CHAPTER II
LITERATURE REVIEW

2.1 Theoretical Background

2.1.1 Epoxidation Reaction

Epoxidation reactions are significant for the chemical industry in order to produce important chemical intermediates. Unlike ordinary ethers, epoxides are quite reactive. The strained three-membered ring easily reacts with a nucleophile. By the reaction with a wide variety of nucleophiles, epoxides can be transformed into useful chemicals (Sreethawong *et al.*, 2006) such as plasticizers, perfumes, epoxy resins, polymers, paints, drug intermediates, and etc. (Jinka *et al.*, 2007, Ingle *et al.*, 2007).

An oxygen atom has only six electrons in its valence shell. It might be expected to act as both an electrophile and a nucleophile in its reaction with an alkene, resulting in the formation of a three-membered ring containing an oxygen called an epoxide. The formation of epoxide is shown in Figure 2.1.
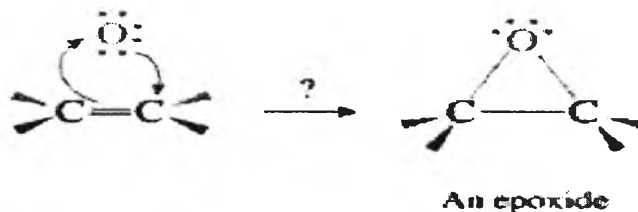

Figure 2.1 The formation of epoxide from alkene.

In the laboratory, percarboxylic acid is used as the oxidant that is able to accomplish this transformation. Namely, a percarboxylic acid has an oxygen–oxygen bond and can act as a source of electrophilic oxygen when reacting with an alkene. The product of this reaction is an epoxide. For example, the formation of ethylene oxide is shown in Figure 2.2.

Although liquid-phase epoxidation with peracids for substituted alkenes are able to accomplish and most widely used method for this reaction, using

peracids results in low reaction rate and large amounts of carboxylic acids as side products (Mandelli *et al.*, 2001).

The other potential oxidants are hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (TBHP), which gives a clean and friendly environment reaction (Khare and Shrivastava, 2004).

A percarboxylic acid   A carboxylic acid
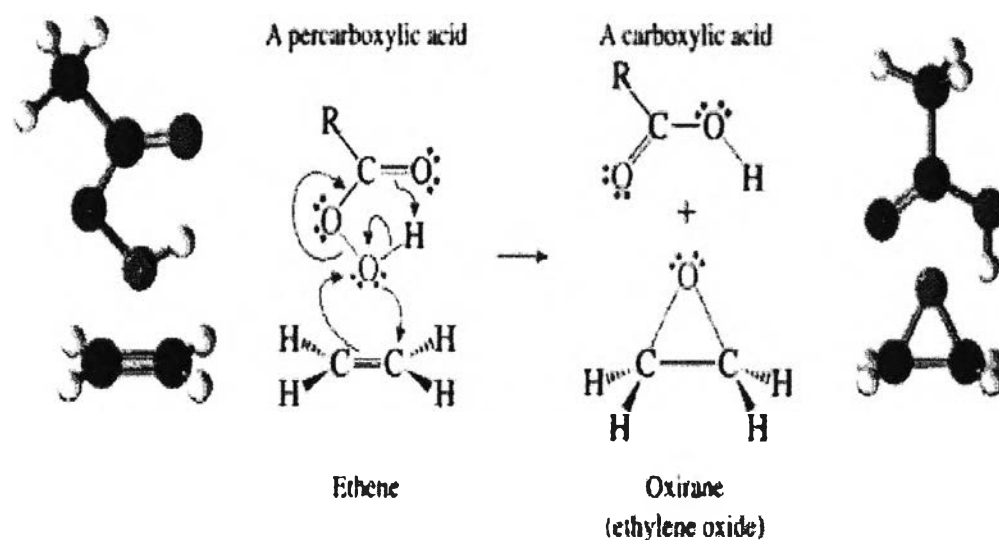
Ethene   Oxirane
(ethylene oxide)

Figure 2.2 The formation of ethylene oxide from ethene (Mandelli *et al.*, 2001).

The epoxidation reaction is concerted. It appears quite complex because of all the bonds that are being made of broken in this one step. A 1,1-elimination of the proton and the oxygen would generate a normal carboxylic acid and an oxygen atom. Addition of the oxygen atom electrophile to the alkene, as illustrated previously, would then produce the epoxide. All of this simply happen in a single step.

Examination of this mechanism suggests that the nature of the R group should not make much difference in the reaction. In fact, a number of different percarboxylic acids can be used to epoxidize alkenes, as illustrated in the following examples. As expected, the additions occur with synthetic stereochemistry. For example, the formation of cyclopentene oxide is shown in Figure 2.3.
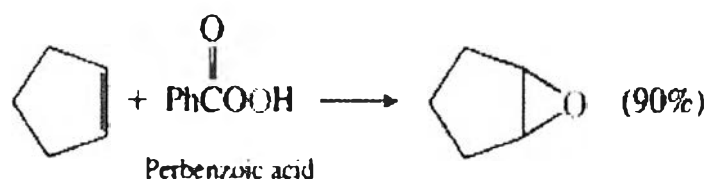
Figure 2.3 The formation of cyclopentene oxide from cyclopentene.

2.1.2 Types of Epoxidation Reaction

2.1.2.1 Jacobsen-Katsuki

The Jacobsen epoxidation allows the enantioselective formation of epoxides from various cis-substituted olefins by using a chiral Mn-salen catalyst and a stoichiometric oxidant such as bleach. Compared to the Sharpless Epoxidation, the Jacobsen Epoxidation allows a broader substrate scope for the transformation: good substrates are conjugated cis-olefins (R: Ar, alkenyl, alkynyl; R': Me, alkyl) or alkyl-substituted cis-olefins bearing one bulky alkyl group. The Jacobsen-Katsuki epoxidation is shown in Figure 2.4.
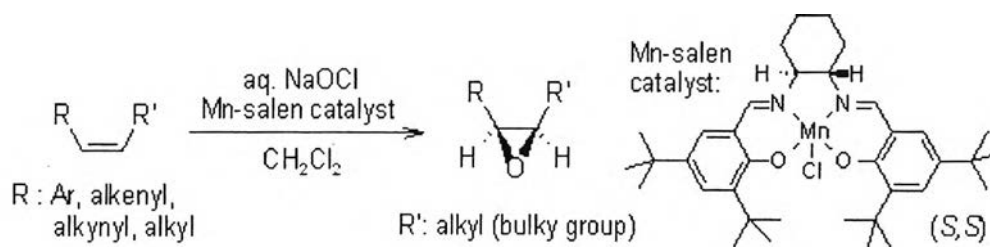

Figure 2.4 The formation of epoxide from Jacobsen-Katsuki epoxidation.

