Gold catalysts for liquid phase epoxidation of terminal alkenes: 1-decene and propene

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Abstract

Gold surfaces have long been regarded as inert and poor catalyst due to their highly stable chemical structures; nevertheless, it has been demonstrated that gold becomes extremely catalytically active when sizes are reduced to < 15 nm and synthesis are performed in the presence of 3d transition metal oxides [1]. The catalytic activity of gold is enhanced by metal oxide supports that have high oxygen mobility, such as TiO_2, Fe_2O_3, NiO_x and CoO_x [2]. Also if gold is deposited as nanoparticles by co-precipitation or deposition-precipitation method, it becomes catalytically active for CO oxidation at temperature as low as 200 K [1].
In this project gold-supported catalyst has been used for the selective epoxidation of terminal alkenes, such as propene and 1-decene, in order to achieve higher conversions to propene and decene epoxides and to sustain an industrial development.

Propene epoxide (PO) is an important intermediate in the chemical industry, and it is used for making propylene glycol, polyethers, glycerol and other products. Currently PO is produced by two in-direct processes that create a large amount of by-products, which are an environmental concern and expensive to dispose of. Therefore, a direct process would be preferred. The liquid-phase epoxidation of propene has been performed in a stainless steel 50 ml Parr autoclave. Standard reaction condition were: 3 barg of propene, 3 barg of oxygen, 24 barg of nitrogen, heated to 90 °C and stirred at 1200 rpm. Bimetallic catalysts composed of supported gold and palladium nanoparticles on titanium dioxide or graphite, synthesized by sol-immobilization method, are used for the direct epoxidation. The reaction is carried out in the presence of benzyl peroxide (BPO) as radical initiator. Various parameters, such as the solvent volume, amount of radical initiator, and catalyst composition, were changed in order to increase conversion and yield in propene epoxide.

1-decene is converted into 1,2-epoxydecane over graphite-supported copper, manganese and gold in the presence of sub-stoichiometric amounts of radical initiator (azobisisobutyronitrile, AIBN). The reaction has been performed in a round-bottom-flask reactor and variation of experimental parameters, such as oxygen pressure, speed of the stirrer, and reaction time, have been performed in order to determine the effects on conversion and selectivity upon epoxide or other terminal oxygenated-C_{10} products.

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1 Introduction

1.1 Terms and definitions

1.1.1 Green Chemistry and Sustainable Development

In the 20^{th} century chemistry changed our lives supplying energy, medicines, foodstuffs and new materials to the modern society. Even though chemistry has had a high impact on us, many problems related to the production of these benefits, such as chemical accidents, pollution, and resources management, have triggered an alarm bell to chemical industries and to the contemporary society. New terms like sustainability development or simply sustainability are commonly discussed. Gadi Rothenberg in his book says: "A sustainable society is one that meets the needs of the current generation without sacrificing the ability to meet the needs of future generations" [3]. Sustainability development can be reached using various approaches, and green chemistry is one of these.

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry technologies provide a number of benefits, including:

- reduced waste, eliminating costly end-of-the-pipe treatments
- safer products
- reduced use of energy and resources
- improved competitiveness of chemical manufacturers and their customers

Rothenberg in his book [3] reports a rephrased version of the 12 principles of green chemistry formulated in 1998 by Anastas and Warner [4,5]

- Prevent waste instead of treating it
- Design atom-efficient synthetic methods
- Choose synthetic routes using nontoxic compound where possible
- Design new products that preserve functionality while reducing toxicity
- Minimize the use of auxiliary reagents and solvents
- Design processes with minimal energy requirements
- Preferable use renewable raw materials

- Avoid unnecessary derivatization
- Replace stoichiometric reagents with catalytic cycles
- Design new products with biodegradable capabilities
- Develop real-time and on-line process analysis and monitoring methods
- Choose feedstocks and design processes that minimize the chance of accidents

Poliakoff and colleagues have reported [6] a mnemonic, PRODUCTIVELY, which captures the essence of the twelve principles of green chemistry and can be shown on a single slide:

- P – Prevent wastes
- R – Renewable materials
- O – Omit derivatization steps
- D – Degradable chemical products
- U – Use of safe synthetic methods
- C – Catalytic reagents
- T – Temperature, pressure ambient
- I – In-process monitoring
- V – Very few auxiliary substances
- E – E-factor, maximize feed in product
- L – low toxicity of chemical products
- Y – Yes, it is safe

Green chemistry economy is supported by three key factors (Figure 1.1): Government legislation, social pressure and economic benefit. [3]

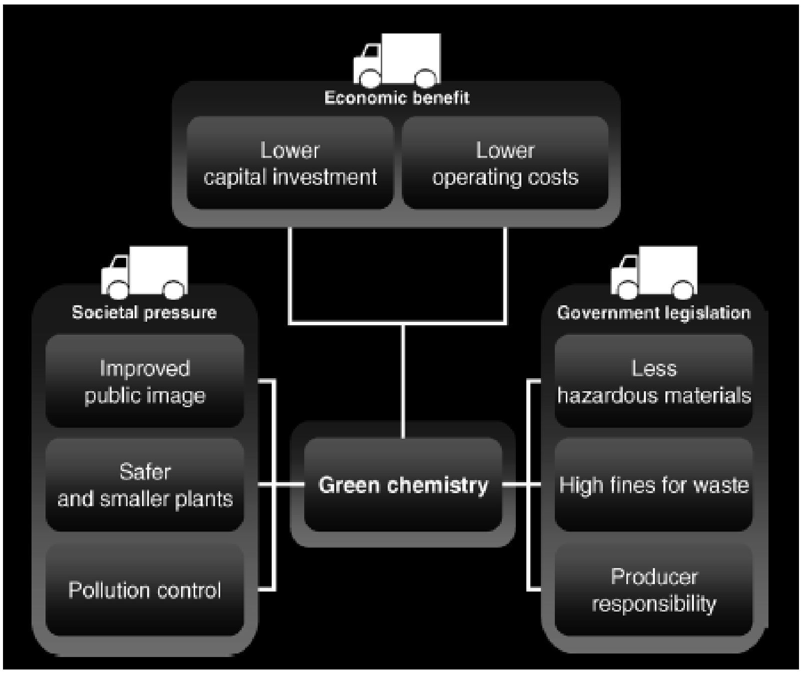


Fig 1.1 *Green chemistry economy key factors [3]*

1.1.2 Efficiency, *E*-factors and Atom Economy

In order to quantify the environmental impact of a chemical process or a chemical reaction is necessary to determine some parameters like efficiency, *E*-factors and Atom economy. The **efficiency** of a chemical reaction is determined by the well-known parameters: reactant conversion, the product selectivity and the product yield over time. Reactant conversion is the fraction of reactant molecules that have transformed to product molecules. The product selectivity is the fraction of a reactant that has converted in a specific product. The yield is the product of multiplying conversion for selectivity.

***E*-factor** is a parameter described by Roger Sheldon [7,8] that measure how is green a chemical process. Formula to calculate *E*-factor is reported below:

$$E\text{-factor} = \mathrm{kg}_{\mathrm{waste}} / \mathrm{kg}_{\mathrm{product}}$$

where “waste” is everything formed in the reaction except for the desidered product (e.g. CO_2, NO_x, water, organic compounds). *E*-factors ignore recyclable factors such as recycled solvents and re-used catalysts, which obviously increases the accuracy but ignores the energy involved in the recovery (these are often included theoretically by assuming 90% solvent recovery). Examples of *E*-factor of chemical process are reported in the Table 1.1 [3] and it could be surprisingly observed that petrochemicals and bulk chemicals have the minimum *E*-factors compared to fine chemicals and pharmaceuticals. This is due to the multistep synthesis (widespread use of classical stoichiometric reagents rather than catalysts) to produce fine chemicals and pharmaceutical products.

Table 1.1 Annual production and *E*-factors in the chemical industry

Industrial sector	**Production/ton y^{-1}**	***E*-factor**
Petrochemicals	10^6-10^8	<0.1
Bulk chemicals	10^4-10^6	1-5
Fine chemicals	10^2-10^4	5-50
Specialties/Pharmaceuticals	10-10^3	20-100

The *E*-factor takes into account only the mass of generated waste. However, the important is not just the amount this waste but also its environmental impact: the nature of the waste must be considered (one kg of sodium chloride is obviously not equivalent to one kg of a chromium salt). Hence, Sheldon introduced the term 'environmental quotient', EQ [7], obtained by multiplying the *E*-factor with an arbitrarily assigned unfriendliness quotient, Q. This measure takes into account both the amount and the nature of the waste. For example, one could arbitrarily assign a Q value of 1 to NaCl and, say, 100-1000 to a heavy metal salt, such as chromium, depending on its toxicity, ease of recycling, etc. The magnitude of Q is obviously debatable and difficult to quantify but, importantly, 'quantitative assessment' of the environmental impact of chemical processes is, in principle, possible. It is also worth noting that Q for a particular substance can be both volume-dependent and influenced by the location of the production facilities. Table 1.2 [3] shows some possible Q values for different by-products. EQ gives a better measure of the environmental impact of a process than *E*-factor or the atom economy alone [3].

Table 1.2 Hazard quotient (Q) values for some common chemical by-products

Compound	Q Value	Compound	Q Value
Nitrogen gas	zero	acids	medium
Carbon dioxide	low	bases	medium
Water	low	Heavy-metal salts	high
NaCl	low	CFC gases	high
Nonmetal salts	medium	Persistent materials	high

Another parameter similar to *E*-factor used to determine the “greenness” of a process is the **atom economy** described by Barry Trost [9]. Atom economy describes how many and which atoms of the reactants remain in the products. For a generic multi-stage reaction:

$A + B \rightarrow C, C + D \rightarrow E, E + F \rightarrow G$

Atom economy = m.w. of G × 100 Σ (m.w. A,B,D,F)

The drawback of atom economy is that assumptions have to be made. For example, inorganic reagents are ignored as they are not incorporated into the final product. Also, solvents are ignored, as the stoichiometry of the reagents.

1.1.3 How Green is a process and Life-Cycle Assessment

In order to determine how eco-friendly is a process it is important to consider not only a chemical reaction but also the hazards, manufacturing costs, transport and store of raw materials involved in the reaction. Hydrogen fuel cells and propene oxide (PO) production are typical examples.

Fuel cell is an electrochemical device that converts chemical energy from a fuel to electricity through a chemical reaction with oxygen or another oxidizing agent [10]. In fuel cells hydrogen is burned and the only by-product is clean water, that represent in “greenness” term a “good waste”. It seems that fuel cells are the ideal source of power compared to the conventional energy sources, but is important to take into account a question related to the hydrogen availability.

Hydrogen is produced from fossil fuels, biomass and water and this costs time, capital and energy, and also his production generates wastes. Another aspect is that then hydrogen must be stored and transported and this requires dedicated infrastructures. All of these factors must be taken into account when calculating the overall environmental impact of fuel cells.

Figure 1.2 [3] compares the efficiency of hydrogen fuel cell with those of various gas-powered and diesel-powered energy sources.

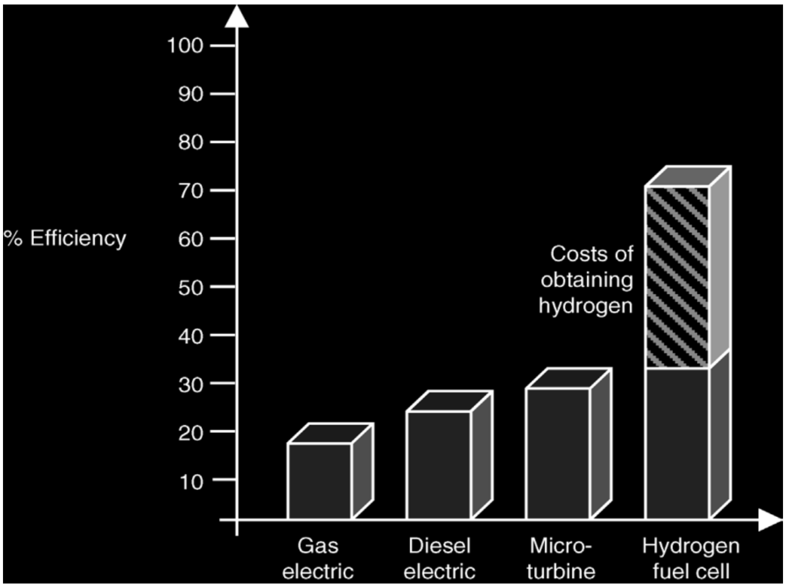


Fig 1.2 *Relative efficiency of various engine types. The column on the right also shows the estimated "hidden costs" of obtaining hydrogen in the case of fuel cells [3].*

PO is an important bulk chemical in the chemical industry; currently there is no catalytic direct process to produce it. Currently PO is produced by two in-direct processes (chlorohydrin and Halcon processes) that create a large amount of by-products which are an environmental concern and expensive to dispose of. Several alternatives, less polluting than the chlorohydrin one, are represented by industrial coupled-processes on which PO and other by products, that have a commercial interest into the market, are produced.

The two examples presented above show what it is necessary to take into account in order to determine the overall environmental impact of a chemical process for an unbiased comparison.

Life-Cycle Assessment (LCA) could help in order to evaluate the environmental impact of a chemical process because gives an overall view on raw materials extractions and acquisitions, chemical reactions, processing, manufacture, packaging, transportation, distribution, consumer use and a end-of-life management.

1.1.4 Catalysis and catalyst

A sustainable process is one that optimizes the use of the available resources while still leaving sufficient amount of them for future generations: catalysis can be the key to sustainability [11].

Catalysis is a chemical phenomenon where the speed of a chemical reaction undergoes changes for the intervention of a substance (or mixture of substances), called catalyst, which is not consumed by the proceeding of the reaction. The term catalysis represents also a branch of chemistry, in particular the one relating to industrial chemistry, which studies synthesis, characterization, design and development of suitable molecules to cover the role of catalysts for the improvement or the implementation of the same various reactions. Catalysts open a selective route to the desired product.

The general principle of catalysis consists in the overall variation of the reaction mechanism and then the various "jumps" (corresponding to the value of activation energy) that the reagents have to undertake in order to be converted into the products. Catalysis works by providing a different reaction pathway or mechanism characterized by a lower activation energy than the un-catalyzed process, with a consequent increase in reaction speed; there are also cases where the presence of a catalyst involves a mechanism that decreases the speed: in this case we talk about negative catalysis or inhibition (and the catalyst is more properly called inhibitor of the reaction). Each step is called elementary step and the slowest one determines the reaction rate. During this step the reactants are in a short-live transition state called activated complex and it has a bonding characteristic of both reactants and products. The energy necessary to reach this transition state and to allow the reaction to carry on is the activation energy; the role of the catalyst is fundamental at this point, in order to form an activated complex with a lower energy, which confers to the reactants a new pathway which require less energy to be transformed into the product. The effect of catalysis is purely kinetic in nature and not thermodynamics: the action of the catalyst in fact changes the intermediate stages of a reaction, but does not change the final state. This means that the catalyst does not affect whether or not a reaction takes place. However a catalyst alters both the forward and reverse reaction, so the equilibrium position is not changed.

An example of the effect of the catalyst in a generic exothermic reaction is shown in the Figure 1.3; the presence of the catalyst opens a different reaction pathway (shown in red) with lower activation energy. The kinetic conditions are different while the thermodynamic ones remain unchanged (energy levels of X, Y and Z).

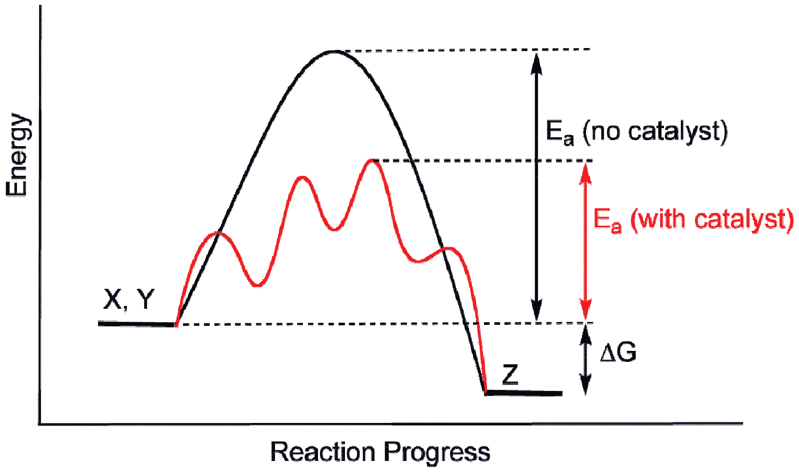


Fig 1.3 *Activation energy for catalyzed (red) and un-catalyzed (black) reaction.*

According to the phase in which the catalyst is, there are two types of catalysis:

- *Homogeneous catalysis*: the catalyst is dissolved in the, same reaction medium in which the reagents are present (i.e. liquid phase);

- *Heterogeneous catalysis*: the catalyst and reactants are not in the same phase (i.e., if the catalyst is a solid finely dispersed in a reaction medium).

There is also the *enzymatic catalysis* when the reaction is performed by a protein called *enzyme.*

To compare the efficiency of different catalysts, their turnover numbers (TON) and turnover frequencies (TOF) need to be considered. TON is the number of cycles that a catalyst run through before it deactivates; TOF is the ratio between TON and time.

1.1.5 Homogeneous catalysis

In homogeneous catalysis, the catalyst is dissolved in the same medium in which the reaction takes place, and this leads to a more difficult and expensive separation of the catalyst from the products than in the case of heterogeneous catalysis (where the catalyst can be recovered by simple separation of liquid-solid, see below). Also, the catalytic site is completely exposed to the action of reagents, so it has a greater catalytic activity but lower selectivity. In order to increase the selectivity of homogeneous catalysts binders are then added, which are functional groups with large steric hindrance that reduce the possibility of attack of the active site by the products. In addition to binders, other ligands are generally present in a homogeneous catalyst, which participate in the reaction mechanism as reagent.

An example of homogeneous catalyst is the complex chloro-*tris*(triphenylphosphine)-rhodium(I) (with the formula [$RhCl(PPh_3)_3$]), also known as Wilkinson's catalyst, used for hydrogenation of alkenes in solution. In this case, the binder action is played by the phenyl groups of triphenylphosphine.

Homogeneous-catalyzed reactions can be in gas or liquid phase. The dehydration of *tert*-butanol to isobutene in the presence of bromidic acid as catalyst, as shown in Figure 1.4, is an example of homogeneous catalysis in gas phase. The acid or basic catalysis is the most important one in the liquid phase; an example of acid catalysis is ester hydrolysis catalyzed by traces of acid (Figure 1.5), while a basic-catalyzed reaction is the aldolic condensation (Figure 1.6).

Fig 1.4 *The bromidic-acid-catalyzed dehydration of tert-butanol to isobutene in gas phase.*

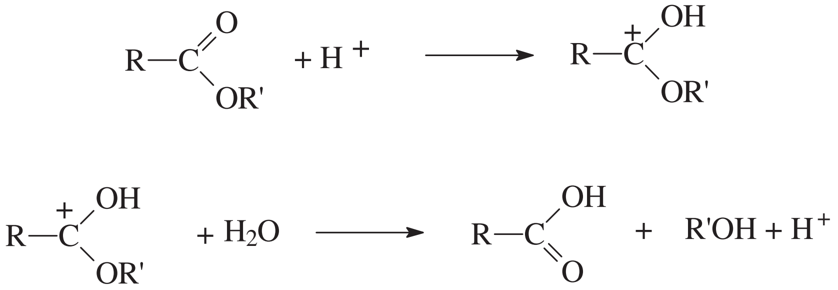
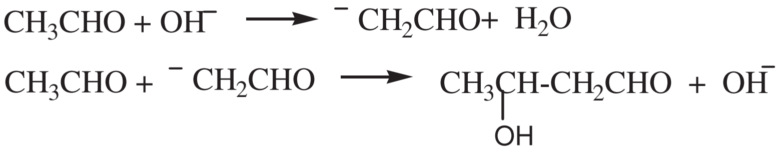


Fig 1.5 *Ester hydrolysis reaction catalyzed by acid.*



$$CH_3CHO + OH^- \longrightarrow {}^-CH_2CHO + H_2O$$

$$CH_3CHO + {}^-CH_2CHO \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}CH_2CHO + OH^-$$

Fig 1.6 *Aldolic condensation, a basic catalyzed reaction.*

Additionally, fine chemistry offers a wide range of homogeneous catalysis, very useful and versatile in many chemical processes, namely:

- *Isomerization*
- *Carbonylation*
- *Oligomerization*
- *Polymerization*
- *Oxidation*
- *Metathesis*

1.1.6 Heterogeneous catalysis

In heterogeneous catalysis the catalyst and reactants are in different phases. The process of heterogeneous catalysis takes place near the interphase between the reactant and the catalyst, which can be of various types, like fluid-solid or liquid-liquid (in the case of two immiscible liquids). The heterogeneous catalytic system can also be formed by a catalyst attached to a solid support. The concept of heterogeneous catalysis is that reactants diffuse to the catalyst surface and adsorb on it with rupture and formation of chemical bonds; after the reaction occurs, the products desorbs from the surface and diffuse away.

Examples of heterogeneous catalysis are the use of rhodium supported on inorganic oxides in the partial oxidation of methane, in order to obtain hydrogen as energy carrier (Figure 1.7), and the reduction of nitriles for instance in the synthesis of phenethylamine with nickel Raney and ammonia (Figure 1.8).

$$CH_4 + \frac{1}{2} O_2 \longrightarrow 2H_2 + CO$$

Fig 1.7 *Partial oxidation of methane, an example of heterogeneous-catalyzed reaction.*

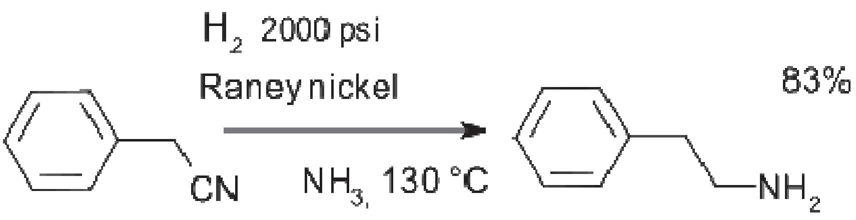


Fig 1.8 *Reduction of nitriles for the synthesis of phenethylamine with Ni-Raney catalyst*

In the refining industry, the most important processes applied to improve the quality and the octane-number of gasoline are based on heterogeneous catalysis:

- *catalytic cracking*
- *alkylation*
- *catalytic reforming*
- *isomerization*
- *desulphurization*

Without going into details, plenty of heterogeneous catalysis processes can be found also in inorganic industrial chemistry:

- Water Gas Shift Reaction (WGSR) (Figure 1.9), for the production of N_2/H_2 mixtures for the ammonia synthesis, is based on conventional Fe_2O_3-Cr_2O_3 catalysts

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Fig 1.9 *Water gas shift reaction*

- Ammonia synthesis from N_2/H_2 mixtures (Haber-Bosch and Montecatini-Fauser processes), which uses iron supported on alumina and K_2O (Figure 1.10)

$$N_2 + 3H_2 \xrightarrow[450 - 500\ ^{\circ}C]{Fe} 2NH_3$$

Fig 1.10 *Ammonia synthesis*

- Ammonia oxidation to NO (Bamag process, Figure 1.11), based on Pt-Rh alloys (up to 10% Rh) in the form of compact grills, which is the first stage in the production of nitric acid (and hence fertilizers)

$$4NH_3 + 5O_2 \xrightarrow[800 - 900\ ^{\circ}C]{Pt - Rh\ alloys} 4NO + 6H_2O$$

Fig 1.11 *Ammonia oxidation to NO*

- Oxidation of SO_2 to SO_3 (Figure 1.12) for the production of sulfuric acid, which uses V_2O_5 supported on silica

$$2SO_2 + O_2 \xrightarrow[500\text{-}600\ ^{\circ}C]{V_2O_5} 2SO_3$$

Fig 1.12 *Oxidation of SO_2 to SO_3*

1.1.7 Enzymatic catalysis

In biochemistry, the action of a catalyst is carried out by enzymes, which are special proteins produced by DNA; enzymes are the catalyst with which all biochemical reactions occur. These compounds are generally macromolecules of molecular mass ranging from 20 to 200 KDa. Their action is based on their ability to complex the reagents and keep them in the right direction and conformation so they can easily react. The reaction products do not remain bound to the enzyme, due to their lower affinity, so the active site is ready for complexing other molecules of reagent. Reagents that bind to the enzyme active site are called "substrate". Enzymes are highly selective and thanks to them reagents follow a precise chemical reaction among the many possible ones (Figure 1.13).

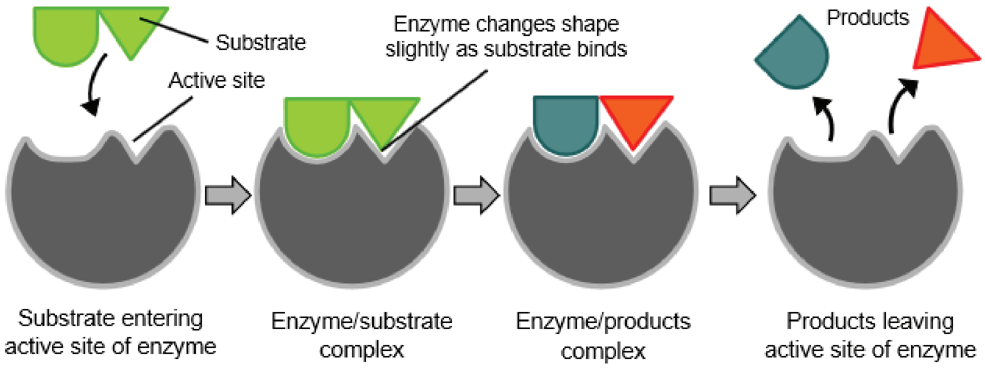


Fig. 1.13 *Representation of the catalytic action of an enzyme*

1.1.8 Promoters

A promoter is a substance added to a catalyst in order to improve the activity, selectivity or the lifetime of the catalyst; a promoter also suppresses the undesired reaction. For example, the modification of copper catalyst with vanadium enhances its catalytic performance of propene epoxidation by oxygen, because the presence of vanadium increase the dispersion of copper and this might contribute to the increase in the catalytic activity [12]. Another example is the trimethylamine (TMA) as a gas phase promoter in the propene epoxidation over supported gold catalyst. One of the explanations is that TMA can poison the Lewis acidic sites of the support, mainly isolated Ti^{4+} centers, which form PO by-products and then the catalyst deactivation. Also TMA could adsorb on the gold surface and suppress H_2 combustion to produce water, which results in an improved hydrogen efficiency [13].

