Solvent Free Alkene Oxidation using Supported nano-Gold Catalysts

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To My Parents and My Wife

Publications

1- Bawaked, S., Dummer, N., Dimitratos, N., Bethell, D., He, Q., Kiely, C., Hutchings, G., *Solvent-free selective epoxidation of cyclooctene using supported gold catalysts.* Journal of Green Chemistry, 2009. **11**: p. 1037-1044.

2- Bawaked, S., Dummer, N., Bethell, D., Knight, D., Hutchings, G., *Solvent-free selective epoxidation of cyclooctene using supported gold catalysts: an investigation of catalyst re-use.* Journal of Green Chemistry, 2011. **13**: p. 127-134.

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Abstract

Oxidation is an important route for the activation of chemical feedstock for the synthesis of chemical intermediates. Alkene epoxidation by the electrophilic addition of oxygen to a carbon-carbon double bond is a major challenge in oxidation catalysis. In particular it is important to use molecular oxygen as the oxidant to avoid the formation of reagent by-products. Although molecular oxygen is the most environmentally benign oxidant in many cases, far more reactive forms of oxygen are required to achieve reaction, and this can lead to by-products with a heavy environmental burden with respect to their disposal. Free solvent selective epoxidation of *cis*-cyclooctene with air and small catalytic amount of radical initiator using supported nano-gold catalysts has been conducted in the liquid phase. Optimization of reaction conditions has been attempted to improve the selectivity by minimizing the background reactions of the support and radical initiator in the absence of the catalyst. Five different radical initiators were tested namely: di-*t*-butyl peroxide (DTBP), *t*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP), azobisisobutyronitrile (AIBN) and dibenzoyl peroxide (DBP). TBHP was selected for more detailed study as it combine the best activity and selectivity in the presence of the catalyst and minimum background reactions in the absence of the catalyst. The influence of the metal nano-particle support was also studied using six different supports. Use of graphite as a support was found to give the best combination of selectivity and conversion. In general the selectivity to the epoxide increased with reaction temperature from 60–80 °C and was highest at 80 °C. Other carbon supports, *e.g.* activated carbon and silicon carbide were found to be less effective. Au supported on TiO_2, SiO_2 and Al_2O_3 catalysts were also selective for the epoxidation reaction and the general order of activity was: graphite $\geq$ SiC $> TiO_2 > SiO_2 \approx Al_2O_3 \approx$ Ac.

Extensive studies concerning the reusability of the gold/graphite catalyst was conducted as catalyst reusability is a key feature of green chemistry. The catalyst is found to be inhibited by the epoxide product but we demonstrate the effect of this is negligible for reused catalysts over a long reaction time. The observation of an induction period may in part be due to the adsorption of the radical initiator blocking surface sites as well as the establishment of the reactive species.

The use of bimetallic catalyst, to be exact Au-Pd supported on graphite, shows significant effect on *cis*-cyclooctene reactivity. The Au-Pd ratio has a major effect on the conversion with very low activities being associated with Au:Pd weight ratios of *ca.* 4:1 and 1:4 which may be associated with structured alloys that can be formed at these compositions. The molar Pd surface percentage were found to have dramatic effect on the conversion as low Pd surface would produce low activity and contrariwise. The selectivity to the epoxide is not affected by the Au:Pd ratio. Catalyst preparation method was also studied and sol immobilization method was found to be the most effective for gold catalyst, however, DP method was the preferred one in the bimetallic catalysts.

The Au-Pd/graphite catalyst series has been further evaluated using crotyl alcohol (*trans*-but-2-en-1-ol) as starting material and using the same reaction conditions that had adopted for the epoxidation of *cis*-cyclooctene. With crotyl alcohol, *t*-butyl hydroperoxide was not required for activity. In the absence of Pd, crotonaldehyde was formed, but the introduction of Pd leads to an isomerisation pathway to 3-buten-1-ol being favored over epoxidation and crotonaldehyde was a minor product. Dimerisation of crotonaldehyde and carbon carbon bond cleavage was observed with Au catalyst. However, with Pd catalysts Wacker-like oxidation of the isomerisation pathway was the major by-product.

Macro abstract

Alkene epoxidation by the electrophilic addition of oxygen to a carbon-carbon double bond is a major challenge in oxidation catalysis. Solvent free epoxidation of *cis*-cyclooctene was performed in ambient condition using supported gold catalyst. The condition of minimum background reaction has been identified and the standard condition as following: 0.12g of catalyst, TBHP ($0.013\text{x}10^{-2}$mole), 80 °C. Different radical initiator and supports have been tested and the radical of choice was TBHP along with graphite as support. The effect of bimetallic catalyst was examined namely Au-Pd system. The activity in *cis*-cyclooctene was varies with AuPd ratio and the best activity was found for the monometallic catalysts. Testing the same Au-Pd series with crotyl alcohol resulted in synergy with maxima at Au-Pd molar ratio of 1:1.86. Sol immobilization method was the method of choice with Au catalyst. However, DP method was the preferred method with Pd and Au-Pd catalysts.

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Chapter One

Introduction

1. Introduction

1.1. Historical background

The beginning of modern chemistry, as known nowadays, dated back to the seventeenth century.[1]. One of the earliest of systematic study was the *Cours de chimie* of Nicolas Lemery, published in 1675 [1]. Chemistry can be defined as the science concerned with composition, behaviour, structure, and properties of matter during chemical reactions [2]. The major role that chemistry plays in other natural science is undeniable. Typically, there are several major sub-disciplines of chemistry one of which is physical chemistry. The foundation of modern physical chemistry is believed to be laid in the 1860s to 1880s [3]. Physical chemistry is the branch of science that combines the principles and methods of physics and chemistry. It provide the basic framework for all other branches of chemistry [4].

Catalysis is an important topic in chemistry. The first known use of catalysis is dated back to 1552 when Valerius Cordus used sulphuric acid to catalyze the conversion of alcohol to ether [5]. The principle of catalysis was first presented by Fulhame in 1794 when she suggested that the presence of small quantities of water was required for the oxidation of carbon monoxide and that the water was unaffected by the chemical reaction [5, 6]. Similar observation was made by Kirchhoff in 1812 when he hydrolyzed starch to sugars using dilute acid and noticed that the acid was not altered by the chemical reaction .[5-7]. It was not until 1836 when Berzelius coined the word catalysis; he reported "*Many bodies have the property of exerting on other bodies an action which is very different from* *chemical affinity. By means of this action they produce decomposition in bodies, and from new compound into the composition of which they do not enter. This power, hitherto unknown, I shall call it catalytic power. I shall also call catalysis the decomposition of bodies by this force.*"[8].

The word catalysis stems from two Greek words, the prefix cata meaning down and the verb lysein meaning to split or break. By 'awaking affinities which are a sleep', a catalyst breaks down the normal forces which inhibit the reactions of molecules. As the understanding of catalysis developed, a more accurate definition has been formulated. At present almost all of our chemicals and materials are produced using catalysis. The chemical industry in the 21st century could not have developed to its current status on the basis of non-catalytic, stoichiomertic reactions alone.

1.2. Catalysis

A catalyst is a substance that alters the rate at which a chemical reaction reaches equilibrium without being consumed in the reaction. However, a catalyst should alter both the forward and reverse reaction so the equilibrium position should not be changed. Most reactions occur through a series of steps. This series of steps is called a pathway or mechanism. The rates at which the slowest step occurs determines the reaction rate. The reaction rate is the rate at which reactants disappear and products appear in a chemical reaction, or, more specifically, the change in concentration of reactants and products in a certain amount of time. While going through a reaction pathway, in order for the reactants to transfer to products it must enter what is called a transitional state where they are no longer reactants, but are not yet products. During this transitional state they form what is called an activated complex. The activated complex is short-lived and has partial bonding characteristics of both reactants and products. The energy required to reach this transitional state and form the activated complex in a reaction is called the activation energy. In order for a reaction to occur, the activation energy must be reached. A catalyst increases the rate of reaction by providing an alternative path that avoids the slow, rate determining step of the un-catalysed reaction. The catalyst forms an activated complex with a lower energy than the complex formed without catalysis. This provides the reactants with a new pathway which requires less energy. The catalyst does not appear in the overall chemical equation for a pathway because the mechanism involves an elementary step in which the catalyst is consumed and another in which it is regenerated. Therefore, according to the Arrhenius equation:

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

Equation 1 Arrhenius equation

Where k is rate coefficient, A is pre-exponential factor; Ea is activation energy, R is the gas constant and T is temperature. The catalyst works by decreasing the activation energy, i.e. it provides a more energetically favorable pathway for the conversion of reactants to product (Fig. 1.1) In some reactions one of the reaction products is a catalyst for the reaction; this phenomenon is called self-catalysis or autocatalysis. An example is the reaction of permanganate ion with oxalic acid to form carbon dioxide and manganous ion, in which the manganous ion acts as an autocatalyst. Such reactions are potentially dangerous, since the reaction rate may increase to the point of explosion.

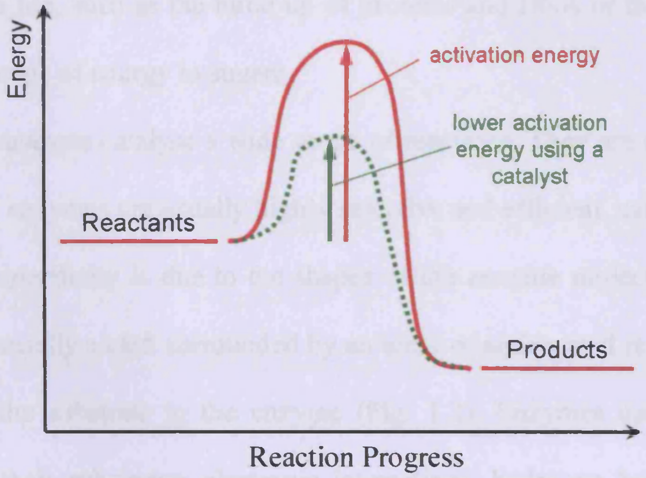

Figure 1.1 Activation energy for catalysed reaction and uncatalysed reaction

Catalysis is important academically and industrially. The application of catalysis has been necessity for the chemical industry for the last 150 years. Catalysis is the workhorse of chemical transformations in the industry; around 85-90% of the chemical industry products are made with the assistance of a catalyst [9]. Apart from its importance in industry, catalysis is important in environmental control which is increasing in demand. There are three main type of catalysis: heterogeneous catalysis, homogeneous catalysis and bio-catalysis. The following paragraphs will briefly discuses the types of catalysis.

1.2.1. Bio-catalysis

Enzymes, which consist of proteins, are a natural catalyst which catalysed the reactions in living organism. The backbone of proteins are amino acids which are linked together by peptide bonds [10]. Enzymes allow biological reactions to occur at the rates necessary to maintain life, such as the build up of proteins and DNA or the breakdown of molecules and the storage of energy in sugars.

Most chemical catalysts catalyse a wide range of reactions. They are not usually very selective. In contrast, enzymes are usually highly selective and efficient, catalysing specific reactions only. This specificity is due to the shapes of the enzyme molecules. The active site of an enzyme is usually a cleft surrounded by an array of amino acid residues. Some of these residues bind the substrate to the enzyme (Fig. 1.2). Enzymes use four kinds of interactions to bind their substrates: electronic interactions; hydrogen bonding; Van der Waals interactions and hydrophobic interactions. The substrate binding at the active site is relatively week, if the substrate bonds strongly it would inhibit the catalytic cycle.

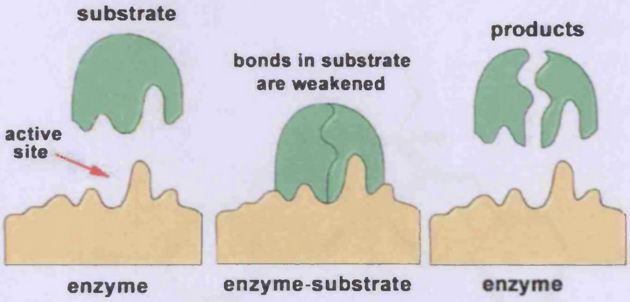

Figure 1.2 Enzyme-substrate binding

1.2.2. Homogeneous catalysis

A homogeneous catalyst is a catalyst in the same phase as the reaction mixture, usually liquid. Currently, 'homogeneous catalysts' are often used in a restricted sense i.e. to refer to catalysis with organometallic and coordination complexes. This is certainly the area which led to the largest number of industrial applications [11]. Many homogeneous catalysts are based on a transition metal stabilised by ligands. Selecting the right metal and the right ligand can improve the catalyst activity, selectivity and stability. An example is the isomerisation and hydration of propylene oxide (Figure 1.3).

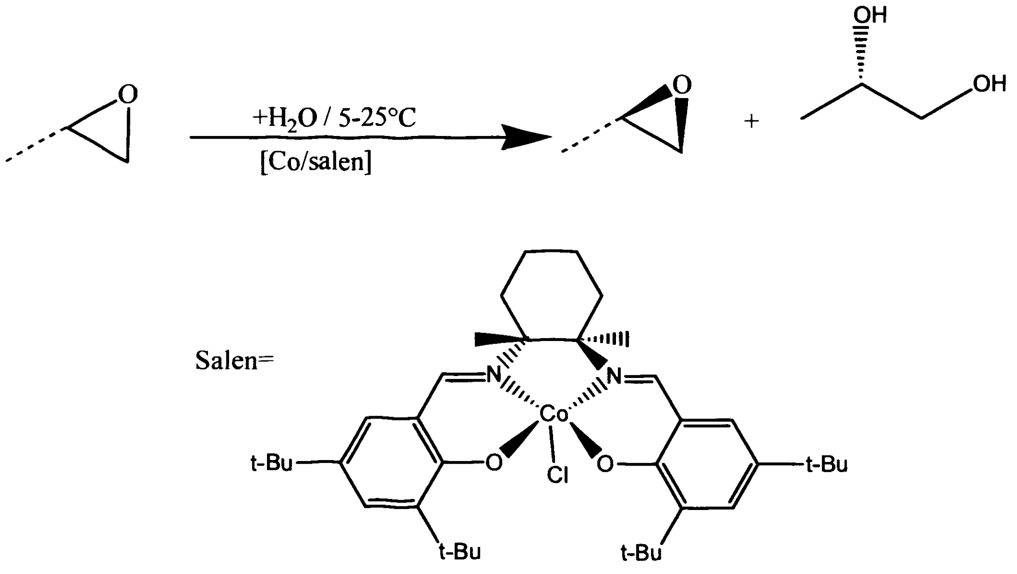

Figure 1.3 Propylene oxide hydration using homogeneous catalyst

Advantages of homogeneous catalysis on an industrial scale are high selectivity, ease of heat dissipation from exothermic reactions and are easily studied from chemical and mechanistic aspects. However, their difficulty of separation from product and their reduced effectiveness on re-use have limited their application in industry.

1.2.3. Heterogeneous catalysis

A heterogeneous catalyst, usually solid, is a catalyst present in a different phase from the reaction mixture, Table 1.1 summarises the difference between homogeneous catalysts and heterogeneous catalysts.

Table 1.1 Comparison between Homogeneous and Heterogeneous catalyst [12]

Criterion	Heterogeneous	Homogeneous
Catalyst form	Solid, often metal or metal oxide	Metal complex
Mode of use	Fixed bed or slurry	Dissolved in reaction medium
Solvent	Usually not required	Usually required- can be product or by-product
Selectivity	Usually poor	Can be tuned
Stability	Stable to high temperature	Often decompose <100°C
Recyclability	Easy	Can be very difficult

Heterogeneous catalytic reactions involve adsorption of reactants from a fluid phase onto a solid surface, surface reaction of adsorbed species, and desorption of products into the fluid phase. Most catalytic activity in heterogeneous catalyst occurs at the surface of the catalyst. An example is the propene hydrogenation using supported metal catalyst (Fig. 1.4). In this reaction, a hydrogen molecule is added to the propene double bond in the presence of metal catalyst (Ni, Pd or Pt). The reaction involved several steps. First, a propene molecule is adsorbed on the catalyst surface. The carbon-carbon double bond breaks and bonds with the surface are created. In the interim, hydrogen molecules are also adsorbed on the catalyst. The H-H bond then breaks, and the H atom move across the metal surface. Eventually, an H atom diffuses close to one of the bonded C atoms. The C-metal bond is then replaced by a C-H bond. When this happens at the other C atom also, the connection with the surface breaks and the new propane molecule diffuses back into the gas phase [10].

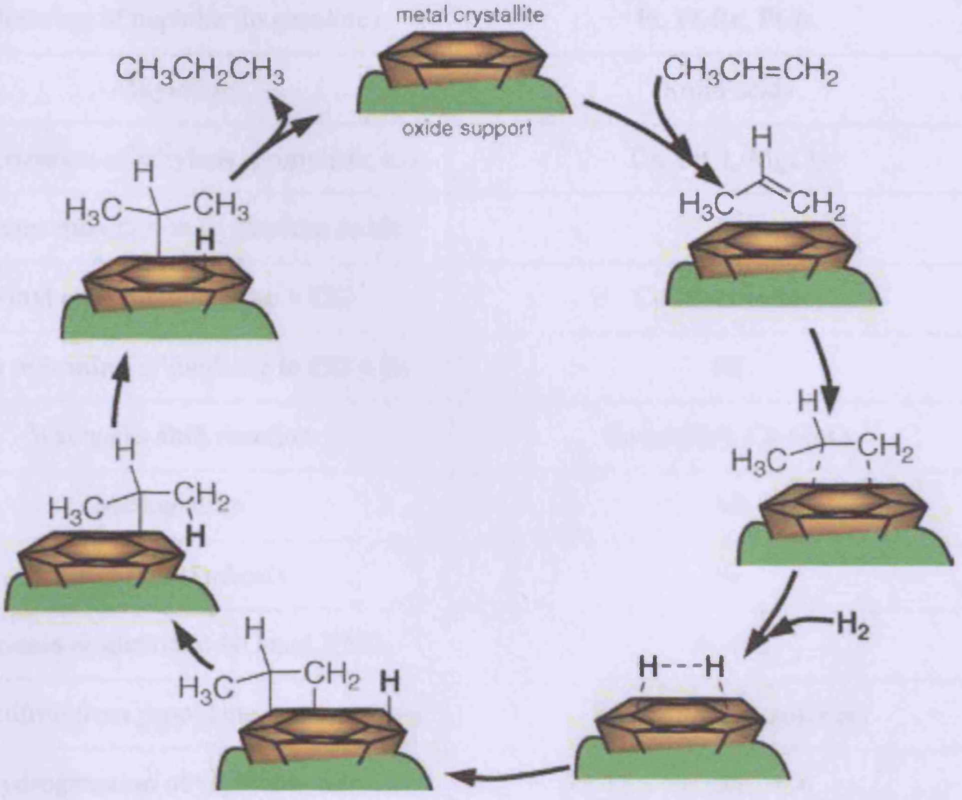

Figure 1.4 Hydrogenation of propene

Heterogeneous catalyst is very important from the academic point of view as well as from the industrial one. Heterogeneous catalysts are the main force for the chemical and petrochemical industry. Table 1.2 illustrates the most important processes in industry based on heterogeneous catalysts.

Table 1.2 Largest processes based on heterogeneous catalyst [9].

Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co-Mo, Ni-Mo, Ni-W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt-Re, Pt-Ir.
Alkylation	Solid acids
Polymerization of ethylene, propylene, a.o.	Cr, $TiCl_x/MgCl_2$
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl_2)	Cu (as chloride)
Steam reforming of methane to CO + H_2	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO_3	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NO_x (in exhaust)	Rh, vanadium oxide

The term "Green Chemistry" was first initiated in 1993 by Anastas and has since been adopted widely by the chemical industry [13].. An alternative term that is currently favored by the chemical industry is "Sustainable Technologies". Green chemistry can be defined as the following: "*Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products" [14].* The concept of green chemistry has been concluded in 12 principles as following:

- Waste prevention instead of redemption
- Atom efficiency
- Less hazardous/ toxic chemicals
- Safer products by design
- Minimize the use of auxiliary regents and solvents
- Energy efficient by design
- Avoid unnecessary derivatization
- Preferably renewable raw material
- Replace stoichiometric regents with catalytic cycles
- Design products for degradation
- Developed real-time and on-line process analysis and monitoring methods
- Choose feedstock and design processes that minimize the chance of accidents

The average mass of waste compared to mass of products can be similar especially in fine chemical and pharmaceuticals industry [14]. This is a direct consequence of using stoichiomertic inorganic regents. The solution is to replace of stoichiomertic methodology with cleaner catalytic alternative.

1.2.4. Adsorption of molecules at catalyst surfaces

Adsorption is the binding of molecules or particles to a surface. This process is the first reactive step in the cycle of heterogeneous catalysis. The solid particle which the adsorption process occurs on it surface is called an adsorbent, whereby the interacting gas molecule is termed the adsorbate. Desorption is the process of disconnection of the molecule from the surface of the adsorbent, which could take two form either as product or as reactant. Depending on the nature of the bond between the surface and adsorbate, there are two type of adsorption.

1.2.4.1. Physisorption

Physisorption (also called physical adsorption) is caused by the forces of molecular interaction which embrace permanent dipole, induced dipole and quadrupole attraction. The fundamental interaction force is caused by Van der Waals force. In this adsorption there is no forming or breaking of chemical bond, however, it is very similar to liquefaction or condensation onto a cold surface. As the molecule approaches the surface the distribution of its electron density will be altered by the influence of the electrons at the surface, which will give arise to Van der Waals force. The introduction of this force will accelerate the molecule towards the surface. The molecule will begin to experience repulsion (an increase in energy) due to the increasing proximity of the outer electronic orbitals of the solid and molecule. Upon collision, energy will be lost to the surface and the resulting velocity of the departing molecule may be less than the velocity required to escape the potential well. In this case, the molecule becomes adsorbed.

1.2.4.2. Chemisorption

Chemisorption (also called chemical adsorption) is adsorption which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate in a monolayer on the surface. Chemisorption is an essential step in the preparation of a molecule for reaction. For a molecule to react catalytically at a solid surface, it must first be chemisorbed. Chemisorption can take one of two forms; the first form is dissociative adsorption which is adsorption with dissociation into two or more fragments, both or all of which are bound to the surface of the adsorbent. Oxidation of CO on metal surface is an example of dissociative adsorption (Fig. 1.5).

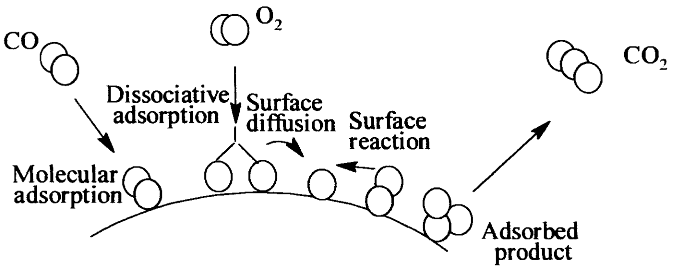

Figure 1.5 Dissociative adsorption of O_2 on metal surface during oxidation of CO [15].

Alternatively, Chemisorption can occur without dissociation on the surface which is known as associative adsorption. The adsorbate molecule interacts with the free valences of adsorbent through either lone-pair or π electrons without fragmentation. For example, the adsorption of ethene on a metal surface is associative adsorption (Fig 1.6).

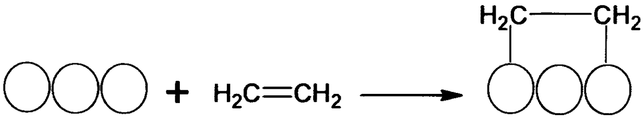

Figure 1.6 Associative adsorption of ethene on metal surface.

1.3. Oxidation catalysis

One of the important reactions in industry is oxidation. It is probably true to say that nowhere is there a greater need for green catalytic alternative in fine chemical manufacture than in oxidation reactions. In contrast to reduction reactions, oxidation is still largely carried out with stoichiometric inorganic oxidant such as permanganate and manganese dioxide. Environmental legislation has imposed increasingly stringent targets for permitted levels of atmospheric emissions. The emission of volatile organic compounds (VOCs) has received particular attention as they have been associated with photochemical smog in urban environment, depletion of atmospheric ozone and the production of ground level ozone [16-19]. Thus, the introduction of heterogeneous catalyst using an oxidant such as O_2 represents a much favoured alternative. Table 1.3 shows some example of industrially oxidation reactions using heterogeneous and homogeneous catalysts in gas and liquid phase.

Oxidation processes can be divided into two types. First, total oxidation or combustion where the normal products for this type of hydrocarbon oxidation are CO_2 and water. This route is thermodynamically favourable as the desired products are the outcome products of the reaction. This process is used in energy production as well as in environmental removal of pollutants. The second type is selective oxidation or partial oxidation where kinetic control must be imposed as the desired products is not thermodynamically stable. In general, the production of chemicals and intermediate is produced through this route. Recently there has been more and more interest in partial oxidation using heterogeneous catalysts. Many metals and metal oxides have been used as catalysts for oxidation reactions. One of these metals which have shown promising results is gold.

Table 1.3 Industrial oxidation reactions using heterogeneous and homogeneous catalysis

Product	Feedstock	Oxidant/process [a]
Styrene	Benzene/ethene	None/G (O_2/L) [b]
Terephthalic acid	*p*-Xylene	O_2/L
Formaldehyde	Methanol	O_2/G
Ethene oxide	Ethene	O_2/G
Phenol	a. Benzene/propene	O_2/L
Acetic acid	b. Toluene	O_2/L
	a. n-Butane	
	b. Ethene	
Propene oxide	Propene	RO_2H/L
Acrylonitrile	Propene	O_2/G
Vinyl acetate	Ethene	O_2/L; G
Benzoic acid	Toluene	O_2/L
Adipic acid	Benzene	O_2/L
ε-Caprolactam	Benzene	O_2/L
Phthalic anhydride	*o*-Xylene	O_2/G
Acrylic acid	Propene	O_2/G
Methyl methacrylate	Isobutene	O_2/G
Maleic anhydride	n-Butane	O_2/G

[a]: L= liquid phase, G= gas phase. [b]: Styrene from propene epoxidation with EBHP.

1.4. Gold catalysis

Gold (Au) has the atomic number of 79 with [Xe]$4f^{14}5d^{10}6s^{1}$ as atomic configuration. It lies in the 11th group of the periodic table and is classified as a transition metal. Gold, along with silver and copper, so called *coinage metals* due to their ability to form many alloys with many other metals [20] (Table 1.4). Because of the softness of pure gold it is usually alloyed with base metals for use in coins and jewellery. Copper is the most commonly used base metals.

Table 1.4 Comparison of some physical properties of group 11 in the periodic table.

Citron	Cu	Ag	Au
Electronic configuration	[Ar]$3d^{10}4s^{1}$	[Kr]$4d^{10}5s^{1}$	[Xe]$4f^{14}5d^{10}6s^{1}$
Atomic number	29	47	79
Atomic weight	63.55	107.86	196.97
Structure	fcc	fcc	fcc
Melting point	1083 °C	961 °C	1064 °C
Boiling point	2570 °C	2155 °C	2808 °C
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)	87	97	193
First ionization energy (kJ/mol)	745	731	890
Metal radius in (12-coordination)/pm	128	144	144
Number of natural isotopes	2	2	1

Gold is unique among metallic element as it shows great resistance toward corrosion and oxidation. Another important feature of gold is it electronegativity where it is considered the most electronegative metal [21]. Due to this high electronegativity gold will not react directly with other electronegativity element such as oxygen and sulphur and will only dissolve in hydrochloric acid when there is strong oxidizing agent such as nitrate ion present (i.e. aqua regia) [20]. The common oxidation states for gold are +1 and +3 states, however, the highest oxidation state is +5 which is only seen in [AuF_6^-]. Fascinating in its complexity for academic chemists, the chemistry of gold has potential applications in material science, medicine and recently in both homogeneous and heterogeneous catalysis.

1.4.1. Historical backgrounds

Gold has been regarded as the noblest metal in the periodic table for a significant period of time. The reason for that is the fully occupied d-band in Au atom. All elements in the eleventh group share this property; however, as consequences of low ionization potentials, Ag and Cu readily lose electrons to yield d-band vacancies resulting in more reactivity in these two elements. In fact, there are at present industrial applications for Ag as well as Cu. Ag is used for ethylene oxide synthesis and Cu is used for methanol synthesis. On the contrary, gold has a high ionization potential and accordingly has a poor affinity toward other molecules. According to the Tanaka-Tamaru rule [22] the surface of Au show no dissociative chemisorption of O_2 or H_2 under 437 K, which implies the lack of reactivity for oxidation and hydrogenation reactions on gold surfaces.

In 1823 Dulong and Thenard [23] observed that gold was among the metals that catalysed the decomposition of ammonia, this could be the first hint that gold might not always exhibit poor activity. Bond and Sermon observed that when a small particles of gold dispersed on SiO_2 it can catalyse the hydrogenation of alkenes and alkynes [24]. It was not until 1980s when two observations changed the general belief that gold is a noble metal and highlighted the fact that small particles of gold are good candidates for catalysts, these two observations are:

a- The successful prediction, then confirmed, that gold would be the best catalyst for acetylene hydrochlorination by Hutchings [25].

b- The low temperature CO oxidation using supported gold nanoparticles by Haruta [26]

These two observations have sparked a flurry of research in the area of gold in the last two decades. Figure 1.7a shows the rapid increase in publication in gold catalysis from years 1900 to 2006 in the homogeneous and heterogeneous catalysis field. Figure 1.7b illustrates the domination of heterogeneous catalysis in the filed of gold over homogeneous catalysis.

The applications for supported gold catalyst are wide and expanding. Gold catalysts are active under mild conditions which makes it unique. The potential applications of gold catalysis cover chemical processing, environmental control and fuel cells. The oxidation of CO at low temperature is one of the important uses for gold catalysis which could be used in industry, fuel cell and car exhaust purification systems [20]. Other uses of gold catalysts includes: hydrogenation of acetylene, oxidation and selective oxidation of hydrocarbon, water gas shift reaction, selective hydrogenation of alkynes and dienes, reduction of NO and production of hydrogen peroxide [27].

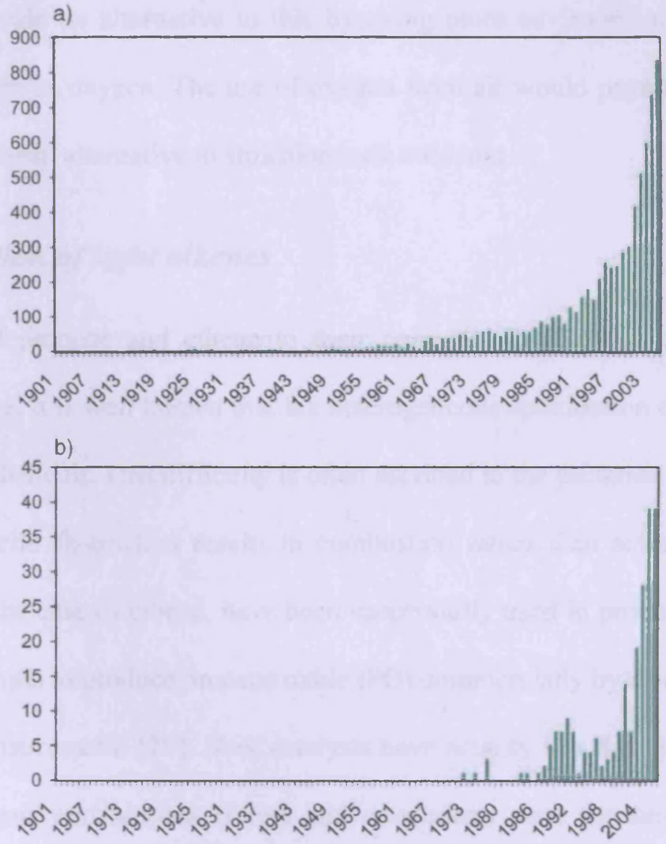

Figure 1.7 Publication on gold catalysis. a) number of publications on gold catalysis. b) number of publications on homogeneous gold catalysis [28].

1.4.2. Selective oxidation of hydrocarbons by gold catalysts

There is an important move in chemistry towards the development of novel environmentally friendly and sustainable processes. The selective oxidation of hydrocarbons is an essential step in pharmaceuticals industry, even though, this remains difficult to be achieve observing the tenets of *green chemistry*. To date, most oxiWEdation processes has been conducted with stoichiomertic oxidants. Gold catalysis seems to have the potential to provide an alternative to this by using more environmental friendly and cheaper oxidants such as oxygen. The use of oxygen from air would provide an abundant, easy to handle and cheap alternative to stoichiomertic oxidants.

1.4.2.1. Epoxidation of light alkenes

Epoxidation of propene and ethene to their corresponding oxides is a process of industrial importance. It is well known that the heterogeneous epoxidation of alkenes other than ethene is very difficult. This difficulty is often ascribed to the presence of labile allylic H atoms, whose facile abstraction results in combustion rather than selective oxidation. Silver catalysts, in the case of ethene, have been successfully used in production of ethene oxide [29]. All attempts to produce propene oxide (PO) commercially by direct oxidation of propene has been unsuccessful [29]. Most catalysts have activity less than 10% with lower selectivity for propene epoxidation. Haruta and co-workers were the first to report the potential of supported gold catalysts in propene epoxidation using oxygen as an oxidant in the presence of hydrogen [30]. According to Haruta [31], >99% PO selectivity with 1% conversion can be achieved for propene epoxidation using Au/TiO_2 in the presence of oxygen and hydrogen. The hydrogen acts as a sacrificial reactant and permits the activation of O_2 where it forms hydrogen peroxide *in situ* and permitting the selective oxidation of propene to occur. There are two other reactions routes competing with epoxidation which is hydrogenation and total oxidation (Fig 1.8).

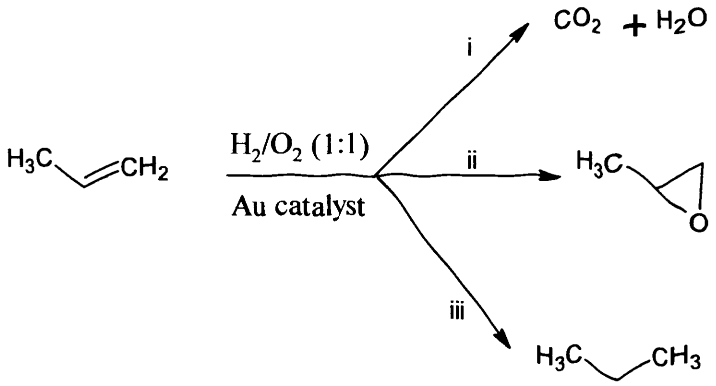

Figure 1.8 Reactions competing with propene epoxidation

A key issue that remains with this experimental approach is the selectivity based on H_2, which can be very low. Haruta and co-workers have tried to address the issue of poor H_2 utilisation and have shown that, using mesoporous titanosilicates as a support [32], improved H_2 consumption with high propene oxide yields (93g/h.kg$_{cat}$ at 160°C). Propene oxide selectivities of >90% were observed at propene conversions of *ca.* 7%, together with a hydrogen efficiency of 40% [33]. However, this H_2 efficiency is far lower that than currently achievable (*ca.* $\geq$ 95%) with indirect H_2O_2 synthesis [34] and so this approach cannot compete with the TS-1 catalysed epoxidation of propene using H_2O_2 [35].

All gold catalysts that exhibit activity for propene epoxidation contain titania as support (including TS-1, Ti-zeolite β, Ti-MCM-41 and Ti-MCM-48) [36-47]. Using the most active catalyst hitherto, selectivities of 80% PO have been obtained at 5% conversion working at 150-200°C [39, 48]. The low gold loading coupled with non-detectable gold particles in TEM micrographs suggested that, in these materials, significant activity is attributable to gold entities smaller than 2 nm [39]. This conclusion seems to be in contrast to a previous hypothesis that gold particles smaller than 2 nm switch the selectivity from PO to propane owing to loss of metallic character [30]. The repeatedly reported low PO yield over Au/TiO_2-based catalysts was attributed to non-Langmuir adsorption noting that an increase in catalyst loading does not lead to a higher yield of propene oxide, either due to consecutive reaction over Ti---O---Ti containing units, or the existence of a PO adsorption–desorption equilibrium over active epoxidation centers [36].

Several parameters have been reported to have an effect on the gold catalytic activity. The addition of water as co-feed in the gas phase has a positive effect on propene epoxidation. The competitive adsorption of water has believed to decrease the PO adsorbed on titania [42]. According to Delgass and co-workers, the pretreatment of gold supported on TS-1 with NH_4NO_3 has result in an increase in the catalytic activity [48]. It has been found that dilution of the active sites represents a way of preventing over-oxidation and deactivation during the epoxidation reaction. In particular, deactivation could be depressed by using TiO_2 dispersed on an inert material such as silica acting as a support [49].

1.4.2.2. Epoxidation of higher alkenes

In contrast to ethene and propene epoxidation, the epoxidation of higher alkenes using supported gold catalyst can be performed without the need of a second regent (i.e. H_2 in the case of propene). The use of peroxide radical initiator to facilitate the epoxidation of alkenes using supported gold catalysts was reported by several groups [50-56]. According to Hutchings [55], the epoxidation of cyclohexene can be performed effectively using supported gold catalyst and *t*-butyl hydroperoxide (TBHP) with good conversion and high selectivity. Cyclohexene can be oxidised to form several possible products, including direct epoxidation to cyclohexene epoxide, followed by ring-opening to cyclohexane-1,2-diol or allylic oxidation to 2-cyclohexen-1-ol plus possible further oxidation to 2-cyclohexen-1-one (Fig. 1.9).

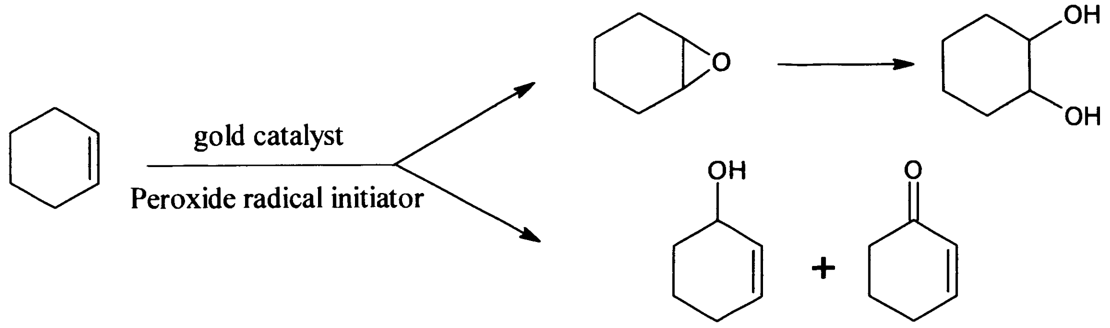

Figure 1.9 Epoxidation of cyclohexene

Cyclohexene epoxidation is highly solvent dependent. Using polar solvent (i.e. water) with TBHP and supported gold catalyst 100% conversions were observed however, the main products were CO_2, formic acid and oxalic acid with no C6 products. Apolar solvent showed opposite results. High selectivity to epoxide (50%) and ketone (26%) at 30% conversion using Au/C and TBHP was obtained in 1,2,3,5-tetramethylbenzene (TMB). Selectivity toward C6 products (98%) were increased significantly by the addition of bismuth to the gold/carbon catalyst [55]. 2,2'-Azoisobutyronitrile (AIBN) was also used as peroxide radical initiator in cyclohexene epoxidation. Corma and co-workers [57] reported that by using Au/CeO_2 as catalyst and AIBN as radical initiator, 20% of cyclohexene oxide together with 15% of 2-cyclohexenol was achievable. The absence of radical initiator or gold from the reaction mixture retards the oxidation reaction. However, the reaction mechanism for this reaction is still not fully understood. According to Corma the radical initiator and the positive gold atoms in gold nanoparticles will form R-Au organogold species on the surface of the gold catalyst which can promote the aerobic oxidation [57].

Epoxidation of styrene can also be carried out by using gold as a catalyst (Fig. 1.10). Hutchings and co-workers demonstrated that the product distribution of styrene epoxidation over 1%Au/C and TBHP using hexafluorobenzene as solvent is 46% benzaldehyde, 29% epoxide and 11% acetophenone at 8% conversion. The basicity of the support was found to play a role in the epoxidation process [55]. By studying gold supported on different kinds of mesoporous alumina with different surface basicity, Yin and co-workers concluded that the activity of the catalyst increases by increasing the surface basicity of the support [50]. This can be attributed to more homogeneous distribution and the smaller average particle size of Au (3.1 nm). Choudhary has investigated a variety of metal oxide supports 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 [52]. The influence of the support on the catalytic activity was found to be strong. Among the studied supports TiO_2 and CuO shows the better performance with respect to epoxidation. Using carbon nanotubes as a support resulted in the most active and selective catalyst for styrene epoxidation with around 95% conversion and 78% selectivity to styrene oxide (SO) with phenylacetaldehyde and benzaldehyde as by-products [58].

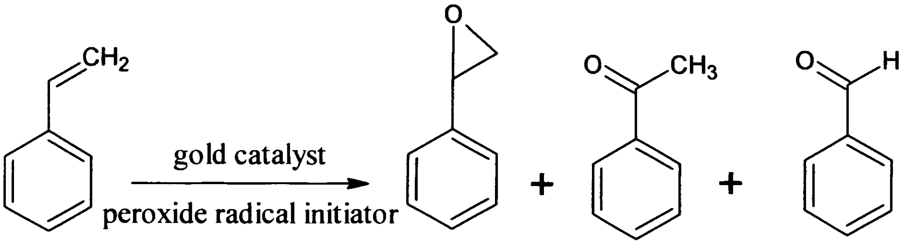

Figure 1.10 Styrene epoxidation

Gold particle size was reported to have an important role in styrene oxidation. Lambert and co-workers reported that small gold entities (~1.4 nm) derived from Au_{55} cluster and supported on inert materials (i.e. boron nitride, silicon oxide or carbon) are efficient for styrene oxidation by dioxygen in the absence of a peroxide initiator [59]. 20% conversion with selectivity of 14% SO using 0.6%Au_{55}/boron nitride as catalyst and dioxygen as oxidant was recorded. Gold particles ≥2 nm are inactive as a catalyst for styrene epoxidation in the absence of radical initiator. This activity of very small gold particles suggests that their capability to dissociate O_2 to yield O ad-atoms which could therefore initiate the partial oxidation [59-61].

