CHAPTER ONE

GENERAL INTRODUCTION AND SCOPE OF THESIS

1.1 Catalytic Epoxidation

The selective epoxidation of olefins is a much discussed topic in the synthesis of intermediates of use in fine and speciality chemistry. Alkenes, either derived from natural resources or generated as products of the chemical industry, are found in great abundance in the realm of organic molecules. One of the most useful transformations of alkenes is via epoxidation (Figure 1.1) whereby two adjacent carbon atoms are functionalized while either of these two adjacent carbons is activated towards nucleophillic attack. This makes the resulting epoxides useful and versatile intermediaries in organic chemistry. Furthermore, in asymmetric synthesis the epoxidation reaction is much preferred since it can produce two chiral carbons in one step [1].

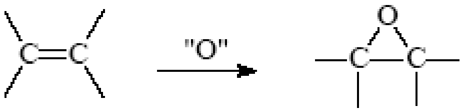


Figure 1.1: Schematic representation of the epoxidation of an alkene.

Prior to this huge amounts of environmentally unacceptable wastes and several other problems like difficulty in separation, recovery and recycling of catalysts after reaction as well as the disposal of liquid and solid wastes, makes catalytic oxidation in the liquid-phase is increasingly important. However, due to increasing environmental demands, the use of classical stoechiometric oxidants for achieving this reaction is no longer optional. In order to make the process cleaner, safer and more efficient, the use of catalysts is almost mandatory [2].

The first example of a liquid phase catalytic oxygen transfer dates back to 1936. The so-called Milas reagents [3] were formed by the reaction of transition metal oxides with a solution of H_2O_2 in *tert*-butanol resulting in soluble inorganic peracids. These catalysts were mainly used for the vicinal dihydroxylation of olefins although with certain metal oxides, e.g. MoO_3 or WO_3, selective epoxidation was also observed. From that point on, a great deal of effort has been put into the development of transition metal based catalysts, both homogeneous and heterogeneous, for the selective epoxidation of a broad range of olefins [4].

Based on the key intermediate involved in the oxygen transfer step, the metal catalyzed oxidations can be divided into two categories [5]. The first one involves a peroxometal, while the second one involves an oxometal pathway (refer to Fig. 1.2). Titanium catalyzed epoxidation has been shown to proceed via a peroxometal pathway [6]. Oxometal species, on the other hand, are generally accepted as the reactive intermediaries in catalytic epoxidations with selenium [7] and chromium [8].

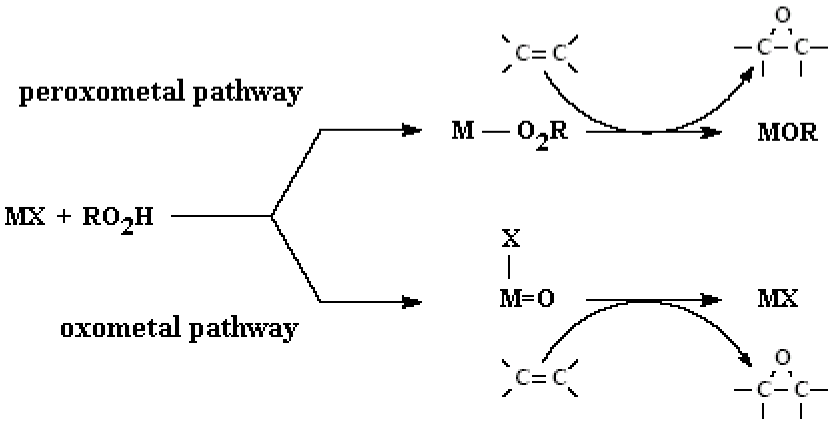


Figure 1.2: Peroxo versus Oxometal Pathways in Catalytic Epoxidation Reaction.

Both heterogeneous as well as homogeneous titanium-catalysts have been extensively studied for their use in liquid phase catalytic epoxidation reactions.

Table 1.1: Advantages and Disadvantages of Homogeneous and Heterogeneous Catalysis.