2.1.2.2 Prilezhaev

The epoxidation of an alkene with peracid gives an oxirane. The commercial available meta-Chloroperbenzoic acid (mCPBA) is a widely used reagent for this conversion, while magnesium mono-perphthalate and peracetic acid are also employed. The Prilezhaev epoxidation is shown in Figure 2.5.
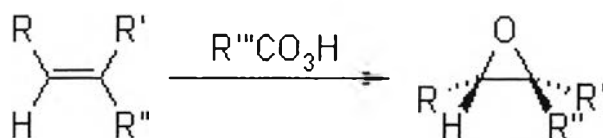

Figure 2.5 The formation of epoxide from Prilezhaev epoxidation.

2.1.2.3 Sharpless

The Sharpless epoxidation allows the enantioselective epoxidation of prochiral allylic alcohols. The asymmetric induction is achieved by adding an enantiomerically enriched tartrate derivative. The Sharpless epoxidation is shown in Figure 2.6.
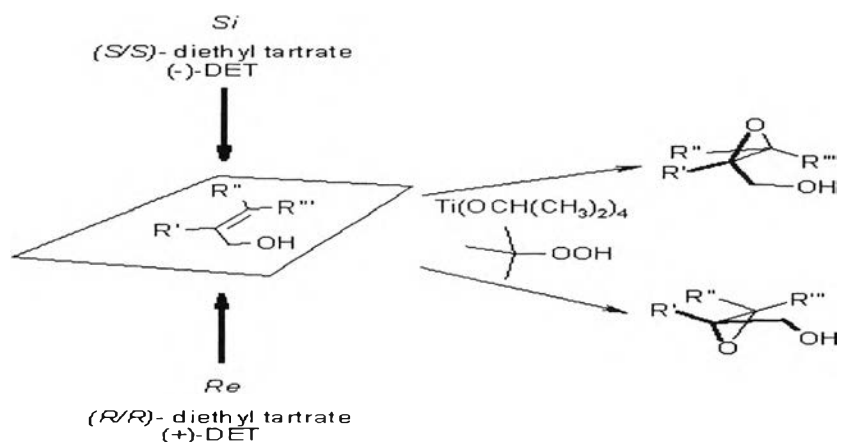

Figure 2.6 The formation of epoxide from Sharpless epoxidation.

Moreover, there are some literatures which have already been researched in an epoxidation reaction to produce epoxide as follows:

Lane *et al.* (2002) had done a research on the epoxidation of alkenes using hydrogen peroxide as the terminal oxidant is promoted by catalytic amounts (1.0-0.1 mol %) of manganese (2^+) salts, and must be performed using at least catalytic amounts of bicarbonate buffer. Various aryl-substituted, cyclic, and trialkyl-substituted alkenes were epoxidized under these conditions using hydrogen peroxide, but monoalkyl-alkenes were not. Additives such as sodium acetate and salicylic acid enhanced the rate of the desired epoxidation reaction by 2-3 times. The reaction is shown in Figure 2.7.
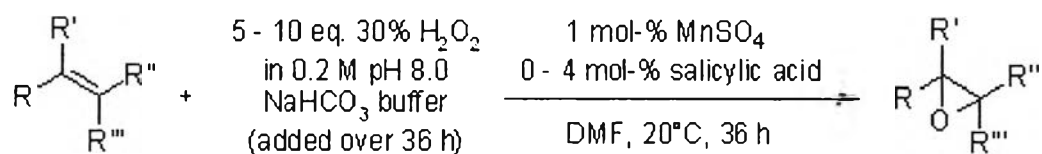

Figure 2.7 An epoxidation of alkenes using hydrogen peroxide.

Zhang *et al.* (2005) had done a study on a new catalytic system for the asymmetric epoxidation of allylic alcohols and has developed featuring high enantioselectivity for Z olefins, catalyst loading of less than 1 mol%, reaction temperatures of 0°C to room temperature over a shorter time, use of aqueous *tert*-butyl hydroperoxide (TBHP) instead of anhydrous TBHP as an achiral oxidant, and simple workup procedures for small expoxy alcohols. The reaction is shown in Figure 2.8.
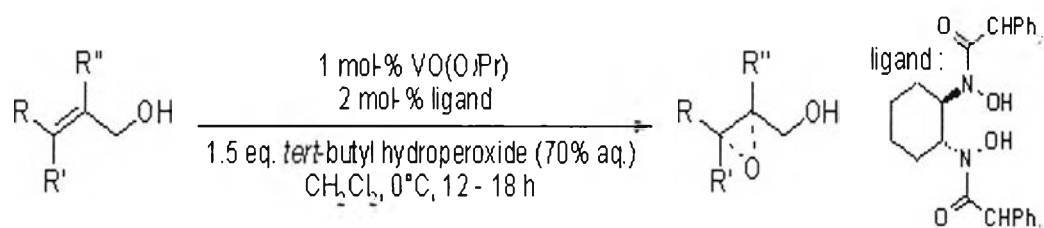

Figure 2.8 An epoxidation of allylic alcohols using new catalytic system.

2.1.3 Incipient Wetness Impregnation Technique

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought in contact with the support. Two methodologies exist. In dry impregnation, also referred to as "pore volume impregnation", just enough liquid (solution of the precursors) is used to fill the pore volume of the support. When the volume of the solution used does not exceed the pore volume of the support, the method is called incipient wetness impregnation. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursors of the active phase. In dry impregnation, the solubility of the catalyst precursors and the pore volume of the support determines the maximum loading available each time of impregnation. In the first step of impregnation, three processes occur:

- transport of solute to the pore system of the support bodies;
- diffusion of solute within the pore system; and
- uptake of solute by the pore wall.

In the case of wet impregnation, a fourth process is operative, *viz.* transport of solute to the outer particle surface. Depending on the process conditions, different profiles of the active phase over the support body will be obtained.