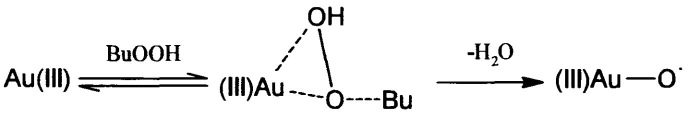

Figure 1.11 Interaction between Gold and TBHP

The mechanism at which the styrene oxidation occurs on the surface of gold has been addressed by several papers [58, 61-64]. The interaction of TBHP with Au(III) in the catalyst to form a hydroperoxy species which undergoes one electron reduction with loss of water and rearranged to give the Au(III)-O_{ad} (Fig1.11) [59]. However it has to be mentioned that this interaction could only be correct if the TBHP was an oxidant rather than as an initiator i.e. used in excess amount. The first step in epoxidation which has been widely agreed is the addition of oxygen to the terminal double bond (Fig. 1.12). Due to the asymmetry of the C=C bond in styrene, two possible oxametallacycles and inequivalent combustion intermediates rise from the interaction between the adsorbed oxygen and the double bond in the styrene molecule (Fig. 1.12). The rate determining step is believed to be the transformation from oxametallacyclic species to the products [61, 63, 64]. From the secondary oxidation of phenylacetaldehyde (product of styrene oxidation) the structure of the combustion intermediate can be drawn. Electronically, the removal of the α-hydrogen in phenylacetaldehyde forms an extended conjugated system that couples the π-electrons through the phenyl ring and the carbonyl group and bonds with surface [65]. DFT calculations have revealed that the formation of styrene oxide is generally easier *via* the two oxametallacycles intermediates than other paths kinetically; suggesting that the formation of the epoxide *via* oxametallacyclic intermediates might be a dominant step. Moreover, the production of styrene epoxide through oxametallacycles intermediate 2 is kinetically favored over that of oxametallacycles intermediate 1 [63].

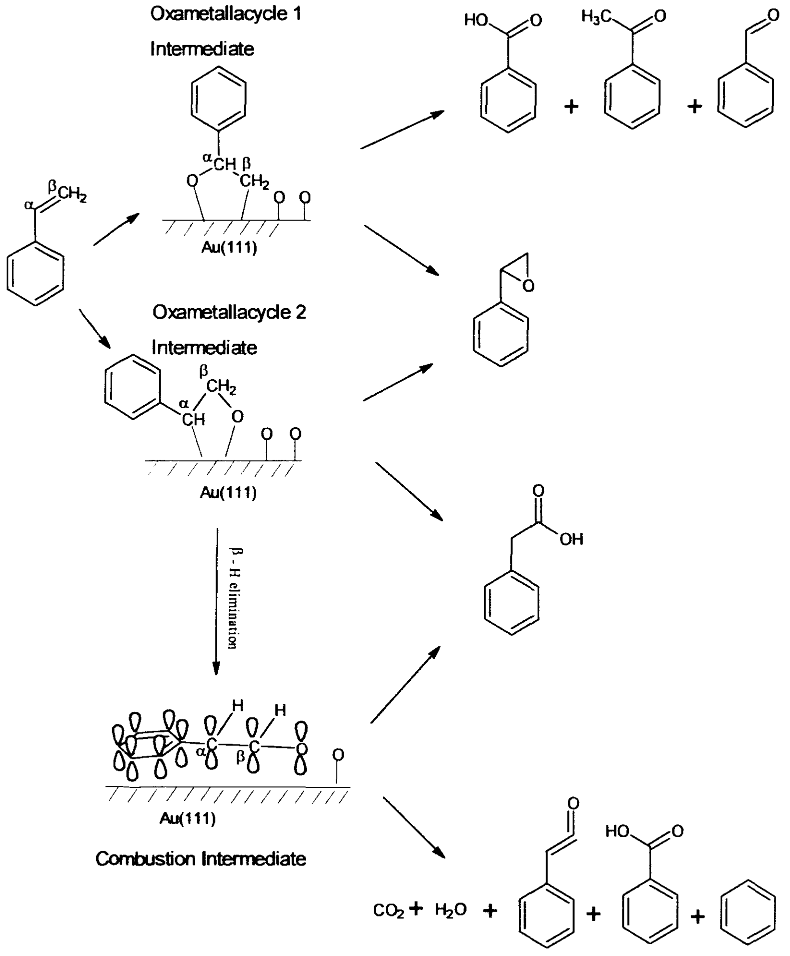

Figure 1.12 Mechanism for styrene oxidation

The use of gold as heterogeneous catalysts for cyclooctene epoxidation has also been reported in the literature (Fig. 1.13). Hutchings and coworkers have investigated the use of Au/C both in the presence and absence of solvents [55]. It was demonstrated that the oxidation of cyclooctene over supported gold catalyst is viable using very small amounts of TBHP with high molar ratio between substrate and TBHP; as high as 300. Screening a variety of solvents, 1,2,3,5-TMB was found as the best solvent with 28% conversion and 94% selectivity to the epoxide. In the absence of solvent 8% conversion and 81% selectivity was achieved using 0.12g of TBHP [55]. The authors suggested that the reaction proceeds *via* radical mechanism where BuOOH act as initiator of a chain reaction which sustained by molecular oxygen. Li and co-workers point out that the epoxidation performance of supported gold catalysts might be essentially related to the nature of the support and gold particles size rather than the surface area of the catalyst. 1% gold supported on carbon nanotubes (CNTs) were found to produce the best results among different supports with 54.6% conversion and 43.9% selectivity for epoxide using TBHP as initiator and CH_3CN as solvent [66]. The amount of TBHP present in the reaction was also found to be an important parameter [55, 66]. Another parameter of importance is the gold loading, which has been found to have an inverse relationship with gold dispersion. Conversion and selectivity increased gradually by increasing the gold loading. However, TOF decreased as a function of gold loading which according to the authors indicate to the importance of the particle size of gold. Particles less than 10 nm in diameter where believed to be responsible for the high activity of Au/CNTs albeit that the product selectivity is less sensitive toward the particle size of gold [66]. Recently, Tsang and coworkers reported the most active catalyst in cyclooctene epoxidation [67]. Nanoparticles gold supported on Si nanowires (SiNWs) achieved 38% conversion with 90% selectivity to epoxide in solvent free condition with TBHP as initiator at mild conditions. The authors suggested that the high loading of gold (66%) and the high surface area of SiNWs is the reason for the high activity of this catalyst. Moreover, the *in situ* reduction of gold over SiNWs surface (Au^{3+} react with Si-H which has strong reducing reactivity) could stabilize and anchor the gold nanoparticles (AuNPs) on SiNWs and isolate or separate the AuNPs [67]. Despite the high activity of Au/SiNWs, the high loading of precious metal (gold) and the use of HF treatment in the preparation of the catalyst demonstrate the need of catalyst system which can operate in mild condition and involve more benign preparation conditions.

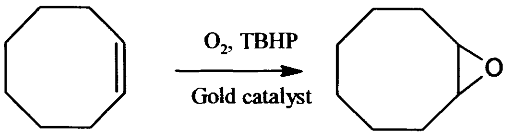

Figure 1.13 Cyclooctene epoxidation

Peroxide can be used as reaction initiator (in catalytic amounts) or as oxidants (in stoichiomertic amounts). Even though most of the reactions mentioned above use hydroperoxide or peroxide as an oxidant in stoichiomertic amounts, which is in direct contrast to the principles of green chemistry, the use of peroxide as reaction initiator in catalytic amounts and the use of air as oxidants have been rarely reported in the literature[54, 55, 66, 67]. Lignier and co-workers reported that by increasing TBHP amounts the reaction rate increases accordingly [54]. Albeit using excess amount of TBHP, Liu and co-workers found that increasing TBHP concentration would result in an increase in the reaction activity [58]. Li and co-workers showed that the activity of the reaction would reach a plateau after certain amounts of TBHP where the concentration of TBHP will not affect the reaction activity. This effect contributed to the change in the rate determining step of the reaction. At low TBHP concentration the rate determining step is believed to be the formation of oxygen free radical species but when TBHP concentration is high, the rate controlling step might turn to the transfer of oxygen free radical species [66]. Performing the oxidation in the absence of catalyst and with TBHP only was reported to produce non-selective conversion of hydrocarbon [54, 55].

1.4.2.3. Selective oxidation of alcohol

Selective oxidation of alcohols is one of the most critical challenges facing the chemical industry. Several reports suggest that catalysis is able to promote the selective oxidation of alcohols, in particular supported nanoparticles gold catalysis were reported to be highly effective [68-73]. In general, organic solvents and /or bases are necessary to achieve high yield and selectivity. An air and moisture –stable oxidation catalyst has to give not only high conversion with some selected alcohols but also has to be chemoselective when the molecule contains other oxidizable functional groups. One important family of alcohols that has industrial relevance is allylic alcohols. Kawanami and co-workers demonstrated that gold supported on TiO_2 can oxidise crotyl alcohol to the aldehyde with high conversion and selectivity (57% and 94% respectively) using O_2 as oxidant and super critical CO_2 as solvent [74]. According to the authors, the double bond between C-C may be stabilized by the aldehyde compounds.

Another example of allylic alcohol is 1-octen-3-ol. 99% Conversion and 90% selectivity toward ketone was achieved when Au/CeO_2 was used as a catalyst and toluene as solvent [75]. An example of benign operating conditions, 1-octen-3-ol was oxidized solely to the corresponding ketone with more than 99% conversion using Au/TiO_2 as catalyst, H_2O_2 as an oxidant and H_2O as solvent [76]. The hydrogen peroxide was believed to facilitate the abstraction of the α-hydrogen as a hydrogen scavenger, leading to the formation of a metalcoholate species during the initial step of the reaction. The Au-alcoholate complex may be further attacked by H_2O_2 or the Au-hydridoperoxide complex generated from the reaction of Au^0 with H_2O_2, to form the final carbonyl compound via a β-elimination pathway (Fig. 1.14). Using glass batch reactors in the absence of solvent at 80°C with O_2 at atmospheric pressure, Corma and coworkers were able to illustrate the efficiency of nanoparticulate gold supported on nanoparticle cerium oxide ($npCeO_2$) to selectively oxidise a large variety of alcohols [73]. Oxidation of 1-octen-3-ol under the previous conditions resulted in 80% conversion with more than 99% selectivity toward the ketone.

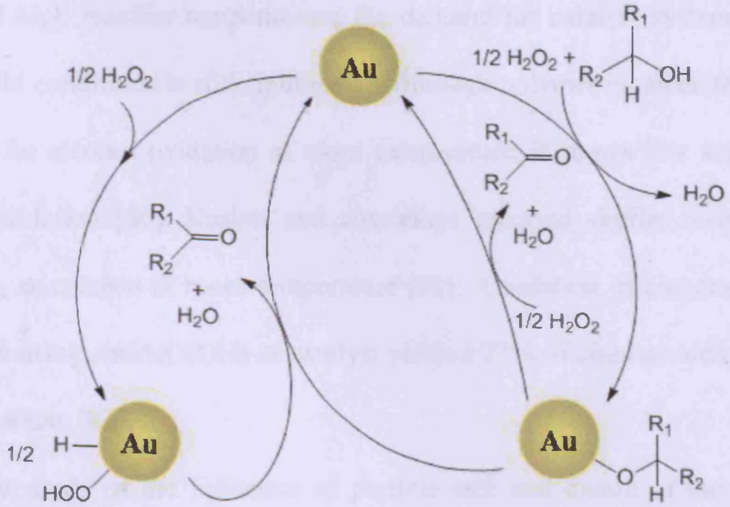

Figure 1.14 mechanism for alcohol oxidation over gold using H_2O_2 as oxidant [76]

Cinnamyl alcohol is considered as a model for allylic alcohol. Moderate activity and selectivity in solvent free conditions was reported for the oxidation of cinnamyl alcohol over $Au/npCeO_2$. Addition of water and base to the reaction resulted in dramatic increase in the activity and selectivity of the reaction, even though, cinnamylic acid was the predominant product [73]. Similar results were found using Au/TiO_2 with aldehyde as the predominate product [77]. Theoretical studies confirm that the -OH groups from the dissociation of water could facilitate the O_2 adsorption on TiO_2 and, therefore, the binding and activation of O_2 could be significantly improved [78]. Qiu and coworkers predicted that the hydrogen species from the dissociation of water would react with the oxygen adsorbed on the catalyst yielding very reactive OOH species that further decompose to form activated oxygen adsorbed on the surface of gold (O^*) [77]. Performing the oxidation of cinnamyl alcohol over Au/TiO_2 with hydrogen peroxide as oxidant resulted in almost complete oxidation to cinnamaldehyde [76]. Gold supported on γ-Ga_2O_3 and $Ga_3Al_3O_9$ was also reported to have high activity in alcohol oxidation [71, 79]. While most of these systems required high reaction temperatures, the demand for catalyst systems which can operate under mild conditions is still significant. Although polymer incarcerated Au cluster is good catalyst for alcohol oxidation at room temperature, it shows low activity toward allylic alcohol oxidation [80]. Karimi and coworkers reported similar results by using $NaAuCl_4/Cs_2CO_3$ as catalyst at room temperature [81]. Oxidation of cinnamyl alcohol at room temperature using Au/AlO(OH) as catalyst yielded 77% of cinnamaldehyde and 23% of cinnamyl cinnamate [82].

A systematic study of the influence of particle size and nature of the support was reported for the aerobic oxidation of cinnamyl alcohol [75]. Increasing the particle size resulted in a decrease in the activity of the catalyst (Au/TiO_2) for cinnamyl alcohol oxidation. However, the selectivity was independent on gold particle size as the aldehyde was the only product. In addition, plotting the total number of external gold atoms at the external surface of the gold crystallites versus the catalytic activity revealed a linear relationship. This finding emphasizes that in order to optimize the catalytic activity of gold for this reaction the metal dispersion should be increased.

To study the effect of the support Corma and coworkers prepared a series of supported gold catalysts with same gold loading and particle size but with a variety of supports [75]. The catalytic activity was as following: npCeO_2>CeO_2>>TiO_2>C. According to the authors the reason for the superior performance of CeO_2, especially in the form of nanoparticles, over titania oxide and carbon was postulated to be due to the abundance of lattice oxygen vacancy in npCeO_2 which favor interaction and physisorption of molecular oxygen. In other words, ceria can act as oxygen "pump" ensuring the oxidation of metal hydrides into water. Furthermore, the effect of gold loading on support was studied [75]. This parameter was found to have a pronounced effect on the catalyst activity where the lower loading of gold being more active, ascribed to the cooperative effect of the support with gold. If the ceria surface is covered by gold to a significant extent then the catalytic activity is reduced. This infers that both gold and ceria surfaces are required in the reaction mechanism.

Kobayashi and coworkers reported that gold embedded in a polystyrene matrix is more effective catalyst for alcohol oxidation at room temperature and atmospheric pressure than Au/npCeO_2 [80]. This is in contrast with what has been reported earlier; that the support plays an important part in alcohol oxidation. Notably the conditions in which these catalysts work is different and it will be useful to compare the two catalysts under the same conditions. It was proposed that the alcohol oxidation using air as the oxidant proceed through a positively charged transition state (Fig. 1.15). Corma and co-workers proposed a three step mechanism in which the oxidation of alcohol occurs using air as oxidant and gold catalysis (Fig. 1.16) [75]. The first step is the formation of metalalcoholate species which will undergo a metal-hydride shift giving rise to the carbonylic product and metal-hydride intermediate in the second step. This step is slow and it considered as rate determining. The third step is the rapid oxidation of the metal-hydride by oxidation to give rise to the initial metallic site and water.

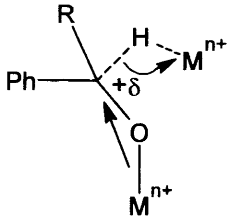

Figure 1.15 The proposed transition state for alcohol oxidation using air as oxidant with gold catalyst [75]

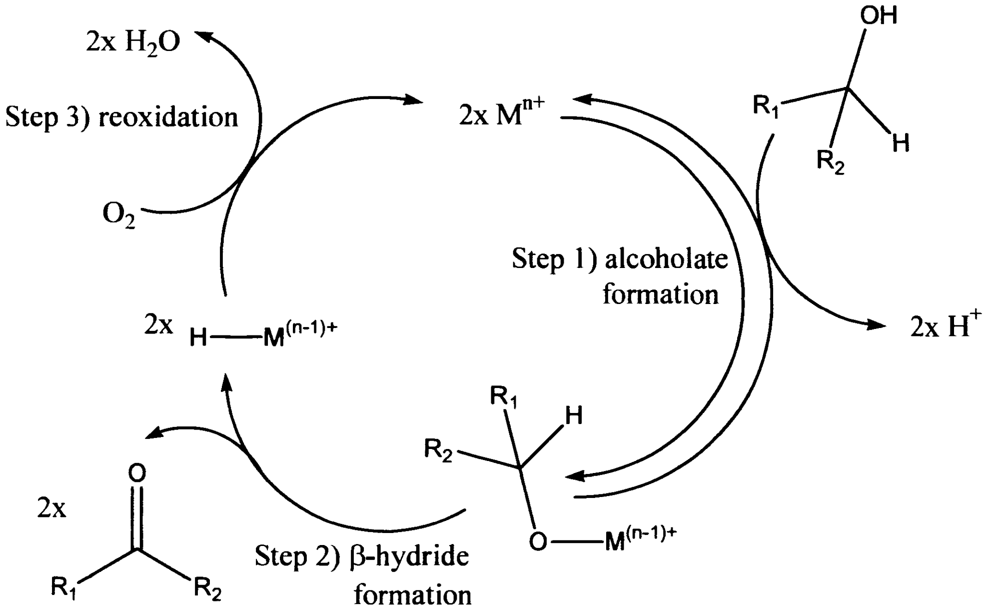

Figure 1.16 Proposed mechanism for the Au/npCeO$_2$ catalysed aerobic oxidation of alcohols [75].

1.4.3. Oxidation by gold-palladium catalysis

Bimetallic nanoclusters attract great interest due to their unique catalytic, electronic and optical properties which differ from those of the corresponding monometallic components [83, 84]. The addition of second metallic component enhances the activity, selectivity and stability of pure metal catalyst [85, 86]. This behavior may originate from an ensemble or a ligand effect [87]. Mixture of Au and Pd can be used in several applications as catalyst.

1.4.3.1. Selective oxidation of hydrocarbons

High turnover frequencies for the oxidation of selected alcohols with oxygen under mild condition have been achieved using Pd supported on hydroxyapatite [88] and titania supported gold (core)-palladium (shell) nanoparticles Fig. 1.17[89]. Screening the literature revealed that the superior activity of bimetallic catalyst over monometallic or the reverse is highly dependent on the nature of the support. Corma and coworkers shows that gold present unique selectivity when compared with Pd and Au-Pd catalyst [90]. Oxidation of 1-octen-3-ol using Au supported on CeO_2 and TiO_2 as catalysts resulted in excellent conversion along with chemoselectivity. However, the presence of palladium in the catalyst (as mono or bimetallic catalyst) was highly detrimental for the catalyst as more isomerisation products were produced [90]. Similar results where found for other allylic alcohols namely; trans-Carveol, 3-octen-2-ol, 2-octen-1-ol and cinnamyl alcohol [90].

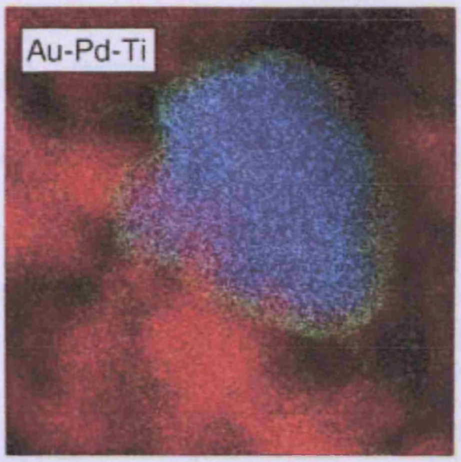

Figure 1.17Core-shell structure of Au-Pd/TiO$_2$ (Ti red, Au blue, Pd green) [89]

In a solvent-less condition supported Pd was found to be more active than supported gold at high temperature (160 °C) however, the reverse behaviour is observed at 120 °C for alcohol oxidation [72]. Figure 1.18 shows the possible competing reaction in the oxidation of allylic alcohol. An explanation for the increasing number of by-products using Pd catalysts over Au catalysts is that the concentration and reactivity of palladium hydride is higher than that of gold hydride [91]. According to Corma and co-workers the metal hydride is formed during the reaction on the metal surface. In the case of gold this hydride is oxidized rapidly and, therefore, its concentration on the surface is very low. This is not the case with Pd, where the oxidation of Pd-H is slow and thus its concentration on the metal surface is high. Metal hydride is known to promote C=C reduction and isomerisation [92].

Hutchings and co-workers demonstrated that Au-Pd/TiO$_2$ is more efficient than pure Pd or pure Au catalysts in alcohol oxidation. For allylic alcohol oxidation turnover frequency as high as 12600 h^{-1} was achieved using Au-Pd/TiO$_2$ [89]. Crotyl alcohol was converted by 81.9% to crotonaldehyde with 31.5% selectivity using H_2O_2 and 2.5%Au-2.5%Pd/ TS-1 as catalyst [93]. Au-Pd supported on polymer was reported to be effective catalyst for alcohol oxidation with activity as following: secondary alcohol > primary alcohol > benzylic alcohol > allylic alcohol > aliphatic alcohol with Au/Pd molar ratio of 8:2 emerged as the most active [94].

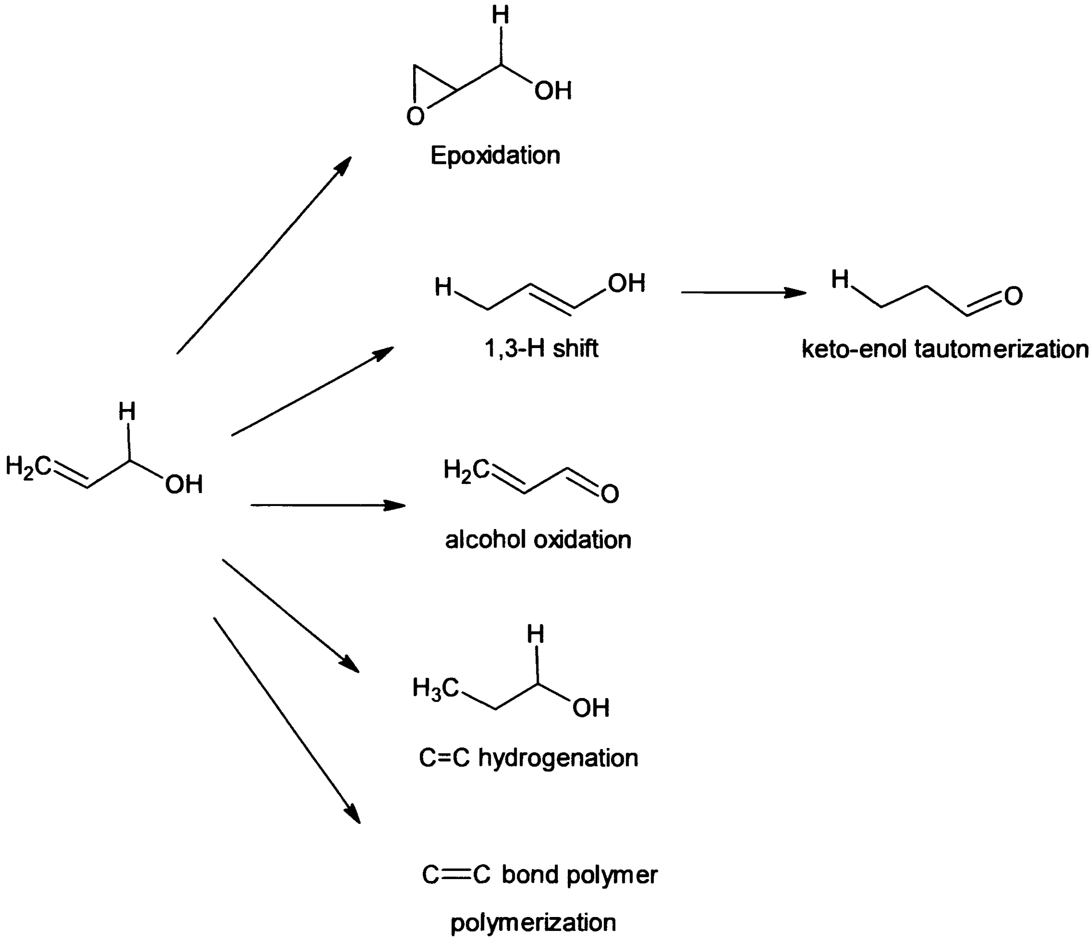

Figure 1.18 Possible competing reactions in allylic alcohols oxidation.

In an XPS study using crotyl alcohol as model, the authors propose that using gold palladium alloys, high palladium surface concentrations should provide the optimum selective oxidation (selox) activity for AuPd alloy nanoparticles with Au_2Pd_3 as the optimum surface alloy composition [95]. Characterization of the active catalyst Au-Pd/TiO_2 after calcination revealed that the surface of the catalyst is significantly enriched with Pd [89]. According to Hou and co-workers PVP-stabilized 1:3 Au:Pd nanoparticles have shown the highest activity for crotyl alcohol oxidation and selectivity toward crotonaldehyde over pure Au or pure Pd [96]. This is in agreement with Villa and co-workers where they illustrated that the bimetallic system (Au/Pd/Activated carbon) is more active than that corresponding to Au and Pd monometallic catalysts [97]. Studying the effect of Au/Pd ratio showed "volcano behavior" with Au_{60}-Pd_{40} catalyst resulting as the most active catalyst in 2-octene-1-ol oxidation in the absence of base. According to the authors an Au:Pd ratio of 9:1, 8:2, 6:4 consist of homogenous alloy whereas Au:Pd = 2:8 shows inhomogeneity of the structure with Pd segregation [97].

It has been proposed that the mechanism of alcohol oxidation over gold and gold rich alloys differs from that over palladium and palladium rich alloy [70, 97]. Oxidation of an alcohol functionality over Pd proceeds as following. The alcohol is dissociatively adsorbed on the palladium surface resulting in an alkoxide and hydride. Then, the H atom on the β-carbon of the adsorbed alkoxide is transferred to the metal surface to form the aldehyde and Pd-H in a rate determining step. Finally, Pd-H oxidized by O_2 to regenerate the metal surface and H_2O_2. Whereas, in the case of gold the rate determining step was thought to involve the H-atom abstraction by a superoxo-like oxygen species adsorbed on Au. Similar finding for gold mechanism has been suggested by different authors[98-100].

1.5. Aims of the study

As described in the literature review, selective oxidation of alkenes (bulky alkene in particular) and alcohol functionality represents a promising and challenging field in heterogeneous gold catalysis. The epoxidation of cyclooctene and crotyl alcohol will be studied using supported gold catalysts and different parameters will be discussed.

The main objectives have been:

1) Identifying the blank conditions in which the epoxidation of cyclooctene can be performed.
2) Systematic study into the effect of reaction parameters on the catalytic activity and selectivity.
3) Exploit the effect of support and radical initiator on cyclooctene epoxidation.
4) Elucidate the chemoselectivity of gold catalysts using bifunctional alcohol namely crotyl alcohol.
5) Study the effect of bimetallic system namely gold-palladium on the epoxidation of cyclooctene epoxidation and crotyl alcohol oxidation and observe the effect of metallic ratio on the reactions activity and selectivity.

Objective 1 is explored in chapter 3, objectives 2 and 3 are dealt with in chapter 3 and 4 and objectives 4 and 5 are explored in chapter 6.

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Chapter Two

Experimental

2. Experimental

2.1. *Introduction*

Experimental techniques represent a very important aspect of chemistry work which can greatly influence the outcome of any scientific research. The reaction of cis-cyclooctene epoxidation will be performed in glass reactors at atmospheric pressure using different supported gold catalysts. In this chapter we will provide detailed information of the catalyst preparation methods, and the catalytic testing. Many characterisation techniques have been used aiming to analyze the catalyst composition and unveil the microscopic mechanism behind reactions catalyzed by various materials. Brief descriptions of the basic principles of the characterisation techniques used in this research are introduced.

2.2. *Catalysts preparation*

Different supports were used in this study namely: graphite, activated carbon, SiC, TiO_2, SiO_2, and Al_2O_3. Graphite was the main support used. Three different preparation methods were evaluated.

2.2.1. *Deposition precipitation*

Unless otherwise stated, catalysts (1 wt% Au/support) were prepared using the following standard deposition precipitation method (denoted DP). A solution of $HAuCl_4.3H_2O$ (5 ml, 2g in 100 ml distilled water) was diluted with water (45 ml). Aqueous sodium carbonate was added with stirring until pH = 10 was attained. This solution was then added, with continuous stirring, to a slurry of the support in water (4.95 g in water 50 ml). The mixture was stirred for 1 h at 20 °C, maintaining the pH at 10. The mixture was heated to 70 °C and formaldehyde was added as a reducing agent. The solid was recovered by filtration and washed with water (1L) until the washings were found to be chloride free by the addition of silver nitrate to the filtrate (presence of chloride will resulted in white precipitate of silver chloride) . The catalyst was dried (110 °C, 16 h) prior to use [1].

Similar to the preparation of 1%Au/support, supported 1%Pd was prepared by DP method using solution of $PdCl_2$ (4.8 ml, 0.5 g in 100 ml distilled water) diluted with water (45 ml) following the procedure reported above.

Similar to the preparation of 1%Au/support, supported 1 %(Au-Pd) was prepared by DP method using required amount of a solution of $PdCl_2$ (0.5 g in 100 ml distilled water) and a solution of $HAuCl_4.3H_2O$ (2 g in 100 ml distilled water) were add simultaneously then diluted with water (45 ml) following the procedure reported above.

2.2.2. Impregnation method

For the impregnation method the support was suspended in distilled water (4.95 g in 100 ml) for 15 min. A solution of $HAuCl_4.3H_2O$ (5 ml, 2 g in 100 ml distilled water) was added to the slurry slowly dropwise over 30 minutes. The mixture was stirred under reflux for 30 minutes; after cooling, formaldehyde was added as a reducing agent. The solid was recovered by filtration and washed with water (1 L) until the washings were found to be chloride free by the addition of silver nitrate to the filtrate (presence of chloride resulted in white precipitate of silver chloride). The catalyst was dried (110 °C, 16 h) prior to use. In a similar way supported 1% (Pd) and 1% (Au-Pd) were also prepared [2].

2.2.3. Sol-immobilization method

For the sol-immobilization method an aqueous solution of $HAuCl_4.3H_2O$ was prepared. Polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, MW = 10 000, 80% hydrolyzed) was added (PVA/Au (by wt) = 0.65); a freshly prepared solution of $NaBH_4$ (0.1 M, Aldrich, $NaBH_4$/Au (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min, the colloid that had been generated was immobilized by adding the support (acidified at pH 1 by sulfuric acid) with stirring. The amount of support material required was calculated so as to have a total final metal loading of 1 wt%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (1 l). The catalyst was dried (110 °C, 16 h) prior to use. In a similar way supported 1% (Pd) and 1%(Au-Pd) were also prepared [3].

2.3. Catalyst testing

All reactions were performed in a glass round bottom flask (50 mL) with a magnetic follower, fitted with a reflux condenser and heated in an oil bath (Fig 2.1). Typically, *cis*-cyclooctene (10 ml) was stirred at the desired temperature at atmospheric pressure. Then the radical initiator was added followed by the catalyst (0.12g) and the reactions were typically carried out for 24 h. Analysis was carried out using a gas chromatography (Varian star 3400 CX) with CP-WAX column and a flame ionization detector.

As conversions were low and the reaction was carried out using solvent-free conditions, alkene conversion was determined on the basis of the concentrations of the observed products, and no CO_x was observed. Experiments were carried out in triplicate and the experimental variation was determined to be $\leq$ 1%, and mass balances were typically 100% within experimental error.

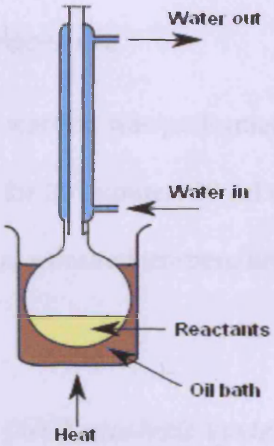


Figure 2.1 Schematic diagram of the glass reactor used in this study

2.3.1. Determination of cyclooctene hydroperoxide

Further experiments were conducted to determine the amount of cyclooctene hydroperoxides, since these products are not detected by the standard gas chromatography analysis. Standard reactions (24 hour and 72 hour) using 1%Au/graphite prepared by deposition precipitation were carried out. After completion of the desired reaction time the reaction mixture was filtered and then divided into two aliquots; (a) stirred for 1 hour with excess amount of triphenylphosphine (PPh_3) in air at room temperature, (b) un-treated with PPh_3. All samples were analysed by GC (FID, CP-wax column, Varian 3400). ^{1}H NMR spectroscopy (Bruker DPX 400 spectrometer) was used to confirm the presence of cyclo-oct-2-enyl hydroperoxide. Samples of all reactions were dissolved in D-chloroform and then ^{1}H NMR was performed. The spectrum for α-H to hydroperoxy exhibit significant downfield shifts of approximately 0.3 ppm compared to the corresponding alcohol. ^{1}H

NMR for alcohol ($CDCl_3$, 400 MHz) δ= 5.48-5.65 (m, 2H), 4.61-4.68 (m, 1H), 2.02-2.23 (m, 2H), 1.85-1.95 (m, 1H), 1.25-1.69 (m, 8H).

2.3.2. Catalyst reusability procedure

To reuse the catalyst a standard reaction was performed then the catalyst was collected by centrifuging the reaction mixture for 20 minutes. 30 ml of acetone was used to wash the catalyst. Then the catalyst was dried at a desired temperature for 16 hours.

2.3.3. Gas chromatography (GC) analysis system

Chromatography is the science of separation which uses a diverse group of methods to separate closely related components of complex mixtures. During gas chromatographic separation, the sample is transported *via.* an inert gas called the mobile phase. The mobile phase carries the sample through a coiled tubular column where analytes interact with a material called the stationary phase. For separation to occur, the stationary phase must have an affinity for the analytes in the sample mixture. The mobile phase, in contrast with the stationary phase, is inert and does not interact chemically with the analytes. The only function of the mobile phase is to sweep the analyte mixture through the length of the column. The gas chromatography instrument used in this study was Varian star 3400 CX, which were fitted with CP-Wax 52 CB capillary column (25m, 0.53mm, 2µm) and a flame ionization detector, the carrier gas was helium.

2.3.3.1. Flame ionization detector

The flame ionization detector (FID), invented by Harley and Pretorious [4], and separately by McWilliams and Dewer [5], evolved from the Heat of Combustion Detector developed by Scott [6]. The FID consists of a stainless steel chamber (jet) constructed so that carrier gas exiting the column flows through the jet, mixes with hydrogen, and burns at the tip of the jet (Fig. 2.2). Hydrocarbons and other molecules which ionize in the flame are attracted to a metal collector electrode located just to the side of the flame. The resulting electron current is amplified by a special electrometer amplifier which converts very small currents to millivolts. The FID is sensitive to almost all molecules that contain hydrocarbons and can detect compounds present in concentration as low as part per million to high part per trillion ranges. The signal for each component is presented as a peak. The area of the peak for each compound is divided by a relative sensitivity factor (RSF) to obtain the true number of the count.

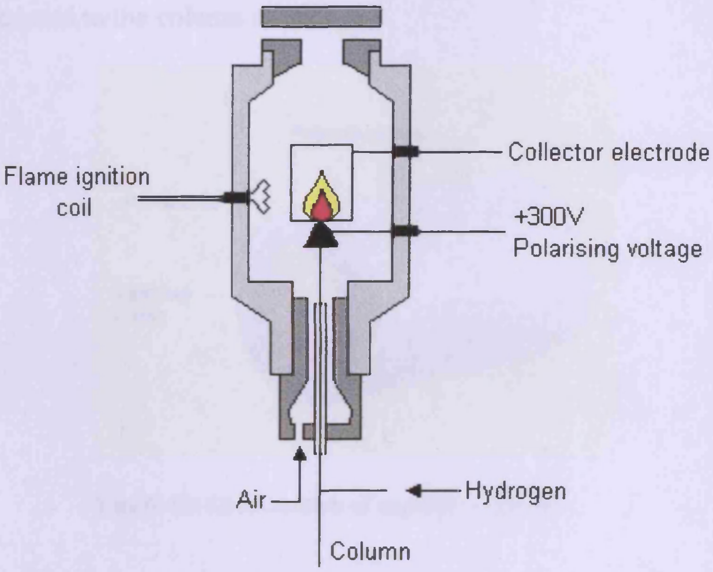


Figure 2.2 Schematic diagram of Flame Ionization Detector

2.3.3.2. Capillary column

There are two type of GC column: capillary column and packed column. Due to it high resolution, capillary column is by far the most used column in gas chromatography. In 1958 the theory of capillary column was first introduced by Golay [7]. Generally, capillary column constructed from quartz tube the diameter of which range between 50-500um, and the length between 5-200m. The column is coated on the outside with a polyamide to reduce breakage. The stationary phase coated on the inner surface of the column (Fig. 2.3). In this study, capillary column CP-WAX 52 CB from Varian was used. The backbone of stationary phase used in this column is made of a polyethylene glycol (Fig. 2.4), by using different functional group the selectivity optimized. The stationary phase is chemically bonded *via* a silane bond to the column surface.

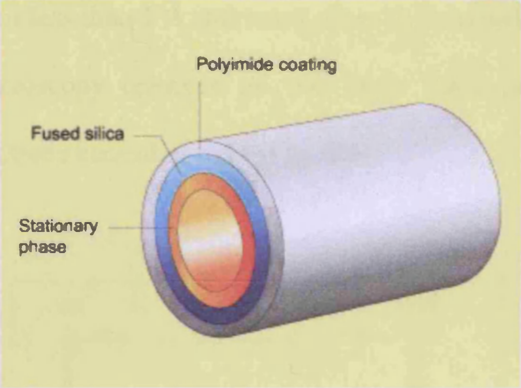
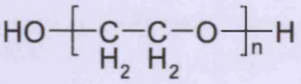


Figure 2.3 Cross section of capillary column



$$HO\left[\underset{H_2}{C}-\underset{H_2}{C}-O\right]_n H$$

Figure 2.4 Polyethylene glycol

2.4. *Catalyst Characterization*

Characterization is an important field in catalysis. The number of physical characterization techniques used to analyse heterogeneous catalysis is large. In this study seven different characterization techniques were used and will be described briefly in the flowing paragraphs.

2.4.1. *Transmission Electron Microscopy (TEM)*

Two German scientists, Ernst Ruska and Max Knoll, developed the first working electron microscope in 1932 after it was apparent the effective role that wavelength has on the theoretical resolution [8]. Electron microscopy is straightforward technique to determine the size, shape and compositions of supported particles. Electrons have characteristic wavelength of less than 1 Å and come close to monitoring atomic detail. The transmission electron microscopy operates on the same basis principle as the light microscope albeit uses electrons instead of light (Fig. 2.5).

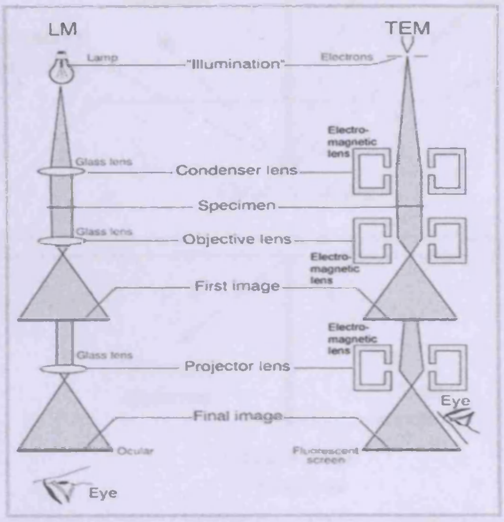


Figure 2.5 Comparison between the optical microscope and TEM [9]

An electron gun at the top of the microscope emits the electrons which pass through a condenser consist of electromagnetic lenses to focus the electrons into a thin beam. After the beam hits the sample, several different types of electron are reflected from the sample surface and disappear (Fig. 2.6). The electrons which transmitted through the sample are magnified by the electromagnetic lenses and then hit fluorescent screen at the bottom of the microscope which used to generate the TEM image. The image can be studied by the operator directly or photograph with a camera. The contrast observed on the TEM image reflections are the interaction between the transmitted electrons and different atoms in the sample. Based on the density of the atom (typically, metals has a higher electrons density than supports, therefore they appear darker in the TEM image (Fig. 2.7)).

