Chapter 2

Theory

2.1 Zeolites

Zeolites[12,45] are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally the zeolites are framework aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens. Zeolites may be represented by the formula $M_{2/n}$ [$(AlO_2)_x$.$(SiO_2)_y$].wH_2O where cations M of valence n neutralize the negative charges on the aluminosilicate framework.

Zeolites are catagorized based on their structures[12,45]. The tetrahedra so called primary building units are linked together to form several types of secondary building units, such as a double 4-ring (D4R), a double 6-ring (D6R), or a sodalite cage (truncated octahedron or β cage). Only the positions of Si and Al are shown at the corners of each building unit shown in Figure 2.1. The oxygen atoms lie near the lines connecting the metal atoms. The connection of these building units in various ways results in different structures, i.e. different types of zeolites.
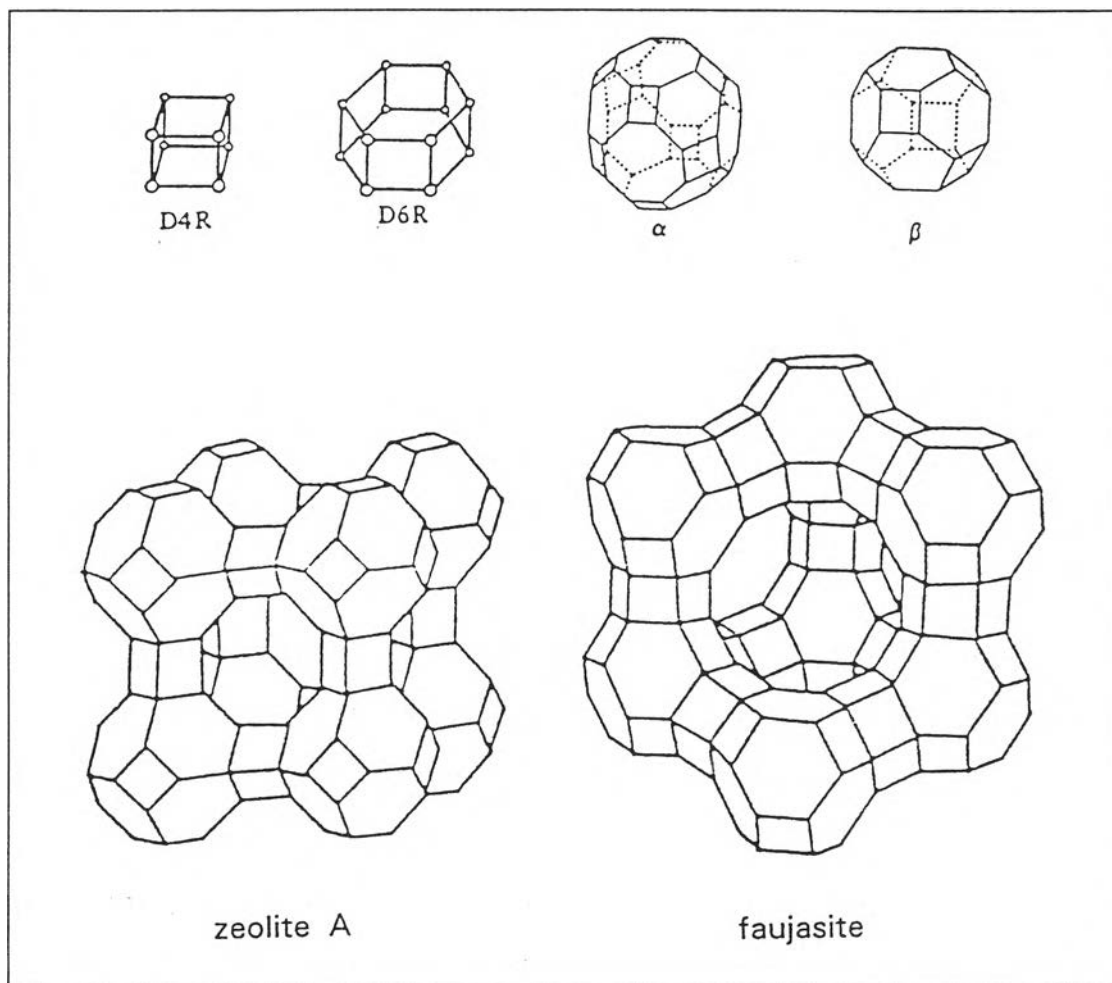
Figure 2.1 Topologies of the structural building units and the structures of zeolite A

and faujasite-type zeolite

For example, Figure 2.1 illustrates the building units and structures of zeolite A and faujasite (including zeolites X and Y). The two structures are formed by connecting the sodalite units with double 4 rings or double 6-rings. A new larger cage is formed at the center which is called supercage (α cage) for both types of structure. The supercage type I belongs to zeolite A structure and supercage type II for faujasite and both are

shown in Figure 2.1. Zeolite X and Y have similar structure but different Si/Al ratio. The Si/Al ratio varies from 1 to 1.5 for zeolite X and from greater than 1.5 to 3 for zeolite Y.

2.1.1 Structure and Chemical Composition of Zeolite Y

In zeolite Y structure, the diameter of the supercage is 12.5 Å while the diameters of the sodalite cage and the double 6-ring are 6.6 and 2.6 Å, respectively. Each supercage contains four windows of 12-membered Al or Si rings with a diameter of 7.4 Å.

The cation sites of zeolite Y are illustrated in Figure 2.2. Type I sites are located at the centers of the hexagonal prisms, type I sites are located in the sodalite cages across the hexagonal faces from type I sites, type II sites are located in the supercages near the unjoined hexagonal faces, and type II' sites are located in the sodalite opposite to the type II sites. Type III sites are located in the supercage, further from the hexagonal faces than the type II sites.

