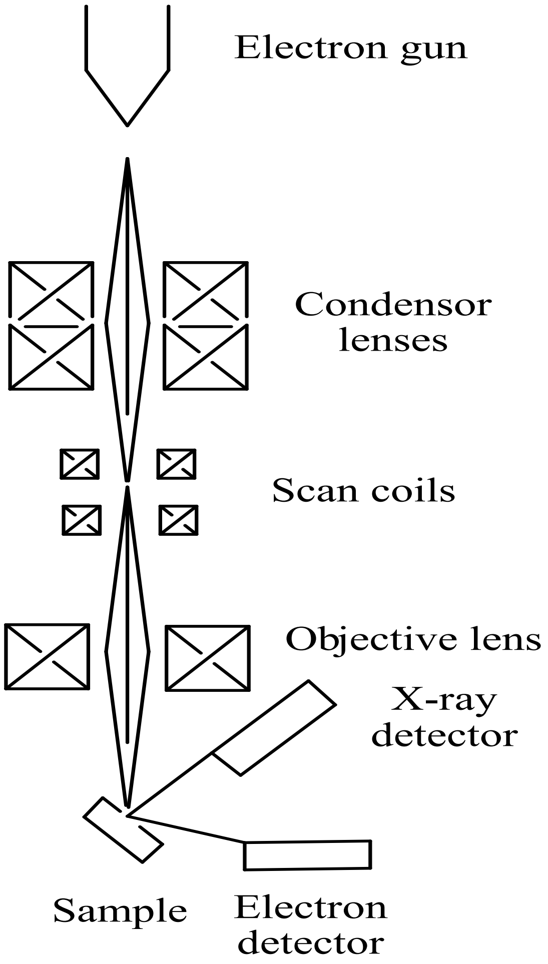

Figure 2.2: Schematic of a SEM/EDX system

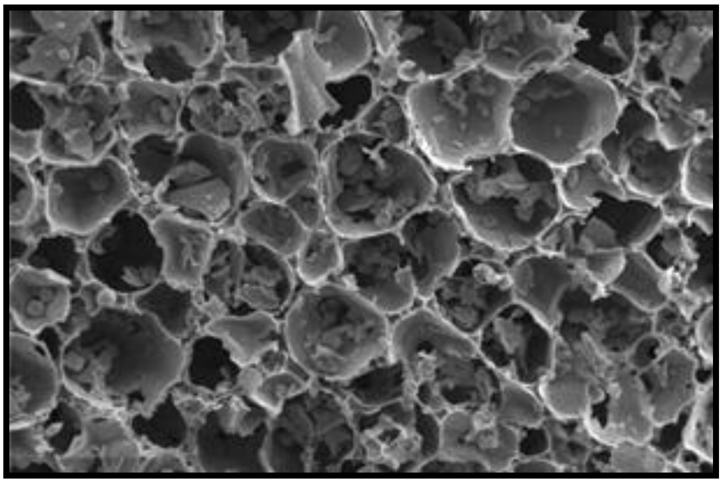

Figure 2.3: SEM image of Au/foam CeO_2.

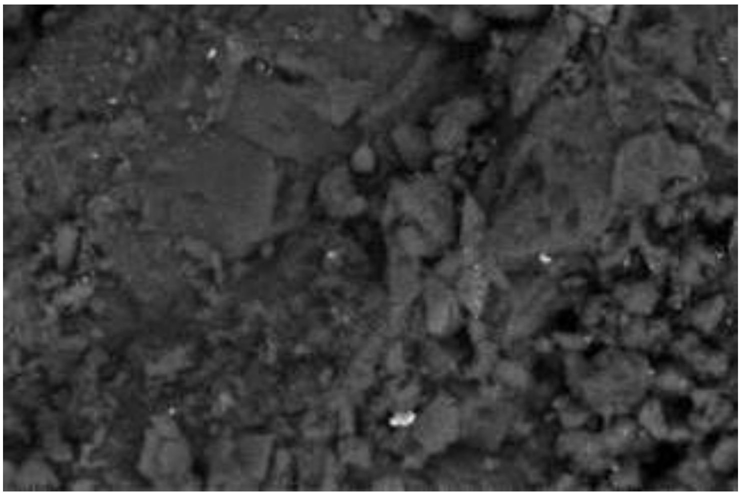

Figure 2.4: SEM image recorded by backscatterd electrons for Pt particles on alumina

2.4.2.2. Experimental

The SEM analysis was performed using a Carl Zeiss EVO 40 SEM fitted with a BSD, an Everhart–Thornley detector, and a variable pressure chamber with a tungsten source.

2.4.3. X-ray powder diffraction (XRD)

2.4.3.1. Background

X-ray diffraction (XRD) is a common technique used to identify crystalline compounds. It can identify the three-dimensional structure of crystalline compounds as regular repeating planes of atoms that form a crystal lattice (Figure 2.5) [8].

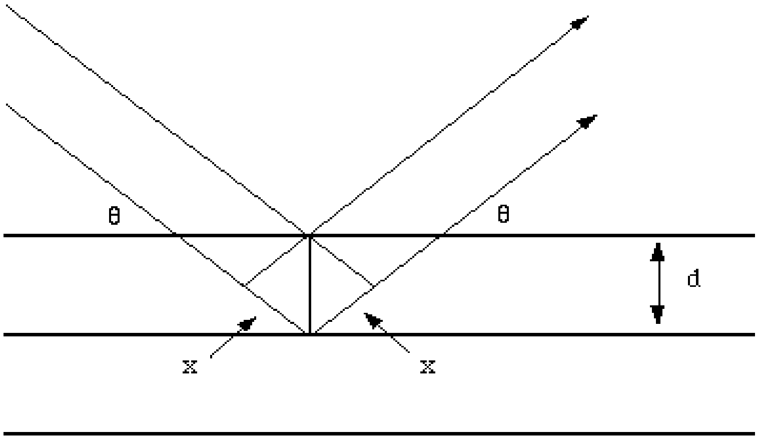

Figure 2.5: Bragg's law of diffraction.

When the X-ray strikes the powdered sample, part of it is diffracted. The distance between the planes of atoms in the sample can be measured by using a mathematical formula called Bragg's law, which is shown in Equation 2.2 [9]:

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

Equation 2.2: Bragg's law.

where **n** is an integer, **λ** is the wavelength, **d** is the spacing between the crystal planes, and **θ** is the diffraction angle.

The X-ray source, a sample, and a detector that collects the diffracted X-ray, are required for the XRD analysis (Figure 2.6).

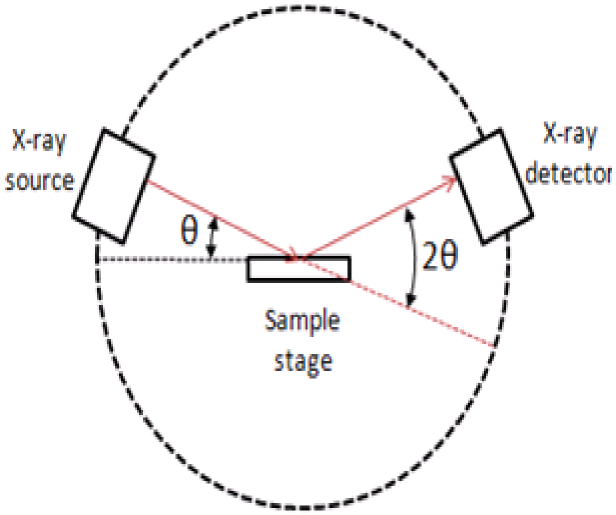

Figure 2.6: Schematic of the X-ray tube, the X-ray detector, and the sample (θ: diffraction angle)

2.4.3.2. Experimental

The catalysts were ground into powder and then placed in a sample holder. The XRD analysis was performed using a PANalytical X’Pert Pro with a CuK_α X-ray source operated at 40 kV and 40 mA fitted with an X’Celerator detector.

2.4.4. Gas chromatography

2.4.4.1. Background

The reaction mixture was analysed by using GC to separate the liquid mixture. The injection port heated the sample until it reached the gas phase and was then transported *via* inert gas (often helium) into a column to separate the substances. It was then analysed by a detector (Figure 2.7).

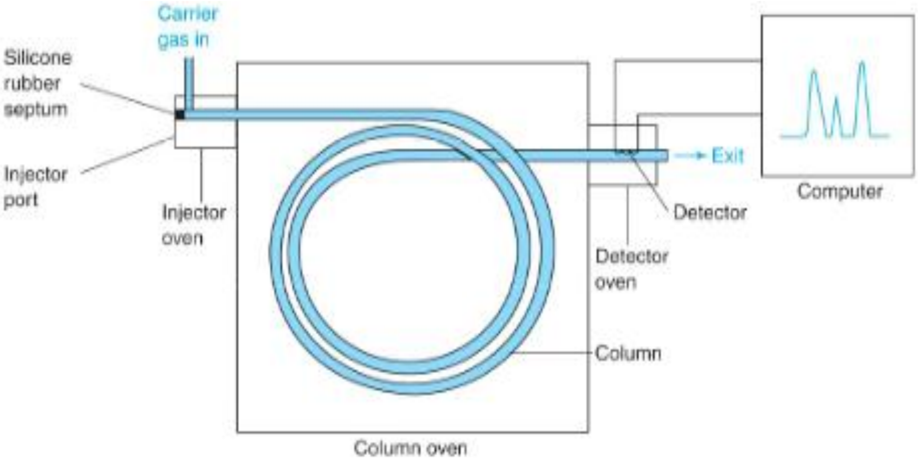

Figure 2.7: Schematic of GC.

In a split injector, the sample was injected using a syringe. The sample was heated at a septum, and then the gas carrier sweept it through an inert packing. At the split point, a small homogenised mixture entered the column, but most passed through the split outlet to the waste vent. The capillary column and the packed column are two types of a GC column. The capillary column is the most commonly used column in GC because of its high resolution and great sensitivity. It is made of quartz tubes and is coated on the outside with polyamide to reduce breakage [10].

A FID is the most commonly used GC detector. It quantifies the components that have been separated in a column. A FID comprises a stainless steel chamber (jet); the gas flow exiting the column passes through this jet, mixes with hydrogen and air, and is burned at the jet's tip (Figure 2.8). Carbon atoms produce CH radicals that produce CHO^+ ions and electrons in flame. The resulting electron current is converted into voltage, which is amplified and then converted into a digital signal [11].

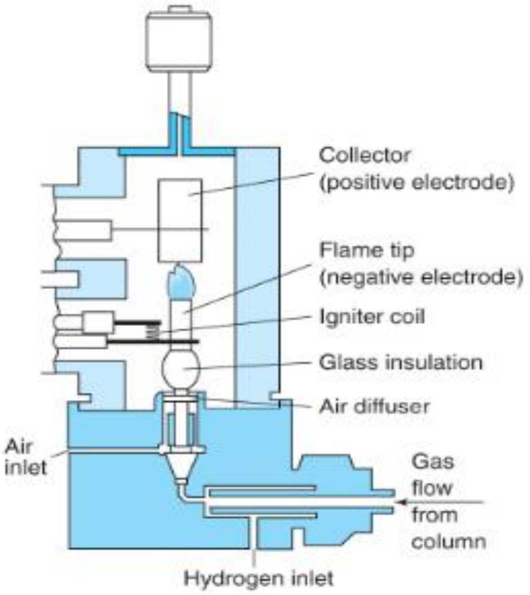

Figure 2.8: Schematic diagram of flame ionization

2.4.4.2. Experimental

The current GC analysis was conducted using GC (Varian star CP-3800) with a CP-wax 52 column (capillary column, 25m, 0.35 mm ID, 0.2 micron) and a FID. A sample (0.02 μl) was automatically injected into GC using a micro syringe.

2.5. References

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Chapter three

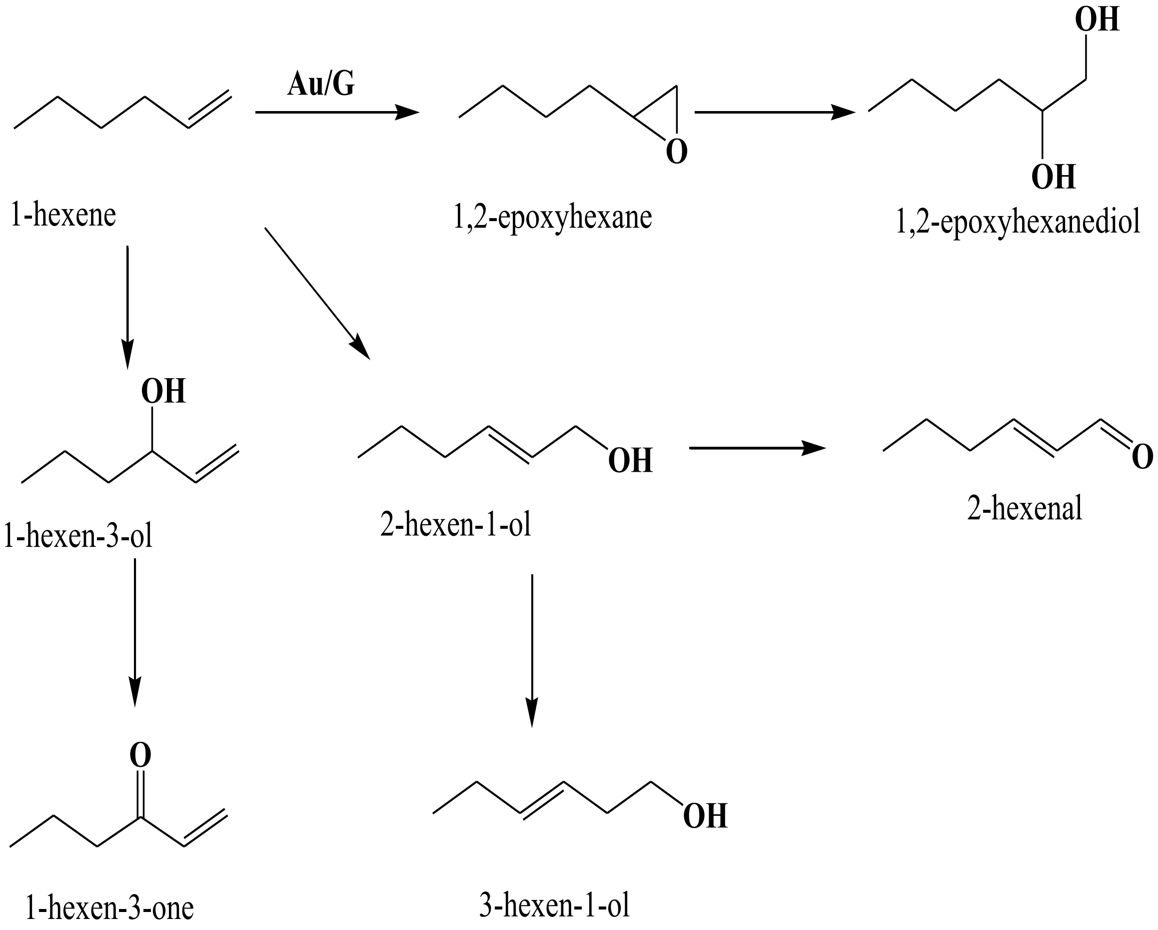
Solvent-free liquid phase oxidation of 1-hexene using supported gold catalysts

3. Solvent-free liquid phase oxidation of 1-hexene using supported gold catalysts

3.1. Introduction

Oxidation reactions are an important step in the synthesis of fine chemicals. Catalytic reactions using oxygen from air are preferred in accordance with the principles of green chemistry. Oxygen is a diradical in the ground state which enables its ease of activation in a number of radical reactions, which can be useful for a range of low temperature oxidations [1-3]. However, at present, many molecules and catalysts are unreactive with molecular oxygen and, therefore, more reactive forms of terminal oxidant are employed; often these involve using a non-green stoichiometric oxygen source such as permanganate or chromates[4, 5].

The oxidation of alkenes has, therefore, become an exciting topic in heterogeneous catalysis and a number of studies have been performed on such oxidations using gold as the catalyst [1, 6-9]. The allylic oxidation of alkenes to allylic alcohols and α,β-unsaturated ketones is an important pathway in natural product synthesis[10-12]. Previous studies have shown that supported gold nanoparticles are active for a range of such alkene oxidations using oxygen as oxidant and TBHP as radical initiator [1, 6, 13]. In this chapter, the previous studies by Hutchings *et al.* [1, 6] concerning the oxidation of cyclic alkenes are extended to investigate whether straight chain alkenes can be oxidised in a similar way. In this study, the use of supported gold nanoparticulate catalysts for the selective, solvent-free oxidation of 1-hexene using oxygen together with catalytic amounts of a peroxy initiator will be examined. In addition, it will be shown that 1-hexene can be oxidised selectively under green conditions with 90% oxidation products accounted for under mild solvent-free conditions (scheme 3.1). Finally, the optimised of the reaction conditions, namely the support, catalyst preparation method and choice of metal will be examined.



Scheme 3.1: Oxidation of 1-hexene using Au/graphite and TBHP

3.2. Characterisation of catalyst

The catalyst chosen for this study is the 1%Au/graphite material, as this has been characterised by Hutchings's group in previous studies[1]. The particle size distribution of the 1 wt% Au/graphite catalyst prepared using the sol-immobilisation method shows this comprises small gold particles, ranging in size mainly between 1 and 5 nm in diameter with most being 2–3 nm in diameter, very few particles greater than 5 nm were detected.

The techniques of XRD, BET and SEM have been used to characterize the support and supported gold catalyst. BET analysis shows that the surface area of 1% Au/graphite was found to be 10 m^2/g. The SEM images (Figure 3.1) show that the surface morphology of undoped graphite and Au/graphite is indistinguishable. The surface morphology for all undoped supports and supported gold that using in this study are shown in Figures (3.3, 3.5 and 3.7). Again, the SEM images show that the difference in morphology between the undoped support and the gold catalyst is negligible except SiO_2 support which had sphere-like morphology with different particle size. After adding gold to it, these spheres agglomerated and lost their spherical morphology due to the stirring effect.

An XRD pattern of undoped supports and supported catalysts show in Figures (3.2, 3.4, 3.6 and 3.8). Comparison with pure support reveals that most of the reflections stem from the support. The main reflection of gold are expected at $2\theta = 38.1803^\circ$ (100%), 44.4° (52%), 64.6° (32%), 77.4° (36%).

