



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Epoxides

Epoxides (also known as oxirane and oxacyclopropane) are compounds containing three membered cyclic ethers consisting of an oxygen atom connected to two adjacent carbon atoms. They can be described as analogs to cyclopropane with a methyl group (-CH₂) being replaced by an oxygen atom as shown in Figure 2.1. Three membered rings are known for their unstable geometry due to its large bond angle strain. The carbons in the structure are tetravalent, normally forming four bonds to other atoms. Usually, each bond would have a stable angle of 109.5 degrees. In order to form a three membered ring, the structure would have the geometry of an equilateral triangle with a bond angle of 60 degrees. The bond angle formed is almost half the stable angle, causing the large amount of bond angle strain. This means that epoxides are very reactive since they are eager to open the ring and use oxygen as the leaving group to release the strain in the bond. Epoxides are known to be much more reactive than the typical acyclic ethers.

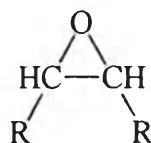


Figure 2.1 The epoxide unit structure.

The nomenclature of epoxides can be done two ways. The first way is by relating the epoxide to its synthesizing source, as the oxide of the alkene. Imagine re-placing the oxygen atom by a double bond, the root name would be the corresponding alkene. Then the name is followed by the suffix “oxide”. The second way is by IUPAC nomenclature, indicating the epoxide as the substituent. The longest chain containing the carbons in the epoxide group is chosen as the root name

and numbered in a way that the carbons in the epoxide unit has the smallest number possible. The name is started with the number of the epoxide unit carbon followed by the prefix “epoxy” and the root name. An example of the nomenclature is shown below in Figure 2.2.

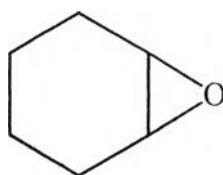


Figure 2.2 The structure of cyclohexene oxide (also known as 1, 2-cyclohexane).

Epoxides are used in a variety of applications due to its exceptional reactivity. Polymerization of epoxides produce epoxy resins (epoxies). They are well known due to their mechanical and electrical properties, structural stability, temperature resistance, chemical resistance, and adhesion to other materials. The largest application of epoxies is surface coating for industrial equipment, electrical equipment, automobile equipment, adhesives, etc. The most popular epoxy resin used is the diglycidyl ethers of bisphenol A.

The objective of this research thesis is to efficiently produce cyclohexene oxide. Therefore, the focus is aimed to the synthesis of epoxides.

2.1.1.1 Synthesis of Epoxides

The synthesis of epoxides is known as epoxidation. There are four types of epoxidation: olefin peroxidation, intramolecular S_N2 Substitution, nucleophilic epoxidation and asymmetric epoxidation.

The majority of epoxides are created by olefin peroxidation. It is basically the preparation of epoxides from oxidation of alkenes by peroxides (peracids) shown in Figure 2.3.

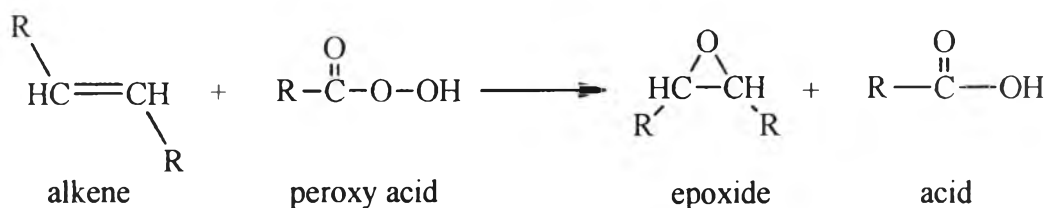


Figure 2.3 Olefin peroxidation (epoxidation) reaction model.

Alkenes (R-C=C-R) are unsaturated hydrocarbons with at least one carbon-carbon double bond in the structure. Peracids (R-COOOH) are acids with an additional oxygen atom in the alcohol functional group. Peracids are powerful oxidizing agents generally having electrophilic properties. Common peracids used are hydrogen peroxide (H₂O₂), peroxydiphosphoric acid (H₄P₂O₈) and peroxydisulfuric acid (H₂S₂O₈). The energy between the oxygen-oxygen bond of the peracid unit is very weak (~35 kcal/mole) with a negative polarity while the hydroxyl group has a positive polarity.

The olefin peroxidation reaction has a one-step mechanism, with everything happening spontaneously. However, for a detailed explanation, the step will be divided into five main parts as shown in Figure 2.4.

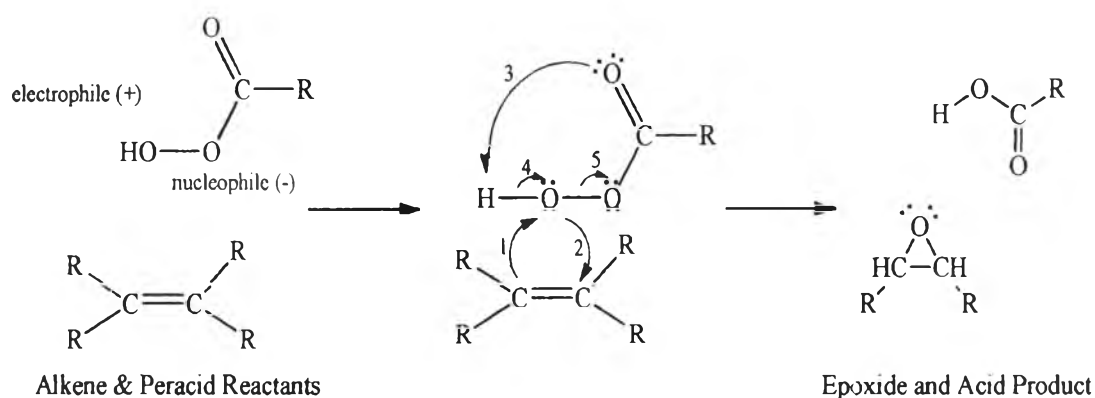


Figure 2.4 Olefin peroxidation mechanism.