Catalysis	Advantages	Disadvantages
Homogeneous	❖ High activity and selectivity at mild reaction conditions. ❖ Relatively ease of characterization of the well-defined active sites.	❖ More sensitive to be poisoned (permanent deactivation via non-competitive inhibitors). ❖ Difficult to achieve product/ catalyst separations.
Heterogeneous	❖ High rates ❖ High throughput ("spacetime yield"). ❖ High productivity of catalyst. ❖ Easy separation of product and catalyst. ❖ Thermal stability ❖ Cleaner technology (less waste)	❖ Lower effective concentration of catalyst since the reaction occurs only on the exposed active surface.

1.1.1 Homogeneous Catalyst

In a homogeneous reaction, the catalyst is in the same phase as the reactants. In the past 15 years, considerable progress has been made in the field of homogeneous catalyzed epoxidations of unfunctionalized olefins. Epoxidation is an important methodology for preparation of highly functionalized organic compounds like; optically active epoxides, which are especially important, intermediates. From many olefins, it is now possible to create in only one step optically active epoxides in nearly enantiomerically pure form. Few systems have been shown to be extremely useful in this field, and have reached the stage of synthetic applicability. The best-known homogeneous catalyst is the Sharpless catalyst [9], which is able to epoxidize allylic alcohols with enantiomeric excesses over 95 %, and yields are generally above 80 %. In this reaction, *tert*-butyl hydroperoxide (TBHP) is used as oxidizing agent and is converted into *tert*-butanol. The catalyst is a complex prepared from titanium-*is*o-propoxide and an enantiomerically pure tartaric acid ester. In general 5-10 % of the titanium-alkoxide is necessary and 10-20 % excess of the tartrate with respect to titanium-*is*o-propoxide.

Molecular sieves are required when performing this reaction catalytically. Since both enantiomers of the tartaric acid derivative are readily available, both enantiomers of the desired epoxide can be obtained with high enantiomeric excess. The catalyst employs the hydroxyl function of the allylic alcohol as a handle to accomplish the high enantioselectivity. Most functionality, except the strongly coordinating protic ones are compatible with this reaction.

Homogeneous catalysts with Ti^{IV}, Ti^{IV}/SiO_2 is very sensitive towards deactivation by strongly coordinating ligands, especially water; for this reason Ti^{IV}/SiO_2 is an ineffective catalyst for the epoxidation with aqueous hydrogen peroxide [10]. This latter problem was overcome with the discovery of TS-1 [11] (titanium silicalite), which due to its hydrophobic character, catalyzes selective epoxidations with aqueous hydrogen peroxide under very mild conditions [12-14].

For industrial purposes, manganese catalysts are preferred since manganese itself is a relatively non-toxic metal. Iron can also be considered but manganese complexes are superior so far in selective epoxidation of olefins, chiefly because they show fewer side reactions than iron complexes. A major obstacle to the commercialization of homogeneous catalysts is that they are often difficult to separate from the reaction products and the solvent.

1.1.2 Heterogeneous Catalyst

Heterogeneous catalysis is an utmost important area of research that has direct impact on the chemical industries. It involves the use of a catalyst in a different phase from reactants. A typical example involves a solid catalyst with the reactants as either liquids or gases. Most examples of heterogeneous catalysis go through the following stage whereby; one or more of the reactants are adsorbed onto the surface of the catalyst at active sites. Adsorption, the binding of molecules or particles to a surface, must be distinguished from absorption, the filling of pores in a solid. The binding to the surface is usually weak and reversible.

An active site is a part of the surface that exposes an array of sites that can chemisorbs an atom or molecule in a localized mode and aids in the reaction [15]. There is an interaction between the surface of the catalyst and the reactant molecules, which makes them more reactive. This might involve an actual reaction with the surface, or some weakening of the bonds in the attached molecules. At this stage, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid. As a result, the product molecules are desorbed.

Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface.

Silver, for example, is not a good catalyst because it doesn't form strong enough attachments with reactant molecules while metals like tungsten, adsorbs too strongly. Meanwhile, metals like platinum (Pt), nickel (Ni) and titanium (Ti) make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products cannot break away.

For heterogeneous liquid phase epoxidation catalysts, the most successful catalyst used in the industry is the Shell catalyst [16] (titanium on silica) and Titanium Silicalite 1 (abbreviated as TS-1) [11].

Table 1.2: Characteristic features of Shell's epoxidation catalyst compared with Titanium Silicalite 1.