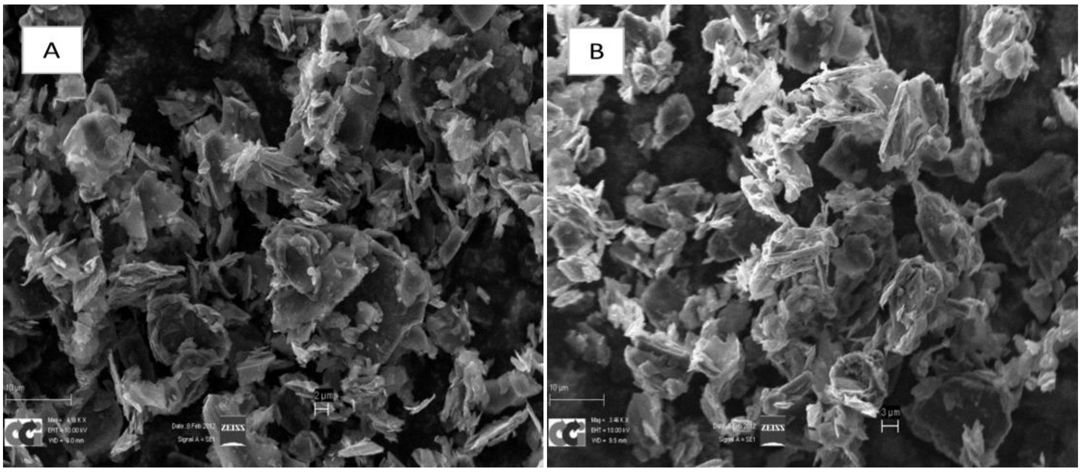


Figure 3.1: SEM image of a) Graphite, b) 1%Au/graphite

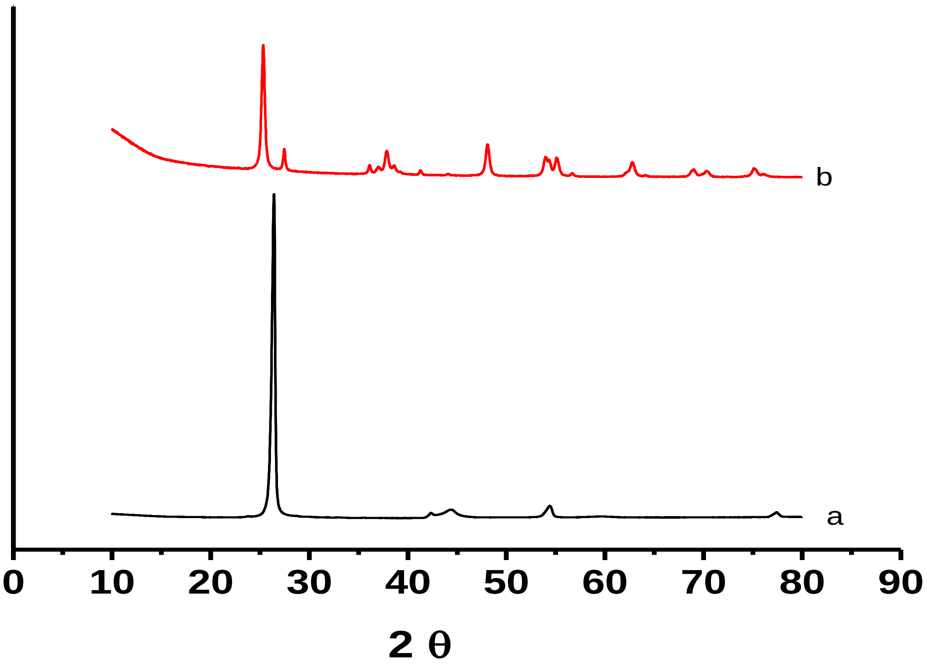


Figure 3.2: The XRD pattern of a) Graphite, b) 1%Au/graphite

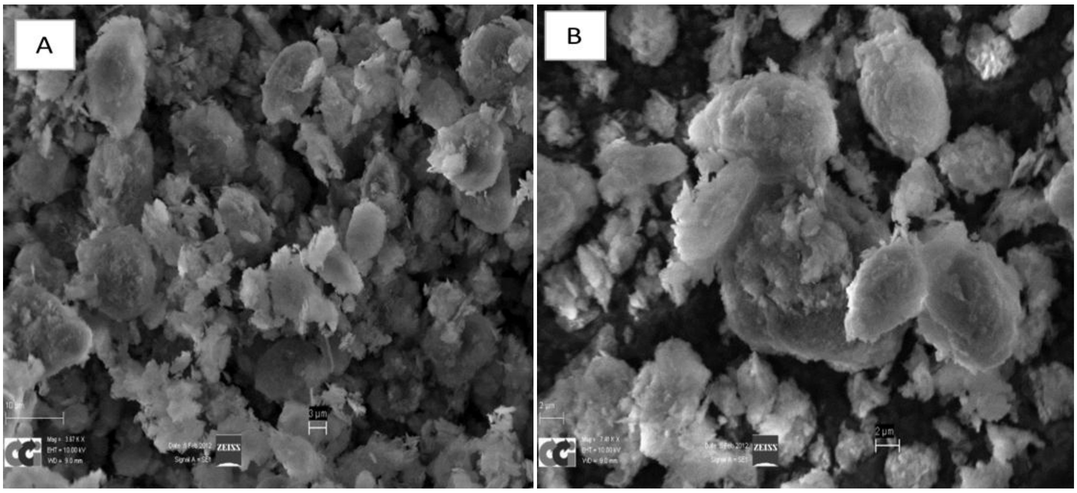


Figure 3.3: SEM image of a) MgO, b) 1%Au/ MgO

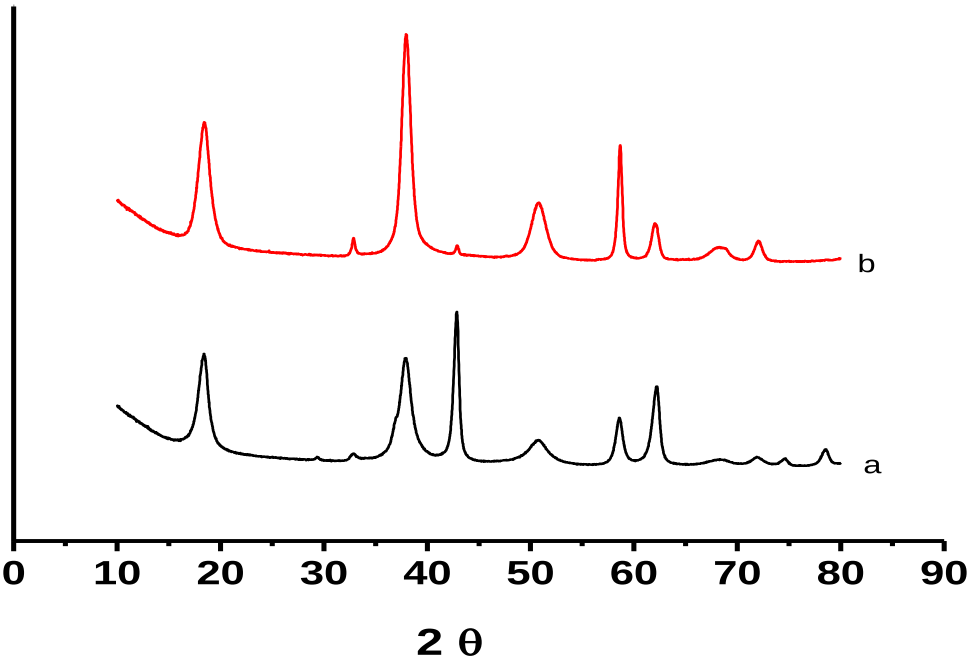


Figure 3.4: The XRD pattern of a) MgO, b) 1%Au/ MgO

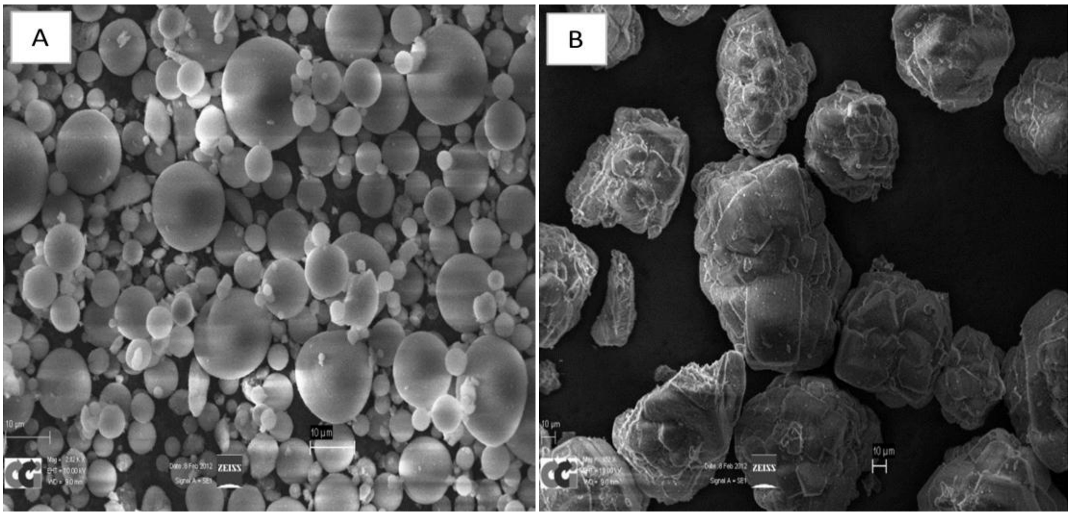


Figure 3.5: SEM image of a) SiO_2, b) 1%Au/ SiO_2

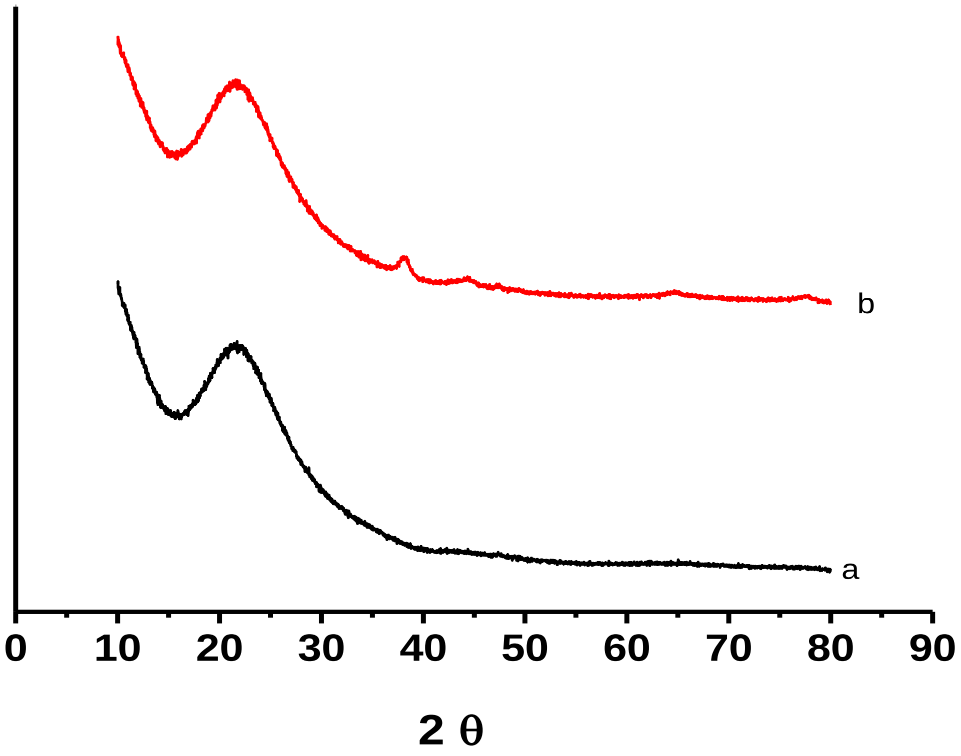


Figure 3.6: The XRD pattern of a) SiO_2, b) 1%Au/ SiO_2

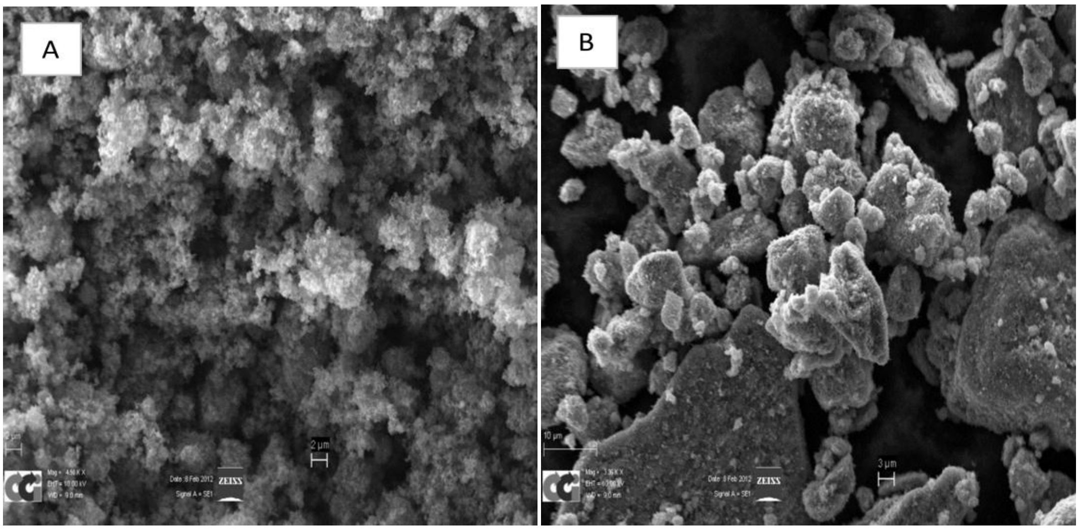


Figure 3.7: SEM image of a) TiO_2, b) 1%Au/ TiO_2

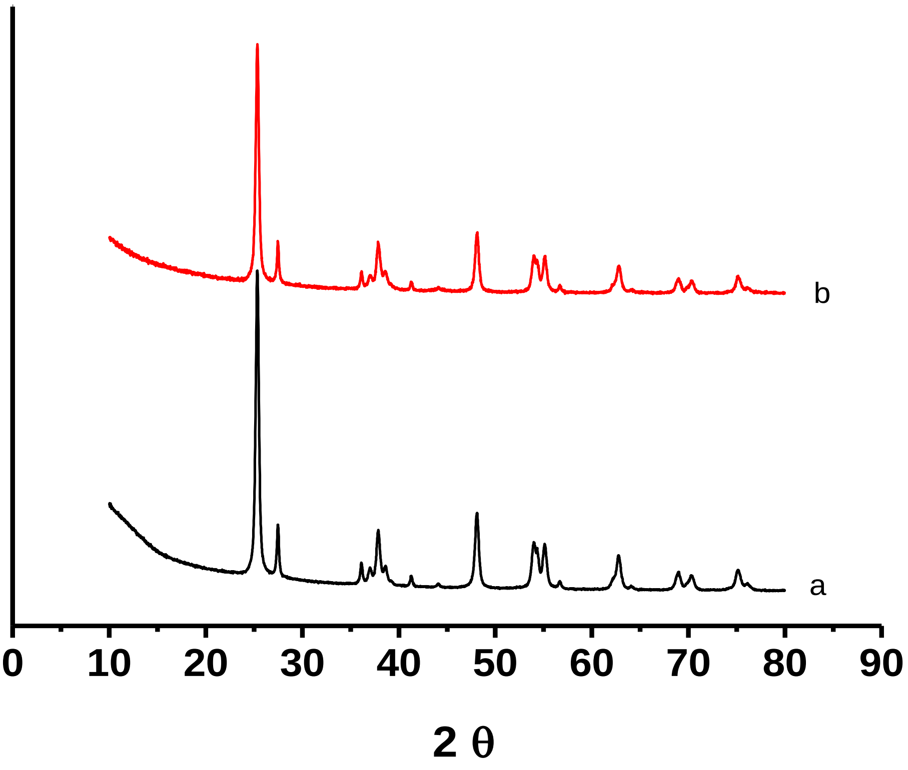


Figure 3.8: The XRD pattern of a) TiO_2, b) 1%Au/ TiO_2

3.3. Results and Discussion

3.3.1. Blank reaction

When using oxygen as a terminal oxidant, it is important to determine the extent the reaction occurs in the absence of the catalyst. Molecular oxygen is a diradical in its ground state and thus can participate in radical reactions in the absence of a catalyst, especially in the presence of radical initiators. In the absence of catalyst and tertiary-butyl hydroperoxide (TBHP), no conversion was observed over the temperature range studied in this study (Table 3.1). A trace of conversion to the epoxide was observed at 40 and 50 ºC after the addition of TBHP to the reaction, as shown in Table 3.1; other products were detected but the yields of these were negligible. To evaluate the effect of radical initiator concentration on 1-hexene oxidation, four different concentrations of TBHP were used (0.064–0.96 mmol): not unreasonably, the oxidaion of 1-hexene is increased by increasing the amount of TBHP present in the reaction media. At low TBHP concentration, no reaction was observed even at 50 ºC. Therefore, a concentration of $0.064\text{X}10^{-2}$ mol TBHP was selected as the standard concentration for further studies (Table 3.1).

Table 3.1: The oxidation of 1-Hexene with/without TBHP in the absence of catalyst

Temp. (°C)	TBHP (mol× 10^{-2})	Conv. (%)	Selectivity (%)				
			1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol
30	0	0	0	0	0	0	0
	0.0064	0	0	0	0	0	0
	0.032	0	0	0	0	0	0
	0.064	0.02	0	54.2	0	33	0
	0.096	0.05	0	40.5	7.7	23.1	5.2
40	0	0	0	0	0	0	0
	0.0064	0.03	0	42.4	0	31.1	0
	0.032	0.1	0	28.1	14.4	30.1	6.9
	0.064	0.1	0	36.1	8.8	25.7	3.4
	0.096	0.1	0	25.4	14	30.8	6.2
50	0	0.03	0	20.6	26.3	22.5	17.4
	0.0064	0.03	0	33.4	10.7	40.7	5.8
	0.032	0.1	3.4	31.4	12.5	35.8	5.3
	0.064	0.2	2.6	27.7	13.7	31.7	5.3
	0.096	0.2	3.4	19.4	17.7	27.8	12.1

Reaction conditions: 10 ml 1-hexene, 24h, atmospheric pressure.

3.3.2. Effect of stirring rate

An important factor in catalysis is mass transport. To examine if the reaction is performed under mass limitation conditions, the stirring speed of the reaction was studied; the results at 40 and 50 ºC are shown in Figure 3.9. It can be seen that, by increasing the stirring speed, the conversion of 1-hexene increases. However, the reactivity of the catalyst stabilised at 800 rpm and above, indicating that the reaction was operating under kinetic control. Therefore, a stirring speed of 800 rpm was selected for subsequent studies.

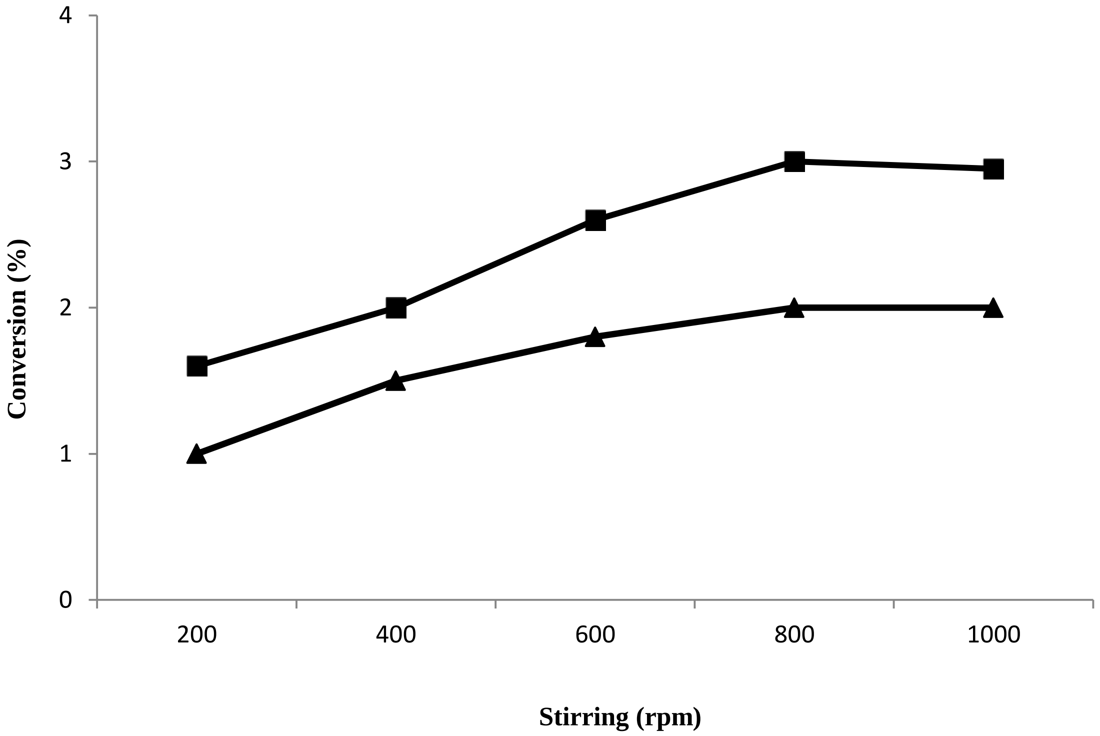


Figure 3.9: The effect of stirring on 1-hexene oxidation using 1% Au/graphite as catalyst. Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP (0.064×10^{-2} mol), glass reactor, 24h, atmospheric pressure at 40 ˚C(▲) and 50 ˚C(■).

3.3.3. Effect of catalyst mass

To study the effect of catalyst mass on 1-hexene oxidation, the catalyst amount was varied in the range 0.05–0.2 g per 10 g of substrate. It can be seen in Table 3.2 that the conversion of 1-hexene increases with increasing catalyst mass, as does the selectivity to 1,2-epoxyhexane. In contrast, the selectivity to 2-hexenal decreases with catalyst mass. There was a significant increase in conversion upon further increasing the catalyst mass to 0.2 g; this suggests there is no mass transport limitation problem under these conditions.

Table 3.2: Effect of catalyst amount on the selectivity of 1-hexene conversion using 1%Au/graphite

Catalyst Amount (g)	Conv. (%)	Selectivity (%)						
		1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol	2-hexen-1-ol	1,2-hexanediol
0.05	1.5	8.2	26.7	16.2	26.4	10.2	2.4	0.8
0.12	2	11.4	29.1	12.5	25.8	8.7	2.2	1.1
0.15	2.1	12	29.8	12.3	25.5	8.6	2	1
0.2	2.4	18.1	28.6	10.4	23.7	7.9	2.2	1

Reaction condition: 10 ml of substrate, TBHP (0.064×10^{-2} mol), 40 °C, glass reactor, 24h, atmospheric pressure.

3.3.4. Effect of radical initiator concentration

To examine the effect of radical initiator concentration, different concentrations of TBHP were used at different reaction temperatures in the presence of 1%Au/graphite and the results obtained are summarised in Table 3.3. In the absence of TBHP, traces of the reaction were observed with no detectable epoxidation; the major product was 1,2-hexandiol. Introducing TBHP to the reaction media resulted in an increase in conversion with allylic oxidation as the major pathway, over the temperature range studied. The selectivity for epoxide formation increases by increasing TBHP concentration along with temperature. These results indicate that the oxidation of 1-hexene in this study system may proceed through a radical mechanism and the rate determining step might be the production of the oxygen free radical, similar results have been reported previously[13, 14]. It was shown that the addition of radical initiator dramatically increased the activity and hence increased the epoxide yield.

The TBHP decomposed to a variety of radicals (Figure 3.10) which can initiate the oxidation of 1-hexene on a gold surface. As shown in Figure 3.10 that $Me_3COO^{\cdot}$, which is very active in abstracting the hydrogen from the allylic position in hydrocarbons, will result from homolysis of O-H bond in TBHP. The O-H bond has high dissociation energy (358.6 kJ/ mol^{-1})[15]. Due to the high energy for O-H homolysis, the concentration of $Me_3OO^{\cdot}$ may be low in the absence of catalyst, however, the gold surface may facilitate the O-H homolysis when catalyst is present and this could explain the dramatic increase in activity when using TBHP as initiator and Au/graphite as catalyst.

Table 3.3: TBHP and temperature effect on 1-hexene oxidation using 1% Au/G

Temp. (°C)	TBHP (mol× 10^{-2})	Conv. (%)	Selectivity (%)						
			1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol	2-hexen-1-ol	1,2-hexanediol
30	0	0.1	0	3.3	0	6.2	1.8	0	88
	0.0064	0.5	4.9	27.9	18.7	27	9.3	2.4	0.6
	0.032	0.8	5.6	27.1	18.1	27.6	9.2	2.5	0.7
	0.064	1	6.3	28.9	18.1	25.7	8.8	2.2	0.5
	0.096	1.2	6.4	27.8	18.2	26.6	8.8	2.4	0.5
40	0	0.1	0	9.6	0	22.6	10.1	0	57.8
	0.0064	1.2	8.5	27.5	13.9	27.3	8.9	2	3
	0.032	1.6	11.1	30.1	8.8	27.7	7.5	2.6	2.1
	0.064	2	11.4	29.1	12.5	25.8	8.7	2.2	1.1
	0.096	2.1	12.4	30.1	11.6	27	8.1	1.8	0.7
50	0	0.1	0	13.6	0	34.8	13.7	0	38
	0.0064	2	18.1	31.8	10	21.3	7	1.6	2.5
	0.032	2.8	15.5	31.8	8.9	25.1	7.6	2.4	2.5
	0.064	3	18	35.4	5.7	25.4	5.3	2.6	0.9
	0.096	3.6	18.4	32.7	8.2	23.8	6.9	1.7	0.7

Reaction conditions: 10 ml 1-hexene, 0.12 g catalyst, 24 h, atmospheric pressure.

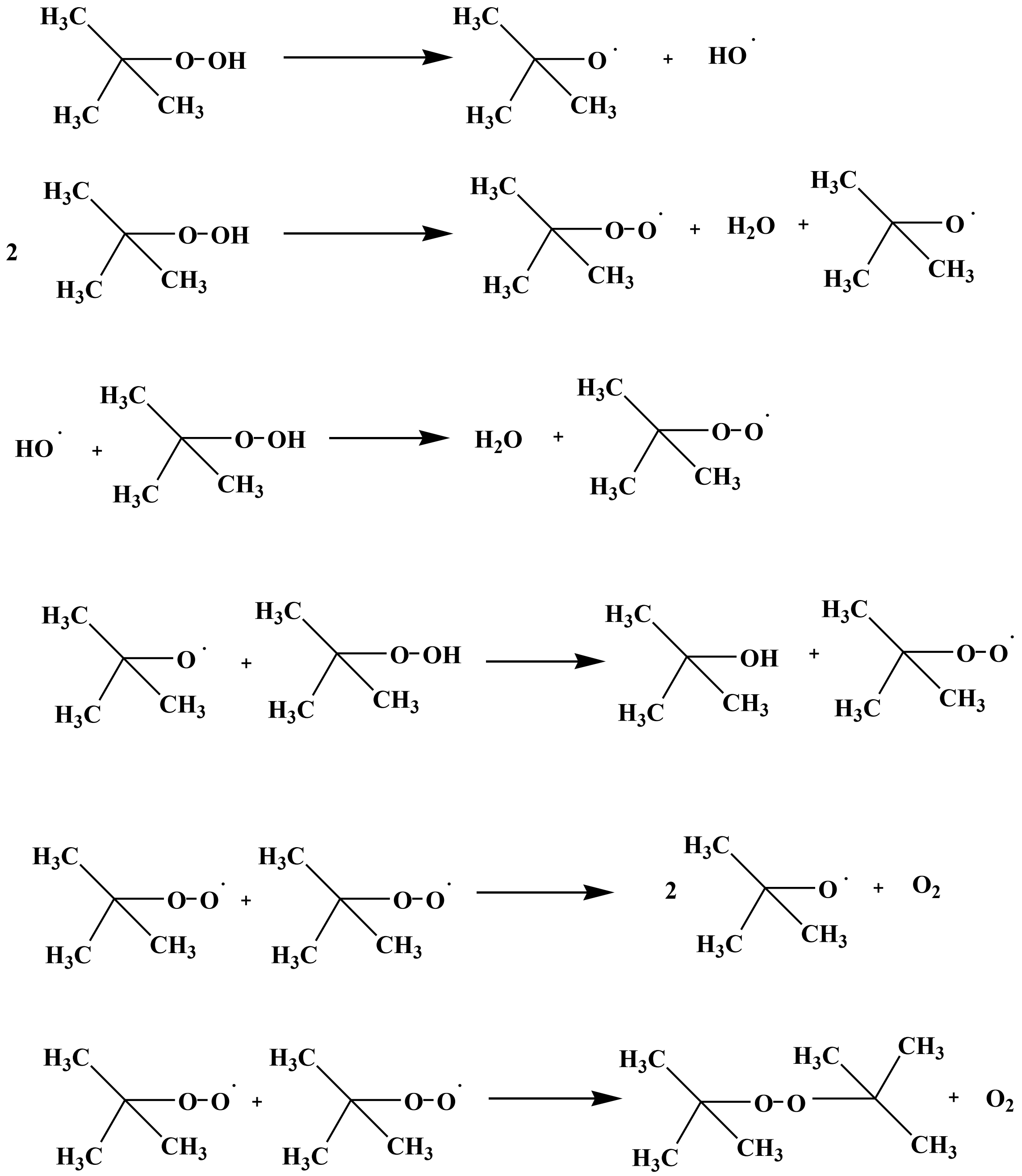


Figure 3.10: ***tert*-Butyl hydroperoxide (TBHP) decomposition[15].**

3.3.5. Evidence for a free radical mechanism

One important characteristic of radical reactions is that the rate of the reaction depends upon the initial concentration of radical initiator [16]. Figure 3.11 show that in the absence of TBHP a trace conversion was observed when the Au/graphite was present. However, performing the reaction in the presence of TBHP the activity increased with the increasing of the TBHP concentration. The increase in activity was more obvious at the beginning of reaction than at higher TBHP concentration and this is consistent with a radical mechanism.

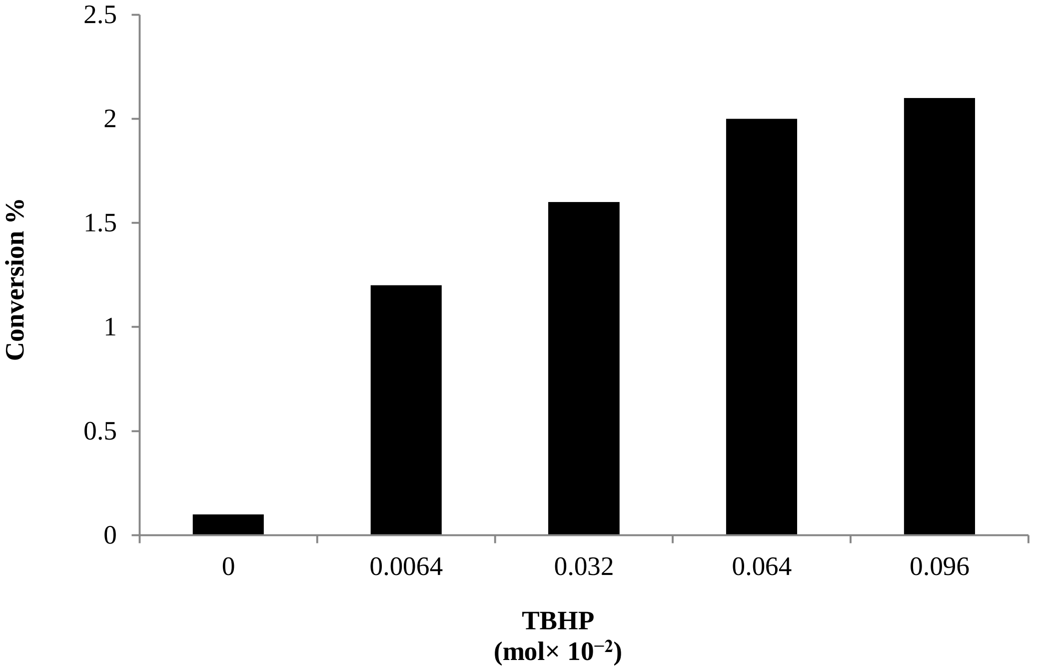


Figure 3.11: Effect of initial concentration of TBHP on the activity of 1-hexene oxidation, Reaction conditions: 10 ml 1-hexene, 0.12 g catalyst, 24 h, 40 °C, glass reactor and atmospheric pressure

Another diagnostic experiment is the reaction in the presence of radical scavenger which should destroy the radical chain reaction. The use of a radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol (BHT), demonstrates that scavenger interact with radicals and terminate the propagation of a radical mechanism. The table 3.4 show that when reaction was performed in the presence of radical scavenger (BHT), no conversion has been achieved.

Table 3.4: Effect of radical scavenger on 1-hexene oxidation

Scavenger	Conversion %
None	2
BHT	trace

Reaction conditions: 10 ml 1-hexene, 0.12 g catalyst, TBHP (0.064×10^{-2} mol), glass reactor, 24 h, 40 °C and atmospheric pressure.

In addition, to confirm that the oxidation of 1-hexene uses oxygen from air, the reaction was performed under Helium atmosphere using Au/graphite as catalyst and TBHP as radical initiator; no conversion has been obtained which indicates that molecular oxygen from the air is involved in the oxidation process.

3.3.6. Effect of the support

The nature of the support is known to play an important role in catalyst activity and different supports may lead to different activities, even under the same conditions[13, 17]. To investigate the role of the support, three different oxides were contrasted with a rather different material, graphite, for the oxidation of 1-hexene; the results are summarised in Table 3.5. The oxide supports used in this study can divided into reducible (TiO_2) and irreducible supports (SiO_2, MgO). Irreducible support has low ability to adsorb or store oxygen[18] which may explain that the higher activity was observed when using TiO_2 relative to SiO_2 or MgO, at 50 ºC. Nevertheless, all such supports resulted in similar activity when the reactions were performed at lower temperature (40 ºC). Overall, all the oxide supports are less effective than graphite which gives very low reactivity in the absence of gold. In addition, graphite support shows the highest selectivity to the epoxide. Hutchings *et al.* [1, 13] have studied the influence of the support on cyclooctene activity using graphite, Al_2O_3, SiO_2 and TiO_2 as support. It was found that graphite showed the highest activity with respect to cyclooctane oxide in the presence of TBHP.

Table 3.5: Effect of support on 1-Hexene oxidation using 1% Au/support

Catalyst	Temp. (^0C)	Conv. (%)	Selectivity (%)						
			1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol	2-hexen-1-ol	1,2-hexanediol
Au/ graphite	40	2	11.4	29.1	12.5	25.8	8.7	2.2	1.1
	50	3	18	35.4	5.7	25.4	5.3	2.6	0.9
Au/TiO_2	40	1.7	10.9	32.5	13.4	24.2	7.9	1.9	0.6
	50	2.5	14.7	33.3	11.3	22.2	7.2	1.5	1.7
Au/SiO_2	40	1.5	4	34.3	15	26.8	8.6	2.2	0.6
	50	2	4.5	38.5	12	24.7	7.9	2	1.5
Au/MgO	40	1.8	13	36.5	9.8	23.6	8.6	2.5	0.2
	50	2	15.1	48.7	12.7	12.2	6	2.1	1.2

Reaction conditions: 10 ml 1-hexene, 0.12 g catalyst, TBHP ($0.064x10^{-2}$ mol), 24h, atmospheric pressure.

3.3.7. Effect of the preparation method

One of the important parameters which can affect the activity of a catalyst is the preparation method[19]. 1% Au/graphite was prepared using three different methods (Table 3.6). Preparing the catalyst by impregnation or deposition precipitation leads to catalysts that display very similar activity. However, a sol-immobilisation method gave catalysts with enhanced activity, possibly due to a higher dispersion of gold with much smaller nanoparticle size[20]. The previous studies by Hutching *et al.* [1] show that the particle size distribution of the 1% Au/graphite catalyst prepared by deposition precipitation and impregnation method is 10–30 nm. This is consistent with the activity of the catalyst that was prepared by impregnation method or deposition precipitation which gave the same activity as shown in table 3.6. Modifying the standard sol-immobilisation by washing the catalyst under reflux resulted in significant improvement in catalyst activity with a selectivity profile similar to that shown by standard sol immobilisation[21]. These results demonstrate that sol-immobilisation is the preferred preparation method for catalysts of this type for 1-hexene oxidation.