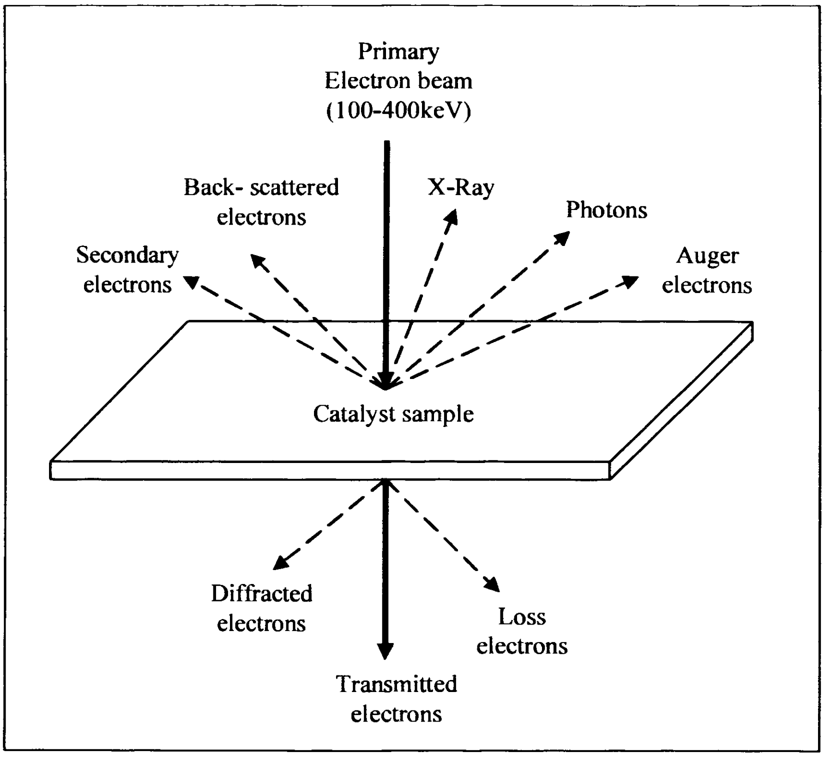


Figure 2.6 Interactions between electrons and specimen

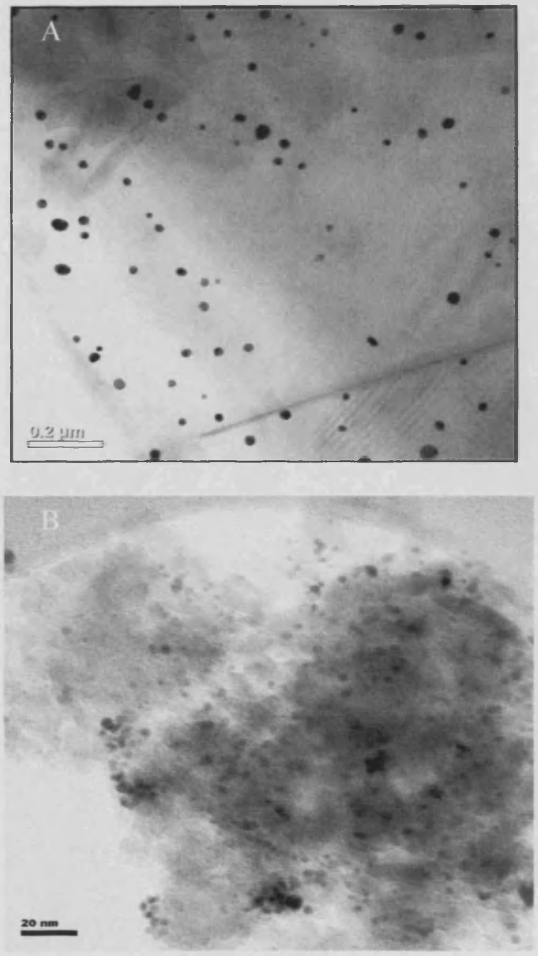


Figure 2.7 TEM image of supported catalyst (a: Au/graphite, b: Pt/SiO_2)

Despite the enormous application of TEM there are a number of drawbacks. The interaction between the highly energetic electron beam and the sample within the electron microscope are always likely to result in permanent structural modification. The extensive preparation of the sample to produce a thin layer to be electron transparent makes TEM analysis time consuming. Due to the relatively small view field, it is possible that the region analysed may not be representative for the whole sample. In spite of these limitations, transmission electron microscopy is one of the techniques most often used for the characterization of catalysts because of it high resolution.

2.4.2. Scanning Electron Microscopy (SEM)

The first modern scanning electron microscope was described by Zworykin *et al* [10].. Similar to transmission electron microscopy (TEM), scanning electron microscopy (SEM) is another kind of electron microscopy using electrons as an alternative of light as source to image the target. Table 2.1 shows the main difference between TEM and SEM (Fig. 2.8).

Table 2.1 comparison between SEM and TEM

SEM	TEM
Electron beam scans over surface of sample	Electron beam passes through thin sample
Sample can be any thickness and is mounted on an aluminium stub	Specially prepared thin samples or particulate material are supported on TEM grids
Specimen stage in the chamber at the bottom of the column.	Specimen stage halfway down column.
Image shown on TV monitor.	Image shown on fluorescent screen
Image is three dimensional of the surface of the sample with lower resolution	Image is a two dimensional projection of the sample with higher resolution

In a typical SEM (Fig. 2.8), an electron beam is emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses that are able to focus and direct the beam toward the sample. When the primary electron beam interacts with the sample (Fig. 2.6), three types of electronic signals emitted from the surface of the specimen: 1) backscattered electrons, 2) secondary electrons and 3) Auger electrons. The first two signals are used in the SEM while the third signal is used in Auger scanning microscope. The de-excitation of atoms also produces a photon within the emission domain ranging from the x-ray to the visible [11]. The secondary electrons are low energy secondary electrons detected by attracting them onto a phosphor screen, and measuring the light intensity with a photomultiplier. Some of the beam's electrons strike atomic nuclei and bounce back. These electrons, known as backscattered electrons, give information on the surface topography and on the average atomic number in the scanned area. The surfaces that face the detector appear brighter than those set at an angle, creating contrast in the image. As the secondary electrons originate from the surface, whereas the backscattered electrons arise from the bulk, SEM gives a "3D" image of the sample. One of the important analytical tool associate SEM is energy dispersive X-ray emission (EDX). By the combination of SEM and EDX elemental analysis can be performed. In EDX technique the elemental analysis is attained by collecting the X-ray emitted from the sample during the interaction of the beam with sample's atoms. X-rays with characteristic energy is emitted by each component in the sample. The signals are displayed as peaks and the intensity of the peak is related to the amount of the component present in the sample.

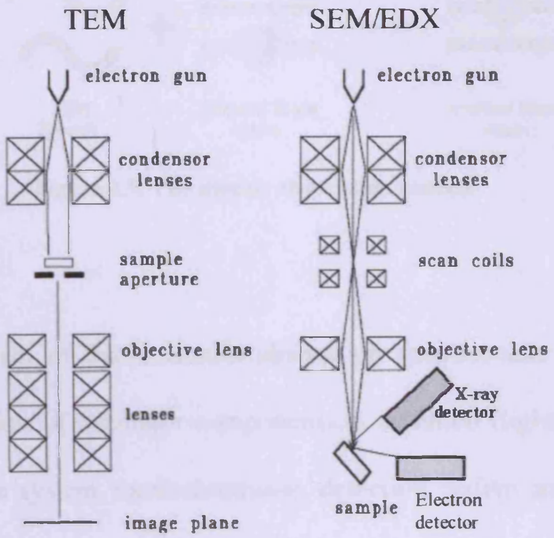


Figure 2.8 Comparison between TEM and SEM/EDX [12]

2.4.3. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a widely used and accepted technique capable of determining trace levels of elements or metals. Optical spectroscopy can be traced to 1672, when Newton observed that sunlight could be separated into colors upon passage through a prism. AAS was first developed independently by Walsh, Alkemade and Melatz in 1950s [13]. AAS involved the measurement of absorption of optical radiation by atoms in the gaseous state and can be used to analyse the concentration of over 62 different metals in a solution. Atomic absorption is the absorption of light by atoms. An atom has several energy levels. Under normal circumstances, most atoms will be in the ground state. For the energy levels E_o (ground state) and E_I (Excited state), a transition from $E_o \rightarrow E_I$ represent an absorption of radiation (Fig. 2.9). As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way.

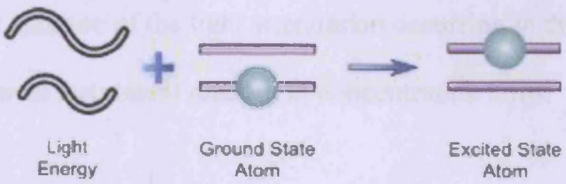


Figure 2.9. The atomic absorption process

A schematic diagram of flame atomic absorption spectrometer is shown in Figure 2.10. It essentially consists of six major components: a radiation (light) source, flame atom cell, sample introduction system, monochromator, detection system and readout. *Radiation source:* the most widely used and accepted radiation source in AAS is the line source, in particular the hollow cathode lamp (HCL). Typically, HCL is a line source, with each new metal or element to be determined requiring a separate lamp. Hollow cathode lamp consist of a glass envelope filled with inert gas, usually neon, argon, or helium, at a pressure of 1 to 5 Torr and the hollow cathode made of the pure metal of interest and the anode is made of tungsten. *Flame atom cell*: the sample is usually introduced to the flame as a fine mist or aerosol. Flames consist of an oxidant and a fuel. The most widely used flames in AAS are air-acetylene (2500 K) and nitrous oxide-acetylene (3200 K). The primary object of the flame is to dissociate the molecule into atoms. Monochromator: the principle function of a monochromator in AAS is to isolate the wavelength (radiation) of interest from the other wavelengths from the radiation source and light emitted by other elements in the flame. *Detecting system*: photomultiplier tube (PMT) is the detection system used most frequently in AAS. The PMT converts the photon flux into electron pulses which are then amplified. It is consist of a photoemissive cathode and several dynodes in a vacuum. The electrical current measured at the anode is directly proportional to the radiation reaching the PMT.

This electrical signal is a measure of the light attenuation occurring in the sample cell and is further processed to generate instrument readout in concentration units.

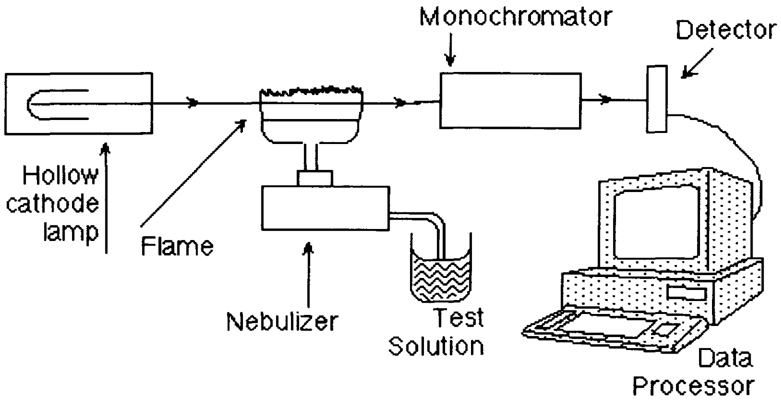


Figure 2.10 Schematic diagram of atomic absorption spectroscopy

Atomic absorption spectroscopy requires calibration with standards of known concentration to obtain accurate results. Calibration curve can be obtained by plotting absorbance as the dependent variable against concentration as the independent variable (Fig. 2.11). The concentration of the element to be determined can be readily derived from this calibration curve.

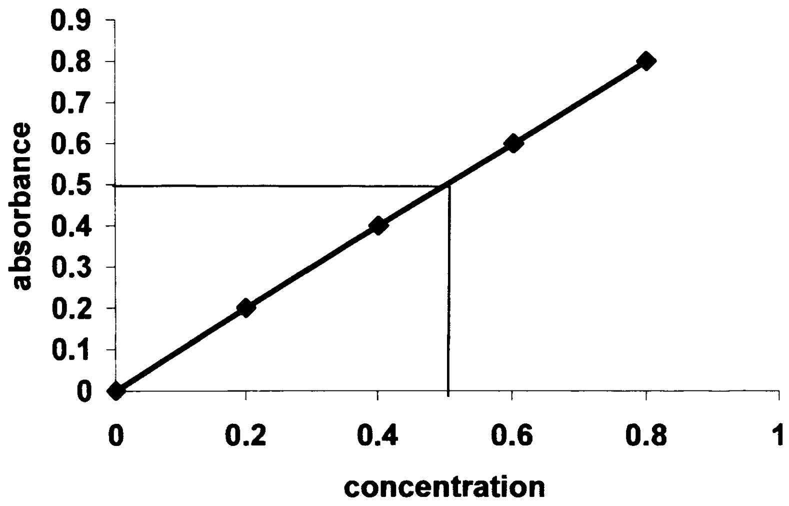


Figure 2.11 Example of a generic AAS calibration curve

2.4.4. Nuclear Magnetic Resonance (NMR)

The signal for Nuclear magnetic resonance (NMR) was first observed by two research groups in Harvard and Stanford universities independently in 1946 [14]. NMR is a technique used to identify the structural information of a compound, especially organic compounds. For NMR to occur, the nucleus of interest must have a non-zero spin angular momentum (I). ^{1}H, ^{13}C, ^{19}F and ^{31}P are some of the common nuclides which all have spin of I=1/2 therefore it have been used more frequently in NMR. On the other hand, ^{14}C and ^{12}C have I=0 which mean they are unable to be detected by NMR spectroscopy.

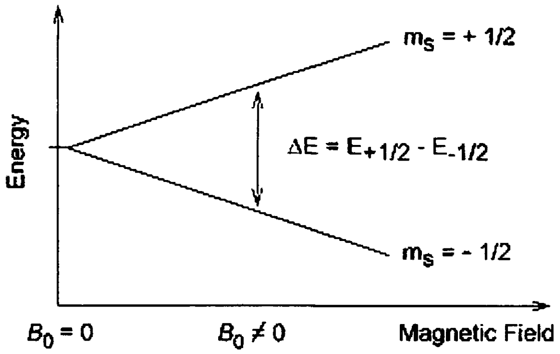


Figure 2.12 The magnetic field B_0 induce energy level splitting in nuclei

The nuclei of all elements carry a charge, when the spins of the proton and neutrons comprising are not paired, the overall spin of the charged nucleus generate a magnetic dipole along the spin axis the resulting spin-magnet has a magnetic moment (μ) proportional to the spin. Exposing the nuclei which display a static magnetic field to a second external magnetic field will produce nuclear magnetic resonance spectrum. The nucleus (with spin I=1/2) has two possible spin state: m=1/2 or m=-1/2 (Fig. 2.12). In the absence of a magnetic field they have the same energy. This degeneracy is removed when a magnetic field is applied. The magnetic moment of the lower energy state 1/2 is aligned with the external filed, but that of the higher energy -1/2 spin state is opposed to the external field. The nuclei can undergo a transition between the two energy states. The transition from the lower to the upper energy level corresponds to absorption of energy, and those in the reverse direction to an emission of energy. Both transitions are possible and equally probable. Due to the population excess in lower level, the absorption of energy is the dominant. In order for this transition to take place the energy of the photons in the electromagnetic field absorbed must exactly match the energy different between the two states (Equation 1). This observed as a signal proportional to the total number of spins in the sample and thus to the concentration.

$$\Delta E = h\nu = \frac{h\gamma}{2\pi} B_0 = h\nu_L$$

Equation 2 Resonance condition

Where: h=Planck's constant

ν = frequency of the applied magnetic field

γ = magnetogyric ratio

B_0 = intensity of applied magnetic field

ν_L =Resonance nuclei frequency

One important feature of NMR is chemical shift. Chemical shift arise because the magnetic field at the nucleus is not equal to the applied magnetic field. Electrons around the nucleus shield it from the applied field. The difference between the applied field and the field at the nucleus is called nuclear shielding. Chemical shift is defined as nuclear shielding / applied magnetic field. Another important feature of NMR is spin-spin coupling which arise from the interaction between neighboring magnetic dipole in a molecule.

There are three essential requirements for an NMR experiment: a strong static magnetic field, a source of radiofrequency radiation to excite nuclei in the sample and a method for detecting the NMR signal (Fig. 2.13)

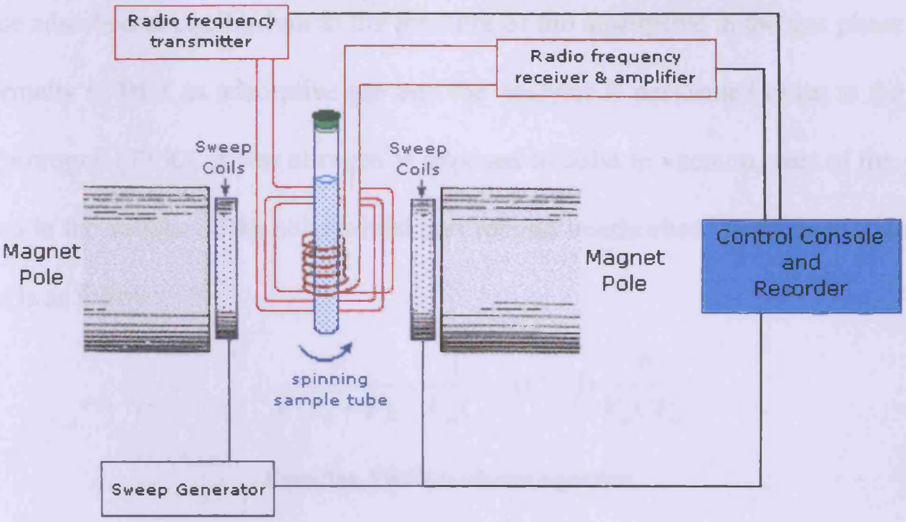


Figure 2.13 Schematic diagram of NMR

2.4.5. BET Surface area analysis

In 1938, Braunauer, Emmett and Teller described a method to determine the surface area for solid materials [15]. This method, abbreviated to the BET method is one of the most common techniques for measuring surface area and widely used in catalysts characterization. BET is based on 3 assumptions:

1- The surface of the adsorbent is flat.

2- There are no lateral interactions.

3- All adsorption occur through the same mechanism.

The total surface area of a solid is related to the volume of gas that is adsorbed on this surface at a given temperature and pressure. There are several theoretical derivations of adsorption isotherm (the function which relates, at constant temperature, the amount of substance adsorbed at equilibrium to the pressure of the adsorptive in the gas phase.). N_2 is used normally in BET as adsorptive gas and the analysis is performed close to the boiling point of nitrogen (77 K). When nitrogen is exposed to solid in vacuum, part of the gas will adsorb on to the surface of the solid whilst part remain unadsorbed. In these condition BET equation is as follow:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + (C-1)\frac{P}{V_m C P_0}$$

Equation 3 BET isotherm equation

Where: P= pressure of nitrogen

V_m= volume of the monolayer of adsorbed gas.

V= volume of adsorbed gas.

P= equilibrium gas pressure

P_0= normal vapor pressure of the adsorbate

C= constant correlated with ΔH of the adsorption process

By plotting $P/V(P_0-P)$ against P/P_0 this should give straight line from which we can determine V_m and C values. The surface area is correlated to V_m by the following equation:

$$SA = V_m N_a \sigma / M V_0$$

Equation 4 surface area equation

Where: SA= surface area

N_a= Avogadro number

V_0= molar volume of gas

M= mass of the sample

σ= area of adsorbate = 0.162 m^2 at 77 K.

2.4.6. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is the study of weight changes of a specimen as a function of temperature. Figure 2.14 represent schematic diagram for typical TGA instrument.

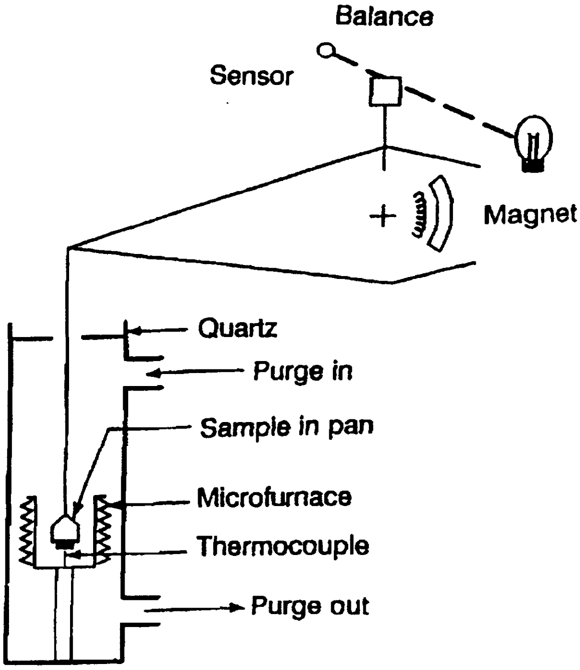


Figure 2.14 Schematic diagram of TGA

TGA consists of essentially: (i) an automatic magnetic re-equilibrating balance with continuous recording of the signal which is capable of detecting weight change as small as 0.1 µg. (ii) A furnace in which the required temperatures can be generated, the heating range from room temperature to 1000 °C. TGA must use high temperature inert sample holders, and quartz, ceramic material and platinum are the most commonly used. A thermocouple passes through the base of the furnace in close proximity to sample but not in contact, so as not to interfere with the free float of the balance and to provide an accurate sample temperature measurement. (iii) A gas flow circuit for controlling the gases environment, an inert atmosphere (N_2, He) or a reactive atmosphere (O_2, H_2).

2.4.7. X-ray Photoelectron Spectroscopy (XPS)

XPS was developed in the mid 1960s by K. Siegbahn and his group. Siegbahn was awarded the noble prize in 1981 for his extensive work in developing XPS to a useful analytical technique [16]. XPS, is also known as electron spectroscopy for chemical analysis (ESCA) and is a useful technique to study the surface composition and oxidation state. Furthermore, it can be used to study the dispersion of supported catalysts. The basic principle for this technique relies on the photoelectronic effect. When a photon (with energy = hv) hit the sample (Fig. 2.15) it interacts with the inner shell electrons and ionizes the atom, producing an ejected free electron with kinetic energy E_{kin} (Equation 5).

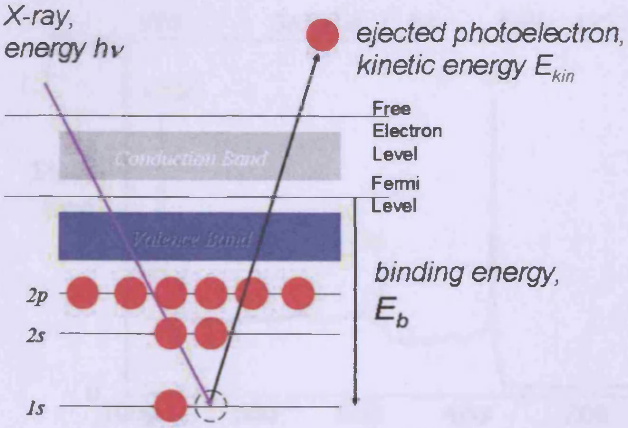


Figure 2.15. Ejected electron by x-ray photon

$$E_{kin} = h\nu - E_b - \varphi$$

Equation 5 Kinetic energy of the ejected electron

Where: hν = the energy of the photon
E_b= electron binding energy
Φ = correction factor

The difference between the photon energy and the ejected electron kinetic energy is approximately equal to the binding energy of that electron. The correction factor (φ) in general is less than 2eV and often ignored. Binding energies of electrons are fully characteristic of element from which the photoelectron originates. Therefore, each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies (Fig. 2.16). The intensity of the peak is related to the concentration of the element in the sample. The electron activated energy varies with oxidation state of a certain element, as the electrons of a cation are bound more strongly than those of a natural atom.

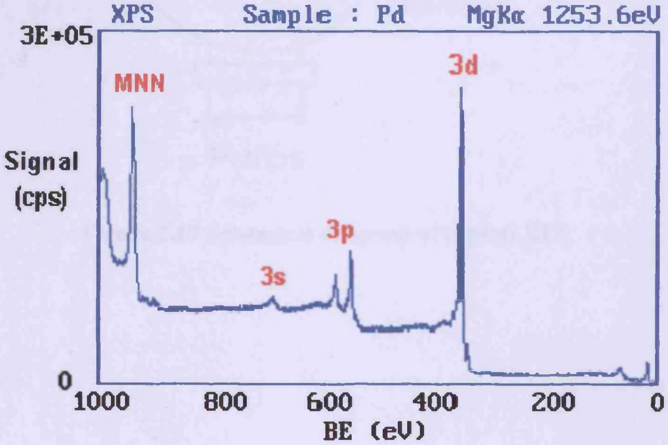


Figure 2.16 Example of XRD spectra for Pd metal

XPS instrument consist of: (i) A fixed X-ray source (the most common x-ray source are Aluminum Kα 1486.6eV and Magnesium Kα 1253.6Ev). (ii) An electron energy analyzer which can disperse the emitted electrons according to their kinetic energy. The most used electron energy analyzer is a concentric hemispherical analyzer (CHA). (iii) A high vacuum environment is required to perform XPS experiment which enables the emitted photoelectron to be analysed without interference from gas phase collision. Figure 2.17 illustrated schematic diagram of typical XPS instrument.

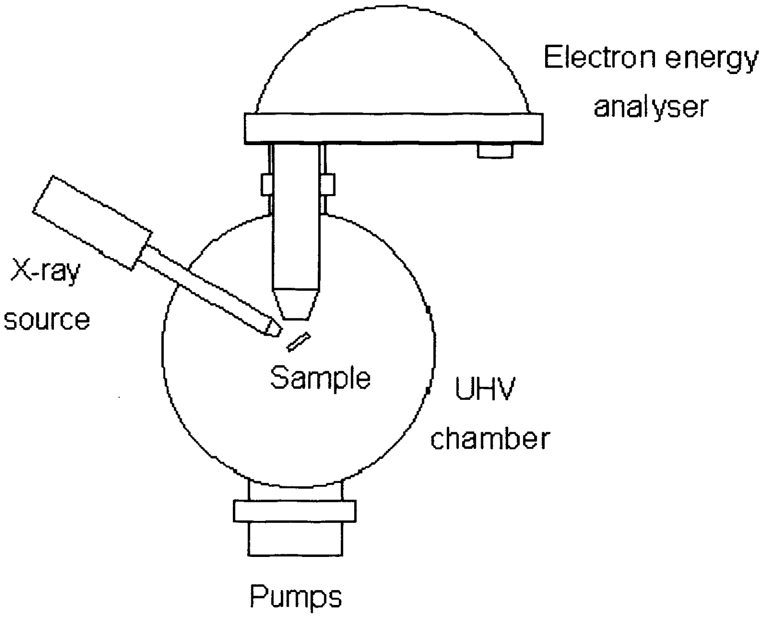


Figure 2.17 Schematic diagram of typical XPS

2.5. ***Reference***

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Chapter Three

Influence of Radical Initiators on Cyclooctene Epoxidation

3. Influence of Radical Initiators on Cyclooctene Epoxidation

3.1. ***Introduction***

Oxidation is one of the major pathways for the synthesis of chemical intermediates. The epoxidation of alkenes by the electrophilic addition of oxygen to a carbon-carbon double bond remains one of the most significant challenges in oxidation. Selective epoxidation of alkenes represents a very intriguing topic in heterogeneous catalysis and the as-formed epoxides are of great commercial and synthetic significance. Of key importance is the use of oxygen as the oxidant, however, in many cases more reactive and less environmentally friendly, sources of oxygen are used. The introduction of catalytic systems using oxygen from air is attractive and presents immense scope for minimising waste and generating green chemical processes. Since the breakthroughs in the 80s regarding the catalytic use of gold [1, 2], the applications of gold for selective oxidation of hydrocarbon have been widely reported. Even though the oxidation of hydrocarbon using radical initiator has been reported by many research groups [3-11], very little effort has been devoted to understand the effect of radical initiator on hydrocarbon oxidation in the absence of the catalyst.

The oxidation of cyclooctene using oxygen from air and radical initiator will be examined in this chapter. The importance of identifying background reactions in the absence of the catalyst will be discussed. The effect of radical initiator choice in cyclooctene oxidation will be conferred.

3.2. Results and discussion

3.2.1. Reactions in the absence of catalyst

Since we are seeking to oxidise cyclooctene with molecular oxygen it is important we determine the reactions that occur in the absence of catalyst. Molecular oxygen is a diradical in its ground state thus it can participate in radical reactions in the absence of a catalyst, especially in the presence of radical initiators.

Hughes and co-worker reported non-selective conversion of cyclooctene in the absence of catalyst [5]. These non-catalysed reactions can often lead to lower selectivities and can, in the extreme cases; mask any catalytic reaction that may be occurring. Hence, the need to determine reaction conditions where no reaction occurs either in the absence of the catalyst or the undoped support.

3.2.2. Radical initiator

In a general sense organic molecules are stable at moderate (~27-127 °C) and elevated (>127 °C) temperatures. Atoms of these compounds are connected by strong chemical bonds with bond dissociation energy (BDE) ~350-500 kJ mol^{-1}. Radical initiators are molecules bearing one weak bond with a low BDE ~100-200 kJ mol^{-1} for example a covalent bond between two oxygen atoms (O-O) [12]. When the temperature of the reaction is sufficiently high, the weakest bond of the radical initiator decomposes *via.* homolysis and produces free radicals. Many free-radical reactions are generated by the addition of this free radical. Organic peroxide is a very versatile source of radicals that at the right temperature will cleave in O-O bond and produce two oxygen-centered radicals. However, these oxyl radicals are rather unstable and believed to be transformed into relatively stable carbon-centered radicals.

3.2.2.1. Radical initiator choice

Hughes and coworkers [5] reported the potential of using 1%Au/graphite as catalyst for cyclooctene epoxidation using *tert*-butylhydroperoxide (TBHP) as radical initiator at 80 °C. To determine the effect of TBHP concentration on cyclooctene epoxidation in the absence of the catalyst a series of concentration of TBHP was studied at different temperatures (Table 3.1). At low TBHP concentration (0.01×10^{-2} mol) there was no activity even at high temperature. Increasing the concentration resulted in an increase in activity at all studied temperature to reach 0.68% conversion and 66.8% selectivity at 80°C.

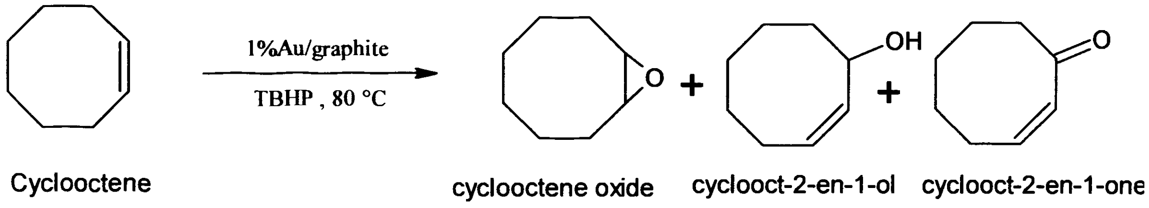

Figure 3.1 Cyclooctene oxidation using 1%Au/graphite and TBHP

Table 3.1 Effect of TBHP concentration on cyclooctene epoxidation at different temperatures.

TBHP/ Mol x10^{-2}	60 °C		70 °C		80 °C	
	Conversion /%	Selectivity (epoxide) / %	Conversion /%	Selectivity (epoxide) / %	Conversion /%	Selectivity (epoxide) /%
0.103	0.04	0	0.11	16.1	0.68	66.8
0.083	0.03	0	0.05	0	0.17	59.5
0.052	0.03	0	0.04	0	0.12	36.9
0.031	0.03	0	0.04	0	0.04	58.3
0.026	0.03	0	0.04	0	0.09	4.3
0.012	0	0	0.02	0	0.04	0
0.0103	0	0	0.02	0	0.04	0

[a] Reaction conditions: cyclooctene (10 ml, 0.077 mol), 24 h, atmospheric pressure.

Four different types of radical initiators (Fig. 3.1) were investigated at 80 °C with alkene/initiator mol ratios between 74.6 and 746, to determine the effect of nature of radical initiator on cyclooctene oxidation and the results are shown in Table 3.2. Tert-butylhydroperoxide (TBHP) and cumene hydroperoxide (CHP) are examples of hydroperoxide radical initiator. Di-t-butyl peroxide (DTBP) and benzoyl peroxide (BPO) are example of dialkyl peroxide and diacyl peroxide, respectively. Azo radical initiators were represented by azobisisobutyronitrile (AIBN). In the absence of the catalyst, CHP was active at all the concentrations evaluated and gave the epoxide with *ca.* 64-70% selectivity. TBHP and DTBP were inactive at the lowest concentration evaluated, but were active at higher concentrations, albeit that TBHP was more selective. The most active radical initiators at all concentrations studied were BPO and AIBN.

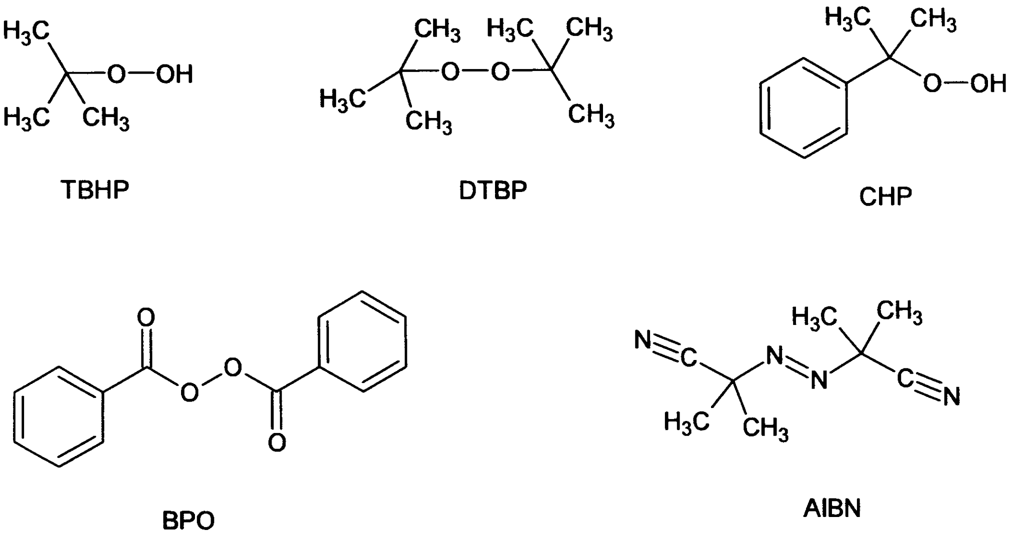

Figure 3.2 Structure of radical initiators used in this study

The addition of the catalyst to the reaction mixture differs in its effect by changing the radical initiator (Table 3.2). Dramatic increase in activity and selectivity of the reaction using TBHP as initiator was observed by addition of 1%Au/graphite as catalyst. Activity was observed to increase when using CHP. There was no effect for the catalyst when used with DTBP or AIBN. In contrast to TBHP, the use of the catalyst with BPO resulted in a small decrease in activity. It can be seen from Fig. 3.3 that TBHP can undergo decomposition to generate a variety of radicals which can initiate the oxidation of cyclooctene on a gold surface. The homolysis of O-H bond in TBHP will result in $Me_3COO^\cdot$ which is very active in abstracting the hydrogen from the allylic position in hydrocarbons. The dissociation energy for O-H is greater than that for O-O bond (358.6 kJ mol^{-1} and 182.5 kJ mol^{-1} respectively) [12]. Due to the high energy for O-H homolysis, in the absence of the catalyst, the concentration of $ROO^\cdot$ may be low however; in the presence of the catalyst the gold surface may facilitate the O-H homolysis which could explain the higher activity observed. Of the initiators examined, CHP, AIBN and BPO have the lowest reported activation energy [12] for homolysis (126, 123.4 and 123.8 kJ mol^{-1} respectively in benzene as a solvent) and are probably the most susceptible to radical-induced decomposition which may explain the high activity of these radicals initiators in the absence of the catalyst. DTBP is reported to have higher activation energy (E_a = 162 kJ mol^{-1}), therefore, the lack of activity using DTBP could be linked to the high activation energy. Moreover, the decomposition of DTBP would only generate $Me_3CO^{\bullet}$ radicals which may not have a strong role in cyclooctene oxidation. To gain more insight on the role of the initiator, TBHP, AIBN and BPO where tested in three reaction temperatures and the results are shown in Table 3.3.

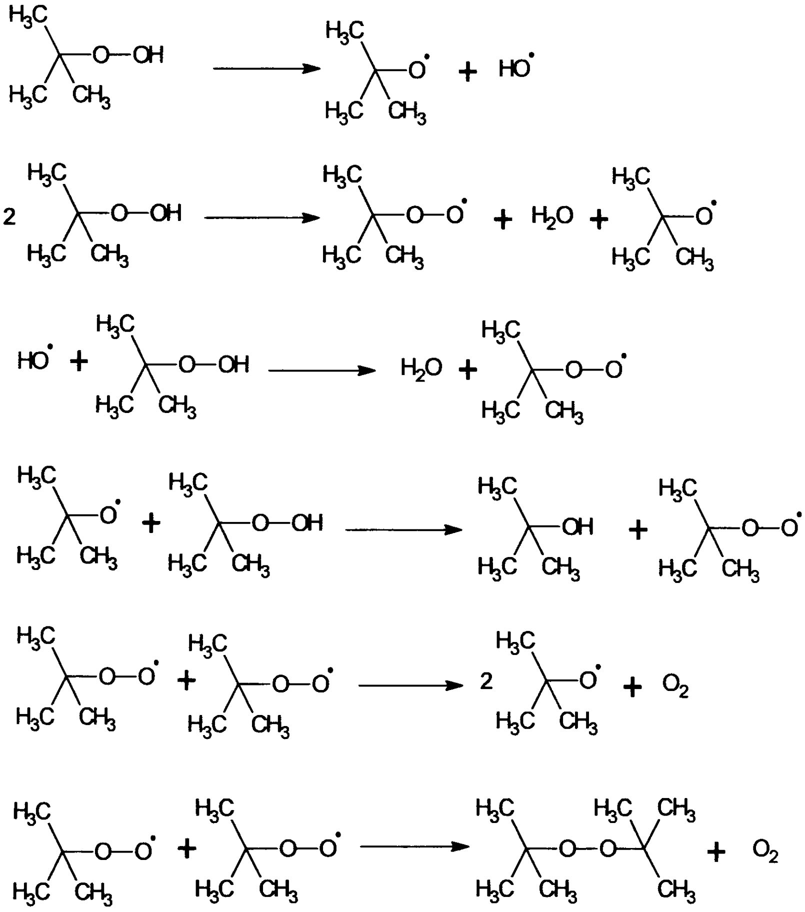

Figure 3.3 TBHP decomposition [12]

Table 3.2 Cyclooctene epoxidation using five different radical initiators.

Peroxy initiator /mol x 10^{-2}		Without catalyst [a]		With 1% Au/graphite [b]	
		Conversion/ %	Selectivity (epoxide)/%	Conversion/ %	Selectivity (epoxide)/%
TBHP	0.1032	0.7	66.8	8.5	78.7
	0.0516	0.1	36.9	6.6	78.7
	0.0103	0.02	0	4.0	78.2
CHP	0.1032	7.0	68.9	8.1	63.9
	0.0516	3.9	69.8	5.8	73.2
	0.0103	1.3	64.1	2.9	79.3
DTBP	0.1032	0.91	36.9	0.5	3.9
	0.0516	0.3	8.0	0.3	0
	0.0103	0.04	0	0.04	0
AIBN	0.1032	7.8	81.1	7.6	75.9
	0.0516	6.3	85.4	5.8	80.5
	0.0103	4.1	82.4	4.1	80.7
BPO	0.1032	8.4	77.1	5.6	79.5
	0.0516	8.9	78.1	5.1	79.7
	0.0103	5.6	83.5	3.3	79.4

[a] Reaction in the absence of catalyst: cyclooctene (10 ml, 0.077 mol), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Table 3.3 Effect of temperature on cyclooctene epoxidation using three different radical initiators.

Temperature / °C			60			70			80		
Peroxy initiator concentration/ mol x10^{-2}			0.010	0.052	0.103	0.010	0.052	0.103	0.010	0.052	0.103
TBHP	Without catalyst[b]	Conversion/ %	0	0.03	0.04	0.02	0.04	0.11	0.04	0.12	0.68
		Selectivity (epoxide)/ %	0	0	0	0	0	16.1	0	36.9	66.8
	With 1%Au/ graphite[a]	Conversion/ %	0.6	1.6	1.9	1.9	2.6	3.9	4	6.6	8.5
		Selectivity (epoxide)/ %	63.9	64.2	68.3	72.3	72.3	71.4	78.2	78.7	78.7
AIBN	Without catalyst[b]	Conversion/ %	0.28	0.85	1.4	1.2	2.6	3.6	4.1	6.3	7.8
		Selectivity (epoxide)/ %	74.7	73.5	70.3	74.5	77.7	79.8	82.4	85.4	81.1
	Withy 1%Au/ graphite[a]	Conversion/ %	0.08	0.85	1.2	1.2	2.9	3.1	4.1	5.8	7.6
		Selectivity (epoxide)/ %	94.9	73.5	69.5	77.7	81.1	84.5	80.7	80.5	75.9
BPO	without catalyst[b]	Conversion/ %	0.36	1.8	2.3	2.7	5.9	8.2	5.6	8.9	8.4
		Selectivity (epoxide)/ %	80.4	77	77.2	76	79.7	84.4	83.5	78.1	77.1
	With 1%Au/ graphite[a]	Conversion/ %	0.22	1.3	2.4	1.5	2.2	2.2	3.3	5.05	5.6
		Selectivity (epoxide)/ %	80.9	78.07	77.6	75.5	78.7	83.5	79.4	79.7	79.5

[a] Reaction in the absence of catalyst: cyclooctene (10 ml, 0.077 mol), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Table 3.3 shows that by increasing the reaction temperature, the conversion and epoxide selectivity was increased with all three radical initiators. AIBN and BPO show high activity and good selectivity toward the epoxide even at low temperatures and low initiator concentrations. However, after the addition of the catalyst the activity of these two initiators remains unchanged at all temperatures studied. On the other hand, TBHP exhibits no activity at low temperature. At higher temperatures and higher concentrations TBHP shows sign of activity. The addition of the catalyst induced activity and selectivity at all temperatures studied for TBHP. The high activity of BPO and AIBN compared to TBHP in the absence of catalyst could be explained by the quicker formation of radicals in the reaction in the case of AIBN and BPO. Figure 3.4 shows that BPO and AIBN will decompose to give radical species quicker than TBHP at the reaction temperature of 80 °C (AIBN has a 10-hour half life at 65 °C, BPO have 10-hour half life at 70 °C and TBHP have 10-hour half life at 170 °C).