2.1.4 Sol-Gel Process

Several key techniques have been adopted to prepare mesoporous TiO_2, such as sol-gel process, hydrothermal process, and ultrasonic irradiation process. The sol-gel process is one of the versatile methods to prepare nono-sized mesoporous materials (Sreethawong and Yoshikawa, 2006). This technique does not require complicated instruments, such as in chemical vapor deposition method. It provides a simple and easy means of synthesizing nano-sized particles, which is essential for nano-catalysts (Wu and Chen, 2004). Besides, it is capable of producing photocatalysts with a high surface area. It involves the formation of metal-oxo-polymer network from molecular precursors, such as metal alkoxides, and subsequent polycondensation as follows:

$$M\text{-}OR \ + \ H_2O \quad \rightarrow \quad M\text{-}OH \ + \ ROH \quad\quad (1)$$

$$M\text{-}OH \ + \ M\text{-}OR \quad \rightarrow \quad M\text{-}O\text{-}M \ + \ R\text{-}OH \quad\quad (2)$$

$$M\text{-}OH \ + \ M\text{-}OH \quad \rightarrow \quad M\text{-}O\text{-}M \ + \ H_2O \quad\quad (3)$$

Where M = Si, Ti, Zr, Al, and R= alkyl group. The relative rates of hydrolysis and polycondensation strongly influence the structure and properties of the resulting metal oxides. Typically, sol-gel-derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and growth and may induce phase transformation (Wang and Ying, 1999).

Factors affecting the sol-gel process include the reactivity of metal alkoxides, pH of the reaction medium, water to alkoxide ratio, reaction temperature, and nature of solvent and additive. The water to alkoxide ratio governs the sol-gel chemistry and the structural characteristics of the hydrolyzed gel. High water to alkoxide ratios in the reaction medium ensures a more complete hydrolysis of alkoxides, favoring nucleation versus particle growth. In addition, an increase in water to alkoxide ratio leads to reduce the crystallitesize of the calcined catalyst. An alternative approach to control the sol-gel reaction rates involves the use of acid or base catalyst. It was reported that for a system with a water to alkoxide ratio of 165, the addition of HCL resulted in the reduction of the crystallite size from 20 to 14 nm

for materials calcined at 450°C. Besides, a finer grain size and a narrower pore size distributioin with a smaller average pore diameter were also attained for the sample synthesized with HCl (Wang and Ying, 1999). The size of alkoxide group in alkoxides also plays an important role in controlling the particle size. The titanium alkoxide containing bulky groups, such as titanium amiloxide, reduces the hydrolysis rate, which is advantageous for the preparation of fine colloidal particles (Murakami et al., 1999).

2.1.5 RuO_2 Catalyst for Epoxidation Reaction

The utilization of RuO_2 in catalysis field has been considerably focused for a number of reactions by being loaded on various kinds of support, such as RuO_2/TiO_2 (Sreethawong et al., 2006), $RuO_2/$zeolite Y for water splitting reaction (Qin and Aika, 1997), and RuO_2/CeO_2 for wet oxidation of acetic acid (Hosokawa et al., 2003). Nowadays, it (in oxide form of RuO_2) has not yet been applied for any epoxidation reactions. 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 RuO_2 in catalytic cyclohexene epoxidation.

2.1.6 Support Material for Epoxidation Reaction

2.1.6.1 Ferrous-Ferric Oxide or Magnetite

Magnetite is a ferrimagnetic mineral with chemical formula Fe_3O_4, one of several iron oxides and a member of the spinel group. The chemical IUPAC name is iron (II,III) oxide and the common chemical name ferrous-ferric oxide. The formula for magnetite may also be written as $FeO \cdot Fe_2O_3$, which consists of two types of iron oxides; 1) wüstite (FeO) and 2) hematite (Fe_2O_3).

The Curie temperature of magnetite (temperature of transformation between ferromagnetism and paramagnetism) is 858 K. Magnetite is the most magnetic of all the naturally occurring minerals on Earth, and these magnetic properties led to magnetite being used as an early form of magnetic compass. Magnetite typically carries the dominant magnetic signature in rocks, and

so it has been a critical tool in paleomagnetism, a science importance in discovering and understanding plate tectonics. The relationships between magnetite and other iron-rich oxide minerals such as ilmenite, hematite, and ulvospinel have been much studied, as the complicated reactions between these minerals and oxygen influence how and when magnetite preserves records of the Earth's magnetic field.

Magnetite has been very important in understanding the conditions under which rocks form and evolve. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that can control oxygen fugacity. Commonly igneous rocks contain grains of two solid solutions, one between magnetite and ulvospinel and the other between ilmenite and hematite. Compositions of the mineral pairs are used to calculate how oxidizing was the magma (i.e., the oxygen fugacity of the magma): a range of oxidizing conditions is found in magmas and the oxidation state helps to determine how the magmas might evolve by fractional crystallization.

Transition metal and alloy nanoclusters are nanoscopic materials with significant value of applications, which can be used to develop various functional materials and devices.

These metal nanoclusters, stabilized only with simple ions and organic solvent molecules, have small particle sizes and narrow size distributions, and can be produced in a large scale. Moreover, the "unprotected" metal nanoclusters can be conveniently separated as precipitates from the original dispersions and purified, which can be then re-dispersed into many kinds of organic solvents to form stable metal colloidal solutions.

γ-Fe_2O_3 and Fe_3O_4 are two kinds of well known magnetic iron oxide, both of them have the cubic inverse spinel crystal structure. They can transform to each other in specific conditions. For example, the oxidation of Fe_3O_4 at about 523 K can produce γ-Fe_2O_3, indicating that γ-Fe_2O_3 is more stable than Fe_3O_4. Difference from the conventional ferromagnetic iron oxides materials with large particle sizes, upon decreasing the particle size to some extent, the iron oxide nanoparticles may exhibit special electronic, magnetic and optical properties. These unique properties endow the iron oxides nanoparticles with extensive application value in the fields of ultrahigh density data storage, bio-separation, controllable

release of medicine, and wave-absorption materials. Currently, the most common method for industrial production of γ-Fe_2O_3 is firstly preparing the ferric hydroxide precursor, followed by calcining the precursor at high temperature resulting in α-Fe_2O_3. Fe_3O_4 is then produced by the reduction of α-Fe_2O_3 with reductive gases, and then oxidized to γ-Fe_2O_3 at high temperature. The required temperature in the preparation process is usually higher than 523 K. using γ-Fe_2O_3 and Fe_3O_4 materials prepared in such a high-temperature method, it is difficult to fabricate nanoscopic materials with small sizes and excellent performances (Wang and Wei, 2004).