First, a carbon from the alkene double bond attacks the oxygen atom in the hydroxyl group of the peracid. Secondly, the same oxygen atom

attacks the other carbon of the alkene double bond. Thirdly, the oxygen atom from the peracid's double bond uses its pi-bond to take the hydrogen away from the hydroxyl group leaving an electron. Fourthly, the electron that is left forms a new lone pair with the oxygen. Lastly, the sigma bonds move the electron to the next oxygen atom in the peracid. The resulting product of the reaction is an epoxide and an acid. It should also be noted that the alkene is trigonal planar. This means that the peracid can attack the alkene from both sides and may produce two different products.

A very common application of olefin peroxidation is the reaction between propylene and either t-butyl hydroperoxide or ethylbenzene hydroperoxide for the production of propylene oxide. Another well-known reaction is the Prilezhaev reaction, shown in Figure 2.5 below.

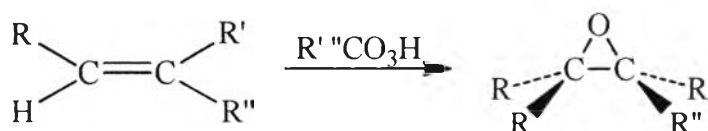


Figure 2.5 Prilezhaev reaction.

The intramolecular S_N2 substitution, another type of epoxidation, uses halohydrins to synthesize epoxides. More than half of the propylene oxide is produced by this method. The mechanism is shown in Figure 2.6.

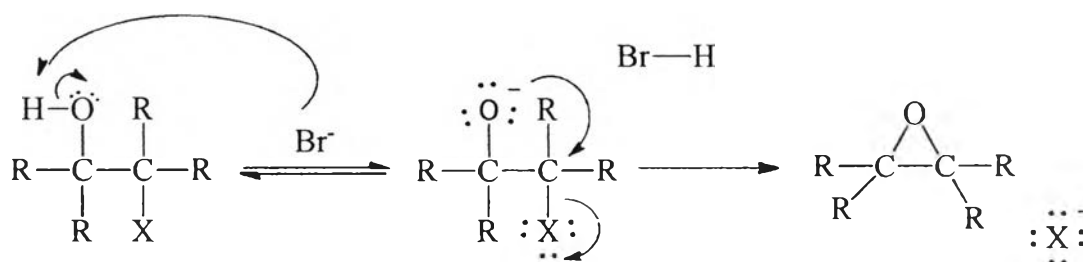


Figure 2.6 Mechanism of halohydrin to epoxide (intramolecular S_N2 substitution).

The first reaction is an acid/base reaction. The base, in this case Br^- , deprotonates the alcohol to form an alkoxide with high nucleophilicity. Then, the alkoxide displaces the halogen (X) within the same molecule by attacking the electrophilic carbon. The precursor compound in the reaction is called a halohydrin.

An application example of this reaction can be found in the Johnson-Corey-Chaykovsky reaction shown in Figure 2.7. The reaction takes place between the sulfur ylides with ketones and aldehydes to form epoxides. The leaving group is the sulfonium instead of the halogen.

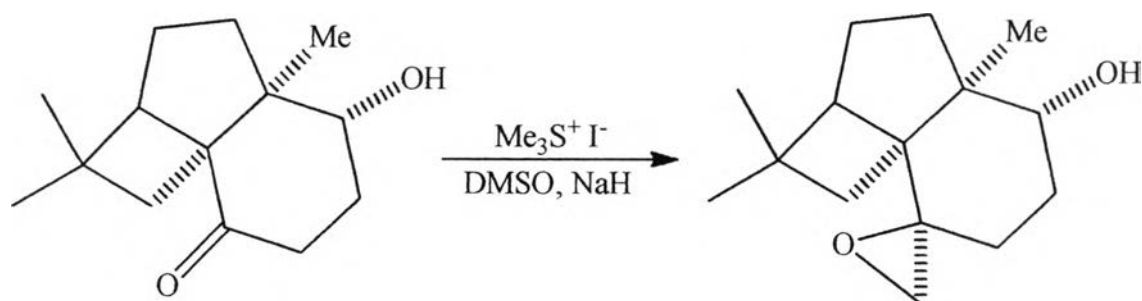


Figure 2.7 An example of the Johnson-Corey-Chaykovsky reaction.

Nucleophilic epoxidation is the epoxidation of electron-deficient alkenes by nucleophilic oxidants. The oxidant act as nucleophiles and the alkene is the electrophile. Electron-deficient alkenes are alkenes which are conjugated with electron withdrawing groups. An example of this reaction is shown in Figure 2.8 where 2-cyclohexen-1-ol reacts with hydrogen peroxide under basic conditions to produce 2,3-epoxycyclohexanone.