1.1.9 Poison

A compound that binds chemically to the active surface sites of a catalyst and reduces its effectiveness by increasing the activation energy of the reaction is called poison. For example, in the CO oxidation reaction over Au/TiO_2 catalyst, moisture could act as a poison if present in a concentration ~ 6000 ppm, because it blocks the active sites of the catalyst [14]. Poison also reduces the metal/substrate interaction. Poisons could enhance the product selectivity by demoting side reactions. For example, if 1-2 ppm of ethene dichloride are added to Ag-catalyzed ethene epoxidation process, chlorine atoms are deposited on the catalyst surface, which retard the total oxidation of ethene to CO_2 and H_2O while increasing the selectivity to ethene oxide as desired [3]. Attempts to recover the original activity of the deactivated catalysts could be done by thermal treatment in gas stream (i.e. oxygen) or by dissolving the organic moieties from the catalyst surface in organic solvents.

1.1.10 Preparation of solid catalyst

Catalysts could be synthesized by several methodologies and their catalytic properties depend strongly on every single step of the preparation, as well as on the purity of the starting materials; every small changes in the synthesis could affect the catalyst performances. In the synthesis of a catalyst, the selection of the right support is also important; the catalyst support should provide optimal dispersion of the active component and stability against sintering. Specific surface area also plays an important role for a right support: the larger the surface area, the better the dispersion (less probability of sintering of the active material). A good support must also be stable at high temperatures in order to prevent catalyst deactivation.

Figure 1.14 shows the main synthetic methods for two solid -catalyst classes, the bulk and the impregnated ones [15,16]. Bulk catalysts are usually made by precipitation, hydrothermal synthesis or fusion (metals, mixed metals or oxides); by this method materials are generated and used as supports for active metal precursor in the synthesis of impregnated catalysts. The second class of catalysts, the impregnated ones, are those made by precious metals or unstable compounds. In this class, a metal precursor is deposited on a porous support (oxides, activated carbon, polymer resin). Figure 1.15 shows the main unit operations and stages in the synthesis of solid catalysts.

Via high-temperature fusion and alloy leaching methods, mixed oxides catalysts can be prepared by fusion of metal precursor at high temperature; this synthetic method creates highly pure and well-dispersed solids. It is possible to obtain a catalyst with different crystalline phases by controlling the cooling of the melt. A nickel-Raney catalyst is an example of this preparation method.

Through precipitation method it is possible obtain high purity materials (precipitation) and stoichiometric mixtures with well-defined mixed crystallites (co-precipitation). Here the precursor solutions are mixed and the desired salt is precipitated as a gel by adding an acid/base or another reagent. Then the resulting gel is aged, filtered, washed, dried and finally calcined. Another method, which allows the synthesis of an important class of catalyst as the zeolites, is the hydrothermal synthesis; this method involves the heating of precipitates, gels or flocculates in the presence of water.

Impregnation of porous supports is a very useful method for making supported catalysts. There are different impregnation methods, which the most used are: wet impregnation, incipient wetness, and vacuum pore impregnation. In wet impregnation the support is immersed in a solution of the catalyst precursor and then the precursor is adsorbed or precipitated on the support there by changing the pH or by inducing another chemical reaction. The catalyst so obtained is then filtered, dried and calcined. Another method is incipient wetness, which involves minor volumes and as a consequence less aqueous waste. By this method a solution of the active precursor is added to the dry porous support in order to fill the pores with the liquid precursor. Through vacuum pore impregnation, the support is first dried and then placed under vacuum, in order to remove air from the pores. Then a volume of precursor solution, equivalent to the pore volume, is mixed with the support under vacuum and this solution is adsorbed. By this method high loadings of active material can be achieved by drying the catalyst and repeating the impregnation process.

The major part of all of these preparation methods involves solvents that must be removed and this can be easy from a crystalline solid but not immediate for gels or hydrogels. In this case it is necessary to proceed removing solvent under mild conditions of temperature in order to prevent the collapse of the porous structure.

Once dried, the catalyst needs to be calcined. The calcination is another process that removes all the water from, decompose the nitrate/carbonate precursors and forms metal-oxide links with the support. It is important to calcine the catalyst under controlled conditions in order to avoid pore collapse. Depending on the final application, catalyst may require activation prior to the reaction.

Finally the catalyst is ready to be formed into a macroscopic sphere or pellets before the use.

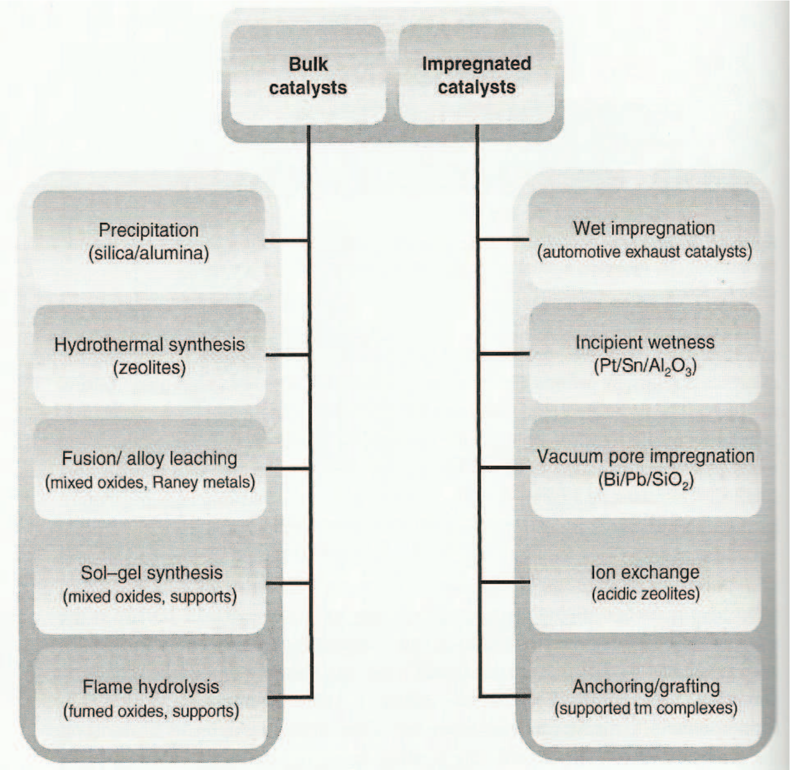


Fig. 1.14 Types and examples of solid catalysts, grouped by preparation methods (tm = transition metals) [3]

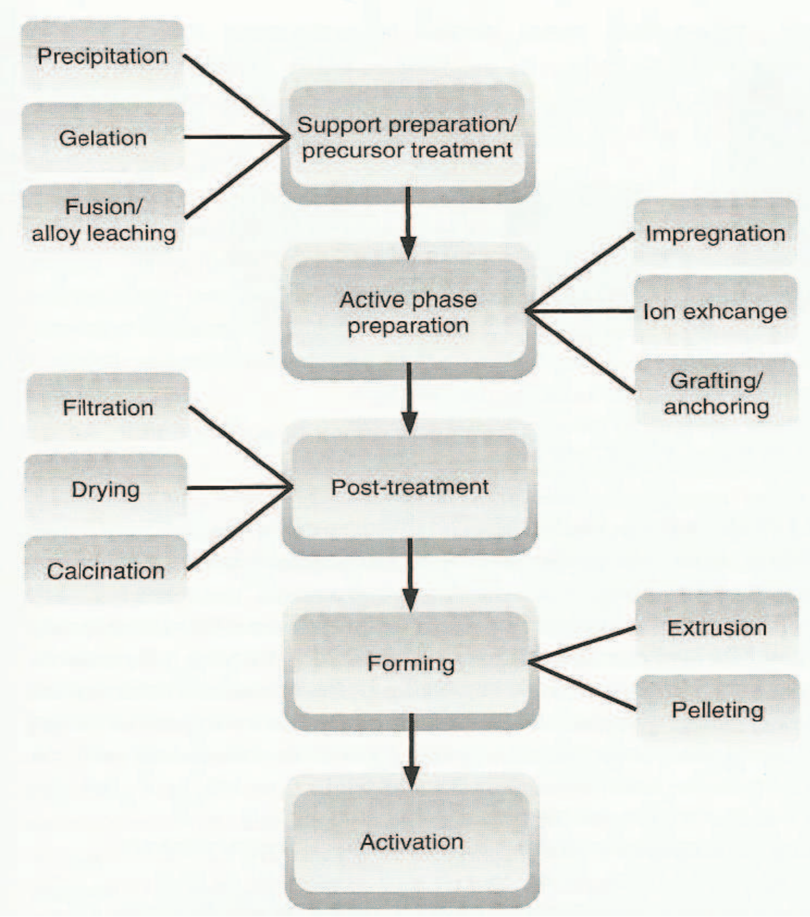


Fig. 1.15 *Main unit operations and stages in solid catalysts synthesis [3]*

1.1.11 Characterization of solid catalyst

"The plethora of catalyst characterization methods makes it easy to see what you want to see. Always try to validate your results, by combining different characterization approaches" [3].

1.1.11.1 Surface area determination

The total surface area of a catalyst is related to the volume of gas that is adsorbed on this surface at a given temperature and pressure. Studying the adsorption of various molecules under controlled conditions yields information regarding the catalyst surface area, pore volume and pore size distribution [17].

Surface characterization is important because in any gas/solid catalytic system the reactant must first be adsorbed on the catalyst surface.

In heterogeneous catalysis the study of the adsorption that involves a monolayer formation followed by filling mesopores (2-50 nm diameter range) is important. Langmuir's model ca efficaciously describe the monolayer formation on a surface. Another common theory useful for the physical adsorption of gas molecules on a solid surface and serves as basis for an important analysis technique for the measurement of the specific surface area of a material is the Brunauer-Emmet-Teller (BET) model; this theory is an extension of the Langmuir theory to multilayer adsorption with the following hypotheses: *i)* gas molecules are physically adsorbed on a solid in layers infinitely; *ii)* there is no interaction between each adsorbed layer; *iii)* the Langmuir theory can be applied to each layer. By this model a monolayer capacity of a solid is determined, and the specific surface area for this solid is given dividing this capacity by the average area which one adsorbate molecule occupies.

The BET measurement of the specific surface area is performed at low pressures and temperatures and consists in the evaluation of the volume V of gas adsorbed at various pressures lower than the saturation pressure. Best results are obtained with small gas spheres (Ar or Kr) but for practical reasons a BET measure is performed using N_2 as adsorption molecules at 77 K.

1.1.11.2 Temperature-Programmed Techniques

The characterization of the physico-chemical properties, structure and surface activity of solids, is extremely important, particularly in the field of catalytic systems. Analytical techniques are Temperature-Programmed Desorption (TPD), Reduction (TPR) and Oxidation (TPO) are extremely useful as they allow to:

- have a qualitative information of the compound analysed;
- have information on the type of bonds and functional groups on the surface;
- assess the influence of different factors on the reactivity of a known compound;
- study the changes in surface reactivity

In particular, the technique TPR is used when you want to determine:

- the number and amount of reducible species present in the sample analyzed;
- the reduction of T reducible species;
- the type and the number of active sites present on the catalytic surface.

Using TPR and TPO techniques it is also possible to monitor the changes that the catalyst precursor goes through during the calcination and activation steps.

1.1.11.3 X-ray diffraction (XRD)

The powder diffraction is one of the most widespread techniques for characterization of materials and is traditionally used as a routine technique for the analysis and quantitative diagnostic of crystalline phases, for the accurate measurement of cell parameters, for studies of texture and preferential orientation, for the analysis of the enlargement of the profiles associated with the size and internal deformation of the crystals, and to measure residual stress. The technique is also usable on solid metallic, ceramic or polymeric materials, therefore the definition of a suitable material covers the number and size of the single crystalline and not their state of aggregation. The ideal polycrystalline sample consists of a very large number of crystalline orientation having statistical, spherical shape and controlled particle size with dimensions of 1-2 µm and anyway lower than 10 µm.

Small-angle X-ray scattering (SAXS) is the analysis of XRD data 2θ angles less than 2° and so it is possible the determination of catalyst particle size in the range of 50-500 nm.

X-ray photoelectron spectroscopy (XPS) is a useful technique for identifying atoms at the catalyst surface [18]; it could also be used to analyze the relative elemental concentrations at the surface as well as to analyze the elemental oxidation states.

1.1.11.4 Electron Microscopy (TEM-SEM)

Electron microscopy is used for determining the size, shape and composition of supported particles [19]. The Transmission Electron Microscopy (TEM) is like an optical microscope where the optical lenses are replaced by electromagnetic ones. In TEM technique an electron beam hits the sample and the transmitted electrons are magnified by the electromagnetic lenses.

In Scanning Electron Microscopy (SEM) an electron beam is scanned over a small area of a sample; this generates lower-energy secondary electrons and back scattered electrons. Secondary electrons escape from the surface of the sample and measure the light intensity. Back-scattered electrons, generated by the collision between the electron beam and the atomic nuclei, bounce back; those give information on the surface topography and on the average atomic number on the surface scanned area.

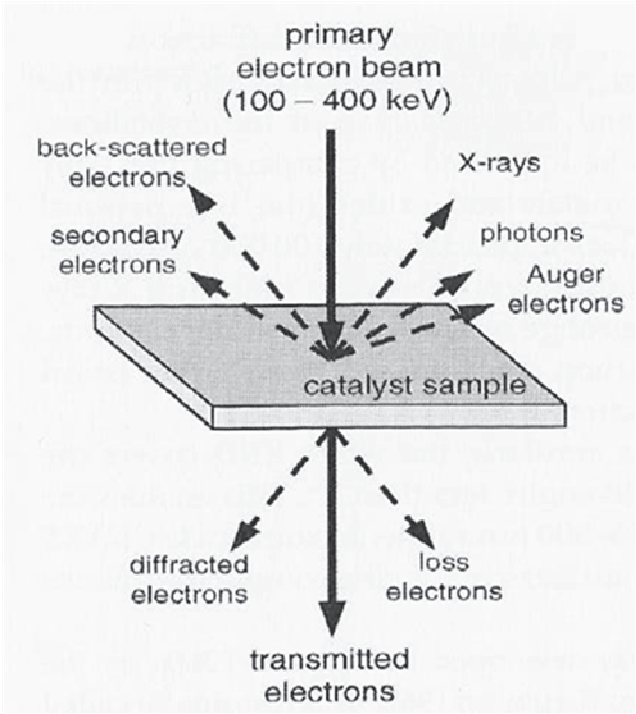


Fig. 1.16 *An electron beam hitting the catalyst surface sets off several processes [3]*

1.1.11.5 Infrared Spectroscopy (IR)

Infrared spectroscopy is a useful technique for studying the surface chemistry of heterogeneous catalysts, and it gives information about the catalyst structure and about the species adsorbed on the catalyst surface [20]. Using probe molecules, such as CO, NO and NH_3, it is possible to qualify and quantify the type and the number of active sites. In IR spectroscopy it is can be also used for detecting the way that molecules are adsorbed on the catalyst surface.

1.2 Gold as catalysts in the selective epoxidation of terminal alkenes

Gold was earlier considered to be chemically inert and regarded as a poor catalyst. However, when gold is prepared in very small particles (in nanometer range) and is highly dispersed on metal oxides, it turns to be highly active. Although gold catalysts posses hydrogenation activity and can be used in a broad range of organic transformations, they are used mainly in selective oxidation reactions.

For example if gold nanoparticles are deposited on semiconducting transition-metal oxides [21] they are active in the oxidation reaction such as carbon monoxide oxidation. Also gold nanoparticles could catalyze the selective oxidation of alcohol in water [22] and the epoxidation of propylene gas using titanium-based oxide supports [23].

The most important selective oxidation regards hydrocarbons; this reaction is very important in the petrochemicals company to produce specific reactions products by the addition of oxygen atoms.

Olefin epoxidation is a widely used way for the production of epoxides, both in laboratory and industrial scales [24], as epoxides they can be used as intermediates for the production of important commercial products, such as polymers, cosmetics and additives [25].

Currently the production of epoxides is not always advantageous, particularly for the lack of direct methods and the formation of harmful and expensive-to-dispose by-products. Propene oxide (PO), the largest propene derivative in production, is used as chemical intermediate for production of polyurethane, polyols and other products. It is worldwide produced at 8 million tons per year by Dow (1.9 Mton/yr), Lyondell (2.1 Mton/yr), Shell/BASF (0.9 Mton/yr); other producers are Sumitomo, Repsol and Huntsman [26].

Currently, the production of PO is generated in a high proportion from the chlorohydrin and hydroperoxide (Halcon) processes.

In the chlorohydrin process, PO is obtained by reaction between propene and HOCl, with the formation of propene chloride, which reacts with $Ca(OH)_2$ to form PO and $CaCl_2$ (Fig.1.17). This reaction produces highly toxic chlorinated by-products, with the consequent problems related to their disposal and ecological issues [27].

In the Halcon process, PO is obtained by reaction between organic peroxides and propene, in the presence of a catalyst together with co-products (Fig. 1.18). The main disadvantages are the market cost of these co-products [28] and the employment of peroxides, which produce acidic waste.

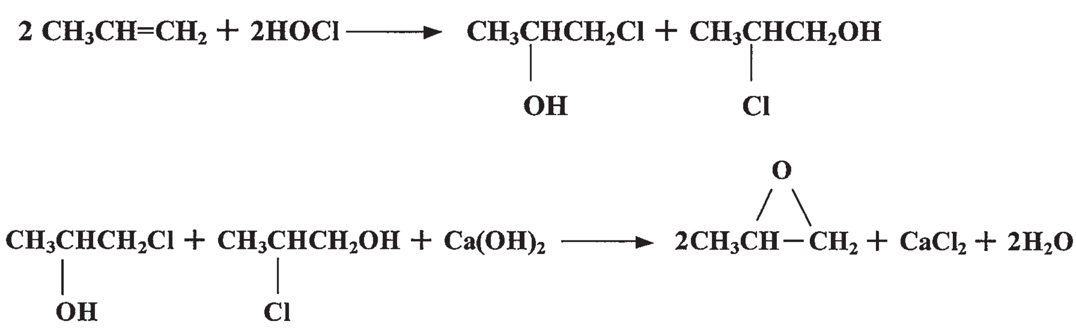


Fig. 1.17 *The chlorohydrin process for the production of PO*

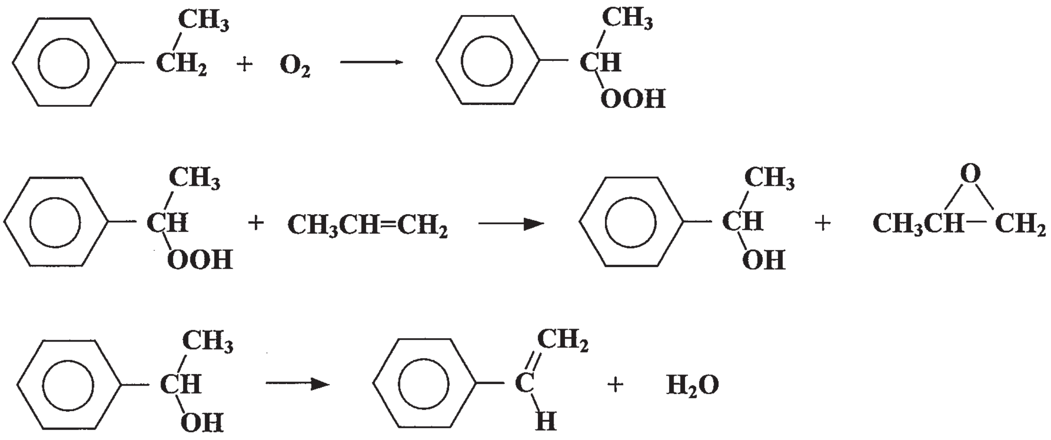


Fig. 1.18 *The Halcon process for the production of PO*

Many attempts has been done in order to find an economic and environmentally-friendly industrial process. One is the styrene monomer propene oxide (SMPO) process, used by Shell and Lyondell (Fig.1.19) [29]. SMPO process is less polluting and couples the epoxide production to that of styrene, but also in this case this route strongly depends on the styrene market cost.

Another alternative is represented by the ARCO/Oxyrane process, over a Mo catalyst, and couples the epoxidation of propene to isobutene oxidation (fig.1.20). Here *t*-butanol, produced as by-product, is then used as a gasoline additive and a starting material for making methyl-*t*-butyl ether (MTBE). Disadvantages of this process are related to the use of toxic heavy metal Mo and MTBE use is being phased out in the US and Europe.

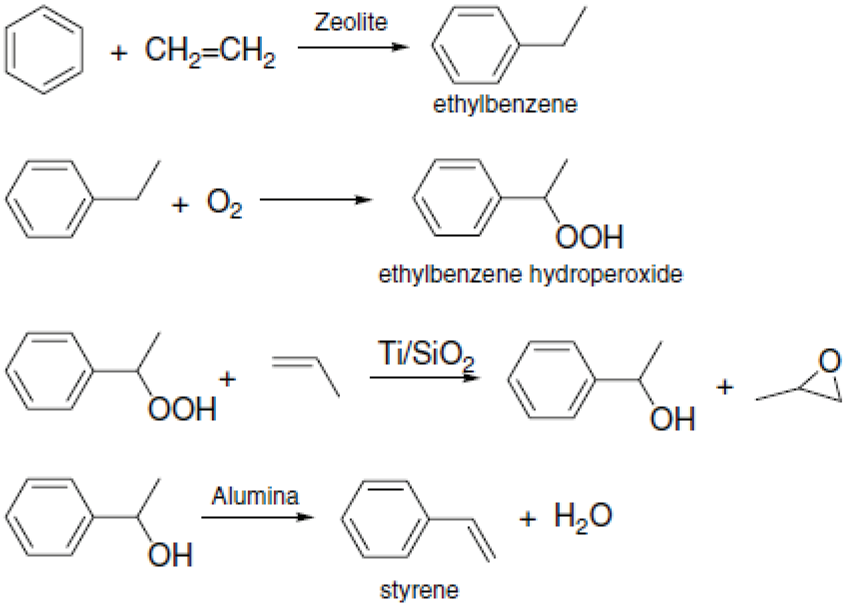


Fig. 1.19 *The SMPO process for the production of PO*

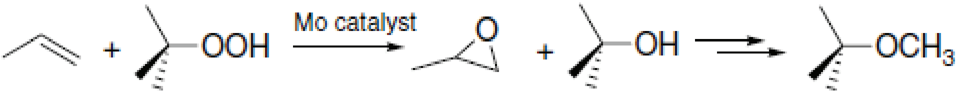


Fig. 1.20 *Propene oxidation over Mo catalyst in presence of t-butyl hydroperoxide*

Also N_2O could be used as epoxidation agent, over supported Fe catalyst or homogeneous polyoxometallate Mn/Zn catalyst [30]; N_2O is a greenhouse gas and contains activated oxygen atoms and the only by-product is N_2. Here the problem is related to the availability of N_2O and on its market cost of this.

For all the issues mentioned, there is a strong interest in developing a new ecological, economic and direct method: heterogeneous catalysis makes a great contribution in the epoxidation of alkenes.

For example gas phase epoxidation of ethene using air or oxygen, catalyzed by a silver catalyst, is an industrially-used process; by the way, other olefins are unable to be epoxidised using just oxygen from air, while hydrogen peroxide [31,32], hydroperoxides [33] or stoichiometric oxygen donors are required.

The main reason of the failure to direct epoxidization of allylic olefins (such as propene) to their corresponding epoxides is the reactivity of allylic C–H bonds. Ethene does not contain any allylic hydrogen atoms and, therefore, it does not undergo auto-oxidation which is a free radical chain reaction where the organic materials (alkene) are converted to hydroperoxides. The auto-oxidation and facile abstraction of allylic hydrogen atoms can be easily understood by the bond dissociation energy of the allylic C–H bond in propene which is 356 kJ/mol, while the vinylic C–H bond strength in ethene is 427 kJ/mol [34]. Thus, electrophilic attack by oxygen and abstraction of one of the allylic C–H bonds in propylene becomes energetically more favourable than electrophilic addition of oxygen across the C=C double bond. Higher alkenes containing allylic hydrogen atoms, can undergo air oxidation to form other oxidation products at suitable conditions while higher olefins without allylic hydrogen atoms can be epoxidised: Eastman Chemical Company prepared 3,4-epoxy-1-butene from 1,3-butadiene [35,36].

Great advances have been made in the field of catalytic propene epoxidation in recent years, and continuously new catalysts and reactions are discovered and new processes developed. Epoxidation of propene with hydrogen peroxide, which does not produce organic co-products is very important. A titanosilicate catalyst like TS-1 in methanol as solvent is used for the reaction in the liquid phase. In a patent by Thiele of Degussa, the reaction is run in a mixed aqueous-organic solvent (methanol and an ether like methyl tert-butyl ether, MTBE) with an added base in solution [37]. The base can be an alkali compound or ammonia, and it generally increases the pH from a level of 2-5 to 8-9 and results in a slight decrease in H_2O_2 conversion, but increases propene oxide selectivity. Stoichiometrically, 1 kg of H_2O_2 is required for the production of 1.7 kg of propene oxide, with a substantial production capacity of H_2O_2 [38]. It would thus be advantageous to have a direct means of producing H_2O_2 from H_2 and O_2 in-situ. This has been achieved using Pd supported on crystalline titanosilicates and an optional solvent (liquid phase) [39], Au/TiO_2 [23], and Pd-Pt/TS1 [40] catalysts (gas phase). However, these catalysts suffer deactivation. Delgass et al [41] reported a stable Au/TS1 catalyst; at 200 ^{o}C and 1 atm, they obtained a propylene conversion of 8.8% with PO selectivity of 81%, and a TOF based on Au of 0.33 s^{-1}.