For industrial application, in virtue of the catalytic function of the metal nanoclusters, the present invention succeeded in preparing a new kind of magnetic transition metals-iron oxides nanocomposite materials at relative low temperature. The main features of the preparation method according to the present invention are first to prepare the colloidal solutions of "unprotected" transition metal or alloy nanoclusters, which are then mixed with the colloidal solutions of ferric hydroxide nanoparticles to form complex sols, followed by the heat treatment in the presence of reductants, such as alcohol, aldehyde and glycolic acid. The obtained products are washed, dried or oxidized to produce the said nanocomposite materials composed of the transition metal nanoclusters and magnetic iron oxides nanoparticles.

The invented nanocomposite materials composed of transition metal nanoclusters and magnetic iron oxides nanoparticles can catalyze the hydrogenation of aromatic halonitro compounds to aromatic haloamines with very high selectivity. The hydrodehalogenation side reaction in the hydrogenation of aromatic halonitro compounds to aromatic haloamines was fully suppressed for the first time over the present nanocomposite catalysts. Moreover, due to the two or more functional components and the cooperative effect between the nanoparticles, the invented nanocomposite materials are of great value for application in the fields of catalyst, magnetic separation, wave-absorption materials, etc (Wang and Wei, 2004).

2.1.6.2 Silicon Dioxide or Silica

Silicon is the second most common element in the Earth's crust, comprising 25.7% of the Earth's crust by weight. It was discovered in 1824 by

a Swedish chemist, Jons Jakob Berzelius. It is shiny, dark gray with a tint of blue. Silicon, atomic number of 14, is a semi-metallic or metalloid, because it has several of the metallic characteristics. Silicon is never found in its natural state, but rather in combination with oxygen as a silicate ion (SiO_4) in silica-rich rocks such as obsidian, granite, diorite, and sandstone. Feldspar and quartz are the most significant silicate minerals. Silicon alloys a variety of metals, including iron, aluminum, copper, nickel, manganese and ferrochromium.

Silica is processed into two intermediate products- silicon and ferrosilicon. Silicon is known in the ferroalloy and chemical industries as "silicon metal." The ultra pure form of silicon (>99.99% Si) is distinguished from silicon metal by the term "semiconductor-grade silicon." The terms "silicon metal" and "silicon" are used interchangeably.

Silicon is used in ceramics and in making glass. Ferrosilicon is crushed into a variety of forms and sold as bulk metal. Depending on its intended use, it can be mixed with aluminum and calcium. It is a very heavy alloy. When it comes into contact with moist air or water, an explosive chemical reaction occurs in which hydrogen is released. Consequently, there are very strict laws about the shipping of ferrosilicon that it must be kept perfectly clean and dry.

Silicon compounds are the most significant component of the Earth's crust. Silicon is recovered from an abundant resource; sand. Most pure sand is quartz, silicon dioxide (SiO_2). Since sand is plentiful, easy to mine and relatively easy to process, it is the primary ore source of silicon. Some silicon is also retrieved from two other silicate minerals, talc and mica. The metamorphic rock, quartzite, is another source (quartzite is metamorphosed sandstone). All combined, world resources of silicon are plentiful and will supply demand for many decades to come.

Silica gel is a granular, porous form of silica made synthetically from sodium silicate. Despite the name, silica gel is a solid. Silica gel is most commonly encountered in everyday life as beads packed in a semi-permeable plastic. In this form, it is used as a desiccant to control local humidity in order to avoid spoilage of some goods.

SiO_2 has a number of distinct crystalline forms in addition to amorphous forms. With the exception of fibrous silica, all of the crystalline forms

involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. Stishovite, the highest pressure form, in contrast has a rutile like structure where silicon is 6 coordinate. The density of stishovite is 4.287 g/cm^3, which compares to α-quartz, the densest of the low pressure forms, which has a density of 2.648 g/cm^3.

Table 2.1 Crystalline forms of SiO_2

| Form	Space group	Stuctural features	Notes
α-quatz	rhombohedral (trigonal)	Helical chains making individual single crystals optically active	α-quatz converts to β-quartz at 573°C
β-quartz	hexagonal	closely related to α-quatz and optically active	β-quartz converts to β-tridymite at 870°C
α-tridymite	orthorhombic	metastable form under normal pressure	-
β-tridymite	hexagonal	closely related to α-tridymite	β-tridymite converts to β-cristobalite 1470°C
α-cristobalite	tetragonal	metastable form under normal pressure	-
β- cristobalite	hexagonal	closely related to α-tridymite	melts at 1705°C
Keatite	tetragonal	Si_5O_{10}, Si_4O_{14}, Si_8O_{16} rings	synthesised from amorphous silica and alkali at high pressure
coesite	monoclinic	Si_4O_8 and Si_8O_{16} rings	high pressure form (higher than keatite)
stishovite	tetragonal	Rutile like with 6 coordinate Si	high pressure form (higher than coesite) and the densest of the polymorphs

| Form	Space group	Stuctural features	Notes
melanophlogite	cubic	Si_5O_{10}, Si_6O_{12} rings	mineral always found with hydrocarbons in interstitial spaces
fibrous	orthorhombic	like SiS_2 consisting of edge sharing chains	-

2.1.6.3 Aluminium Oxide or Alumina

Aluminium oxide is an amphoteric oxide of aluminium with the chemical formula Al_2O_3. It is also commonly referred to as alumina or aloxite in the mining, ceramic and materials science communities. It is produced by the Bayer process from bauxite. Its most significant use is in the production of aluminium metal, although it is also used as an abrasive due to its hardness and as a refractory material due to its high melting point.

The most common form of crystalline alumina, α-aluminium oxide, is known as corundum. Corundum has a trigonal Bravais lattice with a space group of R-3c. Each unit cell contains six formula units of aluminum oxide. The oxygen ions nearly form a hexagonal close-packed structure with aluminium ions filling two-thirds of the octahedral interstices.

