Chapter 2

Theory

2.1 Zeolites

Zeolites[31] 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 categorized based on their structures.[32-33] 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.
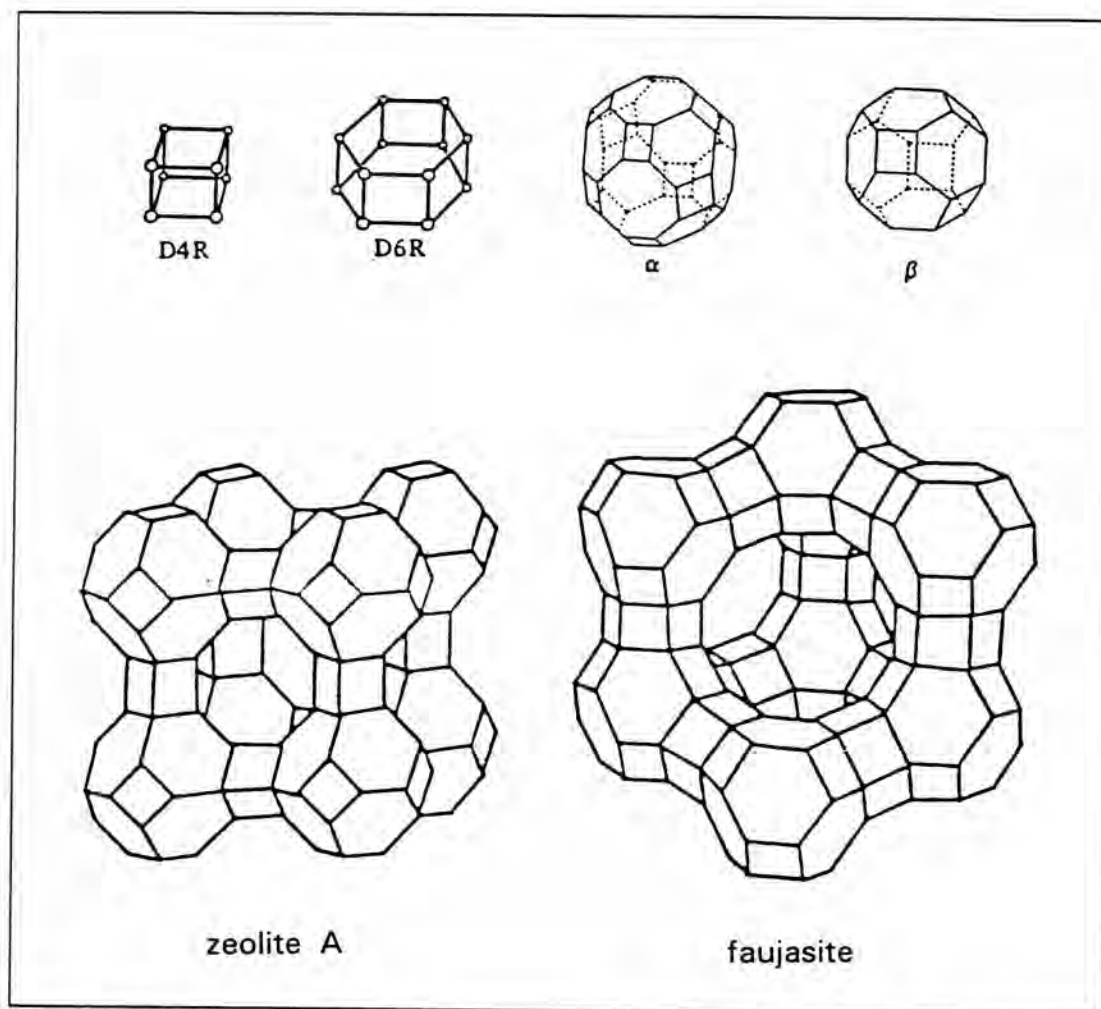

zeolite A   faujasite

Figure 2.1 : Topologies of the structural building units and the structures of zeolite A and faujasite-type zeolites.