For full hydrated zeolite NaY with a Si/Al ratio of 2.3, the chemical formula for a unit cell will be $Na_{58}[(AlO_2)_{58}(SiO_2)_{134}].235H_2O$. In dehydrated zeolite NaY (58 Na^+ ions), a cation distribution of 7.63 Na^+ ions at site I, 19.84 Na^+ ions at site I, and 30.53 Na^- ions at site II was reported[12]. There are 8 supercages per unit cell of zeolite NaY, therefore, 3.82 Na^+ ions on average reside in the supercages. With four single 6-rings

per supercage, there is about 1 Na$^+$ ion per single 6-ring of the supercage. Zeolite Y can contain up to approximately 235 water molecules per unit cell which are distributed in both the large supercages and the small sodalite cages.
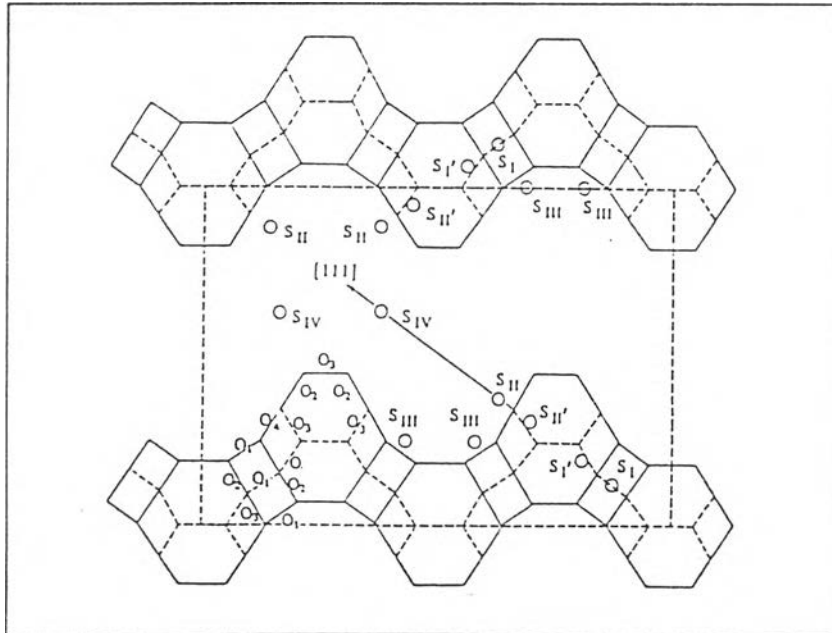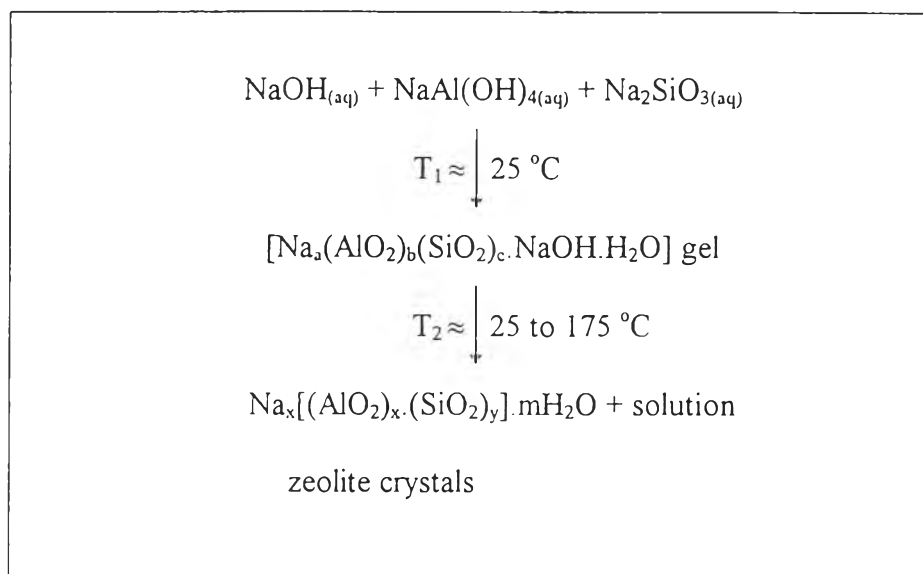

Figure 2.2 Locations of cation sites in zeolite Y

2.1.2 Process of Zeolite Formation

In a four-component system $Na_2O-Al_2O_3-SiO_2-H_2O$,[45] zeolite is commonly crystallized from a molecularly inhomogeneous system referred to as a gel. The gel is defined as a non-crystalline hydrous metal aluminosilicate which is formed by a process of copolymerization of the silicate and aluminate ions in a basic environment. The gel preparation and zeolite crystallization are represented in Scheme 2.1.