Table 3.6: Effect of the preparation methods on 1-Hexene oxidation using 1% Au/G

Preparation Method	Conv. (%)	Selectivity (%)						
		1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol	2-hexen-1-ol	1,2-hexanediol
MSI	2.4	11.8	29.7	11.8	24.8	8.5	2.2	0.8
SI	2	11.4	29.1	12.5	25.8	8.7	2.2	1.1
IMP	0.9	3.7	31.3	29	15.2	8.4	2.3	0.2
DP	0.9	4.5	26.7	24.2	20.8	10.6	2.7	0.4

Reaction conditions: 10 ml of 1-hexene, 0.12 g of catalyst, TBHP (0.064×10^{-2} mol), 40 ^{0}C, 24h, atmospheric pressure. MSI = modified sol immobilisation, SI = sol immobilisation, IMP = impregnation, DP = Deposition precipitation

Sol-immobilization methods utilise colloidal sols having a well-defined particle size distribution, in which the nanoparticles are stabilised in solution by the adhesion of specific surfactant and polymer molecules ensuring that nanoparticles cannot interact[22]. The stabilised nanoparticles are then typically deposited onto a solid surface to enable them to have utility in a chosen application[23]. However, removal of these stabilising molecules is problematic and until recently has only been successfully achieved using thermal and oxidative methods that lead to extensive growth in the size of the nanoparticles[24-28]. However, recent work by Hutchings *et al.* has shown that when PVA is used as a stabilising ligand it can be removed after the nanoparticles have been supported by extraction with water[21]. It can be seen from table 3.6 that when a catalyst prepared by the sol immobilisation method was extracted with hot water, it displayed enhanced activity when compared to material derived from a standard sol method. Analysis of Figure 3.12 reveals that the activity of the extracted catalyst increases with time. In addition, increasing reaction temperature resulted in an increase in catalytic activity of the extracted sol catalyst as shown in table 3-7. Furthermore, the enhancement in the catalytic activity between standard sol and washed sol catalyst increase by increasing the reaction temperature from 11% at 30 °C to 23% at 50 °C. However, the selectivities for standard and washed sol method were quite similar (Table 3.7).

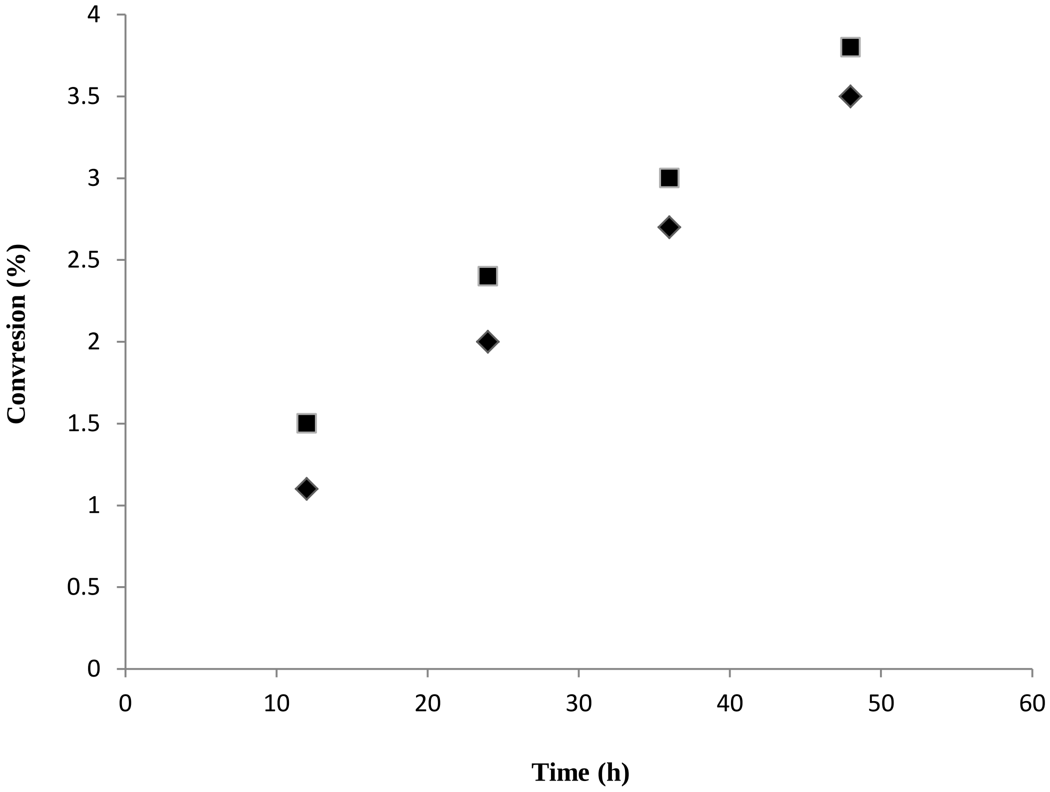


Figure 3.12: Effect of reaction time and washing catalyst, ♦ sol immobilised catalyst, ■ washed sol immobilised catalyst. Reaction conditions: 10 ml 1-hexene, 0.12 g catalyst, TBHP ($0.064 x 10^{-2}$ mol), 40 ^{0}C, atmospheric pressure.

The selectivity toward 2-hexenal decreases with increasing temperature and is coupled with an increase in epoxide formation. The reactivity of graphite alone in the absence of gold was fairly minimal with 2-hexenal and 1-hexen-3-one being the major products (Table 3.7).

Table 3.7: Effect of the preparation methods on 1-hexene oxidation using graphite, 1%Au/graphite and 1%Au/graphite (refluxed)

Temp. (°C)	Catalyst	Conv. (%)	Selectivity (%)						
			1,2-epoxyhexane	1-hexen-3-one	2-hexenal	1-hexen-3-ol	3-hexen-1-ol	2-hexen-1-ol	1,2-hexanediol
30	Graphite	0.3	0.7	32.1	33.1	15.2	7.2	2.2	0
40		0.3	0.9	32.9	33.3	14.8	6.8	2	0
50		0.5	1.4	35.8	34.6	10.8	6.7	1.8	0
30	1%Au/G	0.9	6.3	28.9	18.1	25.7	8.8	2.2	0.5
40		2.0	11.4	29.1	12.5	25.8	8.7	2.2	1.1
50		3	17.1	33.5	6.2	24.1	5.9	2	1.1
30	1%Au/G (refluxed)	1	8.6	29.3	11.4	32.1	9.2	2.9	1.9
40		2.4	11.8	29.7	11.8	24.8	8.5	2.2	0.8
50		3.7	19.1	35.3	6.1	24	5.8	1.9	1

Reaction conditions: 10 ml 1-hexene, 0.12g of catalyst, TBHP (0.064×10^{-2} mol), 24h, atmospheric pressure.

3.3.8. Bimetallic catalysts

Alloying gold with a second metal has been shown to lead to enhancement in the activity of gold catalysts, particularly for the oxidation of alcohols.[29, 30] with this in mind a series of bimetallic gold palladium catalyst were synthesised, these catalysts were prepared using the sol-immobilisation method. The previous reports show that the effect of bimetallic catalytic oxidations was not observed with the epoxidation of cyclic alkenes[31]. Table 3.8 compares the activity of supported Au, Pd and Au-Pd catalysts for 1-hexene oxidation. It can be seen that the highest activity was for Au and Au-Pd catalysts with 2% conversion. However, it was noted that there appeared to be no synergistic effect on conversion, upon addition of Pd to Au, for this oxidation reaction. This is in distinct contrast with two other redox reactions that have previously studied in detail, namely the oxidation of primary alcohols[29] and the direct synthesis of hydrogen peroxide[32] where very pronounced synergistic effects are observed, both on activity and selectivity. The palladium catalyst shows the lowest activity; however some activity was observed compared to the blank reactions.

Table 3.8: Effect of bimetal on 1-hexene oxidation

Catalyst		Au/G	Au-Pd/G	Pd/G
Conversion		2	2	0.8
Selectivity (%)	1.2-epoxyhexane	11.4	10.9	3.7
	1-hexen-3-one	29.1	29.5	20.2
	2-hexenal	12.5	11.9	22
	1-hexen-3-ol	25.8	25.6	23.9
	3-hexene-1-ol	8.7	10.3	15.4
	2-hexen-1-ol	2.2	2.4	3.9
	1.2-hexandiol	1.1	1.4	1.4

Reaction condition : 10 ml of substance , 0.12 g of catalyst , TBHP ($0.064x10^{-2}$ mol), 40 °C , glass reactor , 24h ,atmospheric pressure

3.3.9. Effect of reaction time

A detailed time on line study of the oxidation of 1-hexene is presented in Figure 3.13. It can be seen that, as expected, by increasing the reaction time, the conversion of 1-hexene increases. It is noted that this increase in conversion appears to be linear with time, which suggests that with longer reaction runs greater conversion of 1-hexene should be achievable.

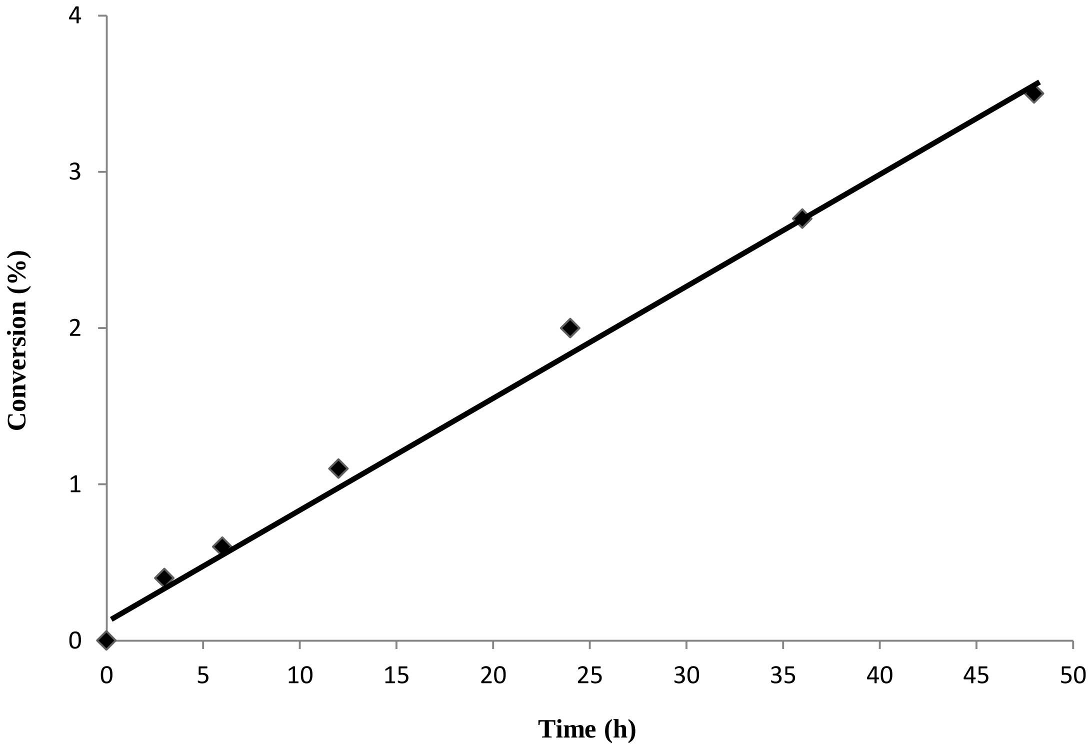


Figure 3.13: Effect of reaction time for the conversion of 1-hexene. Reaction conditions: 10 ml 1-hexene, 0.12 g of catalyst, TBHP ($0.064x10^{-2}$ mol), 40 ^{0}C, atmospheric pressure

The effect on selectivity however, was very marked (Figure 3.14): the selectivity towards the epoxide product dramatically increases with reaction time suggesting that this is one of the initially formed products of the oxidation. In contrast, the selectivity to 2-hexenal decreased dramatically as the reaction proceeded suggesting although this may initially be formed, it is either oxidised to another product or it is the result of an impurity in the starting material. The selectivity of 1- hexen-3-one also increases with reaction time, which is likely to be a result of the oxidation of 1-hexen-3-ol, which remains quite constant throughout the reaction time, suggesting it is oxidised at a similar rate to which it is formed.

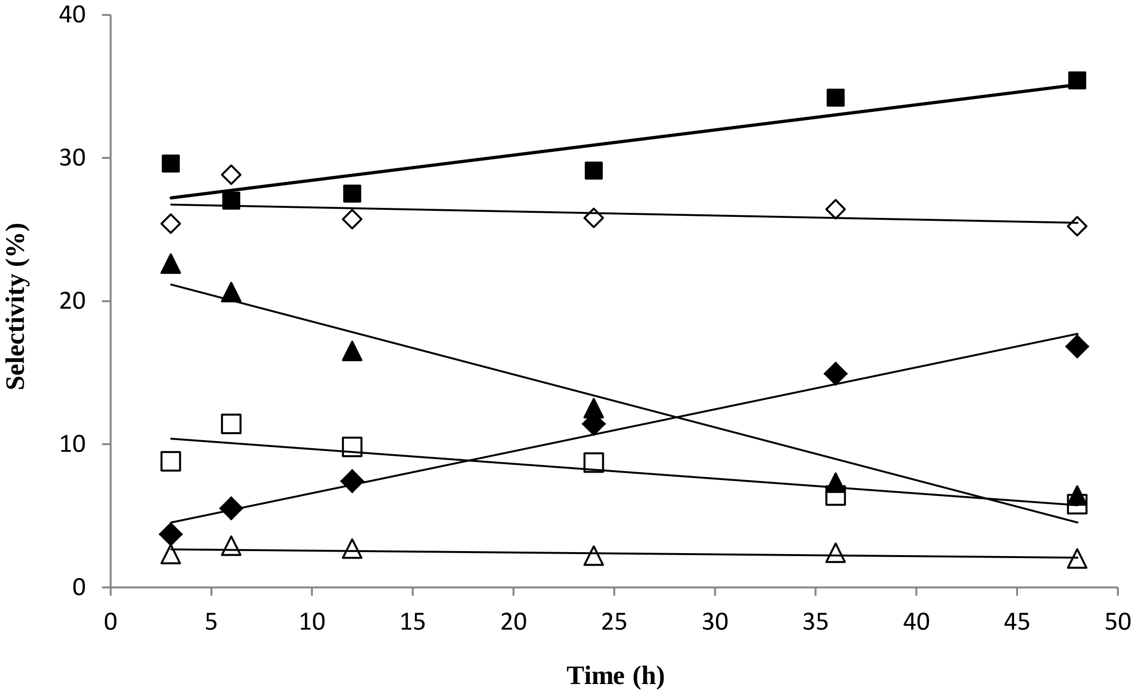
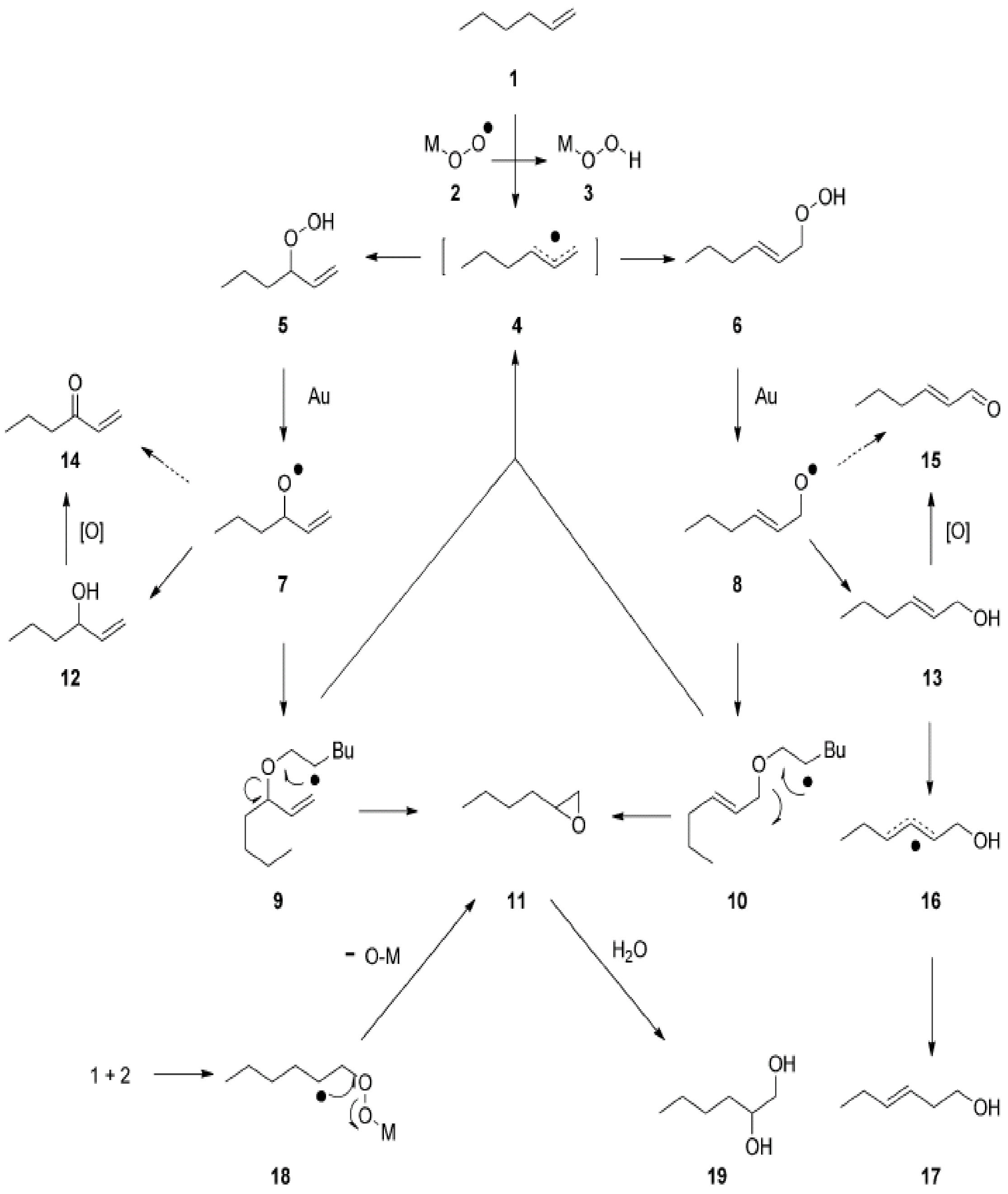


Figure 3.16: Effect of reaction time for the selectivity during the oxidation of 1-hexene. 1,2-epoxyhexane (♦), 1-hexen-3-one (■), 2-hexanal (▲), 1-hexen-3-ol (◊), 3-hexene-1-ol (□), 2-hexen-1-ol (△). Reaction conditions: 10 ml 1-hexene, 0.12 g of catalyst, TBHP (0.064×10^{-2} mol), glass reactor, 40 °C, atmospheric pressure.

Performing the reaction of 2-hexenal under standard reaction conditions did not result in the formation of any 1,2-epoxyhexane, consistent with the latter arising from a different reaction pathway, as argued below.

Based on these experimental observations likely pathways for these oxidations are proposed in Scheme 3.2. The reaction is initiated by cleavage of the ^{t}BuO-OH bond over the surface of the gold catalyst to form peroxy radical species (**2**) which is converted into the neutral species (**3)** as the key intermediate allylic radical (**4**) is formed. The major pathway that the peroxy radical species (**2**) could abstracts a hydrogen radical from 1-hexene (**1**) by breaking an allylic C–H bond and produces the allylic radical (4) which converted into the corresponding hydroperoxides (**5)** and (**6)**. Peroxide bond cleavage, possibly induced by metallic gold would then lead to the alkoxy radicals (**7)** and (**8)**, both of which could then abstract a proton, most likely from 1-hexene (**1**) to produce the two allylic alcohols (**12)** and (**13)**, which are formed in yields of approximately 25 and 2%, respectively. Both of these would be readily oxidised to the corresponding carbonyls (**14)** and (**15)**, formed in yields of approximately 30 and 12 %, respectively. An alternative pathway, which does not require the intermediacy of the alcohols (**12)** and (**13)**, involves 1,2-hydrogen shifts to give more stable allylic radicals (not shown) which, upon loss of a hydrogen radical, would lead to the observed carbonyls (**14)** and (**15)**.



Scheme 3.2: Possible pathway which account for the observed products from 1-hexene oxidation

The alternative path way that the epoxide could form in two ways as shown in scheme 3.2: the highly reactive alkoxy species (**7**) and (**8**) could add to the terminus of the former to provide the ether radicals (**9**) and (**10**) which, being secondary carbon-centred species, are much more stable. Both of these could then decompose to give the epoxide (**11**), formed in around 11% yield, together with the originating allylic radical (**4**). The epoxide (**11**) could also be formed by an alternative pathway initiated by direct addition of the peroxy radical species (**2**) to 1-hexene (**1**) to provide the secondary carbon-centred radical (**18**), decomposition of which in a manner related to that involving the related radicals (**9**) and (**10**), would leave the epoxide (**11**). The very small amount of diol (**19**) [≈1%] most likely arises by epoxide hydration. Finally, the significant amount of the 3-hexen-1-ol (**17**) which is formed [≈ 10%] presumably features reformation of an allylic radical (**16**) followed by proton abstraction. This homoallylic product would be much more difficult to oxidise and hence formation of the corresponding aldehyde was not observed. Indeed, performing the reaction of 3-hexen-1-ol (**17**) under standard reaction conditions, no reaction was observed.

3.4. Conclusions

.

- Reaction condition of 40 °C, TBHP (0.064×10^{-2} mol**)**, 800 rpm with 0.12 g of catalyst are effective under mild, solvent-free conditions using oxygen from air as the oxidant, thus representing a significant improvement in the environmental impact of this reaction.
- Gold supported on graphite is a promising catalyst for the oxidation of 1-hexene with the addition of a catalytic amount of a peroxy initiator. Beside graphite supported , gold nanoparticles supported on TiO_2, SiO_2 and MgO were tested for 1-hexene oxidation. The activity of gold supported on different supports at 50 °C was as following: graphite > TiO_2 > MgO = $SiO_{2.}$
- The effect of radical initiator was studied under different reaction temperatures. In the absence of TBHP, trace of the conversion was observed. However, the activity increase with the increasing of the TBHP concentration, as does the selectivity to 1,2-epoxyhexane. The reaction with radical scavengers has confirmed that the radical initiator (TBHP) was necessary for 1-hexene oxidation.
- Catalyst prepared by the sol-immobilisation method is more active for the oxidation of 1-hexene than those prepared by impregnation or deposition precipitation. Furthermore, modifying the standard sol-immobilisation by washing the catalyst under reflux resulted in significant improvement in the catalyst activity.

3.5. References

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Chapter four

Selective oxidation of alcohols using supported gold-palladium nanoparticles

4. Selective oxidation of alcohols using supported gold–palladium nanoparticles

4.1. Introduction

Oxidation reactions are important for the synthesis of fine chemicals, of which the selective oxidation of alcohols to aldehydes or ketones is one of the most important and useful transformations[1]. There are numerous reports that demonstrate that various catalysts are able to promote the selective oxidation of alcohols, in particular supported gold nanoparticles have been found to be highly effective catalysts[2-7]. The oxidation of alcohols under solvent and/or base–free conditions has also been reported[8], but tends to be more sluggish[9]. Catalysed reactions using oxygen from air are preferred in accordance with the principles of green chemistry[10]. Oxygen is a diradical in the ground state which enables its ease of activation in a number of radical reactions, which can be useful for a range of low temperature oxidations [11-13]. However, at present many combinations of substrate and catalysts do not show any activity with molecular oxygen and therefore more reactive forms of oxygen are often employed, these are typically non-green stoichiometric oxygen donors such as permanganate or a chromate[14, 15].

Allylic alcohols are one important family of alcohols that has great industrial relevance. In this chapter, the use of gold-palladium alloy nanoparticles supported on TiO_2 for the solvent free oxidation of *trans*-2-hexen-1-ol and 1-hexene-3-ol is reported and demonstrates that these catalysts can be extremely effective for this reaction.

The effect of preparation method, catalyst mass, support, gold: palladium ratio and temperature on the oxidation of *trans*-2-hexen-1-ol and 1-hexene-3-ol will also be examined. In this study, it will be investigate if either the alcohol or alkene functional group can be selectively oxidised in *trans*-2-hexen-1-ol and 3-hexen-1-ol.

4.2. Results and discussion

4.2.1. Oxidation of *trans*-2-hexen-1-ol

4.2.1.1. Blank reaction

During oxidations it is important to determine the extent the reaction occurs in the absence of the catalyst. Molecular oxygen is a diradical in its ground state and thus it can participate in radical reactions in the absence of a catalyst. To determine the level of such auto-oxidation, blank reaction was carried out at a range of temperatures as shown in Table 4-1, a trace of conversion was observed for *trans*-2-hexen-1-ol reaction in the absence of the support or the catalyst. The addition of titania leads to an increase in the conversion (Table 4-1): at 70 °C, the conversion increased from 1.7 to 4.9%. However, this conversion was still significantly lower than that observed in the presence of the catalyst. The major product from oxidation of *trans*-2-hexen-1-ol under auto-oxidation conditions or in the presence of titania was *trans*-2-hexenal which was increased when TiO_2 was present.

Table 4-1: Oxidation of *trans*-2-hexen-1-ol in the absence of catalyst

Catalyst	Temp. (° C)	Conv. %	Selectivity %					
			2-hexene	hexanal	*trans*-2-hexenal	*trans*-3-hexen-1-ol	4-hexen-1-ol	*trans*-2-hexenoic acid
Blank	40	0.8	0	3	62.1	15.5	16.9	2.5
TiO_2		1.4	0.6	5.8	65.9	11.8	13.3	2.6
Blank	50	0.8	0	4.4	62.5	13.2	18.7	1.2
TiO_2		1.4	0.5	2.5	74.5	7.9	11.4	3.2
Blank	60	0.8	0	5	64.2	15.2	15.1	0.6
TiO_2		2.3	0.4	3.6	80.7	6.1	7.3	2
Blank	70	1.7	0	13.4	51.7	24.1	9.1	1.7
TiO_2		4.9	0.1	2.2	85.4	3.4	3.4	5.4

Reaction conditions: - Substrate (5ml), TiO_2 (0.06 g), glass reactor, 24 h, air (1 bar).

4.2.1.2. Effect of the preparation method

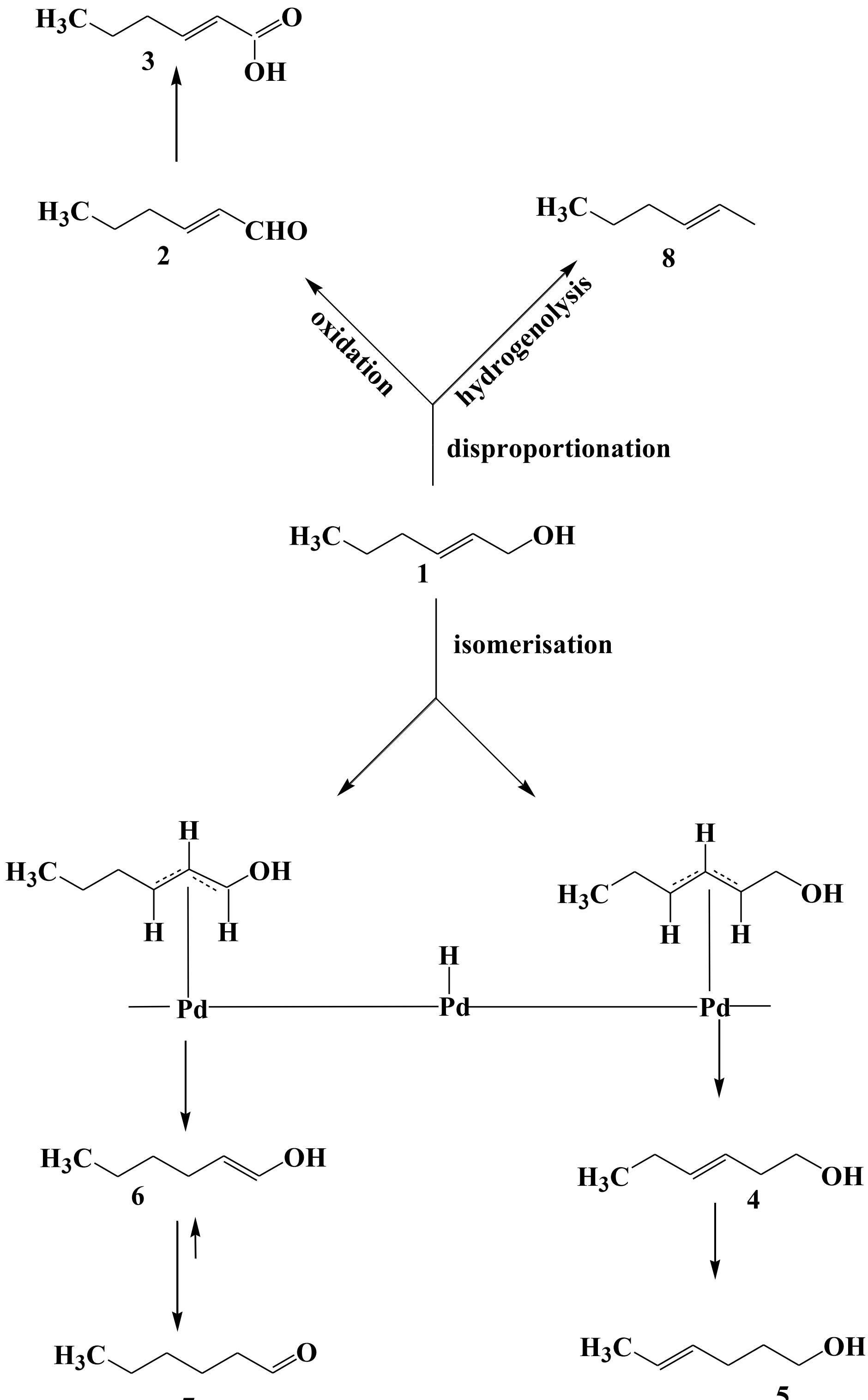
To test the effect of the preparation method, a range of 1%Au-Pd catalysts were prepared by a number of methods: impregnation, deposition precipitation and sol-immobilisation (Tables 4-2). The reaction was initially carried out at 50 °C as the blank reaction and the reaction in the presence of only the titania support at this temperature displayed low conversion. The catalysts prepared using the sol-immobilisation technique proved the most active for *trans*-2-hexen-1-ol reaction. Previous work has shown that this method leads to catalysts with the narrowest particle size distribution of all the preparation methods used in this work [8]. The selectivity observed for *trans*-2-hexen-1-ol reaction shows that the preparation method that are known to give the smallest average particle size [16, 17], namely the sol-immobilisation method, gave the greatest number of products due to the disproportionation reaction. Previous work [11] shows that particle size distributions for impregnation method and deposition precipitation were very similar. This is supported by the activity of the catalysts that were prepared by impregnation method or deposition precipitation methods, which gave almost the same activity, as shown in Table 4.2.