Aluminium oxide is the main component of bauxite, the principal ore of aluminium. The largest manufacturers in the world of alumina are Alcoa, Alcan and Rusal. Companies which specialise in the production of speciality aluminium oxides and aluminium hydroxides include Alcan and Almatis. The bauxite ore is made up of impure Al_2O_3, Fe_2O_3, and SiO_2. Bauxite is purified by the Bayer process:

$$Al_2O_3 + 3\ H_2O + 2\ NaOH \rightarrow 2NaAl(OH)_4$$
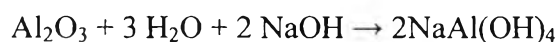
The Fe_2O_3 does not dissolve in the base. The SiO_2 dissolves as silicate $Si(OH)_6^{2-}$. Upon filtering, Fe_2O_3 is removed. When the Bayer liquor is cooled, $Al(OH)_3$ precipitates, leaving the silicates in solution. The mixture is then calcined (heated strongly) to give aluminium oxide: The formed Al_2O_3 is alumina.

$$2Al(OH)_3 + heat \rightarrow Al_2O_3 + 3H_2O$$
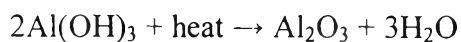
2.1.6.4 Titanium Dioxide or Titania

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

Titanium dioxide 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 cell, gas sensors, pigments and cosmetics. To explore novel approaches for the nanostructured titania of various nature with the control of the particlesize in nanometer-scale and the morphology is quite interesting, since the performance of titania in its various applications depends on its crystalline phase state, dimensions and morphology.

Titanium dioxide is a lustrous silver-white metal that occurs naturally in three crystalline modification; anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The last one is not common. Calcination of titanium salts is at moderately low temperatures around 880°C. 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. Surface area in the range of about 10 m^2/g to 50 m^2/g (Degussa P-25) are available.

Typically, fumed titania consists of mixture of anatase and rutile, the ratio varying somewhat with the manufacturing process. Degussa P-25 is report to be about 85 to 90% anatase, 10 to 15% rutile (Satterfield, 1991).

For Nanocrystalline mesoporous TiO_2 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 te surface and at the grain boundaries result in an increased surface energy. Then, the surface of nanocrystalline TiO_2 provides an active substrate for catalysis. In addition, the reactants are operated across the porous system in

several applications, sufficiently uniform pore size of 2-50 nm in the mesopore 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 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 catalysts and subsequent surface reactions (Sreethawong et al., 2006).

2.1.7 Porous Materials

The classification of pores according to size has been under discussion for many years, but in the-past, the terms "micropore" and "macropore" have been applied in different ways by physical chemists and some other scientists. With an attempt to clarify this situation, the limits of size of the different categories of pores included in Table 2.2 have been proposed by the International Union of Pure and Applied Chemistry (IUPAC) (Ishizaki et al., 1998 and Rouquerol et al., 1999). As indicated, the "pore size" is generally specified as the "pore width", i.e. the available distance between the two opposite walls. Obviously, pore size has a precise meaning when the geometrical shape is well defined. Nevertheless, for most purposes, the limiting size is that of the smallest dimension, and this is generally taken to represent the effective pore size. Micropores and mesopores are especially important in the context of adsorption.

Table 2.2 Definitions about porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 5 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Surface area	Extent of total surface area determined by given method under stated conditions

According to the IUPAC classification, porous materials are regularly organized into three categories on a basis of predominant pore size as follows:

- Microporous materials (pore size < 2 nm) include amorphous silica and inorganic gel to crystalline materials, such as zeolites, aluminophosphates, gallophosphates, and related materials.

- Mesoporous materials (2 nm ≤ pore size ≤ 50 nm) include the M41S family (e.g. MCM-41, MCM-48, MCM-50, and etc.) and other non-silica materials synthesized via intercalation of layered materials, such as double hydroxides, metal(titanium, zirconium) phosphates, and clays.

- Macroporous materials (pore size > 50 nm) include glass-related materials, aerogels, and xerogels.

Nowadays, micro- and mesoporous materials are generally called "nanoporous materials". Particularlyt, mesoporous materials are remarkably very suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation if high loading is sought.

2.2 Literature Review

The catalytic oxidation of olefins to epoxides is of great importance to the chemical industry, because epoxides are valuable intermediates for a wide variety of bulk chemicals, polymers, and fine chemicals (Ramachandran *et al.*, 2007), and as flexible intermediates and precursors to many useful chemical products as well. Moreover, epoxides find a range of applications in pharmaceutical industry as drug intermediates, preparation of epoxy resins, perfumes, pesticides and paints (Jinka *et al.*, 2007, Ingle *et al.*, 2007, Sreethawong *et al.*, 2006).

The selective oxidation of hydrocarbons and other organic compounds is still a challenge in chemical industries and academic field. Therefore, much effort is devoted to the development of new active and selective catalysts for cyclohexene epoxidation that circumvent the formation of large amounts of by-products because several side reactions can take place (Costa *et al.*, 2007, Mandelli *et al.*, 2001).

Transition metal complexes of Co, Ti, Mn, Mo, were used as the catalyst, and high selectivity of epoxides of cyclic olefin such as cyclohexene has been reported. Among all, cobalt complexes have been extensively used for the epoxidation of various alkene substrates. Accordingly, epoxidation of cycloalkenes with cobalt(II)-exchanged zeolite X catalysts using molecular oxygen was conducted by Jinka *et al.* The experiments were carried out in presence of cobalt(II) exchanged zeolite X based catalysts by using molecular oxygen as oxidant. Effect of temperature (353–418 K) and pressure (30–150 psi) was studied to obtain the optimum conditions for the reaction. The best results were obtained at 60 psi pressure and 373K using NaCoX96 catalyst with cycloalkene conversion and epoxide selectivity for cyclohexene, cycloheptene and *cis*-cyclooctene were obtained in the range 26–47 and 48–100% respectively. Alkali and alkaline earth cationic promoters were introduced into the zeolite catalyst in order to study the effect of basicity of the catalyst on the cycloalkene conversion and epoxide selectivity. The catalyst was observed to be recyclable as conversion and selectivity were retained even after four catalytic reaction cycles . In addition, the reaction pathway and the active species formed in the reaction a separate experiment were studied which a