$$NaOH_{(aq)} + NaAl(OH)_{4(aq)} + Na_2SiO_{3(aq)}$$

$$T_1 \approx \bigg| \; 25 \; ^\circ C$$

$$[Na_a(AlO_2)_b(SiO_2)_c.NaOH.H_2O] \; gel$$

$$T_2 \approx \bigg| \; 25 \; to \; 175 \; ^\circ C$$

$$Na_x[(AlO_2)_x.(SiO_2)_y].mH_2O + solution$$

zeolite crystals

Scheme 2.1   Gel preparation and crystallization in the Na_2O-Al_2O_3-SiO_2-

H_2O system

The gel material is subsequently transformed to the nuclei crystals in the liquid phase. A schematic mechanism of the crystallization of an amorphous aluminosilicate gel to a zeolite is given in Figure 2.3. The gel structure, represented hereby in two dimensions, is depolymerized by the hydroxyl ions which produce soluble aluminosilicate species that may regroup to form the nuclei of the ordered zeolite structure. In this version the hydrated cation acts as a template. The size and charge of the hydrated cation species which serve as a nucleation site for the polyhedral structural unit. Eventually, zeolite crystals are formed by the chemical interaction between the nucleation centers and another alumino silicate gel so called reactant mixture.
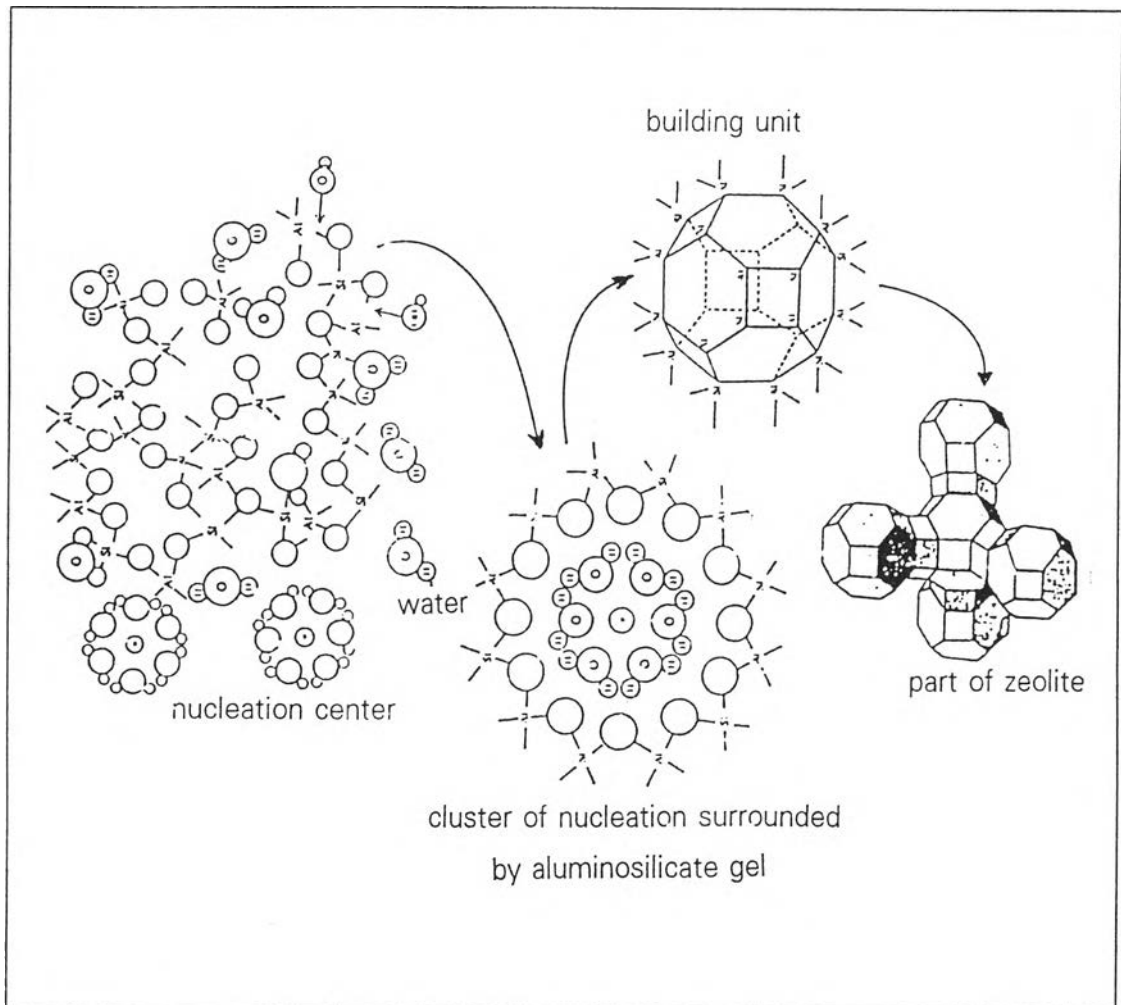
building unit

water

nucleation center

cluster of nucleation surrounded
by aluminosilicate gel

part of zeolite

Figure 2.3   Mechanism of the formation of zeolite crystals in a hydrous gel

2.1.3 Factors Influencing Zeolite Formation

Three variables have a major influence on zeolite structures[44-34]: the gross
composition of the reaction mixture, temperature, and time. There are, in general, also
some other factors which are sometimes called history-dependent factors such as
digestion or aging period, stirring, nature (either physical or chemical) of the reaction

mixture, and order of mixing. A list of individual factors contributing to the synthesis of zeolite structure is provided below :

● Gross composition

    1. SiO_2/Al_2O_3

    2. [OH⁻] or basicity

    3. Cations

          a. Inorganic cations

          b. Organic cations

    4. Anions (other than [OH⁻])

    5. H_2O content

● Time

● Temperature

● History-dependent factors

    1. Aging

    2. Stirring

    3. Nature of mixture

    4. Order of mixing

2.1.3.1 Reactant Mixture Components

Each component in the reactant mixture contributes to specific characteristic properties of the gel and to the final material obtained[46-47]. Table 2.1

provides a broad listing of individual components of the mixture and the primary influence within that reaction mixture. The SiO_2/Al_2O_3 ratio, the hydroxide content of the gel, and the presence of inorganic cations will also contribute to determine which structure(s) will finally crystallize. The crystallization of a particular zeolite structure from the gel system containing these components strongly depends on the SiO_2/Al_2O_3 ratio of the starting gel mixture. The inorganic or organic cations not only influence the crystal structure, but they may also influence other features of the final crystalline products, such as morphology and crystal size. The hydroxide content enhances the formation of soluble silicates but too much hydroxide concentration catalyzes the formation of dense materials such as quartz. The latter inhibits zeolite formation.