Table 4-2: Effect of preparation methods on *trans*-2-hexen-1-ol oxidation

Preparation method	Conv. %	Selectivity %					
		2-hexene	hexanal	*trans*-2-hexenal	*trans*-3-hexen-1-ol	4-hexen-1-ol	*trans*-2-hexenoic acid
Sol- immobilisation	12.4	17.1	9.3	52	15.3	4.2	2.1
Impregnation	6.7	1.9	3.9	73	9.7	7.4	4.1
Deposition precipitation	6.9	7.7	5	44.2	25.1	15.1	3

Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), glass reactor, 24 h, air (1 bar)

A proposed reaction scheme for the oxidation of *trans*-2-hexen-1-ol is shown in Scheme 4-1: *trans*-2-hexen-1-ol (**1**) can be oxidised to form *trans*-2-hexenal (**2**) and subsequently *trans*-2-hexenoic acid (**3**). Oxidation of *trans*-2-hexenal (**2**) using standard conditions and using Au-Pd/TiO_2 as catalyst resulted in *trans*-2-hexenoic acid (**3**) as major product. The alternative pathway was an isomerisation reaction to form *trans*-3-hexene-1-ol (**4**) and subsequently 4-hexene-1-ol (**5**), a related isomerisation pathway, in which the alkene bond was moved in the opposite direction, initially to give an enol (**6**), would lead to hexanal (**7**). The final product 2-hexene could occur if there was a disproportionation reaction, a reaction that Hutchings *et al.* have previously reported during the oxidation of benzyl alcohol over Au-Pd catalysts[18]. The disproportionation of *trans*-2-hexen-1-ol would yield equimolar quantities of *trans*-2-hexenal (**2**) and 2-hexene (**8**). Such a mechanism was much more likely than hydrogenolysis to give 2-hexene, as no saturated products were observed, which would be expected if hydrogenolysis/hydrogenation reaction were taking place.



Scheme 4-1: Principal pathway for transformation of *trans*-2-hexen-1-ol in air catalysed by Au and Au-Pd on TiO_2

4.2.1.3. Effect of catalyst mass

To check for mass transport limitation, the catalyst amount was varied in a range between 0 – 0.12g using Au-Pd/TiO_2 at 50 ˚C. It can be observed from Figure 4-1 that the conversion of *trans*-2-hexen-1-ol increases with increasing catalyst mass. This suggests there are no mass transport limitations under these conditions. The catalyst amount had no effect on selectivity, as shown in Figure 4-2.

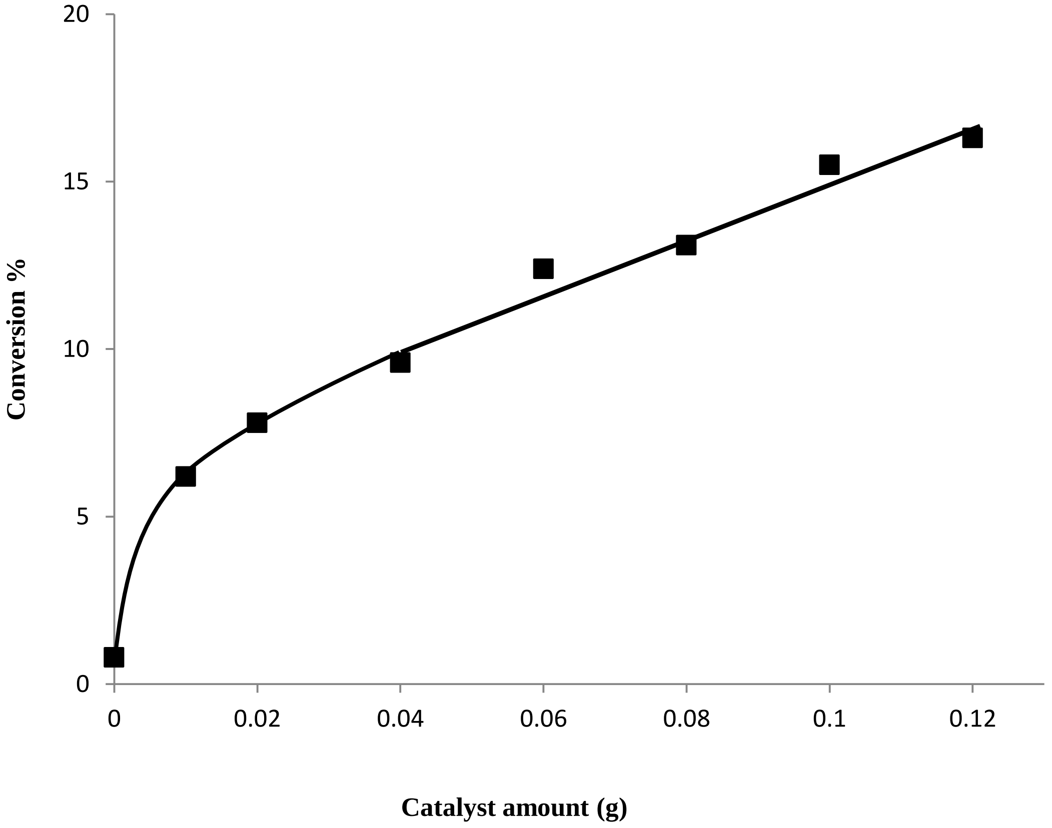


Figure 4-1: The effect of catalyst on the conversion of *trans*-2-hexen-1-ol. Reaction conditions: - Substrate (5ml), glass reactor, 4 h, 50 °C, air (1 bar)

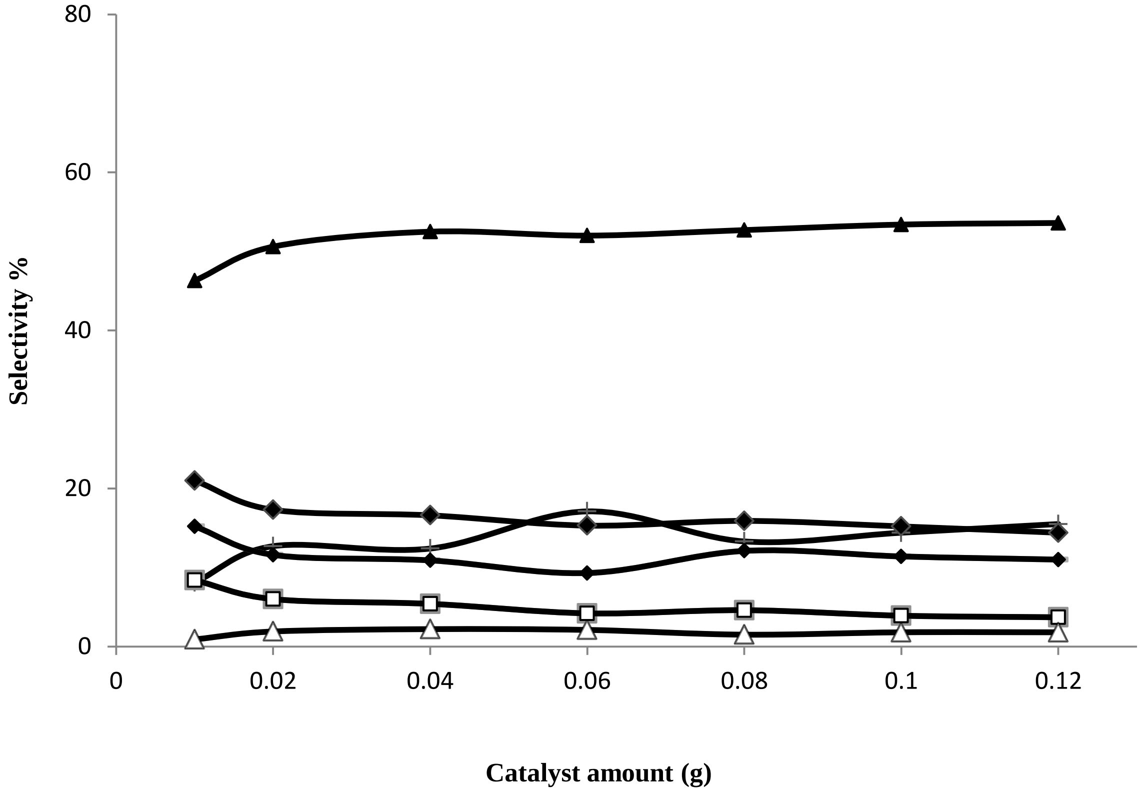


Figure 4-2: Catalyst mass effect for the selectivity during the *trans*-2-hexen-1-ol. Reaction conditions: - Substrate (5ml), glass reactor, 24 h, 50 °C, air (1 bar). 2-hexene (■), hexanal (♦), *trans*-2-hexenal (▲), *trans*-3-hexen-1-ol (●), 4-hexen-1-ol (□), *trans*-2-hexenoic acid (Δ)

4.2.1.4. Effect of the support

To investigate the influence of the support on *trans*-2-hexen-1-ol reaction, Au-Pd catalysts were synthesised on a variety of different supports namely TiO_2, MgO, graphite, SiO_2, and MnO_2, all of which were prepared by the sol-immobilisation method; the results are summarised in Table 4-4. Once again conversion was observed when the pure supports alone were used for the oxidation; however, in all cases this effect was minimal. In general, all oxide supports provide catalysts which were more active than graphite for the oxidation of the *trans*-2-hexen-1-ol in this study. However, the highest selectivity toward oxidation pathway products (*tras*-2-hexenal and *trans*-2-hexenioc acid) was achieved when using graphite as support (76% and 3% respectively). Table 4.3 show the surface area of these supports by BET method. It was clear that the highest activities for trans-2-hexen-1-ol was achieved with the supports have highest surface area (MnO_2 and SiO_2) and the lowest activity was obtained when using graphite as support which has lowest surface area.

Table 4.3: Surface area of supports by BET method

Support materials	Surface area (m^2/g)
TiO_2	46
MgO	40.1
Graphite	10
SiO_2	241
MnO_2	74

Previously, Hutchings *et al.* have reported that the use of MgO as a support can switch off the disproportionation reaction for benzyl alcohol [18, 19] and when MgO was used as the support in this work the same effect was observed, the formation of 2-hexene was negligible. It was noteworthy that this effect also seems to occur when using MnO_2 as the support, an effect that has not been previously reported. In these cases it is interesting to consider the remaining product distribution in order to assess the prevalent reaction pathway in the absence of products produced from disproportionation. In these cases only around 22% of the products are from the oxidation pathway and the isomerisation pathway was dominant. However, when using TiO_2, graphite and SiO_2 as support the oxidation pathway was dominant in this reaction.

Table 4-4: Effect of support on *trans*-2-hexen-1-ol oxidation

Catalyst	Conv. %	Selectivity %					
		2-hexene	hexanal	*trans*-2-hexenal	*trans*-3-hexen-1-ol	4-hexen-1-ol	*trans*-2-hexenoic acid
TiO_2	1.4	0.5	2.5	74.5	7.9	11.4	3.2
0.5%Au-0.5%Pd/TiO_2	12.4	17.1	9.3	52	15.3	4.2	2.1
MgO	0.9	0	5.7	65.6	14.2	13.6	0.8
0.5%Au-0.5% Pd/MgO	14.8	0.7	26.4	23.6	39.6	9.5	0.2
Graphite	1.2	0	5.6	59.9	11.9	15.4	7.1
0.5%Au-0.5%Pd/G	8.9	0.8	2	76	12	6.3	3
SiO_2	1	0	8.9	57.2	15.4	15.4	3.1
0.5%Au-0.5%Pd/ SiO_2	19.5	5.9	10.3	49.8	22.9	4.9	6.2
MnO_2	0.9	0	3.3	71.8	12.2	12.3	1
0.5%Au-0.5%Pd/MnO_2	19.8	1.3	25.5	20.6	41.9	10.6	0.1

Reaction conditions: - Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar)

4.2.1.5. Effect of gold: palladium ratio

Hutchings *et al.* have previously reported the effect of metal composition on the oxidation of benzyl alcohol and the direct synthesis of hydrogen peroxide[20]. To investigate the effect of Au:Pd molar ratio on the oxidation of *trans*-2-hexen-1-ol, a range of catalysts with different metal compositions were prepared. A series of reactions were carried out using the 1% Au-Pd/TiO_2 catalysts containing 1 wt% total metal concentration but with varying Au:Pd ratios. These were prepared by the sol-immobilisation method and the reaction was carried out under solvent-free conditions using air as the source of oxygen. A reaction temperature of 50 °C was selected as the conversion for the blank reaction and the reaction using only titania was minimal at this temperature (0.8 and 1.4% respectively). The results (Figure 4-3) show that the molar ratio of the metals has a marked effect on the conversion of *trans*-2-hexen-1-ol. The observed maximum activity was in the range of Au:Pd molar ratio of 1:1 to 0.1:0.9 for *trans*-2-hexen-1-ol oxidation. In general, the activity was very poor when using monometallic 1% Au/TiO_2 as the catalyst, but on increasing the Pd content the activity was significantly increased.

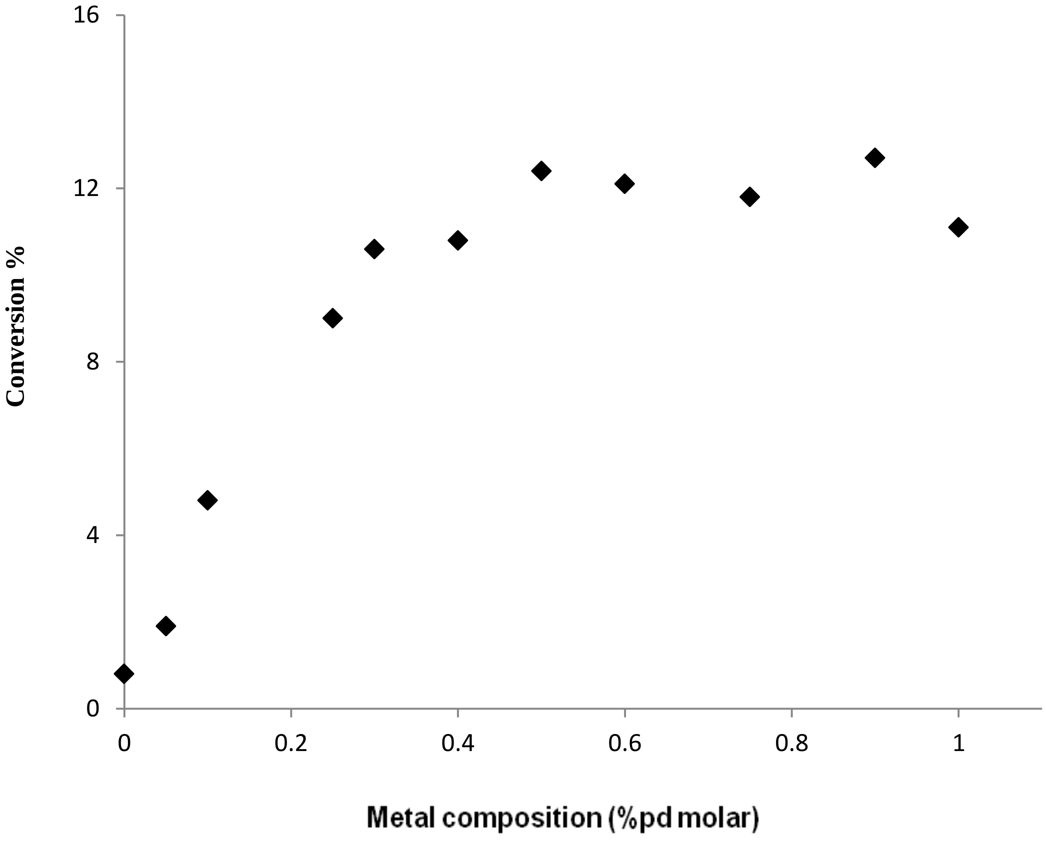


Figure 4-3: Effect of gold:palladium ratio on *trans*-2-hexen-1-ol oxidation. Reaction conditions: Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar)

The effect of the metal ratio on product yield of *trans*-2-hexen-1-ol reaction is shown in Figure 4-4. As expected when monometallic gold was used as the catalyst the oxidation product, *trans*-2-hexenal was favoured, there was some evidence of isomerisation but the disproportionation reaction did not appear to be occurring at all.

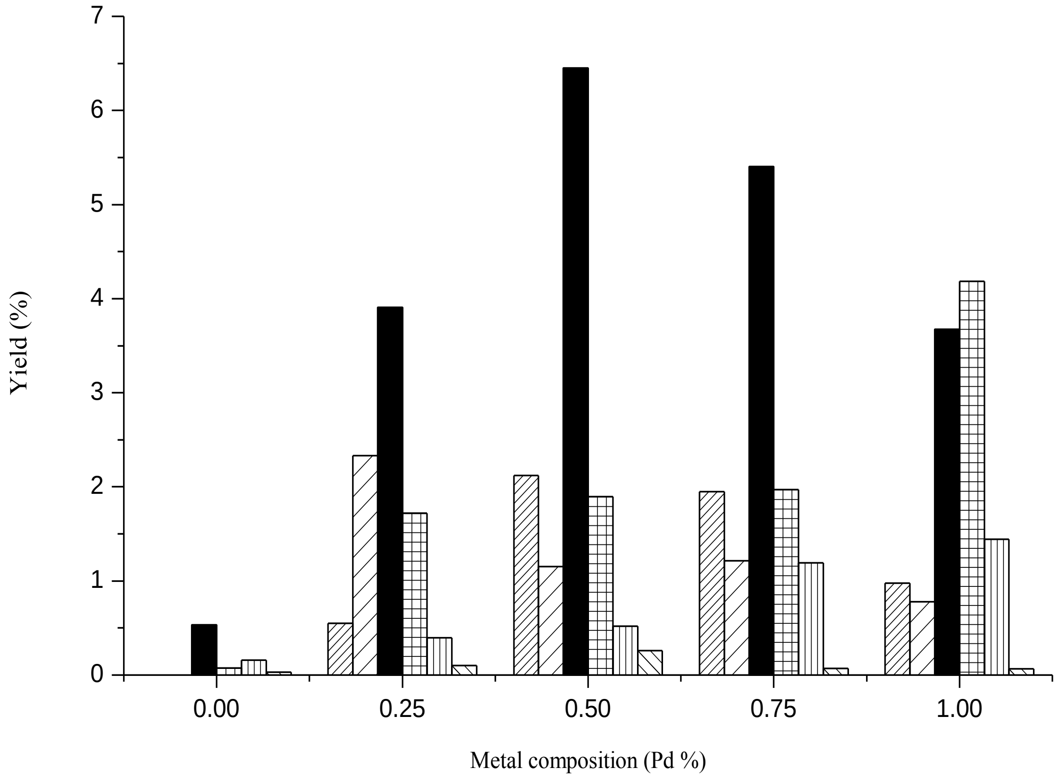


Figure 4-4: Effect of gold: palladium ratio on product yield of *trans*-2-hexen-1-ol conversion. Reaction conditions: - Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar). 2-hexene (▨), hexanal (▨), *trans*-2-hexenal (■), *trans*-3-hexen-1-ol (▦), 4-hexen-1-ol (▥), *trans*-2-hexenoic acid (▧)

As soon as the catalyst contains any palladium, the yield of the isomerisation products immediately increases; in the case of the monometallic palladium catalyst, isomerisation products were the most significant. The 1:1 Au:Pd catalyst was the most active; however, the disproportionation reaction was the most prevalent in this catalytic system suggesting that there may be mass transport limitations with respect to oxygen in this system. The oxidation of *trans*-2-hexen-1-ol was demonstrated with all catalyst compositions, the highest yield of *trans*-2-hexenal was observed with highest conversion (1:1 ratio catalyst), suggesting that the high catalyst activity was associated with the oxidation pathway. The previous report show that gold is promotes/favour alcohol oxidation *via* O_2 or a radical species derived from O_2 on the metal surface[21].

4.2.1.6. Effect of temperature

To test the effect of temperature, a range of reaction temperatures were used for the reaction of *trans*-2-hexen-1-ol. In this reaction pure oxygen was used as the oxidant. Figure 4-5 shows that increasing the temperature and changing the oxidant leads to a significant increase in the conversion of *trans*-2-hexen-1-ol. The reaction time of 4h was considerably shorter than the 24h previously used, demonstrating the enhanced activity that was achieved by using pure oxygen as opposed to air.

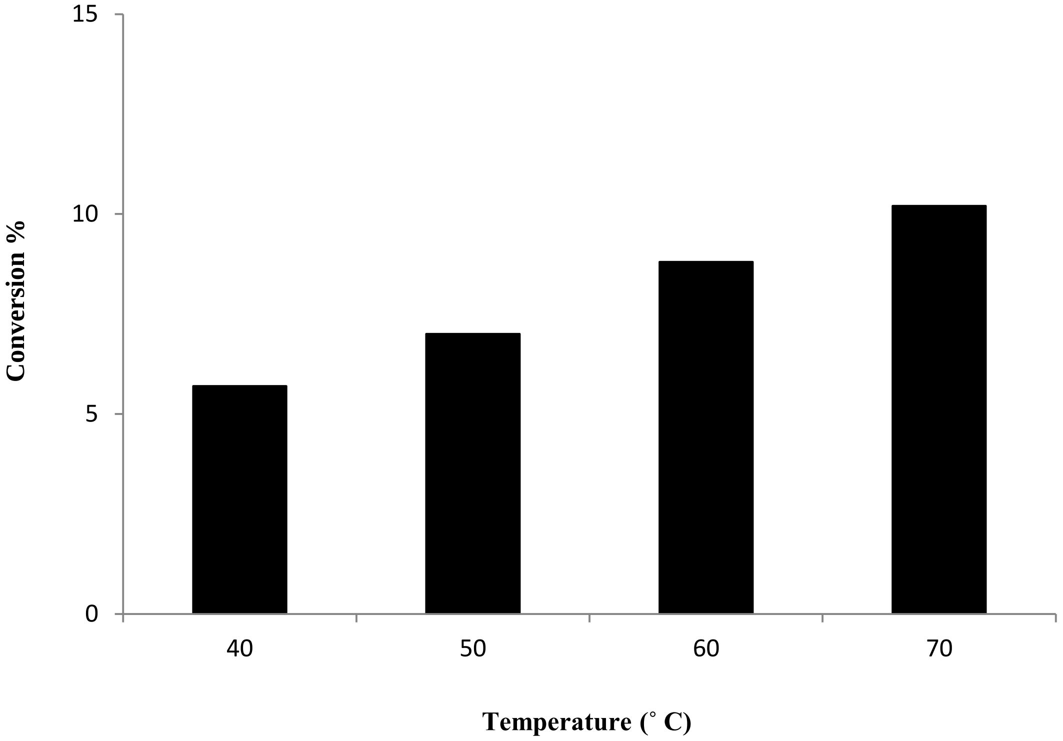


Figure 4-5: Temperature effect for the conversion of *trans*-2-hexen-1-ol. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 4 h, O_2 (balloon)

The selectivity data of *trans*-2-hexen-1-ol oxidation for these four reaction temperatures was shown in Figure 4-6. It was clear that the selectivity to the isomerisation products (hexanal, *trans*-3-hexen-1-ol and 4-hexen-1-ol) decreases with increasing temperature. The selectivity to the oxidation product *trans*-2-hexenal was slightly increased with increasing temperature. The disproportionation reaction increases slightly with increasing temperature: a previous study noted that the disproportionation reaction is not favoured at low temperature but rather increases with increasing temperature [19].

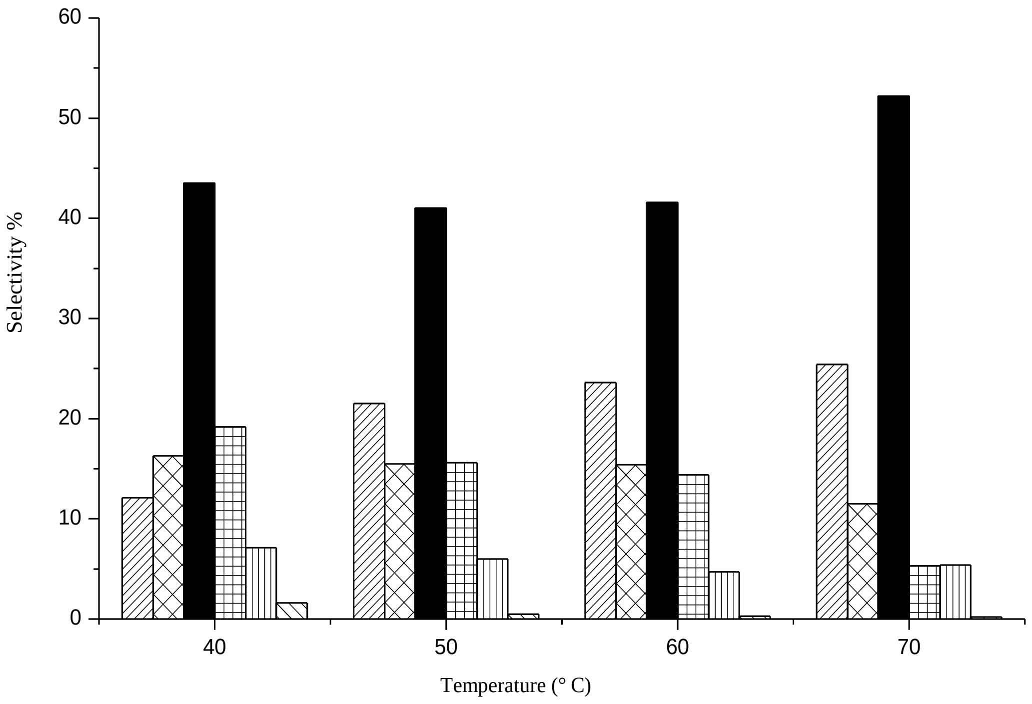


Figure 4-6: Temperature effect for the selectivity during the *trans*-2-hexen-1-ol oxidation. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 4 h, O_2 (balloon). 2-hexene (▨), hexanal (▨), *trans*-2-hexenal (■), *trans*-3-hexen-1-ol (▦), 4-hexen-1-ol (▥), *trans*-2-hexenoic acid (▧)

4.2.1.7. Effect of reaction time

The effect of the reaction time for the *trans*-2-hexen-1-ol oxidations was investigated using the optimised 0.5% Au-0.5% Pd/TiO_2 sol-immobilisation catalyst at the optimal conditions, the result of which is shown in Figure 4-7. Under these conditions, it can be observed that, as expected, there was a steady increase in the conversion with reaction time. There was also no apparent deactivation of the catalysts in this reaction although it must be noted that this was at lower conversions.