Gold nanoparticles supported on graphite or metal oxides, synthesized by a co-precipitation or deposition precipitation methods, have high selectivity in the hydrocarbon oxidation under mild conditions [1,42]. Additionally, Haruta and co-workers reported that gold nanoparticles can epoxidize alkenes, using hydrogen to activate the molecular oxygen [43, 44].

Hutchings and co-workers have shown that Au supported carbon catalysts have significant potential for selective epoxide formation rather that the competing allylic oxidation. However, parameters involved in the catalyst preparation need to be tuned in order to have catalysts that can have a practical impact at the commercial level. Yields need to be improved and also catalyst stability and performance need to be enhanced [45].

1.2.1 Efficient Au catalyst for the propene epoxidation reaction

There are four important factors for the synthesis of gold catalysts used in the direct epoxidation of propene; these factors are: method of synthesis, support materials, size of the Au particles and use of additives.

1.2.2 Effect of the method of synthesis

Haruta and co-workers have shown that gold catalyst on titania prepared by deposition precipitation (DP) method produce PO with 100 % of selectivity and 1% of conversion [23,46], because other methods such as impregnation gives only CO_2 [47]. This high selectivity is related to the state of dispersion and the contact structure of gold nanoparticles on the titania support: with DP method, gold nanoparticles of dimension of 2-5 nm are deposited in hemispherical shape at the flat planes ({111} planes) of the support [48]. This contact structure allows the longest distance between each gold particle on the perimeter interface.

1.2.3 Effect of the support

The appropriate selection of the support has a vitality role in the product selectivity. It has been shown that among different metal oxides supports, only titania in anatase crystalline phase form makes Au selective for the reaction at temperature below 323 K [49]. However this temperature is similar to the boiling point of the PO (307 K) and the small conversion of propene is due to the absorption of PO on the surface catalyst. An increase in the temperature reaction causes a lower PO selectivity, until the product completely disappears when the temperature is above 393 K [49]. The stabilization of PO and the increase in PO yields (conversion up to 5% at >90% PO selectivity) [50,51] due to the desorption of PO is possible at higher temperature using titanosilicates as supports.

1.2.4 Effect of Au particle size

The size of the gold particles is a very important factor for the catalyst performance. Only gold supported nanoparticles in a range of 2-5 nm are catalytically efficient in the propene epoxidation reaction. If the size of the particle is smaller than 2 nm complete hydrogenation of propene to propane comes off; if the particle size is above 5 nm, CO_2 and H_2O are the only product of the reaction (Fig. 1.21) [49].

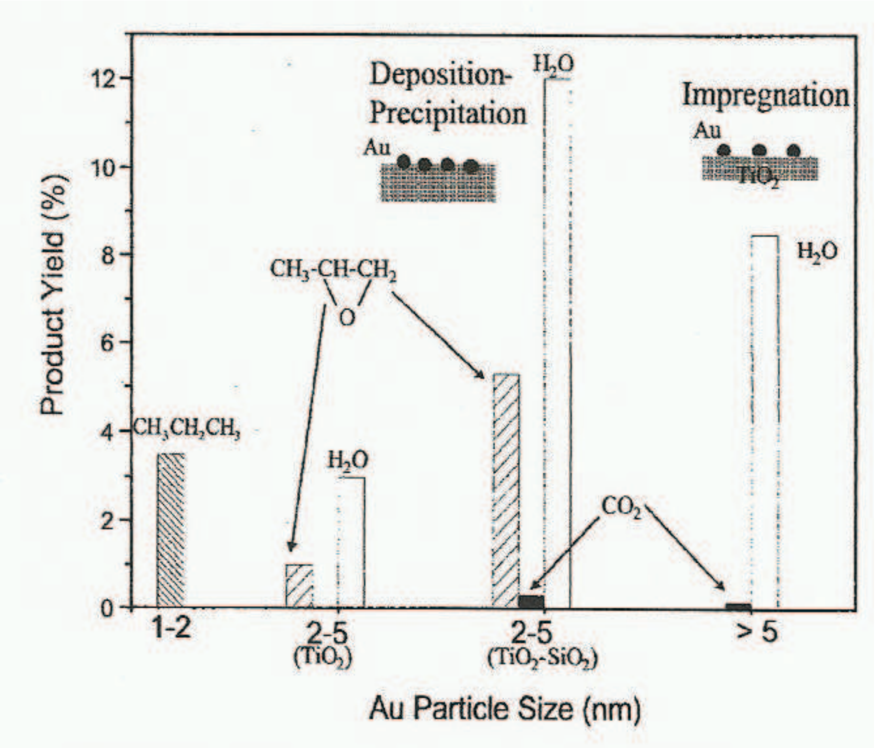


Fig. 1.21 *Influence of Au particle size and synthesis method of PO yield* [49].

1.2.5 Effect of additives

Many alkaline and alkaline-earth salts work as good promoters in PO production and may play an important role in the selectivity [50,52]; studies to understand the optimum amount and the mechanistic role of these promoters are under performing.

1.3 Role of the moisture in the catalytic activity of Au catalyst

Moisture could influence the catalytic activity of Au if adsorbed on the catalyst. The effect of the moisture in gold catalysts has been investigated mainly for CO oxidation because of the extremely low reaction temperature (< 273 K) and because of the remarkable effect of moisture. It has been observed that the influence depends on the type of metal oxides and it could enhance the catalytic activity for Au/Fe_2O_3, Au/TiO_2, Au/Al_2O_3 and Au/$Mg(OH)_2$, while none or negative effects for Au/$Fe(OH)_3$, Au/$Ti(OH)_4$, and Au/TiO_2 [49]. In the case of Au/TiO_2, used in the CO oxidation reaction, the effect of the moisture is related to its concentration; in this studies moisture could enhance the catalytic activity if present up to 200 ppm, but a further increase in its concentration (~ 6000 ppm) suppress the activity of the catalyst (Fig.1.22) [53]. This decrease to the blocking of the active sites.

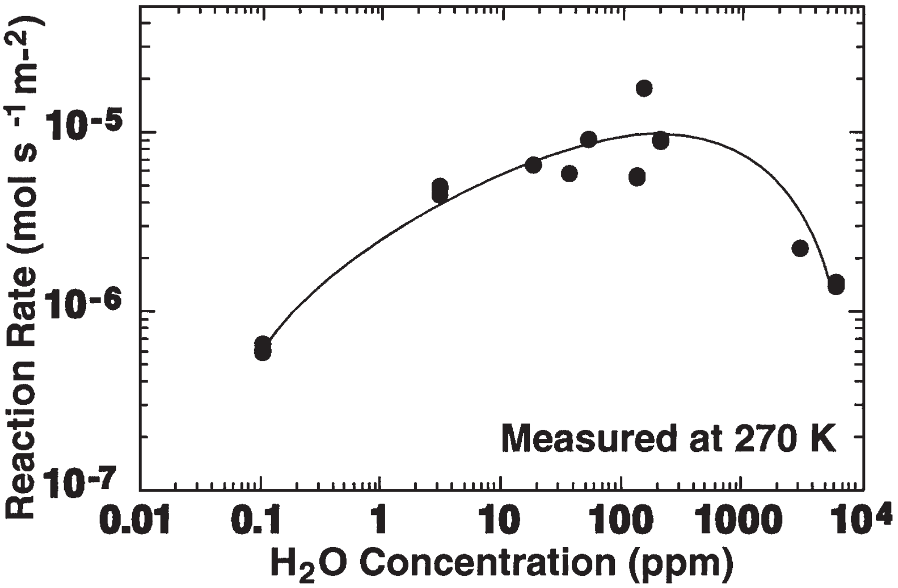


Fig.1.22 *Effect of the moisture concentration on the CO oxidation reaction rate* [53].

The role of the moisture in the enhancement of the catalytic activity has been related to its possibility to activate the oxygen and decompose the carbonate. A possible reaction mechanism at the perimeter interface between Au and metal oxide is represented in Fig. 1.23: moisture could activate oxygen (reaction 2a and 2b) reacting with the CO (adsorbed on the catalyst surface) to form an intermediate, which reacts to CO_2 (reaction 3). The activity of the catalyst decreases due to the carbonate species that are accumulated on the active sites during the reaction (reaction 5a and 5b Fig. 1.24). The deactivated catalyst can be regenerated by the addition of moisture in the reactant gas [54]. In the Figs.1.23 and 1.24 (p) represents adsorption at the perimeter interfaces, (s) the adsorption at the support surfaces and (Au) adsorption at Au the surfaces, (g) denotes the gas phase, and O* indicates the activated oxygen species.

$$CO + H_2O \not\longrightarrow CO_2 + H_2 \qquad 1$$

$$O_2(p) + H_2O\,(s) \longrightarrow O^*(p) + 2OH\,(p) \qquad 2a$$

$$2OH\,(p) \longrightarrow O^*\,(p) + H_2O\,(s) \qquad 2b$$

$$CO\,(Au) + O^*\,(p) \longrightarrow COO\,(p) \longrightarrow CO_2\,(g) \qquad 3$$

Fig.1.23 *Step reaction of the moisture in the oxygen activation*

The role of the moisture in the decomposition of the carbonate has been proposed by Costello et al [55], as shown in the reaction 4a and 4b (Fig. 1.24), where carbonates species are formed in the reverse reaction 4a and also in the reaction 5a and 5b.

$$CO_3\,(p) + H_2O\,(s) \longrightarrow CO_3H\,(p) + OH\,(p) \qquad 4a$$

$$CO_3H\,(p) \longrightarrow CO_2\,(g) + OH\,(p) \qquad 4b$$

$$CO\,(Au) + O_2\,(p) \longrightarrow CO_3\,(p) \qquad 5a$$

$$COO\,(p) + O^*\,(p) \longrightarrow CO_3\,(p) \qquad 5b$$

Fig.1.24 *Step reaction of the moisture in the carbonate decomposition*

Nijhuis and Weckhuysen studied the effect of water on the rate of the gas phase propene epoxidation reaction over Au/TiO_2 catalyst.

In their work, the propene epoxidation and the water production reactions have a strong influence one each other [56]. The addition of water in the gas stream reduces the catalyst deactivation due to the absorption on the titania, but at the same time the presence of water reduces the catalytic activity. The authors concluded that both reactions either share the same reaction site or have a common reaction intermediate, because only in the propene epoxidation reaction Au supported catalyst are deactivated [56].

1.4 Influence of copper in the PO epoxidation

In recent years copper has made a strong contribution in the epoxidation of propene; studies have been conducted and are ongoing in order to discover the intrinsic characteristic of this metal (i.e. oxidation state, the activation by promoters) that enhances the epoxidation reaction. Copper started attracting the attention on this reaction when Lambert and co-workers indicated that Cu surfaces were more selective than Ag surfaces for the epoxidation of alkenes with allylic C–H bonds [57,58]. Studies proposed that the epoxidation is favoured by the nucleophilicity of oxygen isolated atoms on Cu surfaces [57,59].

Many attentions have been focused, and studies are still ongoing, on the oxidation state of the copper responsible for the epoxidation (difficult to determine) as main aspect of the catalyst performances. Monnier and Hartley pointed out that the epoxidation is not favoured by metallic copper catalyst because it may be readily oxidized into Cu_2O or CuO in the presence of O_2 [60]. On the other hand, studies of copper supported catalysts such as NaCl-modified $VCe_{1-x}Cu_x$ oxide [61], NaCl-modified Cu/SiO_2 [62], and Cu/SiO_2 [63] demonstrate that these catalyst could work for the epoxidation of propene, metallic copper is proposed as the active site of these catalysts, and the transformation of metallic copper to oxidised copper species is considered detrimental for the propene epoxidation. Whang et al in their studies suggested that Cu^I species generated during the reaction works as the active site for C_3H_6 epoxidation by O_2 [64].

Recently Whang and co-workers showed that the modification of copper with vanadium enhances the catalytic performance in the propene epoxidation with oxygen. This improvement has been attributed by the ability of vanadium to increase the dispersion of copper, which might contribute to the rise in catalytic activity [12]. In their characterization results, it has been deducted that Cu^{I} is the active site for propene epoxidation and vanadium species at lower valence states (V^{III} and V^{IV}) may also play a role in the activation of O_2. Furthermore the presence of vanadium species suppresses the reactivity of lattice oxygen in the working catalyst. As a conclusion it is clear that more studies are required to gain further information about the role of copper in C_3H_6 epoxidation by O_2.

1.5 A proposed plant for propene and 1-decene epoxide production

A schematic scenario of the plant which could be used for batches productions is depicted in Fig.1.25.

The catalyst, the solvent and the radical initiator are pre-mixed in D1 and then charged in the jacketed reactor R. Olefin is added and the system is pressurized by oxygen and heated to the process temperature. In the case of 1-decene liquid phase oxidation, 1-decene itself could be used to prepare a slurry of the catalyst rather than the solvent.

Reactor is finally vented and the process effluent cooled and sent to centrifuge PC in order to separate exhaust catalyst (a sparkler-like filtration system could be used instead of the centrifuge to collect solid particles).

An optional technological issue could be an ”*in situ*” regeneration plant of the catalyst.

Liquid reaction mixture is sent to storage tank D2 and then to distillation column C. Crude epoxy products are collected from the top and optionally sent to further purification, heaviest (alcohols, alkanoic acids and the like) are harvested from the bottom.

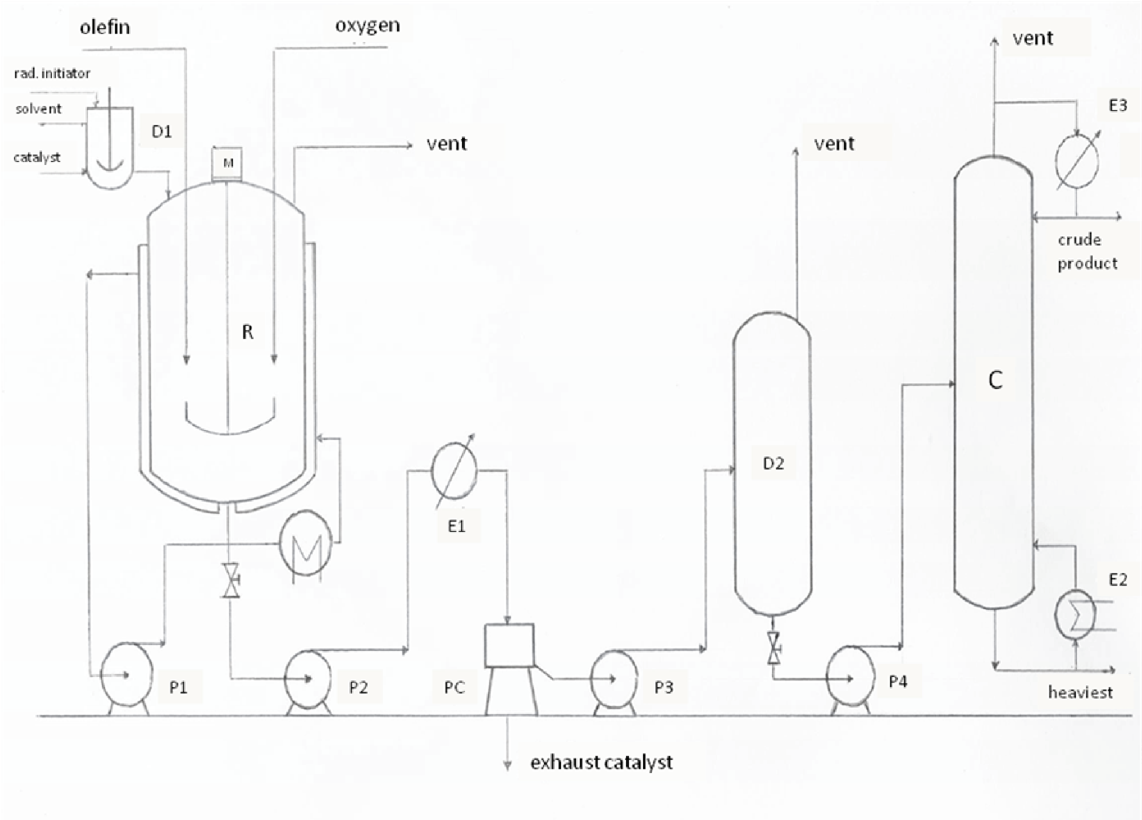


Fig.1.25 *Schematic plant for the epoxides synthesis*

1.6 Toxicological studies on PO

Unlike decene epoxide, which has not been found toxicological hazard for humans, "Report on Carcinogens" reports that "Propene oxide is *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in experimental animals" [66]. Report argued that the exposure to propene oxide by inhalation can cause different benign and malignant tumors in rats and mice of both sex.

The data available from epidemiological studies are inadequate to evaluate the relationship between human cancer and exposure specifically to propylene oxide [66]. Cohort studies have been conducted on humans but from the results it was not possible to evaluate the specific effects of propene oxide, and IARC (International Agency for Research on Cancer) concluded that "the case-control study was not informative because of limitations in exposure assessment and potential confounding by others risk factors" [65].

Guidelines [65]

American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit value – time-weighted average (TLV-TWA) = 2 ppm.

National Institute for Occupational Safety and Health (NIOSH)

Immediately dangerous to life and health (IDLH) limit = 400 ppm.

Listed as a potential occupational carcinogen.

1.7 Objectives of the present studies

In spite of the enormous progress made in alkenes epoxidation, this MPhil program will be focused on the study and synthesis of gold supported catalysts for the liquid phase propene epoxidation, without the use of any reductant. The target is the achievement of the highest PO yield in order to sustain industrial development. Initially, we investigated the effects of different solvents in the propene epoxidation reaction and the reactivity of benzene (breakdown product of common radical initiator); the aim is to determine whether the oxidation of propene competes with benzene at the catalyst surface and if propene may be able to generate benzene under reaction conditions. It was found that only acetonitrile as solvent was able to facilitate PO production. Furthermore, we compared the effects of Au-Pd nanoparticles supported on graphite or titanium dioxide (35% rutile – 65% anatase), and we evaluated the effects of the solvent volume, the amount of radical initiator and catalyst in order to develop the reaction process and improve the PO yield.

As part of an initial training, the liquid phase 1-decene epoxidation reaction has been studied. The objectives of this work has been conducted in order to evaluate the:

- effects of oxygen pressure, stirring speed and time with 1% Au/Graphite, prepared by incipient wetness impregnation.
- effect of reactor and reaction conditions in order to compare which experimental procedures give the best results in terms of 1-decene conversion, epoxide selectivity and terminal C_{10} oxygenate products.
- performance 1% Cu – 1%Mn/Graphite, prepared from different precursor by incipient wetness impregnation, at different oxygen pressures and reaction times.

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CHAPTER TWO

EXPERIMENTAL PART

2. Experimental

2.1 Introduction

The selective epoxidation of propene has been performed in the liquid phase. Bimetallic catalysts composed of supported gold and palladium nanoparticles on titanium dioxide or graphite, synthesized by sol-immobilization method, are used for the direct epoxidation of propylene. The reaction, performed in a 50 mL autoclave, is in presence of benzoyl peroxide (BPO) as radical initiator and a mixture of gases composed of propene, oxygen and nitrogen. Various parameters were changed in order to increase the conversion and the yield of propene epoxide such as the solvent volume, the amount of radical initiator and catalyst composition.
Experimental details will be described later.

The liquid-phase selective epoxidation of 1-decene has been performed in a round bottomed flask reactor. Gold and copper-manganese catalysts supported on graphite were synthesized by incipient wetness impregnation (IWI) and evaluated in 1-decene epoxidation. The reactions were performed under mild conditions and using AIBN (Azobisisobutyronitrile) as a radical initiator. Different experimental parameters were changed in order to test the effects on 1-decene conversion; epoxide and C_{10} terminal oxygenate selectivity. Experimental details will be described later.

2.2 The liquid phase propene epoxidation

2.2.1 Materials

In the propene epoxidation the following materials were used: $HAuCl_4 \cdot 3H_2O$ (Aldrich, 99.999%) and $PdCl_2$ (Aldrich, 99.999%) were used as precursors for the synthesis of the catalysts; benzoyl peroxide (BPO) (Merck, 75%, water content 25% used as stabilizer) was used as radical initiator; propene, nitrogen and oxygen (BOC, high purity) were used as received; graphite (powder, <20 micron, synthetic Aldrich) and titanium dioxide (Degussa P25) were used as support for the catalysts; sodium borohydrate (Aldrich, 99.99% trace metal basis) and polyvinyl alcohol (Aldrich, 99.99%) were used in the preparation of the catalysts; o-xylene (Alfa Aesar, 99%) was used as internal standard. Propene oxide (Aldrich, ≥99%) has been used to evaluate the stability of PO.

2.2.2 Catalyst used in the propene epoxidation reaction

In the propene epoxidation a bimetallic 0.5%Au- 0.5%Pd (% are w/w) on graphite and titanium dioxide catalysts have been synthesized by sol-immobilization (SI) method as reported below:

A 1% solution of PVA was added to an aqueous $HAuCl_4 \cdot 3H_2O$ and $PdCl_2$ solution ($1.65 \cdot 10^{-4}$ M) under vigorous stirring (PVA/Au+Pd= 0.05 w/w); a 0.1 M freshly prepared solution of $NaBH_4$ ($NaBH_4$/Au+Pd= 5 w/w) was then added to form a metallic sol. After 30 min of sol generation, the colloid was immobilized by adding graphite or titania (35% rutile – 65% anatase) as supports (acidified to pH 1 using sulphuric acid) under vigorous stirring. The amount of support was calculated to give a total final metal loading of 0.5%Au and 0.5%Pd. After 2 h the slurry was filtered, the solid washed thoroughly with distilled water to remove the dissolved species, such as Na^+, Cl^- and dried overnight at 110 °C.

2.2.3 Characterization techniques

The catalysts tested in the propene epoxidation reaction were characterized using a Powder X-ray diffraction (XRD) in order to identify the crystallographic phases present in the catalyst and though N_2 physisorption to determine the specific surface area of the sample.

Powder X-ray diffraction (XRD) is a technique widely used in catalyst identification [1]; it is used to identify the crystallographic phases present in the catalyst and to calculate average crystallite sizes. XRD diffraction patterns were collected in an X'Pert Pro diffractometer with a monochromatic Cu Kα source ($\lambda = 0.154$ nm) operated at 40kV and 40 mA. The scans were recorded in the 2θ range between 10 o and 80 o using a step size of 0.016 o and scan step time of 55 seconds. Samples were ground and placed in an aluminium sample holder.

The most widely used method to determine the specific surface area of a solid surface is that reported by Brunauer, Emmet and Teller (BET analysis) [2]

For the BET surface area analysis, powder samples are first degassed at 120 °C to remove surface adsorbates. The analysis begins with evacuation of the chamber in order to remove adsorbed molecules from the surface followed by the N_2 deposition step at 77.4 K. The measurements were performed using Autosorb AS-1 (Quantachrome).

2.2.4 Flammability diagram in the propene epoxidation procedure

Flammability diagrams show the regimes of flammability in mixtures of fuel, oxygen and an inert gas, typically nitrogen. Mixtures of the three gasses are usually depicted in a triangular diagram, also known as a Ternary plot.

In Figure 2.1 a diagram of flammability for the system composed by propene, nitrogen and air is shown [3], from which is possible calculate the values for propene, nitrogen and oxygen system.

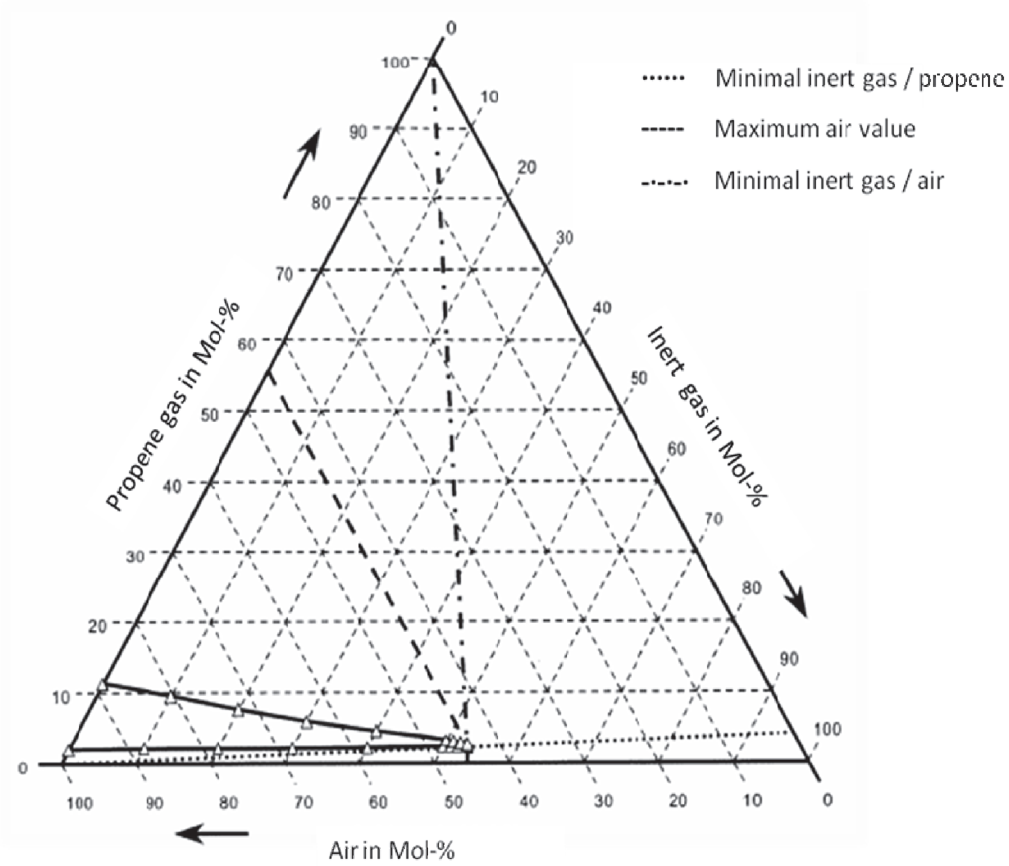

Figure 2.1 *Diagram of flammability for propene/nitrogen/air*

From the propene flammability diagram is possible to know the flammability range of propene in air which is between 2.0 – 11.1 %.