Table 2.1   The effect of variables on the zeolite crystallization.

Reaction mixture composition (mole ratio)	Primary influence
SiO_2/Al_2O_3	Framework composition
H_2O/SiO_2	Rate, crystallization mechanism
OH^-/SiO_2	silicate molecular weight, OH^- concentration
Inorganic cation(s)/SiO_2	Structure, cation distribution
Organic additives/SiO_2	Structure, framework aluminum content

2.1.3.2 Temperature

Temperature influences several factors in zeolite synthesis; it can alter the obtained zeolite phase and can change the induction period before the start of crystallization[12,48]. This induction period decreases with increasing temperature. Also, for any mixture as the temperature increases, the rate of crystallization increases. However, as the temperature changes, conditions may favor formation of other phases.

2.1.3.3 Time

Time can be optimized in the synthesis of many zeolites[12,48]. Many of interesting zeolites are metastable phase, and can recrystallize to other more stable structures which can be observed under certain conditions with prolonged reaction time. Crystallization parameters must be adjusted to minimize the production of other unrequired phases while also minimizing the time needed to obtain the desired crystalline phase.
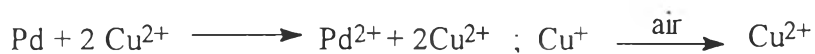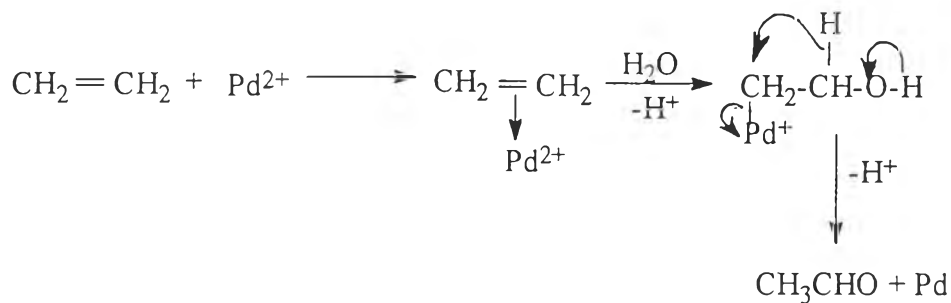
2.2 Oxidation

The term "oxidation[49] is utilized for the processes lead to the incorporation of oxygen or the removal of hydrogen from a molecule; those which result in the partial removal electrons are included only where they are employed *en route* to the introduction of oxygen or the removal of hydrogen, as in the conversion of toluene into benzaldehyde *via* benzyl chloride.

The explanation is not intended to be comprehensive but is limited to those processes which have proved to be synthetically valuable. Thus, the mechanisms of oxidations by such reagents as cobalt (III) and cesium (IV) ions have been widely studied but are not included because the reagents have not proved to be widely applicable in synthesis.

The different techniques used in industrial and laboratory processes are stressed. In the laboratory, reactions are normally carried out at comparatively low temperatures and at atmospheric pressure, and with group-selective and/or stereoselective reagents which are often expensive. Industrial reactions are more often conducted in the gas phase, at high temperature and pressure, and over catalysts, followed by efficient fractionation of the mixture of products, but the first essential is cheapness. Thus, the use of osmium tetroxide (£15 or about $25 per gram), which is justified on a small scale in the laboratory, is not an industrial proposition. The natural industrial oxidant is air, a large number of processes involving air and a catalyst are used, many of which are not fully understood or as yet employed in the laboratory. For example, there is a recently developed continuous processes for converting ethylene

into acetaldehyde, in the presence of palladium(II), copper(II) ions, and air which may be represented as follows[49]:

$$CH_2 = CH_2 + Pd^{2+} \longrightarrow CH_2 = CH_2 \xrightarrow[-H^+]{H_2O} CH_2\text{-}CH\text{-}O\text{-}H$$

$$CH_3CHO + Pd$$

$$Pd + 2\ Cu^{2+} \longrightarrow Pd^{2+} + 2Cu^{2+} \ ; \ Cu^+ \xrightarrow{air} Cu^{2+}$$

.................(2.1)

2.2.1 Organic Oxidation

Oxidation is normally brought about in one of the following ways[49]:

1. By removal of an electron, as in the oxidation of phenols by ferricyanide. The requirement for the oxidizing agent is that it should be capable of electron reduction (here, Fe(III) to Fe(II) characterized by a suitable redox potential. The requirement for the organic compound is that it should give a relatively stable radical on oxidation[49], e.g.
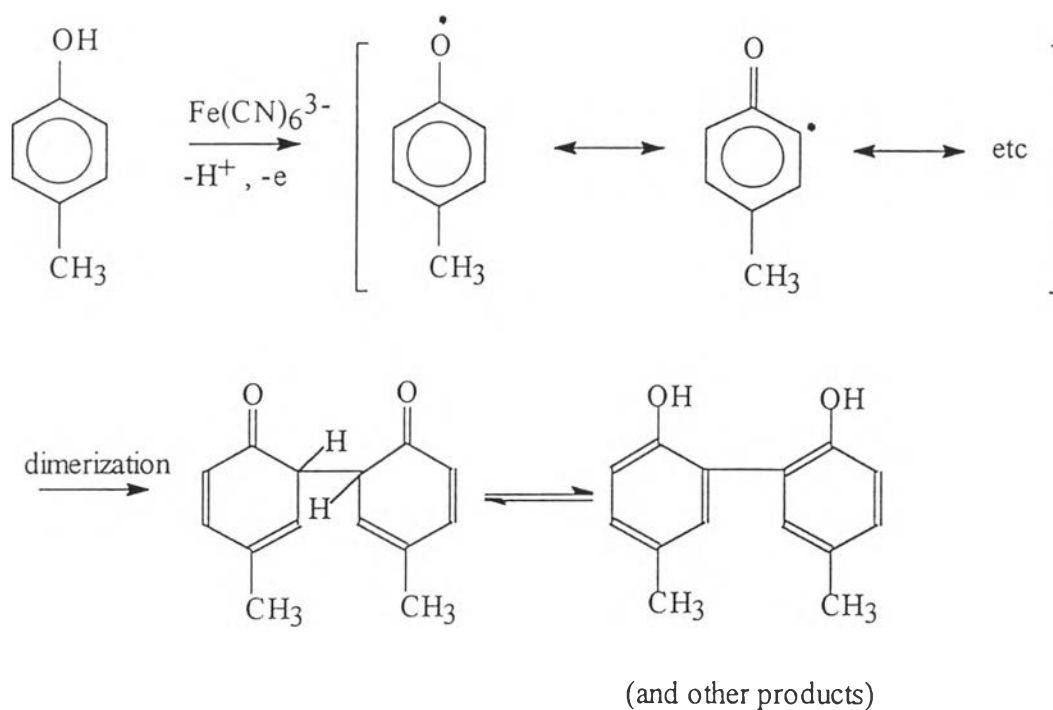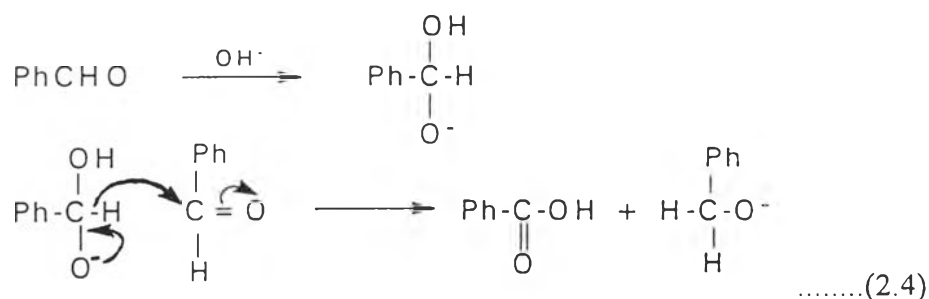
$$\cdots\cdots(2.2)$$

2. By removal of a hydrogen atom, as in the radical-catalyzed autooxidation of
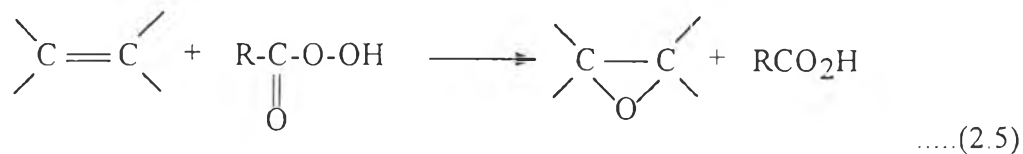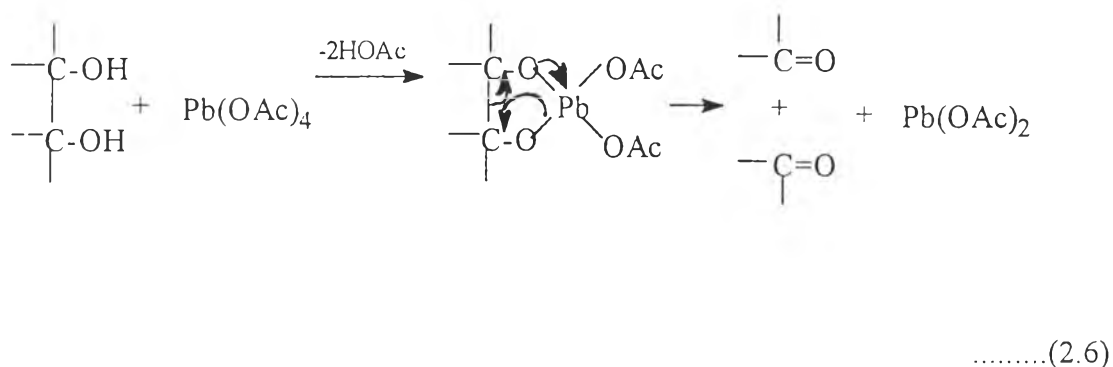
aldehydes:
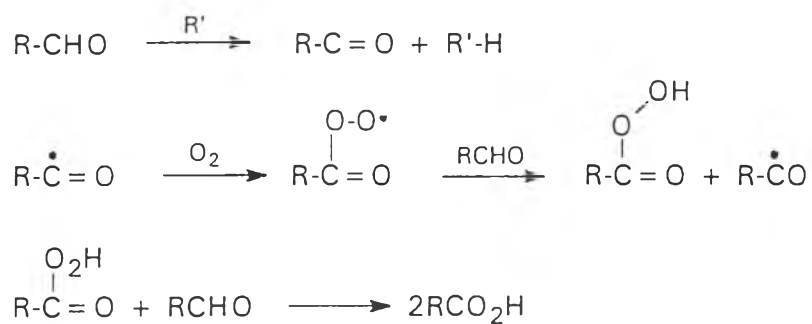
$$\cdots\cdots(2.3)$$

3. By removal of hydride ion, as in the *Cannizzaro* reaction[49], *e.g.*

$$\cdots\cdots(2.4)$$

4. By insertion of oxygen, as in the epoxidation of an olefin by a peracid[49]:

$$\text{C}=\text{C} + \text{R-C-O-OH} \longrightarrow \text{C}-\text{C} + RCO_2H$$

.....(2.5)