The use of a radical initiator to try and increase the initial activity was also investigated; the addation of the radical initiator tert-butyl hydroperoxide (TBHP) made no difference to the conversion of *trans*-2-hexen-1-ol reaction as shown in Figure 4-7. Furthermore, the selectivity to products with and without the TBHP shows the same trend, an effect that has been previously reported[21].

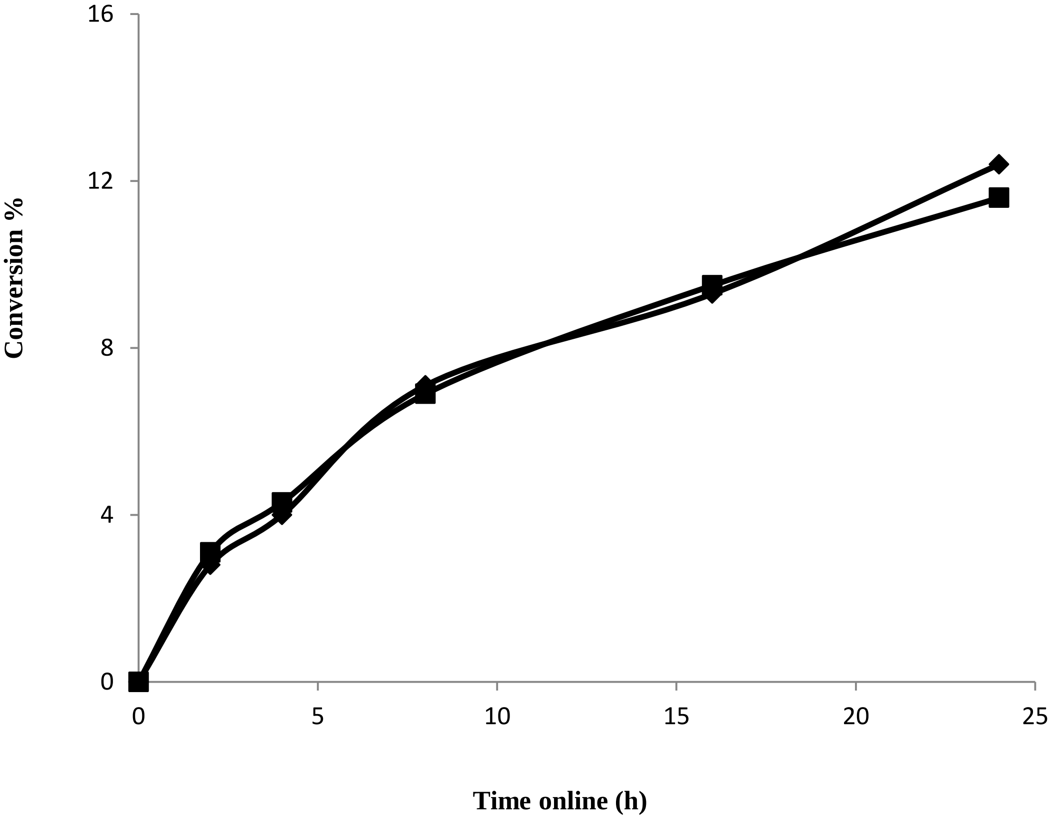


Figure 4-7: Effect of reaction time for the conversion of *trans*-2-hexen-1-ol (■), *trans*-2-hexen-ol with TBHP (♦). Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 50 °C, 4 h and air (1 bar)

The effect of the reaction time on selectivity, however, showed no variation in the selectivity of the products with increasing conversion (Figure 4.8) suggesting that all the reaction pathways were occurring in parallel.

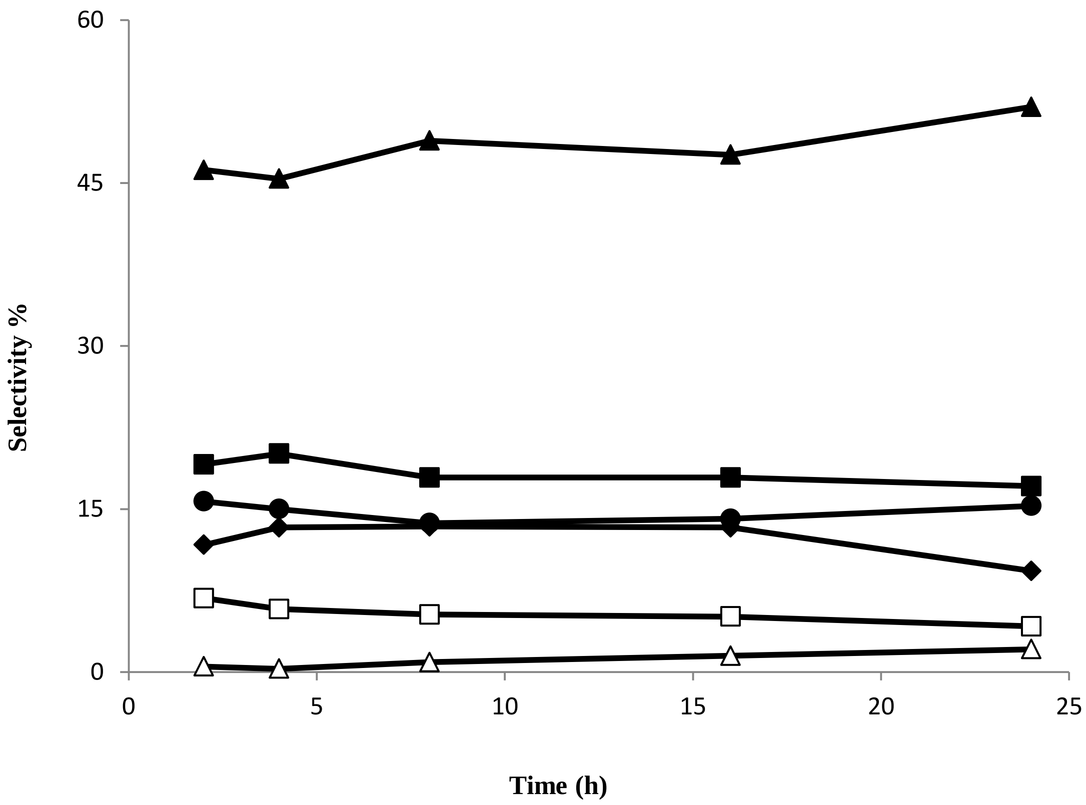


Figure 4-8: **Effect of reaction time for the selectivity during the oxidation of *trans*-2-hexen-1-ol. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 4 h, 50 °C and air (1 bar). 2-hexene (■), hexanal (♦), *trans*-2-hexenal (▲), *trans*-3-hexen-1-ol (●), 4-hexen-1-ol (□), *trans*-2-hexenoic acid (Δ)**

4.2.2. Oxidation of 1-hexen-3-ol

To determine whether the alcohol carbon-carbon double bond would be preferentially oxidised or whether the potential disproportionation reaction and isomerisation pathways would dominate in this system, the 1-hexen-3-ol reaction was performed under the same green conditions that were used for the *trans*-2-hexen-1-ol reaction.

4.2.2.1. Blank reaction

To determine the level of such auto-oxidation, the oxidation of 1-hexen-3-ol was carried out at a range of temperatures in the absence of catalyst. As shown in table 4-5, there was almost no activity for the oxidation of 1-hexene-3-ol and in contrast to *trans*-2-hexene-1-ol; the addition of TiO_2 did not cause an increase in reaction. Under auto-oxidation condition, the major product from oxidation of 1-hexen-3-ol was 1-hexen-3-one and the selectivity towards 1-hexen-3-one was increased when TiO_2 was present.

Table 4-5: Oxidation of 1-hexen-3-ol in the absence of catalyst

Catalyst	Temp. (°C)	Conversion %	Selectivity %			
			1-hexene	3-hexenone	1-hexen-3-one	3-hexanol
Blank	40	0.1	0	0	79	0
TiO_2		0.1	0	0	93.5	0
Blank	50	0.1	0	0	79.4	0
TiO_2		0.1	0	0	93.3	0
Blank	60	0.1	0	0	81	0
TiO_2		0.1	0	0	92.9	0
Blank	70	0.1	0	0	81.1	0
TiO_2		0.1	0	0	91.2	0

Reaction conditions: - Substrate (5ml), TiO_2 (0.06 g), glass reactor, 24 h, air (1 bar)

4.2.2.2. Effect of the preparation method

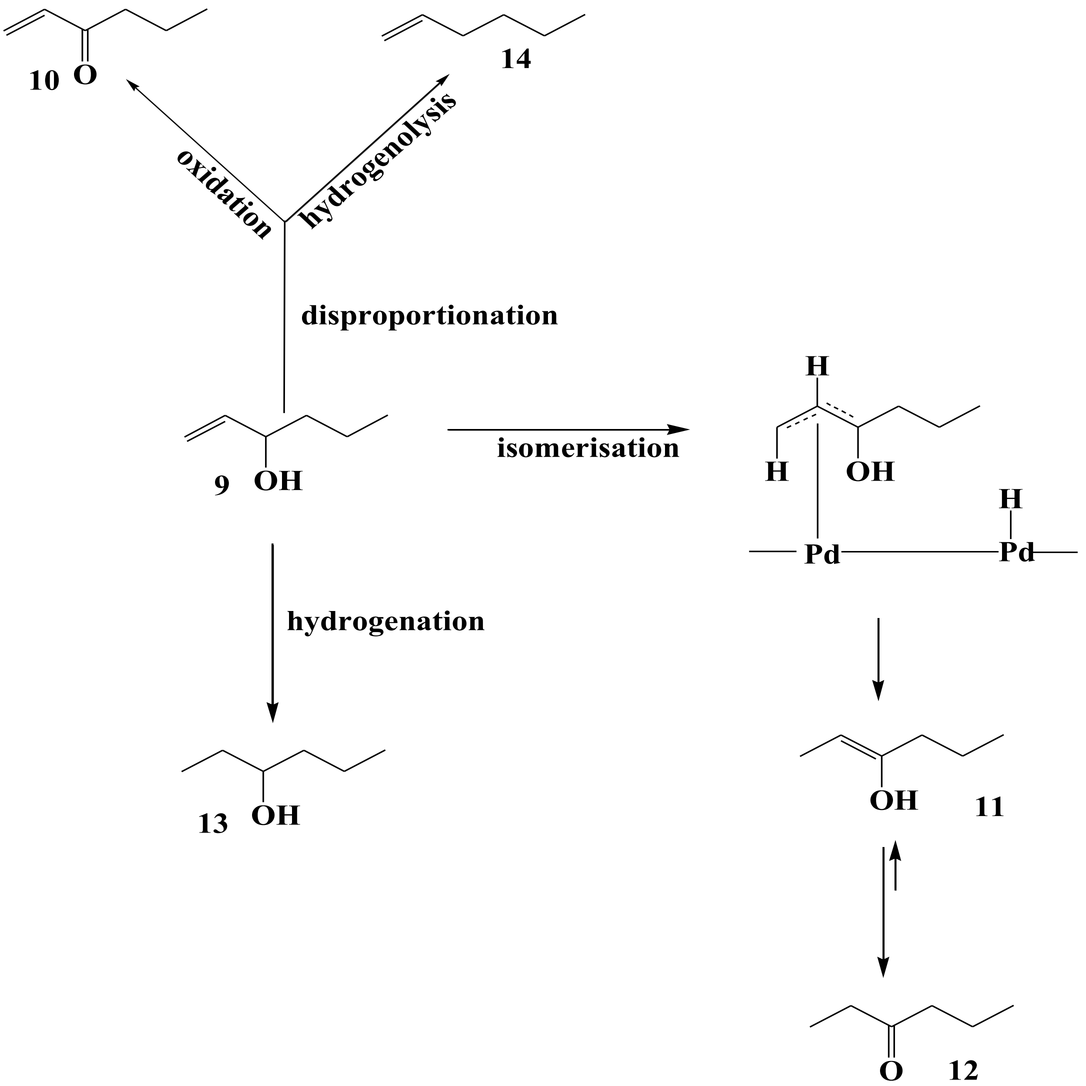
One of the important parameter which can affect the activity of catalyst is the preparation method. To test the effect of preparation method, a range of 1% Au-Pd catalysts prepared using three different preparation methods: impregnation, deposition precipitation and sol-immobilisation. As discussed for the *trans*-2-hexen-1-ol reaction, the catalyst prepared by sol-immobilisation gives catalyst with enhanced activity which could be due to a higher dispersion of gold with much smaller nanoparticle size. The result shown in table 4-6 demonstrates that sol-immobilisation method was significantly the most active for 1-hexen-3-ol reaction but the isomerisation product was the main product. Again as with *trans*-2-hexen-1-ol oxidation, the preparation methods that are known to give the almost same average particle size [11], namely the impregnation method and deposition precipitation, gave the same activity as shown in table 4.6. The selectivities observed for 1-hexen-3-ol followed a similar pattern for *trans*-2-hexen-1-ol reaction: the sol-immobilisation and deposition precipitation methods, gave the greatest number of products due to the disproportionation reaction.

. **Table 4-6: Effect of preparation methods on 1-hexen-3-ol oxidation**

Preparation method	Conversion %	Selectivity %			
		1-hexene	3-hexanone	1-hexen-3-one	3-hexanol
Sol- immobilisation	98	6.5	62.2	29.2	2.1
Impregnation	26.3	1.7	35.1	50.6	12.8
Deposition precipitation	27.9	7.5	43.6	41.8	7.1

Reaction conditions: Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), glass reactor, 24 h, 50 °C and air (1 bar)

A reaction pathway for 1-hexen-3-ol (**9**) is shown in Scheme 4-2. The product of an oxidation reaction would be 1-hexen-3-one (**10**), the isomerisation pathway, in which the alkene bond was moved in the opposite direction, initially to give an enol (**11**), would lead to 3-hexanone (**12**), 3-hexanol (**13**) would be observed if C-C double bond hydrogenation occurred. The disproportionation reaction with this substrate would lead to 1-hexen-3-one (**10**) and 1-hexene (**14**) in equimolar quantities. When gold was used as the catalyst it would be expected that the oxidation reaction would be the primary pathway, however when palladium was the catalyst the isomerisation pathway would be expected to be favoured.



Scheme 4-2: Principal pathway for transformation of 3-hexen-1ol in air catalysed by Au and Au-Pd on TiO_2

4.2.2.3. Effect of catalyst mass

To study the effect of catalyst mass on 1-hexen-3-ol oxidation, the catalyst amount was varied in a range between 0 – 0.12g using Au-Pd/TiO_2 at 50 ˚C. It can be observed from Figure 4-9 that the significant increase in conversion upon further increasing the catalyst mass to 0.12g. This suggests there were no mass transport limitations under our reaction conditions.

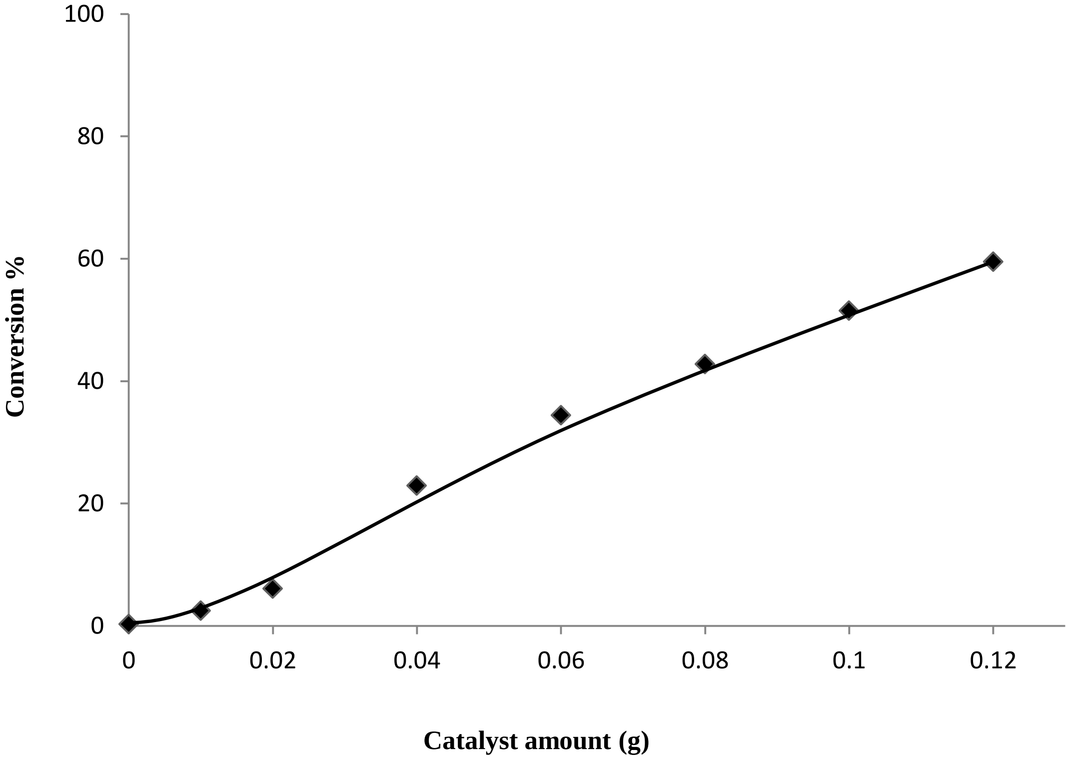


Figure 4-9: The effect of catalyst mass on the conversion of 1-hexen-3-ol. Reaction conditions: - Substrate (5ml), glass reactor, 4 h, 50 °C, air (1 bar)

The effect of variation in the catalyst mass on the selectivity during the 1-hexen-3-ol oxidation was shown in Figure 4-10. Formation of 3-hexanone was slightly increased as the catalyst amount was increased while, in contrast, the selectivity to 1-hexen-3-one decreased with increased catalyst amount.

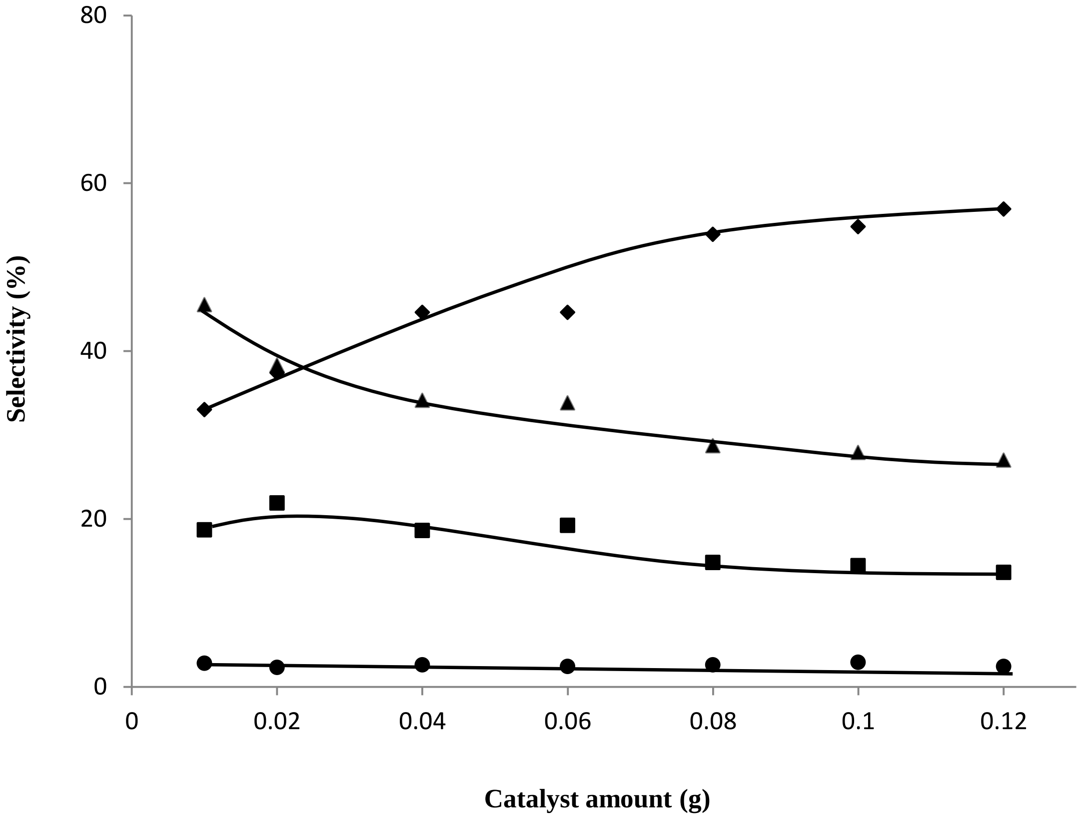


Figure 4-10: **Catalyst mass effect for the selectivity during the 1-hexen-3-ol oxidation. Reaction conditions: - Substrate (5ml), glass reactor, 4 h, 50 °C, air (1 bar). 1-hexene (■), 3-hexanone (♦), 1-hexen-3-one (▲), 3-hexanol (●)**

4.2.2.4. Effect of the support

To investigate the role of the support on 1-hexen-3-ol reaction, Au-Pd catalysts were synthesised on a variety of different supports namely TiO_2, MgO, graphite, SiO_2, and MnO_2, all of which were prepared by the sol-immobilisation method; the results were summarised in table 4-7. Once again a trace of conversion was observed with undoped supports. The result of reactivity observed for the supports repeated the results for the oxidation of *trans*-2-hexen-1-ol: the oxide supports appear to be more effective for this oxidation than the graphite support. However, the highest selectivity toward oxidation pathway products (1-hexen-3-one) was achieved when using graphite as support (46% selectivity to 1-hexene-3-one). Again both MgO and MnO_2 supports seem to almost completely switch off the disproportionation reaction. In this reaction system, with the 1:1 Au:Pd catalyst, isomerisation was the dominant reaction pathway, the oxide supports all having <40% selectivity to the oxidation product 1-hexen-3-one with up to 60% selectivity towards the isomerisation product 3-hexanone. With 1-hexen-3-ol reaction the hydrogenation product, 3-hexanol was far less favoured with selectivity <8% observed on all supports.

Table 4-7: **Effect of Support on 1-hexen-3-ol oxidation**

Catalyst	Conv. %	Selectivity %			
		1-hexene	3-hexanone	1-hexen-3-one	3-hexanol
TiO_2	0.1	0	0	93.3	0
0.5%Au-0.5%Pd/TiO_2	98	6.5	62.2	29.2	2.1
MgO	0.1	0	0	87	0
0.5%Au-0.5% Pd/MgO	66.7	0.5	59.9	34.1	5.4
Graphite	0.1	0	0	80	0
0.5%Au-0.5%Pd/G	35.8	18	35	46.1	0.9
SiO_2	0.2	0	0	69	0
0.5%Au-0.5%Pd/ SiO_2	54.5	8.5	51.2	38.4	2
MnO_2	0.3	0	0	85	0
0.5%Au-0.5%Pd/MnO_2	63.6	0.6	46.9	40.5	8.3

Reaction conditions: - Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar).

4.2.2.5. Effect of gold: palladium ratio

To investigate the effect of Au:Pd molar ratio on the oxidation of 1-hexen-3-ol, a range of catalysts with different metal compositions were prepared using the sol-immobilisation method. The reaction was carried out using the 1% Au-Pd/TiO_2 catalyst containing 1 wt% total metal concentration but with varying Au:Pd ratios. The reaction was carried out under solvent-free conditions using air as the source of oxygen.

A reaction temperature of 50 °C was selected as the blank reaction and the reaction using only titania was unaffected at this temperature (0.1%). The results (Figure 4-11) show that the molar ratio of the metals has a marked effect on the conversion of 1-hexen-3-ol. The observed maximum activity was with A-Pd molar ratio of 1:1. It can be seen from Figure 4-11 that the oxidation of 1-hexen-3-ol was dependent on the ratio of Au and Pd.

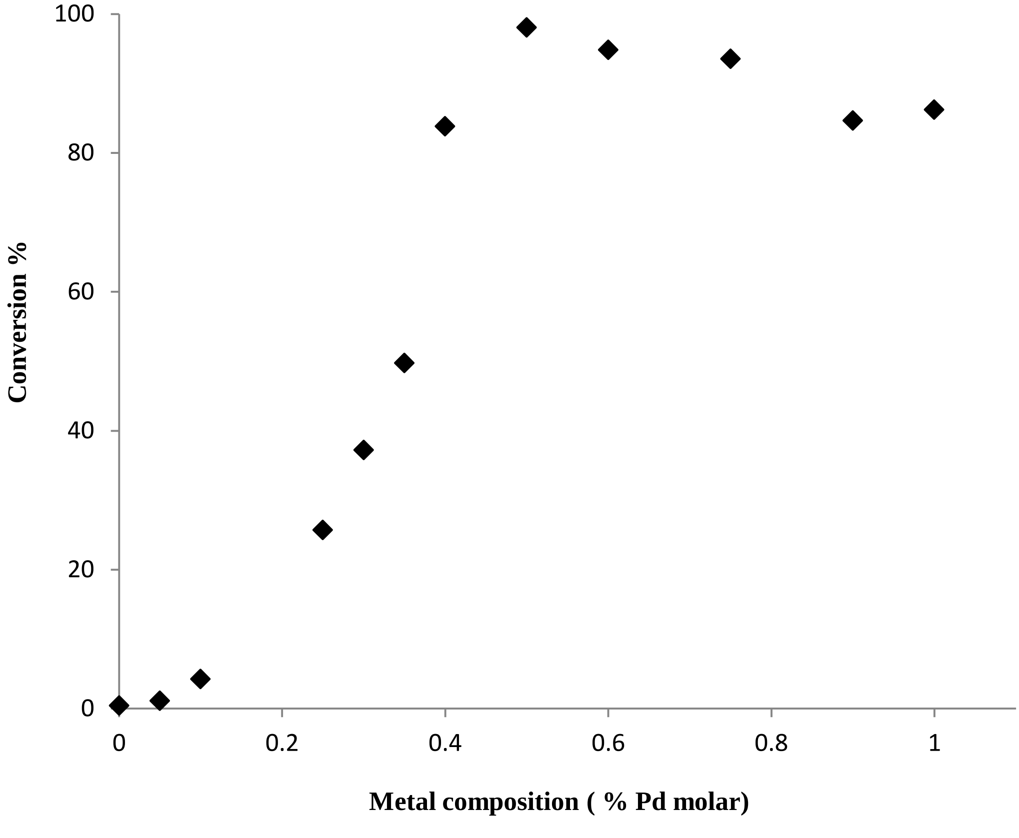


Figure 4-11: Effect of gold: palladium ratio on 1-hexen-3-ol oxidation. Reaction conditions: Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar)

There was a trace conversion observed for the monometallic gold catalysts and the preferred pathway for 1-hexen-3-ol was oxidation, but when Pd was present the activity increases and the isomerisation pathway was dominant as shown in Figure 4-12; the highest activity was achieved for the 1:1 metal ratio catalysts. This also gave the highest yield of 3-hexanone, an isomerisation product which illustrates that both the Pd and Au-Pd catalysts facilitate such alkene migrations. In the cases of all the catalysts where there was a high ratio of palladium (Figure 4-12), the isomerisation product was obtained in the highest yield. In agreement with the oxidation of *trans*-2-hexen-1-ol, the disproportionation pathway in the 1-hexe-3-ol reaction was most prevalent with the 1:1 ratio bi-metallic catalyst. It was noteworthy that the highest yield of 3-hexanone was achieved with the highest conversion, suggesting that the high catalyst activity was associated with isomerisation, which swamps a relatively invariant oxidation rate for alcohol oxidation. Interestingly, the highest yield of the oxidation product was observed for the palladium monometallic catalyst which also gave the highest yield of the hydrogenation product, 3-hexanol (≈7%). Hydrogenation in low yields under oxidative conditions has been reported previously [22] and this is consistent with the known hydrogenation activity of palladium[23]. Abad and co-workers have reported that the stability of Pd-H and Au-H plays an important role in the reaction pathway, if the reaction proceeds through both oxidation or hydrogenation routes. The stability and therefore steady state concentration of Au-H and Pd-H on the metal surface during the reaction had been proposed as the reason for high selectivity of gold compared to palladium[1]. The Pd-H species is postulated to be responsible for promoting the isomerisation and hydrogenation reaction in Au-Pd and Pd catalyst.