Parameter	**Shell Catalyst**	**TS-1**
Structure	Amorphous, silica based	Crystalline microporous structure
Ti incorporation	Several Ti siloxy sites; from monopodal to tetrapodal	Isomorphous replacement of T-atom sites
Substrate size	No limitations with regard to substrate size	Micropores of 5.6^{O}A diameter impose severe limitations
Oxidant	Limited to organic peroxides	Aqueous hydrogen peroxide

The Shell catalyst was patented in 1971 by Shell Oil and is industrially used for the commercial epoxidation of propene with ethylbenzene hydroperoxide delivering 93-94% yield and 96% hydroperoxide selectivity. This titanium(IV) silicon dioxide catalyst is prepared by impregnating silica with $TiCl_4$ or an organo-titanium compound, followed by calcination. Removing the residual Bronsted acid Si-OH groups with an organic silylating agent results in particularly effective catalysts [17].

The catalyst has been reported to leach catalytically inactive titanium (Ti) species during the initial stages of the epoxidation reaction after which the catalyst becomes truly heterogeneous [18]. Initially the structure of the active site has been suggested to be an isolated siloxy bonded titanyl species, but later studies, which also concerned zeolitic systems, suggests that the truly active site is more like a tripodally or tetrapodally attached titanium [19] (Figure 1.2).

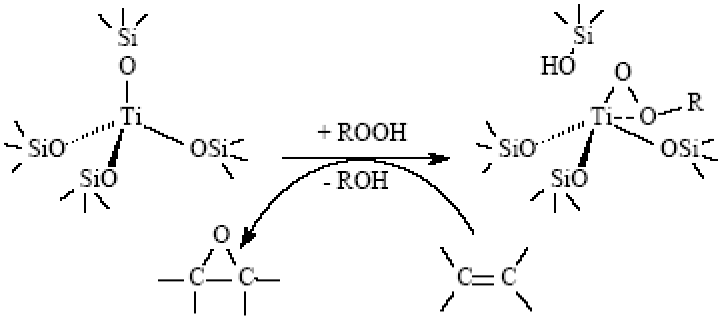


Figure 1.3: Alkene epoxidation catalyzed by a four coordinated Ti(IV) site

In the resulting search for non leaching heterogeneous liquid phase oxidation catalysts, a lot of attention is paid to the catalytic performance of the catalysts, rather than looking at the fundamental questions of which properties are responsible for the specific activity of a catalyst. In fact, a lot of catalysts consisting of a metal oxide on an inert carrier owe their catalytic activity to rapid leaching of the metal from the surface to form active homogeneous catalysts metal from the surface to form active homogeneous catalysts [20].

1.2 Industrially Used Catalysts

An important factor to consider when choosing a catalytic system is whether to choose a homogeneous or heterogeneous catalyst. The advantages for homogeneously catalyzed reactions, in which the catalyst is in the same phase as the reactants, are high activity and selectivity at mild reaction conditions. Another important factor is the relative ease of characterization of the well-defined active sites, which makes tuning of the catalysts possible.

Unfortunately, ease of recovery and thermal stability, properties that homogeneous catalysts generally lack, are considered very important by industry. This results in the overall use of heterogeneous catalysts, which do possess these handling properties, in industrial bulk processes. However, homogeneous catalysts are still used in small scale manufacturing of fine specialty chemicals, in which the costs of catalysts are relatively irrelevant.

Research interests lie in heterogeneous catalysis for use in pollution abatement, and in deriving a fundamental understanding into catalyst operation through combined studies on model and practical catalytic systems. Current projects include the development and characterization of new heterogeneous catalysts for use in liquid phase reactions, e.g. in acid catalyzed and selective oxidation reactions. Additional interests include the development of new combinatorial methodologies for parallel catalyst preparation and screening.

The general target is the development of new clean epoxidation methods, which can supply the needs for improvements in epoxide synthesis. Generally, these needs concern cleaner, more selective epoxidation methods with preferably heterogeneous recyclable catalysts, and with safe, cheap and preferably regenerable oxidants. The application of this approach to the design of new heterogeneous catalysts will improve the efficiency with which new catalyst formulations are discovered.