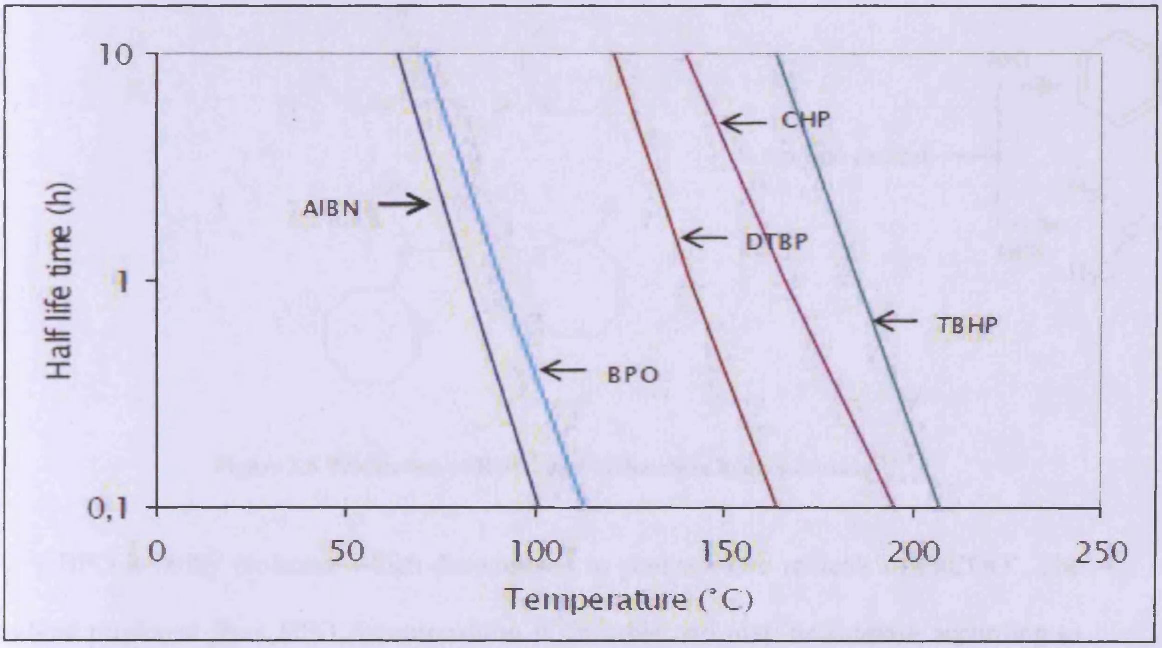

Figure 3.4 half life times of radical initiator as function of temperature [13]

Furthermore, the type of radical produced from the homolysis of TBHP, AIBN and BPO is different. AIBN and BPO will decompose to produce $R^{\bullet}$ radical (Fig. 3.6 and 3.7) which could interact with oxygen and produce $ROO^{\bullet}$(Fig. 3.5). Abstraction of hydrogen from hydrocarbons with $ROO^{\bullet}$ and producing cyclooctene hydroperoxide is facile. The produced hydroperoxide could then initiate cyclooctene oxidation. In contrast, in the absence of gold catalyst, TBHP may decompose to yield an $RO^{\bullet}$ radical which could have poor activity in initiating cyclooctene oxidation. However, the presence of gold would facilitate the homolysis of TBHP to produce $ROO^{\bullet}$ radical hence the improved activity.

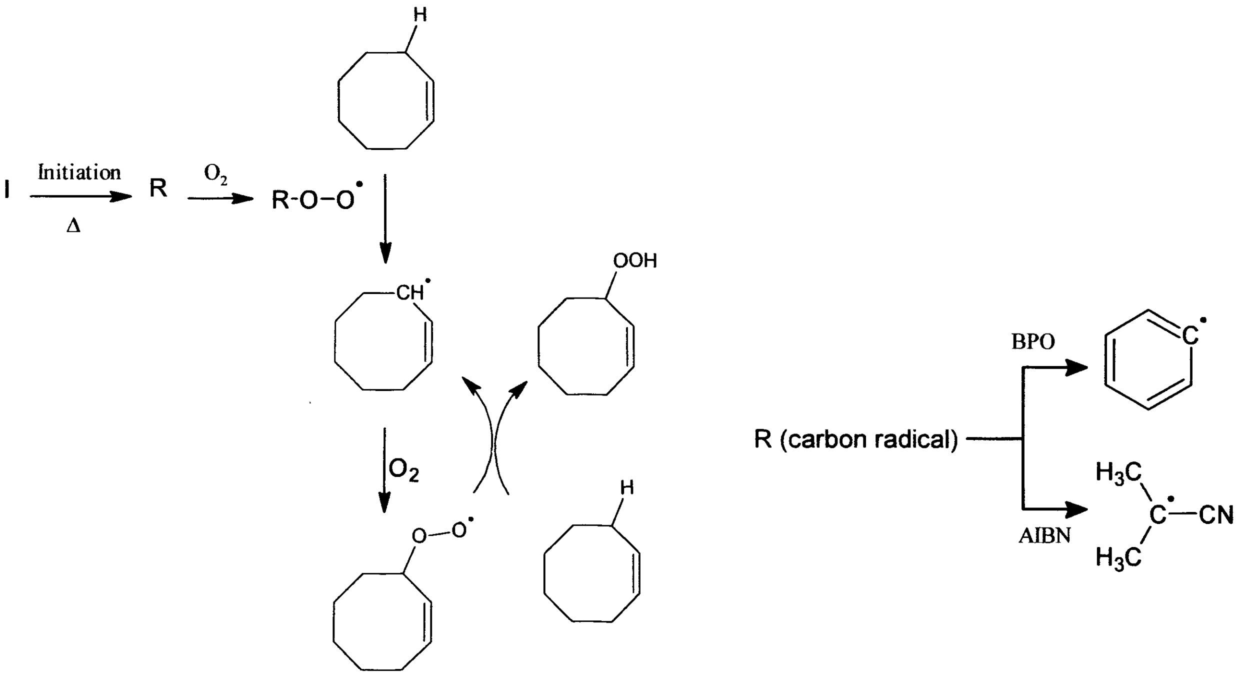

Figure 3.5 Production of $ROO^{\bullet}$ and cyclooctene hydroperoxide

BPO is bulky molecule which decomposes to generate two radicals of $PhCOO^{\bullet}$. The radical produced from BPO decomposition is unstable and may decompose according to figure 3.6 to generate CO_2 along with a phenyl radical. Due to the bulkiness of BPO and the generated radicals, in the presence of gold, the benzene ring may adsorb on the surface of the catalyst and poison the surface. Furthermore, $PhCOO^{\bullet}$ could abstract a proton from the alkene and produce benzoic acid which has been reported to poison the gold surface [14, 15]. Therefore, cyclooctene oxidation over a gold surface may not be observed using BPO as radical initiator and the activity could only come from the homolysis of BPO.

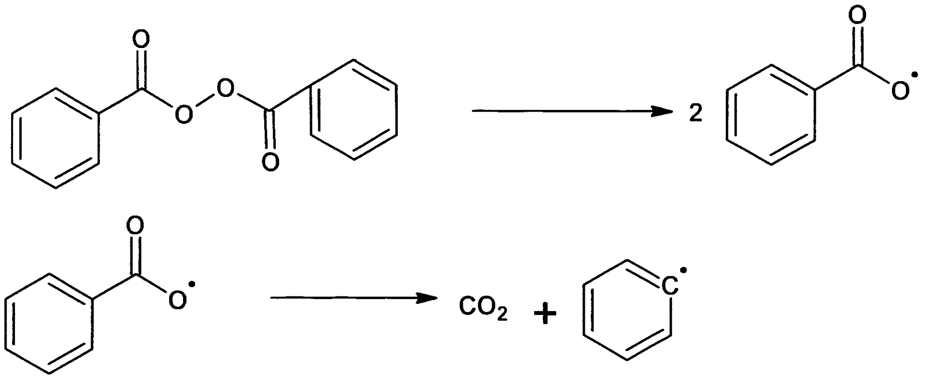

Figure 3.6 BPO decomposition [12]

AIBN decomposes to produce nitrogen and 1-cyano-1-methylethyl radical (carbon centre radical) (Fig. 3.7). The rate at which carbon centre radical ($R^{\bullet}$) react with oxygen to produce $ROO^{\bullet}$ and consequently initiate cyclooctene oxidation can be fast. However, the rate of cyclooctene oxidation over gold surface is slow. Consequently, AIBN decomposition and reacting with oxygen to initiate cyclooctene oxidation could overwhelm the activity of the gold surface which may explain the identical results for the oxidation using AIBN with and without the catalyst (1%Au/graphite). Moreover, the role of gold, presumably, in the case of TBHP is to facilitate the production of ROO$^•$. This is not the case with AIBN as ROO$^•$ is produced by the fast interaction of R$^•$ and oxygen.

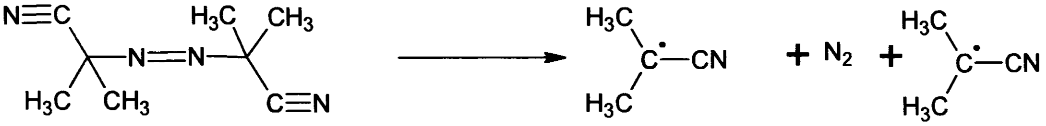

Figure 3.7 AIBN decomposition

Corma and co-workers reported alkene oxidation using AIBN and Au/CeO_2 with 12 bars of oxygen in the presence of cumene [3, 16]. According to the authors, AIBN is able to facilitate the production of cumene hydroperoxide over the surface of Au/CeO_2 which then epoxidized the alkene in the presence of oxygen (Fig. 3.8). CeO_2 is known to have abundant of lattice oxygen vacancies [17] such that CeO_2 can act as oxygen "pump". Thus the contribution of ceria oxide to the oxidation process is significant. Furthermore, the pressurized system (12 bars of oxygen) which the reaction is performed in greatly influences the oxidation process. In the current system, gold is supported on graphite which is inert to the oxidation of cyclooctene (further discussion on the role of support will be presented in chapter 4). In addition, with the current system, oxidation is performed under atmospheric pressure for (oxygen represents 21% of the volume of air) which may not be enough to produce the gold-peroxo intermediate on gold surface (Fig. 3.8). For those reasons, AIBN may not work with the gold in this system as the amount of oxygen present comparable to the system reported by Corma.

A common feature between BPO and AIBN is that both generate carbon centre radical which did not work with 1% Au/graphite for cyclooctene oxidation. Thus, TBHP was selected with concentration of 1.03×10^{-4} mol^{-1} as the standard concentration for the subsequent studies.

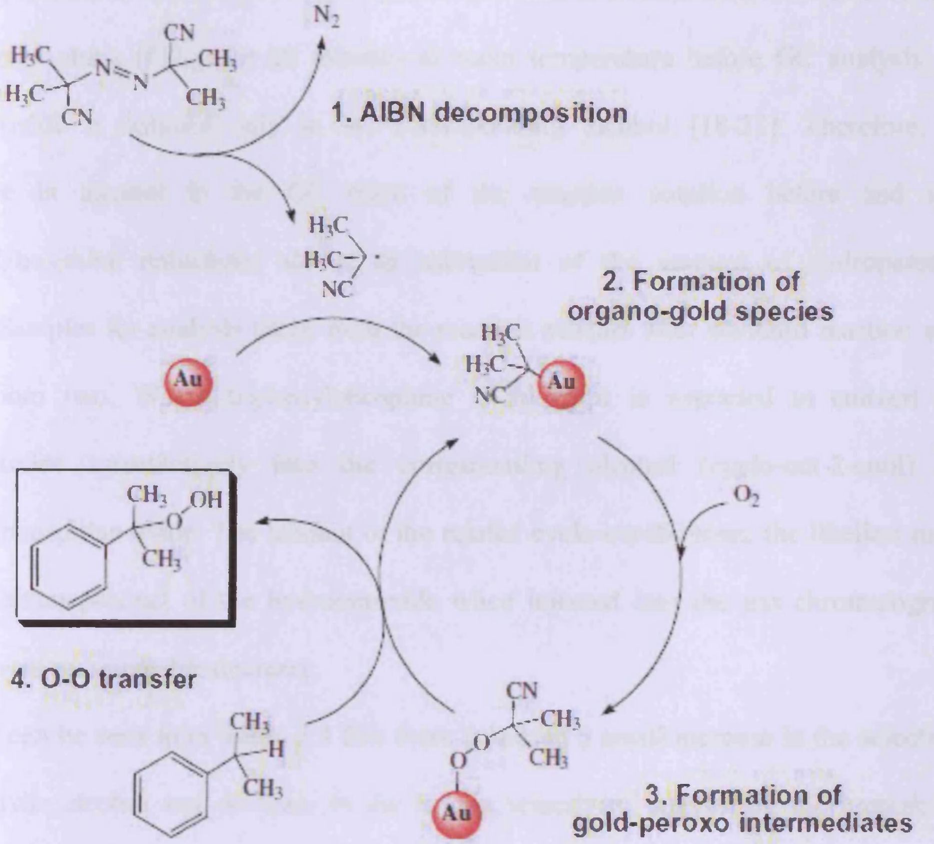

Figure 3.8 mechanism for the production of hydroperoxide in situ using AIBN and Au/CeO$_2$ for alkene oxidation [3].

3.2.3. Presence of cyclooctene hydroperoxide in the reaction

One of the possible products for alkene oxidation is the corresponding hydroperoxide [3] formed by the free radical reaction.

$$RH + O_2 \rightarrow ROOH$$

If RH is a hydrocarbon and RO_2H the corresponding hydroperoxide, the concentration of hydroperoxides (ROOH) in the reaction cannot be determined directly from the GC chromatograms. These compounds decompose in the GC injector due to the high temperature. If the sample of the reaction solution is treated with an excess of solid triphenylphosphine (PPh_3) for 20 minutes at room temperature before GC analysis, the hydroperoxide is reduced only to the corresponding alcohol [18-21]. Therefore, the difference in alcohol in the GC trace of the reaction solution before and after triphenylphosphine reductions allows an estimation of the amount of hydroperoxide present. Samples for analysis taken from the reaction mixture after standard reaction were divided into two. Where triphenylphosphine is added it is expected to convert any hydroperoxide quantitatively into the corresponding alcohol (cyclo-oct-2-enol) and triphenylphosphine oxide. The amount of the related cyclo-oct-2-enone, the likeliest major decomposition product of the hydroperoxide when injected into the gas chromatograph, should show a comparable decrease.

It can be seen from Table 3.4 that there is indeed a small increase in the selectivity to the allylic alcohol and decrease in the ketone selectivity, suggesting the presence of fairly low levels of the allylic hydroperoxide, as expected if it is formed and then consumed as an intermediate species in epoxidation. Direct confirmation of the presence of the hydroperoxide was obtained using ^1H NMR spectroscopy. Comparing ^1H NMR spectra of the peroxy with the spectra of the allylic alcohol, the difference in the chemical shift for the alpha-H (allylic position proton (Fig. 3.9)) should be around 0.3 ppm [22]. Examination of the spectrum of product samples, taken after 24 and 72 hours reaction without treatment and with triphenylphosphine, showed two multiplets (dt) centered at δ 4.63 and 4.93, the former arising from the proton on the allylic carbon atom bearing the hydroxyl group in authentic cyclo-oct-2-enol and the other assigned to the corresponding proton in the hydroperoxide. After phosphine treatment, the signal at δ 4.93 had disappeared (Figure 3.9). The addition of PPh_3 to the reaction crude in air or in N_2 atmosphere does have an effect in transfering the cyclo-oct-2-enyl hydroperoxide to cyclo-oct-2-enol.

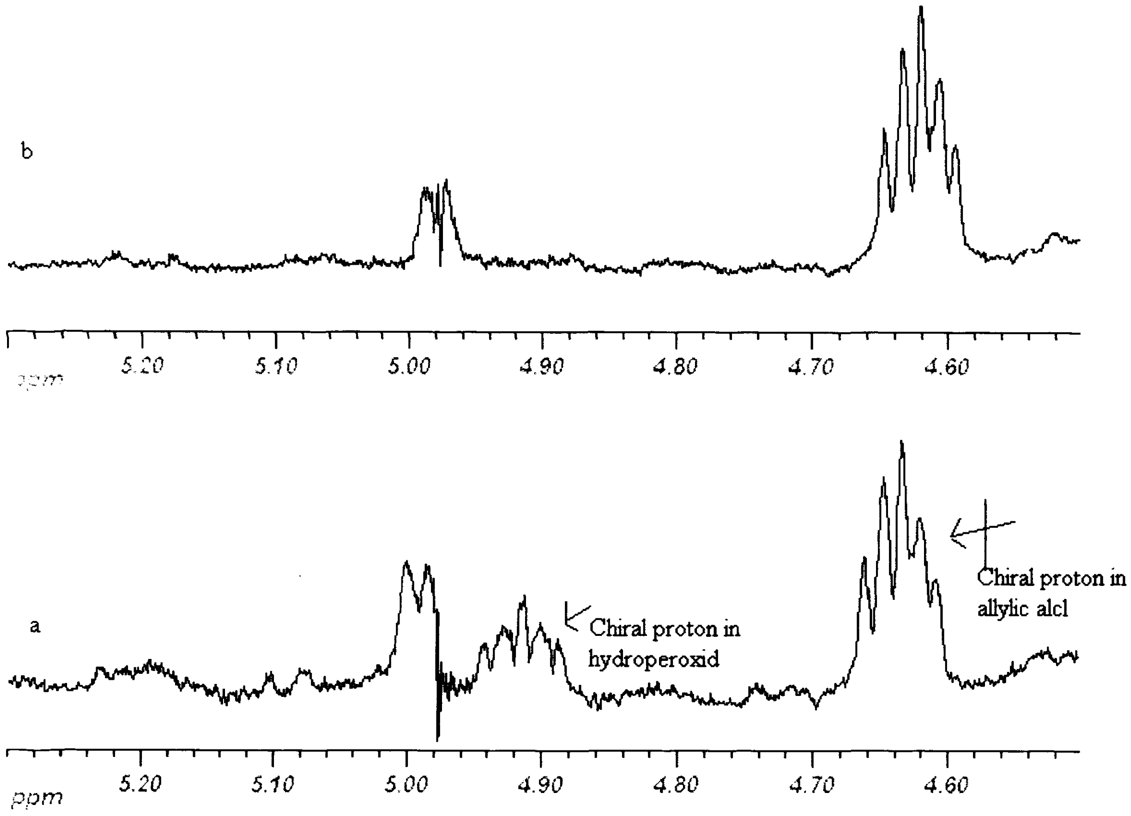

Figure 3.9 NMR spectrum for a: cyclooctene after 72 hour standard reaction without PPh_3 treatment, b: cyclooctene after 72 hour standard reaction with PPh_3 treatment

Table 3.4 Effect of addition of triphenylphosphine on alcohol selectivity in cyclooctene oxidation

Reaction time	Conversion %	Selectivity without PPh_3			Selectivity with PPh_3 in air			Selectivity with PPh_3 in N_2		
		epoxide	alcohol	ketone	epoxide	alcohol	ketone	epoxide	alcohol	ketone
24 h	4.9	74.3	8.3	6.4	71.4	13.0	4.2	71.0	13.0	4.2
72 h	20.3	77.3	5.4	5.4	75.6	7.3	4.8	76.6	7.0	4.7

Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 °C, atmospheric pressure.

Alcohol peroxide

Figure 3.10 Alpha-H in allylic position for peroxide and alcohol.

3.2.4. Time on line analysis

Time on line analysis was conducted for cyclooctene epoxidation using TBHP as radical initiator at 80 °C. It can be seen from Figure 3.11 that in the absence of the catalyst; the support (graphite) and radical initiator there was no reaction. Additionally, in the absence of gold, cyclooctene oxidation with only TBHP did not occur. Traces of activity start to appear by using graphite and TBHP in the reaction mixture. However, remarkable enhancement in activity was observed by the addition of 1% Au/graphite to the reaction mixture in the presence of TBHP. These results indicate that the direct addition of oxygen to cyclooctene in the absence of catalyst and radical initiator is not viable.

It can be seen from figure 3.11 that the high selectivity to the epoxide was maintained in these systems. The results at low conversion indicate that the cis-cyclooctene epoxide is formed initially and the other reaction products observed, such as alcohol and ketone, are the consequence of a sequential oxidation process. The time online curves demonstrate that the partial oxidation C_8 products are relatively stable in the present catalyst system. Analyzing the oxidation of cyclooctene using low (0.01x10-2 mol) and high (0.1 mol) TBHP concentration reveal the presence of induction period using low TBHP concentration (Fig. 3.12). This can be explained by the formation of cyclooctene hydroperoxide which oxidise cyclooctene. At low TBHP concentration at the beginning of the reaction the amount of alkene hydroperoxide produced is small and this increases by extending the reaction time. However, by using higher concentration of TBHP, the amount of $Me_3COO^{\cdot}$ present in the reaction media is higher which assists the increased production of cyclooctene hydroperoxide and thus the induction period is retarded.

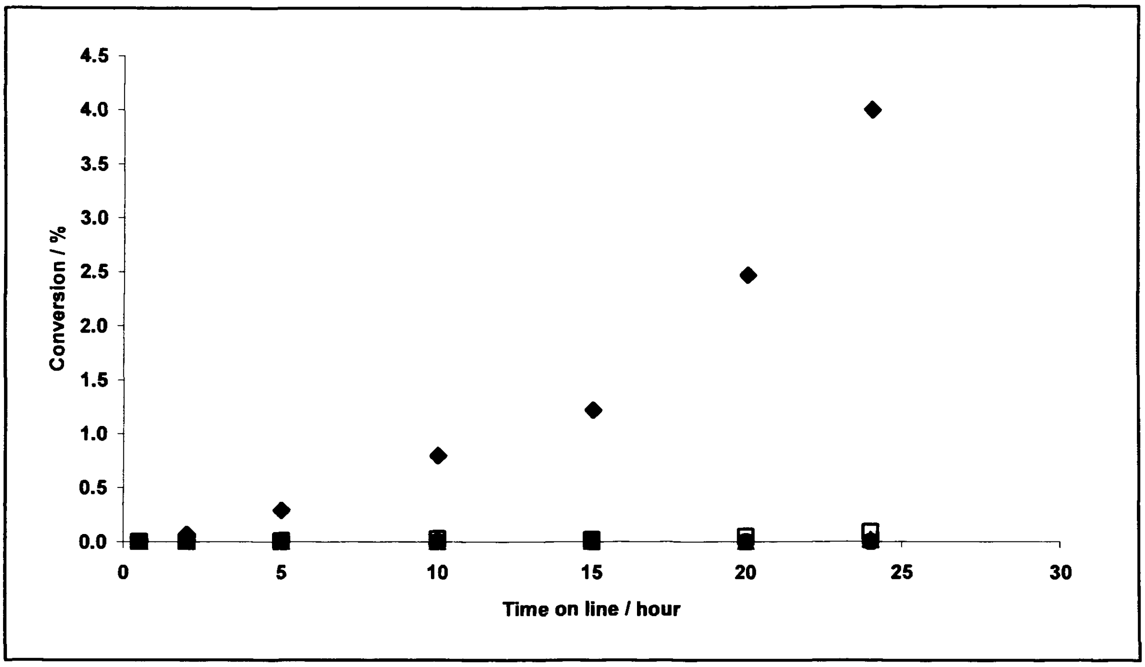

Figure 3.11 Time on line study for cyclooctene oxidation (conversion), (close diamond) 1%Au/graphite, (open square) graphite, (close triangle) TBHP, (open circle) cyclooctene, reaction conditions: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 °C, and atmospheric pressure.

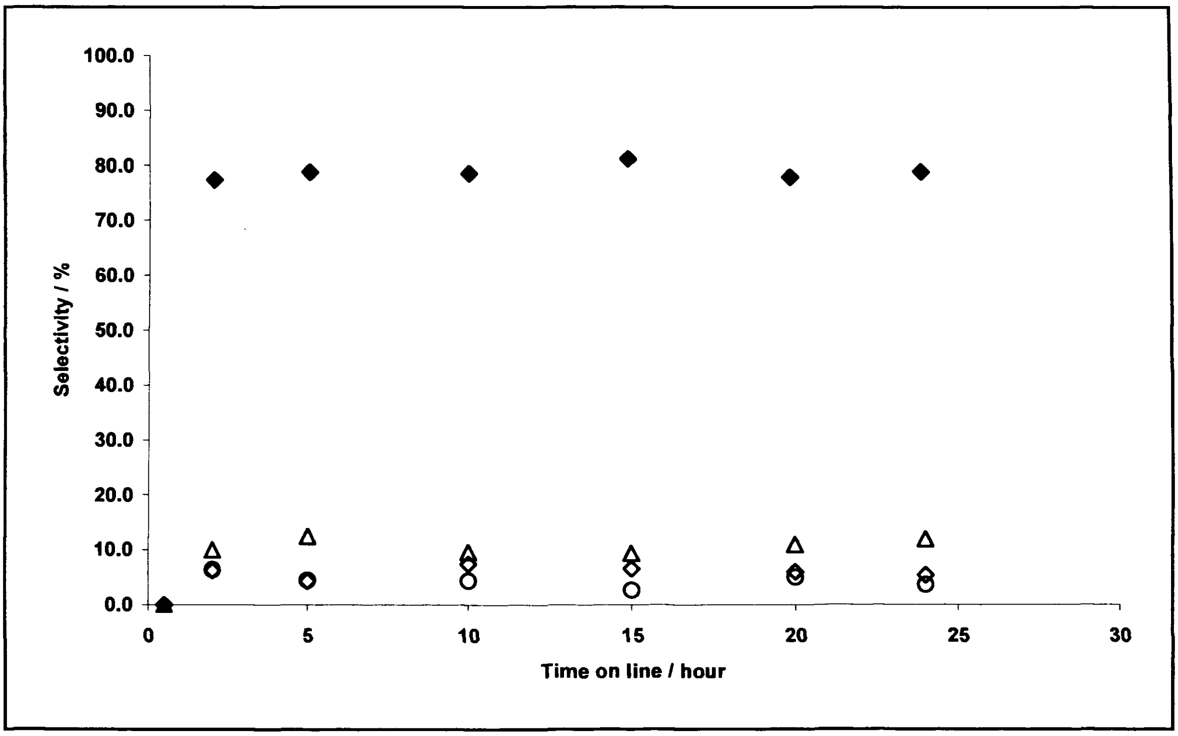

Figure 3.12 Time on line study for cyclooctene oxidation (selectivity), (close diamond) Epoxide, (open triangle) alcohol, (open diamond) ketone, (open circle) others, reaction conditions: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 °C, and atmospheric pressure.

3.2.5. 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 [23]. Figure 3.13 demonstrates that by increasing the TBHP concentration from $0.01x10^{-2}$ mol to $0.1x10^{-2}$ mol the reaction rate increased dramatically in the beginning of the reaction. Indeed, at the higher TBHP amount the induction period almost disappears. This is consistent with a radical mechanism. It should be noted that the rate of conversion at the end of the period studied is roughly the same for both levels of TBHP. This could be interpreted as indicating that the function of the initiator is merely to activate the catalyst surface and this is achieved more quickly with the higher amount of TBHP. Since the amount of catalyst was the same in both experiments, the same rate is eventually reached in both experiments. The mechanism of activation by TBHP could possibly involve O-centred radical species reacting either directly with the metal surface or with surface contaminants (the mechanism of the reaction will be discussed in detail in chapter 4).

Furthermore, performing the reaction in the absence of TBHP resulted in negligible reactivity when measured after 24 h reaction (Fig. 3.10). Another diagnostic experiment is the reaction in the presence of radical scavenger which should destroy the radical chain reaction. Table 3.5 shows that by using two different radical scavengers with cyclooctene oxidation in the presence of TBHP the reaction were terminated. The use of two different radical scavengers demonstrates that radical chemistry is highly involved in the present reaction.

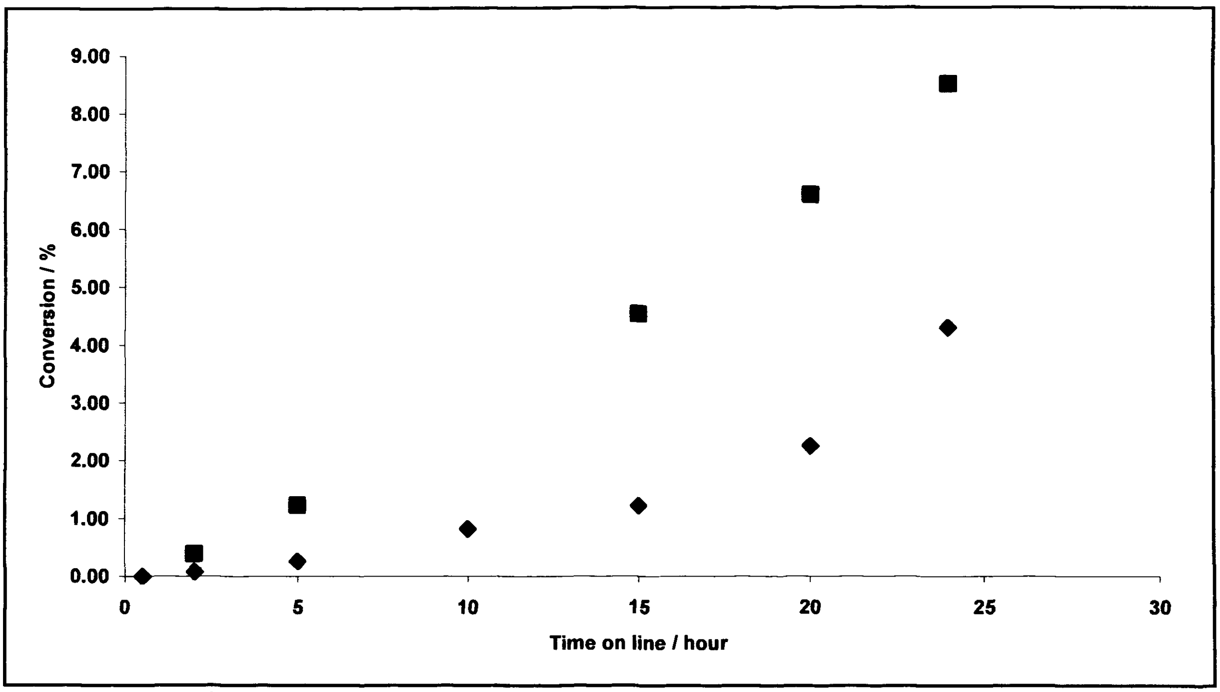

Figure 3.13 Effect of initial concentration of TBHP on the rate of cyclooctene oxidation, (close diamond) 0.01×10^{-2} mol, (close square) 0.1×10^{-2} mol, reaction condition: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80°C, and atmospheric pressure.

Table 3.5 Effect of radical scavenger on cyclooctene oxidation

scavenger	Conversion %	Selectivity (epoxide)%
-	4	78.2
BHT [a]	0.36	-
PS-TEMPO [b]	0.21	Trace

Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 °C, atmospheric pressure.

[a] BHT = 2,6-di- tert-buttyl-4-methylphenol

[b] PS-Tempo = 2,2,6,6-Tetramethylpiperidine-1-oxyl supported on a polymer (polystyrene PS)

Oxidation of 0.077 mole of cyclooctene with 0.0001 mole of TBHP produce 0.0024 mole of cyclooctene oxide with a mole ratio of epoxide to peroxide of 24 which indicates that molecular oxygen from the air is involved in the oxidation process. This is confirmed by performing the oxidation under helium in which less than 1% of cyclooctene oxide is yielded. The fact that there was no reaction observed in the absence of catalyst and presence of TBHP indicates that the reaction is occurring in or near the catalyst surface.

3.3. *Conclusion*

In summary, the oxidation of cyclooctene was performed in solvent free conditions using radical initiators; 1%Au/graphite as catalyst and oxygen from air as oxidant at mild temperature. The effect of radical initiator was studied using five radical initiators. CHP, AIBN and BPO proved to be very active in the absence of catalyst this was attributed to the fast homolysis of these radicals. The presence of carbon radical centres with AIBN and BPO was able to facilitate the production of cyclooctene hydroperoxide which oxidise cyclooctene. TBHP was the only radical initiator which shows enhancement in activity in the catalysed reaction. The cooperative effect of gold with TBHP to produce a variety of radicals was postulated to be the cause for this enhancement. DTBP shows poor activity in cyclooctene oxidation with and without the catalyst which could be due to the high activation energy of homolysis. The addition of catalyst to AIBN and BPO did not result in improvement in catalytic activity which could be due to the bulkiness of BPO and the fast rate of AIBN radical reaction with oxygen.

The presence of cyclooctene hydroperoxide was confirmed in small concentration at the end of the reaction by using triphenylphosphine. Time on line study revealed that the products of cyclooctene oxidation are stable during the reaction time. Even though several experimental observations support the claim that the reaction proceeds through radical mechanism (section 3.2.5), the absence of reactivity without the gold catalyst suggest that the reaction is occurring on or near the catalyst surface.

3.4. References

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Chapter Four

Cyclooctene Epoxidation: Influence of Metal Supports and Catalyst Reusability

4. Cyclooctene Epoxidation: Influence of Metal Supports and Catalyst Reusability

4.1. Introduction

One class of reactions has attracted significant attention, namely the epoxidation of alkenes. Cyclooctene oxidation has been used as model reaction for cycloalkene epoxidation. Chapter three established the conditions for cyclooctene oxidation to occur in the liquid phase with minimal back ground contribution. As noted in chapter three for the epoxidation of *cis*-cyclooctene there are key components of the reaction system that are required for high epoxide selectivity, namely a suitable supported gold catalyst and a radical initiator, as without the radical initiator low epoxide selectivities are observed [1, 2]. The use of a radical initiator such as *tert*-butylhydroperoxide (TBHP) to perform cyclooctene oxidation has been proven to be essential in the catalysed reaction. Gold supported on graphite was shown in the previous chapter to be effective catalyst for cyclooctene epoxidation. To improve the activity and selectivity of cyclooctene oxidation the optimized conditions of the reaction such as temperatures, catalyst preparation methods and catalyst supports must be identified.

In this chapter, the influence of the gold support will be explored and whether an alternative to graphite can improve the performance of gold in cyclooctene oxidation. The reusability of the catalyst will also be examined as this is a key aspect of green chemistry that has not been explored previously with these catalysts to the best of our knowledge.

4.2. *Experimental*

4.2.1. *Carbon support wash procedure*

Supports were pre-treated either with 100 mL water (silicon carbide) or 100 mL 5%HNO_3 (activated carbon (G60) for 3 hours at ambient temperatures whilst stirring followed by filtration and dried for 16 hours at 110 °C.

4.2.2. *Characterisation of catalyst*

The techniques of XRD, BET and SEM have been used to characterize the support and supported gold catalyst. In selected cases, X-ray photoelectron spectra (XPS) of the catalyst was performed, which was recorded with an ESCALAB 220 spectrometer using an achromatic AlKα source and an analyser pass energy of 100eV. In addition, AAS is used to detect if there is gold leaching after the reaction

4.2.3. *Catalyst testing*

4.2.3.1. *Procedure for the addition of a second aliquot of TBHP*

The reactions were performed in a stirred glass round bottom flask (50 mL) fitted with a reflux condenser and heated in an oil bath. Cis-cyclooctene (10 mL) was stirred at 80 °C. Then 0.01mmol of TBHP was added followed by 1%Au/graphite (0.12 g). After a desired time, a second aliquot of TBHP (0.01 mmol) was added to the reaction mixture and the reaction was carried out for the desired time.

4.2.3.2. The addition of cyclooctene oxide to the reaction mixture

The reactions were performed in a stirred glass round bottom flask (50 mL) fitted with a reflux condenser and heated in an oil bath. Cis-cyclooctene (10 mL) was stirred at 80 °C. Then 0.01mmol of TBHP was added followed 1%Au/graphite (0.12g). Cyclooctene oxide (0.3g) was added to the reaction and the reaction was carried out for 24 hour.

4.3. __Results and discussion__

4.3.1. Catalysts and supports characterisation

BET analysis shows that the surface area of graphite and 1%Au/graphite was found to be 10 and 12 m^2/g respectively. It can be seen from SEM images (Fig. 4.1) that the surface morphology of undoped graphite and gold supported on graphite is indistinguishable. An XRD pattern is shown in Figure 4.2 for the graphite and Au-graphite catalysts. Comparison with pure graphite reveals that most of the reflections stem from the support. The main reflections of gold are expected at 2θ= 38.2° (100%), 44.4° (52%). 64.6° (32%), 77.4° (36%).

The surface morphology for all the undoped supports and supported gold catalysts is shown in Figure 4.1, 4.3, 4.5, 4.7, 4.9, 4.11. It can be seen from SEM images that the difference in morphology between the undoped support and the gold catalyst is negligible. However, XRD pattern (Fig. 4.2, 4.4, 4.6, 4.8, 4.10, 4.12). reveals the presence of gold in the expected area as discussed above.