For example, Figure 2.1 illustrates the building units and structures of zeolite A and faujasite (including zeolites X and Y). The 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 differrent 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 across the type II sites. Type III

sites are located in the supercage, further from the hexagonal faces than the type II sites.

For hydrated 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 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 repotrted.[31] There are 8 supercages per unit cell, therefore, 3.82 Na^+ ions on average reside in the supercages. With four 6-rings per supercage, there is about 1 Na^+ ion per 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.
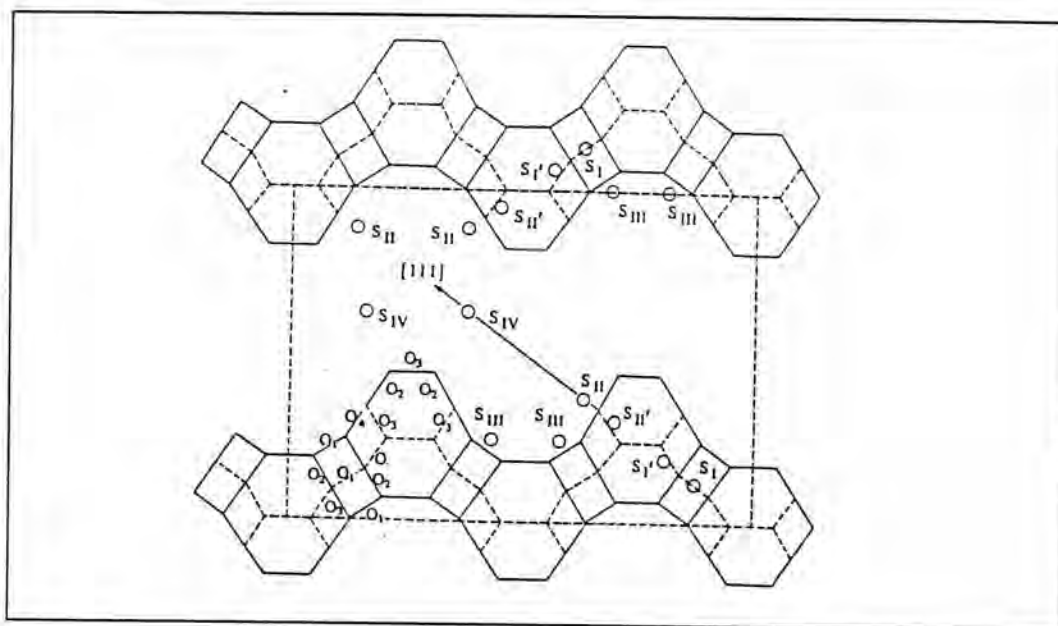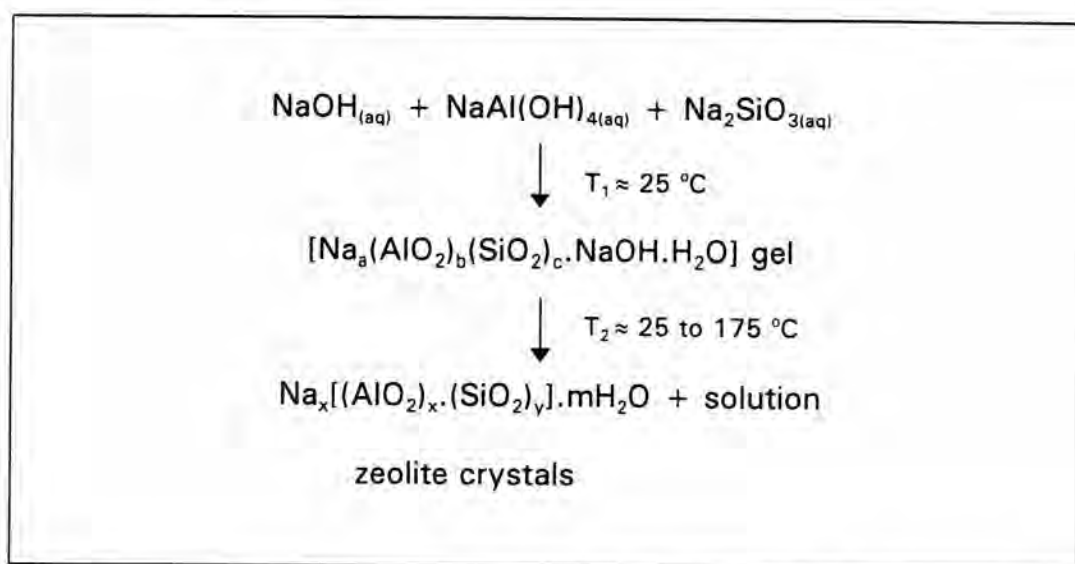