Epoxidation reactions are very important industrially due to the wide variety of processes that utilize epoxides as a substrate. Epoxides are useful building blocks in organic synthesis as they participate in numerous reactions. They can be reacted to provide industrially important products, such as surfactants, personal care, cosmetics, antistatic- or corrosion- protection agents, hydraulic and functional fluids, plastics, polymers, adhesives, sealants, epoxy resins, inks, additives to laundry detergents, fuel additives, lubricating oils, and textiles.

In existing industrial processes, the epoxide is produced by reacting the unsaturated compound with a peracid either preformed [21] or synthesized *in situ* [22] with an organic acid, usually acetic or formic acid, and hydrogen peroxide. Using this procedure, the yields to epoxide are relatively low as a consequence of the low hydrogen peroxide selectivities. Thus, it would be interesting to replace the processes based on peracids by a more desirable catalytic one [23-27].

Reported below are several interesting industrially used catalysts.

1.2.1 Jacobsen's Catalyst

[(R,R)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato-(2-)]manganese (III) chloride

Jacobsen's catalyst opens up short pathways to enantiomerically pure pharmacological and industrial products via the synthetically versatile epoxy function. In 1990, Professor E.N. Jacobsen reported that chiral manganese complexes had the ability to catalyze the asymmetric epoxidation of unfunctionalized alkenes, providing enantiomeric excesses that regularly reaching 90% and sometimes exceeding 98%.

1.2.2 Sharpless catalyst

Allylic alcohols can be converted in a single reaction into the corresponding epoxide with high stereoselectivity. The efficient procedure for the epoxidation of allylic alcohols was developed by Sharpless *et.al*. [28]. A variety of allylic alcohols can be epoxidized using this catalyst and the enantiomeric excesses usually exceed 90 % and yields are generally above 80%.

1.2.3 Manganese trimethyl-triazacyclononane epoxidation catalysts

The manganese trimethyl-triazacyclononane (Mn-TMTACN) systems were originally developed as bleach catalysts for stain removal by Unilever Research [29]. Besides displaying bleach activity in combination with H_2O_2, the complex was also active as epoxidation catalyst (Figure 1.4). High turnover numbers (> 400) were reported using styrene as the substrate [30].

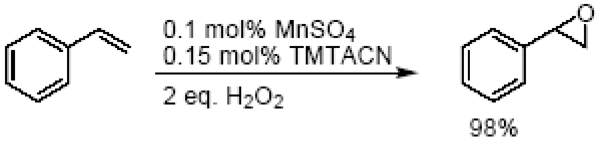


Figure 1.4 The Mn-TMTACN catalyzed epoxidation

1.2.4 Tungsten catalyzed epoxidations

The group has developed a salt free method for olefin epoxidation with H_2O_2 of Noyori (Figure 1.5) [31]. The catalyst in this case is Na_2WO_4 and only 0.2 – 2 mol% of this salt have to be used. Yields in general range from 60 to 80 % for functionalized (alcohols, ketones and esters) alkenes and above 90% for aliphatic alkenes [32].

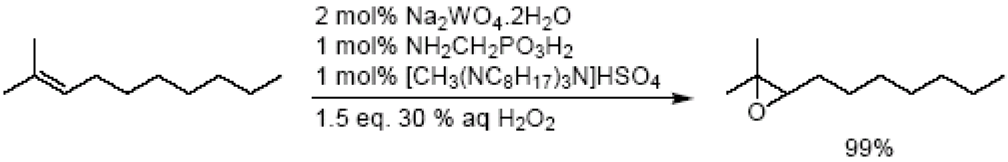


Figure 1.5 The tungsten catalyzed epoxidation

In terms of substrate used which is an aliphatic alkenes, this tungsten catalyzed epoxidation reaction possess similar concept of the epoxidation reaction of my work task in this thesis. This work of thesis is further described in topic 1.4, scope of thesis.

1.3 Commercial Review

Today the epoxy industry amounts to more than $5 billion in North America and about $15 billion worldwide. It is made up of approximately 50 - 100 manufacturers of basic or commodity epoxy resins and hardeners of which the big 3 are Resolution Polymers (formerly Shell; whose epoxy tradename is "Epon"), Dow Chemical (tradename "D.E.R."), & Huntsman Advanced Materials (formerly Ciba; tradename "Araldite"). The other 50+ smaller epoxide manufacturers primarily produce epoxides only regionally (not world-wide), produce epoxide hardeners only, produce specialty epoxides, or produce epoxide modifiers.