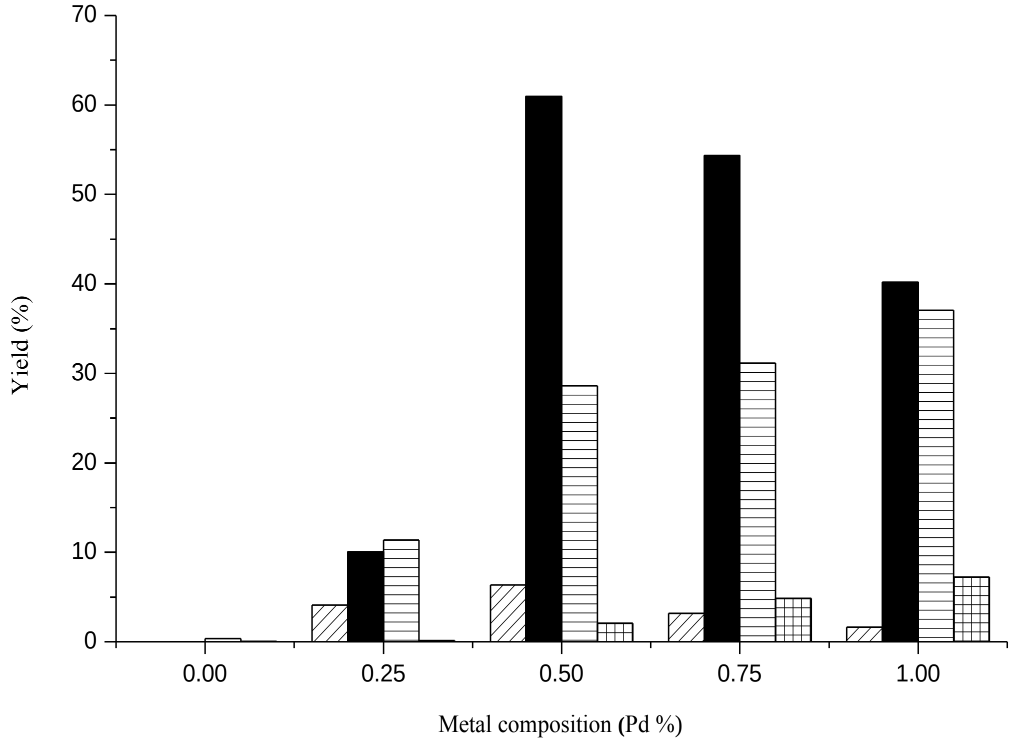


Figure 4-12: Effect of gold: palladium ratio on product yield of 1-hexen-3-ol conversion. Reaction conditions: - Substrate (5ml), catalyst (0.06 g), glass reactor, 24 h, 50 °C, air (1 bar). 1-hexene (▨), 3-hexanone (■), 1-hexen-3-one (▤), 3-hexanol (▦)

4.2.2.6. Effect of temperature

A range of reaction temperatures were tested for the reaction of 1-hexen-3-ol. In this reaction pure oxygen was used as the oxidant. As with *trans*-2-hexen-1-ol reaction, Figure 4-13 show that increasing the temperature and changing the oxidant leads to a significant increase in the conversion of 1-hexen-3-ol oxidation. The reaction time of 4h was considerably shorter than the 24h previously used, demonstrating the enhanced activity that was achieved by using pure oxygen as opposed to air.

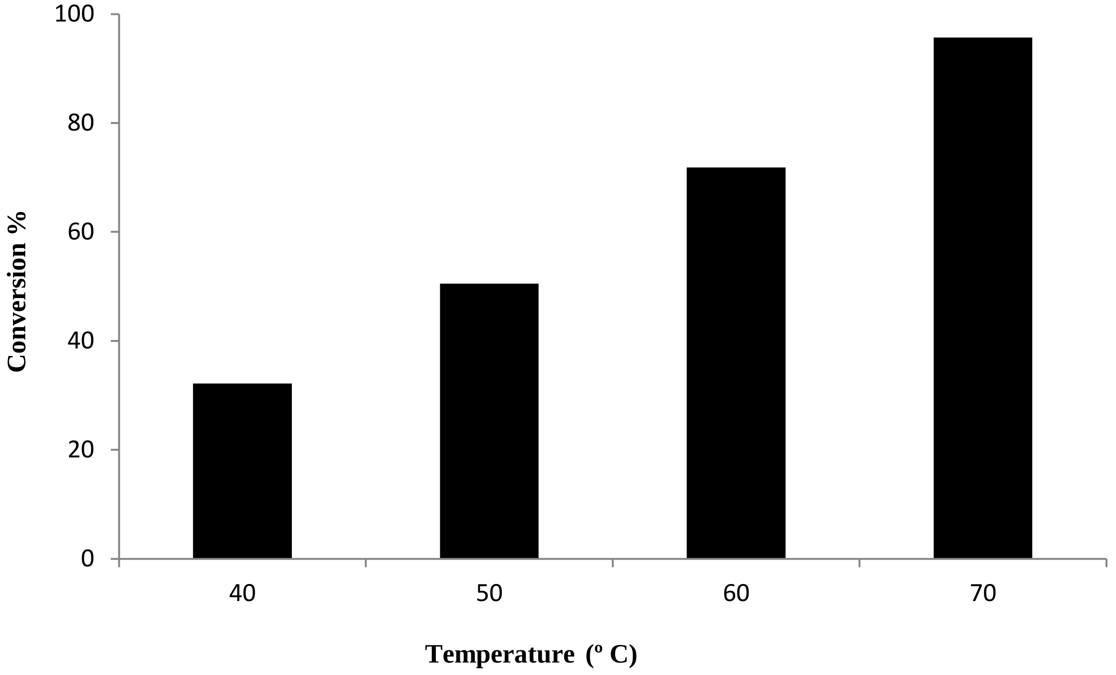


Figure 4-13: Temperature effect for the conversion of 1-hexen-3-ol. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 4 h, O_2 (balloon)

The influence of temperature on selectivity for 1-hexen-3-ol oxidation with O_2 under pure oxygen was shown in Figure 4-14. Again the selectivity to the preferred pathway increases with increasing temperature. In this reaction the isomerisation pathway was preferred rather than the oxidation pathway. Indeed, the selectivity to 3-hexanone increases with increasing temperature and the selectivity to the oxidation product

1-hexen-3-one decreases. The formation of the hydrogenation product 3-hexanol decreased with increasing temperature. In agreement with the oxidation of *trans*-2-hexen-1-ol, the disproportionation reaction increases slightly with increasing temperature: it was previous noted that the disproportionation reaction is not favoured at low temperature but rather increases with increasing temperature[19].

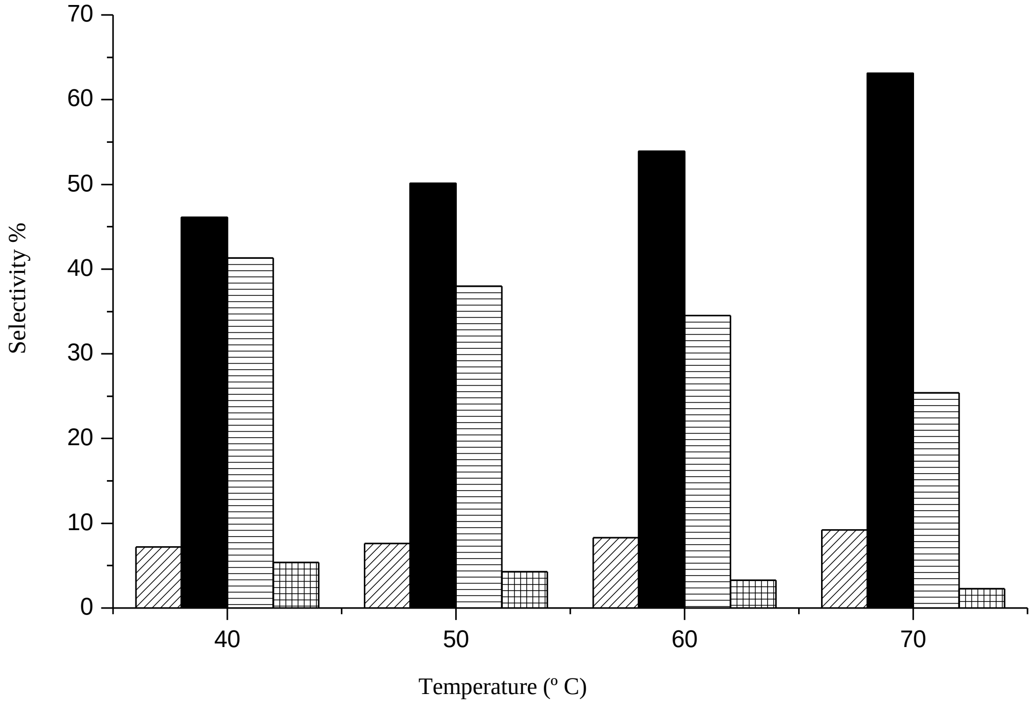


Figure 4-14: Temperature effect for the selectivity during the 1-hexen-3-ol oxidation. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO$_2$ (0.06 g), 4 h, O$_2$ (balloon). 1-hexene (▨), 3-hexanone (■), 1-hexen-3-one (▤), 3-hexanol (▦)

4.2.2.7. Effect of reaction time

The effect of reaction time for 1-hexen-3-ol oxidation was investigated using the optimised 0.5%Au-0.5% Pd/TiO_2 sol-immobilisation catalyst at the optimal conditions, the result of which is shown in Figure 4-15. Under these conditions, it can be observed that, as expected, there was a steady increase in the conversion with reaction time. It was apparent that there is no deactivation of the catalyst and high conversions can be achieved.

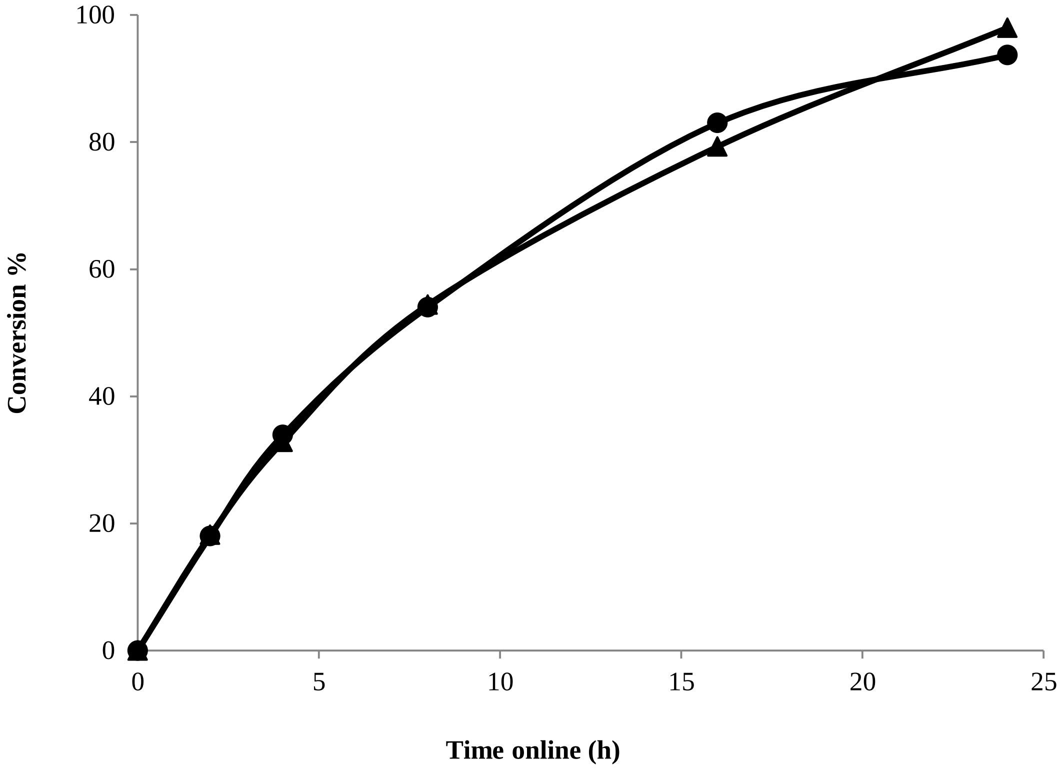


Figure 4-15: Effect of reaction time for the conversion of 1-hexen-3-ol (▲), 1-hexen-3-ol with TBHP (●). Reaction conditions: Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 50 °C and air (1 bar)

The use of a radical initiator to try and increase the initial activity was also investigated; the addition of the radical initiator tert-butyl hydroperoxide (TBHP) made no difference to the conversion of the 1-hexen-3-ol reaction as shown in figure 4-15. Previous studies on the oxidation of alcohol shown that alcohols can be oxidised in the absence of radical initiator[21].

The effect on selectivity during the oxidation of 1-hexen-3-ol, however, was more significant as shown in Figure 4-16: at short reaction times (1-2h) the selectivity towards the oxidation product and the isomerisation product (1-hexen-3-one and 3-hexanone respectively) were formed at similar levels, however there was a significant amount of the disproportionation product 1-hexene, indicating that a large quantity of the apparent oxidation product would have arisen from this pathway. However as the reaction proceeds both the disproportionation and oxidation products decrease whilst the isomerisation product increases in selectivity. This indicates that the isomerisation pathway was the major component in the reaction system. A plot of the yield of each product versus reaction time (Figure 4-17) indicates that all the reaction pathways were occurring in parallel as the yield to all the products steadily increases. The exception to this was the formation of 1-hexene which under such reaction conditions could be oxidised back to 1-hexen-3-ol as discussed previously in chapter 3. The selectivity towards the hydrogenation product (3-hexanol) was minimal at all reaction times.

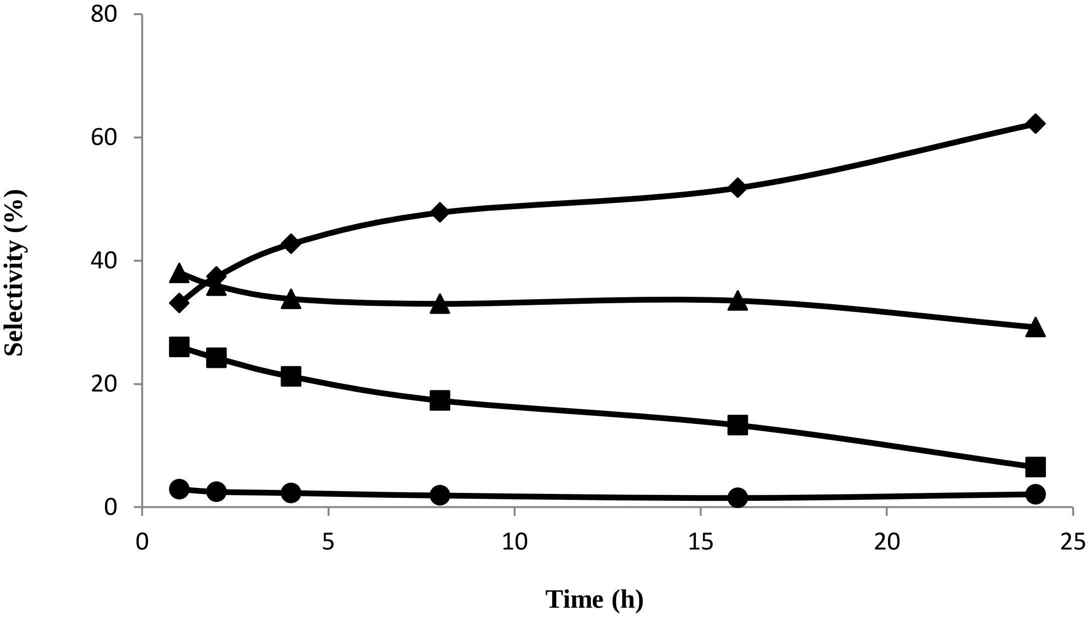


Figure 4-16: **Effect of reaction time for the selectivity during the oxidation of 1-hexen-3-ol. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 50 °C and air (1 bar). 1-hexene (■), 3-hexanone (♦), 1-hexen-3-one (▲), 3-hexanol (●)**

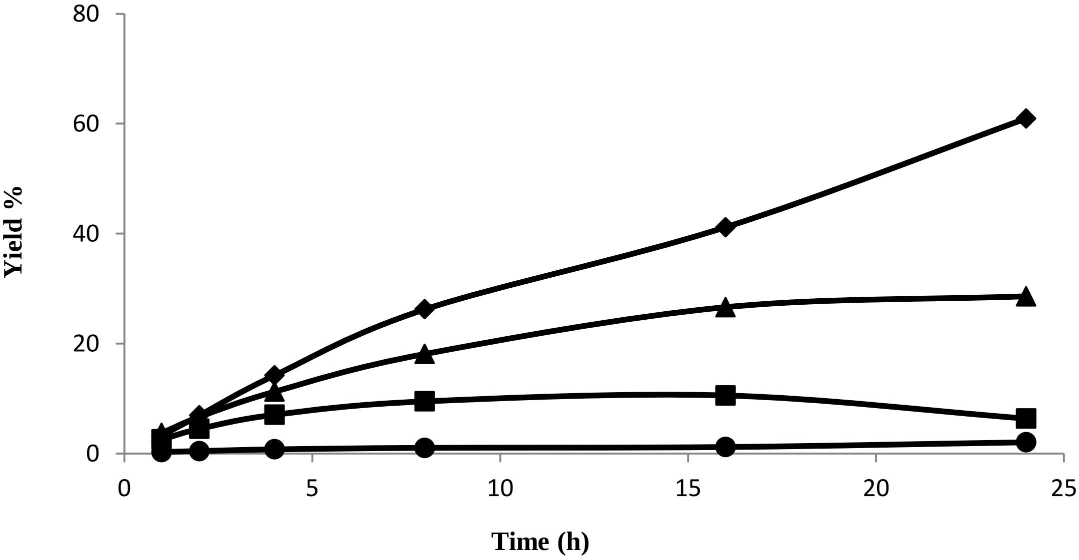


Figure 4-17: **Effect of reaction time for the yield during the oxidation of 1-hexen-3-ol. Reaction conditions: - Substrate (5ml), 0.5%Au-0.5%Pd/TiO_2 (0.06 g), 50 °C and air (1 bar). 1-hexene (■), 3-hexanone (♦), 1-hexen-3-one (▲), 3-hexanol (●)**

4.3. Conclusions

- Reaction condition of 50 ºC with 0.06 g of catalyst are effective under mild, solvent-free conditions using oxygen from air as the oxidant
- We have found that there were four main reaction pathways that occur in these systems. The oxidation pathway was much less prevalent than has previously been assumed with isomerisation being the main reaction under almost all conditions. Furthermore, manipulation of the catalyst design process has shown that a significant amount of the putative oxidation products arise from a disproportionation reaction and not from an oxidation pathway. However, it was demonstrated that the design of the catalysts and control of the reaction conditions can afford a certain degree of control over the reaction products.
- As has been demonstrated for benzyl alcohol and crotyl alcohol, bimetallic gold palladium on supported were the most effective catalyst for solvent free oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol.
- Catalysts prepared by the sol-immobilisation method that give the smallest average particle size was more active for the oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol than impregnation and deposition precipitation methods.
- The conversion of *trans*-2-hexen-1-ol and 1-hexen-3-ol depend on the ratio of Au and Pd. Monometallic Au/TiO_2 was observed to have a low activity and the oxidation pathway was preferred. However, as soon as the catalyst contains any palladium, the activity increased with significant increasing to isomerisation products.

- The oxide supports were more active for the oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol than graphite support, however, the highest selectivity toward oxidation pathway products were achieved when using graphite as support. In addition, MgO and MnO_2 supports seem to almost completely switch off the disproportionation reaction.

4.4. References

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Chapter five

Epoxidation of cycloalkene using supported gold nanoparticles

5. Epoxidation of cycloalkene using supported gold nanoparticles

5.1. Introduction

Hydrocarbon oxidation reactions are important in the synthesis of fine chemicals, catalytic oxidation reactions using oxygen from air represent the greenest method of carrying out these reactions[1]. Gold catalysts have been shown to be effective for several types of oxidation reaction particularly the oxidation of alcohols[2-4] and the direct synthesis of hydrogen peroxide[5]. The gold catalyst was successful catalyst for 1-hexene oxidation as investigated in chapter 3. Moreover, the previous studied by Hutchings and co-workers[6] that show gold catalyst was active for epoxidation of *cis*-cyclooctene. Selective electrophilic addition of oxygen to an alkene to form an epoxide is one of the major challenges in oxidation chemistry. The epoxidation of ethene using molecular oxygen is carried out industrially using a silver catalyst[7, 8]. However, gold catalyst can be used for epoxidation of higher alkenes which they are generally epoxidised using a radical initiator [9-13].

In the first part from this chapter, the effect of ring size on the oxidation of cyclic alkenes using supported gold nanoparticles will be investigated under solvent free conditions using air as the oxidant with catalytic amounts of radical initiator. The second part from this chapter will be investigated the influence of the removing stabiliser from cycloalkene under solvent free conditions using air as the oxidant in the absence of radical initiator.

5.2. Characterisation of catalyst

The catalyst chosen for this study was the 1%Au/G material, as this has been characterised by using the techniques of XRD, BET and SEM in chapter 3. The particle size distribution of the 1 wt% Au/graphite catalyst prepared using the sol-immobilisation method shows this comprises small particles, ranging in size mainly between 1 and 5 nm in diameter with most being 2–3 nm in diameter, very few particles greater than 5 nm were detected[6].

5.3. The influence of ring size on the selective epoxidation of cycloalkenes using supported metal catalysts

In the first part from this chapter, it will expand on previous studies by Hutchings *et al.* [6, 14] on the study of the epoxidation of cyclooctene using supported gold nanoparticles. The previous studies[1] have shown that supported gold catalysts were active for cyclooctene oxidation with significant selectivity to epoxide. In the same work it was demonstrated that the cyclohexene can be oxidising over a supported gold catalyst under mild conditions with poor selectivity to epoxide. In this study, the effect of ring size on the epoxidation of the range of cyclic alkenes using supported gold and gold-palladium nanoparticles, under solvent free conditions using air as the oxidant will be investigated with catalytic amounts of radical initiator. The effect of reaction temperature, the support and the preparation method on the range of cyclic alkenes will be examined. The interesting effect on the selectivity of the epoxide related to the size of the ring has not been reported in the literature before to the best of our knowledge.

5.3.1. Results and discussion

5.3.1.1. Reaction in the absence and presence of catalyst

As reported in the previous chapters, it is important to determine the extent of the blank reaction when using oxygen as a terminal oxidant. To test for auto-oxidation blank reactions with no catalyst present were carried out for a range of temperatures, depending on the boiling point of the cyclic alkenes. It has previously been shown that the oxidation of cyclic alkenes requires a radical initiator and for this reason, the catalytic amount of TBHP have used in this part of study [1, 6, 12-15]. In the range of temperatures selected the conversion of the alkenes was generally very low (< 1%) (Table 5.1), the exceptions to this were cycloheptene, which had a maximum conversion of 6.5% at 70 °C, and cyclododecene, of which 4.8% was converted at 120 °C. The previous work[1] shows that a trace conversion was observed for oxidation of cyclohexene and cylooctene in the absence of catalyst under mild conditions.

Table 5.1: The oxidation of cycloalkenes in the absence of catalyst

Cycloalkene	Temperature (°C)	Conversion (%)	Selectivity %		
			Epoxide	Cy-one	Cy-ol
Cyclopentene	22	0.08	4	49	46
	26	0.1	7.3	65.6	27
	30	0.1	3.8	33.2	34.4
Cyclohexene	40	0.01	0	43.9	56.1
	50	0.04	4.6	52.8	42.6
	60	0.05	4.3	51.5	44.3
Cycloheptene	50	1.7	15.3	26.5	58.2
	60	2	24	31	44
	70	6.5	24	26	48
Cyclooctene	70	0.01	56.1	0	43.9
	80	0.03	47.6	13.1	39.3
	90	0.2	65.1	1.1	8.8
Cyclododecene	120	4.8	75	23	-

Reaction conditions: 10 ml of substrate, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

The effect of the addition of the graphite support to these reactions was shown in Table 5.2. In most cases the presence of graphite did not make a significant difference to the conversion of the cyclic alkene. Graphite is known to have neutral surface and this could explain the low activity in the absence of gold especially at low temperature. However, in the case of cyclooctene at 90 °C there was a significant increase in the conversion upon the addition of graphite to the reaction mixture, from 0.2 to 5.4%. The effect of temperature on the activity of cyclooctene in the presence of graphite is shown in Figure 5.1. This increase in conversion was also observed for cyclododecene oxidation, which was also carried out at 120 °C, suggesting that at higher temperatures graphite alone can catalyse the reaction. The previous report shows that graphite can act as a catalyst for the oxidation of cyclooctene at temperatures $\geq$100 °C[6]. In addition, the homolysis rate of TBHP would be faster at higher temperatures which could increase the activity in the presence of graphite only and this may also explain why the increase in the conversion was more significant at higher temperatures.

Table 5.2: The oxidation of cycloalkene using graphite

Cycloalkene	Temperature (°C)	Conversion (%)	Selectivity %		
			Epoxide	Cy-one	Cy-ol
Cyclopentene	22	0.1	3.2	36.4	39
	26	0.2	5.3	42.9	41.6
	30	0.4	7.9	39.7	37.6
Cyclohexene	40	0.01	0	48	52
	50	0.03	0	49.3	41.9
	60	0.14	4.3	49.5	43.8
Cycloheptene	50	2.4	13	26.5	60.5
	60	4.9	17.6	29.5	52.9
	70	6.2	34.4	34.9	30.6
Cyclooctene	70	0.1	66.8	5.3	27.8
	80	0.4	79.7	4.5	15.8
	90	5.4	86.3	4.7	7.2
Cyclododecene	120	8	88	10	-

Reaction conditions: 10 ml of substrate, 0.12g of graphite, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

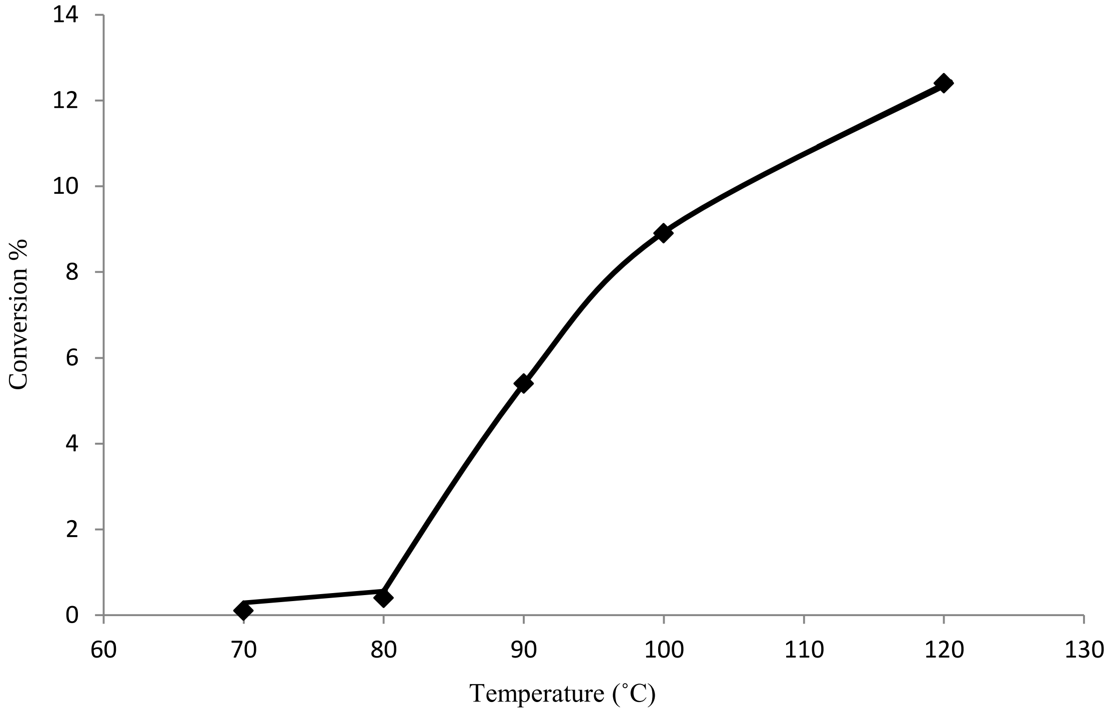


Figure 5.1: The effect of addition graphite on cyclooctene oxidation in presence of graphite

The addition of gold supported on graphite, however, leads to a significant increase in the conversion of the cyclic alkenes at all the reaction temperatures studied as shown in table 5.3. In the presence of gold catalyst, the gold surface may facilitate the O-H homolysis in TBHP to produce $Me_3COO^{\bullet}$, which is very active in abstracting the hydrogen from the allylic position in hydrocarbons at mild temperature[14] and this could explain the dramatic increase in activity when adding gold supported on graphite.