tentative reaction mechanism for cyclohexene epoxidation has been proposed to proceed as shown in Figure 2.9 (Jinka *et al.*, 2007).
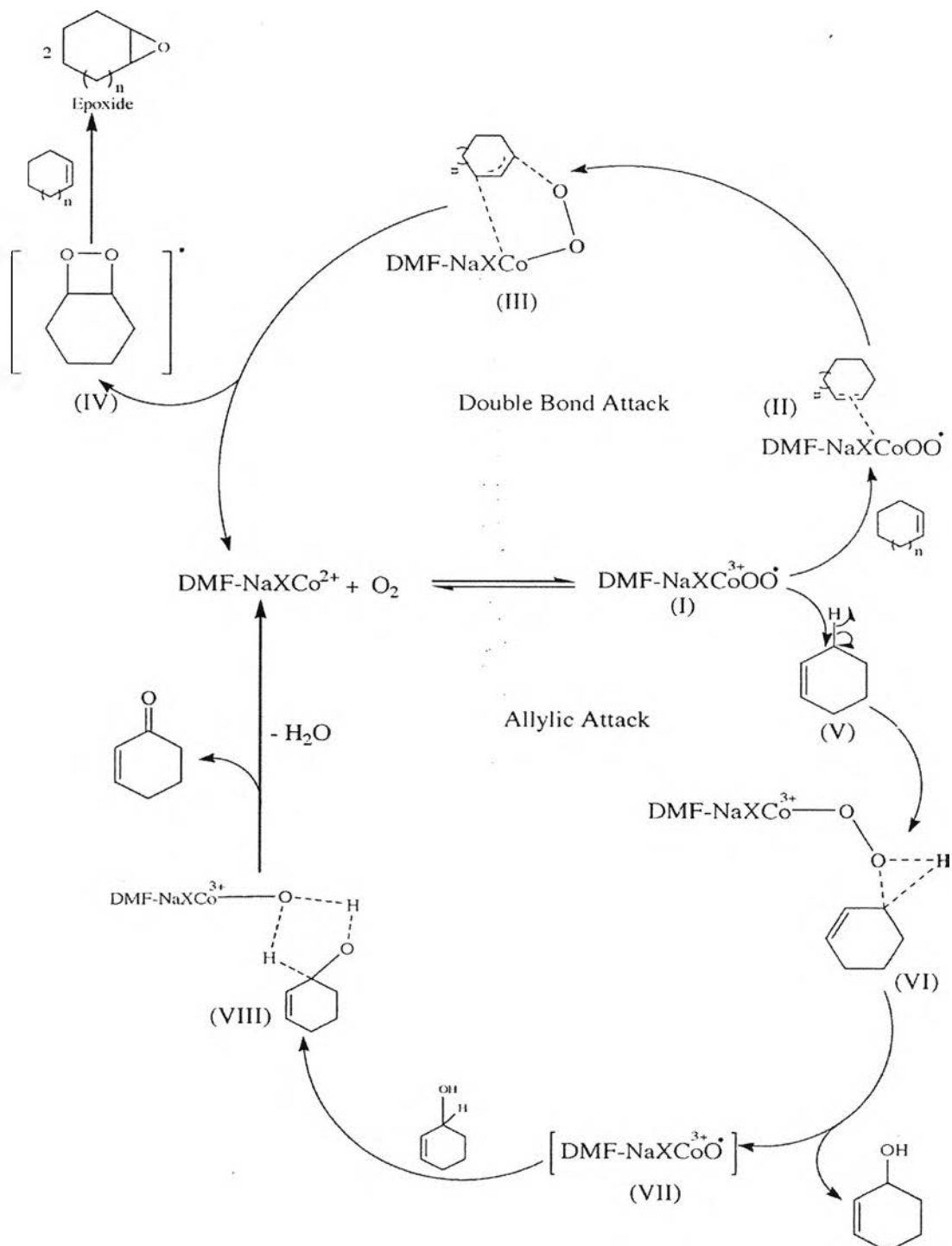

Figure 2.9 Tentative reaction mechanism for epoxidation of cyclohexene (Jinka *et al.*, 2007).

Many catalytic systems containing transition metal ions have been exploited for the epoxidation of alkenes. In recent years, transition metal-substituted catalysts have gained considerable interest due to their multi versatilities for the oxidation of organic substrates. Transition metal-substituted polyoxometalates (TMSP) generally provide higher conversion and better selectivity for epoxides. Amongst the TMSP, vanadium-substituted polyoxometalates are the most studied ones that have attracted the attention as catalysts. Accordingly, alkene epoxidation catalyzed by vanadomolybdophosphoric acids supported on hydrated titania was conducted by Ingle *et al.* The experiments were carried out with vanadomolybdophosphoric acids wet-impregnated on hydrated titania ($TiO_2 \cdot xH_2O$), making an efficient catalytic system for the epoxidation of a variety of alkenes with organic solvent extracted TBHP as the oxidant. By an appropriate choice of solvent, the catalyst can be reused at least three times without much loss in the activity for subsequent runs. XRD shows that the heteropoly acid is uniformly dispersed over the support and up to 15 wt% loading of the heteropoly acid, no additional peak of the same can be seen in the XRD pattern of the catalyst. The reactivity varied with the nature of alkene but the major product was always the corresponding epoxide. The catalytic system is free of high temperature calcination steps and tedious multi-step procedures, normally encountered in the heterogenization of heteropoly acids (Ingle *et al.*, 2007). Moreover, transition-metal substituted α-titanium arsenate is also studied because it provides good catalytic systems in terms of separation of reaction products from the catalyst. Consequently, epoxidation of cyclohexene catalyzed by transition-metal substituted α-titanium arsenate using *tert*-butyl hydroperoxide as an oxidant was researched by Khare *et al.* The experiments were carried out with epoxidation of cyclohexene, using transition-metal substituted α-titanium arsenate {α-TiMAs, where M=Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III)} as a catalyst and dry *tert*-butyl hydroperoxide as an oxidant. In the epoxidation reaction, cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. It was found that the reactivity of the epoxidation reaction decreased in the order α-TiRuAs > α-TiMnAs > α-TiFeAs > α-TiCrAs > α-TiCoAs > α-TiCuAs. A maximum selectivity for epoxidation of cyclohexene (89.89%) was observed for α-TiRuAs/dryTBHP system

after 4 h of reaction when concentrations of the catalyst and the substrate were 0.20 and 20 mmol, respectively (Khare and Shrivastava, 2004).