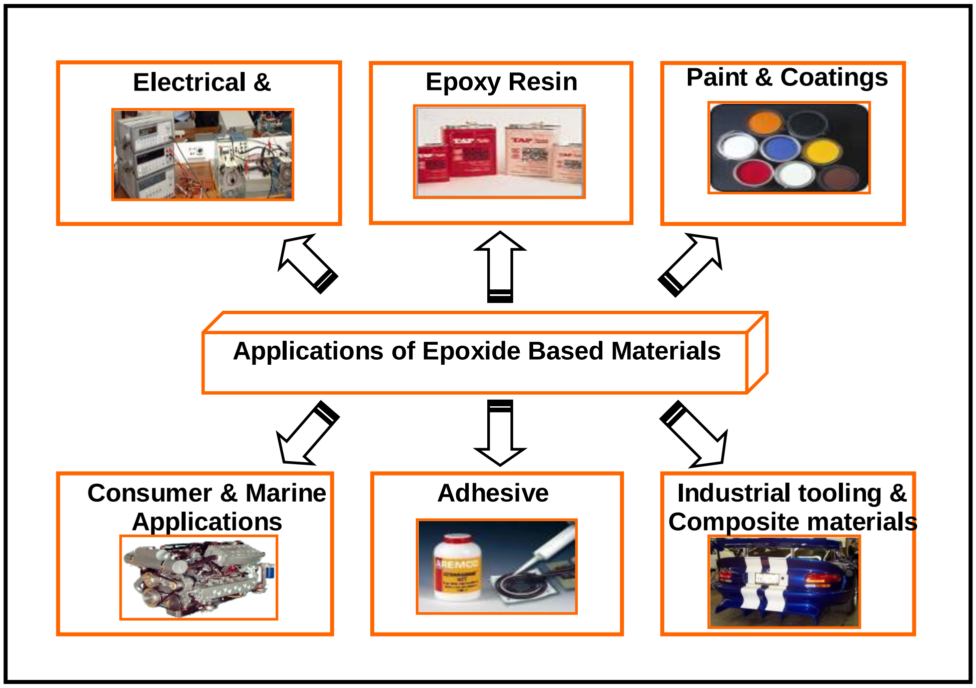
These commodity epoxide manufacturers mentioned above typically do not sell epoxy resins in a form of usable to most end users, so there is another group of companies that purchase epoxide raw materials from the major producers and then compounds (blends, modifies, or customizes) epoxy systems out of these raw materials. This class of companies is typically known as “formulators”. The vast majority of the epoxide systems sold is produced by these smaller formulators and they account for greater than 60% of the dollar value of the overall epoxide market.

There are hundred of ways that these formulators can modify epoxides - by adding mineral fillers (talc, silica, alumina), by adding flexibilizers, viscosity reducers, colorants, thickeners, accelerators, adhesion and also promoters. These modifications are made to reduce costs, to improve performance, and to improve processing convenience. As a result, a typical formulator sells dozens, hundreds, or even thousands of formulations – each carefully tailored to the requirements of a particular application or market.

The applications for epoxide based materials are extensive and include coatings, adhesives and composite materials like carbon fiber and glass-reinforced plastic (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxides and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties.

In general, epoxides are known for their excellent adhesion, chemical and heat resistance, good to excellent mechanical properties and very good electrical insulating properties, but almost any property can be modified (for example silver-filled epoxies with good electrical conductivity are widely available even though epoxides are typically electrically insulating).

Epoxides find significant use in many applications including the following:



1.3.1 Paints & Coatings

Today, paints/coatings are used almost everywhere in daily life; such as on buildings, furniture, cabinets, refrigerators, wires of electrical motors, cassettes and videotapes, compact discs, inside and outside of cans, ships, aircrafts, steel bridges, storage tanks and also cars. They are used for decoration purposes as well as for protecting surfaces against various environmental effects like UV-radiation, chemical invasion and mechanical stresses.

Other examples include powder coatings for washers, driers and other "white goods". Epoxy coatings are widely used as primers to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Metal cans and containers are often coated with epoxy coatings to prevent rusting especially for foods like tomatoes that are acidic.