In order to evaluate if our experimental conditions (propene, O_2= 3 barg, N_2= 24 barg) are outside the flammability region it is possible calculate the composition of the gas mixture and then verify with the diagram.

The moles of gases are calculated by the formula and reported in Table 2.1

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

R = gas constant = 0.0821 L · atm / mol ·K

T = temperature = 20 $^{\circ}$C = 293 K

V reactor = 0.05 L

Table 2.1 – Values for gases involved in the mixture

	P (bar)	P(atm)	Moles n°	%
Propene	3	2.96	0.006	9.84
Nitrogen	24	23.67	0.049	80.32
Oxygen	3	2.96	0.006	9.84

From the moles of oxygen is possible calculate the moles of air which are 0.029 and then by difference between the moles of air and the ones of oxygen, moles of nitrogen in air are obtained which are 0.023. The final moles of nitrogen are then calculated by difference between the moles of nitrogen (0.049) and the ones of nitrogen in the air (0.023) which are 0.026. The moles of propene still the same 0.006.

Table 2.2 – Final values for gases involved in the mixture

	Moles n°	%
Propene	0.006	9.84
Nitrogen	0.026	43.33
Air	0.029	46.84

Controlling the % composition of the mixture in the flammability diagram is possible note that the experimental parameters are outside the flammability region.

2.2.5 The propene epoxidation procedure

The epoxidation of propene reactions were performed in a 50 mL Parr® 5500 Series Compact reactor (Figure 2.2 – 2.3). Catalysts, radical initiator and solvents were added to a Teflon liner that is in turned placed in a steel vessel of the autoclave. The reactions were performed directly in the vessel when 20 and 30 mL of solvent were used. The reactor is then filled with the reaction gas up to 30 barg: 3 barg of propene, 3 barg of oxygen, 24 barg of nitrogen and heated to 90 °C. When the reactor attained 90 °C, the solution was stirred at 1200 rpm. The quantity of catalyst and BPO (~ 75%, Merck) varied from 0.02 g to 0.04 g and from 0.028 g to 0.056 g respectively. The quantity of solvent was varied from 10 to 30 mL. After reaction, the reactor was cooled down in an ice bath at around 2°C, the reaction products were filtered and 100 microliters of internal standard (*o-xylene* 99%, Alfa Aesar) were introduced before the GC analysis.

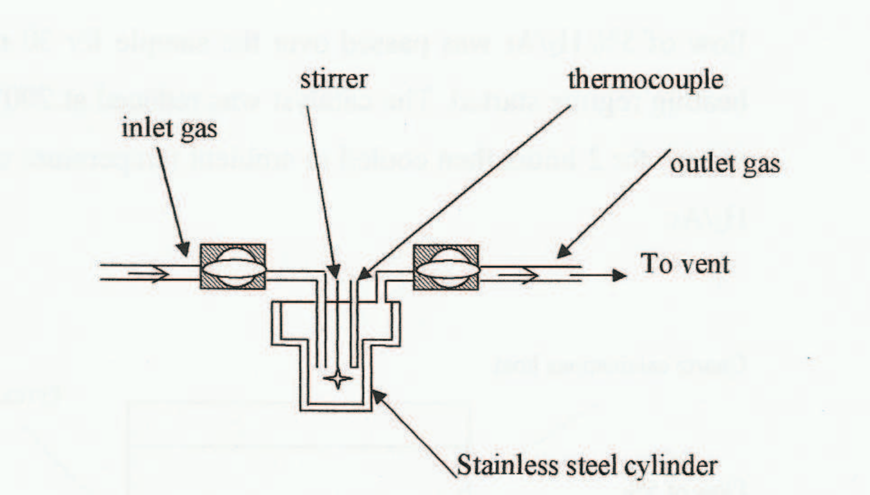

Figure 2.2 *Schematic representation of the autoclave reactor*

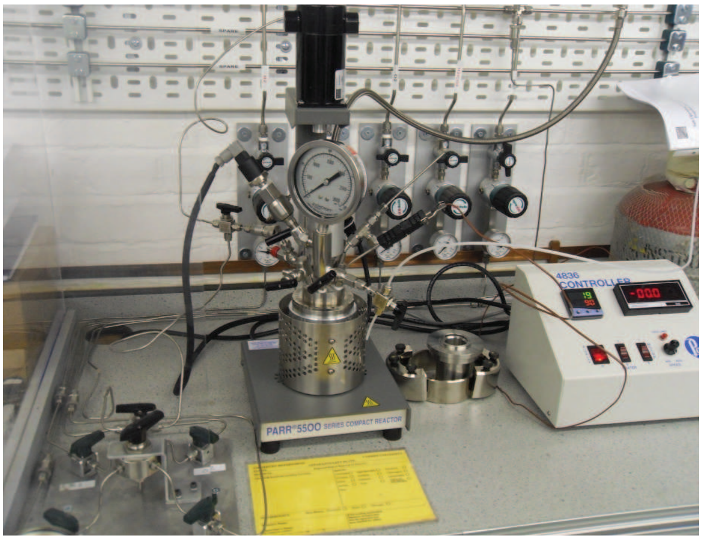

Figure 2.3 *Picture of the* Parr® 5500 Series Compact reactor

2.2.6 Product analysis

The reaction mixture was analyzed on a Varian GC 3300 fitted with Zebron ZB-Wax plus (L=60m, I.D=0.53) column and a flame ionization detector (FID). The column was maintained isothermal at 40°C for 5 minutes, followed by a ramp of 10°C/min, until 200°C and held at this temperature for 6 minutes; injector and detector was maintained at 150°C and 200°C respectively.

The flame ionization detector is a detector used in gas chromatography 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 high sensibility, robustness and a low noise makes FID one of the most common detectors and of more general use in gas chromatography. The FID consists in a stainless steel chamber where the outflow from the column is mixed with air and hydrogen and burned. The FID is sensitive for detecting hydrocarbons and other easily flammable components and can detect compounds present in concentration in a range between $10^{-9} \div 10^{-12}$ g. FID are insensitive to H_2O, CO_2, CS_2, SO_2, CO, NO_x, and noble gases because they cannot be ionized by the flame [7].

Calibration curves for PO, acetone, methanol, acrolein, acetaldehyde and BPO break down products (*p*-benzoquinone, phenol, benzene, benzoic acid) were performed using the internal standard and their response factor obtained. Response factor for the various products were calculated by the formula:

$$\frac{Aa}{As} = Rf \cdot \frac{Ca}{Cs}$$

to obtain the *Response Factor*

$$Rf = \frac{Aa}{As} \cdot \frac{Cs}{Ca} \qquad \text{Eq. 2.1}$$

Ca and Cs : concentration of the analyte and internal standard

Aa and As : peak area of the analyte and internal standard

Rf : response factor

The concentration of each product is calculated by the formula:

$$Ca = \frac{Aa}{As} \cdot \frac{Cs}{Rf} \qquad [Ca] = \text{mol/l} \qquad \text{Eq. 2.2}$$

and dividing the value obtained for 100 that is possible obtain the concentration in 10 mL, while the concentration in 20 and 30 mL is the double or triple of the one in 10 mL. Below the equations for the determination of the experimental details are reported; results will be presented later in the respective chapter.

In table 2.3 the products detected with their own retention time were reported.

Table 2.3 – Products with retention time and response factor in the propene epoxidation

Products	**Retention Time (min)**	**Response factor (Rf)**
Propene	1.63	not determined
Acetaldehyde	1.85	0.0555
PO	2.15	0.0841
Acrolein	2.85	0.1898
Methanol	3.18	0.0756
Benzene	4.15	0.7287
Acetonitrile	5.87	not determined
o-xylene	9.67	not determined
p-benzoquinone	15.94	0.0082
Phenol	20.34	0.7645
Benzoic acid	26.41	0.3514

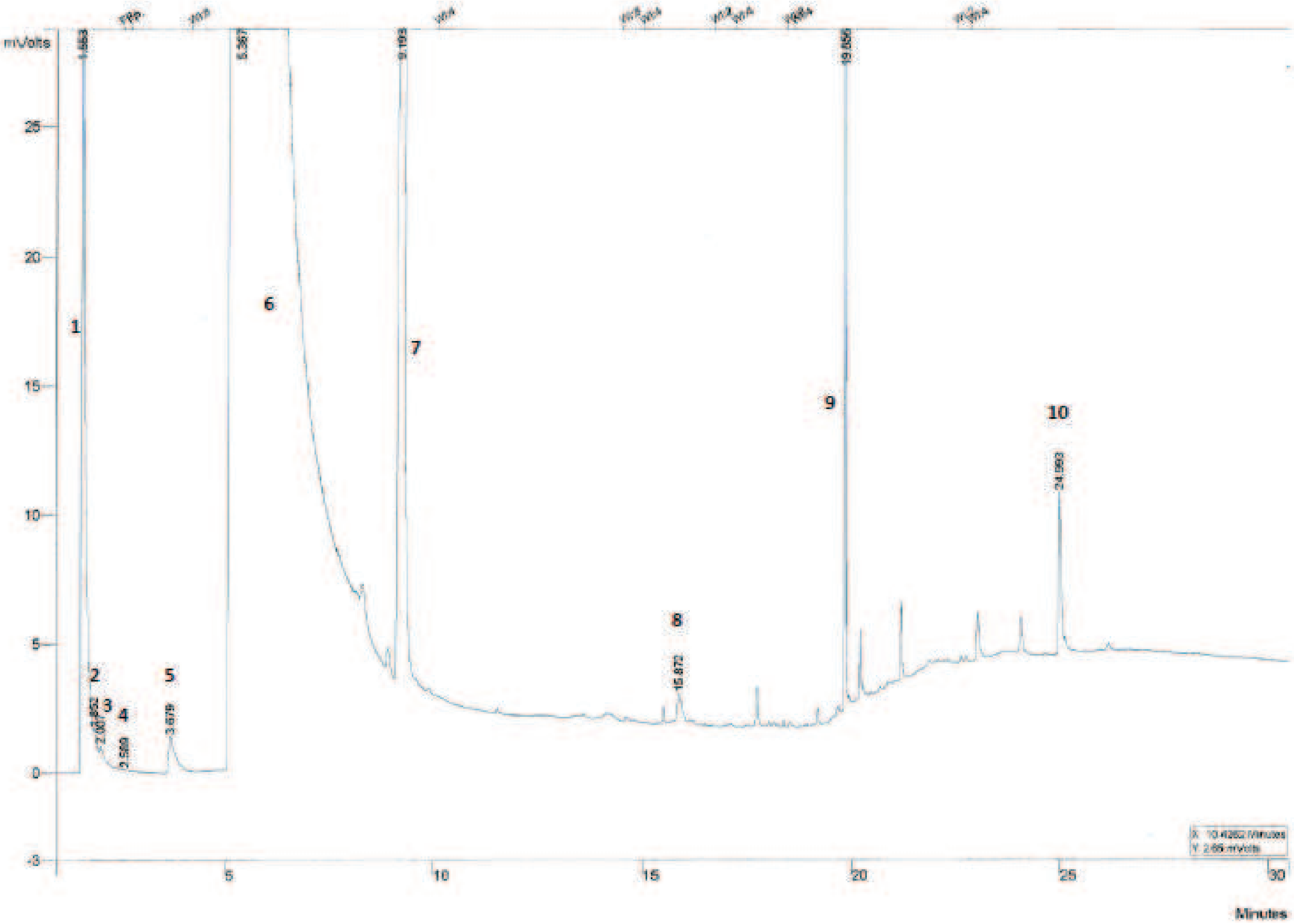

Figure 2.4 *Product separation with Zebron ZB-Wax Plus column in propene epoxidation*

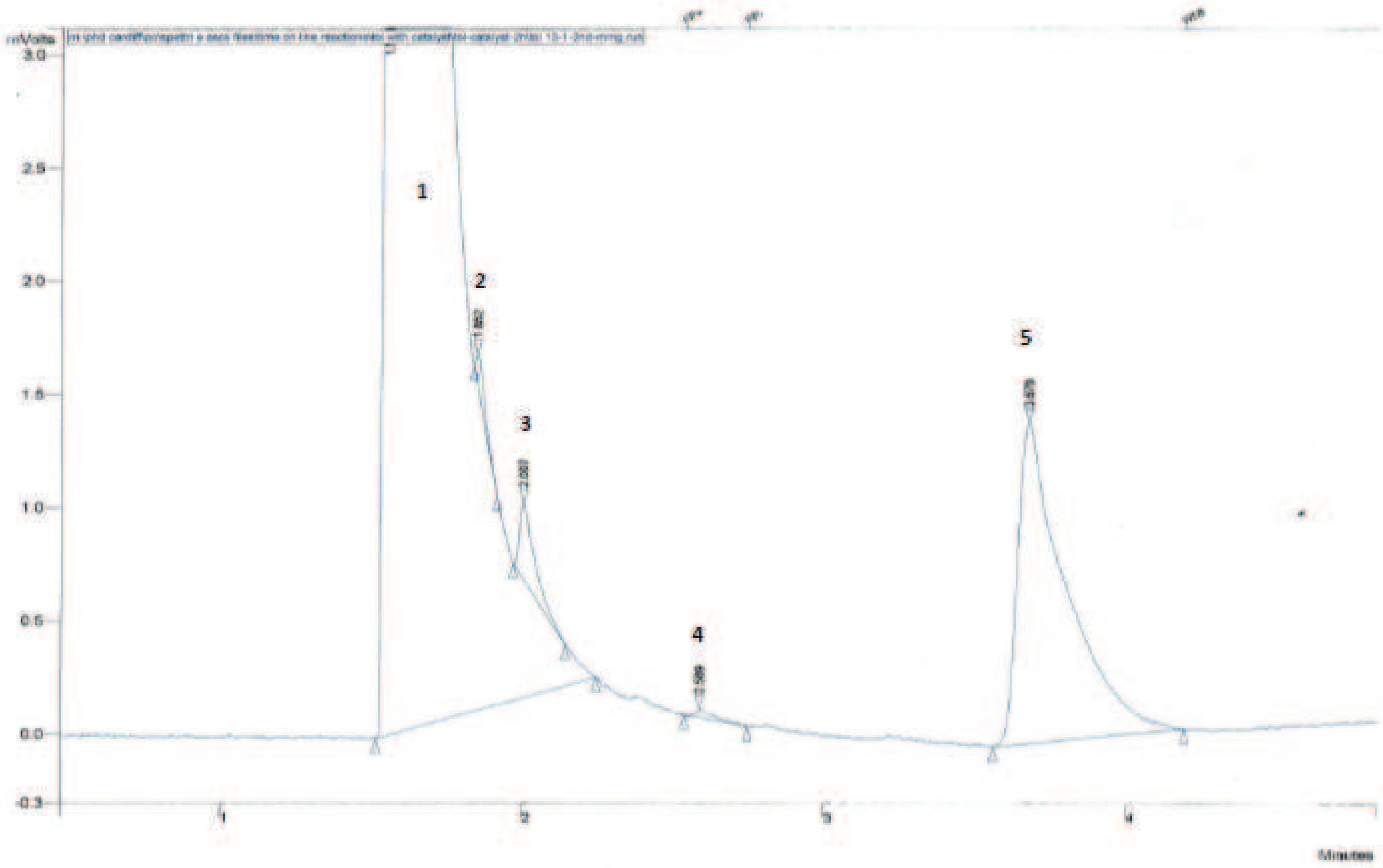

Figure 2.5 *Product separation with Zebron ZB-Wax Plus column in propene epoxidation*

Figures 2.4 shows a typical spectra of the products separation obtained after the GC analysis. The peaks are: 1st propene, 2nd acetaldehyde, 3rd PO, 4th acrolein, 5th benzene, 6th acetonitrile, 7th o-xylene, 8th p-benzoquinone, 9th phenol, 10th benzoic acid. Other peaks showed in the chromatogram are not related to propene epoxidation reaction. Figure 2.5 is the enlargement of Figure 2.4 in order to make possible the vision of the secondary products of propene epoxidation reaction.

PO yield (X) was calculated in according to the formula:

$$\text{PO yield} = \frac{n_{(\text{PO})\text{formed}}}{n_{(\text{propene})\text{in}}} \times 100 \qquad \text{Eq. 2.3}$$

The amount of propene in the reactor is calculated by the formula:

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

Total volume of reactor = 50 mL

Volume of headspace = $\frac{1}{3}$ x volume of reactor = 16.67 mL

Volume of solvent used = 10 mL.

$\Rightarrow$ volume of reactor occupied by gas (V) = (50 – 16.67 – 10) mL = 23.33 mL.

Propene pressure (P) = 3 bar = 2.9608 atm

R = gas constant = 0.0821 L · atm / mol ·K

T = temperature = 20 °C = 293 K

$$n = \frac{2.9608\,\text{atm} \times 0.0233\,\text{L}}{0.0821\,\text{L.atm.mol}^{-1}\text{K}^{-1} \times 293\,\text{K}} = 0.002831 \text{ moles}$$

$$= 2.831 \times 10^{-3} \text{ moles}$$

If volume of solvent = 20 mL $n_{(propene)in} = 1.642 \times 10^{-3}$ moles

If volume of solvent = 30 mL $n_{(propene)in} = 4.103 \times 10^{-4}$ moles

Propene conversion was calculated by the formula below:

$$\mathrm{Conv} = \left[1 - \left(\frac{n_{(propene)in} - \sum n_{products}}{n_{(propene)in}}\right)\right] \cdot 100 \qquad \text{Eq. 2.4}$$

2.3 The liquid phase epoxidation of 1-decene

2.3.1 Materials

In 1-decene epoxidation were used: : $HAuCl_4 \cdot 3H_2O$ (Aldrich, 99.999% trace metal basis), $PdCl_2$ (Aldrich, 99.999%), $Cu(NO_3)_2$ hemipentahydrate (Sigma Aldrich, 98%), $Mn(NO_3)_2$ hexahydrate (Aldrich, 98%) and $MnSO_4$ monohydrate (Sigma Aldrich, ≥ 98%) were used as precursors for the synthesis of the catalysts; graphite (Powder, <20 micron, synthetic, Aldrich) was used as support for the catalysts; 1-decene (purity >96% obtained from Alfa Aesar) were used as received; α,α-Azoisobutyronitrile (AIBN) (purity 97.5%, Molecula) was used as radical initiator.

2.3.2 Catalysts used in 1-decene epoxidation reaction

In 1-decene epoxidation reaction 1%Au on graphite and 1%Cu – 1% Mn on graphite (% are in w/w) have been used as catalyst and synthesized by incipient wetness impregnation (IWI) method. In Incipient wetness impregnation a solution of the active precursor is added to the dry support powder until the pores of the support are filled with the liquid.

In the synthesis of 1%Au/graphite, 1 ml of aqueous stock solution (20 mg/ml of Au) of chloroauric acid was diluted with distilled water to make 2 ml of total gold solution. This means that 1 ml of gold solution (equivalent to 20 mg of gold) was taken in a glass vial and diluted with 1 ml of distilled water. The gold solution was added dropwise to the graphite powder followed by air drying at various intervals (60-90 minutes). After complete addition of metal solution it was air dried overnight and finally dried for 16 h at 110 °.

Also 1%Cu – 1% Mn/graphite was prepared by incipient wetness impregnation; two batches were synthesized starting from a combination of different precursors: $Cu(NO_3)_2$ hemipentahydrate, $Mn(NO_3)_2$ hexahydrate and $MnSO_4$ monohydrate. Dried 1%Cu – 1% Mn/graphite was calcined at 450 °C, under nitrogen atmosphere, with heating rate of 5 °C/minute and holding for 3 hours at desired temperature.

2.3.2.1 The calcination of 1%Cu – 1% Mn/Graphite

1%Cu – 1% Mn/graphite was pre-treated before use with the apparatus illustrated in Figure 2.6 in order to remove water from the catalyst, to decompose the nitrate precursors and form metal-oxide links with the support. Catalyst sample (2 g) was placed in a ceramic calcination boat and inserted into a Pyrex tube furnace. The oven programme was programmed with heating rate of 5 °C/minute and held for 3 hours at 450 °C; a continuous flow of N_2 was passed over the sample for the duration of the operation and during cooling to room temperature.

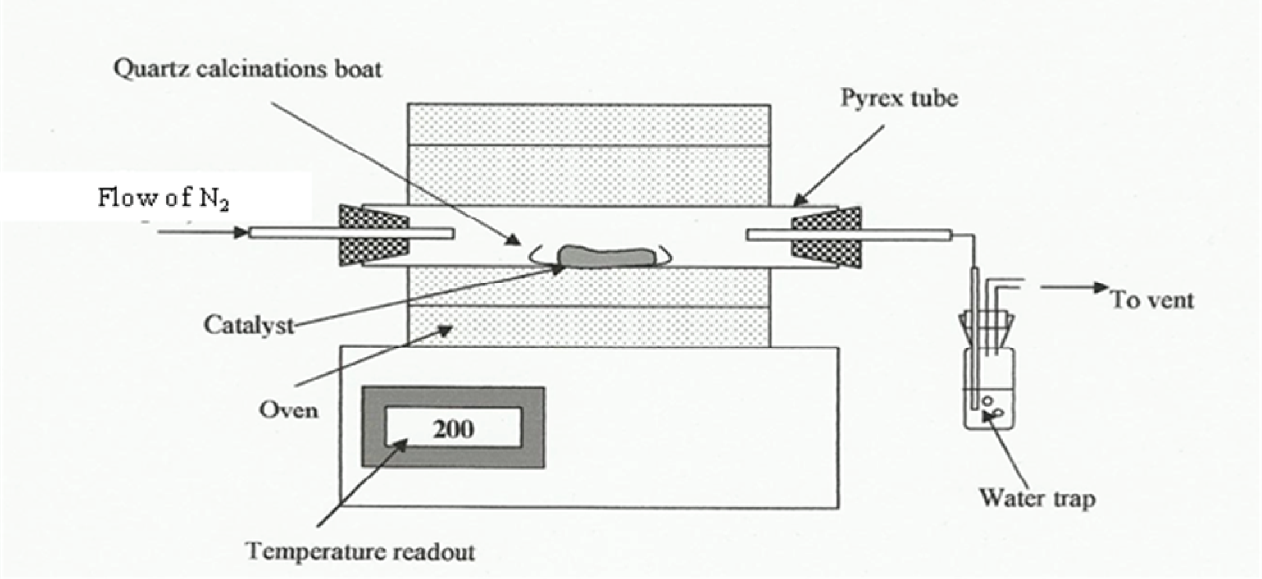

Figure 2.6 *Apparatus for catalyst reduction*

2.3.3 The 1-decene epoxidation reaction procedure

Round bottomed flask reactor and a high pressure reactor were evaluated in the epoxidation of 1-decene in order to determine which gives better performance for 1-decene conversion, epoxide selectivity and terminal C_{10} oxygenated products; both modes of reaction are reported below. After reaction, the reactor was cooled down at around 25 °C, the reaction products were filtered and GC analysis performed.

Round bottomed flask (RBF): 1-Decene oxidation was performed in presence of AIBN (α,α-Azobisisobutyronitrile) as radical initiator in a round bottomed flask equipped with a reflux condenser under atmospheric air (Figure 2.7). 1-Decene (10 mL) of was placed in a round bottomed flask (50 mL) to which the catalyst (typically 0.1 g) and radical initiator (typically 3.5×10^{-2} mmol) was added and refluxed (90 °C) with stirring under required reaction condition.

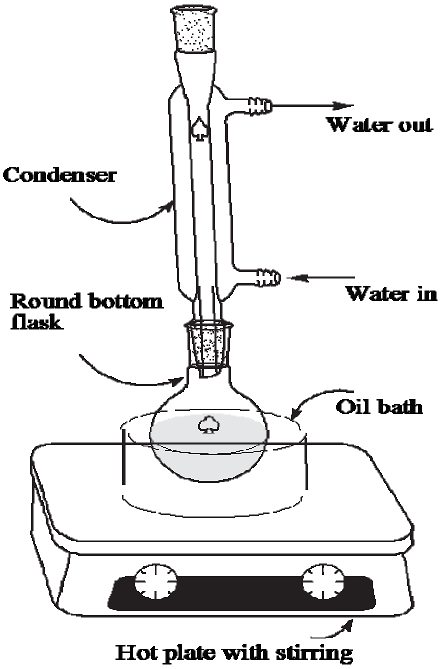

Figure 2.7 *Schematic version of the round bottomed flask reactor*

High pressure reactor (open/closed): In high pressure reactor the same reaction was performed in a glass reactor under pressure of oxygen (Figure 2.8). The terms open or closed indicate the opening or closing of the reactor to the oxygen line. The reagents were always added in the same quantities, the reactor heated in oil bath and stirred under required reaction conditions.

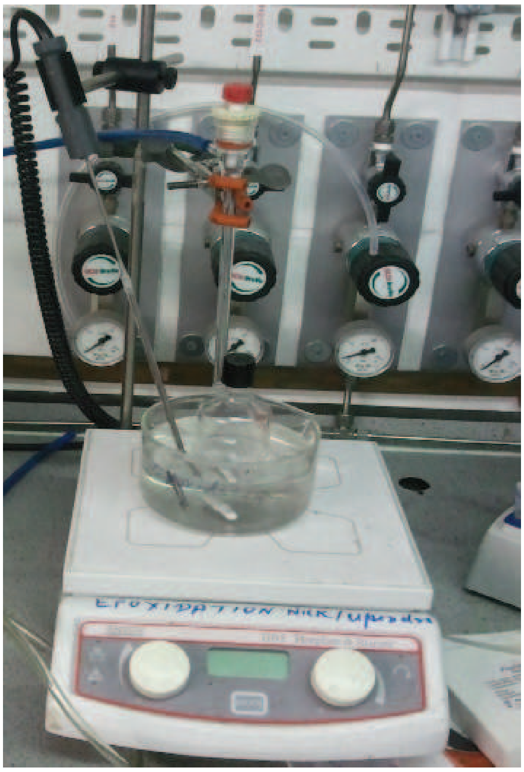

Figure 2.8 *Picture of high pressure reactor*

2.3.4 Product Analysis

The reaction mixture was analyzed on a Varian GC 3300 fitted with Zebron ZB-Wax plus (L=60m, I.D=0.53) column and a flame ionization detector (FID). The injector and detector temperature of the GC was maintained at 250 °C throughout analysis. During the analysis the column was heated from 60 °C to 200 °C at a heating ramp rate of 10 °C/minute and held at the final temperature for 26 minutes.