Sreethawong et al. (2005) prepared nanocrystalline mesoporous TiO_2-based catalysts by a surfactant-assisted templating sol-gel process which were tested on cyclohexene epoxidation. The mesoporous TiO2 showed exceptional potential for epoxidation of cyclohexene, exhibiting both higher cyclohexene conversion and higher cyclohexene oxide selectivity than non-mesoporous commercial TiO2 powders, i.e. Ishihara ST-01 and Degussa P-25. The oxides of Fe, Co, Ni, and Ru were also loaded by incipient wetness impregnation method onto the synthesized mesoporous TiO2, aiming to enhance the catalytic performance. Among metal oxide-loaded catalysts, RuO2-loaded mesoporous TiO2 was proved to possess noticeably high catalytic performance based on cyclohexene oxide selectivity. The 1 mol% RuO2-loaded mesoporous TiO2 was the best catalyst, showing the highest cyclohexene oxide selectivity and lowest cyclohex-2-en-1-ol (undesired product) selectivity. In addition, the plausible reaction pathway and the active species formed in the reaction for cyclohexene epoxidation has been proposed to proceed as shown in Figure 2.10.
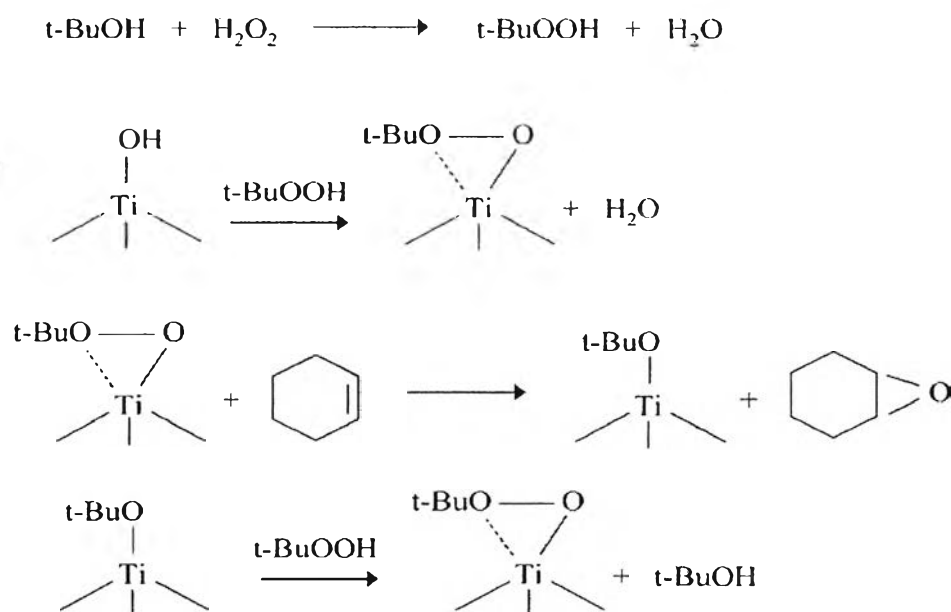
$$t\text{-}BuOH + H_2O_2 \longrightarrow t\text{-}BuOOH + H_2O$$

Figure 2.10 Proposed pathway for cyclohexene epoxidation at TiO_2 surface (Sreethawong et al., 2005).

Sreethawong *et al.* (2006) had done a study optimization of reaction conditions for cyclohexene epoxidation with H_2O_2 over nanocrystalline mesoporous TiO_2 loaded with RuO_2. The support TiO_2 prepared by surfactant-assisted templating sol–gel method is nanocrystalline and has mesoporous structure with narrow monomodal pore size distribution. An activator of 1 mol% RuO_2 was loaded onto the synthesized TiO_2 by incipient wetness impregnation method. The resultant catalyst was characterized by XRD, N_2 adsorption–desorption and TEM analyses. Reaction conditions in the epoxidation reaction, namely reaction temperature, amount of catalyst and concentration of H_2O_2 in terms of cyclohexene/H_2O_2 ratio, were systematically optimized to obtain maximum selectivity to cyclohexene oxide.

Catalysts based on inorganic rhenium compounds are much more readily available, since no organometallic synthesis is required. Consequently, epoxidation of alkenes with hydrogen peroxide catalyzed by ReO_4–SiO_2·Al_2O_3 and ReO_4–Al_2O_3 was studied by Mandelli *et al*. The experiments were carried out with rhenium oxides supported on zeolite Y, mixed silica–alumina and pure alumina prepared by impregnation of the supports with Re_2O_7 or NH_4ReO_4. The materials are active catalysts in the epoxidation of cyclooctene and cyclohexene with anhydrous H_2O_2 in EtOAc. Stable catalysts ReO_4–Al_2O_3 with ReO_4^- contents up to 12 wt.% can be prepared. Higher contents result in extensive metal leaching and catalysis in the homogeneous phase. The catalyst ReO_4 (12 wt.%)–Al_2O_3 was reused in three catalytic runs, without loss of activity. Selectivities for cyclooctene epoxide were around 96% . (Mandelli *et al.*, 2000).

Mandelli *et al.* (2001) had done a study in Alumina-catalyzed alkene epoxidation with hydrogen peroxide. Because Al_2O_3 was inexpensive, it can be used as a simple catalyst for alkene epoxidation, using anhydrous hydrogen peroxide as oxidant. This system is active and selective in the epoxidation of several alkenes. Besides the epoxidation of the terpenes limonene, and α-pinene, we studied the epoxidation of cyclohexene and cyclooctene, as well as α-olefins, such as 1-octene and 1-decene. Productivities of up to 4.3 g products per gram catalyst were obtained and the catalyst was recycled without significant loss of activity. Moreover, the reaction mechanism of the Al_2O_3/H_2O_2-catalyzed alkene epoxidation has been proposed in Figure 2.11
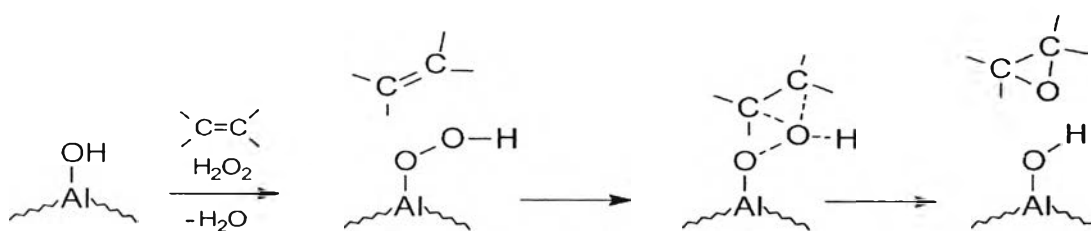
Figure 2.11 Proposed mechanism for the Al₂O₃-catalyzed alkene epoxidation (Mandelli *et al.*, 2002).