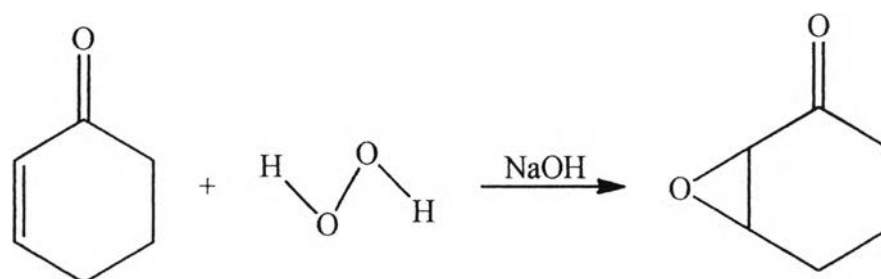


Figure 2.8 Epoxidation of 2-cyclohexen-1-ol to 2,3-epoxycyclohexanone.

The mechanism of this reaction consists of a two-step reaction. The first step is the formation of the peroxide ion from the nucleophilic conjugate addition by the oxygen. Then, the carbanion attacks back the oxygen forming a ring.

Sometimes, depending on the geometry of the reactant and the reaction mechanism, the epoxide produced may have stereogenic geometry. Most of the time, the reaction goes through a two-step mechanism which can produce stereoisomers (*cis-trans*). This is called asymmetric epoxidation. An example of the epoxidation producing a stereoisomer is shown in Figure 2.9, an epoxidation of *cis*-alkene to produce *cis*-epoxide and *trans*-epoxide.

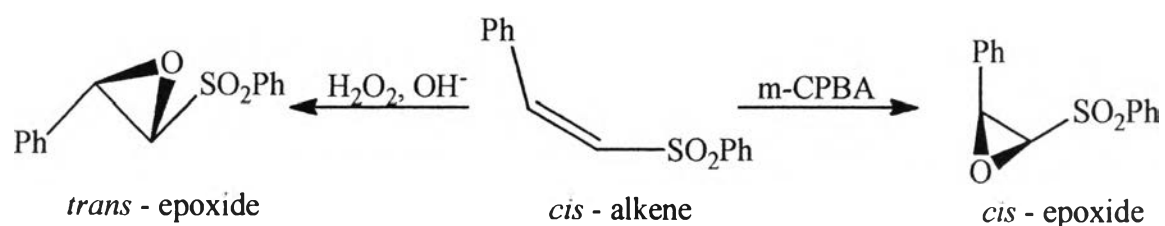


Figure 2.9 Epoxidation of *cis*-alkene to produce *cis*-epoxide and *trans*-epoxide.

A well-known example of the asymmetric epoxidation is the Sharpless epoxidation (Figure 2.10), the Jacobsen epoxidation (Figure 2.11) and the Shi epoxidation (Figure 2.12).

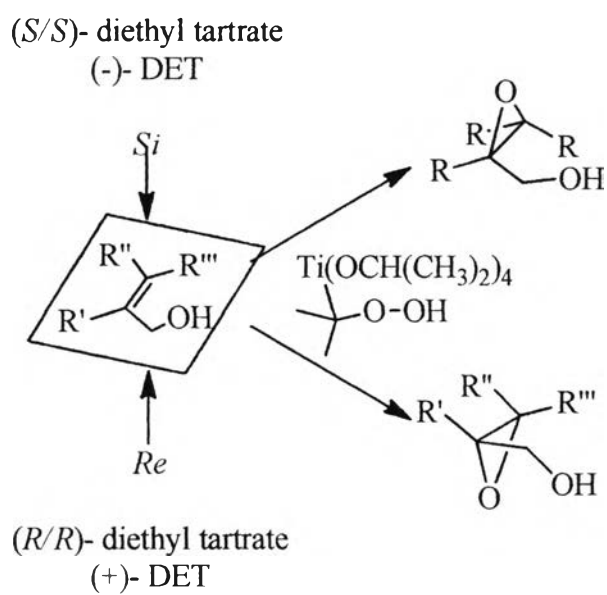


Figure 2.10 Sharpless epoxidation.

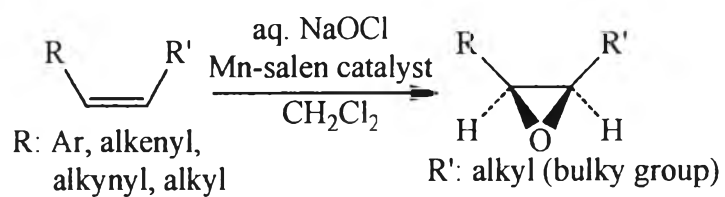


Figure 2.11 Jacobsen epoxidation.

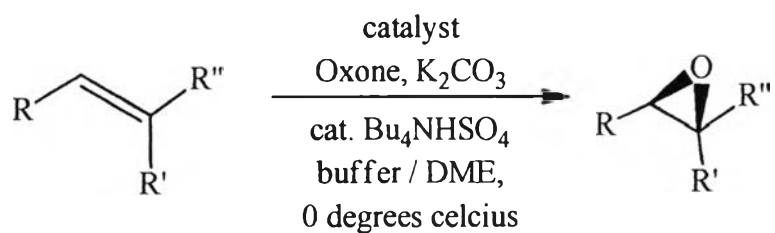


Figure 2.12 Shi epoxidation.