5. By a concerted reaction in which the oxidizing agent undergoes a two electron reduction, as in the oxidation of glycols by lead tetraacetate:

$$-\text{C-OH} + Pb(OAc)_4 \xrightarrow{-2HOAc} \longrightarrow -\text{C=O} + -\text{C=O} + Pb(OAc)_2$$

.........(2.6)

6. By catalytic dehydration, as in the palladium-catalyzed conversion of cyclohexane to benzene. Alicyclic rings which contain some unsaturation can be dehydrogenated on those catalysts which are successful for hydrogenation. Palladium on charcoal or asbestos is the most commonly used, *e.g.* the reduced isoquinolines obtained by the Bischler-Napierralski synthesis are usually oxidized in this way:

$$\xrightarrow[-H_2]{Pd-C}$$

............(2.7)
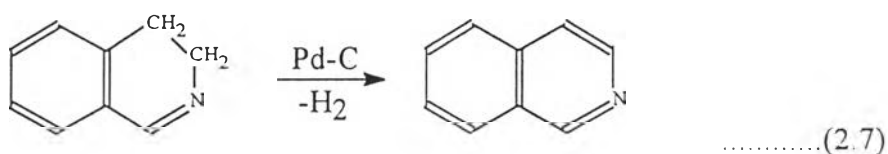
2.2.2 Oxidation of Olefinic Double Bonds

1. *Epoxidation*[49]. Olefinic double bonds react with peracids to give epoxides. The process involves electrophilic attack on the olefin and a simplified representation is:

.........(2.8)
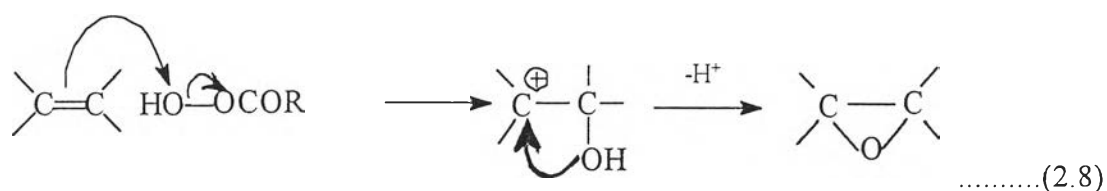
Consequently, electron-releasing groups in the olefin and electron-attracting groups in the peracid facilitate the reaction. In fact, the two steps are closely synchronous, so that a true representation is[49]:


.............(2.9)
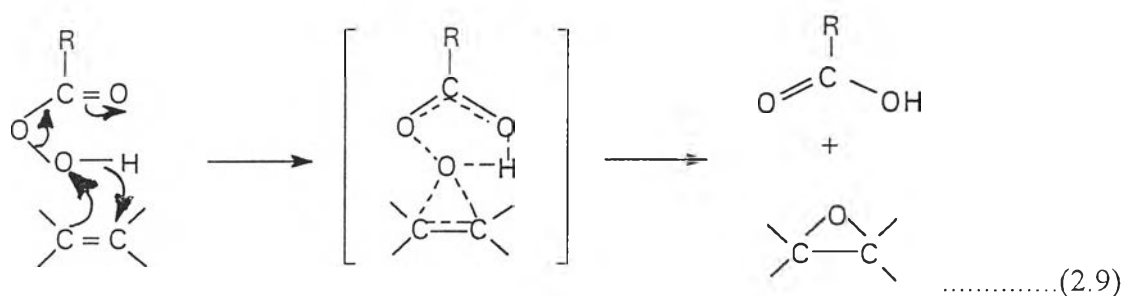
Industrially, ethylene oxide is made by the oxidation of ethylene with atmospheric oxygen at pressure up to 300 psi over a silver catalyst at 200 - 300 °C. The most important use is in the production of ethylene glycol which is required; for example, for the manufacture of terylene.

The use of transition-metal complexes as catalysts for epoxidation reaction has been received attention for the past 2 decades. There are many reasons for this increased interest, *e.g.* the requirement for functionalization of lower alkenes formed as by products in the manufacture of gasoline by oil cracking, the interest in

understanding reaction of biological molecules, the need for selective oxidation, and the preparation of compounds with a specific structure. The transition-metal complexes seem to fulfill some of these requirements, and today many different systems are available so that one can utilize a variety of oxygen sources for the epoxidation reaction. The transition metals which can catalyze epoxidation are the group IVB (Ti, Zr, Hf) until group IB (Cu, Ag, Au).

For example, titanium (IV) alkoxides catalyze the epoxidation of alkenes with an alkyl hydroperoxide as oxygen donor[50]. The reaction is as follows:


$$\dots\dots\dots\dots(2.10)$$
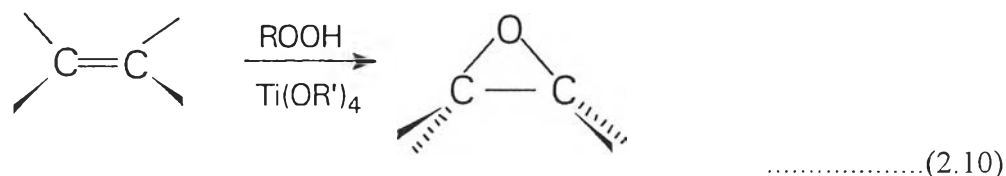
It has been claimed that propylene is oxidized to propylene oxide in 93 - 94 % yield at 96% ethyl hydroperoxide conversion[51].