Epoxy resins are also used for high performance & decorative flooring applications especially terrazzo flooring. In industrial flooring applications, self-leveling polyurethane or epoxy/ polyurethane multiplayer systems offer good chemical and mechanical properties and benefits such as minimal shrinkage, high mechanical strength and durability and favourable cost of installation. They are broadly used for wear- and crack-resistant floorings on parking decks, for concrete protection in assembly areas, as well as in large kitchens or slaughterhouses due to ease of cleaning.

1.3.2 Adhesives

Epoxy adhesives are a major part of the class of adhesives called "structural adhesives" or "engineering adhesives" (which also includes polyurethane, acrylic, and cyanoacrylate). These high performance adhesives are used in the construction of airplanes, automobiles, bikes, golf clubs, skis, snowboards, and many other applications where high strength bonds are required. Epoxy adhesives can be developed that meet almost any application.

They are exceptional adhesives for wood, metal, glass, stone, and some plastics. They can be made flexible or rigid, transparent or opaque/colored, fast setting or extremely slow. Epoxidized soybean oil (ESO) as a plastic additive has a relatively stable market of approximately 100,000 tons/year [33].

Epoxy adhesives are almost unmatched in heat and chemical resistance among common adhesives. In general, epoxy adhesives cured with heat will be more heat and chemical resistant then the same formulation cured at room temperature.

1.3.3 Epoxy Resins

Epoxy resins, a group of synthetic resins are referring to a family of molecules or oligomers containing more than one epoxide group (Oxirane). These products are solid or liquid with the consistency of honey and have the ability to react via the epoxy end-groups to generate three-dimensional networks providing the final material with rigidity, hardness and the inability to reflow.

The chemical chosen to react with these epoxides is referred to as the *curing agent* (or *hardener*), and it typically has active hydrogen attached to nitrogen, oxygen, or sulfur. The selection of the curing agent depends on many parameters and will determine, to a large extent, the performance of the final epoxy thermoset.

This family of thermosets is used in many applications like composites, plastics, coatings, adhesives and encapsulating materials. These materials are noted for their versatility, but their relatively high cost has limited their use. High resistances to chemicals and outstanding adhesion, durability, and toughness have made them valuable as coatings. Because of their high electrical resistance, durability at high and low temperatures, and the ease with which they can be poured or cast without forming bubbles, epoxy resin plastics are especially useful for encapsulating electrical and electronic components.

Epoxy resin adhesives can be used on metals, construction materials, and most other synthetic resins. They are strong enough to be used in place of rivets and welds in certain industrial applications. The most common epoxy resins are glycidyl ethers of alcohols or phenolics. Liquid epoxy resin is the diglycidyl ether of bisphenol A (DGEBA) and represents greater than 75% of the resin used in industrial applications.

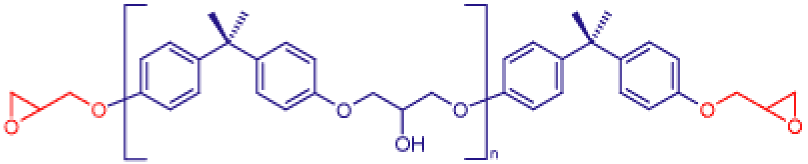


Figure 1.6: Structure of DGEBA resin

This resin has the consistency of honey. The epoxide group on the end of these molecules serves as the reactive site for cross-linking in these thermoset polymers. The chemical chosen to react with these epoxide is referred to as the curing agent, and it typically has active hydrogen attached to nitrogen, oxygen, or sulfur. Amine curing agents are the most common and can be primary or secondary, aliphatic or aromatic, or cycloaliphatic. The amines typically have greater than three reactive sites per molecule that facilitate the formation of a three-dimensional polymer network when mixed with the epoxy resin (Figure 1.7).