Table 5.3: The oxidation of cycloalkene using 1%Au/graphite

Cycloalkene	Temperature (°C)	Conversion (%)	Selectivity %		
			Epoxide	Cy-one	Cy-ol
Cyclopentene	22	2.2	17.2	43	23
	26	4.4	12.4	43.6	23.9
	30	8.3	10.9	43.3	33.3
Cyclohexene	40	6.5	8.2	43.3	45.5
	50	8.2	6.4	50.5	41.4
	60	11.6	5.9	53.8	40.2
Cycloheptene	50	9	17.8	35.2	47
	60	10.1	18.2	43.5	38.4
	70	11.2	19.8	47.9	32.3
Cyclooctene	70	2.6	81.1	6.3	12.6
	80	6.8	85.9	4.8	9.3
	90	11.5	86.3	5.3	7.8
Cyclododecene	120	10.2	60.5	37	-

Reaction conditions: 10 ml of substrate, 0.12g catalyst, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

The experimental conditions show that oxidation of the larger ring sizes requires the use of higher temperatures. This makes direct comparison of the reactivity of the alkenes difficult. However, as shown table 5.3, at 30 °C, cyclopentene shows comparable conversion over 1%Au/graphite to cyclohexene at 50 °C, suggesting the smaller ring was more reactive toward oxidation. The conversion of cyclohexene and cycloheptene at 50 and 60 °C appear similar for the supported Au catalyst but the significantly higher reactivity in the absence of Au for cycloheptene may suggest that the metal catalysed conversion of cyclohexene was actually the greater. In the case of cyclooctene and cyclododecene higher temperatures were required and yet conversions using 1%Au/graphite did not significantly increase. These observations suggest that the reactivity of the cyclic alkenes decreases as the ring size increases. There was also a significant trend in the selectivity to the epoxide when the gold catalyst was present. The selectivity to the epoxide was relatively low for the smaller ring sizes (between 6 and 20% for C_5-C_7). However, the selectivity to the epoxide was significantly increased for the C_8 and C_{12} rings (86% and 60% respectively).

5.3.1.2. Bimetallic catalysts

Alloying gold with a second metal has been shown to lead to enhancement in the activity of gold catalysts, particularly for the oxidation of alcohols[3, 16-18] and the selective oxidation of toluene[19, 20]; with this in mind a series of bimetallic gold palladium catalysts were synthesised, these catalysts were prepared using the sol-immobilisation method. A previous report[15] shows that the effect of bimetallic catalytic oxidations was not observed for the epoxidation of cyclooctene. The effect of mono Au or Pd and bimetallic Au-Pd on cycloalkene is shown in Table 5.4. It was clear that the bimetallic catalyst was not more active than monometallic gold catalyst, the most active catalyst for any of the cycloalkenes studied; the gold monometallic catalyst gives the highest conversion. In most cases the palladium catalyst shows the lowest activity; however some activity was observed compared to the blank reactions. The bimetallic catalysts tend to have an activity between that observed for the monometallic catalysts suggesting that the palladium was in this case acting as an inhibitor or a diluent for the active gold phase. The effect of bimetallic on selectivity was shown in table 5.4. There does appear to be a significant trend between the metal and the selectivity towards the major products, although it appears that the previously discussed trend towards the epoxide with the larger ring size still applies whichever metal was present in the catalyst, however it was observed that for the smaller ring sizes the addition of palladium to the catalyst leads to an increase in the selectivity of the allylic alcohol product.

Table 5.4: Effect of bimetal on cycloalkene oxidation

Cycloalkene	Temperature (°C)	Catalyst	Conversion (%)	Selectivity (%)		
				Epoxide	Cy-one	Cy-ol
Cyclopentene	26	Au/G	4.4	12.4	43.6	23.9
		Au-Pd/G	3.5	14.7	20.9	36.9
		Pd/G	1.4	11.8	20.1	38.4
Cyclohexene	50	Au/G	8.2	6.4	50.5	41.4
		Au-Pd/G	4.5	6.6	14.4	78.9
		Pd/G	2.5	15.2	32.2	50.8
Cycloheptene	60	Au/G	10.1	18.2	43.5	38.4
		Au-Pd/G	7.8	16.7	40.6	42.7
		Pd/G	9.6	20.2	30.4	49.5
Cyclooctene	80	Au/G	6.8	85.9	4.8	9.3
		Au-Pd/G	2.5	85	5.4	9.6
		Pd/G	2.8	85.4	5.3	9.4
Cyclododecene	120	Au/G	10.2	60.5	37	-
		Au-Pd/G	8.2	81.2	16	-
		Pd/G	10	65.7	10.3	-

Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

5.3.1.3. Effect of the support

The activity of catalyst is often affected by the nature of support. Previous studies on gold catalyst have shown a significant support effect on both the conversion and selectivity. A series of supported gold catalysts were prepared on a range of different oxide supports and these were tested for the oxidation for the different cyclic alkenes. These catalysts were prepared using the sol-immobilisation method. Initially the undoped supports were tested as shown in table 5.5, for the majority of the alkenes there was not a significant improvement in conversion compared to the blank tests (Table 5.1), the exceptions were cycloheptene and cyclododecene where there was significant conversion of the alkene with the addition of the support alone. In the case of cycloheptene, it was only the graphite support that leads to a significantly enhanced conversion. In the case of cyclododecene, there was significant conversion with all the supports tested, however, this may be associated with the temperature that these reactions were carried out at temperature above 100 ºC, as discussed previously in section 5.3.1.1.

Table 5.5: The oxidation of cycloalkene using undoped support

Cycloalkene	Temperature (ºC)	Catalyst	Conversion %	Selectivity %		
				Epoxide	Cy-one	Cy-ol
Cyclopentene	26	Graphite	0.2	5.3	42.9	41.6
		TiO_2	1.3	12	44	26
		SiO_2	0.2	20	25	49
Cyclohexene	50	Graphite	Trace	0	69.8	30.2
		TiO_2	Trace	0	68.0	31.0
		SiO_2	0	0	0	0
Cycloheptene	60	Graphite	4.9	17.6	29.5	52.9
		TiO_2	3.0	21.0	25.0	53.0
		SiO_2	2.5	21	44	34
Cyclooctene	80	Graphite	0.4	17.6	29.5	52.9
		TiO_2	0.2	33	33	36
		SiO_2	0.1	50	20	30
Cyclododecene	120	Graphite	8	88	10	-
		TiO_2	7.3	91	8.2	-
		SiO_2	7.4	93	6.9	-

Reaction conditions: 10 ml of substrate, 0.12 g of support, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

The addition of gold to the support in all cases leads to a significant enhancement in the conversion of the cycloalkene as shown in table 5.6. The enhancement in the conversion was most significant at lower temperatures with cyclopentene and cyclohexene displaying the most significant improvement when compared to both the blank reaction and reaction of undopped support. The effect of support on selectivity was shown in table 5.6. The same selectivity trend as has been previously discussed with the gold on graphite catalyst was shown with all the supports tested, the selectivity towards the epoxide product greatly increases when the ring size increases in the case of cyclooctene and cyclododecene. All of the supports tested for this reaction showed similar activities. However, due to high surface area (240 m^2/g), SiO_2 generally being the either the most active support of showing very similar activity to the most active support in each case.

Table 5.6: The oxidation of cycloalkene using Au/ support

Cycloalkene	Temp. (ºC)	Catalyst	Con. %	Selectivity %		
				Epoxide	Cy-one	Cy-ol
Cyclopentene	26	1%Au/Graphite	4.4	12.4	43.6	23.9
		1%Au/TiO_2	5.7	11.3	40.2	25.2
		1%Au/SiO_2	5.2	9	44.8	11.5
Cyclohexene	50	1%Au/Graphite	4.4	12.4	43.6	23.9
		1%Au/TiO_2	6.7	9.9	25.6	61.2
		1%Au/SiO_2	7.9	6.2	51.1	41.8
Cycloheptene	60	1%Au/Graphite	10.1	18.2	43.5	38.4
		1%Au/TiO_2	10.7	19.1	42.7	38.2
		1%Au/SiO_2	14.1	18	40.5	41.5
Cyclooctene	80	1%Au/Graphite	6.8	85.9	4.8	9.3
		1%Au/TiO_2	6.6	81.4	5	7.6
		1%Au/SiO_2	4.6	87.4	5	7.7
Cyclododecene	120	1%Au/Graphite	10.2	60.5	37	-
		1%Au/TiO_2	9.4	65.9	33	-
		1%Au/SiO_2	8.6	60.9	35	-

Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, TBHP (0.064×10^{-3} mol), glass reactor, 24 h, atmospheric pressure

5.3.1.4. Effect of the preparation method

As investigated in the previous chapters that the important parameters which can affect the activity of a catalyst is the preparation method. To test the effect of the preparation method a range of 1%Au catalysts were prepared by different methods namely, impregnation and deposition precipitation, these catalysts were compared to the sol-immobilisation prepared catalysts. Although there was variation between the substrates in all cases the catalysts prepared using the sol-immobilisation technique provided the most active catalyst. Previous work[21] has shown that the sol-immobilisation method leads to catalysts with the narrowest particle size distribution of all the preparation methods used in this study, the higher activity was displayed when the sol-immobilisation method was used supporting the theory that the small gold particles proved the most active for cycloalkene oxidation. There was also a broad grouping between the preparation method that has a washing step incorporated into their methodologies, namely the deposition precipitation method and the method that has not washing step, namely impregnation suggesting that the removal of excess chloride ions has an influence on the activity. It has been previously reported [22] that the chloride ions may act as a poison for several catalytic reactions and the washing process removing chloride ions. At the higher temperatures used for the oxidation of cyclododecene all the catalysts performed similarly once again suggesting that at this temperature auto-oxidation was the principal mechanism.

Table 5.7: The effect of preparation method on cycloalkene oxidation

Cycloalkene	Temp. (ºC)	Method	Conv. (%)	Selectivity		
				Epoxide	Cy-one	Cy-ol
Cyclopentene	26	SI	4.4	12.4	43.6	23.9
		IMP	1.3	16	28	36
		DP	1.8	10.7	49.4	39.9
Cyclohexene	50	SI	8.2	6.4	50.5	41.4
		IMP	6	6.6	16.3	77
		DP	5.4	11.4	38.5	44.5
Cycloheptene	60	SI	10.1	18.2	43.5	38.4
		IMP	6.6	17.3	33.2	49.5
		DP	7.6	18.1	30.7	51.2
Cyclooctene	80	SI	6.8	85.9	4.8	9.3
		IMP	3.2	86.3	4.5	9.2
		DP	3.7	80.2	4.1	15.7
Cyclododecene	120	SI	10.2	60.5	37	-
		IMP	9.2	66.4	33	-
		DP	10.2	57.9	31	-

Reaction condition: - 10 ml of substrate, 0.12 g of Au/graphite catalyst, TBHP (0.064×10^{-3} mol), glass reactor, 24h, atmospheric pressure. SI = sol immobilisation, IMP = impregnation, DP = Deposition precipitation

5.3.1.5. Effect of reaction time

The effect of the reaction time for the cycloalkene oxidations was investigated using the optimised 1%Au/graphite sol-immobilisation catalyst at the optimal conditions; the results were shown in Figure 5.2. Under these conditions, it can be observed that, as expected, there was increase in the conversion with reaction time, generally the trend was that the conversion increases as the size of the ring increases, it must be kept in mind however the temperature of the reaction was also increasing as the larger size of the ring coincides with the higher boiling point of the cycloalkene facilitating the increase in temperature in the reaction conditions.

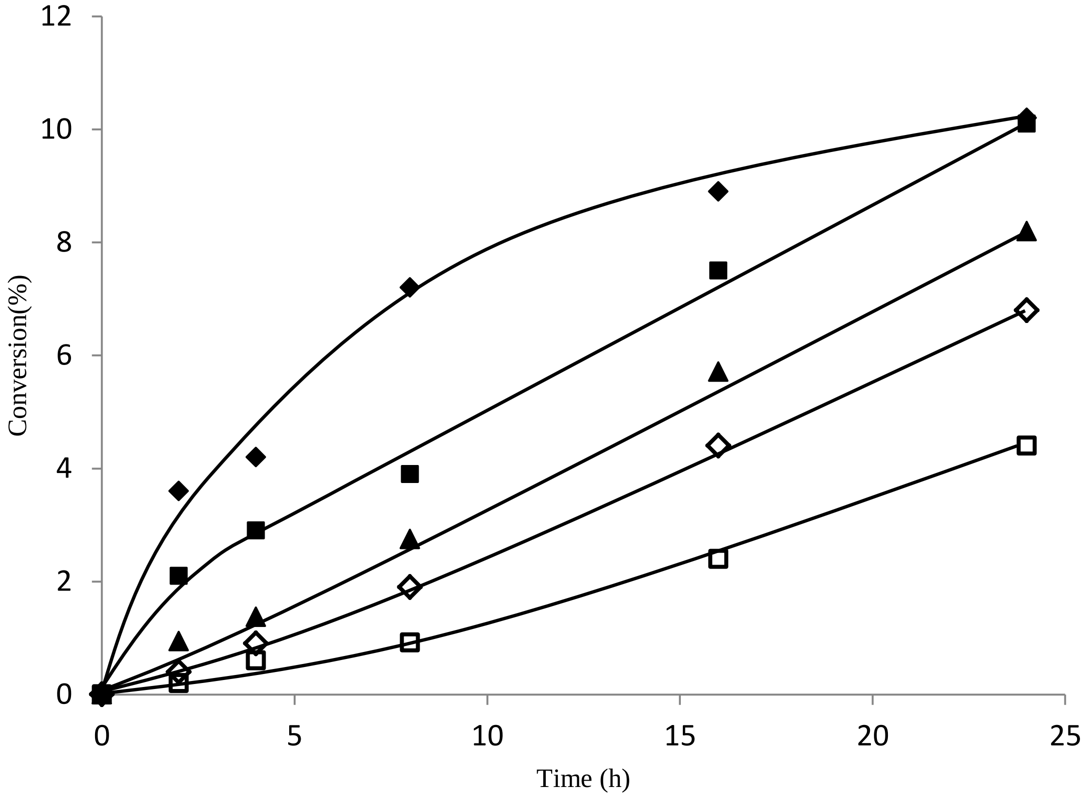


Figure 5.2: Effect of reaction time for the conversion of cycloalkene. Reaction conditions: - 10 ml of substrate, 0.12 g of Au/graphite catalyst, TBHP ($0.064x10^{-3}$ mol), glass reactor, atmospheric pressure. Cyclopentene(□), cyclohexene(▲), cycloheptene(■), cyclooctene(◊) and cyclododecene(♦)

Figure 5.3 shows the selectivity towards the epoxide, there was a clear bimodal distribution in the selectivities, with the previously discussed trend outlined by the time on line data. At the conversion levels achieved in this work the selectivity towards the epoxide product was consistent over the time period studied for all substrates.

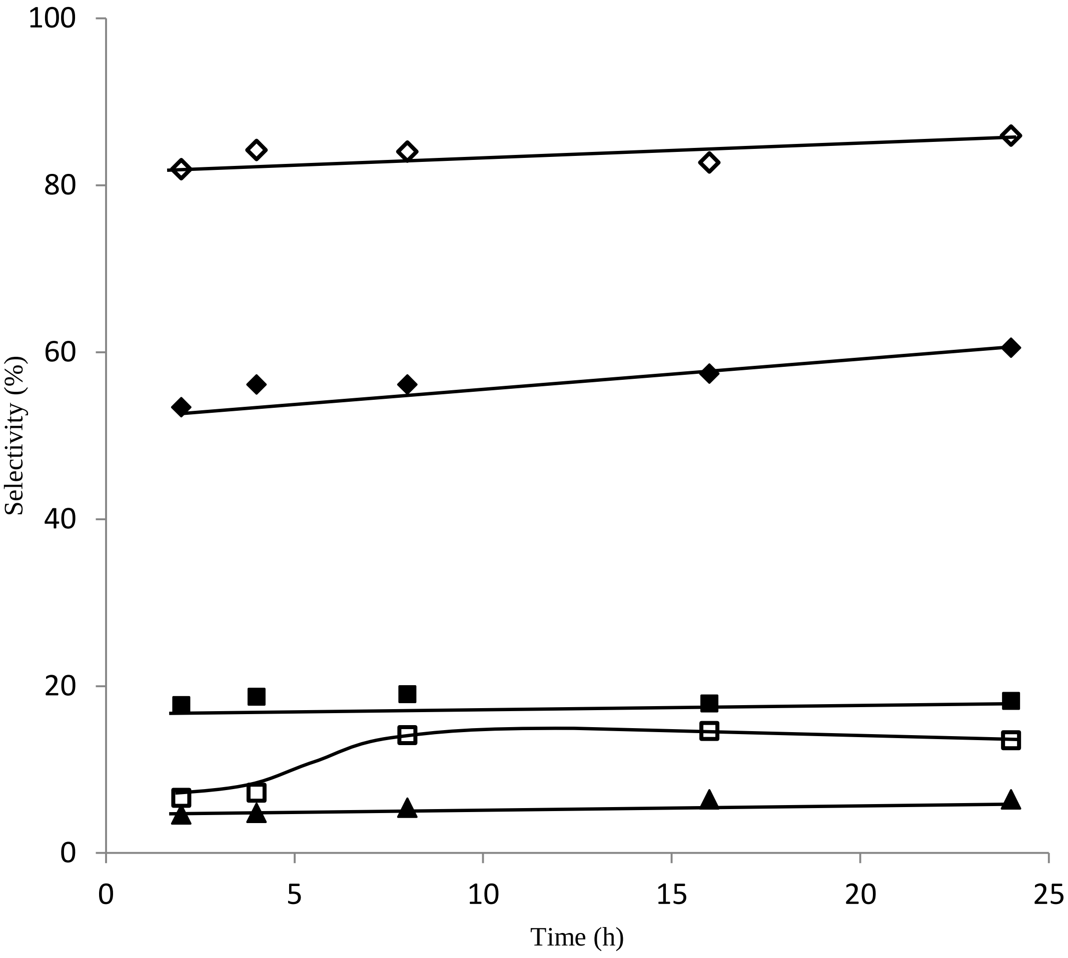
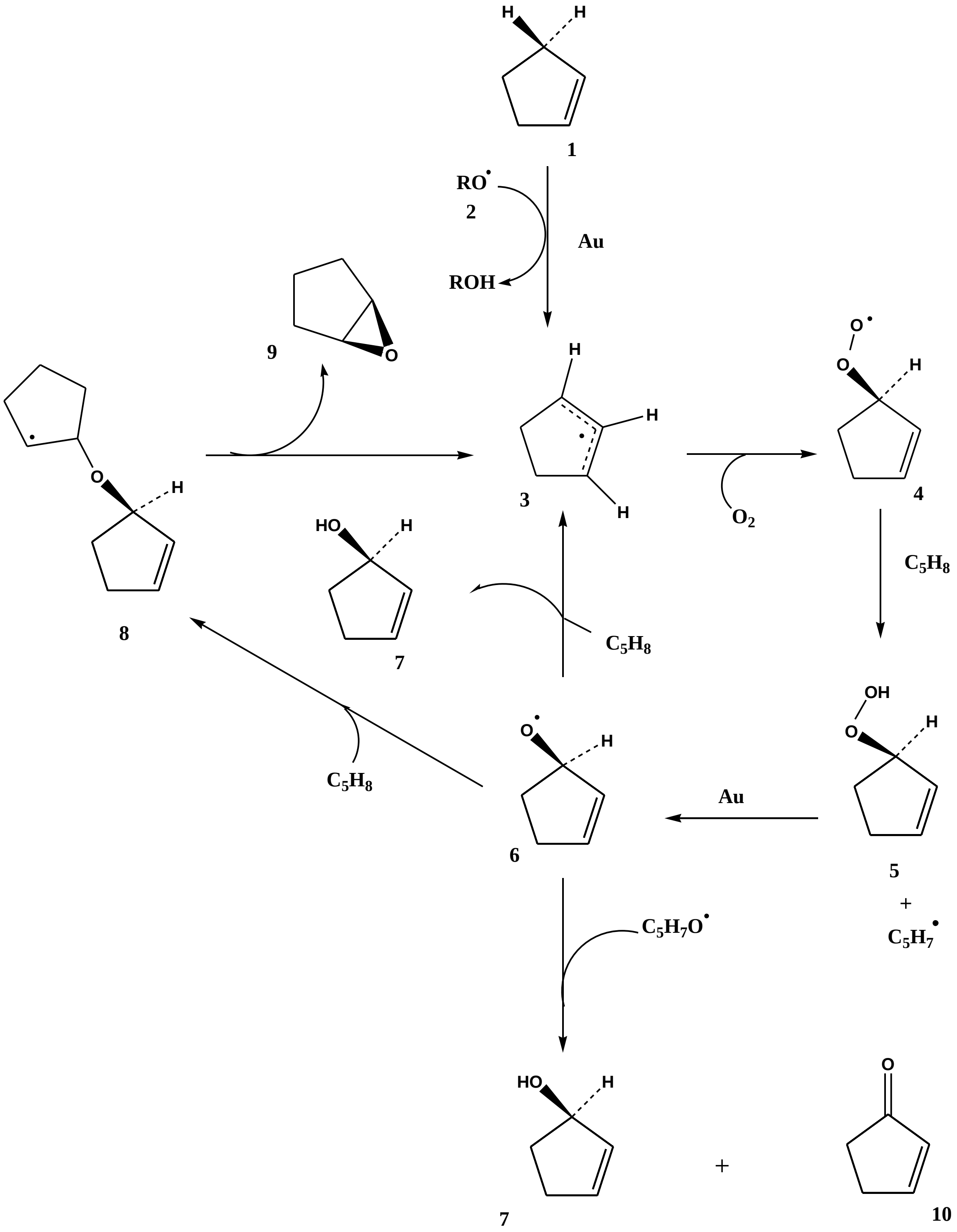


Figure 5.3: Effect of reaction time for the selectivity of epoxidation of cycloalkene. Reaction conditions: - 10 ml of substrate, 0.12 g of Au/graphite catalyst, TBHP (0.064×10^{-3} mol), glass reactor, atmospheric pressure. cyclopentene oxide(□), cyclohexene oxide(▲), cycloheptene oxide(■), cyclooctene oxide(◊) and cyclododecene oxide(♦)

5.3.1.6. Comments on the reaction mechanism

The reaction mechanism of cycloalkene oxidation involves radical species in the catalytic cycle. The proposed mechanism for cyclopentene, as an example substrate, in a way to emphasise how the different oxidation products can be explained is shown in scheme 5.1. The reaction was initiated by cleavage of the ^{t}BuO-OH bond over the surface of an Au particle to form surface bound radicals. This reaction has been found to be energetically favourable and practically barrierless in DFT calculations[23]. The peroxy radical species (**2**) could abstract hydrogen from cyclopentene (**1**) by breaking an allylic C-H bond to give the radical (**3**). In turn **(3)** will capture molecular oxygen to form a peroxy radical (**4**) which in turn can abstract hydrogen from another molecule of substrate to produce the hydroperoxide (**5**) and further carbon centred radical (**3**). Peroxide bond cleavage, possibly induced by metallic gold would then lead to the alkoxy radicals (**6**). At this point there are three possibilities; firstly the alkoxy radical **(6)** can react with further substrate with H abstraction from an allylic position to produce alcohol (**7**) and a further allylic radical. Secondly, interaction between the alkoxy radical **(6)** and the double bond of the cycloalkene will result in the intermediate (**8**) which can ring close to form the epoxide product (**9**) and a further allylic radical (**3**). Either of these pathways generates the allylic radical (**3**) and so the reaction can continue to consume more substrate. The third alternative involves the reaction of two molecules of alkoxy radicals (**6**) with H abstraction to produce the allylic ketone (**10**) and the alcohol (**7**). In this case radical species are lost and so this can be thought of as the termination step of the process.



Scheme 5.1: Proposed mechanism for cyclopentene oxidation

In the mechanism set out in Scheme 5.1 the selectivity of the reaction was controlled by the relative importance of the three reaction pathways available to allylic oxygen radical (**6**). DFT calculations were carried out by Dr. David J. Willock to consider the effect of ring size on the production and reaction of allylic oxygen radical (**6**) by comparing the potential energy surfaces calculated for cyclopentene and cyclooctene. Figure 5.4 shows that for both the cyclopentene and the cyclooctene systems the formation of intermediate (**8**) was both energetically favourable and occurs with a small potential energy barrier. However, for the C5 ring system the barrier to ring closure to form the epoxide was 13 kJ mol^{-1} higher than that for the C8 case. Hence, for the C8 system, once the intermediate was formed, it was more likely that an epoxide will be produced than in the C5 ring case.