2.1.1.2 Oxidants for Epoxidation

The oxidant is the source of the oxygen atom which will be incorporated into the alkene to produce the epoxide. The most straightforward method is simply using molecular oxygen, not only are they abundant in nature, they are also cheap. However, the usage of the diatomic oxygen comes with many drawbacks. One of the first challenges is its effortless uncontrollable auto-oxidation. Not to mention the oxygen atom's asymmetry once its pair atom is used in the reaction. The majority of catalytic reactions use active oxygen in some form. The active oxygen is either activated directly or indirectly.

This dissertation will be using hydrogen peroxide (H_2O_2) which owes its attractiveness to water, the only by-product produced. Therefore, it is known to be an environmentally friendly oxidant. Hydrogen peroxide is also easy to handle and has a high content of active oxygen.

2.1.2 Sol-gel Process

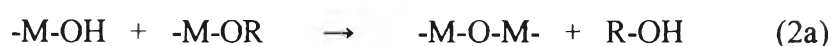
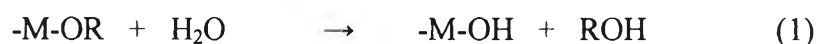
The sol-gel process was first discovered centuries ago during the 1800s, known as the chemical solution decomposition. However, the process has gained much attention during the past decades due to its ease of processing and control. The process stands out due to its high purity, preparation at low temperatures, addition of multicomponents in a single step, production of various physical forms, ability to change physical characteristics and molecular level control of compositional homogeneity.

The process mainly involves the production of an inorganic network through the formation of a sol followed by a gel. A sol is a colloidal suspension of solid nanoparticles (precursor) in a liquid (solvent). The liquid is therefore the continuous phase while the solid particles are in the dispersed phase. The solid nanoparticles condensate and forms a three dimensional network within the liquid called a gel. The transition from a sol to a gel is called gelation. A gel is produced when the continuous phase is the solid network while the dispersed phase is the liquid. The liquid is basically encapsulated by the solid network. Removal of the liquid can be done by either evaporative drying or supercritical drying to obtain the solid catalyst structure known as a xerogel and aerogel, respectively. The whole sol-

gel process can be explained in further detail having 5 key steps: formation of sol, sol-gel transition, gel aging, removal of solvent and heat treatment.

The principle of producing a sol is to have solid nanoparticles (1~1000nm) suspended in a liquid. The solid nanoparticle is known as the precursor. The precursor generally used is metal alkoxides due to its purity and availability. The liquid is normally a solvent appropriately chosen to match the precursor. Since the solid nanoparticles are very small and light, they tend to defy the rules of gravity and interact by weaker forces such as van der Waals, columbic and steric forces. The negligence of gravitational force allows the solid particles to be suspended and dispersed.

Under appropriate conditions, the sol-gel transition occurs when the suspended solid nanoparticles agglomerate and form a network within the liquid. Gelation is usually automated but for some reactions, an additive is added playing the role of a 'glue' to help agglomerate the solid nanoparticles. The viscosity of the solution approaches infinity as the gel is formed. The gelation process can be simplified to undergo two main types of reaction, hydrolysis (reaction 1) and ploycondensation (reaction 2a and 2b):



Where M = Ti, Ce, Ru and R = alkyl group. The first reaction is hydrolysis with the addition of water. The alkoxide group (OR) is replaced by the hydroxyl group (OH). Subsequently, ploycondensation occurs where the metal replaces the hydrogen in the hydroxyl group forming a continuous three dimensional structure with the template of -M-O-M- with water and alcohol as byproducts. Factors affecting the rate and formation of the gel include type of precursor, type of solvent, pH, water content, precursor concentration and temperature.

Once the gel is formed, aging occurs. During this stage, the gel undergoes many changes and transformation including further condensation. Aging promotes and more static and firm cross-linked network structure. However, too

much aging may cause the gel to undergo syneresis, where the solvent is completely extracted from the gel. Many parameters affect aging which include time, temperature, pH and aging environment.

The next step is drying in order to remove the solvent from the gel. Once the solvent is removed, the solid network is left with small pores of various sizes causing differential pressure. The pressure may cause the pores to collapse. The decrease of pores is undesirable as it also decreases the surface area for the reaction to occur. To resolve the issue, studies have been done to lower both the differential and capillary pressure. A narrow pore size distribution, addition of solvent with low surface tension and elimination of the liquid-vapor interface by supercritical drying can lower the capillary pressure. The factors that should be taken into consideration in this step are drying method, temperature, heating rate, pressure, pressurized rate, and time.

The last step in the process is the heat treatment called calcination. The high heating temperature may change both physical and chemical properties of the solid catalyst. The catalyst is likely to crystallize into various structural forms. The calcination of the xerogel/aerogel is aimed to remove any residual organics and oxidize/reduce the surface of the catalyst. Factors affecting this step include temperature, heating rate, time, and gaseous environment.

2.1.3 Catalyst Reactive Components

This research will be studying the $\text{CeO}_2\text{-RuO}_2\text{-TiO}_2$ catalyst.

2.1.3.1 *Titanium Dioxide (TiO_2)*

The reducible metal oxide is one of the most important supports, which provide a strong metal-support interaction (SMSI), particularly TiO_2 support. It has been known that TiO_2 exhibits a strong metal-support interaction effect with group VIII noble metals.