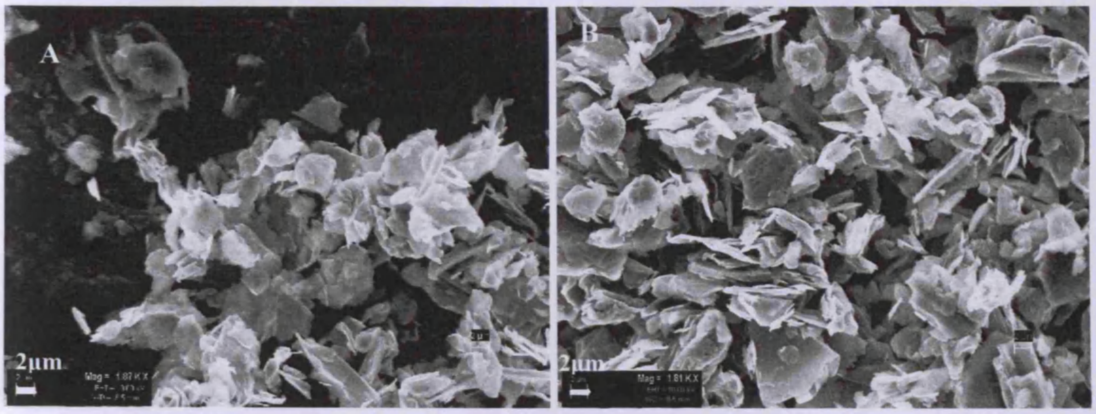

Figure 4.1 SEM image of a) graphite , b) 1%Au/graphite

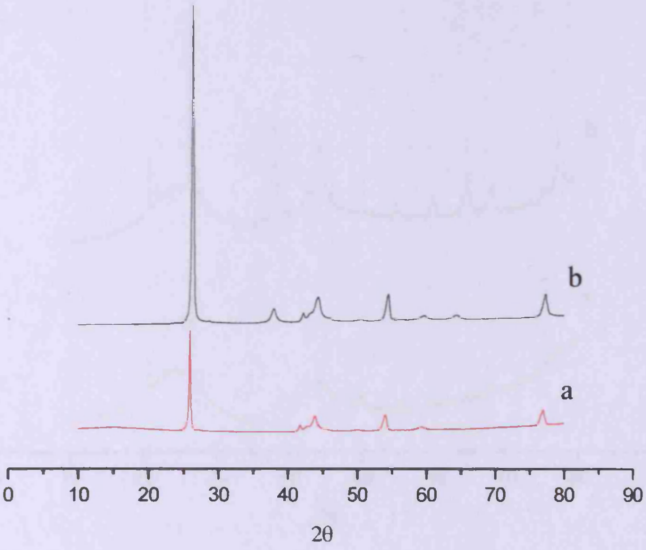

Figure 4.2 The XRD pattern of a) graphite , b) 1%Au/graphite

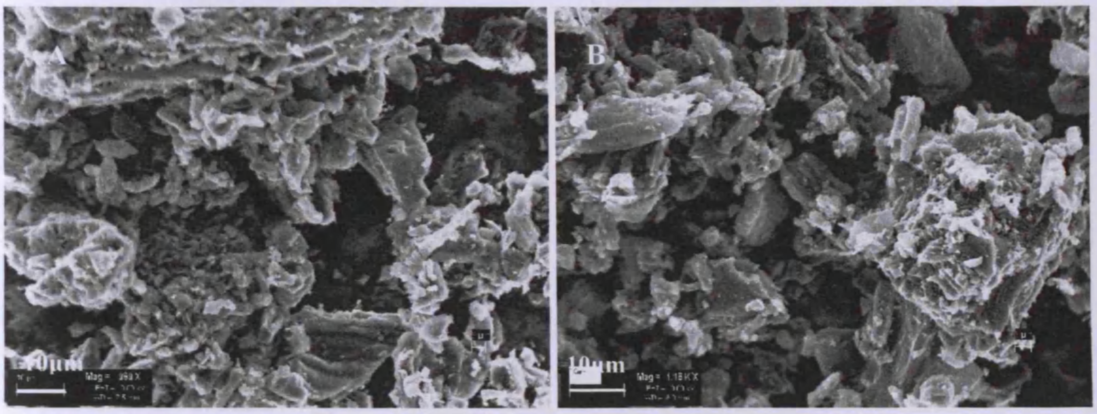

Figure 4.3 SEM image of a) activated carbon, b) 1%Au/activated carbon

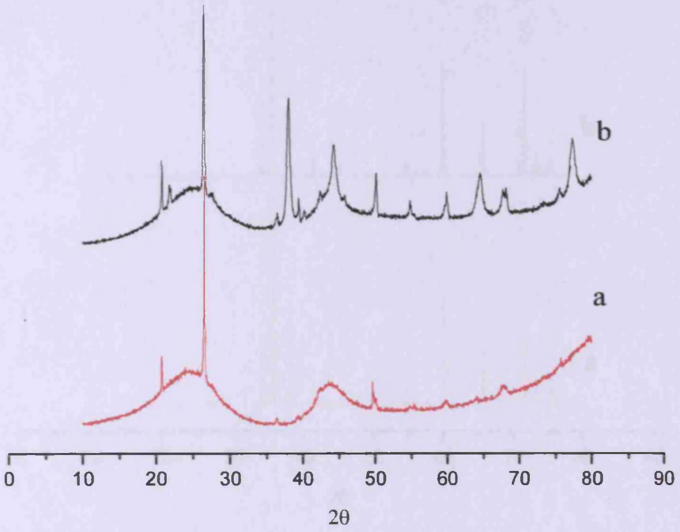

Figure 4.4 The XRD pattern of a) activated carbon, b) 1%Au/activated carbon

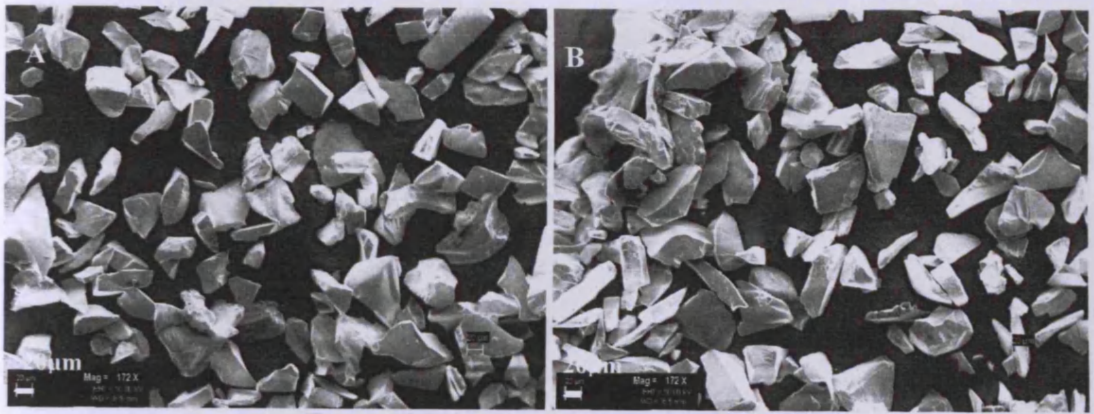

Figure 4.5 SEM image of a) SiC , b) 1%Au/SiC

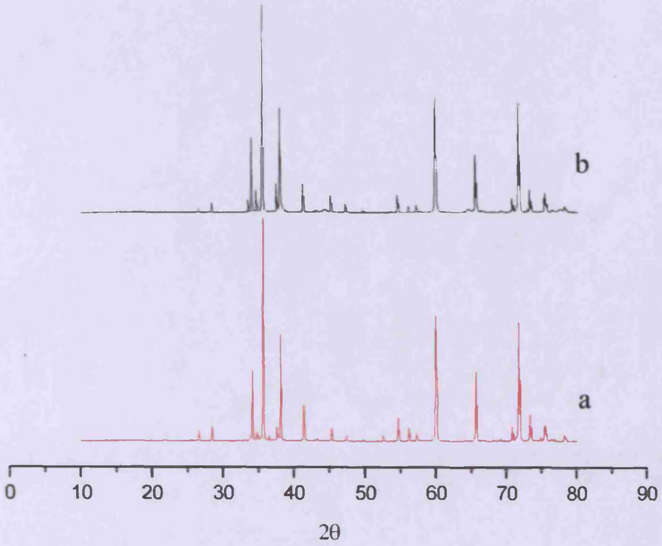

Figure 4.6 The XRD pattern of a) SiC , b) 1%Au/SiC

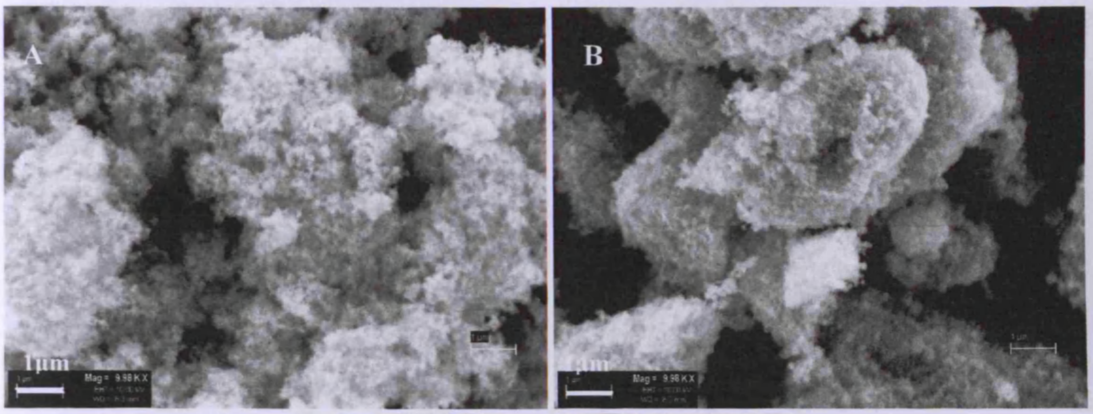

Figure 4.7 SEM image of a) TiO_2, b) 1%Au/TiO_2

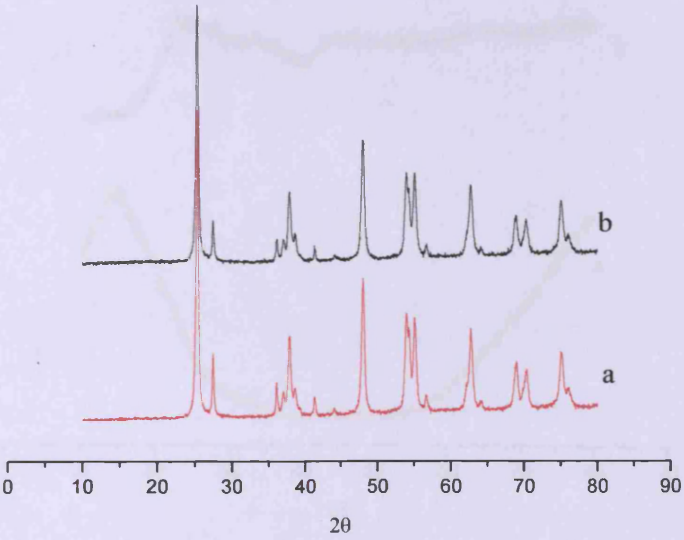

Figure 4.8 The XRD pattern of a) TiO_2, b) 1%Au/TiO_2

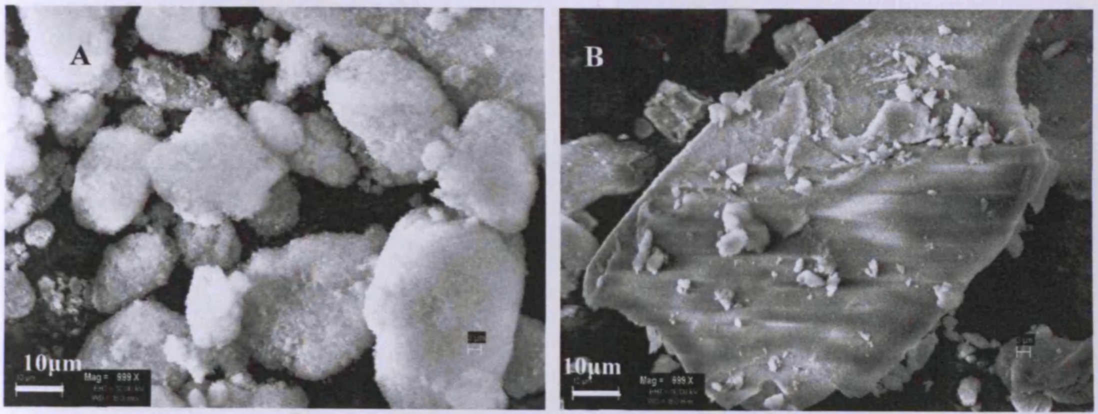

Figure 4.9 SEM image of a) SiO_2, b) 1%Au/SiO_2

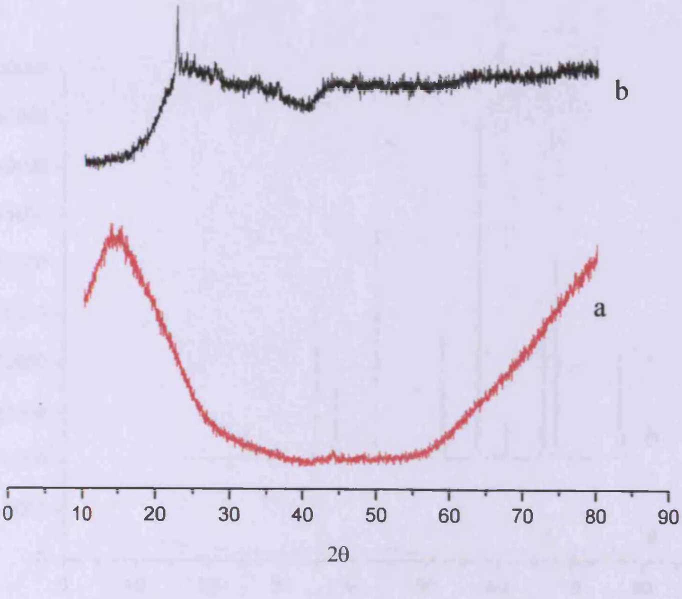

Figure 4.10 The XRD pattern of a) SiO_2, b) 1%Au/SiO_2

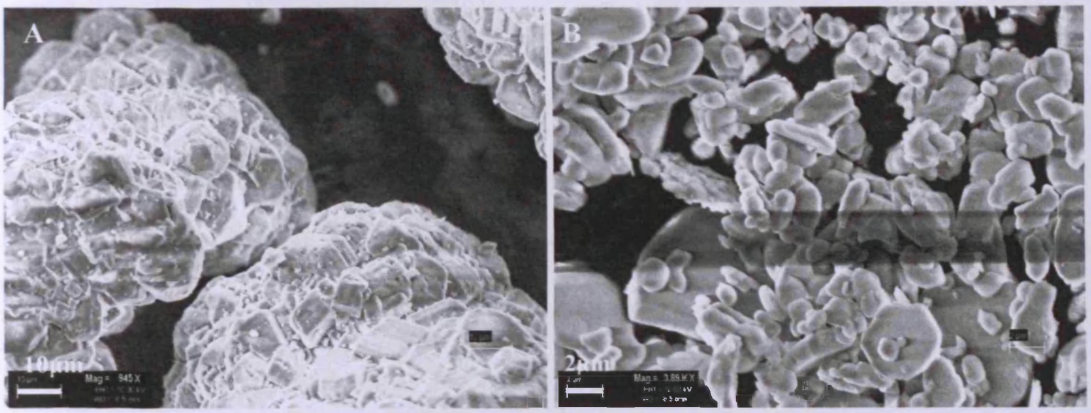

Figure 4.11 SEM image of a) Al_2O_3, b) 1%Au/Al_2O_3

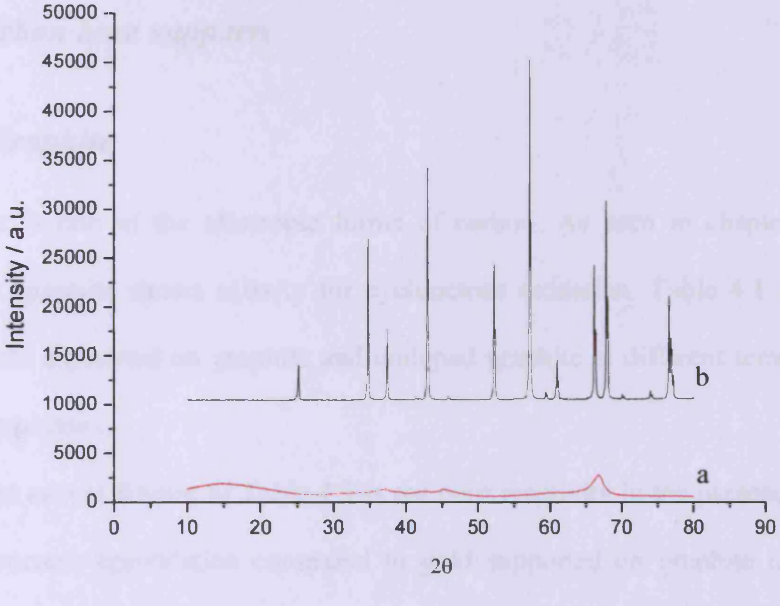

Figure 4.12 The XRD pattern of a) Al_2O_3, b) 1%Au/Al_2O_3

4.3.2. Testing of Catalysts and Supports

The support of metal nano-particles is one of the important parameters which can be highly influential on the activity of any giving reaction in heterogeneous catalysis. For supported gold catalysts the surface of support has been reported to act as a nucleating agent, and therefore the properties of the support play a predominant role in the adsorption of gold which finally influences the catalytic activity [3-5]. To study the effect of the support on cyclooctene oxidation, six different support materials were used. The supports used in this study are divided into two main groups: carbon based supports and metal oxide based supports

4.3.2.1. Carbon base supports

4.3.2.1.1. Graphite

Graphite is one of the allotropic forms of carbon. As seen in chapter three, gold supported on graphite shows activity for cyclooctene oxidation. Table 4.1 compares the activity of gold supported on graphite and undoped graphite at different temperatures and TBHP concentrations.

The most salient feature of Table 4.1 is the poor reactivity in the presence of graphite toward cyclooctene epoxidation compared to gold supported on graphite mostly at low temperatures. Indeed, at lower temperatures the 1 % Au/graphite is significantly more active and in the presence of gold the selectivity to the epoxides is greatly enhanced and, importantly, is independent of the TBHP concentration. Increasing the temperature increases the activity of graphite particularly at high TBHP concentrations. In fact, at reaction temperatures ≥100 °C the support is as active as the gold catalyst and shows the highest selectivity to the epoxide. However, for 1%Au/graphite increasing the temperatures resulted in an increase in selectivity of epoxide to peak at 80 °C with ca. 78%.

Table 4.1 Comparison between gold supported on graphite and undoped graphite.

TBHP / mol x 10^{-2}	Temperature. °C	Graphite [a]		1%Au/graphite [b]	
		Conversion /%	Selectivity /%	Conversion /%	Selectivity /%
0.1032	60	0.40	58.4	1.9	68.3
0.0516		0.16	30.7	1.6	64.2
0.0103		0.01	0.01	0.6	63.9
0.1032	70	0.9	63.2	3.9	71.4
0.0516		0.36	64.5	2.6	72.3
0.0103		0.04	86.4	1.9	72.3
0.1032	80	4.5	74.2	8.5	78.7
0.0516		1.8	62.6	6.6	78.7
0.0103		0.1	42.6	4.0	78.2
0.1032	100	12.9	79.1	12.9	73.2
0.0516		9.9	78.8	11.1	76.1
0.0103		3.3	80.5	10.9	79.7
0.1032	120	16.4	77.1	13.4	71.4
0.0516		14.2	77.7	14.0	72.8
0.0103		13.9	77.3	14.6	73.6

[a] Reaction using graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Graphite is known to have neutral surface, at the same time, there are several functional groups that can be attached to graphite surface including hydroxyl group, hydrophobic functional groups and inorganic impurities [6]. Plausibly, this may explain the non-selective low activity, especially, at low temperatures for cyclooctene epoxidation in the absence of gold. According to Xu, pretreatment of graphite with acid or base prior to gold loading did not improve the activity of gold/graphite catalyst in hydrocarbon oxidation [7]. As discussed in chapter three, the activity of TBHP for cyclooctene oxidation increases un-selectively by increasing the temperature. Thus, at temperatures above 100 °C the homolysis rate of TBHP would be faster which could increase the un-selective oxidation of cyclooctene and hence the slight decline in selectivity using 1%Au/graphite as catalyst. Furthermore, cyclooctene oxidation is a temperature analogue reaction as increasing the temperature the reactivity of cyclooctene toward auto-oxidation increases. In the liquid phase auto-oxidation of alkenes, temperature is, therefore, an important factor. Figure 4.13 demonstrates that at moderate temperatures (<100°C) there was no conversion which confirms that the absence of auto-oxidation at standard reaction temperature (80°C) as described in chapter three section 3.2.4. However, at temperature ≥100 °C the auto-oxidation of cyclooctene is promoted and the rate increases rapidly by increasing the temperature. In the presence of TBHP the effect of temperature was more pronounced which may explain the comparable results between graphite and gold supported in graphite at temperature ≥100°C.

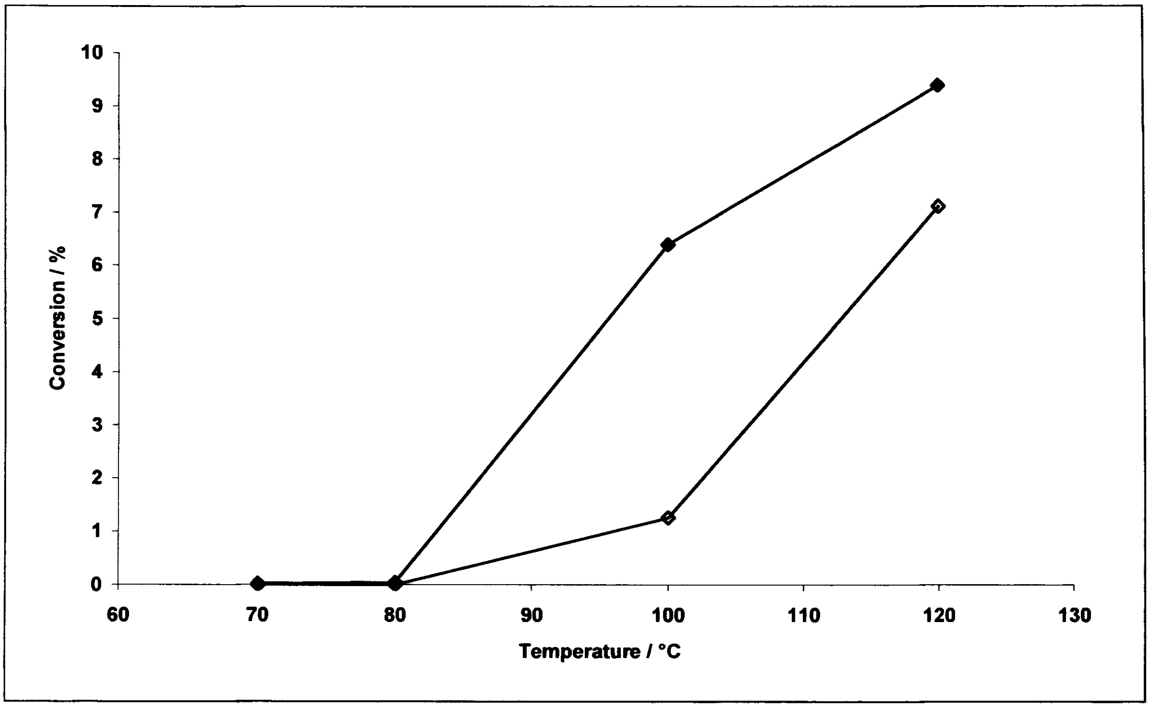

Figure 4.13 Auto-oxidation of cyclooctene in the absence of catalyst. Open symbol cyclooctene without TBHP, close symbol cyclooctene with TBHP

4.3.2.1.2. Activated Carbon

Activated carbons are widely used as supports and hence we contrasted their reactivity with that of graphite. Wood, coal, lignite, coconut shell and peat are the most important raw material for the production of activated carbon, although other materials such as fruit pits, synthetic polymer or petroleum processing residues can also be used [8]. The reactivity of a range of different activated carbon supports manufactured from wood, coconut shell and coal were examined and the results are shown in Table 4.2.

Table 4.2 Effect of carbon source on cyclooctene oxidation

Carbon	Source	Conversion / %	Selectivity (epoxide)/%
Aldrich G60	Wood	2.21	77.11
1wt% Au/Aldrich G60	Wood	1.6	69.3
Norit Rox 0.8	Wood	0.1	59.4
1 wt% Au/ Norit Rox 0.8	Wood	0.06	65.5
Norit GCN-3070	Coconut shell	0.01	-
1 wt%Au/ Norit GCN-3070	Coconut shell	0.01	32.9
Norit PDKA 10x30	Coal	0.6	82.7
1 wt%Au/ Norit PDKA 10x30	Coal	0.2	67.6

Reaction condition: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.1 mmol), 80 °C, 24 h, atmospheric pressure.

In general, activated carbons prepared from coal were the most selective for epoxide formation. The activity for all carbon used in this study apart from Aldrich G60 was poor. Despite the fact that both originated from wood, Aldrich G60 and Norit Rox 0.8 has shown distinctly different behavior toward cyclooctene oxidation. However, the addition of gold was not observed to enhance the catalytic activity for all activated carbon studied. In fact a decrease in activity was the common feature for all carbon examined, although the presence of Au did lead to slightly higher epoxide selectivity in some cases.

Figure 4.14 shows the effect of temperatures on oxidation of cyclooctene with activated carbon G60. It can be seen that the activity of G60 decreases with decreasing the temperature, however, at temperatures as low as 40°C, G60 yet shows sign of activity. The addition of gold to G60 did not result in an improvement in activity at those low temperatures. The surface chemistry of an activated carbon influences the catalyst manufacture and the performance of catalyst. The presence of impurities like ashes and salts, which are potentially poisoning and/or pore plugging materials, depends on the washing treatment [8, 9]. Washing activated carbon with acid has been reported to have beneficial effect on gold catalysts [10]. To investigate this further, G60 was washed with diluted nitric acid and then tested in cyclooctene oxidation. It can be seen from Table 4.3 that the acid pre-treatment of carbon resulted in decrease in activity and in selectivity compared to the untreated carbon. The acid treatment led to a decrease in active site for the nonselective oxidation of cyclooctene on the surface of carbon. The addition of gold to the pre-treated carbon resulted in complete lost of activity. The added gold particle could decorate sites on the support that are otherwise active for the oxidation of cyclooctene.

Table 4.3 effect of acid washing in activity of activated carbon (G60)

Catalyst	Conversion / %	Selectivity / %
Unwashed G60	2.21	77.1
1%Au/unwashed G60	1.6	69.3
Acid washed G60	0.32	62.1
1%Au/acid washed G60	0.03	0

Reaction condition: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.1 mmol), 80 °C, 24 h, atmospheric pressure.

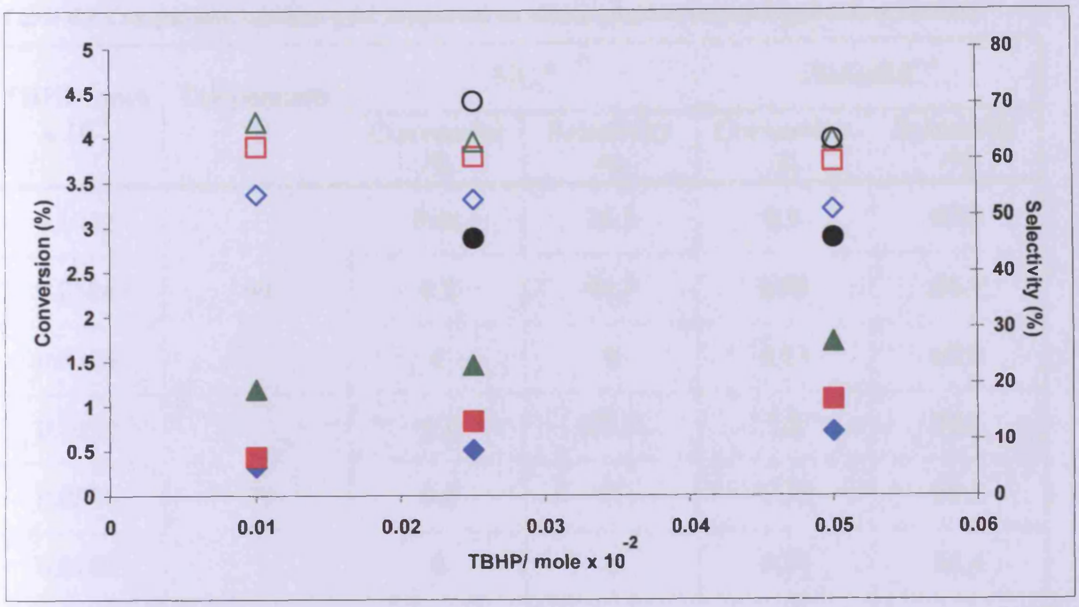

Figure 4.14 Effect of temperature and TBHP concentration on cyclooctene oxidation using Aldrich G60 as support. Open symbols; selectivity, closed symbols; conversion, 40 °C; ♦, 50 °C; ■, 60 °C; ▲, 70 °C; ●.

4.3.2.1.3. Silicon carbide

The interest in silicon carbide (SiC) as support has risen from it physical and chemical properties. SiC exhibits a high thermal conductivity, high resistance towards oxidation, high mechanical strength and chemical inertness [11]. All of these advantages led to the conclusion that silicon carbide can be a promising support in heterogeneous catalysis. Yet, gold supported on silicon carbide has been rarely reported in the literature [12]. Table 4.4 summarized cyclooctene oxidation using SiC and gold supported on SiC.

Table 4.4 Comparison between gold supported on silicon carbide and undoped silicon carbide

TBHP / mol x 10^{-2}	Temperature. °C	SiC [a]		1%Au/SiC [b]	
		Conversion /%	Selectivity /%	Conversion /%	Selectivity /%
0.1032	60	0.64	36.2	0.9	67.6
0.0516		0.2	44.5	0.63	66.4
0.0103		0	0	0.13	63.5
0.1032	70	2.1	72.7	3.2	72.1
0.0516		0.8	71	1.38	69.7
0.0103		0	0	0.74	64.4
0.1032	80	6.9	76.1	11	73.4
0.0516		4.4	78.3	7.7	71.4
0.0103		0.32	59.4	4.8	75.2

[a] Reaction using SiC: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1%Au/ SiC: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure

Silicon carbide shows similar behavior as for graphite in cyclooctene oxidation (Table 4.4). At low temperature and low TBHP concentration there was no activity for SiC in cyclooctene oxidation. Increasing the temperatures and TBHP concentration increases the conversion, expectedly, to peak at ca. 6.9%. The addition of the gold resulted in great enhancement in activity along with selectivity at all temperatures and TBHP concentrations studied. Even though, silicon carbide is regarded as inert with respect to chemical reactions, the impurities and ashes present on the surface of SiC may play a role in the activity at higher temperature and TBHP in the absence of gold.

The presence of impurities in silicon carbide has been reported previously by different groups [13, 14]. It known that such impurities could affect the contact of gold with support, and eventually, affect the activity of catalyst. Furthermore, as cyclooctene oxidation required the presence of radical initiator; the presence of ionic impurities in the reaction media could trigger the oxidation even in the absence of gold. To verify this assumption cyclooctene oxidation was performed using un-doped, washed and un-washed silicon carbide. The activity of unwashed silicon carbide was ca. 1.45%, however, simple wash of SiC with water resulted in almost total loss of activity to ca. 0.1% conversion.

4.3.2.2. Metal Oxide supports

4.3.2.2.1. Titanium dioxide (TiO_2)

One of most used metal oxide as catalyst support is titanium oxide. Titanium oxide exists in a number of crystalline forms the most important of which are anatase and rutile. TiO_2 used in this study was supplied from Degussa and consists of 80% anatase and 20% rutile. TiO_2 can be regarded as reducible support. Preparation of metallic gold nanoparticles on reducible support has been reported to facilitate the formation of active catalyst [15]. The oxidation of cyclooctene with undoped TiO_2 and 1% gold supported on TiO_2 is summarised in Table 4.5.

Table 4.5 Comparison between gold supported on titanium oxide and undoped titanium dioxide

TBHP / mol x 10^{-2}	Temperature. °C	TiO_2 [a]		1%Au/TiO_2 [b]	
		Conversion /%	Selectivity /%	Conversion /%	Selectivity /%
0.1032	60	1.1	65.7	1.8	67.7
0.0516		0.8	71.2	1.3	69.1
0.0103		0.3	85.6	0.9	71.6
0.1032	70	1.7	78.7	3.8	73.4
0.0516		1	77.0	3.0	64.9
0.0103		0.13	75.2	2.0	75.4
0.1032	80	5	80.4	8.8	77.7
0.0516		2.3	83.1	6.3	79.0
0.0103		0.07	78.8	0.3	78.3

[a] Reaction using TiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1%Au/ TiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure

In line with the results obtained from graphite and silicon carbide, titanium oxide shows limited activity in the absence of gold particularly at low TBHP concentration (Table 4.5). High activity of TiO_2 was associated with high temperature and high TBHP concentration in cyclooctene oxidation. Epoxide selectivity was increased by increasing the temperature. Gold supported on titanium oxide display higher activity compared to the undoped titania. Activity as high as ca. 8.8% was achievable using TBHP concentration of $0.1x10^{-2}$ mole and Au/TiO_2 as catalyst at 80 °C.

4.3.2.2.2. Silicon dioxide (SiO_2)

There are several forms of manufactured silica including glass, fumed silica and colloidal silica. Due to it high surface area, fumed silica was chosen as support in this study. Table 4.6 illustrates the difference between silica and gold supported silica in cyclooctene oxidation.

Table 4.6 Comparison between gold supported on silicon oxide and undoped silicon oxide

TBHP / mol x 10^{-2}	Temperature. °C	SiO_2 [a]		1%Au/SiO_2 [b]	
		Conversion /%	Selectivity /%	Conversion /%	Selectivity /%
0.1032	60	0.4	64.5	0.9	64.8
0.0516		0.4	67.8	0.7	66.7
0.0103		0.1	0.1	0.4	67.8
0.1032	70	0.9	70.8	1.8	80.3
0.0516		0.3	74.5	1.3	81.1
0.0103		0.1	75.4	0.9	75.0
0.1032	80	4.5	74.5	6.0	80.2
0.0516		2.0	77.1	4.0	83.8
0.0103		0.1	0.1	2.7	79.7

[a] Reaction using SiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1%Au/ SiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure

It can be seen from table 4.6 that the behavior of silica toward cyclooctene oxidation is comparable to titania despite the fact that SiO_2 is a non-reducible support. As expected, the activity increases by increasing the temperatures and TBHP amount. Compared to titania, silicon dioxide shows lower activity to oxidation in absence of gold. The presence of gold resulted in increase in activity and selectivity to epoxide particularly at higher temperature

4.3.2.2.3. Aluminum oxide (Al_2O_3)

The most common occurring crystalline form of aluminum oxide is α-alumina which also called corundum. The oxidation of cyclooctene using gold supported on aluminum oxide and un-doped alumina is reported in Table 4.7.

Aluminum oxide and silicon oxide both categorized as non-reducible supports, therefore, the activity toward cyclooctene oxidation is similar for both of them (Table 4.7). In similar behavior to other oxide supports, the activity and selectivity of alumina was poor in the absence of gold. However, the introduction of gold resulted in huge improvement in activity and selectivity. Comparing alumina with other metal oxide used in this study revealed the lower selectivity toward epoxide for alumina.

Table 4.7 Comparison between gold supported on aluminum oxide and undoped aluminum oxide

TBHP / mol x 10^{-2}	Temperature. °C	Al_2O_3 [a]		1%Au/Al_2O_3 [b]	
		Conversion /%	Selectivity /%	Conversion /%	Selectivity /%
0.1032	60	0.25	53.6	0.55	52.1
0.0516		0.09	71.8	0.48	49.7
0.0103		0	0	0.13	54.2
0.1032	70	1.2	61.7	1.8	62.4
0.0516		0.43	48.7	1.3	63.6
0.0103		0.01	72.5	0.38	63.3
0.1032	80	4.4	71.4	6.3	72.6
0.0516		0.2	46.7	4.6	74.04
0.0103		0	0	2.6	71.8

[a] Reaction using Al_2O_3: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

[b] Reaction using 1%Au/ Al_2O_3: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure

4.3.2.3. Summary of choice of support

The role of the metal support in catalysis is fundamental. The interaction between gold and the support may influence the activity of the supported gold catalyst in heterogeneous reactions. Six different supports were investigated for cyclooctene oxidation using TBHP as radical initiator. Three carbon based supports were used namely graphite, activated carbon and silicon carbide. The carbon surface contains a number of heteroatoms in the form of functional groups (Fig. 4.15). The presence of these groups may affect the catalytic properties of the catalyst by adding chemical functionalities such as acid, basic or electron donating/ withdrawing properties [13, 16]. The effects of this functionality were more pronounced in the case of activated carbon and silicon carbide. It was stated in the previous sections that using undoped activated carbon and SiC used as received resulted in high activity which may be linked to the ashes and functional group present on their surfaces. Washing activated carbon with acid (diluted nitric acid) and silicon carbide with water resulted in a decrease of activity. Graphite, on the other hand, is known to have neutral surface, thus it exhibits no activity in the absence of gold. In fact, Xu reported that the pre-treatment of graphite with acid has no effect on activity [7].

Metal oxides used in this study can be divided into reducible (TiO_2) and non-reducible support (SiO_2 and Al_2O_3). All of these supports exhibit no activity at low temperature in the absence of gold. The presence of gold induced activity with all metal oxide. Despite the fact that the non-reducible support has low ability to adsorb or store oxygen, these catalysts show comparable activity to TiO_2.

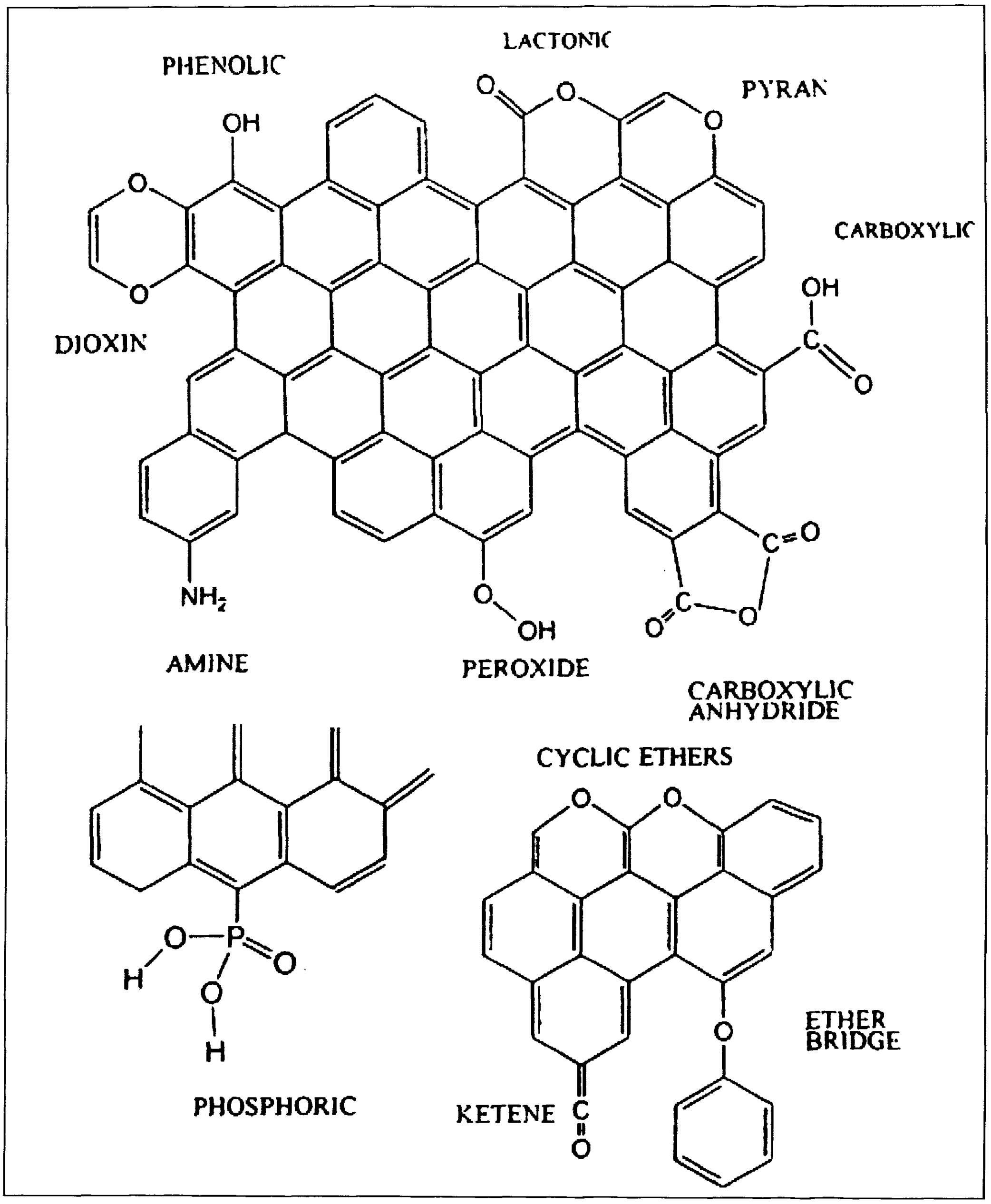

Figure 4.15 structure of some functional groups presented on the surface of carbon [17].

Figure 4.16 and Figure 4.17 compare gold supported on all supports used in this study. It can be seen that based on activity the supports have the following order: SiC > graphite ≈ TiO_2 > Al_2O_3 ≈ SiO_2 ≈ Ac and for selectivity to the epoxide the order is graphite ≈ SiO_2 ≈ TiO_2 > SiC ≈ Al_2O_3 ≈ Ac (Fig. 4.16 and Fig. 4.17). Even though silicon carbide exhibits the highest activity among supports, this could be due to presence of functional groups adsorbed as surface species, as a simple water washing may not be enough to clean the surface. Furthermore, the selectivity for silicon carbide is lower than graphite or titania. In view of this we selected the 1 wt% Au/graphite catalyst for detailed studies on catalyst re-uses.

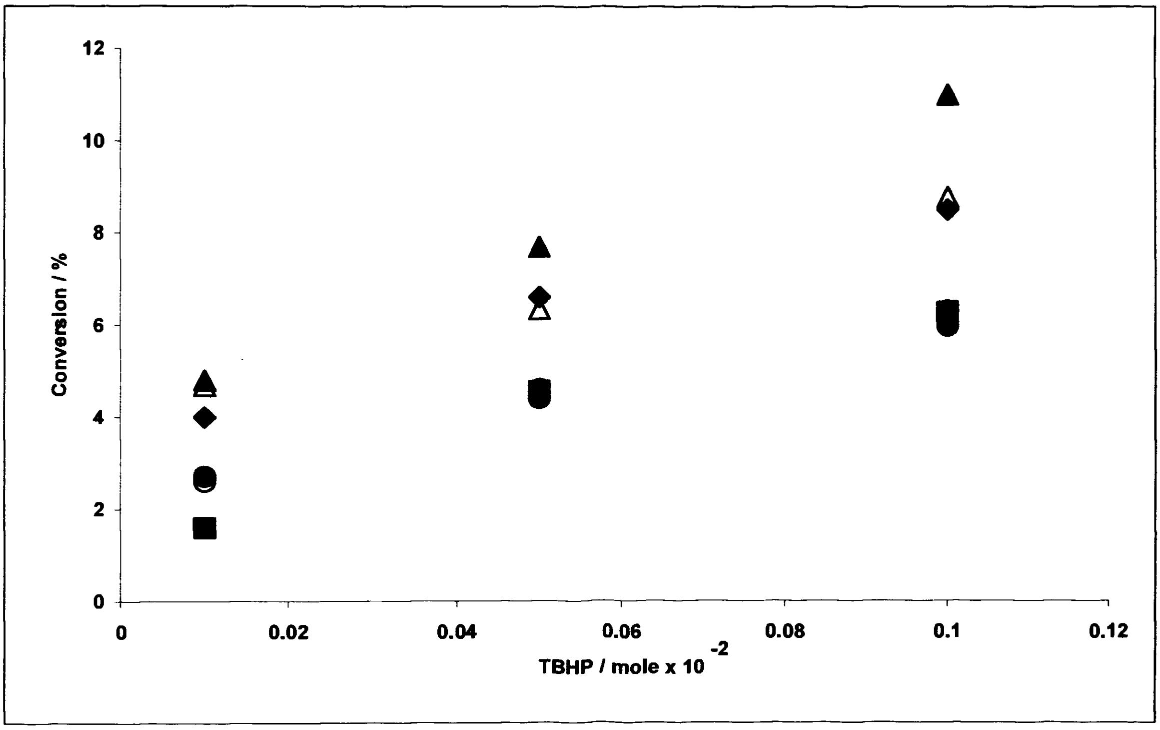

Figure 4.16 Support affect on cyclooctene oxidation (conversion), (close triangle) 1%Au/SiC, (dark close diamond) 1%Au/graphite, (open triangle) 1%Au/TiO_2, (open circle) 1%Au/Al_2O_3, (close square) 1%Au/activated carbon, (close circle) 1%Au/SiO_2, reaction conditions: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01x10^{-2} mol), 80 °C, and atmospheric pressure.

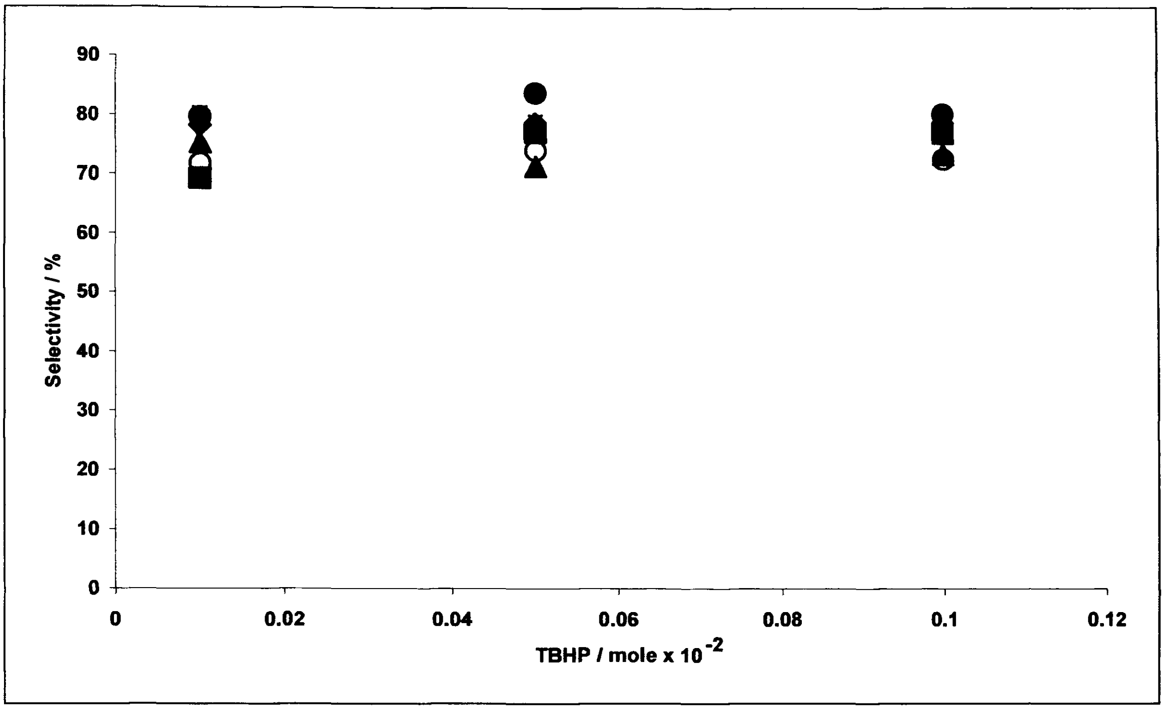

Figure 4.17 Support affect on cyclooctene oxidation (selectivity), (close triangle) 1%Au/SiC, (dark close diamond) 1%Au/graphite, (open triangle) 1%Au/TiO_2, (open circle) 1%Au/Al_2O_3, (close square) 1%Au/activated carbon, (close circle) 1%Au/SiO_2,, reaction conditions: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 °C, and atmospheric pressure.