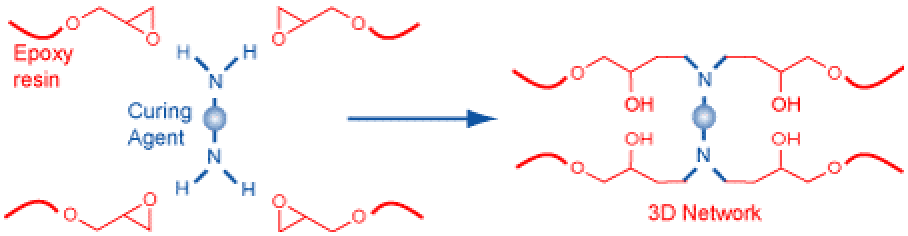


Figure 1.7: Curing mechanism of Epoxy resins

While the reaction of amines and epoxides occurs at room temperature and below, care must be taken in the selection of the curing agent to insure that a complete reaction takes place. Amines designed for room temperature applications typically employ plasticizers to insure complete reaction. Amines designed for heat-cured reactions use little or no plasticizers and typically give thermosets with higher strength and thermal performance.

The final products generally exhibit:

- Excellent electrical properties
- Good adhesion due to presence of polar groups
- Low shrinkage
- Good impact resistance
- Moisture resistance

1.3.4 Industrial tooling & Composites

Epoxy systems are also used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids.

This "plastic tooling" replaces metal, wood and other traditional materials and generally improved the efficiency and either lowers the overall cost or shortens the lead-time for many industrial processes. They can also be used to bind porous filler materials and rubber particles to produce composites for sport tracks and playing fields [34-35].

Just recently research has been started to use oleochemicals to build up matrices for natural fiber reinforced or composite parts [35]. They are more expensive than polyester resins and vinyl ester resins, but generally produce stronger more temperature resistant composite parts. The use of natural fibers, such as flax, hemp, sisal, and yucca is of increasing interest for various applications, among them the automotive industries, where the composites could be used in door pockets, covers, instrument panels, and sound insulation. Other applications could be in the manufacturing of furniture.

1.3.5 Electrical & Electronics

Epoxy resin formulations are also important in the electronics industry and are used in many parts of electrical systems. In electrical power generation, epoxy systems encapsulate or coat motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulation materials and they protect electrical components from short-circuiting and from dust, humidity and other environmental factors that could damage the electrical equipment.

In the electronics industry, epoxy resins are the primary resin used in making printed circuit boards. The largest volume type of circuit board - an "FR4 board" - is nothing but a sandwich of several layers of glass cloth bonded together into a composite by an epoxy resin. Epoxy resins are also used in the production of circuit traces on the circuit boards and are a major component of the green solder mask used on many circuit boards. Other miscellaneous electronic applications exist in the production and assembly of electronic components.

1.3.6 Consumer & Marine Applications

Epoxides are sold in many hardware stores - typically as two component kits. They are also sold in many boat shops as repair resins for marine applications. Epoxides typically are not the outer layer of a boat because they are negatively affected by long-term exposure to UV light. But they are often used during boat repair and assembly and then are over coated with polyester gel coats or marine varnishes that protect the epoxides from UV exposure. Epoxides are fairly easy to distinguish from polyester thermosets, as commercially marketed epoxy materials typically use 1:1 ratio of resin to hardener, or similar convenient mix ratio, while polyester thermoset materials typically use a ratio of at least 10:1 between resin to hardener (or "catalyst"). Also, epoxy materials tend to harden somewhat more gradually, while polyester materials tend to harden more abruptly.

1.3.7 Lubricants

Fatty acids esters are getting closer attention as synthetic lubricants. Among the unique but desirable characteristics of synthetic lubricants are good lubricities, minimum viscosity change with temperature, low temperature fluidity, high thermal and oxidation stability, low volatility, excellent additive response and high fire and flash points. Simple monobasic acid esters such as methyl stearate, oleate, butyl oleate, butyl stearate and hexyl laurate are used in lithium-base grease, mould releasing agents, rolling oils and cutting oils. Monobasic acid esters of branched polyols such as neopenthyl alcohol and neopenthyl glycol are also important lubricants since the absence of hydrogen atoms on the highly branched carbon atom of the alcohol portion of the molecule provides high thermal and oxidative stability.

1.3.8 Companies Specialized on Formulation

There are a lot of companies that are specialized on to formulate products based on epoxy resins and its hardeners. One of them is Polipox that is based on Brazil. They have formulated products to be applied in flooring, paints, adhesives, and electronics.