TiO_2 is an n-type semiconductor and a typical photocatalyst, attracting much attention from both fundamental and practical viewpoints. It has been used in many industrial areas, including environmental purification, solar cells, gas sensors, pigments, and cosmetics. To explore novel approaches for the nanostructured TiO_2 , the control of the particle size in nanometer-scale and the

morphology is quite interesting, since the performance of TiO_2 in various applications depends on its crystalline phase state, dimensions, and morphology.

TiO_2 is a lustrous silver-white metal that occurs naturally in three crystalline polymorphs: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The last one is, however, not common. Rutile is the thermally stable form at all temperatures, but conversion of anatase to rutile is so slow that it may be unimportant in most catalytic reactions. Anatase typically has a higher surface area than rutile. TiO_2 with surface areas in the range of about $10 \text{ m}^2/\text{g}$ to $50 \text{ m}^2/\text{g}$ (Degussa P-25) is commercially available. Typically, fumed TiO_2 consists of mixture of anatase and rutile, with the ratio varying somewhat with the manufacturing process. Degussa P-25 is reported to contain about 85 to 90 % anatase and 10 to 15 % rutile (Satterfield *et al.*, 1991).

For nanocrystalline mesoporous TiO_2 , it generally possesses high catalytic efficiency because of its unique properties conferred by very small physical dimensions. The large specific surface area and high volume fraction of atoms located both on the surface and at the grain boundaries result in an increased surface energy. Then, the surface of nanocrystalline mesoporous TiO_2 provides an active substrate for catalysis. In addition, the reactants are operated across the porous system in several catalytic applications. Sufficiently uniform pore size between 2 and 50 nm in the mesoporous region is more suitable if loading of cocatalysts/dopants is required as not to become easily blocked as in the case of microporous materials (pore size $< 2 \text{ nm}$). Therefore, the surface of nanocrystalline TiO_2 particles with a mesoporous structural network will be more promising because catalytic activity can be further enhanced due to the enlarged surface area for facilitating better reactant accessibility to the catalyst surfaces and subsequent surface reactions (Sreethawong *et al.*, 2006).

2.1.3.2 Cerium (IV) Oxide (CeO_2)

CeO_2 is an oxide of the rare earth metal cerium. CeO_2 can be formed by calcining cerium (IV) diammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. CeO_2 is the most stable phase at room temperature and under atmospheric conditions. CeO_2 is generally used in ceramics, to sensitize photosensitive glass, as a catalyst and a catalyst support, and to polish glass and stones. It is also used in the walls of self-

cleaning ovens as a hydrocarbon catalyst during the high-temperature cleaning process. While it is transparent for visible light, it absorbs ultraviolet radiation strongly. So, it is a prospective replacement of ZnO and TiO₂ in sunscreens.

CeO₂ has been used in catalytic converters in automotive applications. Since CeO₂ can become non-stoichiometric in oxygen content depending on its ambient partial pressure of oxygen, it can release or take in oxygen in the exhaust stream of a combustion engine. In association with other catalysts, CeO₂ can effectively reduce NO_x emissions, as well as convert harmful carbon monoxide to the less harmful carbon dioxide. CeO₂ is particularly interesting for catalytic conversion economically because it has been shown that adding comparatively inexpensive CeO₂ can allow for substantial reductions in the amount of platinum needed for complete oxidation of NO_x and other harmful products of incomplete combustion. Due to its fluorite structure, the oxygen atoms in a CeO₂ crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies. As the number of vacancies increases, the ease at which oxygen can move around in the crystal increases, allowing the CeO₂ to reduce and oxidize molecules or co-catalysts on its surface. It has been shown that the catalytic activity of CeO₂ is directly related to the number of oxygen vacancies in the crystal, frequently measured by using XPS to compare the ratios of Ce³⁺ to Ce⁴⁺ in the crystal (Deshpande *et al.*, 2005). CeO₂ can also be used as a co-catalyst in a number of reactions, including the water-gas shift and steam reforming of ethanol or diesel fuel into hydrogen gas and carbon dioxide, the Fischer-Tropsch reaction, and selected oxidation (particularly with lanthanum). In each case, it has been shown that increasing the CeO₂ oxygen defect concentration will result in increased catalytic activity, making it very interesting as a nanocrystalline co-catalyst due to the heightened number of oxygen defects as crystallite size decreases. At very small sizes, as many as 10 % of the oxygen sites in the fluorite structure crystallites will be vacancies, resulting in exceptionally high diffusion rates.

2.1.3.3 Ruthenium Oxide (RuO₂)

There has continually been application of RuO₂ incorporated in the catalysis field for various reactions. The most dominant use is being loaded on various kinds of support, such as RuO₂/TiO₂ (Sreethawong *et al.*, 2006),

RuO₂/zeolite Y for water splitting reaction (Qin and Aika *et al.*, 1997), and RuO₂/CeO₂ for wet oxidation of acetic acid (Hosokawa *et al.*, 2003). However, only Ru in many complex forms has been extensively used for numerous epoxidation reactions, such as epoxidation of propene, octene, cyclohexene, cyclooctene, styrene, etc. (Cetinkaya *et al.*, 1998). Therefore, it is a good probability to extend the application of supported RuO₂ in catalytic cyclohexene epoxidation.