Response factors for the various products were taken in account when calculating the conversion and product distribution. Due to the wide range of products produced, an internal standard cannot be used for GC analysis. Because of this reason, conversion of 1-decene was calculated using conversion formula (Equation 2.5). Known and unknown products area obtained from gas chromatogram are added to the 1-decene area and considered as total reactant. Conversion of 1-decene was calculated by dividing the sum of known and unknown products area by the total reactant area. However, epoxidation of 1-decene produces gaseous products such as CO, CO_2 etc. which is not counted in the conversion and product selectivity.

In order to quantify the amount of the 1-decene reaction products, response factors have been calculated either using commercial available standards or theoretically (Effective Carbon Number (ECN) calculation) or the results has been compared with literature [8-11]. The response factor (Rf) of each product was calculated by analysing the known amount of available products in GC. Three different solutions were prepared with the possible products available. The first calibration solution contained 1-decene (10 g), the possible products (20 mg). The second and third solutions contained the same mixture but with 30 mg and 50 mg of possible products. Rf was the average of three different calibration solutions (20 mg, 30 mg and 50 mg of available product) using the equation below:

$$\mathrm{Rf} = \frac{(\text{GC count of product})/(\text{wt\% of product})}{\left(\text{GC peak area of 1-decene}\right)/(\text{wt\% of 1-decene})} \qquad \text{Eq. 2.5}$$

Rf: response factor

Conversion (X), product selectivity (S), products yield (Y) were calculated from the GC peak areas according to the formula:

$$\text{Conversion (X)} = \frac{\Sigma \text{ Total products in liquid}}{(\Sigma\text{Total products in liquid} + \Sigma \text{ Dec-1-ene})} \times 100 \qquad \text{Eq. 2.6}$$

Selectivity (S) of epoxide and known products was calculated according to the formula:

$$\text{Selectivity (S)} = \frac{\text{Product}}{\Sigma\text{Products}} \times 100 \qquad \text{Eq. 2.7}$$

Product yield (Y) of epoxide and known products was calculated according to the formula:

$$\text{Yield (Y)} = \frac{\text{Selectivity (S)} \times \text{Conversion (X)}}{100} \qquad \text{Eq. 2.8}$$

Response factor for known products were calculated (Table 2.4) and used to determine 1-decene conversion and product selectivity. Response factor for unknown products are considered as 1.

Table 2.4 Products with retention time and response factor in the 1-decene epoxidation

Products	**Retention Time (min)**	**Response factor**	**Method of calculation**
1-decene	2.99	1.00	Experimental
Heptanal	4.51	0.86	Experimental
Octanal	5.70	0.87	Experimental
Cyclododecane	6.23	1.00	ECN Calculation
3-nonanone	6.52	0.89	Experimental
Nonanal	6.97	0.89	Experimental
1-heptanol	7.70	0.77	Experimental
Epoxide	7.79	0.76	Experimental
2-decanone	8.21	0.90	Experimental
1-decen-3-one	8.39	0.90	ECN Calculation
1-octanol	8.89	0.80	Experimental
2-decenal	9.97	0.90	Experimental
1-decen-3-ol	10.06	0.83	Experimental
3-nonen-1-ol	10.25	0.82	Experimental
Cyclodecanol	10.40	0.84	ECN Calculation
2-decen-1-ol	11.88	0.83	Experimental
Heptanoic acid	13.36	0.75	Experimental
Nonalactone	13.88	0.81	ECN Calculation

Octanoic acid	14.28	0.78	Experimental
C16 epoxide	14.95	0.93	ECN Calculation
Nonanoic acid	15.66	0.80	Experimental
1,2-decanediol	18.10	0.71	Experimental
2-decenoic acid	19.82	0.81	ECN Calculation
Unknown products		1.00	

All the unknown products have a retention time in a range between 7.10 and 18.50 minutes.

Figure 2.9 shows a typical spectra of the products separation obtained after the GC analysis. The peaks are: 1st acetone, 2nd 1-decene, 3rd heptanal, 4th octanal, 5th cyclododecane, 6th 3-nonanone, 7th heptanol, 8th 1,2 epoxidecane, 9th 2-decanone, 10th 1-decen-3one, 11th 1-octanol, 12th 2-decenal, 13th 1-decen-3ol, 14th 3nonen-1ol, 15th cyclodecanol, 16th 2decen-1-ol, 17th heptanoic acid, 18th nonalactone, 19th octanoic acid, 20th C_{16} epoxide, 21th nonanoic acid, 22th 1,2 decanediol and 23th 2-decenoic acid

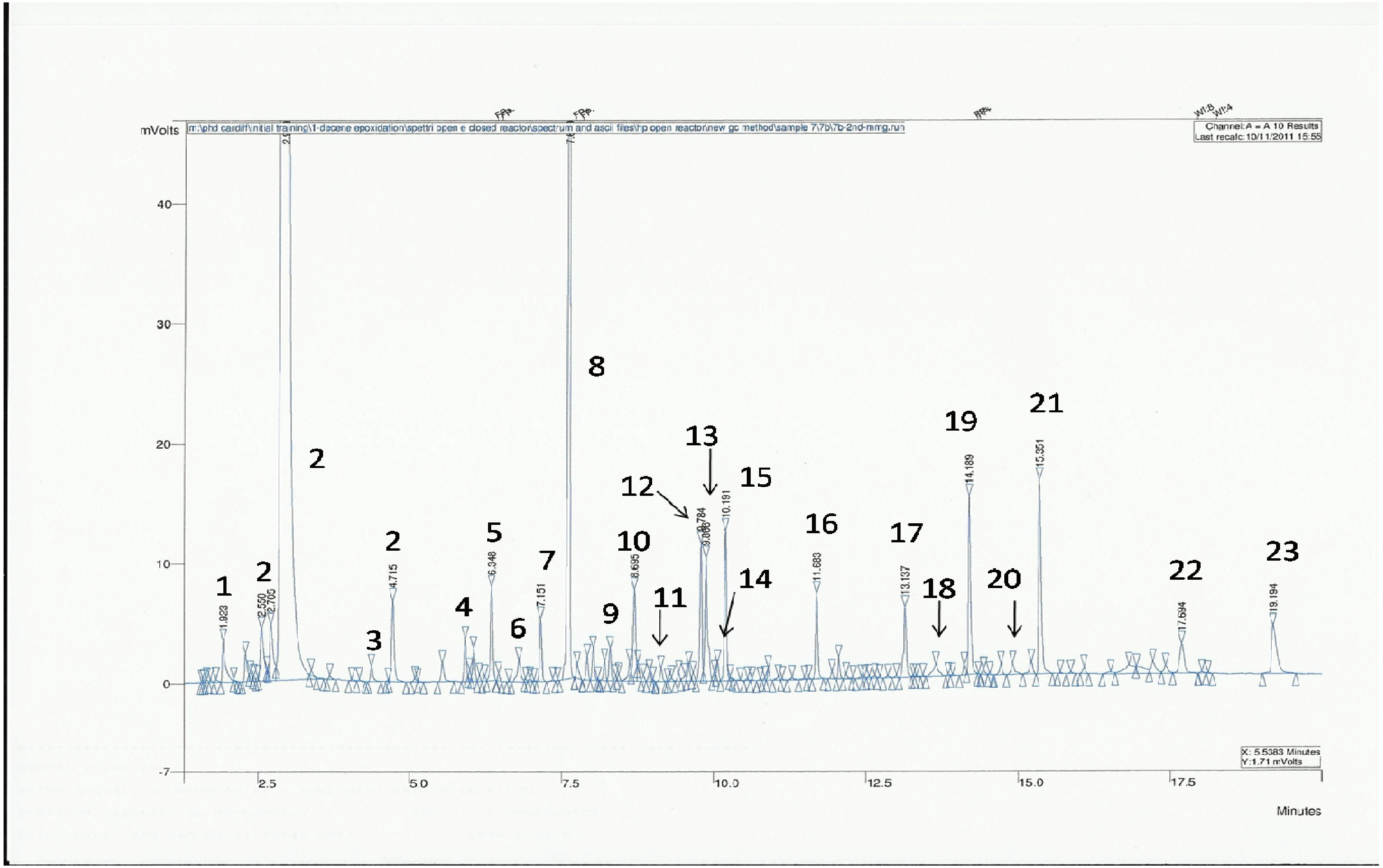

Figure 2.9 *Product separation with Zebron ZB-Wax Plus column in 1-decene epoxidation*

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CHAPTER THREE

THE LIQUID PHASE EPOXIDATION OF PROPENE

3. The liquid phase epoxidation of propene

3.1 Introduction

The liquid phase epoxidation of propene (Figure 3.1) over bimetallic catalyst supported on graphite and titanium dioxide has been performed without the use of any reductant in a 50 mL stainless steel autoclave. Reaction gas up to 30 barg: 3 barg of propene, 3 barg of oxygen, 24 barg of nitrogen and benzoylperoxide (BPO) as radical initiator were used in the reaction. The primary objective of this investigation is to find the experimental reaction conditions to achieve the highest PO yield in order to sustain industrial development.

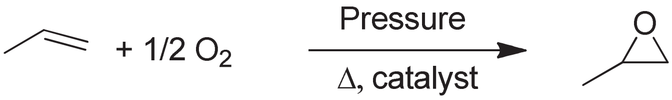

Figure 3.1 *The liquid phase propene epoxidation reaction*

The effects of different solvents in the reaction and the reactivity of benzene (breakdown product of common radical initiator) have been investigated; the aim is to determine whether the oxidation of propene competes with benzene at the catalyst surface and if propene may be able to generate benzene under reaction conditions. Furthermore, the effects of Au-Pd nanoparticles supported on graphite or titanium dioxide (35% rutile – 65% anatase) were compared and the effects of the solvent volume, the amount of radical initiator and catalyst evaluated in order to develop the reaction process and improve the PO yield. Products analysis has been performed on a Varian GC 3300 fitted with Zebron ZB-Wax plus (L=60m, I.D=0.53) column and a flame ionization detector (FID) as reported in section *2.2.6* and propene conversion and propene epoxide yield has been determined with equation *2.3* and *2.4* reported in section *2.2.6* of chapter two.

3.2 Catalyst characterization

3.2.1 Powder X-ray diffraction

The Powder X-ray diffraction has been performed as reported in section *2.2.3*. In the pattern shown in Figure 3.2, only the presence of titania has been identified because is not possible detect the presence of the metals, due to their low concentration. The search and match pattern, performed with an Inorganic Cambridge Software Database (ICSD) software detect only the presence titania composed by its crystalline forms anatase (green lines) and rutile (blue lines). This is the same for Figure 3.3 where only the presence of the support, in this case carbon graphite, has been identified; in fact no gold and palladium were detected after XRPD analysis due to the low concentration of them. The search and match pattern, performed with an Inorganic Cambridge Software Database (ICSD) software detect only the presence carbon in its crystalline forms graphite.

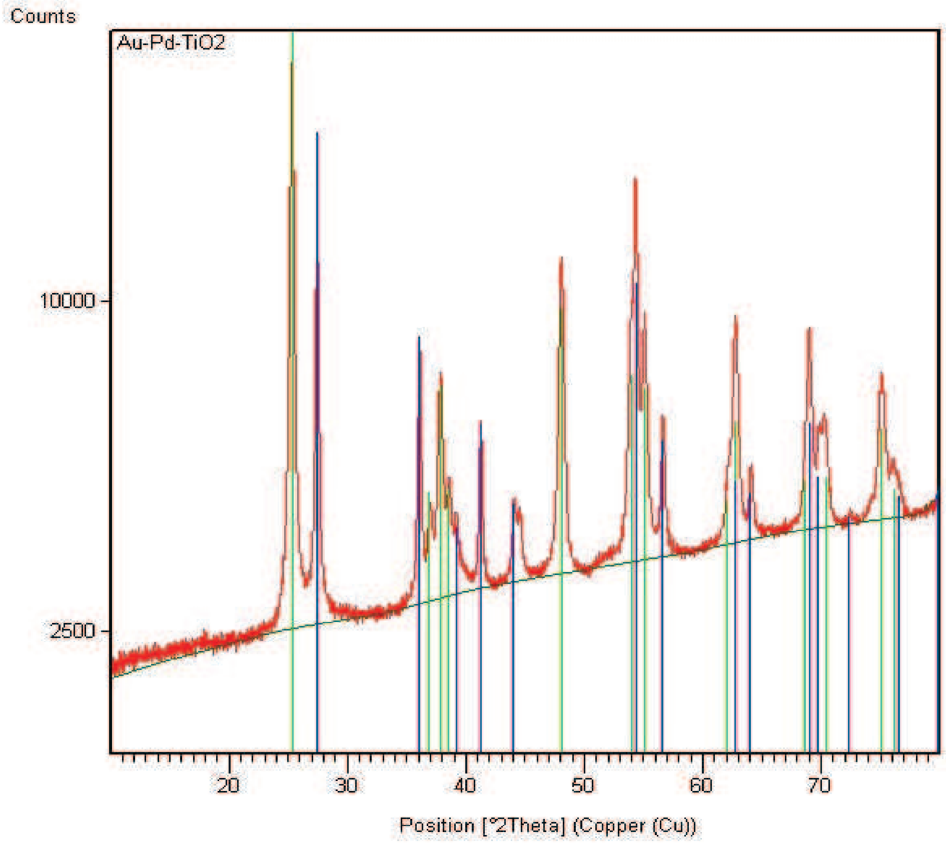

Figure 3.2 *XRPD pattern of 0.5%Au-0.5%Pd/TiO$_2$*

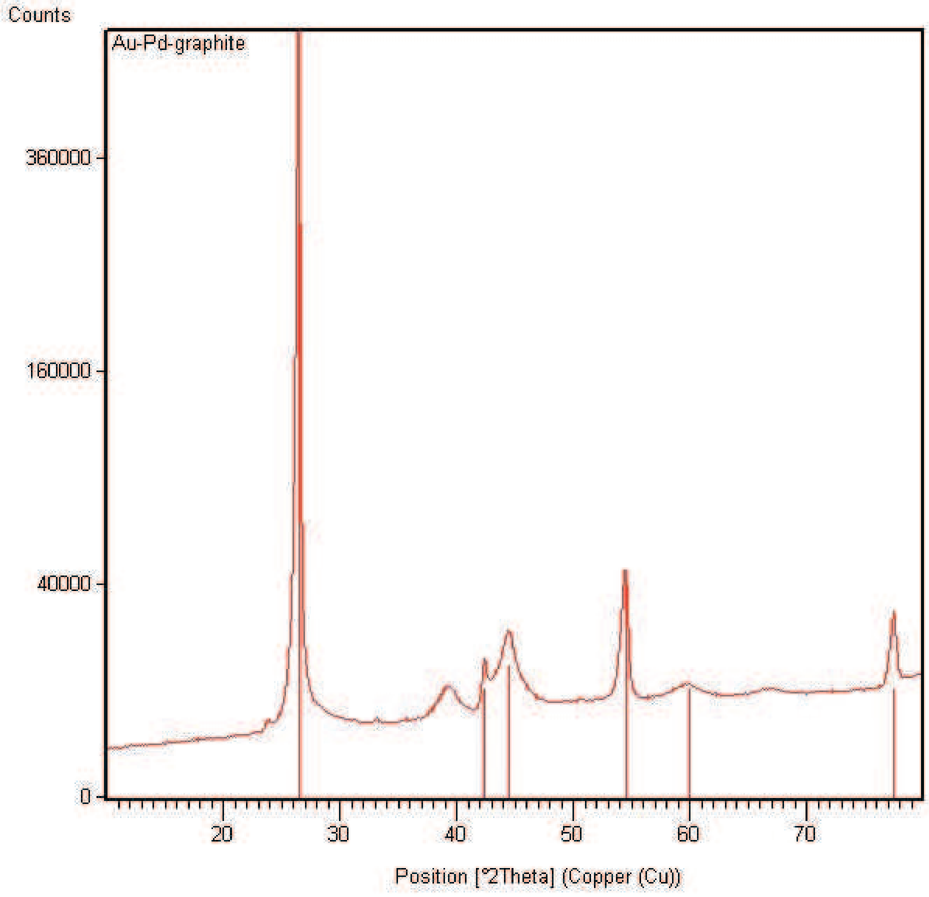

Figure 3.3 *XRPD pattern of 0.5%Au-0.5%Pd/graphite*

3.2.2 N_2 physisorption

The N_2 physisorption has been performed as reported in section *2.2.3*. The specific surface area (SSA) of the catalysts used is 60.94 m^2/g for 0.5%Au- 0.5%Pd supported on titania. The specific surface area (SSA) of the catalysts 0.5%Au- 0.5%Pd supported on graphite is 114.79 m^2/g.

3.3 Results and discussion

3.3.1 The effect of the solvents

Different solvents have been studied in order to determine their effects on the propene epoxidation reaction. Solvents tested were: acetonitrile (CH_3CN), methanol (MeOH), ethanol (EtOH) and water. The aim is to identify which solvent gives better results in terms of propene oxide yield, which is considered to be related to the solubility of propene.

In the literature it has been reported that methanol is a good solvent for the production of propene oxide [1] (TS-1 with stoichiometric amounts of hydrogen peroxide (H_2O_2)) and the Handbook of Chemistry and Physics reports that the propene is very soluble in water, ethanol and acetic acid [2].

As reported in Table 3.1, of those solvents tested only acetonitrile is suitable for obtaining propene oxide (entry 5 was repeated with acetonitrile to confirm the data). The reason that despite the increased solubility of propene in other solvents acetonitrile appears to facilitate epoxidation will be object of determination. Indeed in the case of reactions with TS-1 and H_2O_2 [1] the rate of epoxidation could be related to the *mole transition energy* (E_T). Mole transition energy is an empirical parameters determined by spectroscopy measurements, dynamics methods and equilibrium of chemical reaction [3] that describe the overall interactions between a solvent and a solute [4]. In literature is reported that E_T has a linear dependence only with log r_0, where r_0 is the initial rate of epoxidation reaction, while with other physical parameters of solvents (dielectric constant, dipole moment, autoprotolysis constant) this linear dependence does not occur [1]. In Figure 3.3 the linear dependence of log r_0 with E_T has been showed: methanol with an E_T of 233 kJ/mol had the highest epoxidation rate compared to the E_T of 193 and 157 kJ/mol for acetonitrile (MeCN) and tetrahydrofuran (THF) in which the rate was progressively poorer. Therefore the propene epoxidation is more active in solvent with a larger E_T.

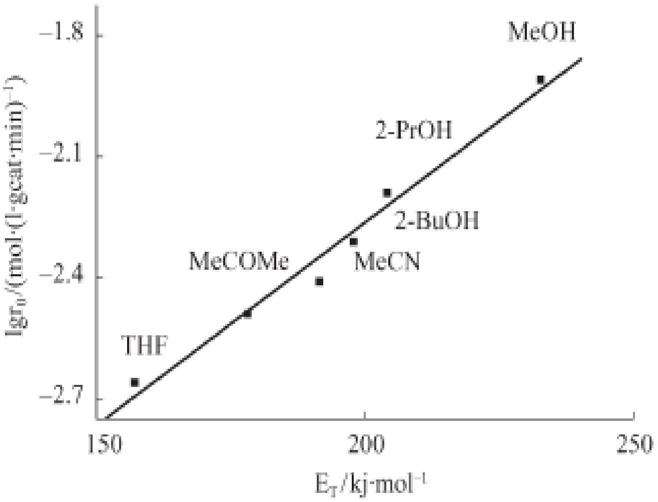

Figure 3.4 *Linear dependence between E_T and log r_0 for propene epoxidation with H_2O_2 on TS-1 [1]*

Table 3.1 - Influence of solvents on propene epoxidation reaction

Entry	Solvent	PO (moles)
1	CH_3OH	0
2	EtOH	0
3	H_2O	0
4	**CH_3CN**	**5.48E-06**
5	**CH_3CN**	**3.36E-06**

Reaction conditions: 0.5%Au-0.5%Pd/C graphite 0.02 g, BPO 0.028 g, Solvent 10 mL, O_2, propene 3 barg, N_2 24 barg, 1200 rpm, 2 h, 90 °C.

3.3.2 Effect of AIBN as radical initiator

Propene epoxidation reaction was performed using AIBN (azobisisobutyronitrile) instead of BPO as the radical initiator. After 2 hours reaction, no PO could be detected by GC analysis. From this observation, studies will continue using BPO as the radical initiator of choice.

3.3.3 Effect of benzene

The effect of benzene on the propene epoxidation reaction has been evaluated in order to determine whether the oxidation of propene competes with that of benzene. Potentially, benzene and CO_2 are generated due to the breakdown of BPO and its subsequent oxidation may restrict further product (PO) formation through competitive adsorption.

A series of reactions were performed using 0.5%Au-0.5%Pd/Graphite catalyst and introducing benzene. The amount of benzene introduced is equal to that generated from the BPO used in the reaction, doubling its concentration. The results of the reactions performed are shown in Table 3.2.

Table 3.2 – Influence of time on the propene epoxidation with benzene

Reaction conditions	Entry	Time of reaction (hours)	PO (moles)
No benzene introduced	1	2	5.48E-06
0.027 g benzene added	2	2	6.10E-06
	3	4	1.54E-06
	4	12	2.14E-06
	5	24	0

Reaction conditions: 0.5%Au-0.5%Pd/C graphite 0.02 g, BPO 8.67E-05 mol, acetonitrile 10 mL, O_2 and propene 3 barg, N_2 24 barg, 1200 rpm, 90 °C

The aim of these reactions is to see if a decreased PO yield was observed over the reaction time. From these initial results it appears that there is no disadvantage due to the addition of benzene to the reaction. Over time the moles of PO decreases which is considered to be due to PO ring opening and the formation of secondary products. From four to twelve hours reaction a slightly increase has been observed; this is only an anomaly, probably due to the low amount of propene and does not affect the diminution trend over the time.

3.3.4 Blank activity

A series of blank reactions were performed in order to evaluate the activity of the catalyst under the reaction conditions used.

All the reactions performed are shown in Table 3.3 and the results are shown in Table 3.4. Benzene, *p*-benzoquinone, phenol and benzoic acid are the break down products of BPO. In Table 3.3, Entry 8 the amount of benzene introduced in the reaction is the same of that generated from the BPO used.

Table 3.3 – List of blank reactions performed (x = used, n = not used)

Entry	**Propene (3 barg)**	**O_2 (3 barg)**	**N_2 (barg)**	**BPO (0.056 g)**	**Au-Pd/TiO_2 (0.04 g)**
1	x	x	24	n	n
2	x	x	24	x	n
3	x	x	24	n	x
4	x	x	24	x	TiO_2
5	n	x	27	x	x
6	x	n	27	x	x
7	x	x	24	x	x
8	n	x	27	Benzene (0.027 g)	x

Reaction conditions: CH_3CN 30 mL, total pressure 30 barg, 2 h, 1200 rpm, 90°C

Table 3.4 – Moles of products in 30 mL of volume from the blank reactions performed

Entry	**PO**	**acrolein**	**benzene**	**p-benzoquinone**	**phenol**	**benzoic acid**
1	0	0	0	2.15E-04*	1.08E-05*	2.04E-05*
2	5.71E-06	6.67E-07	7.59E-06	4.93E-05	7.18E-05	5.10E-05
3	0	0	0	0	8.91E-06*	1.85E-05*
4	2.41E-06	8.88E-07	6.02E-06	1.36E-04	6.95E-05	4.27E-05
5	0	0	1.35E-05	1.21E-04	7.29E-05	1.19E-05
6	1.06E-06	3.14E-07	8.32E-05	1.30E-04	4.88E-06	7.18E-05
7	7.24E-06	1.74E-06	9.43E-06	2.51E-04	8.62E-05	5.52E-05
8	0	0	2.29E-04	4.36E-05*	7.40E-07*	1.10E-05*

* Impurities present inside the reactor and syringe

Table 3.4 shows the number of moles obtained performing the blank reactions. Performing the reactions with propene but without the radical initiator (Entries 1, 3), no benzene is detected after GC analysis. Furthermore, the amount of the other break down products remains in the same dimensional range as others, so benzene does not react to form them. It is considered that propene reacts to form propene oxide only and does not make benzene. The amount of the break down products marked with the asterisk its due to the impurities inside the reactor and syringe (as stated in a footnote of the Table 3.4) because they can only be generated from BPO.

3.3.5 Effect of the catalyst support: graphite versus TiO_2

Titania, in the anatase form has been shown to be the appropriate phase and support that makes gold nanoparticles selective in reactions performed below 373 K, whereas the rutile form causes the complete oxidation to form CO_2 [5]. This difference could be correlated to the disposition of Ti cations in the crystalline lattice of TiO_2; in the case of anatase Ti cations are relatively isolated from one each other than the rutile, where the Ti cations are densely packed [6]. In literature is reported that amorphous TiO_2, produce CO_2, acetone and propene oxide [6]. When amorphous TiO_2 is calcined in air at 400°C, after gold particles has been deposited, his crystalline structure rearrange in a rutile and anatase; in this case the products selectivity are determined by a combination of rutile and anatase, probably because the structure of rutile is not fully crystallized and the undesidered oxidation reaction are depressed than on well crystallized rutile [6].

In this study, in order to improve the yield of propene oxide, a 0.5% Au-0.5%Pd/TiO_2 catalyst (35% rutile, 65% anatase Degussa P25) synthesized by sol immobilization method has been tested in the reaction. This was compared to the 0.5%Au-0.5%Pd/graphite catalyst and the results obtained using both catalysts are reported in Tables 3.5 and 3.6. Reactions were performed changing the amount of catalyst, radical initiator and solvent to form a matrix of reaction conditions and the effect on PO yield reported.

Table 3.5 and Figure 3.4 illustrate the performances of both catalysts tested in the reaction performed using 0.02 g of catalyst, 0.028 g of BPO and varying the solvent volume from 10 to 30 mL. Table 3.6 and Figure 3.5 report the performances of both catalysts tested in the reaction performed using 0.04 g of catalyst, 0.056 g of BPO and varying the solvent volume from 10 to 30 mL. The notation “trace” refers to all products observed performing the GC analysis on which the quantification has not been possible with an acceptable error due to the lowest amount of them.