1.4 Objective of Thesis

The objectives of this research include:

- To study the synthesis and characterization of Ti-MCM-41 catalyst system towards 1-octene and methyl oleate epoxidation reaction.
- To optimize reaction parameters for optimum epoxide yield.

- To study the effect of silylation towards epoxidation of 1-octene and methyl oleate.

1.5 Scope of Thesis

The goal of research in this thesis is to obtain a more profound understanding of the catalyst characterization, catalytic activities and reaction mechanisms in the selective epoxidation of 1-octene as model compound and C-18 unsaturated fatty acid methyl esters, methyl oleate, (MO) as the actual feedstock, using titanium-based catalysts, Ti-MCM-41. Very stable organic peroxide, *tert*-butylhydroperoxide (TBHP) is used as an oxidant. In the first stage of this study, 1-hexene is used as the model compound. However, after a series of reactions, the molar balance discovered to be very low, 75%. This proved that 1-hexene is inefficient feedstock for epoxidation reaction; probably due to its volatile characteristic and possess low boiling point, around 60 ^{o}C. Hence, 1-octene is chosen to be the next model compound and it's found to be better, whereby the molar balance has improved to 90% and above.

The choice of oxidant in this reaction studies are based on the fact that TBHP contains much lesser amount of water (± 8%) compared to hydrogen peroxide (± 70%). The hydrophilic nature of titanium-on-silica prohibits the use of oxidant with high content of water.

Nevertheless, even when only organic reactants are used, the needs for hydrophobic Ti-MCM-41 are of interest, as to achieve highly active and selective epoxidation catalyst. In this case, a large number of silanol groups in Ti-MCM-41 have to be reduced by reaction with organosilanes or known as silylation technique.

Process based on utilizing non-silylated Ti-MCM-41 as well as silylated Ti-MCM-41 is done for all Si/Ti ratios of prepared catalyst on the model compound, 1-octene in order to select the most promising catalysts for reactions with methyl oleate.

Process optimizations are done for each catalyst on 1-octene epoxidation reaction by looking into several parameters. Firstly is the effect of Si/Ti ratio, followed by the temperature, molar ratio, and time. The latter section involves reaction with actual feedstock, mo, using the selected catalyst and optimized conditions, since MO is very expensive. Characterizations of catalysts developed in this work are done to understand the structural, thermal and chemical properties and its correlation with catalytic activities of Ti-MCM-41 group catalysts. Summary on each chapter are discussed below.

In the introduction of this thesis, a general overview on catalytic epoxidation is presented. Topics on factors to consider when choosing a catalytic system, whether to choose for homogeneous or heterogeneous catalysts are revealed. This introduction chapter also includes the industrially used catalysts in epoxidation reactions. The final part of the introduction discloses some industrial uses of vegetable oils and fatty esters/ derivatives.

Chapter 2 contains literature review and background of research done on Ti-MCM-41. Already available epoxidation technologies are compared and a new catalytic system is proposed. Special emphasis is placed on correlating the catalytic activity with intrinsic properties of the catalysts. Due to instability of Ti-MCM-41 during epoxidation and the problems encounter with the use of 1-hexene as mentioned earlier, elaboration on this matter is necessary towards the change of feedstock. The focus of this chapter is on epoxidation of vegetable oils, particularly palm-base (MO).

Chapter 3 discloses the preparation, characterization and properties of Ti-MCM-41 in details. Methodology of catalyst synthesis including materials and reagents are revealed. The reaction procedure and set-up as well as labeled picture are described.

Chapter 4 contains the results and discussion for the epoxidation of model compound (1-octene) and MO based on utilizing silylated and non-silylated Ti-MCM-41. Effects of different reaction conditions and catalysts ratio on product distribution and substrate conversion are analyzed. One of the aims is to optimize products yields under as mild as possible reactions conditions. The final part of this chapter will show the influence of degree of silylation on the olefin's conversion and products yield.

Finally, chapter 5 summarizes the best reaction conditions for MO and the best Ti-MCM-41 sample, which exhibits high catalytic activity as well as high selectivity to the desired epoxide. When comparing silylated and non-silylated samples, it's found that silylated samples show higher catalyst activity, and the conversion and TON increased three times as compared to non-silylated samples.