4.3.3. Catalyst reusability

One of the key advantages of heterogeneous catalysts is that when operated in a batch mode the catalyst can be readily recovered by filtration for re-use. The successful recovery and re-use of heterogeneous catalysts is therefore an essential aspect of green chemistry. To the best of our knowledge the reusability of the Au/graphite catalysts for alkene epoxidation has not been considered to date.

Following reaction of *cis*-cyclooctene under standard conditions for 24 hours the catalyst was recovered by centrifugation. Several treatments for the drying of the catalyst prior to reuse was investigated. In all cases a larger batch of catalyst was used in the initial experiment so that following recovery and drying a sufficient amount of catalyst could be added to the reactor in the re-use experiments. This ensures that any loss in activity is not due to any discrepancy in the catalyst mass used. The way in which the recovered catalyst was dried after an initial washing treatment with acetone was also investigated (Table 4.8).

Table 4.8 Drying temperature effect on catalyst re-usability

Drying temperature	Conversion / %	Selectivity / %
Fresh catalyst	4	78.2
20 °C, 16 h	0.44 [b]	67.1
110 °C, 1h	1.1 [b]	66.9
110 °C, 16 h	2.4 [b]	75.0
150 °C, 16 h	2.4 [b]	79.0
170 °C, 16 h	2.4 [b]	78.6

[a] Reaction conditions: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), TBHP (0.01×10^{-2} mol), 80 ° C, glass reactor, 24 hour, atmospheric pressure; after use the catalyst was recovered by centrifugation, washed with acetone (30 ml), and dried at the temperature and time specified in the table, [b] conversion on first reuse.

Drying at 20 °C for 16 h did not recover the activity or selectivity, nor did drying at a higher temperature for 1h. Drying at temperatures of 110-170 °C for 16 h recovered the selectivity of the catalyst but the activity of the catalyst was at best *ca.* 60% compared with the activity of the fresh catalyst for a 24 h reaction. However, a catalyst that had been re-used once could be successfully re-used retaining this lower activity on subsequent reactions (Figure 4.18). The effect of the drying atmosphere (Table 4.9) was also found to have a marked effect. Drying with static air gave the best results and use of flowing air or H_2 gave a slightly decreased activity on re-use. However, flowing O_2 gave a much poorer performance for the re-used catalyst.

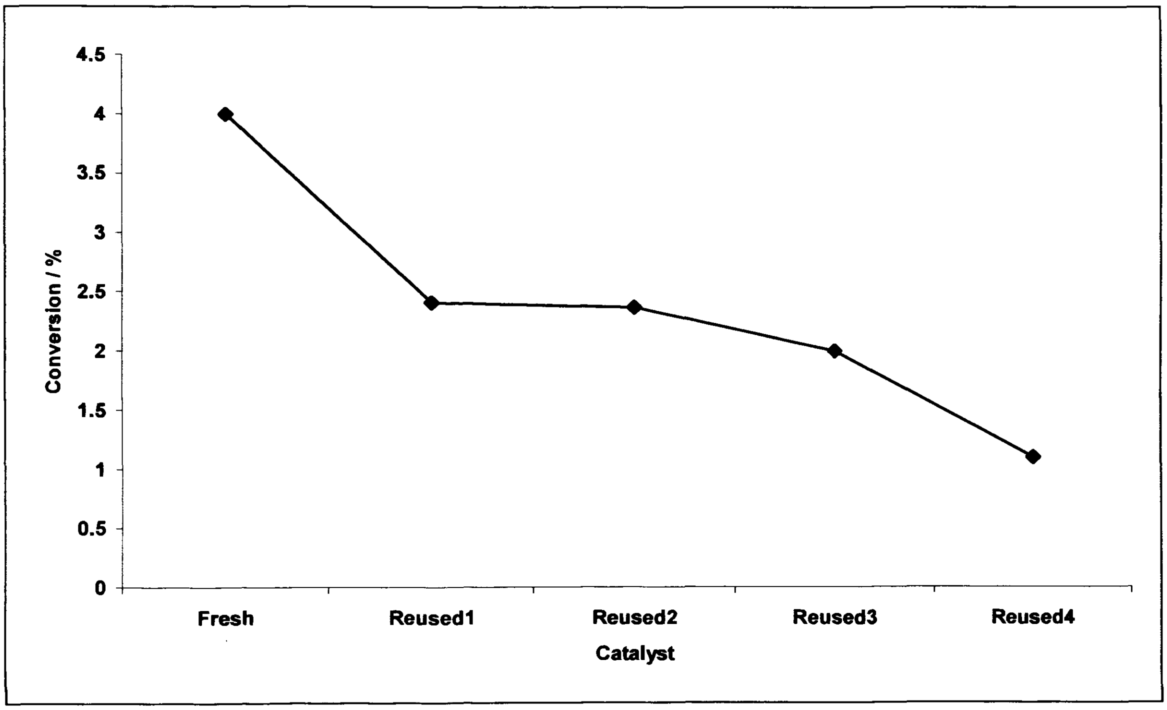

Figure 4.18 Reusability of 1%Au/graphite in cyclooctene oxidation Reaction condition: cyclooctene 10ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 h, atmospheric pressure.

Table 4.9 Effect of drying atmosphere on reusability of 1%Au/graphite in cyclooctene oxidation

drying condition	Conversion (%)	Selectivity (%)
Fresh catalyst	4	78.2
Static air, 150 °C, 16 h	2.4[b]	78.6
Flowing air, 150 °C, 16 h	2.1[b]	78.3
flowing 5% H_2/Ar, 150 °C, 16 h	2.2[b]	76.8
flowing O_2 at 150 °C, 16 h	1.1[b]	71.6

[a] Reaction condition: cyclooctene 10 ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 hour, atmospheric pressure; after use the catalyst was recovered by centrifugation, washed with acetone (30 ml), and dried at the temperature and time specified in the table; [b] conversion on first reuse.

The solvent used in the catalyst treatment prior to drying was also found to be important (Table 4.10). If no solvent treatment was used then the activity was only marginally lower than if an acetone washing step was employed, and the selectivity was retained at a high level. Washing with water, diethyl ether, ethanol, aqueous sodium hydroxide, dilute nitric acid or toluene all led to no activity being observed in the recovered catalyst. These results demonstrate the sensitivity of the catalyst to any treatment with a solvent and the best results are attained either using no solvent treatment or using acetone.

Investigation using recovered cyclooctene, after it had been used for an initial reaction, was conducted (Table 4.11). In this case, fresh (not recovered) catalyst and TBHP were added and the reaction was allowed to proceed for either an additional 2 or 24 h. The conversions observed were similar to those observed with increasing reaction time for the conversion of cyclooctene. Stopping the reaction after 6 h and removing the catalyst before adding fresh catalyst and TBHP did not lead to any enhancement in activity and hence a conclusion was made that reused cyclooctene behaves normally, giving conversions that are indistinguishable from standard reactions carried out for the same time.

Table 4.10 Effect of washing medium on 1%Au/graphite reusability in cyclooctene oxidation

Washing conditions	Conversion (%)	Selectivity (%)
Fresh catalyst	4	78.2
Without washing, dried static air, 110 °C, 16 h	2.1[b]	79.2
Washed with acetone, dried static air, 110 °C, 16 h	2.4[b]	75.0
Washed with H_2O, dried static air, 110 °C, 16 h	0[b]	0
Washed with acetone then H_2O, dried static air, 110 °C, 16 h	1.6[b]	79.5
Washed with diethyl ether, dried static air, 110 °C, 16 h	0[b]	0
Washed with ethanol, dried static air, 110 °C, 16 h	0.1[b]	83.2
Washed with 2% NaOH, dried static air, 110 °C, 16 h	0[b]	0
Washed with 2%HNO_3, dried static air, 110 °C, 16 h	0[b]	0
Washed with Toluene, dried static air, 110 °C, 16h	0[b]	0

[a] Reaction condition: cyclooctene 10 ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 hour, atmospheric pressure; after use the catalyst was recovered by centrifugation, washed with solvent (30 ml), and dried at the conditions specified in the table; [b] conversion on first reuse.

Table 4.11 Reuse of cyclooctene following reaction with 1% Au/graphite

Catalyst /conditions[a]	Conversion (%)	Selectivity (%)
Standard reaction for 24 h	4.0	78.2
Standard reaction for 24 h, fresh catalyst and TBHP for 2 h	5.2	79.9
Standard reaction for 24 h, fresh catalyst and TBHP for 24 h	13.3	81.9
Standard reaction for 6 h then fresh catalyst and TBHP for 24 h	4.5	79.2

[a] Standard reaction condition: cyclooctene 10 ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, atmospheric pressure. After the standard reaction the mixture was filtered and the recovered cyclooctene was reused for the stated time. The conversion is reported after the total reaction time.

To investigate further, the fate of TBHP was followed in the reaction by gas chromatography and NMR spectroscopy and we observed that the TBHP was no longer detected in solution after the first 15 minutes of reaction. This can be due to adsorption of TBHP onto the catalyst surface as the half life of homogeneous TBHP decomposition under these conditions is of the order of 10-15 h. It is possible that slow decomposition of the surface-bound TBHP leads to two effects. First it could clean the active sites so that effective catalytic species are established and secondly it participates directly in establishing the intermediates that propagate the reaction. In both cases this would lead to an induction period which is observed. Therefore, an investigation on the addition of TBHP during the course of the reaction was conducted (Table 4.12, Figs. 4.19 and 4.20). Addition of a second aliquot of TBHP at 2, 6 or 24 h had a dramatic effect by increasing the activity and also enhanced the selectivity when added in the earlier period. Moreover, the second addition of TBHP resulted in rate enhancement where the rate increases from 0.16 mmol/h before the addition to 0.22 mmol/h after the addition. Indeed, the addition of the second aliquot of TBHP had immediate effects and did not involve a further induction period. This suggests that the TBHP acts as a source of active (radical) intermediates immediately. This is consistent with the first aliquot aiding the cleaning of the catalyst surface as suggested. These results show that by carefully manipulating the experimental conditions, enhanced activity and selectivity can be achieved.

Table 4.12 Effect of second addition of TBHP during cyclooctene oxidation

Reaction condition	Conversion (%)	Selectivity (%)
Standard reaction, 24 h	4	78.2
Second aliquot of TBHP added at 2 h, 24 h total reaction	4.6	80.6
Second aliquot of TBHP added at 6 h, 24 h total reaction	5.8	81.8

[a] Standard reaction condition: cyclooctene 10 ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 h, atmospheric pressure, TBHP (0.01×10^{-2} mol) was added to the reaction mixture without stopping the reaction.

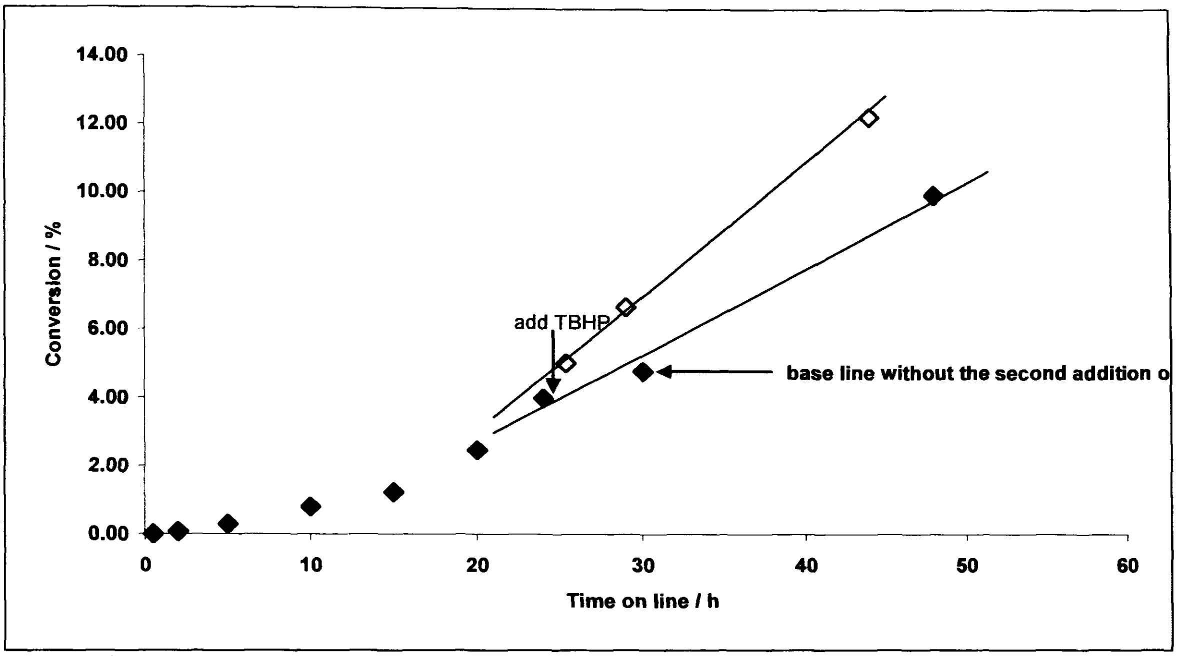

Figure 4.19 Effect of addition of TBHP after 24 h standard reaction on the conversion of cyclooctene oxidation, reaction condition: cyclooctene 10ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 h, atmospheric pressure, TBHP (0.01×10^{-2} mol) was added to the reaction mixture without stopping the reaction.

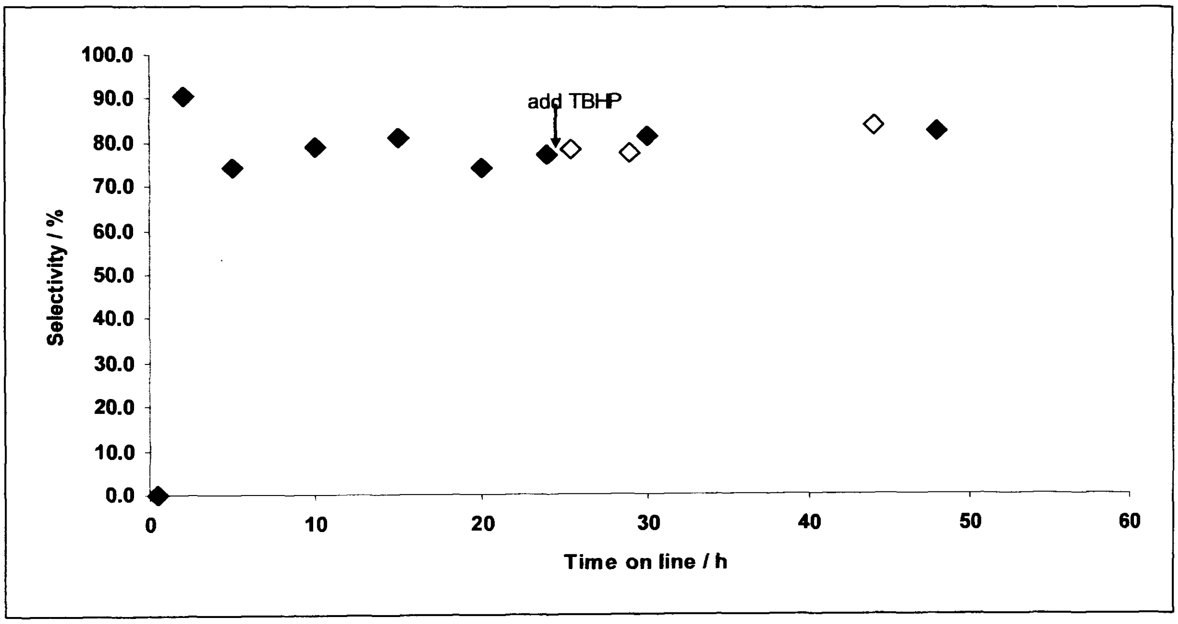

Figure 4.20 Effect of addition of TBHP after 24 h standard reaction on the selectivity of cyclooctene oxidation, reaction condition: cyclooctene 10ml, catalyst 0.12 g, TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, 24 h, atmospheric pressure, TBHP (0.01×10^{-2} mol) was added to the reaction mixture without stopping the reaction

As the cyclooctene could be re-used effectively (Table 4.11) the cause of the deactivation of the catalyst after the initial use was investigated. The addition at the start of the reaction of the epoxide at a range of concentrations up to the concentration expected for 4% conversion and 80% selectivity after a 24 h reaction was examined. This epoxide was added together with the fresh catalyst and TBHP. The conversion at the end of the 24 h reaction period was 2.4%; *i.e.* identical to that of the reused catalysts that had been recovered, washed with acetone and dried in static air (Tables 4.8-4.10). Furthermore, TGA analysis for the washed catalyst and fresh catalyst revealed a mass lost of ca. 6% of the reused catalyst after 200 °C which could come from the adsorbed epoxide on the catalyst surface (Fig. 4.21). Hence it is apparent that minor quantities of the epoxide are retained on the surface of the catalyst and a product inhibition is observed.

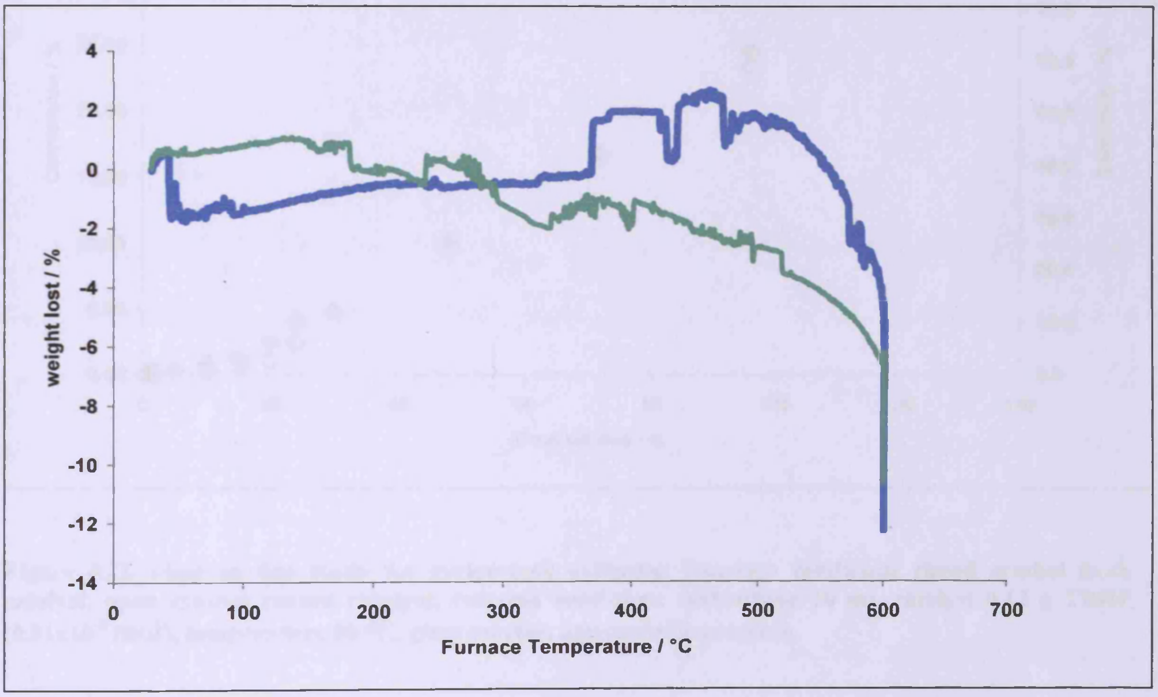

Figure 4.21TGA analysis of fresh catalyst (blue line) and used catalyst (green line)

Reaction of the recovered catalyst was extended for longer reaction periods (Fig. 4.22). It is apparent that at longer reaction times the activity of the catalyst is fully recovered and consequently the activity of the initially fresh catalyst and the reused catalyst are indistinguishable; inhibition is only evident by comparison of fresh and recovered catalysts at short times and low epoxide conversions. Consequently the catalyst can be re-used efficiently over longer reaction times, an important facet of a green chemical process.

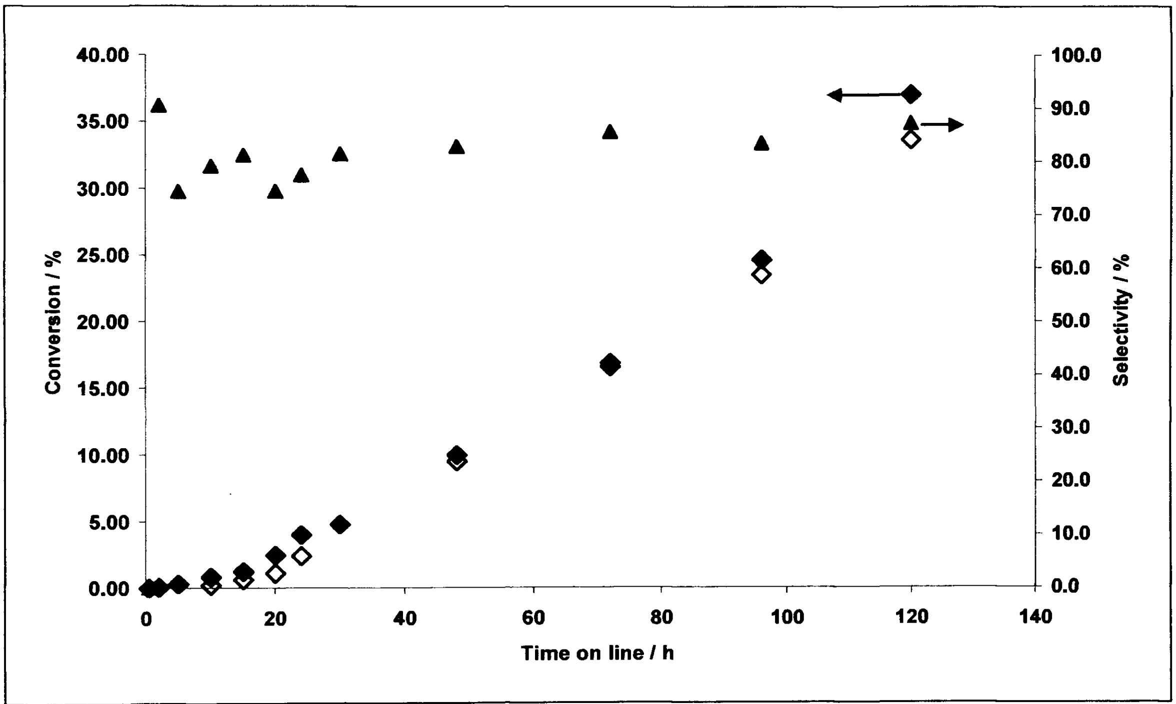

Figure 4.22 Time on line study for cyclooctene oxidation Reaction conditions closed symbol fresh catalyst, open symbol reused catalyst, reaction condition: cyclooctene 10 ml, catalyst 0.12 g TBHP (0.01×10^{-2} mol), temperature 80 °C, glass reactor, atmospheric pressure.

4.3.4. Comments on the reaction mechanism

Commenting on the reaction mechanism of cyclooctene oxidation in the present catalyst system (TBHP as radical initiator and 1%Au/graphite as catalyst), cyclooctene oxidation is believed to involved free radicals at some stage in the catalytic cycle as discussed in chapter three (section 3.2.5). In the absence of catalyst, the epoxidation seems to be a higher temperature analogue of epoxidation by peroxycarboxylic acids. In particular, the selectivity to epoxide increases with TBHP concentration in the uncatalysed reaction but is constant in the catalysed process (Table 4.1). If the uncatalysed peroxide were generating a reactive free radical species capable in part of O-transfer to the alkene, its partitioning between the various pathways should be roughly independent of peroxide concentration. In particular, the competition between epoxidation and allylic oxidation should be independent of TBHP concentration. This is not observed and this suggests that there is a direct O-transfer between the hydroperoxide and the alkene at temperatures below that necessary for homolysis of the O-O linkage.

With Au, hydroperoxides seem necessary and that suggests that a surface O-species may be produced that is capable of O-transfer, either to an adsorbed alkene or an alkene in the liquid phase. In the presence of gold (Fig. 4.23), TBHP may decompose to produce $(CH_3)_3COO^\cdot$ radical or, more probably (see below), $(CH_3)_3CO^\cdot$ radical attached to the surface of the gold catalyst. The radical so formed abstracts a hydrogen atom from cyclooctene and produces the allylic radical (**1**) which, via the oxygen adduct (**2**), produces cyclooctene hydroperoxide (**3**), evidence for the presence of which was presented earlier (see section 3.2.3).

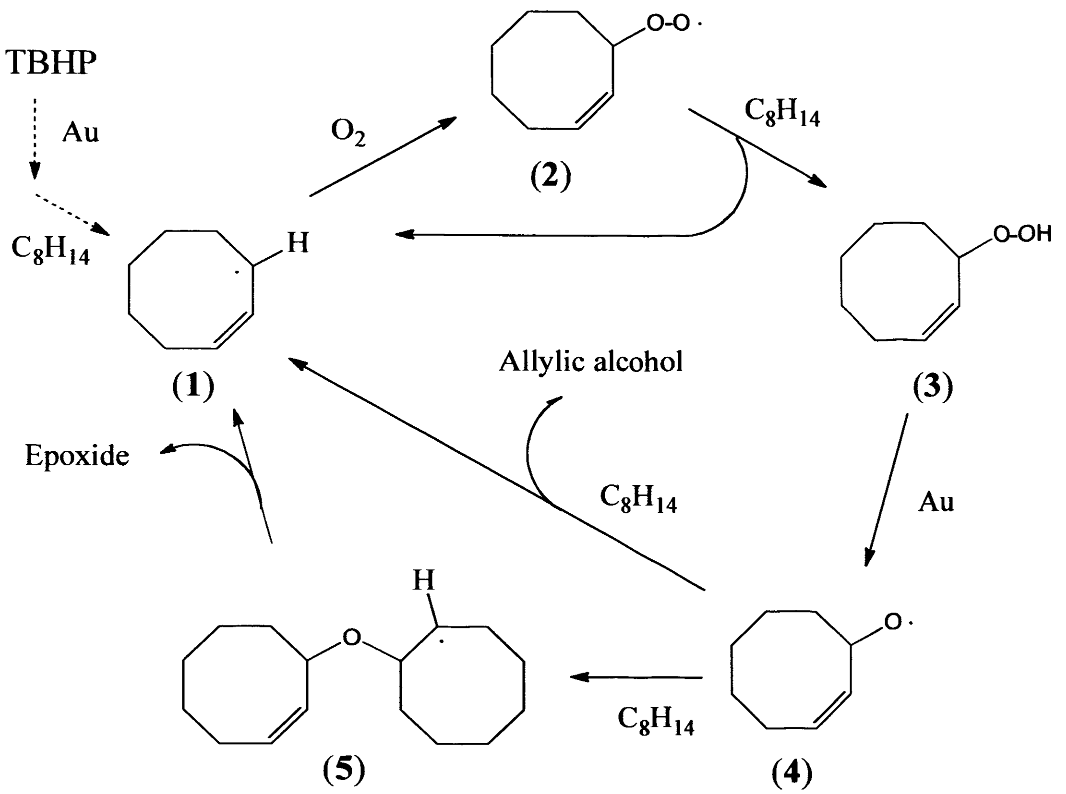

Figure 4.23 Proposed mechanism for cyclooctene oxidation using 1%Au/graphite as catalyst

This step could account for the induction period, after which the concentration of cyclooctene hydroperoxide is sufficient to sustain the oxidation of cyclooctene on the gold surface. This is postulated to proceed by transformation of (3) into the cyclooctenyloxy radical (4) which has been demonstrated by DFT calculations [18] that, on a ten atom gold cluster, hydrogen peroxide dissociates into two HO˙ radicals attached to gold atoms on the surface. It is the masked radical (4) that believed to be a key intermediate in the catalytic cycle. the selectivity to epoxide predicted by the catalytic cycle in Figure 4.23 depends critically on the partitioning of the cyclooctenyloxy radical (4) so as to complete the catalytic cycle between (i) allylic hydrogen abstraction from a further molecule of cyclooctene or (ii) attachment to the double bond of cyclooctene, thereby forming radical

(**5**). Cleavage of (**5**) affords a molecule of the epoxide and the allylic radical (**1**) to complete the cycle; only epoxide is produced in this way. Hydrogen atom abstraction from cyclooctene by (**4**) would on the other hand produce a molecule of the allylic alcohol together with (**1**). Our observation of epoxide selectivities in the range 70-80% would require that both routes are available. After O-transfer to the alkene, the surface species would have to be reconstituted either directly from gaseous O_2 or indirectly via formation of the intermediate allylic hydroperoxide.

4.4. Conclusions

Gold supported catalysts have been demonstrated to be an effective catalyst for cyclooctene oxidation using TBHP as radical initiator at 80 °C. Gold nanoparticles supported on graphite, silicon carbide, TiO_2, SiO_2 and Al_2O_3 exhibits activity in cyclooctene oxidation, whereas the supports alone were identified to be rather inactive mostly at low temperatures and TBHP concentration. The functionality presented on the surface of carbon supports, particularly, activated carbon and silicon carbide was found to play determinate role in cyclooctene oxidation. Prewashing of activated carbon and silicon carbide supports resulted in enhancement in catalytic activity. The activity of gold supported on different supports was as following: $SiC > graphite \approx TiO_2 > Al_2O_3 \approx SiO_2 \approx Ac$ and for selectivity to the epoxide the order is $graphite \approx SiO_2 \approx TiO_2 > SiC \approx Al_2O_3 \approx Ac$, therefore, graphite was concluded to be the support of choice.

The reusability of 1%Au/graphite was investigated in this chapter. The treatment of the used catalyst was proven to be of importance. The catalyst sensitivity toward the solvent used in washings recovered catalyst was high as the best results were obtained using only acetone or without solvents treatments. The optimized conditions for catalyst reusability is: acetone as solvent and 150°C as drying temperature in static air. Despite the reduced activity of the reused catalyst (60% of original activity over 24 h), the catalyst can retain this low activity for a further 2 subsequent uses. The unreacted cyclooctene was recovered and recycled successfully into the reaction. *Tertiary* butyl hydroperoxide is found to be the most effective initiator but under reaction conditions it does not persist long setting up the reactive species that are propagated by the catalytic oxidation reaction. The catalyst is found to be inhibited by the epoxide product but the effect of this is negligible for reused catalysts over a long reaction time. A tentative mechanism that is consistent with most of this study observation is set out in Figure 4.23. Although largely modeled on the behavior of free radicals in auto-oxidation chains, the dramatic increase in epoxide selectivity in the presence of the gold catalyst suggests that the chemistry takes place on or near the metal surface. Accordingly, speculated about the possible existence and nature of chain-terminating processes was not attempted.

4.5. References

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Chapter Five

Alkene Oxidation:
Bimetallic catalysts

5. Alkene Oxidation: Bimetallic Catalysts

5.1. ***Introduction***

The epoxidation of cis-cyclooctene with supported gold catalysts can be used in high efficiency. Recent interest in gold catalysed selective oxidation reaction has led to the investigation of bimetallic variant, most notably involving gold and palladium. The addition of Au to Pd catalysts has been reported to improve not only the catalytic activity but also the selectivity to the desired product [1, 2]. In comparison with Pd and Pt, Au is more resistant to deactivation by chemical poisoning or overoxidation, and it displays a higher intrinsic chemoselectivity [3]. Indeed the chemoselectivity of gold for the oxidation of hydroxyl group in the presence of other functional group in the molecule is high when compared to Pd [4].

In this chapter, the epoxidation of *cis*-cyclooctene using different composition of Au-Pd catalysts will be performed. The effect of the preparation methods of gold –palladium catalysts on *cis*-cyclooctene epoxidation will also be examined. The activity of the supported Au-Pd catalysts prepared by different methods will be examined on crotyl alcohol, as it contains two functional groups. The effect of gold-palladium composition on cyclooctene epoxidation, or any other high alkene, has not been reported in the literature before to the best of our knowledge.

5.2. Experimental

5.2.1. Catalyst characterization

Different techniques have been used to characterize the bimetallic catalysts used in this study including XRD and TEM. TEM imaging was carried out on a JEOL 2000FX microscope operating at 200 kV. Samples were prepared for TEM examination by dispersing the catalysts powder in ethanol, and then allowing a drop of the resulting suspension to dry on a holey carbon film supported on a 300 mesh Cu grid.

5.2.2. Catalyst testing

5.2.2.1. Crotyl alcohol oxidation

The reactions were performed in a stirred glass round bottom flask (50 mL) fitted with a reflux condenser and heated in an oil bath. Typically, crotyl alcohol (10 mL) was stirred at 80 °C. Then 0.01 mmol of the desired radical initiator (i.e. TBHP or AIBN) was added followed the desired catalyst (0.12 g) and the reaction was carried out for 24 hours.

5.3. Results and Discussion

5.3.1. Catalyst characterization

Table 5.1 summarises particles size obtained from TEM and Pd/Au molar ratio obtained from XPS for represented points of Au-Pd series used in this study.

Table 5.1 XPS, theoretical Pd/Au molar ratios and TEM particle size for the 1% Au-Pd/C catalysts

Au theory wt %	Pd theory wt %	theory Pd/Au molar ratio	XPS Pd/Au corrected molar ratio	Particle size (nm)
1	0	0	0.00	32
0.837	0.163	0.36	0.91	23
0.5	0.5	1.86	6.38	18
0.163	0.837	9.54	6.22	16
0	1	146.2	41.1	8

TEM analysis of Au-Pd series (Fig 5.1-Fig.5.5) shows that it comprises nano-crystalline Au and Pd particles with a broad size range from 5nm to 50nm. The size of the gold particles increases by increasing the gold loading. Despite the fact that Pd and Au are not uniformly distributed, EDX analysis shows the presence of bimetallic particle formation between gold and palladium. Small particles agglomerate tends to be Pd rich and bigger particles are Au rich.

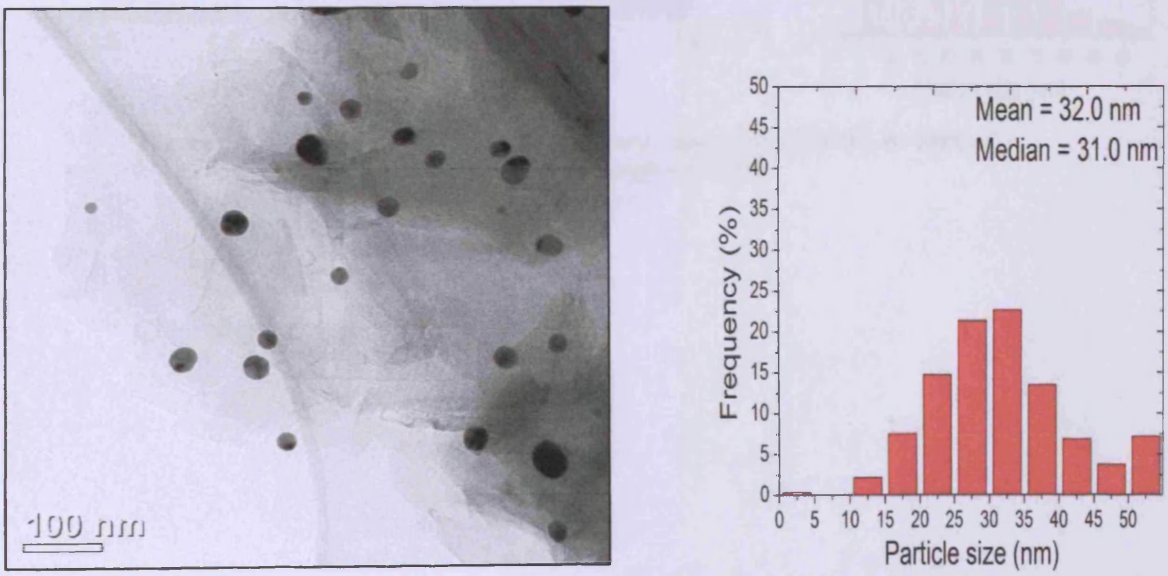


Figure 5.1 Bright field transmission electron microscopy (TEM) of 1%Au/G catalyst

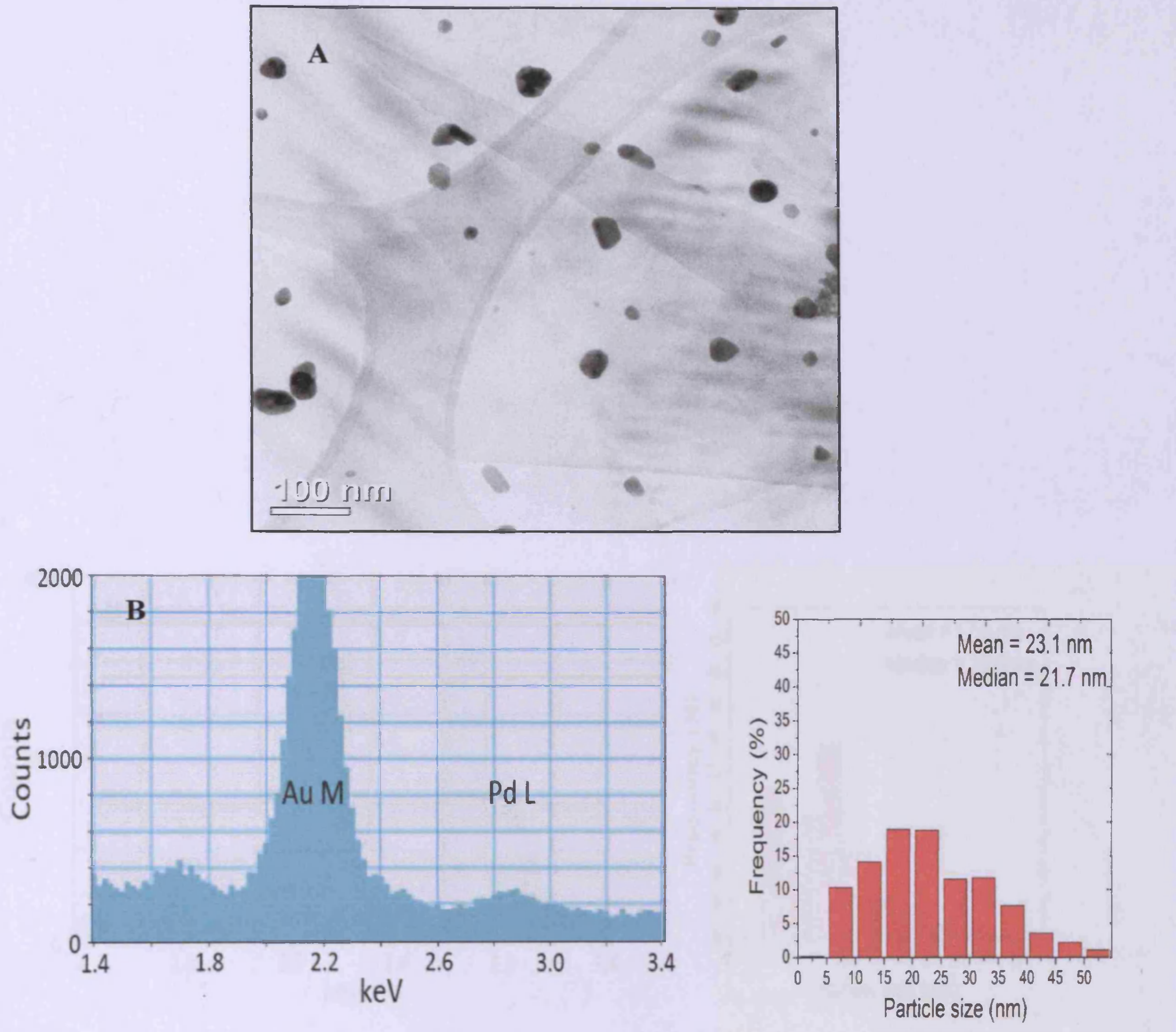


Figure 5.2 A: Bright field transmission electron microscopy (TEM), B: EDX of 0.84%Au-0.16%Pd/grapite catalyst