Figure 2.2 : Locations of cation sites in zeolite Y.

2.1.2 Process of Zeolite Formation

In a four-component system $Na_2O-Al_2O_3-SiO_2-H_2O$,[31] zeolite is commonly crystallized from a molecularly inhomogeneous system referred to as a gel. The gel is defined as a 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 crystallization is represented in Scheme 2.1.

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

$$\downarrow \quad T_1 \approx 25\ ^\circ C$$

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

$$\downarrow \quad T_2 \approx 25\ to\ 175\ ^\circ C$$

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

zeolite crystals

Scheme 2.1 : Gel preparation and crystallization in the $Na_2O-Al_2O_3-SiO_2-H_2O$ system.

The gel material dissolves contiuously and are transported to the nuclei crystals in the liquid phase. A schematic representation 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.
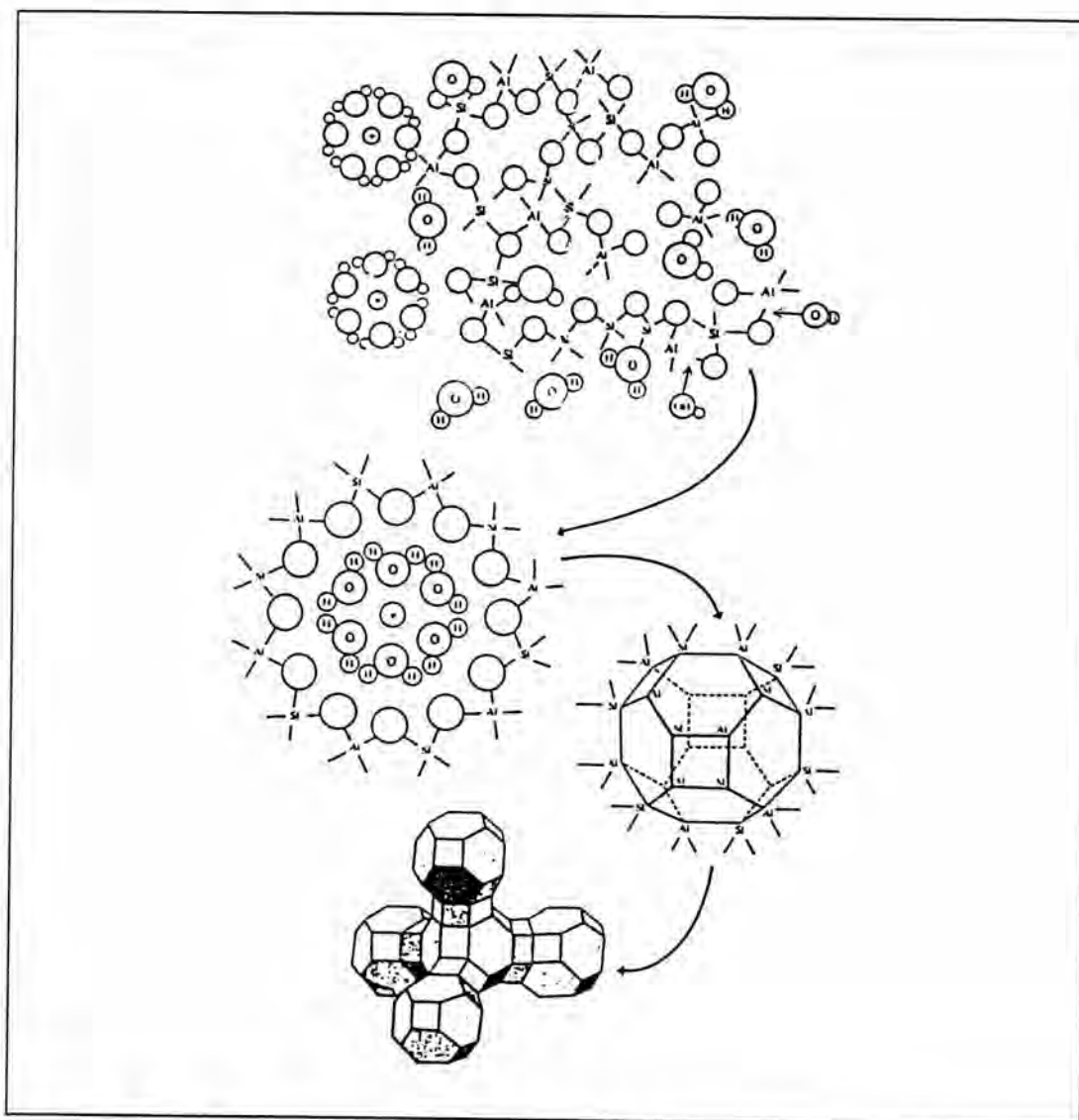