2.2 Literature Review

The chemical industry has always been interested in the epoxidation of alkenes. Lambert *et al.* (2004) did a study on the development for the heterogeneous epoxidation of alkenes, mainly ethane and propane. The first epoxidations of alkenes was catalyzed by silver (Au) catalysts. The silver active sites were the oxygen adatoms at the surface. The minimum condition for epoxidation to occur was the π -adsorbed alkene and the adatom. Additions of halogens were added to promote the reaction. When an alkali was present with nitrous gases, there was high enhancement of the selectivity due to the mechanism pathway. Copper (Cu) is expected to be a better catalyst due to its selectivity compares to silver.

Nam, Kim *et al.* (2001) studied the epoxidation of cyclohexene catalyzed by the electron-deficient iron porphyrins and m-CPBA compared with the oxoiron (IV) porphyrin cation containing and electron-rich porphyrin ligand. The electron-deficient iron porphyrins and m-CPBA prefers epoxidation over allylic oxidation and the oxoiron (IV) porphyrin cation containing and electron-rich porphyrin ligand produces both epoxides and allylic alcohol.

Farias *et al.* (2003) synthesized mixed oxide catalysts, including the SiO₂-TiO₂ catalyst, by the sol-gel method. The catalyst showed amorphous structure after calcination at 600°C. The titanium containing catalyst gave the best activity and selectivity when tested in the cyclooctane epoxidation with *tert*-butyl hydrogen peroxide as the oxidant. The highest yield achieved was 45 %.

Epoxidation of cyclohexene using cumyl peroxide as the oxidant was studied with the TiSBA catalyst by Bonardet *et al.*(2004). The TiSBA catalyst is titania incorporated into mesoporous silica structures. The catalyst synthesis was

successful with satisfactory conversion to epoxides. The Ti-OH group is believed to be the active site of the reaction.

Optimization of hydrogen peroxide as the oxidant in cyclohexene epoxidation by silica-supported catalysts has been studied by Fraile *et al.* (2003). It was concluded that slow addition of hydrogen peroxide greatly enhanced the yield and selectivity of the reaction due to the oxygen produced in the decomposition of hydrogen peroxide. Silica-supported titanium showed low yield and selectivity due to its hydrophilic surface.

Silica-based catalysts were put on hold due to its hydrophilic surface decreasing the efficiency of the catalyst. Rhee *et al.* (2000) synthesized titanium containing activated carbon and silica-carbon composite catalyst hoping to gain better epoxide selectivity. The catalysts were tested by the liquid phase epoxidation of cyclohexene with tertbutylhydroperoxide (TBHP) and hydrogen peroxide (H_2O_2). The titanium was successfully loaded on the carbon-silica composite and gave a higher yield of epoxide compared to the silica based catalyst for both oxidants, especially for the 3 wt. % Ti. The higher yield is explained by the hydrophobic environment from the carbon surface. It was also shown that using tertbutylhydroperoxide as the oxidant gave a higher epoxide yield and selectivity. Ti-containing mesoporous catalysts have been gaining a lot of attention due to their exceptional properties, especially mixed oxides with silica. However, they are mostly amorphous and have high defect on the silano group, creating a hydrophilic surface. The problem arises in oxidative reactions, especially those using hydrogen peroxide (H_2O_2). The surface silinols strongly attract water molecules from the hydrogen peroxide blocking the pathway for organic compounds to reach the active site.

Addition of pore-directing amines in the sol-gel process has proven to effectively increase the porosity of the catalysts. A.R. Oki *et al.* (2007) studied the effect of various amine lengths used in the sol-gel synthesis of mesoporous TiO_2 - SiO_2 mixed oxides. The main comparisons done were between Hexylamine (HXA), Dodecylamine (DCA) and Octadecylamine (ODA). The porous structure parameters achieved from the research is shown in Table 1. It is observable that the dodecylamine gave the highest surface area, pore volume and pore size.

Table 2.1 Porous structure parameters of TiO₂-SiO₂ templated by various amines

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
TiO ₂ -SiO ₂	476	0.256	2.5
TiO ₂ -SiO ₂ -HXA-1	664	0.442	2.5
TiO ₂ -SiO ₂ -DDA-1	704	1.008	6.4
TiO ₂ -SiO ₂ -ODA-1	694	0.848	2.7-11.0

The solvent's role in the reaction is to promote a single phase between the reactants and the products. M.D. Romero *et al.* (2008) investigated the effects of solvents used in the epoxidation of cyclohexene with hydrogen peroxide as the oxidizing agent. The solvents were divided into three groups; protic molecules, polar aprotic solvents and nonpolar aprotic solvents. It was concluded that the solvent shouldn't be strongly polar nor strongly nonpolar. The best results indicated the alcohol (methanol in the study), to be the best choice as it had medium values of dielectric constant and dipole moment. Methanol exhibits high toxicity leading the author to recommend the use of alcohol replacement.