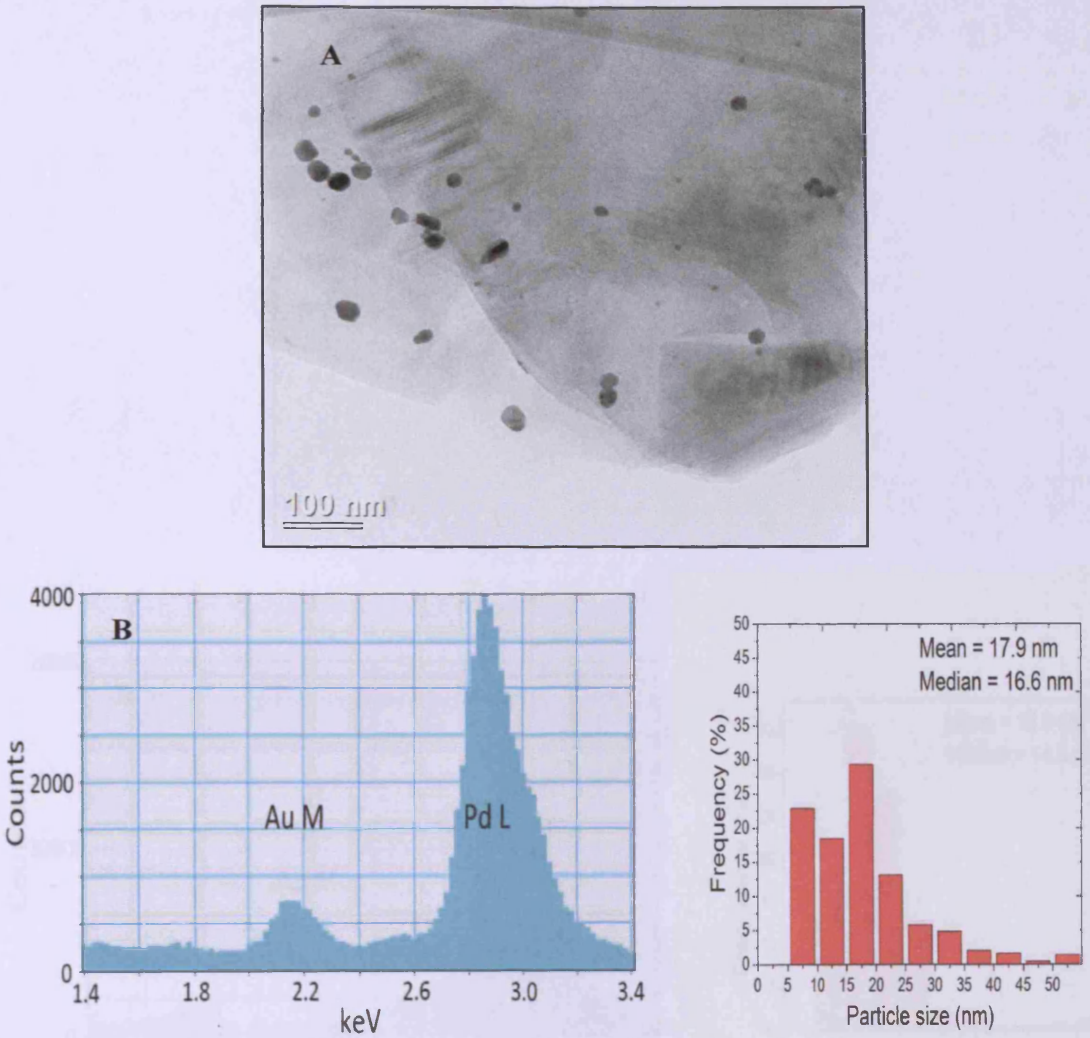


Figure 5.3 Bright field transmission electron microscopy (TEM), B: EDX of 0.5%Au-0.5%Pd/graphite catalyst

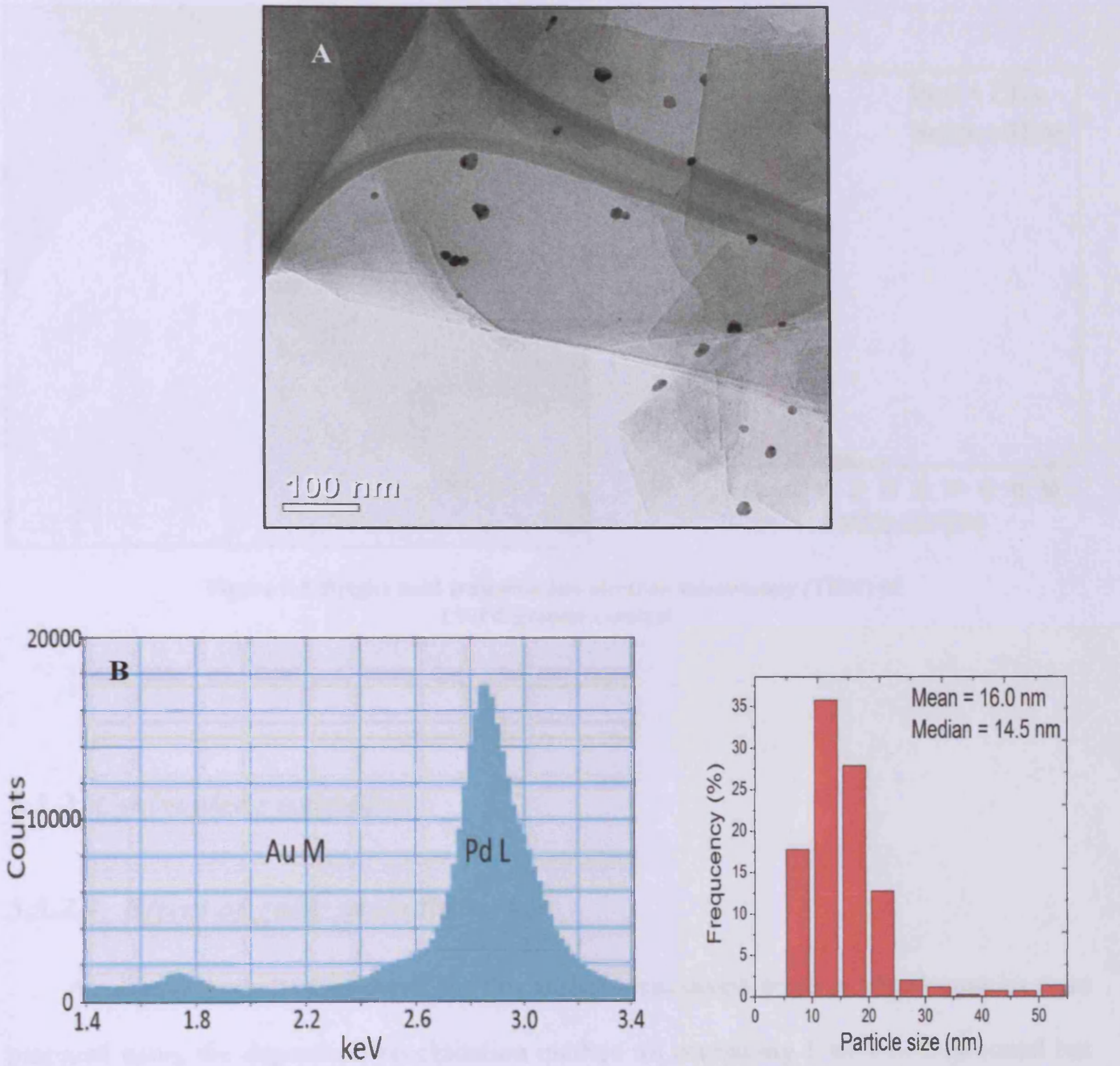


Figure 5.4 Bright field transmission electron microscopy (TEM), B: EDX of 0.16%Au-0.84%Pd/grapite catalyst

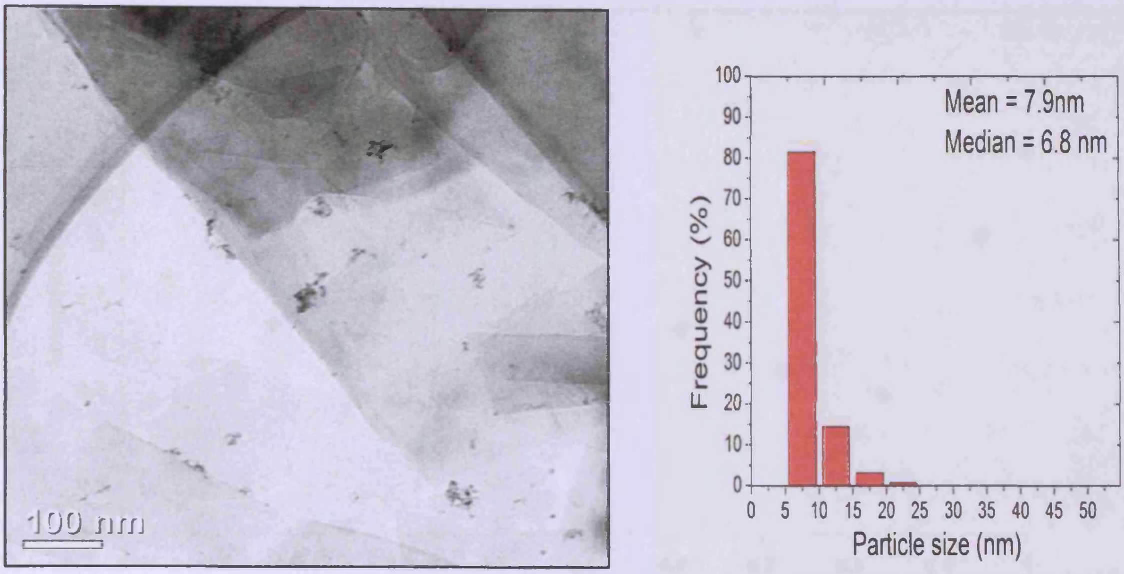


Figure 5.5 Bright field transmission electron microscopy (TEM) of 1%Pd/grapite catalyst

5.3.2. Cyclooctene oxidation

5.3.2.1. Effect of gold: palladium ratio

A range of graphite supported Au-Pd catalysts was investigated in which samples were prepared using the deposition precipitation method all containing 1 wt% of total metal but with varying Au:Pd ratios and the effect of the Au:Pd ratio on activity is shown in Figure 5.6. It is apparent that this variable has a major effect on the observed activity with two minima in activity being observed with Au:Pd weight ratios of 1:4 and 4:1 and a distinct maximum at Au:Pd = 1:1. However, the monometallic Au and Pd catalysts showed marginally higher activity when compared with the bimetallic Au-Pd = 1:1 catalyst. The selectivity to the epoxide was unaffected by the Au:Pd ratio and was *ca.* 75-80% across the composition range (Figure 5.7).

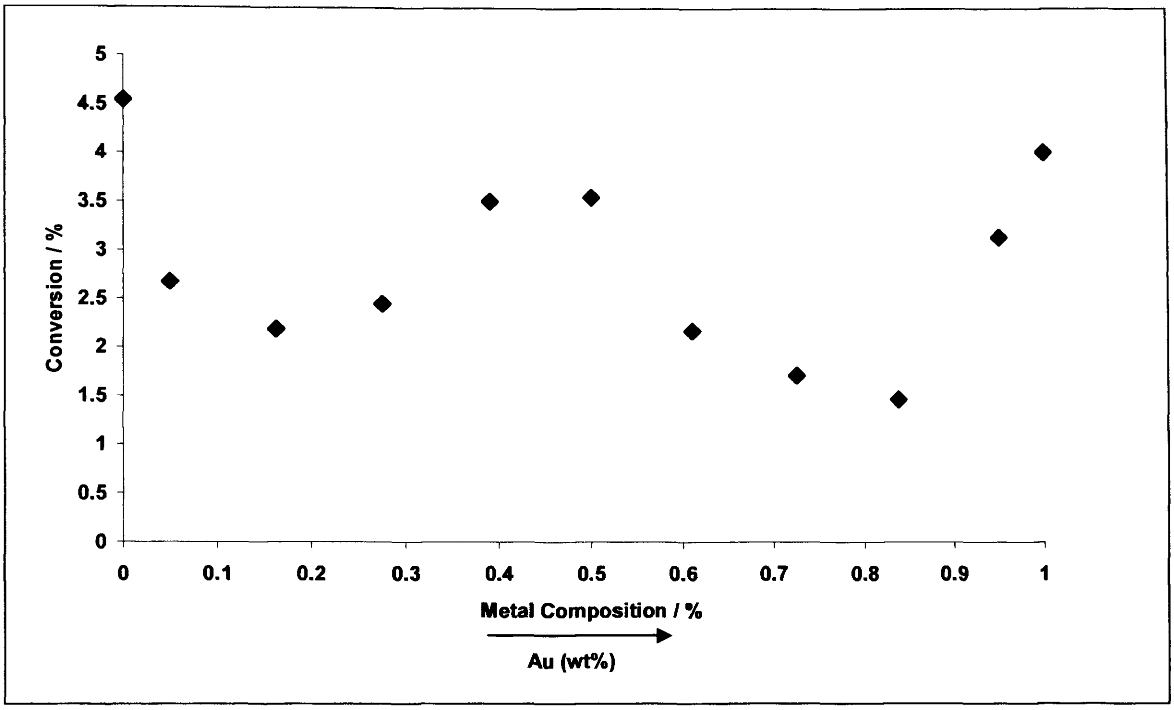


Figure 5.6 Effect of metal composition on cyclooctene conversion. Reaction conditions: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01ml, 1.03×10^{-4} mol), temperature 80 °C, 24 h, atmospheric pressure.

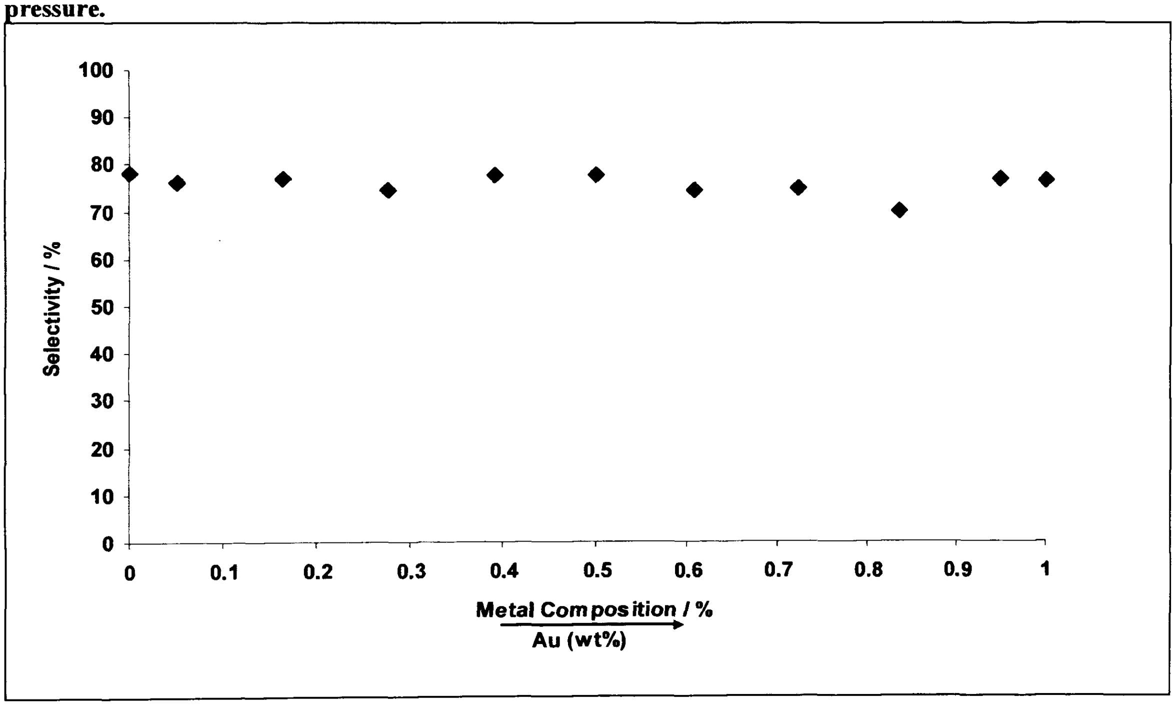


Figure 5.7 Effect of metal composition on the selectivity of cyclooctene oxide. Reaction conditions: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01ml, 1.03×10^{-4} mol), temperature 80 °C, 24 h, atmospheric pressure.

The combination of gold and palladium has been reported to have dramatic enhancement in catalytic activity in redox processes. Although gold alone is very effective catalyst in alcohol oxidation in the absence of solvent [5], the alloying of gold with palladium led to a 25-fold enhancement in activity [6]. While palladium alone is an exceptional catalyst for hydrogenation of molecular oxygen to hydrogen peroxide [7], the alloying with gold significantly enhances the activity and selectivity [8-13]. Moreover, Pd catalysts when dioxygen is used as the oxidant often show deactivation due to over oxidation [14, 15]. However, this synergetic effect is not general in all redox reactions. Especially in alcohol oxidation there has been reports [4, 16] of superior performance for the pure metal compared to bi-metal catalysts.

According to Figure 5.6 oxidation of cyclooctene with Au-Pd did not show any sign of synergy as pure metals shows better performance than the bimetallic catalyst. However, the activity is affected by changing the Au:Pd ratio. It is known that gold particle sizes play an important role in gold catalysis activity. TEM study for representative points of Fig. 5.6 reveals that there are no correlation between particle size of the metal and conversion of cyclooctene (Fig. 5.8). This rejects the possibility that the gold particle size has a major role in this reaction.

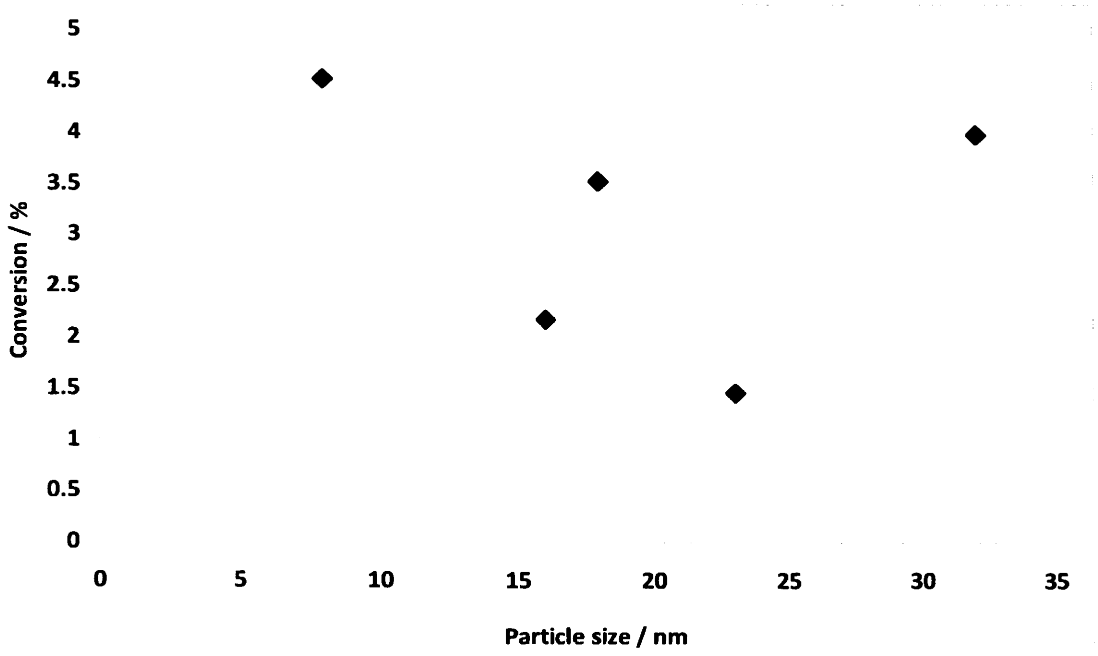


Figure 5.8 Relationship between gold particle size and conversion in cyclooctene epoxidation

The change in activity of Au-Pd catalysts by changing the ratio between Au and Pd could be rationalized as the effect of the order and disorder of Au-Pd formation. According to the phase diagram of Au-Pd alloy by changing the composition of Au-Pd the alloy changes from ordered to disorder alloy. The ordered phases of Au-Pd system was believed to occur when the gold –palladium composition is 1:4 and 4:1 at room temperature. It can be seen from Figure 5.9 that the minimum activity region coincides with the ordered region of the alloy. Moreover, the disordered regions correspond with high activity regions. Similarly, an activity trend has been reported in the literature for the gold system [17]. The activity of the Au-Cu system was reported to change for benzyl alcohol oxidation by changing the composition of the catalyst.

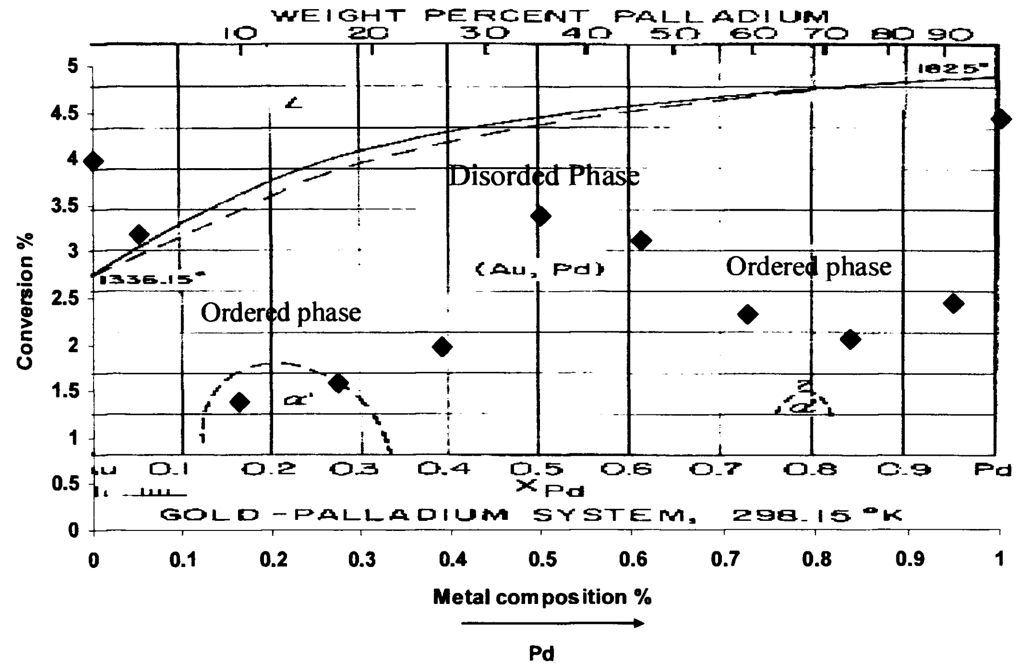


Figure 5.9 Correlation between the Au:Pd alloy ratio and phase diagram of Au-Pd.

To explore further the effect of AuPd ratio an XPS study has been conducted on these catalysts to examine the effect of the catalyst surface composition in cyclooctene oxidation. Fig. 5.10 shows that the percentage of palladium on the catalyst surface plays a detrimental effect on the catalytic activity of the catalyst. When the Pd concentration on the catalyst surface is low the catalyst exhibit low activity. However the activity of the catalyst increases by increasing the Pd present on the catalyst surface. Thus, at the minimum activity region (Fig. 5.9) the Pd surface concentration was low, however, when the concentration of Pd at the surface of the catalyst increases the activity increase in an appropriate manner.

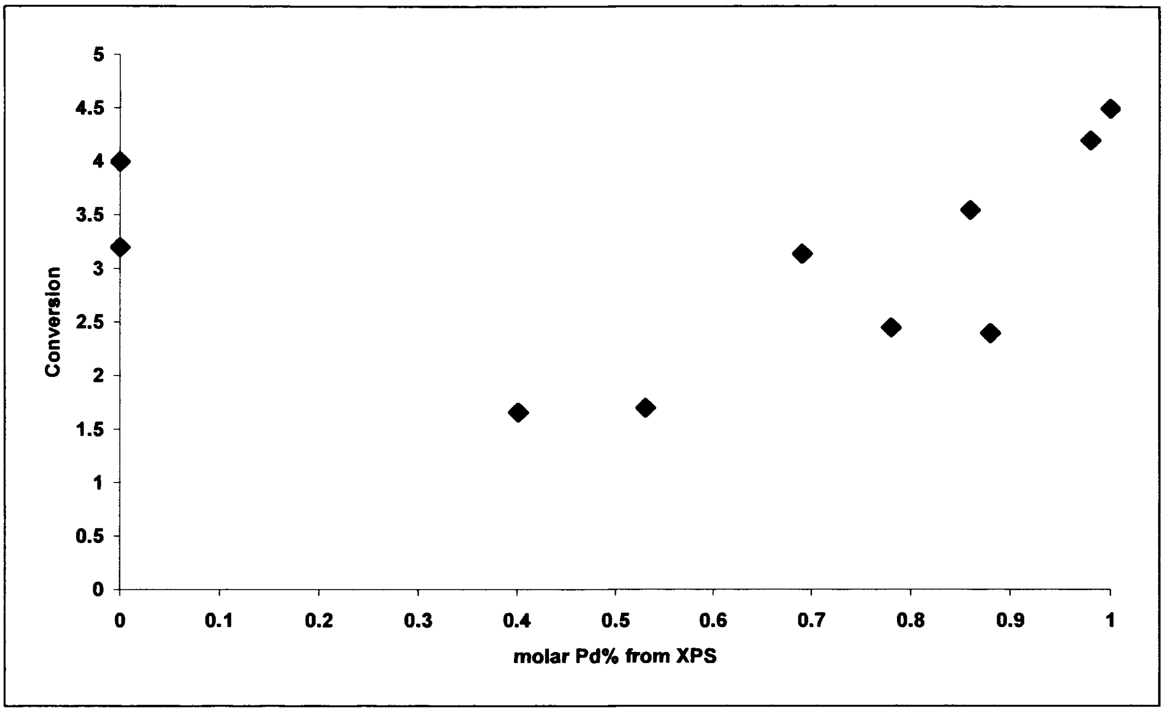


Figure 5.10 The influence on the cyclooctene conversion of the mean molar % of surface Pd determined by XPS Reaction conditions: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01 ml, 1.03x10^{-4} mol), temperature 80 °C, 24 h, atmospheric pressure.

5.3.2.2. Preparation method effect

One of the important parameter which can affect the activity of catalyst is the preparation method. Three different preparation methods were studied on the oxidation of *cis*-cyclooctene using gold, palladium and gold-palladium graphite-supported catalysts and the results are shown in Table 5.2.

Table 5.2 Effect of the preparation method on *cis*-cyclooctene oxidation using graphite-supported catalysts [a]

Preparation method	1%Au		1% Pd		1% (Au/Pd)	
	Conv.(%)	Sel.(%)	Conv.(%)	Sel.(%)	Conv.(%)	Sel.(%)
DP	4	78.9	4.4	78	3.3	82.9
Sol immobilization	7.7	81.5	2.16	79	1.6	72.7
Impregnation	4.2	71.3	2.5	75.9	4.8	76.1

[a] Reaction condition: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01ml, 1.03×10^{-4} mol), temperature 80 °C 24 hour, atmospheric pressure

The selectivity observed was very similar for all preparation methods, namely the main product was the epoxide with *ca.* 80% selectivity and the major by-product was the allylic alcohol. Using deposition precipitation or the standard impregnation method did not result in major differences in activity. However, it was noted that there appeared to be no synergistic effect on addition of Pd to Au for this oxidation reaction. This is in distinct contrast with two other redox reactions have previously studied in detail in Hutchings group, namely the oxidation of primary alcohols [6] and the direct synthesis of hydrogen peroxide [18] where a very pronounced synergistic effect is observed both on activity and selectivity. It can be seen from table 5.2 that the monometallic catalysts perform better with respect to cyclooctene oxidation compared to the bimetallic catalyst. This can be due to the rate of TBHP decomposition which is faster on the bimetallic catalyst.

Gold particle size has been reported to be an important factor in epoxidation. The catalytic activity of gold is directly related to the particle size in the nanometer length scale. It has been reported [19-22] for many reactions that gold catalyst activity decreases dramatically if not completely by increasing the gold particle size. One of these well known reactions is CO oxidation. The optimum particle size for this reaction has been identified as ~3 nm, increasing the particle size further would demolish any activity [23]. Nevertheless, the gold particle size required for hydrocarbon oxidation dose not seems to be the same. Figure 5.8 shows that in cis-cyclooctene oxidation the particle size did not affect the gold catalyst activity if the particle size was ≥ 15nm. According to Carrettin and coworkers [24] the optimum particle size for glycerol oxidation is about 20 nm using gold supported on graphite. Li and co-workers also observed high activity of supported gold catalyst with relatively big particle size in cyclooctene oxidation [19]. Using different preparation method in this study resulted in different gold particle size as sol immobilization resulted in mean particle size of 3-4nm while DP and impregnation method resulted in 25nm mean particle size. Despite the difference in particle size this was not reflected in the same magnitude in conversion. Another important observation is that the selectivity to epoxide is independent of gold particle size. Similar results were reported for cinnamyl alcohol oxidation [25].

In view of this TiO_2-supported catalysts (Table 5.3) were inspected and observed similar results, *i.e.* no synergistic effect was apparent for the addition of Pd to Au. Again the selectivity to the epoxide was *ca.* 80% and the allylic alcohol was the major by-product. It can be seen that when prepared by sol immobilization method the highest activity and selectivity was observed for a supported gold catalyst. However, Pd and Au-Pd catalyst exhibit very low activity with cis-cyclooctene oxidation, this may result from the instant decomposition of TBHP that is believed to take place with these catalysts at low TBHP concentration.

Table 5.3 Effect of the preparation method on *cis*-cyclooctene oxidation using titanium dioxide-supported catalysts [a]

Preparation method	1%Au		1% Pd		1% (Au/Pd)	
	Conv.%	Sel. %	Conv. %	Sel. %	Conv. %	Sel. %
DP	4.6	80.4	6.3	79.8	2.2	77.2
Immobilization	6.3	92.8	0.27	8.4	0.15	70.4
Impregnation	1.8	74.0	0.34	85.1	3.01	77.9

[a] Reaction condition: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01 ml, $1.03\text{x}10^{-4}$ mol), temperature 80 °C, 24 hour, atmospheric pressure

Consequently, the effect of the reducing agent, formaldehyde, on the catalytic activity was investigated (Table5.4). It can be seen that the improved results were obtained when formaldehyde was used as a reducing agent. For palladium catalyst, lower activity and selectivity were attained in the absence of formaldehyde. However, for the bimetallic catalyst calcination of the catalyst resulted in a reduction of the activity which could be due to the centering of the palladium particle along with possible change in alloy structure as seen in section 5.3.2.1.

Table 5.4 Effect of reduction with formaldehyde during preparation of graphite-supported catalysts for cyclooctene epoxidation [a]

Catalyst	Reduced with formaldehyde		unreduced		Unreduced and Calcined at 300 °C	
	Con. %	Sel. %	Con. %	Sel. %	Con. %	Sel. %
1%Au/graphite	4.0	78.2	3.7	83.0	4.6	74.9
1%Pd/graphite	4.4	78	3.0	70.3	5.2	71.7
0.5%Au-0.5%Pd/graphite	3.3	82.9	2.6	79.6	0.84	70.1

[a] Reaction conditions: catalyst (0.12 g), cis-cyclooctene (10 ml, 0.077 mol), TBHP (0.01ml, $1.03\text{x}10^{-4}$ mol), temperature 80 °C, 24 hour, atmospheric pressure.

5.3.3. Crotyl alcohol oxidation

The results shown above strongly suggest that, using Au supported on graphite, solvent free and a small amount of TBHP as initiator, selective oxidation of cyclooctene can be finely tuned. In addition, the solvent free selective oxidation of *cis*-cyclooctene is environment friendly as an effective selective oxidation without solvent and represents a major tenet of green chemistry. In a subsequent study, the selective oxidation of crotyl alcohol has been studied. This opens the possibility of a gold catalyst providing tuneable activity for the selective oxidation of aliphatic alkenes. The second reason for studying the oxidation of crotyl alcohol over Au/graphite catalyst was to determine if gold supported on graphite can chemoselectivity oxidize C=C in the presence of another functional group.

5.3.3.1. Effect of gold: palladium ratio

The effect of the Au:Pd ratio was investigated on the activity and selectivity for the reaction of crotyl alcohol. Crotyl alcohol was selected as there are two functional groups present that can be oxidized (Fig. 5.11). In these initial experiments the same reaction conditions that had been adopted for the epoxidation of *cis*-cyclooctene, and in particular TBHP was present as a radical initiator in catalytic amounts, was used. The catalysts were prepared by the deposition precipitation method all containing 1 wt% of total metal but with varying Au:Pd molar ratios and the effect of the Au:Pd molar ratio on activity is shown in Figure 5.12.

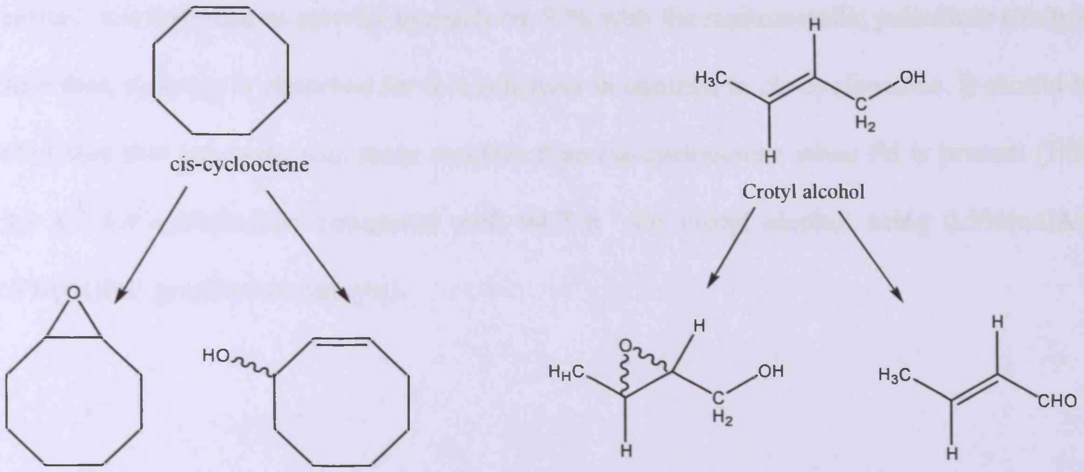


Figure 5.11 ***Cis*-cyclooctene and trans-crotyl alcohol, together with their principal expected products under heterogeneous epoxidation conditions**

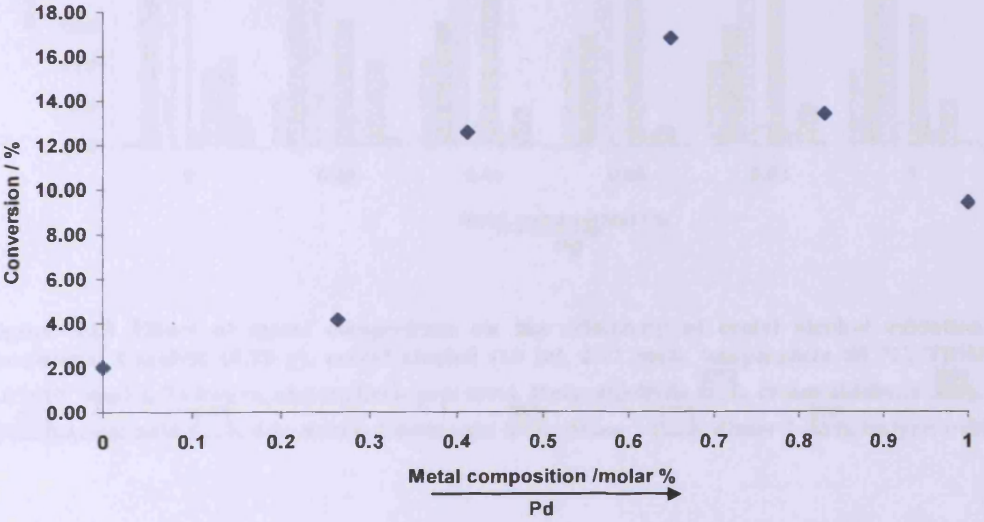


Figure 5.12 Effect of metal composition on crotyl alcohol conversion (Reaction condition: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03x10^{-4} mole), 24 hours, atmospheric pressure).

The conversion of crotyl alcohol steadily increases as Pd is added to the catalyst composition to peak at a Au:Pd molar ratio of 3.5:6.5 (*ca.* 16.9%). Further addition of Pd resulted in a decrease in activity to reach *ca.* 9 % with the monometallic palladium catalyst. Therefore, synergy is observed for this substrate in contrast to cis-cyclooctene. It should be noted that this substrate was more reactive than *cis*-cyclooctene when Pd is present (TOF 13.1 h^{-1} for cyclooctene compared with 94.7 h^{-1} for crotyl alcohol using 0.5%(wt)Au-0.5%(wt)Pd/ graphite as catalyst).

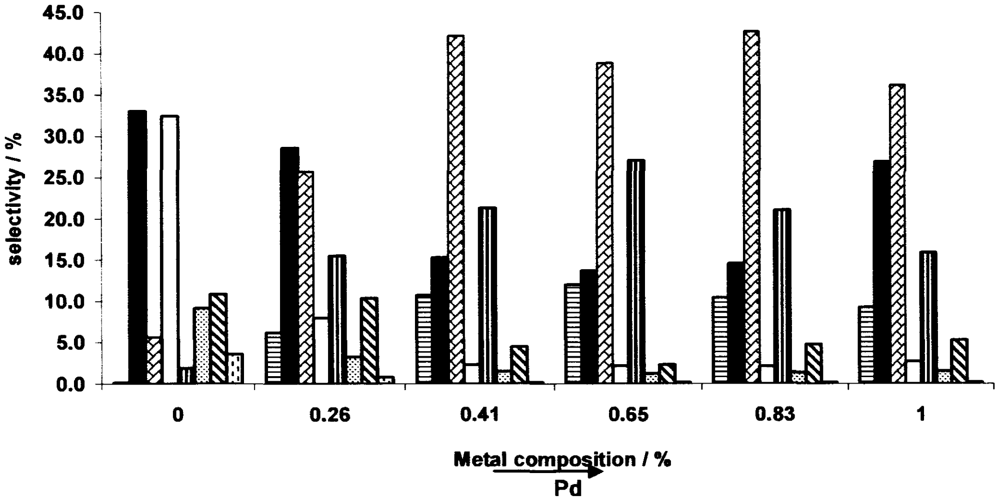


Figure 5.13 Effect of metal composition on the selectivity of crotyl alcohol oxidation (Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), 24 hours, atmospheric pressure). Butyraldehyde (▤), crotonaldehyde (■), 3-buten-1-ol (▨),acetic acid (□), 4-hydroxy-2-butanone (▥), dimer 1 (▒), dimer 2 (▧), butyric acid (▦).

The effect on the selectivity was, however, very marked (Figure 5.13) with different reactions occurring in the same time. With catalysts comprising mainly Pd, the isomerisation reaction was dominant as 3-buten-1-ol was the major product and modest levels of oxidation were observed. Additionally, 4-hydroxy-2-butanone was detected in significant quantities when Pd is present and is considered to form *via* oxidation of 3-buten-1-ol through Wacker type oxidation [26-28]. Only when the catalysts became rich in gold, with low surface Pd concentration, was the oxidation of the alcohol functional group observed. Oxidation of the alcohol group was observed with all catalyst formulations, however, where gold is higher in surface concentration the yield of crotonaldehyde is increased (Fig. 5.14). The exception to this is the Pd only catalyst which has a higher selectivity to crotonaldehyde than the Au-Pd catalysts. Gold promotes/favors alcohol oxidation via O_2 or a radical species derived from it on the metal surface. Similarly, with the pure Pd catalyst, This indicates that the Pd and Au-Pd catalysts facilitate isomerisation, which may be due to the generation of π-allyl intermediates by chemisorption with allylic C-H dissociation at C-1 and C-3

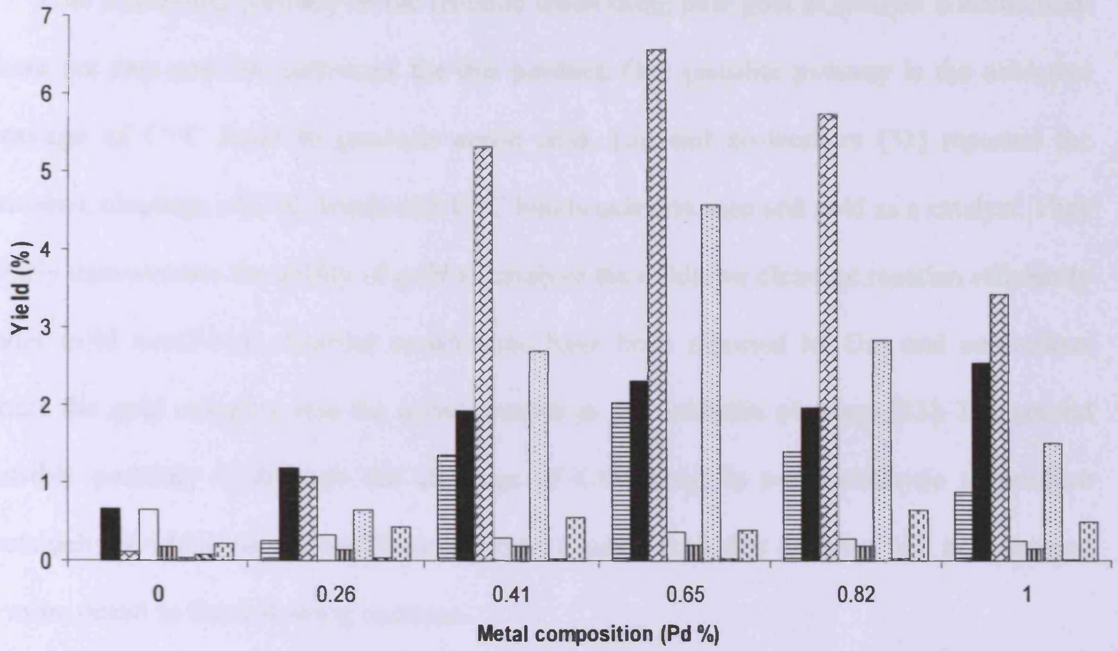


Figure 5.14 Effect of metal composition on the product yield of crotyl alcohol conversion. Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 mL, 1.03x10^{-4} mol), 24 hours, atmospheric pressure. Butyraldehyde (▤), crotonaldehyde (■), 3-buten-1-ol (▨), acetic acid (☐), Dimer 1 (░), 4-hydroxy-2-butanone (▥), Dimer 2 (▧), butyric acid (▒).

Hou and co-worker [29] reported the oxidation of crotyl alcohol over Au-Pd catalyst with product distribution of 34% crotonaldehyde and 40% 3-buten-1-ol. Similar isomerisation products were reported by Abad and coworkers [4, 16].. Palladium is known for it high activity in hydrogenation reaction [30, 31]. According to Abad and co-workers the stability of Pd-H and Au-H play an important role in the reaction path way i.e. if the reaction will proceed through oxidation route or hydrogenation route [16]. The Pd-H species (which is more stable than Au-H) is postulated to be responsible for promoting the isomerisation and hydrogenation reactions in Au-Pd and Pd catalysts.

One interesting pathway of the reaction when using pure gold as catalyst is acetic acid. There are two possible pathways for this product. One possible pathway is the oxidative cleavage of C=C bond to produce acetic acid. Liu and co-workers [32] reported the oxidative cleavage of C≡C bonds and C=C bonds using oxygen and gold as a catalyst. They clearly demonstrate the ability of gold to catalyse the oxidative cleavage reaction efficiently under mild conditions. Similar conclusions have been reported by Das and co-workers where the gold complex was the active species in the oxidative cleavage [33]. The second possible pathway is through the cleavage of C=C bond in crotonaldehyde to produce acetaldehyde which in turn oxidises to produce acetic acid, this pathway will be discussed in more detail in the following sections.