Titanium dioxide,[52] oxotitanium diacetylacetonate and oxotitanium porphyrin[53] have been used as catalysts for epoxidation with *tert*-butyl hydroperoxide (TBHP) as oxygen donor but the catalytic properties of these complexes are not as good as those of the silicon dioxide supported titanium complexes. The reaction is as follows:


$$\dots\dots\dots(2.11)$$
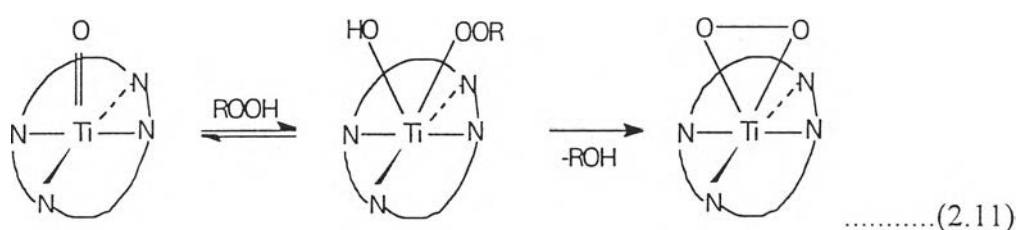
Molecular oxygen has also been applied as oxidant in vanadium-catalyzed epoxidation. $CpV(CO)_4$, $VO(acac)_2$ and V_2O_5 have been found to be able to catalyze

the stereoselective oxidation of cyclohexene to *cis*-1,2-epoxycyclohexan-3-ol as the major product[54].

$$\text{(cyclohexene)} + O_2 \xrightarrow{\text{V-catalyst}} \text{(cis-1,2-epoxycyclohexan-3-ol)}$$

.................(2.12)
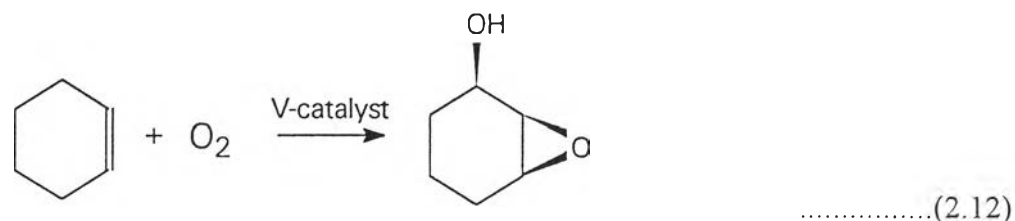
Oxochromium (V) complexes formed from chromium (III)-salen or -*meso*-tetraphenylporphyrinato (TPP) complexes with iodosobenzene also achieve the conversion of alkene to epoxide[55]. The oxygen atom is successively transferred from the oxidant, *e.g.* iodosobenzene, to the chromium (III) complexes acting as catalysts and hence to the alkene.

$$\text{C}{=}\text{C} + \text{PhIO} \xrightarrow[\text{Cr(III)TTP}]{\text{Cr(III) salen or}} \text{(epoxide)} + \text{PhI}$$
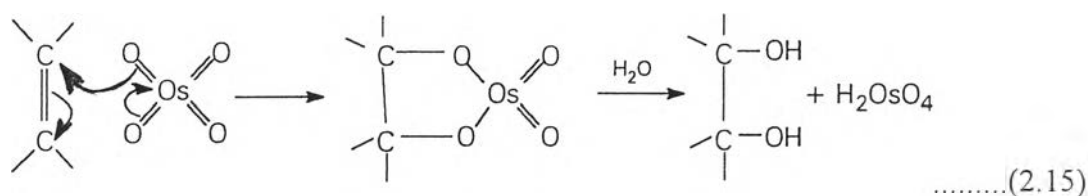
.............(2.13)
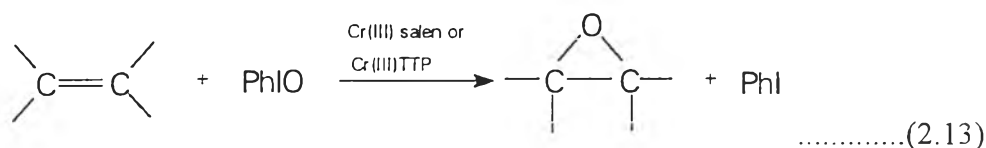
Silver is a uniquely effective catalyst for heterogeneous epoxidation with molecular oxygen as oxidant, but the reaction is mainly restricted to the selective oxidation of ethylene oxide[56]. The epoxidation of alkenes other than ethylene results in low epoxide yield, and little use of silver catalysts has been made for other alkenes.

$$\text{C}{=}\text{C} + 1/2 O \xrightarrow{\text{Ag}} \text{H}{-}\text{C}{-}\text{C}{-}\text{H}$$

.............(2.14)
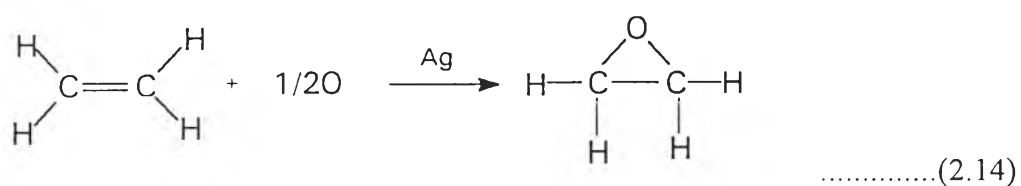
2. Diol formation

Olefin can be directly converted into diol by the use of osmium tetraoxide as catalyst. The addition of an olefin to osmium tetraoxide in ether causes the rapid
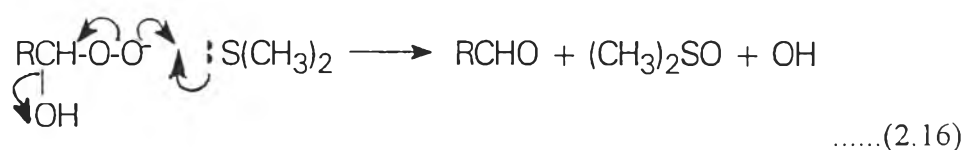
precipitation of a cyclic osmate ester. Pyridine, which complexes the osmium atom in the ester, is often added as a catalyst. The ester is then hydrolyzed, commonly with aqueous sodium sulphite, to give a *cis*-1,2-diol:

$$\begin{array}{c}\text{(structure)} \xrightarrow{} \text{(cyclic osmate ester)} \xrightarrow{H_2O} \quad \begin{array}{l} \overset{|}{C}-OH \\ \overset{|}{C}-OH \end{array} + H_2OsO_4 \end{array}$$
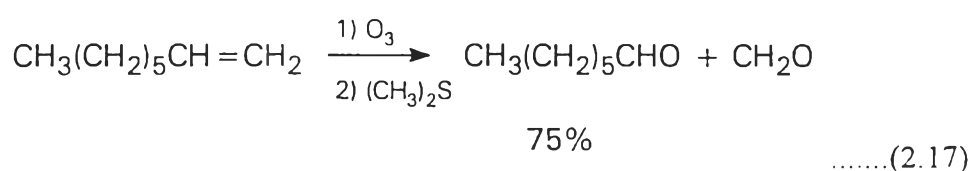
..........(2.15)

Osmium tetroxide is both highly toxic and expensive, but it is a valuable reagent because of its specificity for olefinic bond and ease of its application.

3. *Cleavage of the double bond*

The reactive double bonds can easily cleaved by ozone, the Lemieux reagent and chromium (VI) oxide, with ozone, the reaction called ozonolysis. It is often more useful to carry out the solvolysis in the presence of a reducing agent with zinc and acetic acid, hydrogen on a metal catalyst, or dimethyl sulphide. In either case, only carbonyl compounds are formed because dimethyl sulphide has the advantages that other reducible groups in the compound are not affected and its suitable system from its ability to reduce hydroperoxy compounds:

$$\underset{\underset{OH}{|}}{RCH\text{-}O\text{-}O} \quad :S(CH_3)_2 \longrightarrow RCHO + (CH_3)_2SO + OH$$

......(2.16)

For example,

$$CH_3(CH_2)_5CH=CH_2 \quad \xrightarrow[\text{2) }(CH_3)_2S]{\text{1) }O_3} \quad CH_3(CH_2)_5CHO + CH_2O$$
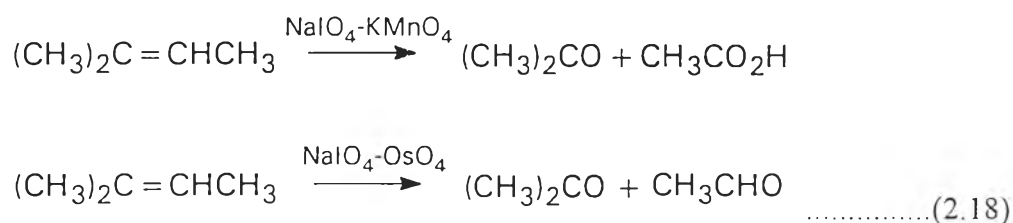
75%

......(2.17)

Acetylenic compounds are also oxidized by ozone, but they generally react at only about one-thousandth the rate of olefins, just as they are less reactive than olefins towards other electrophiles. Reaction with acetylenes give carboxylic acids, together with small amounts of α-dicarbonyl compounds, probably by a mechanism analogous to that for olefins.

Ozone is unpleasant to handle and is not selective for olefins: *e.g.* secondary alcohols may be oxidized to ketones and tertiary C-H bonds to alcohols. Ozone has therefore largely been replaced by the Lemieux reagent, which consists of dilute aqueous solution of sodium periodate, with a catalytic quantity of potassium permanganate or osmium tetroxide. In each case, the olefin is first oxidized to the *cis*-diol which is then cleaved by the peroxidate to give aldehydes and/or ketones. The permanganate reagent then oxidizes aldehydic products to caboxylic acids. The low-valent state of manganese and osmium generated during the reaction are reoxidized by the peroxidate to their original state, so that only catalytic quantities are required. The reactions are rapid at room temperature and are selective for olefins, *e.g.*:

$$(CH_3)_2C = CHCH_3 \xrightarrow{NaIO_4\text{-}KMnO_4} (CH_3)_2CO + CH_3CO_2H$$

$$(CH_3)_2C = CHCH_3 \xrightarrow{NaIO_4\text{-}OsO_4} (CH_3)_2CO + CH_3CHO \quad \text{................(2.18)}$$

According to the toxicity of osmium tetroxide, the cleavage of olefinic bonds with chromic oxide is the alternative. The cleavage of olefinic bonds with chromic oxide is competitive with oxidation of allylic C-H bonds; *e.g.* cyclohexene gives a mixture of 3-cyclohexenone and adipic acid:

...............(2.19)
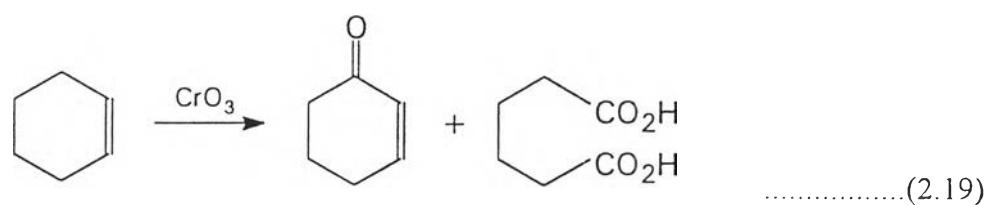
The use of partially aqueous medium favors the cleavage process, whereas anhydrous medium such as glacial acid favors allylic oxidation. In addition, cleavage is promoted by the presence of phenyl substituents, evidently because the first step involves the formation of a carbonium ion which is stabilized by adjacent aromatic ring:

...............(2.20)