Sreethawong *et al.* (2005) investigated the catalysis of cyclohexane with tert-butanol as the solvent and hydrogen peroxide as the oxidant. The mesoporous TiO₂-based catalyst, synthesized by sol-gel method, was used in the reaction. The experiments were done in comparison with the commercial non-mesoporous TiO₂ catalysts. The synthesized TiO₂ catalyst exhibited higher conversion and selectivity towards the cyclohexene oxide. Loading of the metal oxides (Fe, Co, Ni, and Ru) on the TiO₂ catalyst was done by the incipient wetness impregnation method. The 1mol% RuO₂-loaded mesoporous TiO₂ gave the best performance for cyclohexene oxide production. A proposed pathway for cyclohexene epoxidation on the TiO₂ surface and cyclohexene auto-oxidation is shown in Figure 2.13 and Figure 2.14, respectively. Sreethawong *et al.* (2006) further mesoporous TiO₂ studied the 1mol% RuO₂-loaded prepared by surfactant-assisted templating sol-gel method. The reaction parameters were optimized for cyclohexene oxide production up to 80% selectivity.

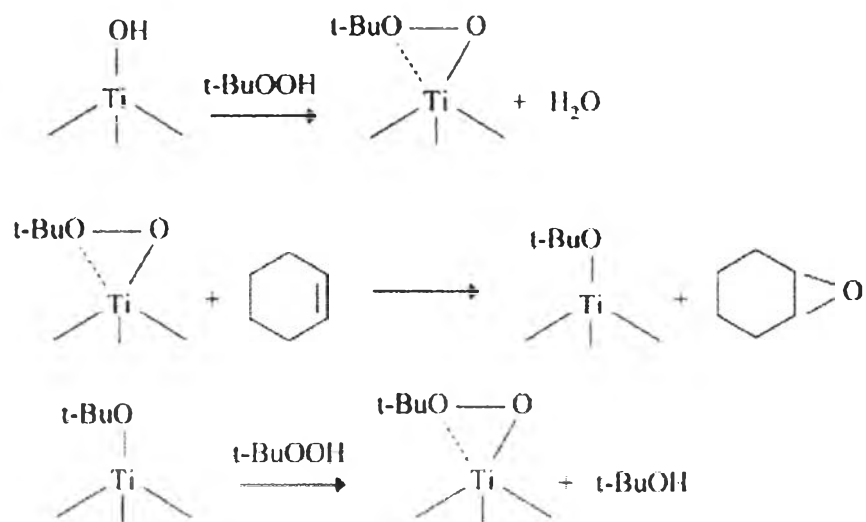


Figure 2.13 Proposed pathway for cyclohexene epoxidation on TiO_2 surface.

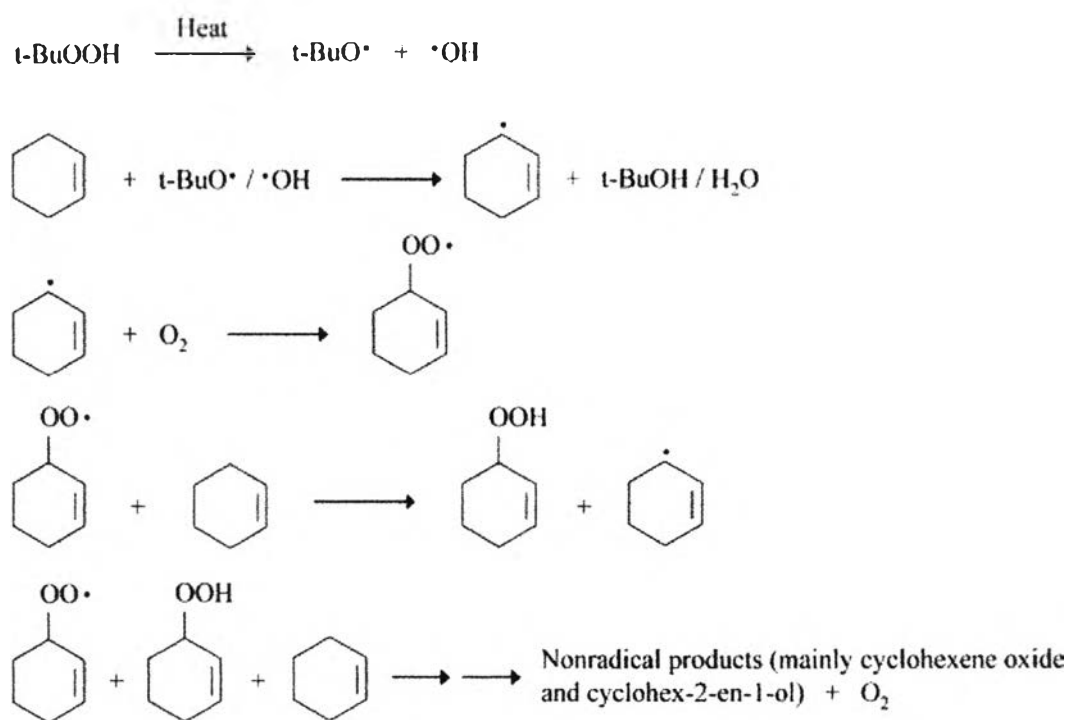


Figure 2.14 Proposed pathway for cyclohexene auto-oxidation.

Investigation of cyclohexene epoxidation with hydrogen peroxide as the oxidant was investigated by Woragamon *et al.* (2010) using RuO₂-loaded mesoporous-assembled TiO₂ catalyst. A comparison of the catalyst synthesis was done between the incipient wetness method and the single-step sol gel method. The 1 mol.% RuO₂/TiO₂ catalyst synthesized by the single-step sol-gel method and calcined at 450°C gave the best performance and recyclability due to its stability.