Figure 2.3 : Representation of the formation of zeolite crystals in a hydrous gel.

2.1.3 Factors Influencing Zeolite Formation

Three variables have a major influence on crystallized zeolite structures[32-34]: the gross composition of the reaction mixture, temperature, and time. There are also 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 4. Anions (other than [OH-])

    2. [OH-]   5. H_2O content

    3. Cations

        a. Inorganic

        b. Organic

● Time

● Temperature

● History-dependent factors

    1. Aging

    2. Stirring

    3. Nature of mixture

    4. Order of mixing

2.1.4.1 Reaction Mixture Components

Each component in the reactant mixture contributes to specific characteristic of the gel and to the final material obtained.[34-35] Table 2.1 provides a broad listing of individual components of the mixture and the primary influence within that reaction mixture.

Table 2.1 : The effect of selected variables on the final crystalline products of 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

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.
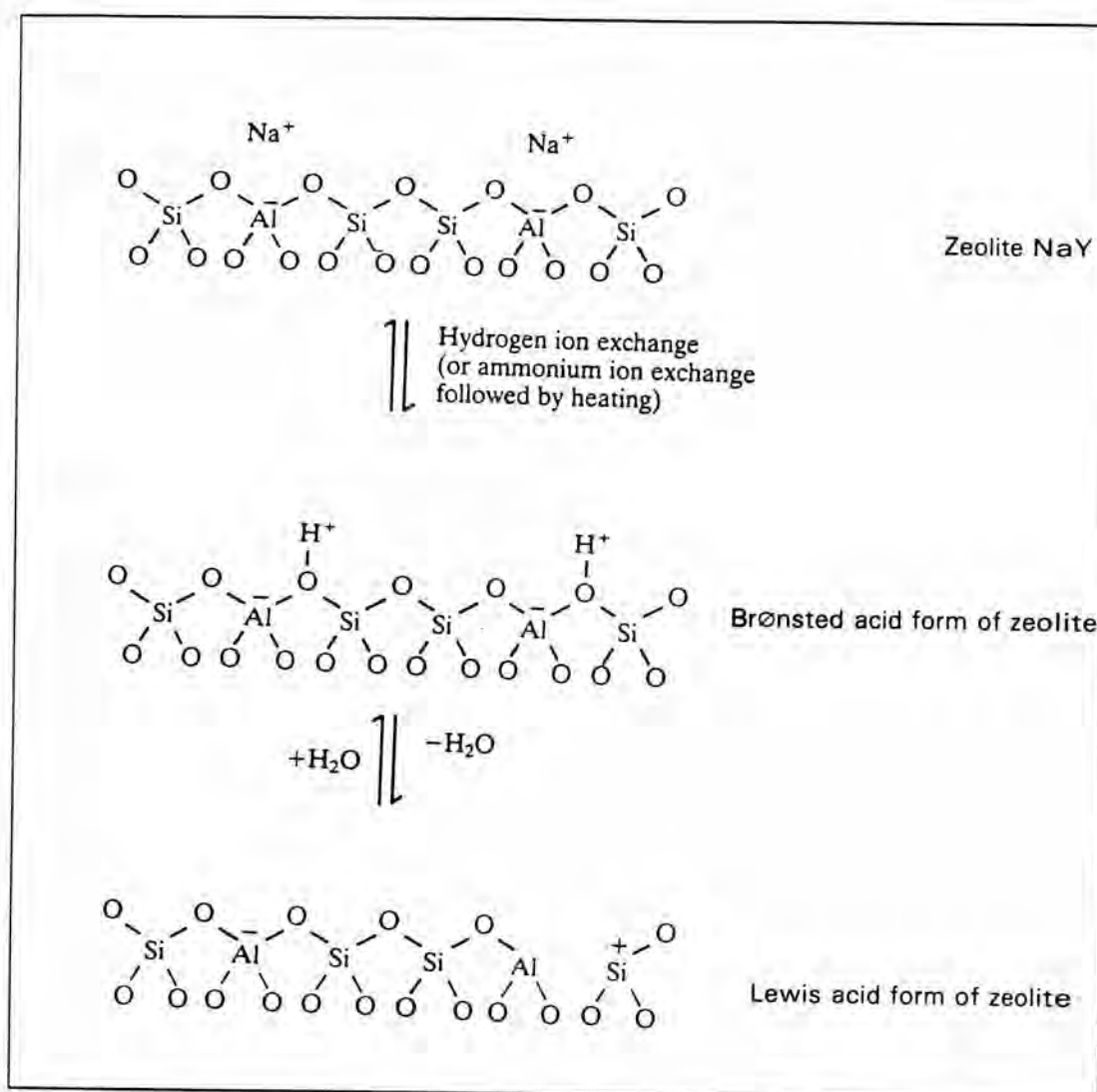
2.1.3.2 Temperature