Using titanium dioxide as the Au-Pd support led to an increase in the PO yield by a factor of two orders over the conditions adopted initially. It appears that a combination of lower propene concentration and titania support have increased the rate of PO formation. This could be related either to the amount of catalyst or to the amount of solvent: perhaps because of a greater dilution, the product has a larger volume to get away from the surface of the catalyst increasing access to its active sites and preventing its deactivation; also the greater the quantity of catalyst and the higher are the catalytic performances. At this initial stage further work is required to determine the background reaction at such conditions. A larger reaction vessel was used in subsequent experiments, in an effort to increase the reaction volume with the moles of propene static. At low volume with low BPO concentrations the TiO_2 supported catalyst performs poorly compared to the graphite supported catalyst. This has been seen before in the case of cyclooctene epoxidation, such that when the initiator concentration has been increased the TiO_2 supported catalyst performs better relative to the graphite supported catalyst [7].

Increasing the volume of the reaction solvent is detrimental in the case of graphite but beneficial in the case of titania catalysts. In order to understand the nature of this phenomenon a study with more propene but at the same concentration in the solvent (for example 3 barg in 10 mL, twice amount in 20 mL and triple amount in 30 mL) could be useful to study the dependence of the catalyst from the amount of propene available; in other terms is possible to check the performances of the catalyst with more propene. Further work with propene at the same concentration of the studies described in Tables 3.5 and 3.6, but keeping constant the volume (for example 3 barg in 10 mL, ½ amount in 10 mL and ¼ amount in 10 mL) could be object of study; in this case is possible to study the effect of the diffusion factor of propene at constant ratio catalyst/solvent. However, under increased catalyst/BPO and solvent conditions the formation of secondary products has occurred with titania catalysts. The presence of benzene in the analysis of these reactions does indicate that despite competitive adsorption the rate of PO formation is increased and preferential to a degree. This is contrary to that with graphite catalysts as all the benzene has reacted to other products.

Table 3.5 – Effect of increasing the volume of solvent

						Amount of products (moles)					
Entry	**CH_3CN (mL)**	**Catalyst**	**BPO (g)**	**Propene Conv. %**	**PO yield %**	**PO**	**Acetaldehyde**	**Benzene**	**p-benzoquinone**	**Phenol**	**Benzoic acid**
1	10	0.02 g Au-Pd/C	0.028	0.50	0.50	1.42E-05	0	7,16E-07	3,89E-05	2,97E-06	1,87E-05
2	10	0.02 g Au-Pd/TiO_2	0.028	0.32	0.32	9.07E-06	trace	2.08E-06	2.53E-03	4.17E-05	8.98E-06
3	20	0.02 g Au-Pd/C	0.028	1.25	1.25	2.06E-05	0	0	5.23E-02	4.76E-04	3.24E-05
4	20	0.02 g Au-Pd/TiO_2	0.028	1.22	1.22	2.00E-05	0	0	1.54E-02	3.30E-04	1.99E-03
5	30	0.02 g Au-Pd/C	0.028	6.58	6.58	2.70E-05	0	0	3.45E-03	1.15E-04	1.18E-04
6*	30	0.02 g Au-Pd/TiO_2	0.028	0	0	0	0	0	3.54E-03	1.14E-04	0

Au-Pd/C = 0.5 %Au – 0.5%Pd/Graphite

Au-Pd/TiO_2= 0.5 %Au – 0.5%Pd/TiO_2

***= performed twice, but no PO was detected in both cases**

Table 3.6 - Influence of the volume of solvent with increased catalyst and BPO concentration.

						Amount of products (moles)						
Entry	**CH_3CN (mL)**	**Catalyst**	**BPO (g)**	**Propene Conv (%)**	**PO Yield (%)**	**PO**	**Acetaldehyde**	**Acrolein**	**Benzene**	**p-benzoquinone**	**Phenol**	**Benzoic acid**
1	10	0.04 g Au-Pd/C	0.056	0.32	0.32	9.02E-06	0	0	0	1.27E-04	6.71E-05	5.23E-05
2	10	0.04 g Au-Pd/TiO_2	0.056	0.71	0.71	2.02E-05	0	0	0	3.51E-03	1.89E-04	0
3	20	0.04 g Au-Pd/C	0.056	0.22	0.22	3.66E-06	0	0	0	8,22E-05	2,39E-05	5,12E-05
4	20	0.04 g Au-Pd/TiO_2	0.056	1.52	1.52	2.50E-05	trace	0	2.18E-06	9.08E-04	6.80E-05	0
5	30	0.04 g Au-Pd/C	0.056	2.27	2.30	9.42E-06	0	0	2,89E-05	1,14E-05	1,04E-05	1,92E-05
6	30	0.04 g Au-Pd/TiO_2	0.056	13.74	12.50	5.13E-05	trace	5.07-06	3.90E-06	3.75E-03	7.20E-05	7.26E-06

Au-Pd/C = 0.5 %Au – 0.5%Pd/Graphite

Au-Pd/TiO_2= 0.5 %Au – 0.5%Pd/TiO_2

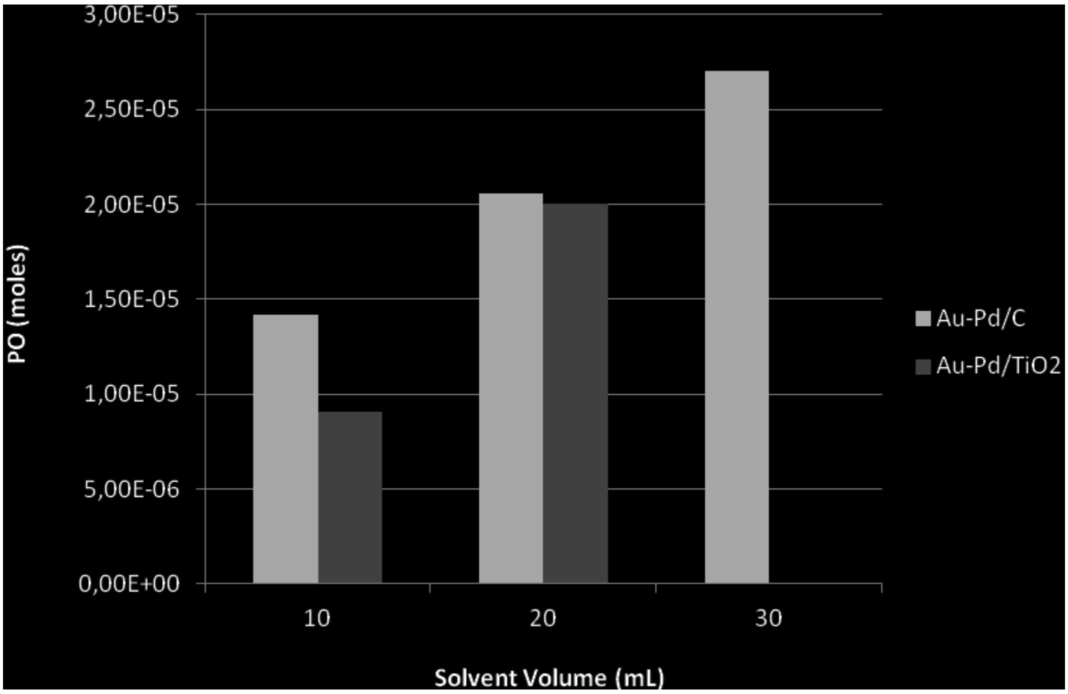

Figure 3.5 – *Moles of PO in 10, 20 and 30 mL of solvent using 0.02 g of catalyst, 0.028 g of BPO*

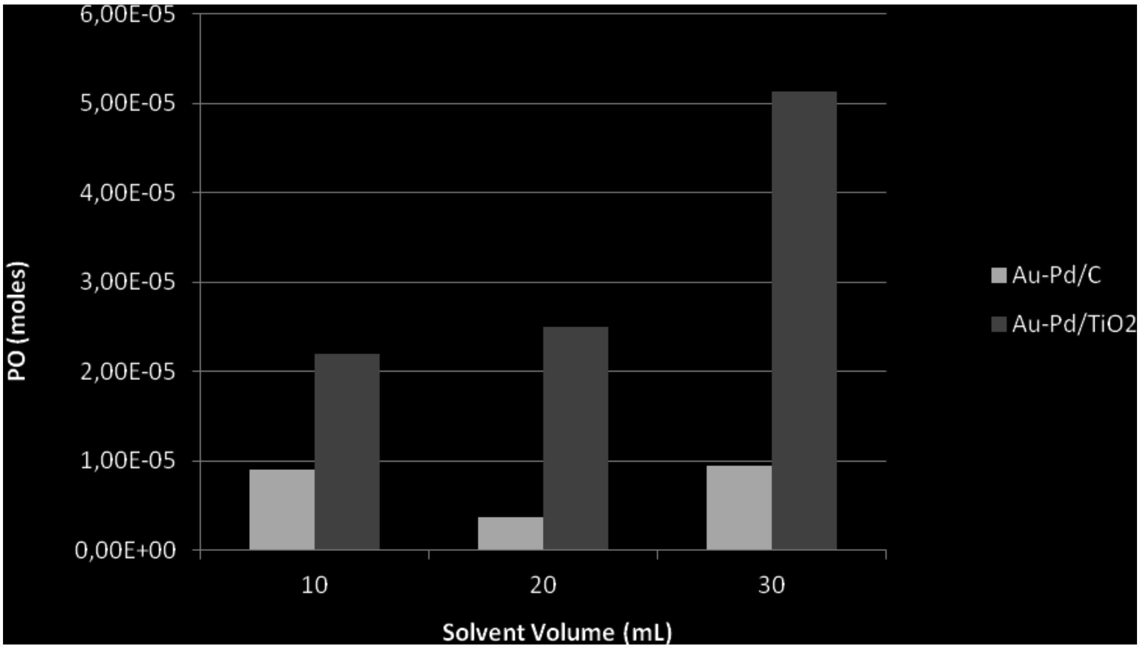

Figure 3.6 – *Moles of PO in 10, 20 and 30 mL of solvent using 0.04 g of catalyst, 0.056 g of BPO*

3.3.6 Study on Au-Pd/TiO_2 in the propene epoxidation

As reported in Section 3.5 the high PO yield has been obtained using bimetallic Au-Pd supported on titanium dioxide catalyst (Table 3.6, Figure 3.5). Time on line reactions have been performed with and without catalyst in order to compare its influence in the reaction, as reported in Table 3.7.

Table 3.7 – Reactions performed

Entry	Propene (barg)	O_2 (barg)	N_2 (barg)	BPO (g)	Au-Pd/TiO_2 (g)
1	3	3	24	0.056	NO
2	3	3	24	0.056	0.04

Reaction conditions: 2h, 90 °C, 1200 rpm, CH_3CN 30 mL, 30 barg total pressure

The reaction in Entry 1 it is a typical blank reaction done in order to determine the amount of PO and the others products obtained without catalyst and the products obtained are reported in Table 3.8. On the other hand, the reaction in Entry 2 is a standard reaction performed with catalyst and the products are reported in Table 3.9. BPO break down products are the total moles obtained by summing of benzene, p-benzoquinone, phenol and benzoic acid. An amount of acetaldehyde reported in the Table 3.8 and acrolein in Table 3.9 has been observed performing the GC analysis; this has been pointed out reporting trace because the quantification of the peak area of the by-products observed in the GC analysis has not been possible with an acceptable error, due the lowest amount of them.

Table 3.8 – Moles products obtained without catalyst

Time (hours)	PO	Acetaldehyde	Acrolein	BPO break down (total moles)	CO_2
1/2	8.48E-06	0	4.24E-07	2.50E-04	1.94E-05
1	2.44E-05	trace	1.24E-06	1.77E-04	2.86E-05
2	1.78E-05	trace	7.97E-07	1.65E-04	3.76E-05
4	5.28E-05	trace	0	1.77E-04	4.19E-05
12	1.53E-06	6.62E-07	2.03E-07	1.85E-04	5.51E-05

Reaction conditions: 90 °C, 1200 rpm, CH_3CN 30 mL, 30 barg total pressure, **NO CATALYST**

Table 3.9 – Moles of products obtained with catalyst

Time (hours)	**PO**	**Acetaldehyde**	**Acrolein**	**BPO break down (total moles)**	**CO_2**
1/2	4.74E-07	0	trace	1.98E-04	2.00E-05
1	3.73E-05	0	1.37E-06	3.90E-04	2.84E-05
2	6.93E-06	2.17E-06	3.62E-07	1.53E-04	5.47E-05
4	3.39E-06	3.30E-06	3.29E-07	1.24E-04	4.97E-05
12	3.73E-07	1.04E-06	trace	1.64E-04	4.28E-05

Reaction conditions: 90 °C, 1200 rpm, CH_3CN 30 mL, 30 barg total pressure

At this initial stage it seems that the reaction performed without the catalyst, under the described reactions conditions, give slightly better PO yield than the one performed with; this is probably related to the deactivation of the catalyst due to the adsorption of PO on its surface. Lowest PO yield are detected in both reactions performed with and without catalyst for half than a hour, where the low PO yield is probably related to the low reaction time, and in longer time reaction (twelve hours). This is probably due to the adsorption of PO on the catalyst surface (in reactions performed with catalyst) and to the epoxide ring opening even if looking the amount of acrolein, acetaldehyde and CO_2 (products derived from the decomposition of PO) is not possible conclude that PO converted to them. Also the amount of the BPO break down products is in the same dimensional range for all the reactions. In the reactions performed with catalyst, the maximum amount of PO is obtained after one hour reaction and for longer reaction times the amount slightly decreases (Figure 3.6). These results suggest that the catalyst play an important role in the synthesis of propene oxide compared to the other experimental conditions, therefore future studies will be oriented in the discovery of a new catalyst that not suffer of deactivation and gives better the propene epoxide yields.

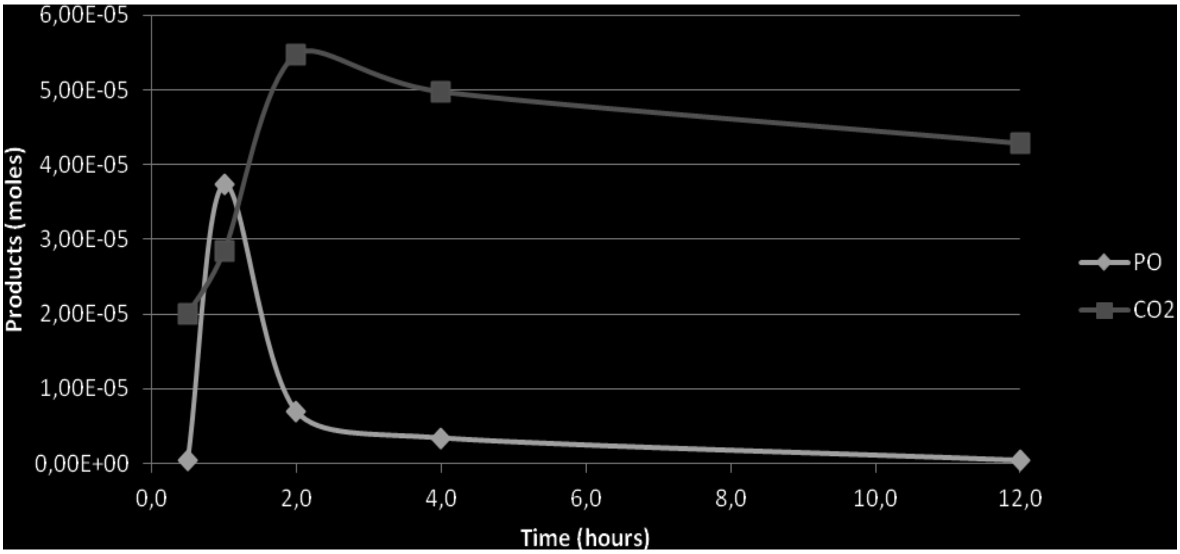

Fig. 3.7 – *Moles of PO and CO_2 obtained in time on line reactions with catalyst*

3.3.7 The stability of PO

The stability of PO has been evaluated performing reactions in which an amount of propene oxide has been introduced in the autoclave. The amount of propene oxide introduced is the double of that obtained during the reaction for one hour with catalyst (Table 3.9). The target is to determine the amount of PO still present after one and four hours reactions. Reactions were performed in acetonitrile and methanol, in order to evaluate the stability of PO in both solvents. Reaction conditions are reported in Tables 3.10 and 3.11 and results are in Table 3.12 and 3.13.

Table 3.10 – Reactions performed for 1 hour

Entry	PO (moles)	Time (hour)	Au-Pd/TiO_2 (g)	BPO (g)	Solvent
1	**7.46E-05**	1	0.04	NO	CH_3CN
2			0.04	0.056	CH_3CN
3			0.04	NO	CH_3OH
4			0.04	0.056	CH_3OH

Reaction conditions: 90 °C, 1200 rpm, solvent 30 mL, O_2 3 barg, N_2 27 barg

Table 3.11 – Reactions performed for 4 hours

Entry	**PO (moles)**	**Time (hours)**	**Au-Pd/TiO_2 (g)**	**BPO (g)**	**Solvent**
5	**7.46E-05**	4	0.04	NO	CH_3CN
6			0.04	0.056	CH_3CN
7			0.04	NO	CH_3OH
8			0.04	0.056	CH_3OH

Reaction conditions: 90 °C, 1200 rpm, solvent 30 mL, O_2 3 barg, N_2 27 barg

Table 3.12 – Amount of PO and products after 1 hour reaction

		Amount of products (moles)						
Entry	**PO**	**acetaldehyde**	**acrolein**	**benzene**	**p-benzoquinone**	**phenol**	**benzoic acid**	**CO_2**
1	6.34E-05 **(88.79 %)**	8.50E-06	0	0	0	5.50E-06*	4.08E-07*	2.14E-06
2	6.37E-05 (**89.21** %)	0	0	9.90E-06	4.24E-06	6.52E-05	1.10E-04	3.01E-05
3	7.00E-05 (**98.04** %)	6.15E-05	6.42E-07	**	0	2.45E-06*	2.28E-06*	1.76E-06
4	5.54E-05 (**77.59** %)	5.73E-06	6.90E-07	**	2.77E-05	5.50E-05	2.90E-04	3.29E-05

*traces in the reactor and in the syringe

** Benzene peak cover by MeOH peak

Table 3.13 – Amount of PO and products after 4 hour reaction

					Amount of products (moles)			
Entry	**PO**	**acetaldehyde**	**acrolein**	**benzene**	**p-benzoquinone**	**phenol**	**benzoic acid**	**CO_2**
5	3.35E-05 (**46.92** %)	0	2.84E-07	0	0	1.06E-07*	7.74E-07*	2.56E-06
6	2.28E-05 (**31.93** %)	3.34E-07	1.10E-07	1.14E-05	4.42E-05	9.51E-05	4.71E-05	5.36E-05
7	9.97E-05***	2.77E-05	2.99E-07	**	0	8.70E-07*	1.70E-06*	3.28E-06
8	2.34E-05 (**32.77** %)	1.28E-05	9.09E-07	**	3.04E-05	3.61E-05	2.97E-04	2.06E-05

** traces in the reactor and in the syringe*

*** Benzene peak cover by MeOH peak*

**** more PO than introduced.*

The amount of the break down products marked with the asterisk its due to the impurities inside the reactor and syringe (as stated in a footnote of the Table 3.12 and 3.13) because they can only be generated from BPO. In Table 3.13 Entry 7, the amount of PO obtained after performing the reaction is more than the one introduced; this reaction has been repeated two times and the same results has been obtained. This results is possible related to some PO that stuck inside the reactor surface and then solubilised by methanol during the reaction or because the solubility of PO in methanol and the absence of radical initiator could have avoided the decomposition of PO though performing a longer time reaction.

3.4 Conclusion

The primary objective of this investigation is to find the experimental reaction conditions to achieve the highest PO yield in order to sustain industrial development.

The initial research work has been performed using a 0.5%Au-0.5%Pd/C graphite catalyst. Since in literature has been reported that methanol is good solvent for the epoxidation of propene [1] and that propene is very soluble in ethanol, water and acetic acid [2] a series of reactions has been performed in order to evaluate which solvent performs better. Results of this work are reported in Table 3.1 and is possible to note that only using acetonitrile is possible detect propene oxide. The right chose of a radical initiator is also a parameter that has been evaluated and only using BPO as radical initiator is possible detect PO.

A consequence of using BPO as radical initiator is that benzene produced from its decomposition could affect the epoxidation rate of propene due to the adsorption on a catalyst surface and a consequent reduction of its catalytic activity. The results are shown in Table 3.2; performing the reaction adding benzene is possible to note that there is no variation in the PO yield and the PO decreasing over the time is related to the ring opening and a formation of a secondary by-products.

In order to reach the target, a different catalyst was studied in the propene epoxidation reaction: 0.5%Au-0.5%Pd/TiO_2; this because in literature is reported that titanium dioxide in the anatase crystalline form is a good catalyst for the epoxidation of propene [4].

A comparison between the catalyst supported on titania and the other one supported on graphite has been done. Notwithstanding at lower catalyst and radical initiator amounts the catalyst supported on graphite performs better than the titania supported one at every solvent volume (Figure 3.5), the highest PO yield has been obtained using the catalyst supported on titania (Figure 3.6) to the condition of doubling its and BPO quantitative. By the way a series of blank reactions highlighted that no many differences in PO yield has been noticed performing the reaction with and without catalyst (Tables 3.8 – 3.9).

In conclusion of our studies, the stability of PO has been studied. PO is stable in methanol and acetonitrile for one and four hours reactions; as mentioned previously the amount of PO over the time decrease due to the ring opening and the formation of secondary by-products (Table 3.13).

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CHAPTER FOUR

THE LIQUID PHASE EPOXIDATION OF 1-DECENE

4. The liquid phase epoxidation of 1-decene

4.1 Introduction

The liquid phase epoxidation of 1-decene (Figure 4.1) has been studied as part of my initial training. The reaction has been performed over catalysts comprising graphite supported metal nano-particles, synthesized by incipient wetness impregnation (IWI) method.

Variation of experimental parameters such as pressure of oxygen, speed of the stirrer and reaction time has been studied in order to determine the effects on conversion, epoxide and terminal C_{10} oxygenate product selectivity. The aim is to identify which experimental procedures give the best results in terms of 1-decene conversion, epoxide selectivity and terminal C_{10} oxygenate products. The standard gold supported on carbon graphite catalyst was compared with copper-manganese supported on carbon graphite catalyst one under different reaction conditions. Reactions were performed reducing the pressure of oxygen and increasing the reaction time, so as to increase the selectivity to epoxide.

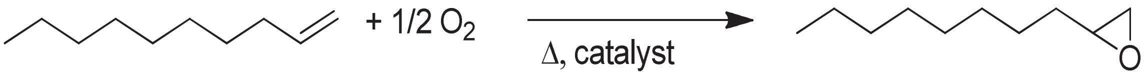

Fig. 4.1 *The liquid phase 1-decene epoxidation reaction*

Products analysis has been performed on a Varian GC 3300 fitted with Zebron ZB-Wax plus (L=60m, I.D=0.53) column and a flame ionization detector (FID) as reported in section *2.3.4* and 1-decene conversion, 1-decene epoxide yield and selectivity has been determined with equation *2.6, 2.7* and *2.8* reported in section *2.3.4* of chapter two.

4.2 Results and discussion

4.2.1 1%Au /graphite as catalyst in the epoxidation of 1-decene

4.2.1.1 Effect of the reactor: comparison of the products from RBF and high pressure (open/closed) reactors

Three reactions were performed respectively in RBF at atmospheric pressure and at higher pressure (open, closed) under 3 barg of O_2 for 24 hours at 90°C and stirred at 600 rpm; AIBN has been used as radical initiator. At the end of the reaction, the products were analyzed at GC and the results are reported in table 1. The increased oxygen pressure has been investigated in an effort to improve the catalyst activity and yield of epoxide. 1-Decene conversion has improved; however, the epoxide selectivity at 24 hours is lower than that obtained in the RBF reactor at atmospheric pressure (air). From the GC analysis, the high pressure reactor in an open state gave better results than where reactor is closed and the O_2 supply finite. For this reason, the experimental studies has been carried out using the open version reactor over both the closed and RBF reactors setups.

Table 4.1 **-** Influence of the reactor setup on 1-decene epoxidation

Reaction Conditions	Conversion (%)	Epoxide Selectivity (%)	C_{10} terminal oxygenates selectivity (%)
RBF	27	28	40
CR, 3 barg O_2	25	19	51
OR, 3 barg O_2	38	26	43

1-decene: 10 mL; Catalyst: 0.1 g; AIBN: 0.006 g; 600 rpm; 90 °C; 24 h

RBF: round bottom flask - CR: closed reactor - OR: open reactor

4.2.1.2 Effect of reaction conditions

The effect of stirrer speed, oxygen pressure and time were further investigated (Table 4.2 and 4.3). The outcomes of a number of the reactions were not intuitive and needs to be repeated. However, general trends have emerged and these will be discussed.

4.2.1.3 Effect of oxygen

Generally, increasing the oxygen pressure, conversion and epoxide selectivity were found to increase, although they are comparable to the RBF under atmospheric pressure. The selectivity to terminal oxygenate products was found to be comparable with all pressures (Table 4.2 and 4.3).

4.2.1.4 Effect of the reaction time

Increasing the reaction time, generally led to best results; however, from 12 to 24 hours the reaction rate has diminished. This may be due to increased competitive adsorption and subsequent reactions of primary and secondary products. Increasing the reaction time further and performing reactions in the presence of primary products may verify whether competitive adsorption is suppressing 1-decene conversion (Table 4.2 and 4.3).

4.2.1.5 Effect of the stirrer speed

Increasing the speed of the stirrer generally led to best results in terms of conversion and selectivity. However, further investigation with lower speeds needs to be performed to confirm this initial observation (Table 4.2 and 4.3).