The transition-metal substituted α -titanium arsenate (α -TiMAs; where M = Cu(II), Co(II), Mn(II), Fe(II), Cr(II) and Ru(II)) was studied for their catalytic activity in cyclohexene epoxidation with TBHP as the oxidant by A. Khare *et al.* (2004). The addition of the Ru(III) metal ion gave the most satisfying selectivity at 89.89% and conversion of 18.41% due its enhanced ability to form a variety of high-valent oxo complexes.

A comparison between Cu, Mn, Fe, Ru and Ti on polybenzimidazole (PBI) support complexes in the oxidation of cyclohexene was researched by G.Olason (1999). The reaction was done using t-butylhydroperoxide and dioxygen as the solvent and oxidant, respectively. In terms of epoxidation, PBI.Ru gave the highest turnover frequency while PBI.Ti showed the highest epoxide conversion.

Cerium-containing catalysts has been gaining interests for their activity and selectivity in the oxydation of many organics. Ceria has unique oxygen storage capacity and redox properties. The lattice oxygen on the surface is also capable of easily shifting between Ce(III) and Ce(IV) when Ce is incorporated with other metal oxides. Some challenges of incorporating cerium ions into network structures is the difference in its atomic size.

M.N. Timofeeva *et al.* (2007) was able to incorporate ceria into the mesoporous silica network by hydrothermal method. The yeild increased as the cerium content increases until reaching its optimum content at 2% when tested by the cyclohexene epoxidation. Then, the yeild decreases owing to the lack of surface OH radicals which are believed to be the active sites in the reaction. The catalytic activity is also proven to be dependent on the quantity and agglomeration of the cerium atoms on the surface of the support.

The iron-cerium oxide catalyst was studied by A.S. Reddy *et al.* (2010). The iron is dispersed on the CeO₂ support at various amounts. The obvious improvement

in the reaction is when the iron is properly dispersed throughout the support. The active sites on the mixed oxide catalyst are believed to be the weak and strong acidic sites. In addition, the successful yield is due to the low reduction temperature and better redox properties. The author also investigated the effects of the solvent on the reaction. Tert-butanol, a nonpolar aprotic solvent, exhibited the highest conversion and selectivity for the reaction as shown in Figure 2.13. This dissertation will be using tert-butanol as the solvent as well.

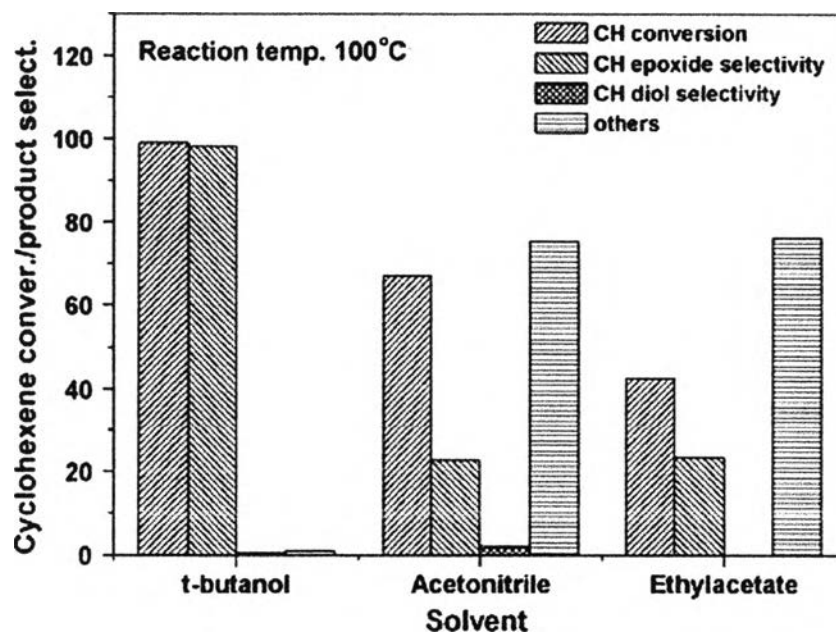


Figure 2.15 Solvent effect on cyclohexene oxidation.

Ce-incorporated mesoporous titania was synthesized by Eguchi *et al.* (2008) via the co-condensation method. The cerium surface concentration reached 69% with Ti/Ce=100 after calcination at 473 K to 673 K. the catalyst was tested in the ethanol-oxygen reaction giving acetaldehyde and acetic acid as the main products.

Rattanapunyakun *et al.* (2011) did a dissertation on the cyclohexene epoxidation with hydrogen peroxide as the oxidant catalyzed by the TiO₂-CeO₂ mixed oxide catalyst. The catalyst was synthesized by the single-step sol-gel method and calcined at 500°C. The 2% CeO₂ mixed oxide achieved the highest performance in cyclohexene oxide yield and selectivity.

Trimellitic mixed oxide was shown to provide better catalytic activity than bimetallic mixed oxide studies by M. Ghiaci *et al.* (2011) for allylic oxidation of cyclohexene. The comparison was done between Ru/Ce, Co/Ce and Ru/Co/Ce mixed oxides. The mixed oxides were prepared by reverse micelle method and precipitated by alkali-hydrolysis. The trimetallic mixed oxide provided a higher surface area and allylic oxidation activity. The author was able to achieve 97.7% cyclohexene conversion at optimum reaction conditions with a 95% selectivity by adjusting many reaction conditions. This research encourages the opportunity for using trimetallic mixed oxide with optimization of reaction conditions to favor the production of cyclohexene oxide.