The incorporation of transition metal ions into microporous or mesoporous molecular sieves is of considerable interest for catalytic applications. Since the discovery of mesoporous molecular sieves MCM-41, it has attracted considerable attention for its potential use in catalytic conversion. MCM-41 pores has a regular hexagonal array in its mesopore structure with a high surface area. Accordingly, V-MCM-41 as selective catalyst for epoxidation of olefins and *trans*-2-hexene-1-ol was conducted by Farzaneh *et al*. In experiments, Vanadium containing MCM-41(V-MCM-41) was synthesized by one pot synthesis and characterized by spectroscopic techniques. The oxidation of olefins such as 1-hexene, cyclohexene, cyclopentene, norbornene and *trans*-2-hexene-1-ol with tertiary butyl hydroperoxide (TBHP) in the presence of V-MCM-41 as catalyst in different solvents(CH_2Cl_2, CH_3CN, $CH_3OH\cdot CHCl_3$) is described. It was found that V-MCM-41 in refluxing $CHCl_3$ was very reactive for epoxidation of *trans*-2-hexene-1-ol with 52% reactivity and 100% selectivity. Oxidation of *trans*-2-hexene-1-ol to the corresponding epoxide in the absence of solvent was successfully carried out with the enhancement of reactivity to 94%. Besides, the reaction mechanism of cyclohexene epoxidation has been proposed in Figure 2.12 (Farzaneh *et al.*, 2004).
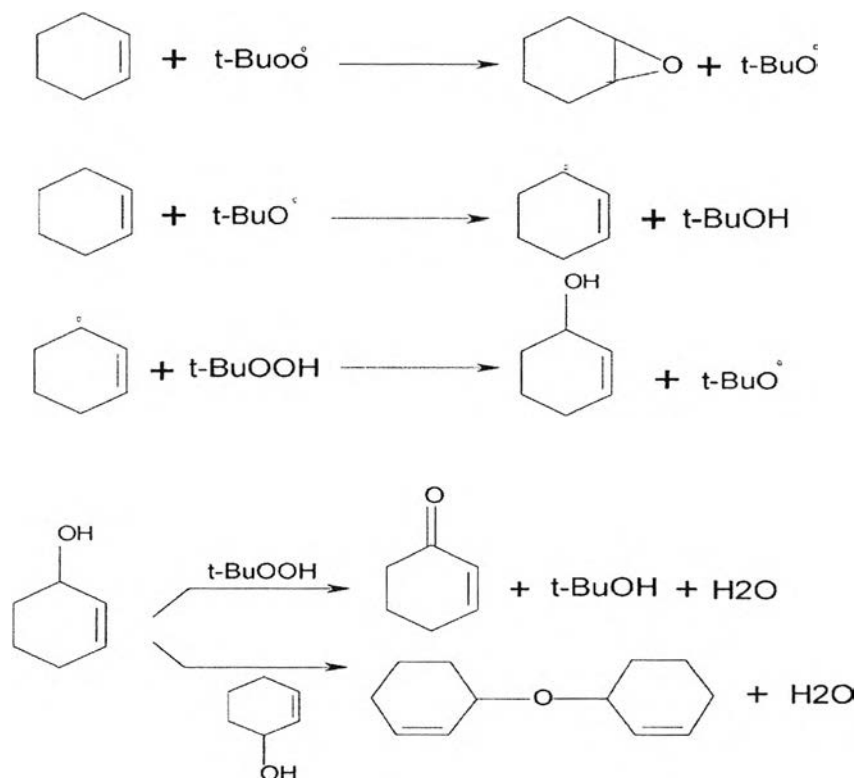
Figure 2.12 The reaction mechanism of cyclohexene epoxidation in the presence of TBHP as oxidant (Farzaneh *et al.*, 2004).

Farahani *et al.* (2002) had done a research in Molybdenum incorporated silicalite as catalyst for epoxidation of olefins. Synthesis of silicalite containing small amount of molybdenum is described. Characterization of this zeolite was carried out with FT-IR, atomic absorption spectroscopy, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). In order to increase molybdenum content in zeolite structure with grafting method, the prepared silicalite-1 underwent reaction with molybdenum hexacarbonyl at high temperature. The incorporation of molybdenum in the structure was increased to 11%. The modified zeolite catalyzed the epoxidation of olefins (cyclohexene and *trans*-2-hexene-1-ol) with about 90% yield and 98% selectivity. In addition, the tentative reaction mechanism of cyclohexene epoxidation has been proposed in Figure 2.13.
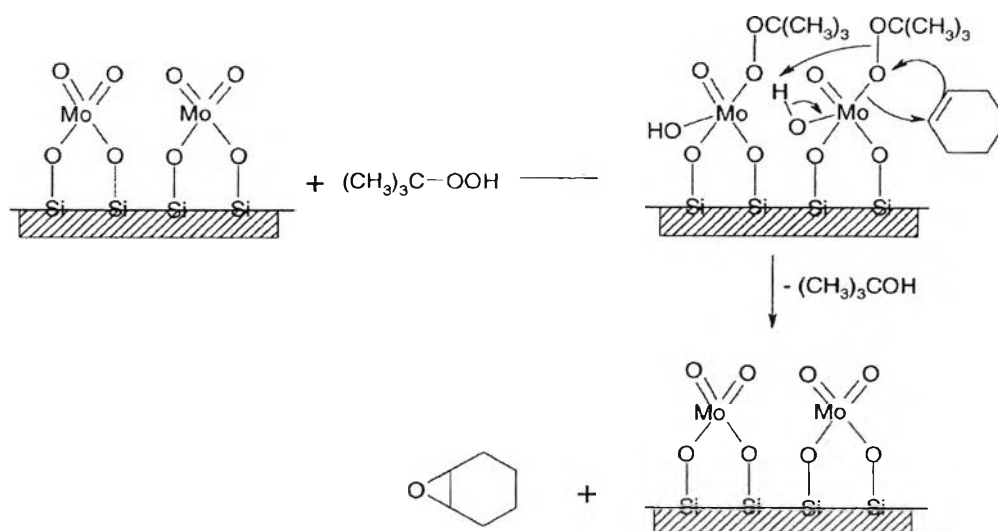
Figure 2.13 Mechanism of cyclohexene epoxidation in the presence of modified Mo-silicalite (Farahani *et al.*, 2002).