Table 4.2-Conversion, epoxide and C_{10} terminal oxygenate selectivity expressed in % at 600 rpm

Time (h)	**1 barg**			**2 barg**			**3 barg**		
	Conv	**Epoxide**	**C_{10}**	**Conv**	**Epoxide**	**C_{10}**	**Conv**	**Epoxide**	**C_{10}**
6	16	30	49	6*	10*	26*	16*	21*	37*
12	20	28	44	25	32	47	10*	9*	48*
24	29	26	48	23*	32*	47*	38	26	43

1-decene: 10 mL; Catalyst: 0.1 g; AIBN: 0.006 g; 90°C

* entries are suspect and needs to be repeated

Table 4.3-Conversion, epoxide and C_{10} terminal oxygenate selectivity expressed in % at 1000 rpm

Time (h)	**1 barg**			**2 barg**			**3 barg**		
	Conv	**Epoxide**	**C_{10}**	**Conv**	**Epoxide**	**C_{10}**	**Conv**	**Epoxide**	**C_{10}**
6	8*	19*	35*	22	35	51	26	23	37
12	19	32	49	22	35	50	29	33	48
24	17*	28*	47*	24	33	47	21*	26*	40*

1-decene: 10 mL; Catalyst: 0.1 g; AIBN: 0.006 g; 90 °C

* entries are suspect and needs to be repeated

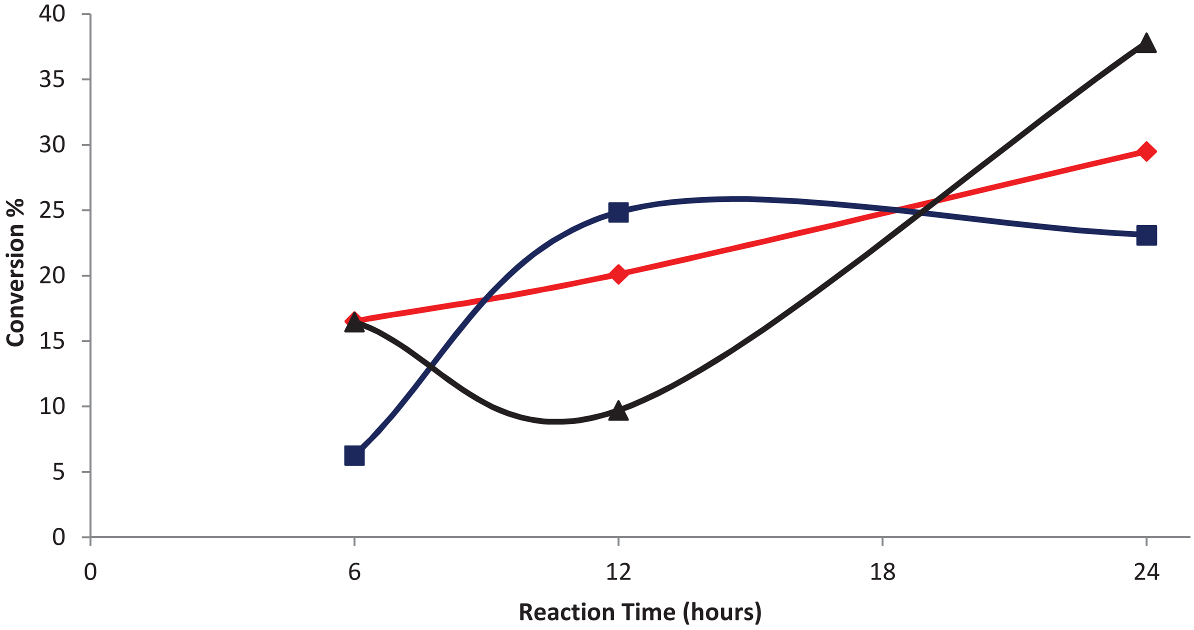

Fig. 4.2 *Influence of pressure on 1-decene conversion at 600 rpm over 6-24 h.* ◆= *1 barg,* ■= 2 barg, ▲ = *3 barg*

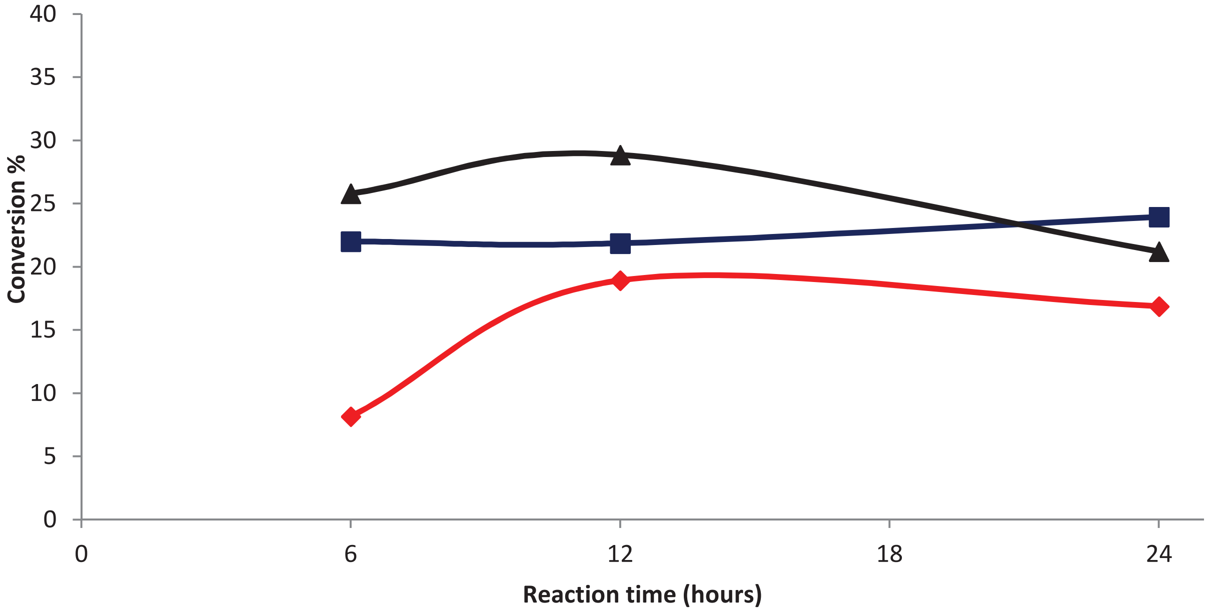

Fig. 4.3 *Influence of pressure on 1-decene conversion at 1000 rpm over 6-24 h.* ◆*= 1barg,* ■ *= 2 barg,* ▲*= 3 barg*

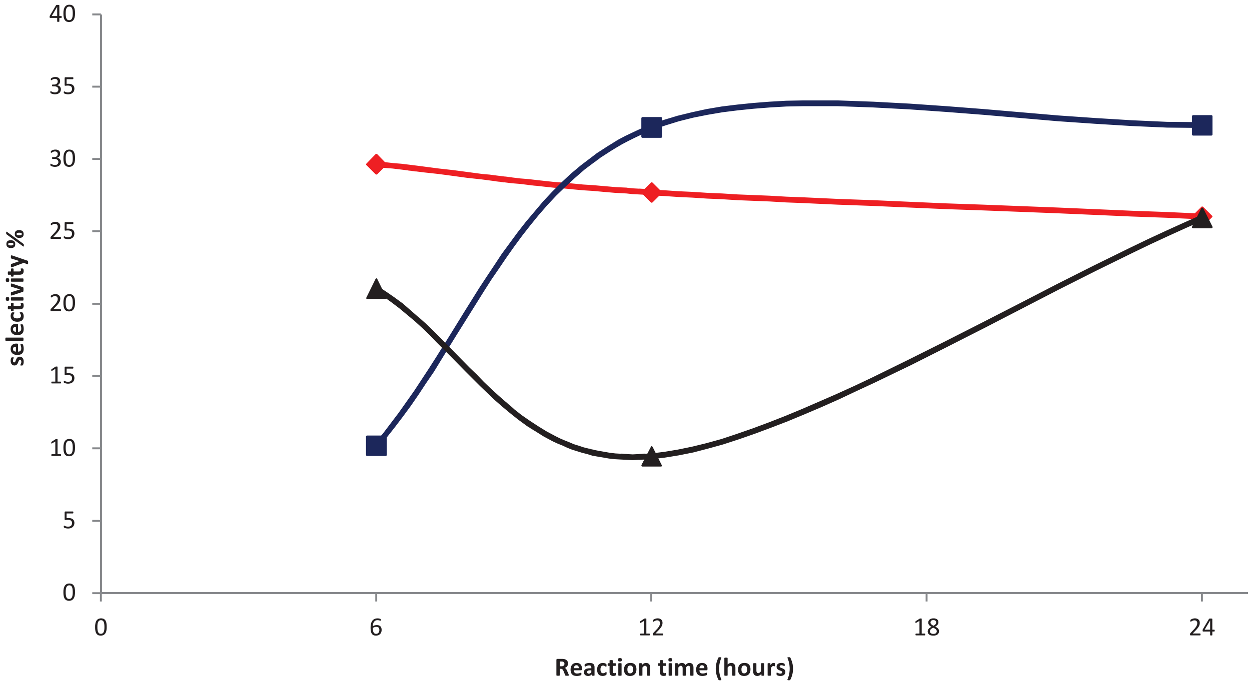

Fig. 4.4 *Influence of pressure on epoxide selectivity at 600 rpm over 6-24 h.* ◆*= 1 barg,* ■ = 2 *barg,* ▲ *= 3 barg.*

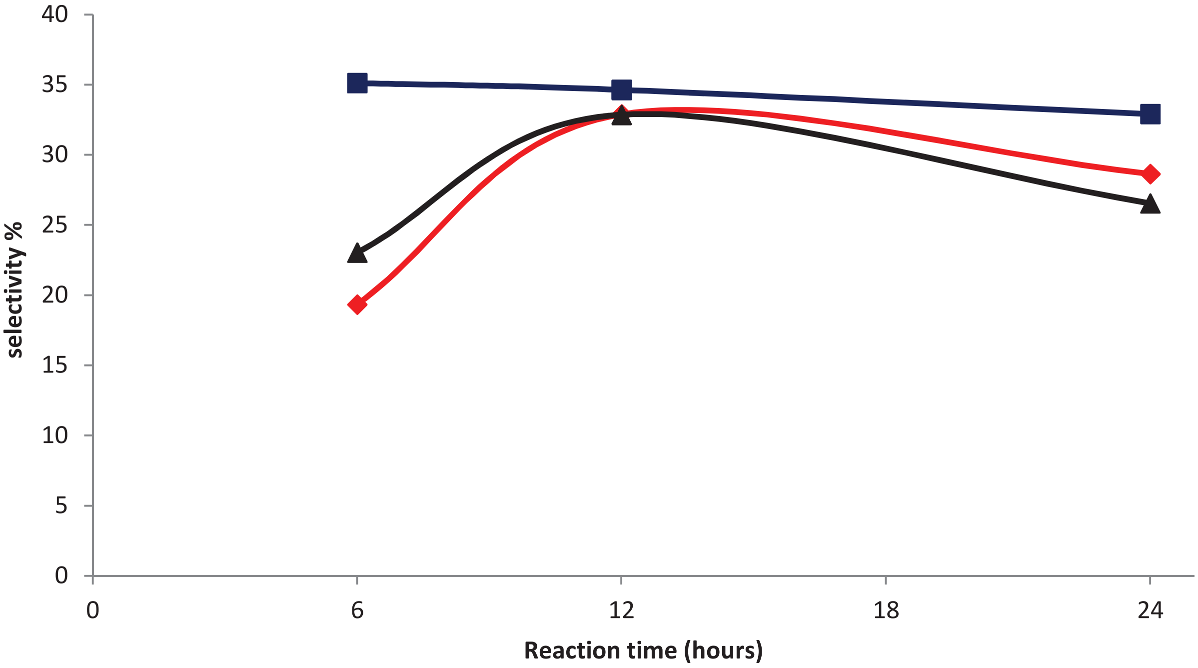

Fig. 4.5 *Influence of pressure on epoxide selectivity at 1000 rpm over 6-24 h.* ◆ *= 1 barg,* ■ *= 2 barg,* ▲ *= 3 barg.*

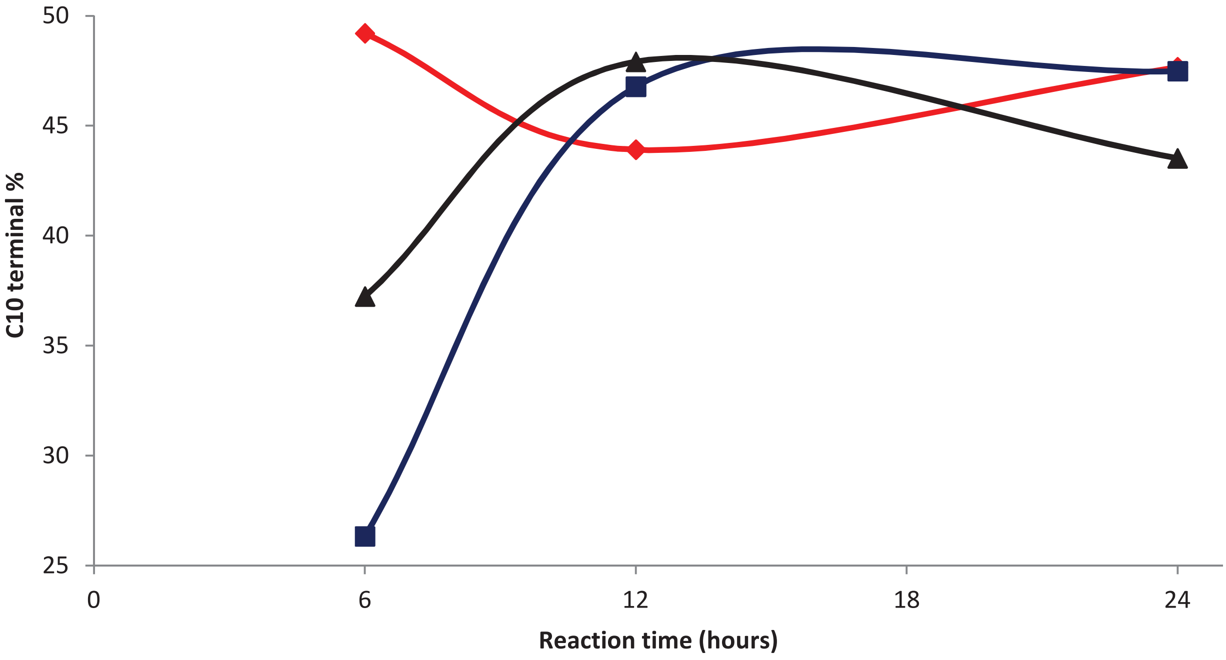

Fig. 4.6 *Influence of pressure on* C_{10} *terminal oxygenates selectivity at 600 rpm over 6-24 h.* ◆ *= 1 bagr,* ■ *=2 barg,* ▲ *= 3 barg.*

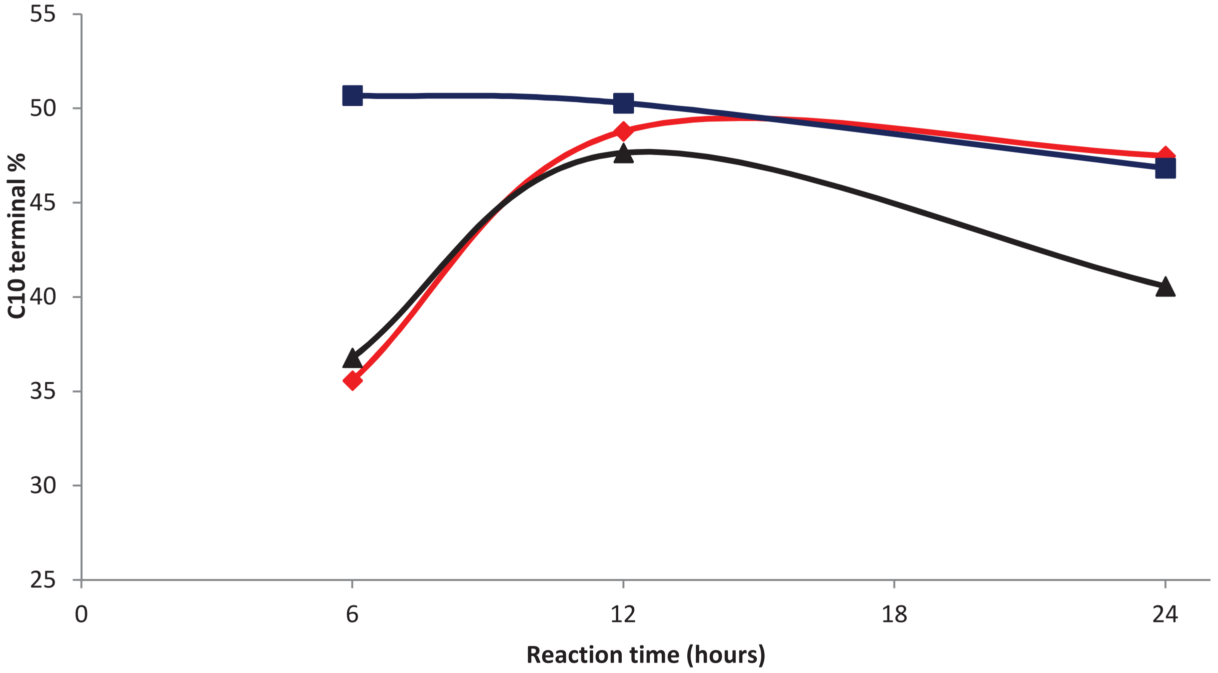

Fig. 4.7 *Influence of pressure on C_{10} terminal oxygenates selectivity at 1000 rpm over 6-24* h. ◆ *=1 barg,* ■ *=2 barg,* ▲ *= 3 barg*

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4.2.2 1%Cu- 1%Mn/graphite as catalyst in the epoxidation of 1-decene

1-decene epoxidation reaction has been performed also using a catalyst comprising 1%Cu-1%Mn/Graphite. Reaction conditions are 90°C, AIBN, 24 h, 3 barg, 1000 rpm. Two batches of 1%Cu-1%Mn/Graphite were prepared, one synthesized from $Cu(NO_3)_2$ hemipentahydrate and $Mn(NO_3)_2$ hexahydrate precursors and the second one from $MnSO_4$ monohydrate and $Cu(NO_3)_2$ hemipentahydrate precursors. These were tested in order to determine which one gave better results, as reported in Table 4.4. Potentially to identify issues with adsorbates from the precursors. After GC analysis, the catalyst synthesized from both nitrate precursors gave better results than the nitrate/sulphate precursor; for this reason, the experimental studies has been carried out using the catalyst from both nitrate precursors. Has been considered that the sulphate persists on the surface of the supported metals, reducing access to active sites.

Table 4.4 - Conversion, epoxide and C_{10} terminal oxygenates selectivity with 1%Cu-1%Mn/graphite catalysts

Catalyst	**Conversion (%)**	**Epoxide Selectivity (%)**	**C_{10} terminal oxygenates selectivity (%)**
1%Cu-1%Mn/graphite **a**	34.46	23.69	35.03
1%Cu-1%Mn/graphite **b**	31.55	15.84	25.54

1-decene: 10 mL; Catalyst: 0.1 g; AIBN: 0.006 g; O_2 pressure: 3 barg; 90 °C; 1000 rpm; 24 h

a: from nitrate precursors – **b:** from nitrate/sulphate precursors

Parameters, such as oxygen pressure and reaction time, were evaluated in order to investigate the dependence of conversion, epoxide selectivity and C_{10} terminal oxygenate products. Reactions were carried out at 1 or 3 barg of oxygen at different reaction times. Comparison of reactions over 48 hours at 1 and 3 barg (Table 4.5 and Figure 4.8) indicate that both pressures are characterized of an initial induction time. However, the induction period persists for a longer time at the higher pressure. The rate of 1-decene conversion at both cases diminished after 24 hours, although the conversion at 48 hours is approximately twice at the higher pressure. There appears to be a balance between the oxygen pressure and the rate which also influences the overall product yield at 48 hours. This could be due to potential transport issues of both 1-decene and oxygen to the active site or a dependence on the availability of radical species. Further work in this area may prove beneficial in enhancing standard reactions such as those in the high pressure autoclave.

Table 4.5 - Influence of oxygen pressure and reaction time in 1-decene epoxidation reaction with 1%Cu-1%Mn/graphite at 90°C and 1000 rpm.

Pressure	**Time (h)**	**Conversion %**	**Epoxide Selectivity (%)**	**C_{10} terminal oxygenates selectivity (%)**
1 barg	1	1.23	8.75	29.72
	3	3.08	13.11	34.14
	6	14.15	25.21	38.66
	12	16.56	30.78	43.99
	24	16.14	27.58	40.39
	48	18.00	30.15	42.23
3 barg	1	0.69	5.37	26.42
	3	1.87	10.71	29.88
	6	8.19	21.04	37.09
	12	26.70	24.56	34.85
	24	30.17	24.81	36.15
	48	30.48	26.14	15.54

1-decene: 10 mL; Catalyst: 0.1 g; AIBN: 0.006 g; 90 °C; 1000 rpm

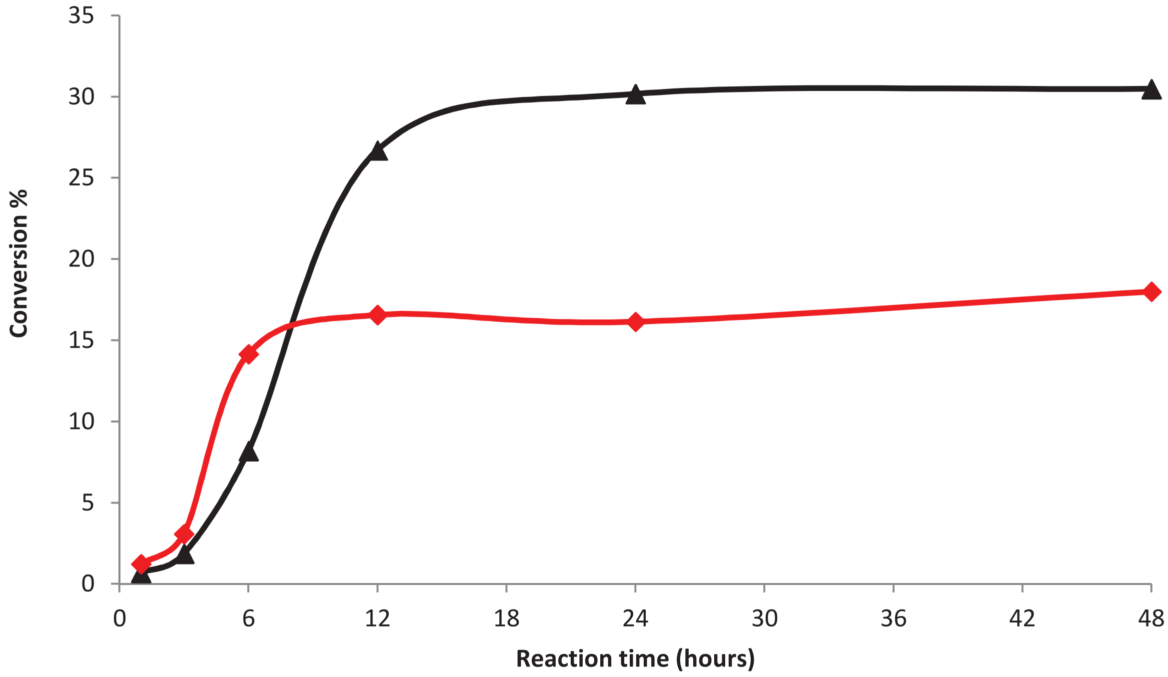

Fig. 4.8 *Influence of pressure on 1-decene conversion at 1000 rpm over 1-48 hours.*

◆ = *1 barg,* ▲ = *3 barg.*

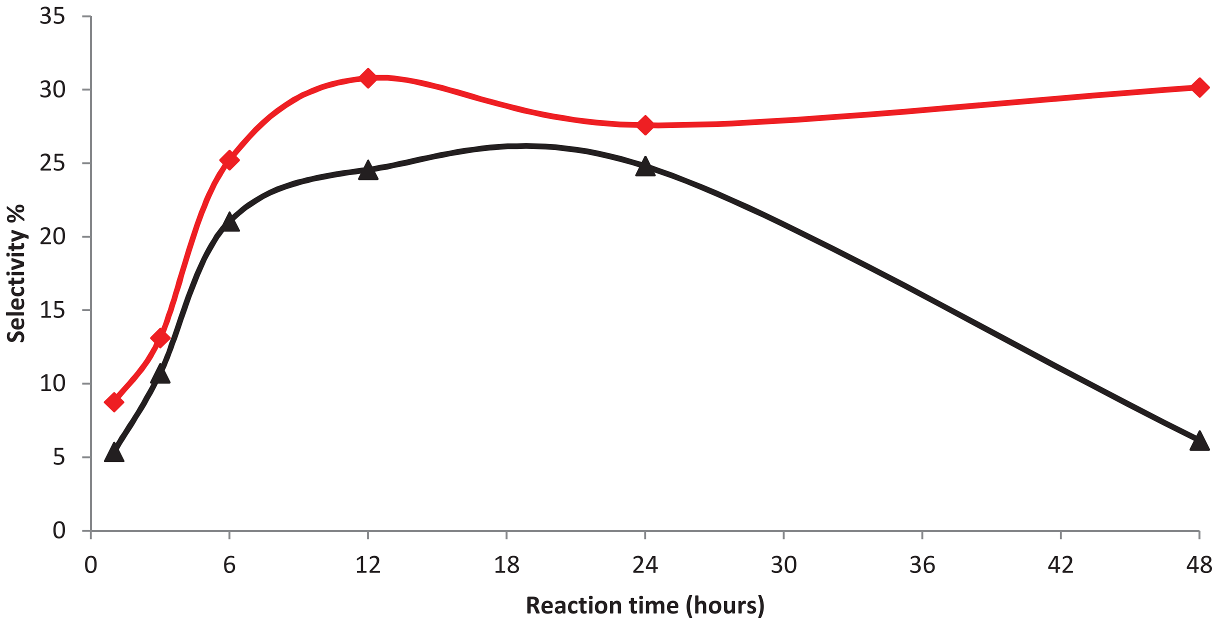

Fig. 4.9 *Influence of pressure on epoxide selectivity at 1000 rpm over 1-48 hours*

◆ = *1 barg,* ▲= *3 barg.*

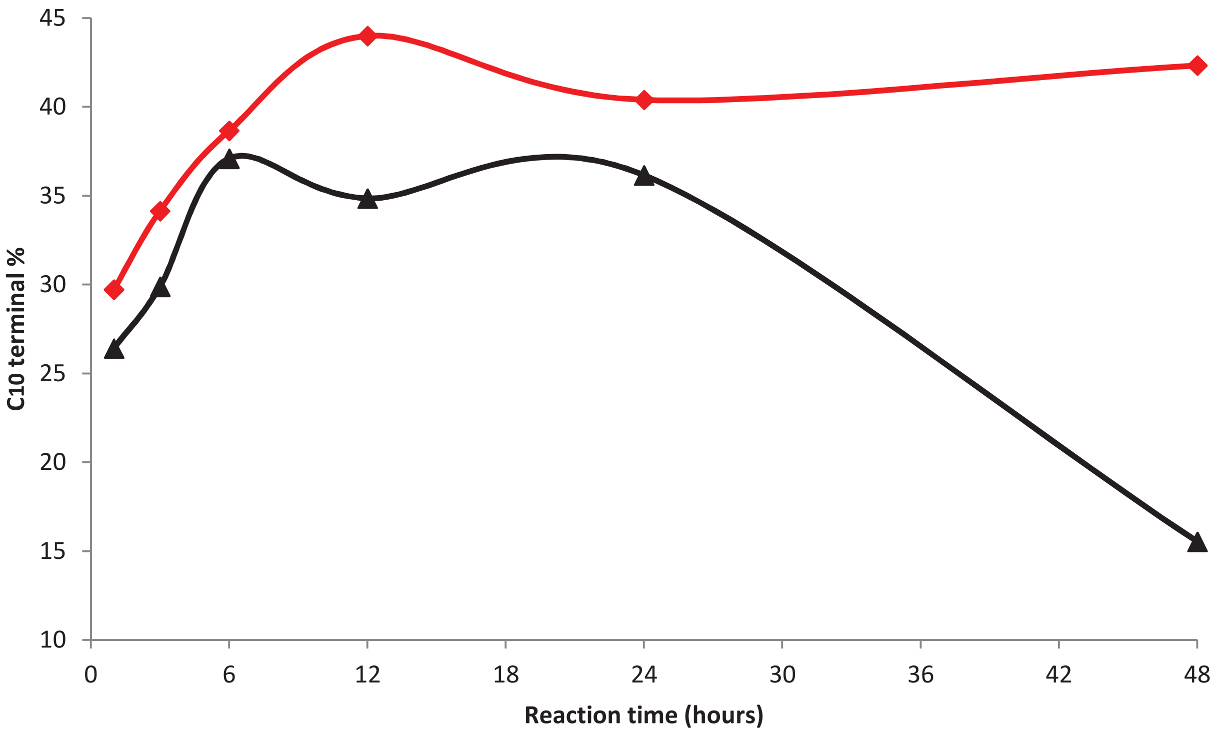

Fig. 4.10 *Influence of pressure on C_{10} terminal oxygenates selectivity at 1000 rpm over 1-48 hours.* ◆ = *1 barg,* ▲ = *3 barg.*

Figure 4.9 and 4.10 shows that epoxide and terminal oxygenate selectivity are both characterized by a long induction time. This may be due to competitive adsorption between the products and starting material, resulting in a diminished 1-decene conversion and increased secondary reactions. This is pronounced with the reaction at 3 barg, where the higher concentration of surface oxygen may facilitate increased reactions of terminal oxygenates.