5.3.3.2. Effect of preparation method

Crotyl alcohol oxidation was investigated using 1 wt% Au supported on graphite prepared using the deposition precipitation, impregnation and sol immobilization methods and the results are shown in Table 5.5. Impregnation and deposition precipitation methods gave very similar activities, while sol immobilization shows lower activity. However, no epoxide was observed and the major product was crotonaldehyde, derived from the oxidation of the alcohol functional group with all catalysts. Four other by-products were observed in significant amounts namely, acetic acid, dimer 1, dimer 2 and 3-buten-1-ol. The product distributions of all three methods were fairly close. However, for sol immobilization method the selectivity towards crotonaldehyde was better than the other two methods. This could be linked to the smaller particle size of gold which was produced in sol immobilization method (3 nm for sol immobilization method compare to 25 nm for DP and impregnation methods). 3-Buten-1-ol, however, derives from the isomerisation of the C=C bond. Nevertheless, for the gold monometallic catalysts the oxidation of the alcohol group was the dominant pathway. The overall reaction pathways are summarised in Figure 5.15.

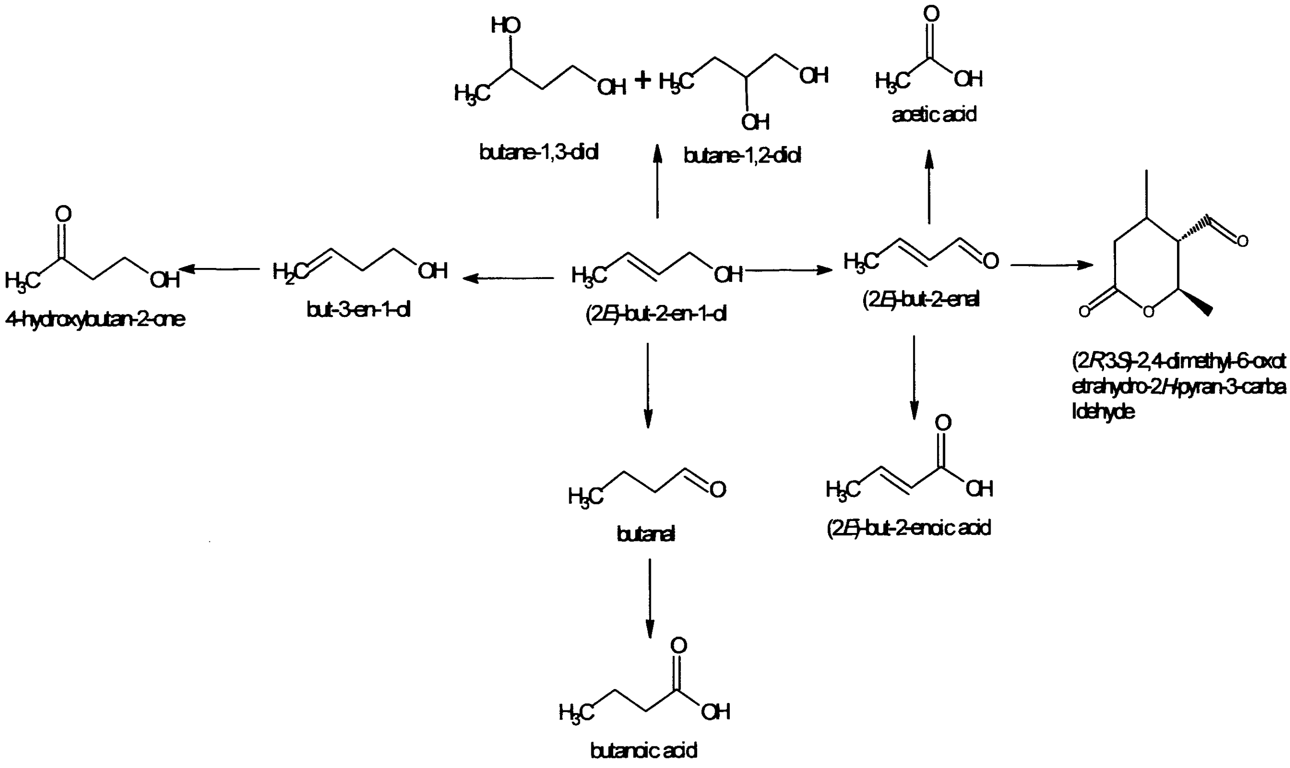


Figure 5.15 Crotyl alcohol oxidation using 1%Au/graphite and TBHP

Table 5.5 Effect of the method of preparation on crotyl alcohol oxidation using 1 wt% Au graphite-supported catalysts [a]

Preparation method		DP	Immobilization	Impregnation
Conversion (%)		2.02	1.94	2
Selectivity (%)	butyraldehyde	0.1	3.3	0.2
	crotonaldehyde	33.0	47.1	31
	3-buten-1-ol	5.6	6.1	5.5
	Acetic acid	32.5	14.6	33.3
	4-hydroxy-2-butanone	1.9	1.5	2
	butyric acid	3.6	1.8	3.4
	dimer 1	9.2	7.1	10
	dimer 2	10.9	16.6	11
	1,2-butandiol	1.0	0.8	1
	1,3-butandiol	1.1	0.5	1.2
	crotonic acid	1.0	0.6	1.4

[a] Reaction condition: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), 24 hours, atmospheric pressure.

5.3.3.3. Radical initiator effect

To examine the effect of TBHP on the course of crotyl alcohol reaction, two sets of gold-palladium catalysts were used with and without TBHP and the results are summarised in Fig. 5.16 and Fig. 5.17. It can be seen from these Figures that the addition of TBHP does not seem to affect the activity of Au-Pd catalysts on crotyl alcohol oxidation. Furthermore, the product distribution of reactions with and without the TBHP shows the same trend. These findings indicate that the oxidation of crotyl alcohol do not proceed through the same route as cyclooctene oxidation over these catalysts. The presence of radicals in the reaction media appear to be irrelevant to crotyl alcohol oxidation as it does not seems to proceed through radical route.

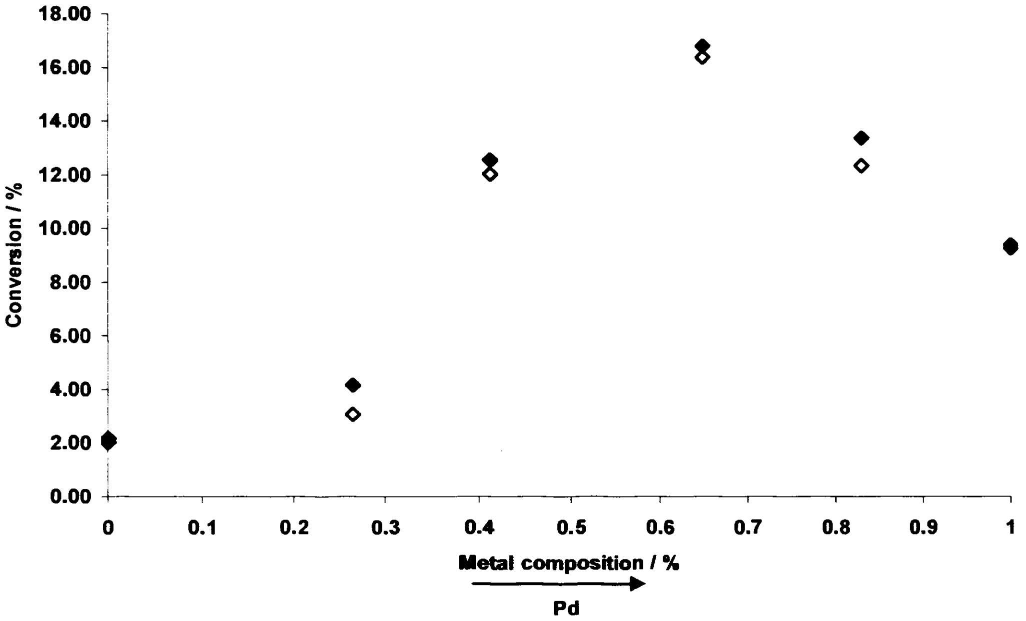


Figure 5.16 Effect of metal composition effect on crotyl alcohol conversion with TBHP (close symbol) and without TBHP (open symbol) (Reaction condition: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), 24 hours, atmospheric pressure

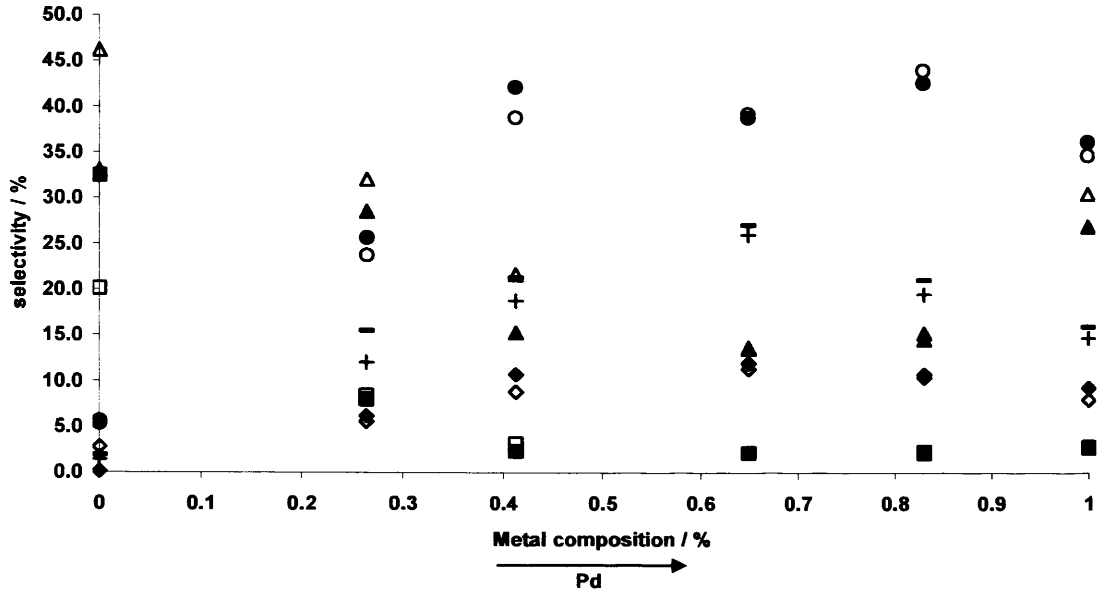


Figure 5.17 Metal composition effect on crotyl alcohol oxidation with TBHP (closed symbol) and without TBHP (open symbol) (selectivity) (Reaction condition: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), 24 hours, atmospheric pressure) crotonaldehyde diamond, 3-buten-1-ol triangle, 1-butanol square, butyraldehyd circle.

Intrigued by these results, AIBN and TBHP as radical initiator has been compared in crotyl alcohol oxidation and the results are presented in Table 5.6. It can be seen from Table 5.6 that TBHP shows better activity in crotyl alcohol oxidation when Pd presented in the catalyst. However, AIBN is more active when only gold is used as catalyst. The selectivity with both initiators is fairly similar. To explore this further a reaction with crotyl alcohol and AIBN in the absence of the catalyst has been performed which yielded a conversion of ca. 7% and selectivity similar to the reaction with catalyst. The same experiment has been performed using TBHP which resulted in very low activity. This finding suggests that crotyl alcohol oxidation using AIBN proceeds through a homogeneous reaction however with TBHP the catalyst play the major role in the oxidation and the reaction proceed heterogeneously.

Table 5.6 Radical initiator effect on Crotyl alcohol oxidation [a]

Catalysts		1%Au/graphite		0.5%Au-0.5%Pd/graphite		1%Pd/graphite	
Radical initiator		TBHP	AIBN	TBHP	AIBN	TBHP	AIBN
Conversion (%)		2.0	7	16.9	6.3	9.4	7.4
Selectivity (%)	butyraldehyd	0.1	0.2	12.1	0.5	9.3	0.3
	crotonaldehyde	33.0	49.9	13.8	50.4	27.1	52.8
	3-buten-1-ol	5.6	2.3	39.0	4.5	36.4	4.8
	Acetic acid	32.5	24.6	2.2	18.1	2.8	20.1
	Unknown 1	9.2	10.5	1.2	11.3	1.6	9.8
	4-hydroxy-2-butanone	1.9	0.9	27.2	2.9	16.0	2.3
	butyric acid	3.6	1.4	0.2	1.4	0.2	1.3
	Dimer 1	9.2	10.5	1.2	11.3	1.6	9.8
	Dimer 2	10.9	6.3	2.3	6.7	5.3	4.8
	1,2-butandiol	1.0	1.2	0.2	1.2	0.2	1.1
	1,3-butandiol	1.1	0.3	0.4	0.2	0.1	0.2
	crotonic acid	1.0	2.4	1.4	2.7	1.0	2.4

[a] Reaction condition: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, radical initiator ($1.03\text{x}10^{-4}$ mole), 24 hours, atmospheric pressure

5.3.3.4. Influence of reaction time

To gain more insight on the reaction route of crotyl alcohol oxidation, the reaction duration was extended and has been performed using two catalysts namely 1%Au/graphite and 0.5%Au-0.5%Pd/graphite and the results are shown in Fig. 5.18- Fig. 5.21.

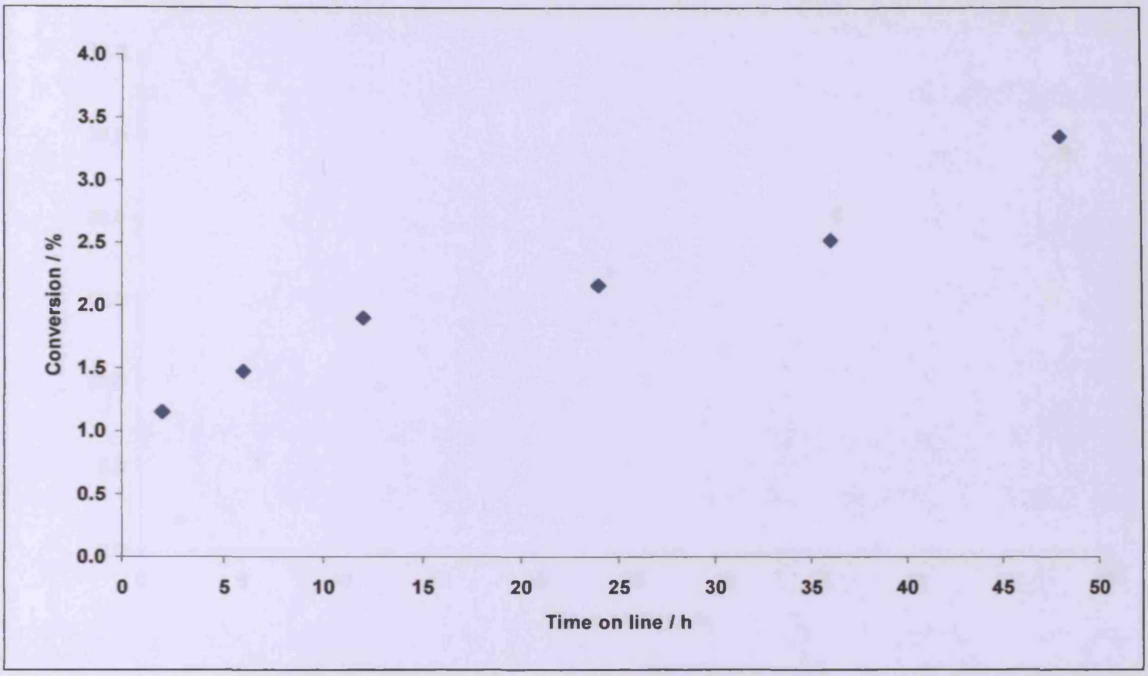


Figure 5.18 Effect of reaction time on the conversion of crotyl alcohol using1%Au/graphite as catalysts. Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), atmospheric pressure.

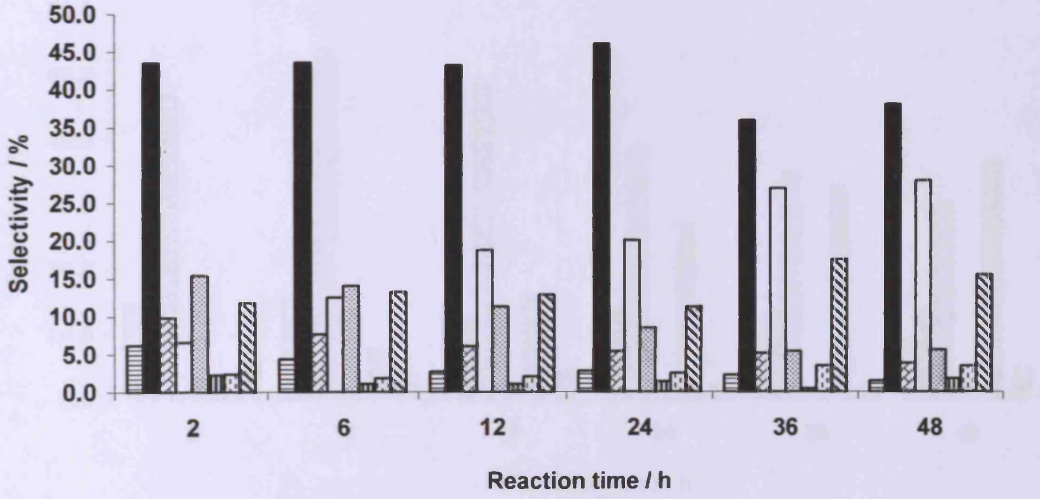


Figure 5.19 Selectivity to products of crotyl alcohol conversion using 1%Au/graphite as catalyst. Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 mL, 1.03×10^{-4} mol), atmospheric pressure. Butyraldehyde (▤), crotonaldehyd(■), 3-buten-1-ol (▨), acetic acid (□), 4-hydroxy-2-butanone (▥), dimer 1 (░), dimer 2 (▧), butyric acid (▦)

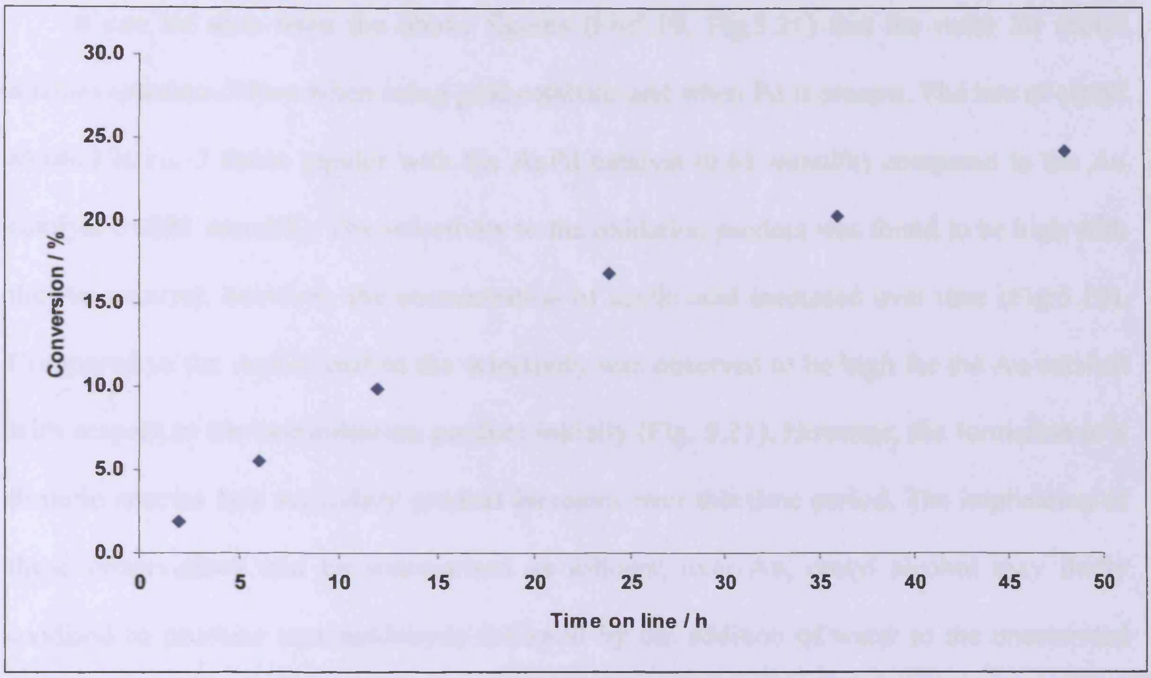


Figure 5.20 Effect of reaction time on the conversion of crotyl alcohol using 0.5%Au-0.5%Pd/graphite as catalysts. Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mole), glass reactor, atmospheric pressure.

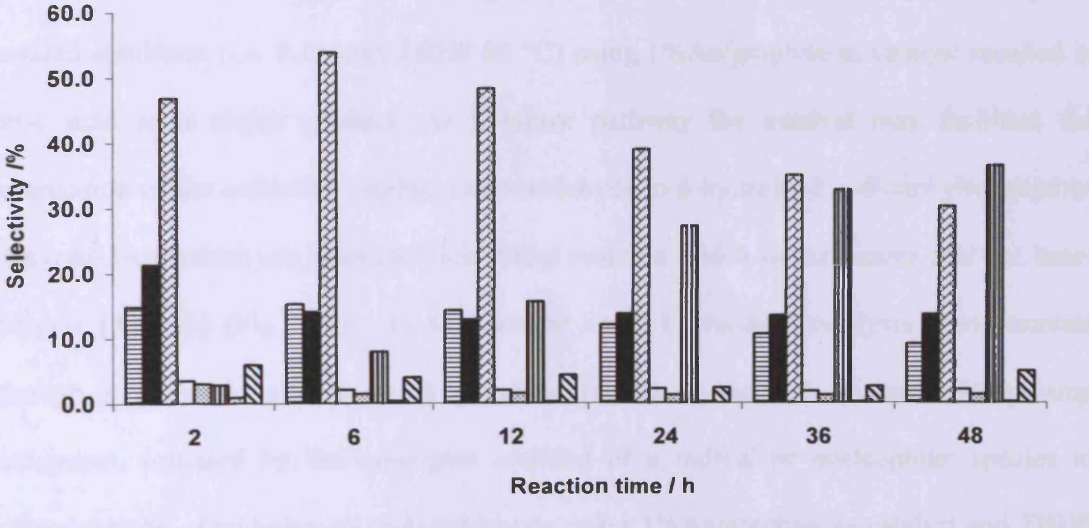


Figure 5.21 Selectivity to products of crotyl alcohol conversion using 0.5%Au-0.5%Pd/graphite as catalyst. Reaction conditions: Catalyst (0.12 g), crotyl alcohol (10 ml, 0.12 mol), temperature 80 °C, TBHP (0.01 ml, 1.03×10^{-4} mol), atmospheric pressure. Butyraldehyde (▤), crotonaldehyd(■), 3-buten-1-ol (▨), acetic acid (☐), 4-hydroxy-2-butanone (▥), dimer 1 (░), dimer 2 (▧), butyric acid (▩)

It can be seen from the above figures (Fig5.19, Fig.5.21) that the route for crotyl alcohol reaction differs when using gold catalysis and when Pd is present. The rate of crotyl alcohol is *ca.* 7 times greater with the AuPd catalyst (0.61 mmol/h) compared to the Au catalyst (0.085 mmol/h). The selectivity to the oxidation product was found to be high with the Au catalyst, however, the concentration of acetic acid increased over time (Fig 5.19). Compared to the AuPd catalyst the selectivity was observed to be high for the Au catalyst with respect to the isomerisation product initially (Fig. 5.21). However, the formation of a dimeric species as a secondary product increases over this time period. The implication of these observations can be summarised as follows; over Au, crotyl alcohol may firstly oxidised to produce crotonaldehyde followed by the addition of water to the unsaturated bond then subsequently through the cleavage of hydrated crotonaldehyde (*retro*-aldol fragmentation), which may produce two acetaldehyde molecules which could then transform to acetic acid as seen in Figure 5.22. Oxidation of acetaldehyde using the standard condition (i.e. 0.1mmol TBHP 80 °C) using 1%Au/graphite as catalyst resulted in acetic acid as a major product. As a minor pathway the catalyst may facilitate the dimerisation of the oxidation product crotonaldehyde to 6-hydroxy-2,4-dimethyltetrahydro-2H-pyran-3-carbaldehyde through Diels-Alder reaction which occurs under acid- or base-catalysis [34, 35] (Fig. 5.23). In the present case, Lewis-acid catalysis could operate although a plausible alternative is a radical (or base-)-induced Michael addition-trap mechanism, initiated by the conjugate addition of a radical or nucleophilic species to crotonaldehyde. Oxidation of crotonaldehyde using 1%Au/graphite as catalyst and TBHP at 80 °C resulted in acetic acid, dimer 1 and dimer 2 in the expected manner. Likewise over the studied Au-Pd catalyst, crotonaldehyde could be formed as discussed above and other possible pathway arises by π-allyl formation when palladium is present (Fig. 5.24). Hydration of such a species adjacent to the hydroxyl group would also generate crotonaldehyde. The implication that a π -allyl species is involved would also account for the formation of both 3-buten-1-ol, another significant product, and of butanal, following alkene isomerisation without hydration. Subsequent oxidation of the former would then lead to the relatively small amount of butanoic acid, observed, as would formation of crotonic acid, by direct oxidation of crotonaldehyde A possible origin of the 3-hydroxy-2-butanone is by a Wacker-type oxidation of 3-buten-1-ol, but could conceivably also arise by rearrangement of the epoxide derived from crotyl alcohol. However, no epoxide or other obvious products arising from it were observed; indeed, epoxidation of the starting alcohol appears not to occur to any detectable level.

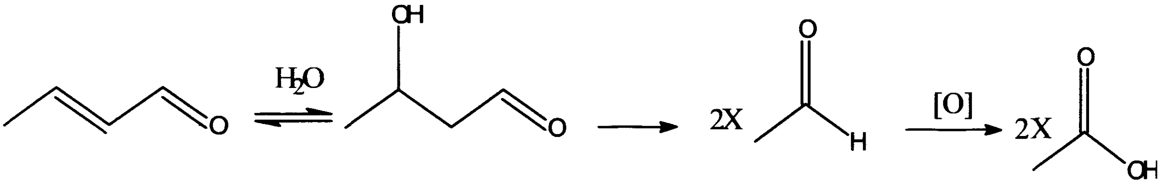
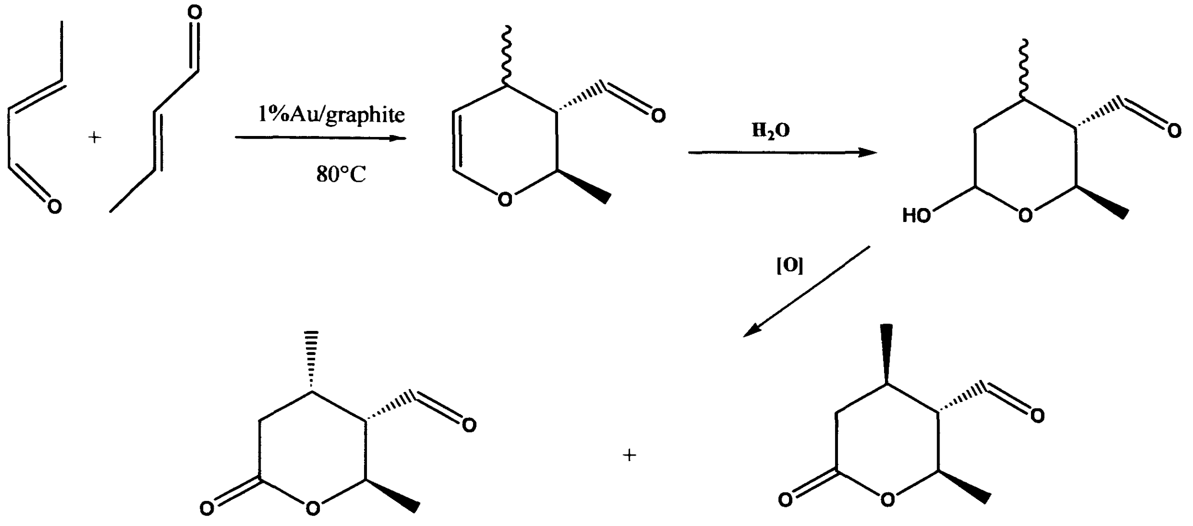


Figure 5.22 Formation of acetic acid from crotonaldehyde in the presence of 1%Au/graphite



(2*R*,3*S*,4*S*)-2,4-dimethyl-6-oxotetrahydro-2*H*-pyran-3-carbaldehyde (2*R*,3*S*,4*R*)-2,4-dimethyl-6-oxotetrahydro-2*H*-pyran-3-carbaldehyde

Dimer 1 Dimer 2

Figure 5.23 Diels-Alder formation of products 6-hydroxy-2,4-dimethyltetrahydro-2H-pyran-3-carbaldehyde from oxidation product crotonaldehyde

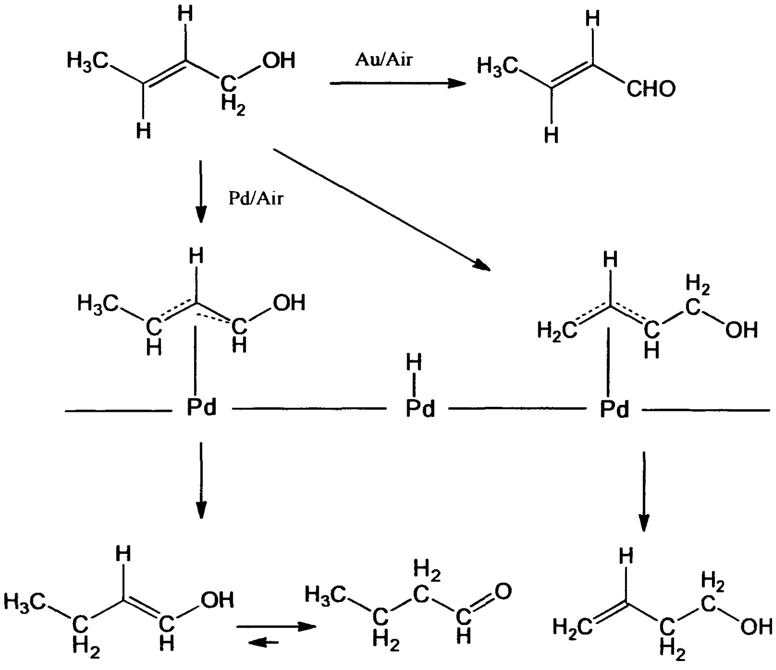


Figure 5.24 Principal pathways for transformation of crotyl alcohol in air catalysed by Au and Au-Pd on graphite

5.4. Conclusions

In this chapter the study of *cis*-cyclooctene epoxidation using mild oxidising conditions has been extended to investigate catalyst preparative methods. The results indicate that although no synergistic effects between Au and Pd were noted with *cis*-cyclooctene, improvements in epoxide yield could be achieved through careful catalyst preparation. Gold catalysts prepared by the sol immobilisation method were found to yield the highest epoxide, however the DP method was found to be the superior method with Pd and bimetallic catalysts. Investigating these Au-Pd mixed catalysts for *cis*-cyclooctene oxidation has revealed the complex nature of such mixtures, through TEM and XPS, and their influence on the activity observed. The interesting activity profile generated under these conditions may suggest that structured alloys were produced, as the minima correspond to regions where the ratio of Au:Pd is 1:4 and 4:1 by weight. Examination by electron microscopy and XPS indicate that the particle size and the mean surface Pd concentration may combine to affect the activity observed so that, where the surface Pd concentration is highest, the activity is correspondingly high.

Oxidation of crotyl alcohol under similar conditions resulted in a larger range of products wherein the influence of Au and Pd could be clearly differentiated. Where Au was present in high concentrations, oxidation to crotonaldehyde was the preferred pathway. However, when Pd was present in the catalyst the dominant pathway was isomerisation which may be followed by Wacker-type oxidation. The conversion of crotyl alcohol is highly dependent on the ratio of Au and Pd. Monometallic Au was observed to have a low activity, whereas mixtures of Au and Pd had the highest activity. This synergistic effect has been observed before with other catalysts and appears to be related to the isomerisation of the starting material when Pd is present. The activity and product distribution of crotyl alcohol oxidation using gold supported on graphite was proven to be irrelevant to the addition of TBHP in sharp contrast to *cis*-cyclooctene oxidation. Despite the fact that the studied preparation method of supported gold catalysts has no affect on the activity of crotyl alcohol, the sol immobilisation method seemed to yield the highest aldehyde concentration which could be related to the gold particle size.

5.5. References

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Chapter Six

Conclusions and Future Work

6. Conclusions and Future Work

6.1. Conclusions

In the last two decades the interest in gold catalysis has risen dramatically after the discovery of it potential uses as catalyst [1, 2]. Selective oxidation of hydrocarbon is one of important reactions which can open the possibility for a variety of intermediates that can be used in industry. One of the intermediate and challenging processes facing the chemical industry is the epoxidation of alkenes. Epoxidation of high alkenes, particularly, are considered a difficult task. The epoxidation of *cis*-cyclooctene has been chosen as model reaction to perform under solvent free oxidation conditions using supported nano-gold catalysts.

The objective for this study was divided into three main parts: firstly, identification of the background reactions which could originate from the radical initiator or the support in the absence of catalyst. These may result in a reduction of the selectivity observed of the desired products. Secondly, study the effect of bimetallic catalyst, in particular Au-Pd, and the effect of the ratio between the two metals in cyclooctene epoxidation. Finally, exploit the chemoselectivity of gold catalysis in oxidising carbon carbon double bonds in the presence of other functional group, namely a hydroxyl group. In all of these studies, the reactions were carried out in solvent free and mild conditions.

In summary, the oxidation of cyclooctene was performed in solvent free condition using radical initiator; 1%Au/graphite as catalyst and oxygen from air as oxidant at mild temperature. The choice of the radical initiator is crucial thus the effect of radical initiator was studied using five radical initiators. The activity of cumene hydroperoxide (CHP), azobisisobutyronitrile (AIBN) and dibenzoyl peroxide (BPO) was high even in the absence of the catalyst at all studied temperatures. On the other hand, Di-t-butyl peroxide (DTBP) was inactive even in the presence of catalyst. *t*-Butylhydroperoxide (TBHP) did not show activity in absence of catalyst especially at low concentration, however, it was the only radical initiator which shows enhancement in activity in the catalysed reaction. The high activity of CHP, AIBN and AIBN was contributed to the fast homolysis of these radical initiators. The presence of carbon radical centre using AIBN and BPO was claimed to facilitate the production of cyclooctene hydroperoxide which oxides cyclooctene. The poor activity of DTBP could be due to the high activation energy of homolysis. The cooperative effect of gold with TBHP to produce a variety of radical species was postulated to be the cause of the enhancement in activity observed in the catalysed reaction. The standard reaction conditions in which the background reactions were minimised were identified as follows: TBHP (0.1mmol) and 80 °C.

Gold supported catalysts have been demonstrated to be an effective catalyst for cyclooctene oxidation using TBHP as radical initiator at 80 °C. To examine if the graphite is the best support for this reaction gold nanoparticles supported on graphite, activated carbon, silicon carbide, TiO_2, SiO_2 and Al_2O_3 were tested. In general, supports such as graphite, TiO_2, SiO_2 and Al_2O_3 were identified to be rather inactive mostly at low temperatures and TBHP concentration. The functionality presented on the surface of carbon supports, particularly, activated carbon and silicon carbide were found to play a determinate role in cyclooctene oxidation as these two supports show activity in absence of gold. Pre-washing of activated carbon and silicon carbide supports resulted in enhancement in catalytic activity. All supported gold nanoparticle exhibit activity in cyclooctene oxidation and the activity was as following: SiC > graphite ≈ TiO_2 > Al_2O_3 ≈ SiO_2 ≈ Ac and for selectivity to the epoxide the order is graphite ≈ SiO_2 ≈ TiO_2 > SiC ≈ Al_2O_3 ≈ Ac, therefore graphite was concluded to be the support of choice.

One of the key aspects of green chemistry is the recovery and re-use of the catalyst. The reusability of 1%Au/graphite was investigated and the treatment of the used catalyst was proven to be of importance. The solvent used in washing the recovered catalyst was demonstrated to be important and the best results were obtained using only acetone or without solvent treatment. The optimized conditions for catalyst reusability are: acetone as solvent and drying (150 °C) in static air. Despite the reduced activity of the reused catalyst (60% of original activity over 24 h), the catalyst can retain this low activity for a further two subsequent uses. The lower activity of the reused catalyst was postulated to be due to the possible strong adsorption of the epoxide products on the catalyst surface. However, this poisoning effect was found to be insignificant over longer reaction times for the reused catalyst.

A mechanism that is consistent with most of this study observation is set out in chapter 4. Despite evidence which suggested that the reaction proceeds through a radical mechanism, the dramatic increase in epoxide selectivity in the presence of the gold catalyst suggests that the chemistry takes place on or near the metal surface. Cyclooctene hydroperoxide was postulated as the active species in this mechanism. The presence of cyclooctene hydroperoxide was confirmed in rather small concentration at the end of the reaction using triphenylphosphine. This is consistence with the postulation that cyclooctene hydroperoxide is formed then consumed in cyclooctene oxidation.

Furthermore, the epoxidation of *cis*-cyclooctene was extended using mild oxidising conditions to investigate bimetallic catalyst effect. By screening various ratios of Au-Pd supported on graphite it can be concluded that there was no synergistic effect between Au and Pd. Nevertheless, the activity was affected by changing the Au-Pd ratio. The interesting activity profile generated under these conditions may suggest that structured alloys were produced, as the minima correspond to regions where the ratio of Au:Pd is 1:4 and 4:1 by weight. XPS reveals that Pd surface concentration may have an effect on the catalytic activity. Moreover, TEM images indicate that the particle size decreases by reducing the Au added to the catalysts. This infers that the particle size and the mean surface Pd concentration may combine to affect the activity observed. Preparing the catalyst by various methods reveals that an improvement in the epoxide yield can be achieved. The sol immobilisation method was the best method for gold catalyst. However, DP was proven to yield the highest epoxide with Au-Pd and Pd catalysts.

The influence of Au-Pd catalysts was also investigated with crotyl alcohol oxidation as it contains two functional groups under the same conditions used with *cis*-cyclooctene epoxidation. Synergy between Au and Pd was identified for this substrate where 1:1 weight ratio is the highest. This synergistic effect has been observed before with other catalysts and appears to be related to the isomerisation of the starting material when Pd is present. However, oxidation of crotyl alcohol under similar conditions as cyclooctene epoxidation resulted in a larger range of product structures wherein the influence of Au and Pd could be clearly differentiated. Where pure gold was present, oxidation to crotonaldehyde was the preferred pathway. However, when Pd was present in the catalyst the dominant pathway was isomerisation followed by Wacker-type oxidation. The addition of TBHP to the reaction mixture did not affect the activity or selectivity in crotyl alcohol oxidation in sharp contrast to *cis*-cyclooctene oxidation. Changing the preparation method of Au/graphite catalysts did not have an effect on the catalyst activity. However, the selectivity toward crotonaldehyde was improved by using sol immobilisation method which could be related to the gold particle size.

*6.2. **Future Works***

The work in this thesis has demonstrated that supported Au catalysts could be used as potential and promising heterogeneous catalysts for selective oxidation of hydrocarbons under mild conditions. The results obtained from these reactions lead to some questions and suggestions which may be beneficial to understand more about the mechanism of hydrocarbon epoxidation and improve the performance of supported gold nanoparticles. The following suggestions may facilitate understanding into the nature of active site of gold catalysis and assist to achieve catalysts with improved activity and selectivity:

(1) Further studies on the role of Au nanoparticles in activating molecular oxygen for the selective oxidation of alkenes under mild conditions. Potentially revealing how Au nanoparticles activate molecular oxygen under mild conditions and how Au particles play their role in the selective oxidation of alkenes. Consequently, it will provide us with a valuable roadmap for pursuing green and sustainable chemistry through control of the reactivity of oxygen.

(2) In this study, a mechanism for oxidation of cyclooctene has been proposed. However, no direct evidence for the mechanism has been shown. Such evidence might be sought from isotopic labelling of both of the sp^2 carbon atoms of *cis*-cyclooctene (or their attached hydrogen), since Figure 4.23 requires that the epoxide ring incorporates only one of the labels, while an alternative direct O-transfer to the double bond would incorporate both.

(3) One of the limitations of this study is the low activity of the reused gold supported on graphite catalyst due to the adsorption of product. Accordingly, other methods are needed to enhance the activity of the reuse catalysts such as a new preparation method.

(4) Bimetallic catalysts represent a very interesting option in the attempt to improve gold catalyst activity. In the current work Au-Pd were primarily tested. Presumably, other bimetallic system would lead to more active and/or selective catalysts. Testing different metal combination namely Au-Cu and Au-Ag and

optimisation of catalyst preparation method. This will help to obtain a more selective catalyst for partial oxidation of alkenes to target oxygenated products.

(5) Optimization of the formulation of supported bimetal catalysts, mainly supported Au-Pd, Au-Ag and Au-Cu catalysts, which aims to improve the activity and selectivity of catalysts for alkene epoxidation. This is a very important factor for influencing the catalytic activity of supported bimetallic catalysts.

(6) It has shown that many parameters can be manipulated to control *cis*-cyclooctene reaction. Investigation of temperature, pressure, stirring speed on the product profile of crotyl alcohol reaction would be interesting. It will also be interesting to try to oxidise *cis*-crotyl alcohol under the same condition as *cis*-cyclooctene after further optimisation.

(7) The fact that oxidation of crotyl alcohol with gold catalyst gave the oxidation of hydroxyl group rather than epoxidation of C=C bond, raises the question if the hydroxyl group was activated by the presence of the π electron in the allylic position. Thus it will be appealing to study the effect of gold catalysis on the oxidation of 2-hexen-1-ol, 3-hexen-1-ol and 4-hexe-1-ol and observe the direction of the reaction.

6.3. References

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