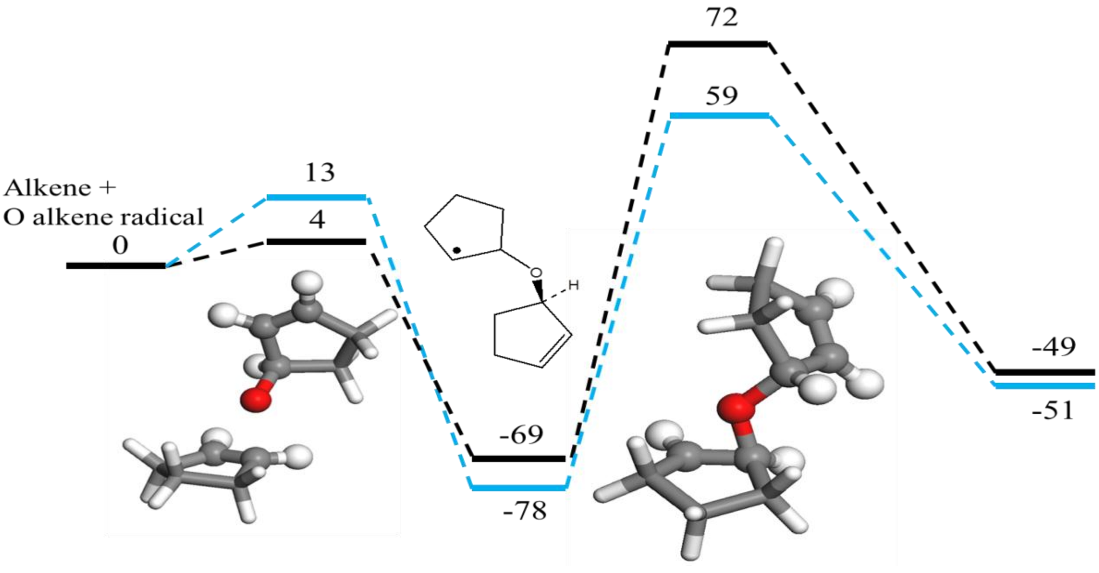


Figure 5.4: Calculated potential energy surface for the formation of intermediate 6 and ring closure to form the epoxide product 10 for C5 (black) and C8 (blue) systems. Calculated at the B3LYP/6-31G(d,p) level. For the molecular graphic insets atoms colours follow; C=grey, O=red and H=white. (Calculated potential energy surface performed by Dr. David J. Willock)

5.4. The influence of removal of stabiliser on the selective oxidation of cycloalkenes using supported metal catalysts

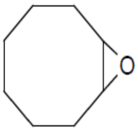
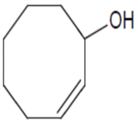
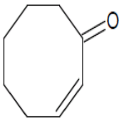
In the second part from this chapter, the influence of the removal of stabiliser from cycloalkenes on their epoxidation using supported gold nanoparticles in the absence of radical initiator will be investigated. Peroxide plays an important role in the oxidation of alkenes which can be used as reaction initiator in catalytic amounts. The use of peroxide as reaction initiator in catalytic amounts and the use of air as oxidants have been reported in the literature [1, 6, 14, 15, 24-27]. In previous publications[6, 14, 15] it was demonstrated that gold supported on graphite was active for the solvent free oxidation of cyclic alkenes, however a catalytic amount of an initiator (either H_2O_2 or TBHP) was required to start these reactions, and no conversion was observed in the absence of initiator. However, in the previous paper by Hutchings *et al.* [1] it was indicated that conversion in the absence of a radical initiator was possible for cyclohexene in the presence of much higher pressures of molecular oxygen.

In this present study, it will investigate the epoxidation of a range of cyclic alkenes; under solvent free conditions can be oxidised in the absence of radical initiators when the cyclic alkenes are free of stabilisers. Stabilisers such as 2,6-bis(t-butyl)-4-methylphenol (BHT) or 3-Octadecyl-(3,5-di-t-butyl-4-hydroxyphenyl)-propaoate (irganox 1076) are typically added to some commercial alkenes as stabilisers to prevent auto-oxidation during storage. In this study, it will be shown that selective cyclic alkene epoxidation can be achieved under solvent-free conditions without the addition of a radical initiator when these stabilisers are removed from cycloalkene by pre-treatment of washing with aqueous potassium hydroxide and subsequent distillation. This work will demonstrate that the only function of the radical initiator is to oxidise the stabilisers present in the cyclic alkenes. This discovery helps to the removal of a sacrificial reactant from the process adheres to the principles of green chemistry.

5.4.1. Results and discussion

The initial studies investigated the epoxidation of *cis*-cyclooctene in the absence of a radical initiator (TBHP) when the stabiliser has been removed. The catalyst (1%Au/graphite) used in this study was prepared by sol-immobilisation as previous studies in this chapter that was shows the most activity for epoxidation of cyclic alkenes. Table 5.8 summarises the performance of the catalyst for *cis*-cyclooctene oxidation, before and after the stabiliser removal treatment, using air as the oxygen source and 1%Au/graphite as catalyst. The results show that, before treatment, *cis*-cyclooctene, which contains irganox 1076 as a stabiliser, 5.6 % conversion with around 83% selectivity towards the epoxide was achieved when TBHP was used as a radical initiator. In contrast, in the absence of radical initiator (TBHP), no cyclooctene conversion was observed. This was consistent with previous studies which confirm that a catalytic amount of initiator is necessary for cycloalkene oxidation [1, 6, 28-30]. The experiment was repeated after removal of the stabiliser, under the same reaction conditions as were used for the oxidation of *cis*-cycloctene without treatment: the conversion with and without TBHP was shown in Table 5.8. It was interesting to note that 5.6% conversion, with 86% epoxide selectivity was achieved, in the absence of radical initiator. Furthermore, the addition of TBHP to the stabiliser free cyclooctene did not lead to any enhancement of the conversion or epoxide selectivity indicating that the radical initiator does not enhance the conversion but instead simply counteracts the effects of the stabiliser by reacting with it.

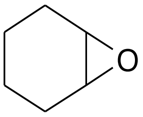
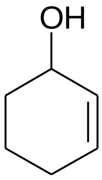
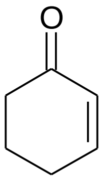
Table 5.8: Comparison of oxidation activity for *cis*-cyclooctene (before/after) treatment, in the presence/absence of TBHP and in the presence of 1%Au/G catalyst

Treatment	TBHP	Conversion %	Selectivity		
					
Before treatment	Yes	5.6	83.7	10	5
	No	0	0	0	0
After treatment	Yes	5.3	86.8	7	5
	No	5.6	86.7	7	5

Reaction conditions: 5 ml of *cis*-cyclooctene, 0.06g Au/G, glass reactor, TBHP ($0.032\text{x}10^{-3}$ mol), 80°C, 24h, and atmospheric pressure

In view of these promising results, the two samples of cyclohexene were tested (both from sigma-Aldrich), firstly a cyclohexene which contained 0.01% BHT as stabiliser, and secondly a sample that was stabiliser-free. Table 5.6 shows that, in the case of the cyclohexene that contained the stabiliser, 8% conversion was achieved when a small amount of TBHP was added as a radical initiator. However, no cyclohexene oxidation was observed in the absence of radical initiator. In contrast, the cyclohexene which was inhibitor-free gave very similar activity and selectivity in the absence or presence of TBHP.

Table 5.9: Comparison of oxidation activity for cyclohexene (with/without) stabiliser, in the presence/absence of TBHP and in the presence of 1%Au/G catalyst

stabiliser	TBHP	Conversion %	Selectivity		
					
Contain stabiliser	Yes	8.2	6.4	41.4	50.5
	No	0	0	0	0
Stabiliser free	Yes	8.9	6.3	46	47
	No	8.7	6.5	41	44

Reaction conditions: 5 ml of cyclohexene, 0.06g Au/G, glass reactor, TBHP ($0.032x10^{-3}$ mol), 50ºC, 24h and atmospheric pressure

In a further set of experiments, cyclopentene and cycloheptene were used as the substrate (Table 5.10). Again, it was found that if the cycloalkene contained stabiliser, no reaction was observed in the absence of a radical initiator but with a small amount of radical initiator the epoxidation occurs. In contrast, the inhibitor-free cycloalkene can be oxidised with almost the same activity and selectivity either in presence or in absence of radical initiator.

Table 5.10: Comparison of oxidation activity for cycloalkene (with/without) stabiliser, in the presence/absence of TBHP and in the presence of 1%Au/G catalyst

cycloalkene	Temp. (ºC)	stabiliser	TBHP	Conve. %	Selectivity %		
					Epoxide	Cy-one	Cy-ol
Cyclopentene	26	Contain stabiliser	Yes	4	12.7	37.6	23.7
			No	0	0	0	0
		Free of stabiliser	Yes	4.4	12.4	43.6	23.9
			No	4.4	12.5	36.2	22.4
cycloheptene	60	Contain stabiliser	Yes	9.1	18.4	41.8	39.7
			No	0	0	0	0
		Free of stabiliser	Yes	10.1	18.2	43.5	38.4
			No	9.4	18.4	43.3	38.3

Reaction conditions: 5 ml of substrate, 0.06g Au/G, glass reactor, TBHP (0.032×10^{-3} mol), 24h and atmospheric pressure

Using these optimised conditions, time-on-line studies were carried out for cyclohexene and *cis*-cyclooctene either containing stabiliser or stabiliser-free. When the cycloalkene contained stabiliser, a small amount of radical initiator (TBHP) was added; the results were shown in Figures 5.5 and 5.6. It was clear that by removing the stabiliser, the activity was identical to that when stabiliser and initiator were present, at all times tested.

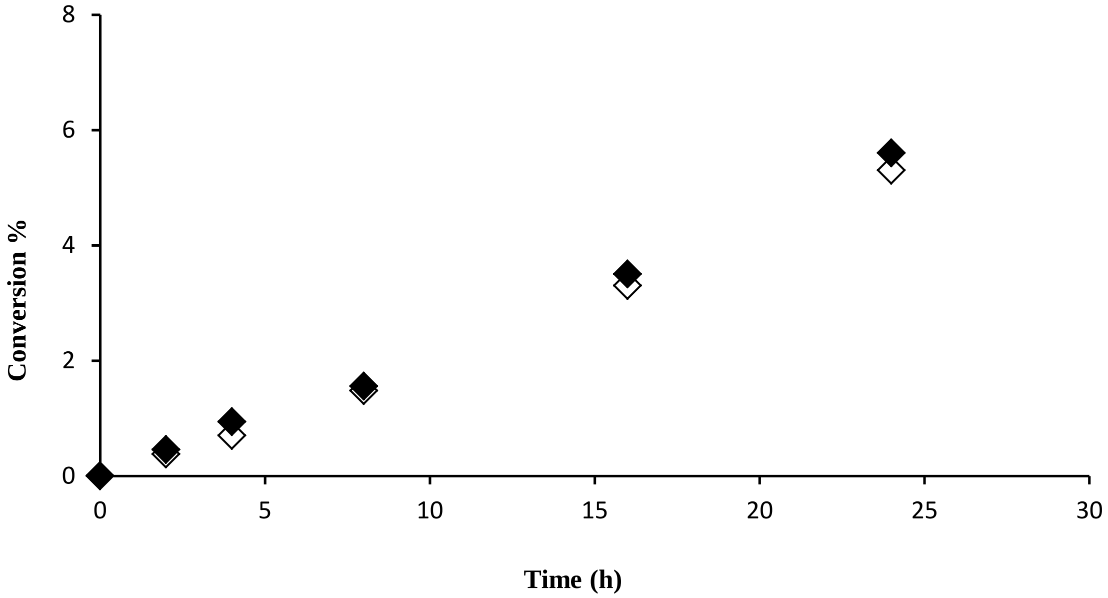


Figure 5.5: Effect of reaction time for the conversion of cis-cyclooctene containing stabilizer with TBHP (solid diamonds) and cis-cyclooctene after removal of stabilizer without TBHP (open diamonds). Reaction conditions: 5 ml of *cis*-cyclooctene, 0.06g Au/G, glass reactor, TBHP ($0.032x10^{-3}$ mol), 80 ºC and atmospheric pressure

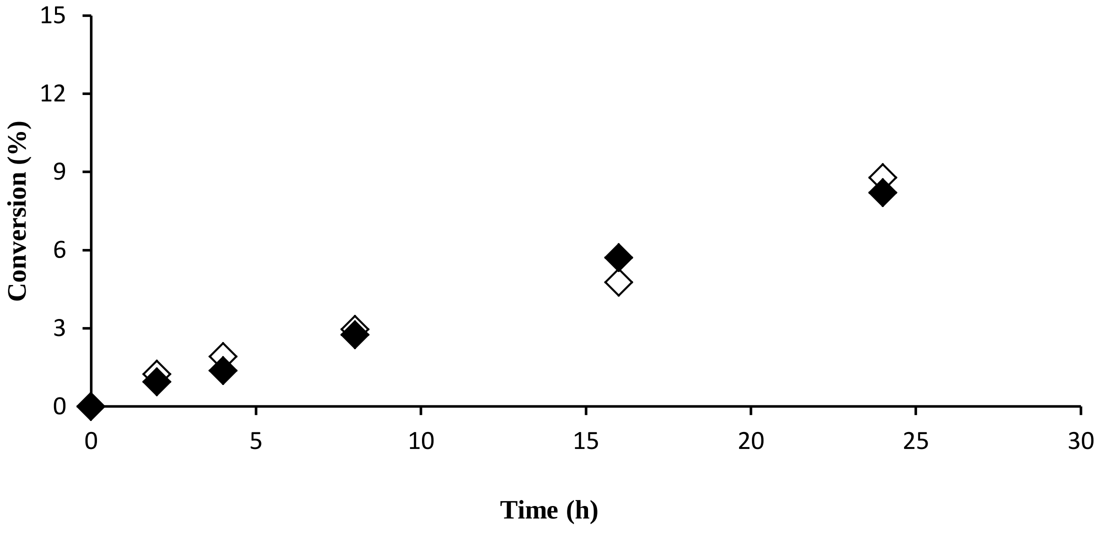


Figure 5.6: Effect of reaction time for the conversion of cyclohexene containing stabilizer with TBHP (solid diamonds) and cyclohexene inhibitor-free without TBHP (open diamonds). Reaction conditions: 5 ml of cyclohexene, 0.06g Au/G, glass reactor, TBHP ($0.032x10^{-3}$ mol), 80ºC and atmospheric pressure

To determine the detrimental effect of the stabiliser (BHT) on the conversion of cyclopentene, small quantities of BHT were doped into stabiliser-free cyclopentene. The effect of this doping was shown in Figure 5.7. It was clear that the addition of even a small amount (10^{-6} M) of the stabiliser had a detrimental effect on the conversion and a concentration of 3 x10^{-5} M was enough to completely stop the oxidation reaction.

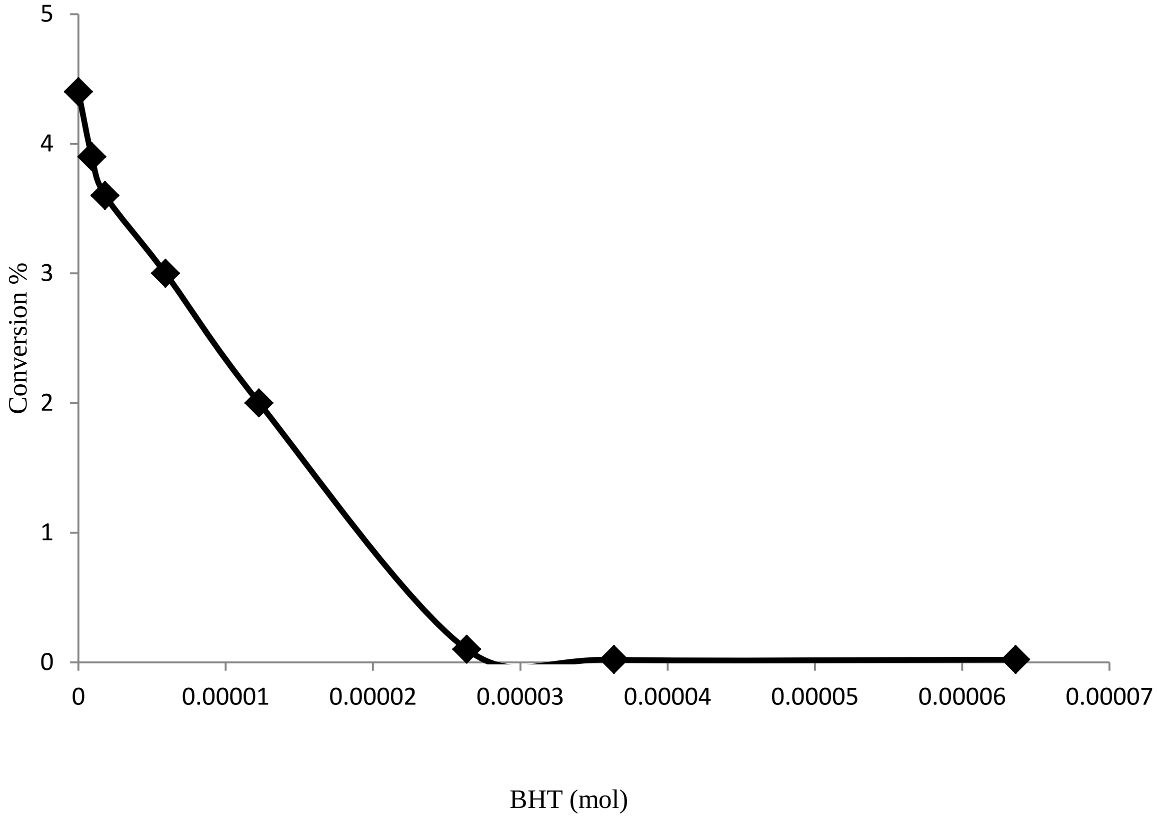


Figure 5.7: Effect of the addition of BHT to cyclopentene (stabiliser free), Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, glass reactor, 24h and atmospheric pressure

This concentration of stabiliser (3 x10^{-5} M) was subsequently used to demonstrate the effect of the amount TBHP on the conversion of stabilised cyclopentene and these result was shown in Figure 5.8. If the TBHP was added in equimolar quantities to the stabiliser there was no conversion, in fact over 10 times the concentration of the stabiliser was required to show any improvement on the negligible conversion. The reaction was carried out with up to 33 times the concentration of the stabiliser relative to TBHP which still only led to below half the stabiliser-free conversion.

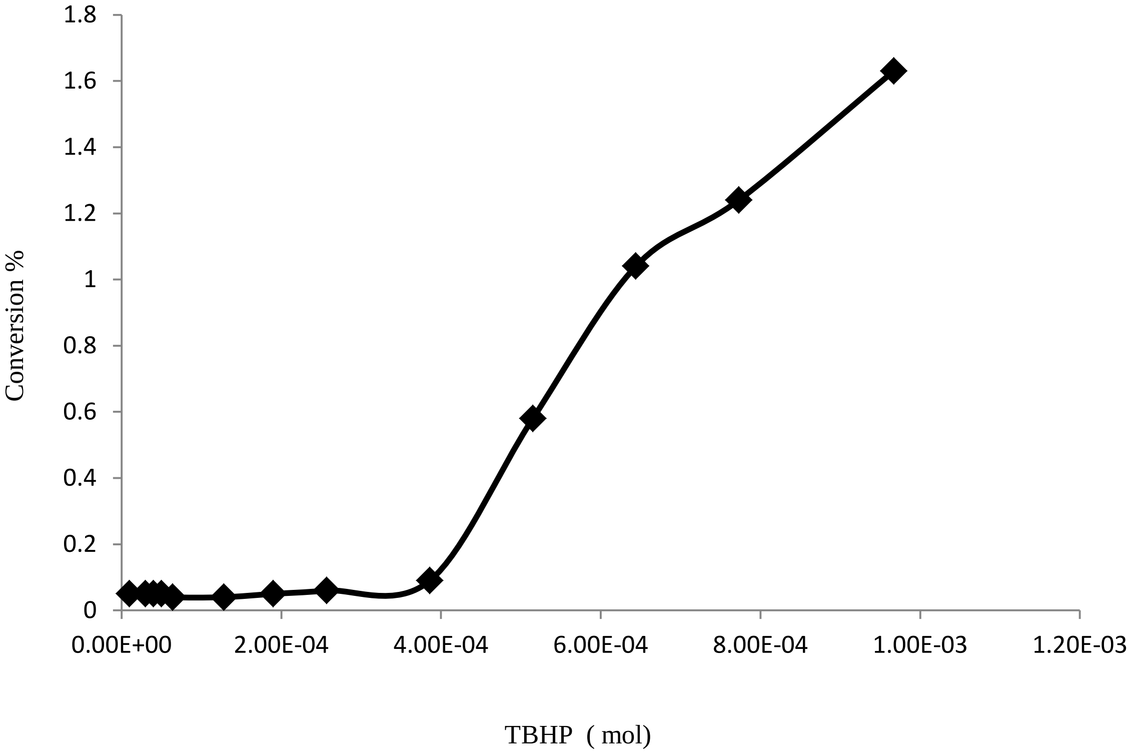


Figure 5.8: Effect of the addition of radical initiator to cyclopentene containing (3x10^{-5} mol BHT), Reaction conditions: 10 ml of substrate, 0.12 g of catalyst, glass reactor, 24h and atmospheric pressure

In summary, this work shows that selective cyclic alkene epoxidation can be achieved under solvent-free conditions without the addition of a radical initiator and have demonstrated that the only function of the radical initiator is to oxidise the stabilisers present in the cyclic alkenes

5.5. Conclusions

- Reaction conditions using oxygen from air as the oxidant with 0.12 g of catalyst were effective under mild, solvent-free conditions using of a range of temperatures, depending on the boiling point of the cyclic alkenes.
- Gold nanoparticles support on graphite is active for cycloalkene oxidation, whereas the graphite alone was inactive especially at low temperatures.
- The effect of ring size on the epoxidation of cyclic alkenes using supported gold under solvent free conditions using air as the oxidant with catalytic amounts of radical initiator was investigated. The selectivity to epoxide was low for the smaller ring sizes (C_5-C_7), increasing significantly for the C_8 and C_{12} rings.
- The larger rings (C8-C12) the selectivity towards the epoxide was significantly higher than the smaller rings (C5-C7), DFT calculations indicate that the barrier to ring closure of radical intermediate was much greater for the smaller ring sizes.
- The influence of bimetallic catalyst was also investigated for cycloalkene oxidation and it was obtained that there was no synergistic effect between Au and Pd.
- Catalyst prepared by the sol-immobilisation method was more active for the oxidation of cycloalken than those prepared by impregnation and deposition precipitation.
- A range of cyclic alkenes were investigated for epoxidation, under solvent free conditions and it has been demonstrated that these alkenes can be oxidised in the absence of radical initiators when alkenes are free of stabilisers.

5.6. References

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Chapter six

Conclusions and future work

6. Conclusions and future work

6.1. Conclusions

Oxidation of hydrocarbons to produce oxygen-containing organic compounds is very important for modern chemistry processes. The oxidation of hydrocarbon such as alkenes and alcohols has been demonstrated using gold catalyst under green chemistry conditions [1-3]. The objective for this thesis was involved three main parts. The first part, in chapter 3, the main aim was to investigate that catalysts that have previously been demonstrated to be useful for oxidation of cyclohexene and cyclooctene can also be applied to the oxidation of straight chain alkenes with all the products identified[4-6]. Furthermore, it was shown that the catalyst was effective under mild, solvent-free conditions using air as the oxidant, thus representing a significant improvement in environmental impact of this reaction. Secondly, in chapter 4, the aim was to determine if either the alcohol or alkene functional group can be oxidises delectivly in trans-2-hexen-1-ol and 3-hexen-1-ol. Finally, in chapter 5, further work into the oxidation of cyclalkene was investigated; the effect of ring size on the selectivity to epoxide and effect of removal of stabilizer from cycloalkene on the reaction.

In chapter 3, liquid phase oxidation of 1-hexene was performed under solvent free condition using oxygen from air as the oxidant and Au/graphite as catalyst with a catalytic amount of TBHP as initiator. The choice of support is crucial thus the effect of support was investigated using different supports, namely TiO_2, SiO_2 and MgO. The activity of gold supported on different supports was as following: graphite > TiO_2 >

$MgO = SiO_2$. Overall, all the oxide supports are less effective than graphite which gives very low reactivity in the absence of gold. Several preparation methods were examined during oxidation of 1-hexene. Catalyst prepared by the sol-immobilisation method was more active for the oxidation of 1-hexene than those prepared by impregnation or deposition precipitation. The sol-immobilisation method gave catalysts with enhanced activity, possibly due to a higher dispersion of gold with much smaller nanoparticle size. Preparation of catalysts using modified sol-immobilisation was found to be effective, particularly when PVA stabiliser was removed by a solvent treatment prior to the reaction. The influence of bimetallic catalyst was also investigated for 1-hexene oxidation. The highest activity was obtained for Au and Au-Pd catalysts. It can be concluded that there was no synergistic effect between Au and Pd. Based on the results obtained, mechanistic pathway have been proposed. It was suggested that the reaction proceeds through a radical mechanism. The major pathway formed allylic products when alkoxy radicals abstract a proton from 1-hexene to produce the two allylic alcohols. The alternative path way that the epoxide could form by direct addition of the peroxy radical species to 1-hexene.

In chapter 4, liquid phase oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol was performed under solvent free condition using oxygen from air as the oxidant and Au-Pd/TiO_2 as catalyst at 50 ˚C. The products of the reactions of *trans*-2-hexen-1-ol and 1-hexen-3-ol using gold, gold palladium and palladium catalysts under green conditions were investigated in detail. It was found that there are four main reaction pathways that occur in these systems. The oxidation pathway is much less prevalent that has previously been assumed with isomerisation being the main reaction under almost all conditions. Furthermore, manipulation of the catalyst design process has shown that a significant amount of the putative oxidation products arise from a disproportionation reaction and not from an oxidation pathway. However, it was demonstrated the design of the catalysts and control of the reaction conditions can afford a certain degree of control over the reaction products. The effect of bimetallic catalyst was also examined for *trans*-2-hexen-1-ol and 1-hexen-3-ol. By testing various ratios of Au-Pd supported on TiO_2 it can be concluded that there was synergistic effect between Au and Pd. The conversion of *trans*-2-hexen-1-ol and 1-hexen-3-ol depend on the ratio of Au and Pd. Monometallic Au/TiO_2 was observed to have a low activity and the oxidation pathway was preferred. However, as soon as the catalyst contained any palladium, the activity increased with significant increase in the selectivity towards isomerisation products. The influence of support was investigated. The oxide supports were more active for the oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol than graphite support, however, the highest selectivity toward oxidation pathway products was achieved when using graphite as the support. In addition, MgO and MnO_2 supports seem to almost completely switch off the disproportionation reaction. Catalyst prepared by sol-immobilisation that give the smallest average particle size was more active for the oxidation of *trans*-2-hexen-1-ol and 1-hexen-3-ol than impregnation and incipient wetness.

In chapter 5, liquid phase oxidation of a range of cyclic alkenes were performed under solvent free condition using oxygen from air as the oxidant and a range of temperatures, depending on the boiling point of the cyclic alkenes. It was found that gold nanoparticles support on graphite was active for cycloalkene oxidation, whereas the graphite gives very low reactivity in the absence of gold especially at low temperatures. The effect of ring size on the epoxidation of cyclic alkenes using supported gold under solvent free conditions using air as the oxidant with catalytic amounts of radical initiator was investigated. The selectivity to epoxide was low for the smaller ring sizes (C_5-C_7), increasing significantly for the C_8 and C_{12} rings. It was proposed based on DFT calculation that the ring closure to form epoxid in C_8 system is more likely to occur than in the C_5 system because the potential energy barrier in C_8 is less than in C_5 system. The effect of preparation method was tested using sol-immobilisation, impregnation, deposition precipitation and incipient wetness. The sol-immobilisation method, which gives smaller particles size, was more active than the others. It was also noted that the sol-immobilisation and deposition precipitation which have a washing step, which helps to remove chloride ions, were more active. More interesting results have been achieved for oxidation of cyclic alkenes without the use of radical initiator. It has been found that these alkenes could be oxidized in the absence of radical initiators when alkenes are free of stabilisers.

6.2. Future work

The further development some of the topics in this thesis is possible. The following suggestions may assist in improving activity and understanding more about the mechanism of hydrocarbon oxidation:

- It was investigated in chapter 3 that 1-hexene can be oxidised using air as the oxidant gas at 40 ˚C. However, performing reaction under high pressure and high temperature in an autoclave would improve the activity.
- The use of various radical initiators such as AIBN, CHP and DTBP for oxidation of 1-hexene. There are reports in literature suggesting that the fast homolysis (short half-life) of these radical initiators lead to enhancement of activity and selectivity.
- Alloying gold with a second metal has been shown to lead to improve gold catalyst activity. The bimetallic catalyst Au-Pd was not effective for 1-hexene oxidation. However, other bimetallic system such as Au-Cu could lead to enhancement in activity or selectivity.
- Due to the enhancement of catalyst activity and selectivity by using pure oxygen as opposed to air in oxidation of trans-2-hexen-1-ol and 1-hexen-3-ol, performing reaction in autoclave may lead to enhancement to oxidation pathway.
- More characterizations needs to done to understand and explain the difference in activity and selectivity that obtained when using different supports.

- It was demonstrated in this study that gold nanoparticles supported on graphite was able to oxidise cycloalkenes in the absence of radical initiator. However it important in the future studies to understanding the mechanism of oxidation cycloalkene in absence of radical initiator.

6.3. References

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