To establish whether this induction period can be decreased two reactions were carried out. The first one with an increased amount of the radical initator AIBN, and the second one with 1,2- epoxydecane. The quantity of epoxydecene introduced is the same that we found at the end of the reaction at 24 hours (Table 4.4). Completion of the table with both increased AIBN concentration and introduction of epoxide at the start for all reaction times studied (Table 4.5) is an on-going concern.

Table 4.6 - Effect of increased AIBN concentration and 1,2-epoxydecane addition at 90°C, 3barg, 24 hours and 1000 rpm.

Conditions	Conversion %	Epoxide selectivity %	C_{10} Terminal selectivity %
standard	30.17	24.81	36.15
2xAIBN	22.71	25.78	37.86
epoxydecene	32.12	18.61	27.13

1-decene: 10 mL; Catalyst: 0.1 g; O_2 pressure: 3 barg; 90 °C; 1000 rpm; 24 h

However, the results indicate that increasing the AIBN lowers the 1-decene conversion over 24 hours, whereas the addition of epoxydecane has not affected this. Tentatively we can say that the induction period is not due to product inhibition. However, the initator may be blocking active sites where upon it undergoes homolysis and reacts with incoming 1-decene. At an increased concentration 1-decene adsorption may be prevented. Further work in this area needs to be carried out in order to elucidate the cause of the induction period.

4.3 Conclusion

In the liquid-phase epoxidation of 1-decene many efforts has been done in order to found better conditions that gives the best results in terms of 1-decene conversion and the selectivity to epoxide and C10 terminal oxygenate products.

Incipient Wetness Impregnation (IWI) is the method used to synthesize the catalysts used in this research work: 1%Au/C graphite and 1%Mn-1%Cu/C graphite.

First part of this research work has been conducted over a gold catalyst supported on graphite and has been related in finding a proper reactor. After a reaction test the high pressure reactor, open to the oxygen line, proved to be the better (even though the epoxide selectivity is slightly smaller than the one obtained in a RBF reactor); this could be related by the constant oxygen feed that probably increase the transport of reactants at the gold surface.

An important factor that led to a results decrease is the reaction time (Tables 4.2 and 4.3). Usually increasing the reaction time better results are obtained; in this case the decreasing of our results could be related to a competitive adsorption on the catalyst surface and the consequent formation of secondary by-products.

Also the stirrer speed plays an important role in the epoxidation reaction; its role has been evaluated in order to increase the 1-decene conversion and the selectivity to epoxide and C_{10} terminal oxygenates. An increase in the stirrer speed could led to an increase of the properties mentioned above but in this case there are no substantial variation.

Epoxidation of 1-decene has been studied also through another catalyst, 1%Mn – 1%Cu/C graphite. The catalyst has been synthesized from metal nitrate and sulphate precursors; the one synthesized from both nitrate precursors performs better than the one synthesized from nitrate and sulphate precursors (Table 4.4); probably the residual sulphates presence could play an inhibitor role for the catalytic activity.

Performing the reactions at different pressure values and reaction time, after an initial induction period observed (Table 4.5) probably due to a competitive adsorption between products and starting materials, the 1-decene conversion increase at nearly twice at high pressure; in this case no substantial differences has been detected performing reactions for 24 and 48 hours.

On the other side an increase in the oxygen pressure and reaction time led to a decreasing in the selectivity to epoxide; the same trend has been observed for the selectivity to C_{10} terminal oxygenates. It seems that under high pressure and longer time reaction there are competitive reactions (ring opening) at the catalyst surface with consequent formation of secondary by-products different from the ones of interest.

CONCLUSION

5.1 Conclusion

The epoxidation of olefins is an important class of catalytic reactions widely used on both a laboratory and industrial scale [1] as they can be used as direct products or as intermediates for the production of important commercial products, such as polymers, cosmetics and additives [2]. Their selective synthesis is a subject of considerable academic and industrial interest.

Currently the production of epoxides is not always facile, particularly for the lack of direct methods and the formation of by-products which can be harmful and expensive to dispose of. One of the most challenges in the selective oxidation of olefins is represented by the electrophilic addition of oxygen to a double bond of an alkene to form an epoxide [3].

The simplest case of what reported above is represented by the silver-catalyzed gas phase epoxidation of ethylene using air or oxygen, that is an industrially established process [4].

In spite of the versatility and importance of olefin epoxides in the chemical processing industry, until very recently, no other olefins had been commercially epoxidized using only molecular oxygen as oxidant as hydrogen peroxide [5,6], hydroperoxides [7] or stoichiometric oxygen donors are required Many explanations have been proposed for the failure to directly epoxidize allylic olefins, such as propylene, to their corresponding epoxides, although the most obvious reason is the reactivity of allylic C–H bonds. Ethylene does not contain any allylic hydogen atoms and, therefore, it does not undergo autoxidation, conversely, other higher alkenes do not behave in the same way as ethylene does. In general, all other higher alkenes containing allylic hydrogen atoms can undergo air oxidation to form various oxidation products at suitable conditions. Autoxidation is a free radical chain reaction where the organic materials (alkene) are converted to hydroperoxide by autoxidation. The autoxidation and facile abstraction of allylic hydrogen atom can be simply understood by the bond dissociation energy of the allylic C–H bond in propylene which is 356 kJ/mol, while the vinylic C–H bond strength in ethylene is 427 kJ/mol [8]. Thus, electrophilic attack by oxygen and abstraction of one of the allylic C–H bonds in propylene becomes energetically more favourable than electrophilic addition of oxygen across the C=C double bond.

On the contrary, higher olefins which do not have allylic hydrogen atom can be epoxidised. This was demonstrated by Eastman Chemical Company who prepared 3,4-epoxy-1-butene from 1,3-butadiene which do not contain allylic hydrogen atom [9,10].

Gold supported on carbon catalysts have significant potential for selective epoxide formation rather than the competing allylic oxidation. However, parameters involved in catalyst preparation can be tuned in order to create catalysts that can have a practical impact at the commercial level [11].

Studies demonstrates that gold nanoparticles supported on graphite or metal oxides, synthesized by a co-precipitation or deposition precipitation methods, have high selectivity in the hydrocarbon oxidation under mild conditions [12, 13]. Additionally, Haruta and co-workers have reported that gold nanoparticles can epoxidize alkenes, using hydrogen to activate the molecular oxygen [14, 15].

According to what reported above, in the present work gold supported catalyst has been synthesized and studied in the liquid phase epoxidation reactions of propene and 1-decene, without the use of any reductant. Experimental parameters has been tuned in order to obtain high propene and 1-decene conversion and increase the selectivity to the respective epoxides.

5.2 Liquid-phase epoxidation of propene

The production of PO is generated in a high proportion from two-stage liquid phase industrial processes: chlorohydrin and hydroperoxide (Halcon) processes Due to the formation of highly toxic chlorinated by-products in the former process and the employment of peroxides (which produce acid waste as by-products economically disadvantageous if there is no market for them) in the latter, growing interests have been directed to develop one step environmental friendly method, based on the electrophilic addition of oxygen to an alkene [16]. The investigation on liquid-phase propene epoxidation founds the following:

- The liquid-phase epoxidation of propene has been performed initially over bimetallic gold and palladium catalyst synthesized by sol immobilization and supported on graphite (0.5%Au-0.5%Pd/Graphite) without the use of any reductant.
- The Powder X-Ray Diffraction (XRPD) performed on the catalysts synthesized, identified the crystalline composition of the supports but not detected the presence of metals due to their low concentration.
- *o-xylene* has been used as an internal standard and introduced at the end of the reaction

- The choice of solvent was carried out according to the solubility of propene and only using acetonitrile was it possible to detect PO. Propene epoxide is also obtained only when using BPO compared to using AIBN.
- The effect of benzene was studied in order to evaluate whether the oxidation of propene competes with that of benzene. Since benzene is generated as breakdown products of BPO its subsequent oxidation may restrict further propene epoxide formation through competitive adsorption on a catalyst surface and a reduction of its catalytic activity. Based on results showed in Table 3.2 the presence of benzene does not affect the epoxidation rate of propene, the PO decreasing observed over the time was related to the epoxide ring opening and the formation of secondary by-products.
- Since in literature is reported that titania in the anatase form has been shown to be the appropriate phase that makes gold nanoparticles selective in reactions performed below 373 K [17], titanium dioxide (65% anatase – 35% rutile) has been studied as support for gold and palladium alloys in the epoxide reaction.
- A series of blank reactions were performed over a 0.5%Au-0.5%Pd/TiO_2 (table 3.3-3.4) to evaluate the activity of the catalyst under the reaction conditions used. The following conclusion were founded:
    - Performing the reaction without the catalyst PO were produced(Table 3.4-Entry 2).
    - The presence of BPO is fundamental in order to obtain PO (Table 3.4-Entry 1-3). This results is in agreement to that reported by Corma et al. about the effect of radical initiator for the epoxidation of alkenes [18]: a catalytic amount of radical initiator is essential for the reaction to take place otherwise no oxidation occurs even when the catalyst is present.
    - TiO_2 alone is selective to the formation of PO (Table 3.4-Entry 4).
    - Propene reacts to propene epoxide only and does not make benzene; benzene is produced as breakdown product of the radical initiator (Table 3.4-Entry 1-3).
- Both catalyst were tested in same reactions in order to evaluate their performances changing parameters such as their amount, the solvent volume and the amount of BPO, (Table 3.5-3.6). Based on results obtained:

  - at low volume and at low BPO and catalyst concentration, the titania supported catalyst performs poorly compared to the graphite one (Table 3.5-Entry 1-2). Since any amount of the two main PO by-products (acrolein and acetaldehyde) has been observed, the PO decreasing is probably due to the adsorption of the product on the catalyst surface and the consequent deactivation of its activity. This is more evident in the reaction carried out in 30 ml of solvent where no PO has been detected.
  - Increasing the volume of reaction is detrimental for graphite catalyst but beneficial in the case of titania one, even though interestingly at higher volume and low amount of catalyst and BPO no PO has been detected (Table 3.5-Entry 6). Study with more propene but at the same concentration in the solvent could be useful to understand the dependence of the catalyst from the amount of propene available.
  - At lower propene concentration with highest amount of catalyst and BPO, Au-Pd supported on titanium dioxide led to an increase in the PO yield (Table 3.6-Entry 6) by a factor of two orders over the conditions adopted initially with Au-Pd supported on graphite (Table 3.5-Entry 5). Probably due to the greater dilution products have larger volume to get away from the surface of the catalyst, preventing its deactivation and increasing access to the active sites.
  - The greater the amount of titania supported catalyst and the higher the catalytic performances are. The effect of the diffusion factor of propene at constant ration catalyst/solvent could be object of further studies.
  - At greater amount of titania supported catalyst, solvent and BPO the formation of secondary by-products (acrolein and acetaldehyde) has occurred (Table 3.6-Entry 6).

- At the initial stage of the project and under the described reaction conditions, seems that the reactions performed without gold-palladium supported on titanium dioxide, led to a slightly better PO yield than the one performed with catalyst. The reported data shows in the reactions performed with catalyst an increase of acetaldehyde, a secondary product deriving from the decomposition of PO (Table 3.8-3.9).

- Due to the epoxide ring opening, the longer the reaction time and the lower the PO amount for reactions carried out with and without catalyst (Table 3.8-3.9). In the case of reactions performed with catalyst the lower PO amount obtained was also due to the epoxide adsorption on its surface.

- Stability of PO has been evaluated performing spike reactions with propene oxide, in order to evaluate the amount of PO moles that are still present after one and four hours reactions. Methanol has been also used as solvent, as well as acetonitrile, in order to evaluate the stability of PO in this solvent. PO is stable in both solvents, and performing the reaction for one hour is possible to get back almost all the PO added (Table 3.12). As supported by previous findings, over the time the concentration of PO decreases due to PO ring opening and the formation of secondary products (Table 3.13).

The investigation in published works about the liquid-phase propene epoxidation with a consequent comparison with the results obtained in this project are reported in Table 5.1.
Table 5.1 shows some published work on propylene epoxidation; results reported are relatives to experiment performed both in gas phase (items 1-2) and in a liquid phase (items 3-5).
Many efforts has been done to increase the epoxidation rate of PO in order to sustain an industrial development. Haruta and co-workers reported of a trimethylsilylated $Ba(NO_3)_2$-Au/titanosilicate (Ti/Si 3:100) catalyst with three dimensional mesoporous titanosilicate as a support for gold nanoparticles in the gas phase epoxidation of propylene with molecular oxygen [19] (Item 1). They argued that a silylation of the silanol sites, with a consequent increasing of the hydrophobicity of the catalyst enhance the PO desorption and the PO yield [19] (Item 1-2). A great contribution in the liquid phase propylene epoxidation has been due by the Hölderich's work which shows how the PO formation is favoured by a small Pd clusters and high fraction of Pd(II) species [20] (Item 3). Item 4 reports the catalytic performances of TS-1 catalyst, synthesized by hydrothermal method in the presence of polymethylmethacrylate (TS-1 PMMA) and polystyrene beads (TS-1 PS) in order to increase the hydrophobic properties of catalyst [21]. The epoxidation of propylene over these catalyst and in presence of hydrogen peroxide led to the best results of propylene conversion and PO selectivity and yield published.
Gold and palladium catalyst synthesized on this research project shows great catalytic properties. Apart from what reported in item 4, the catalytic performances of Au-Pd/TiO_2

are comparable and sometimes better to those of the catalyst reported in Table 5.1. It seems that the bimetallic combination of gold and palladium works as a benefit to the propylene epoxidation. The catalyst show a quite high selectivity to PO but conversion and yield must be increased in order to find out a practical application of it. It is noteworthy to observe that gold and palladium catalysts of this project can be prepared by means of a novel and much simple way with respect to the reported ones. In addition, polyoxometalates derivatives (Item 5) [22] besides their high yield and selectivity, chemical complexity (stoichiometry, polymorphism and so on) lead to high developmental costs. It is also known to those skilled in the art that using hydrogen peroxide in combination with organic solvents could cause the accumulation of organic peroxides in the reaction mixtures, thus potentially compromising the process from the safety point of view. On the other hand, based on the raw data of this research project, explosiveness incidence resulted not to be a critical point. Finally, although susceptible of successive optimization work, the process temperature could be considered "low" with respect to other current investigation works.

Table 5.1 – State of the art about propylene epoxidation

Item	**Catalyst**	**Catalyst specifications**	**C_3H_6 conversion (%)**	**PO selectivity (%)**	**PO yield (%)**
1	Au-$Ba(NO_3)_2$/TS-1	0.3 %wt Au – 1 %wt $Ba(NO_3)_2$ 3 % mol Ti	8.5	93	7.9
2	Au/Ti-MCM-48	2 % mol Ti	2.3	95.5	2.19
3	Pd-Pt/TS-1	1 %wt Pd-0.02 %wt Pt/TS-1	25.4	46	11.7
4	TS-1	1.4 %wt Ti	96	87.5	84
	TS-1 PMMA	1.5 %wt Ti Polymethylmethacrylate bead	98	92.5	90
	TS-1 PS	1.4 %wt Ti Polystyrene bead	99	96	95
5	$(Bu_4N)_4 \cdot [\gamma\text{-}SiW_{10}O_{34}(H_2O_2)]$	Keggin-type polyoxometalate	90.9	> 99	90
6	Au-Pd/TiO_2	0.5 %wt Au - 0.5 %wt Pd/TiO_2	13.7	91	12.5

1 - 2 Reaction conditions: 10 % Vol each of C_3H_6, H_2, O_2 in Ar (SV 4000 $cm^3h^{-1}g^{-1}$ cat.); 0.5 h; 160 °C

3 - Reaction conditions: 15 g MeOH; 5 g H_2O; 10 g C_3H_6; 7 bar O_2; 15 bar N_2; 10 bar O_2; 2 h; 43 °C

4 - Reaction conditions: 80 ml MeOH; 5.2 ml H_2O_2 30%; 7 atm C_3H_6; 1.5 h; 40 °C

5 - Reaction conditions: 6 ml CH3CN; 1 mmol H_2O_2 30%; 5 mmol C_3H_6; 8 h; 32 °C

6 - Reaction conditions: 30 ml CH_3CN; 0.056 g BPO; C_3H_6 3 barg; O_2 3 barg; N_2 24 barg; 2 h; 90 °C

5.3 Liquid-phase epoxidation of 1-decene

Since 1-decene can be used as a co-monomer in certain co-polymers and as an intermediate in the production of epoxides, amines, oxo alcohols, synthetic lubricants, synthetic fatty acids and alkylated aromatics [23], the epoxidation of α-alkenes using 1-decene as a model reactant has been here studied using molecular oxygen and catalytic amounts (non-stoichiometric) of α,α-azoisobutyronitrile (AIBN) as radical initiator. C_{10} terminal oxygenates products (2-decenal, 2-decen-1-ol and 2-decenoic acid) were also object of studies as they could be used to produce plastics, detergents, paints, cosmetics and food additives. The investigation on liquid-phase 1-decene epoxidation founds the following:

- Gold and copper-manganese catalysts supported on graphite synthesized by incipient wetness impregnation were evaluated with 1-decene epoxidation.
- Over 1%Au/Graphite the higher results were obtained performing the reactions in the high pressure reactor, open to the oxygen line (constant pressure of 3 barg over 24 hours). This implies that increased transport of reactants and oxygen were able to facilitate increased catalytic activity at the gold surface and terminal oxygenates selectivity. However, a portion of the data appears inconsistent (Table 4.2-4.3) with the above statement and anomalies obtained are to be repeated as part of further work.
- The effect of 1%Cu – 1%Mn/Graphite with 1-decene epoxidation was also investigated. The catalyst synthesized from both nitrate precursors gave better conversion, selectivity to epoxide and C_{10} terminal products than the one synthesized from nitrate and sulphate precursors (Table 4.4); the residual sulphates presence could persist on the catalyst surface and play an inhibitor role for the catalytic activity.

- The dependence of conversion, epoxide selectivity and C_{10} terminal oxygenates from the oxygen pressure and reaction time were evaluated (Table 4.5). Based on results obtained the following conclusion were founded:
    - the conversion of 1-decene is influenced by the oxygen pressure and increased at nearly twice at high pressure (Figure 4.8) for longer time reactions. This could be due to a potential transport issue of reactants to the active sites of the catalyst or a dependence on the availability of radical species.
    - The selectivity to epoxide and to C_{10} terminal oxygenate products were increased reducing the oxygen pressure up to 1 barg (Figure 4.9-4.10). Under high pressure competitive reactions occur at the catalyst surface with the consequent formation of secondary by-products.
    - Due to competitive adsorption on the catalyst surface between products and starting materials with a resulting decrease of 1-decene conversion and increase of secondary reactions, both reactions performed at 1 and 3 barg are characterized by an initial induction time; based on findings the induction time is not depended by the inhibition of the product (Table 4.6-Entry 3). Also doubling the amount of AIBN (Table 4.6-Entry 2) the desidered effect has not been obtained: the greater amount of radical initiator may be blocking the active sites of the catalyst.
- Interestingly copper-manganese catalyst showed performances comparable to that of gold one. Parameters involved in the catalyst preparation need to be tuned, yields need to be improved and also catalyst stability and performance need to be enhanced in order to have catalysts that can have a practical impact

The investigation in published works about the liquid-phase 1-decene epoxidation with a consequent comparison with the results obtained in this project are reported in Table 5.2. Table 5.2 shows some published work on liquid phase 1-decene epoxidation (item 1-4) and the results of this thesis work are reported (item 5).

It is possible to observe that the better results in terms of conversion, yield and selectivity were obtained again using polyoxometalates derivatives as catalyst [22]. As stated before in the propylene epoxidation conclusions (Table 5.1), the chemical complexity (stoichiometry, polymorphism and so on) of these catalyst led to high developmental costs.

Also the use of hydrogen peroxide in combination with organic solvents could cause consequent problems to the process related to the safety point of view.

Same conclusion about the use of hydrogen peroxide could be done for other works reported in Table 5.2. In fact, apart from the experimental work of Psaro et al. [24] in which the epoxidation of alkenes has been performed over CuO/Al_2O_3 catalyst mediated by the *in-situ* formation of cumene hydroperoxide as oxygen carrier, all other works involve the use of hydrogen peroxide has reductant agent [25-26].

Despite the conclusion reported above, is very interesting to observe how catalyst used in these works [24-26] perform; in fact they are only made by oxides and metal nanoparticles are not used with a consequent reduction of manufacturing costs. Highest selectivity to epoxide, close to 100 %, are achieved over metal oxide catalysts.

Gold and copper-manganese catalysts synthesized and studied on this research project shows great catalytic properties. Reactions were performed under mild conditions and without the use of any reductant. The catalysts show a quite high 1-decene conversion and 1,2-epoxydecane yield compared to other works; however selectivity, the lowest achieved compared to other works, to 1,2-epoxydecane must be increased in order to find out a practical application of it.

Noteworthy are the catalytic properties of copper-manganese supported on carbon graphite catalyst: those shows quite similar properties to that obtained using gold as active metal. This is a great discovery because lead to a costs reduction, even if parameters must be tuned in order to enhance performances.

Table 5.2 – State of the art about 1-decene epoxidation

Item	Catalyst	Catalyst specifications	1-decene conversion (%)	1,2-epoxydecane selectivity (%)	1,2-epoxydecane yield (%)
1	Al_2O_3	Bohemite crystal structure	18	100	18
2	CuO/Al_2O_3	7.6 % wt CuO/Al_2O_3	29	94	27
3	(silica gel-O2)(EtO)Si-L^1-VO(L^2)	Silica supported vanadium(V)oxo-aroylhydrazone complex	33	100	33
4	$(Bu_4N)_4 \cdot [\gamma\text{-}SiW_{10}O_{34}(H_2O_2)]$	Keggin-type polyoxometalate	90.9	> 99	90
5	Au/C graphite	1% wt Au/C	38	26	43
	Cu-Mn/C graphite	1% wt Cu-1%wt Mn/C	34	24	35

1 - Reaction conditions: 10-25 mmol 1-decene; 20-25 mmol H_2O_2 (24 % ethyl acetate); 25 ml ethyl acetate; 1 h; 90 °C

2 - Reaction conditions: 10 mmol 1-decene; 30-35 ml min^{-1} O_2; 20 ml cumene; 6 h; 100 °C

3 - Reaction conditions: 1.0 mmol 1-decene; 3 ml CH_3CN; 3.0 mmol H_2O_2; 1.0 mmol $NaHCO_3$; 5 h; 80 °C

4 - Reaction conditions: 6 ml CH3CN; 1 mmol H_2O_2 30%; 5 mmol C_3H_6; 8 h; 32 °C

5 - Reaction conditions: 10 ml 1-decene; 0.006 g AIBN; 3 barg O_2; 24 h; 90 °C

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