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.[34,36] 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, as a parameter, can be optimized in the synthesis of many zeolites.[34,37] 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 the other phases while also minimizing the time needed to obtain the desired crystalline phase.
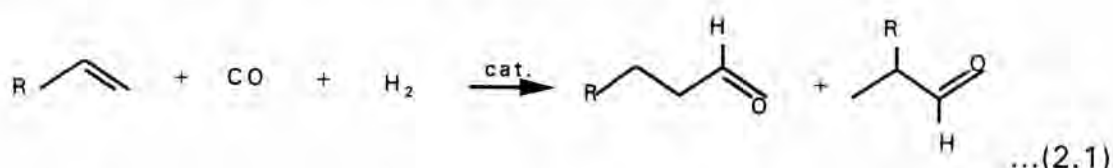
2.1.4 Hydrogen-Form of Zeolites

In a normal sodium-form zeolite, a sodium cation balancing a negative charge of each AlO_2^- tetrahedron can be, in some cases, readily exchanged for protons by direct reaction with an acid, giving surface hydroxyl groups-the Bronsted sites. Alternatively, if the zeolite is not stable in acid solution, the hydrogen form can be generated by exchange with ammonium ions from an aqueous solution of ammonium chloride or ammonium nitrate, and subsequent heating above 375 °C so that ammonia is driven off, leaving protons as the counter ions of the framework. This method is known as deammination of the ammonium-form zeolites. Further thermal treatment at higher temperature results in a loss of water from two neighboring hydroxyl groups. This process is generally called dehydroxylation. The dehydroxylation causes the loss of one oxygen per water molecule removed, exposing a tricoordinated Al ion, which is an electon-pair acceptor; this is identified as a Lewis acid site. The formation of these sites[31] is shown in Scheme 2.2.

Scheme 2.2 : Generation of acid sites in zeolites.

2.2 Hydroformylation

The reaction of an alkene with carbon monoxide and hydrogen, catalyzed by metal carbonyl complexes, to form an aldehyde is called hydroformylation (or sometimes the oxo process).[38-40] The general equation may be represented by Equation 2.1:
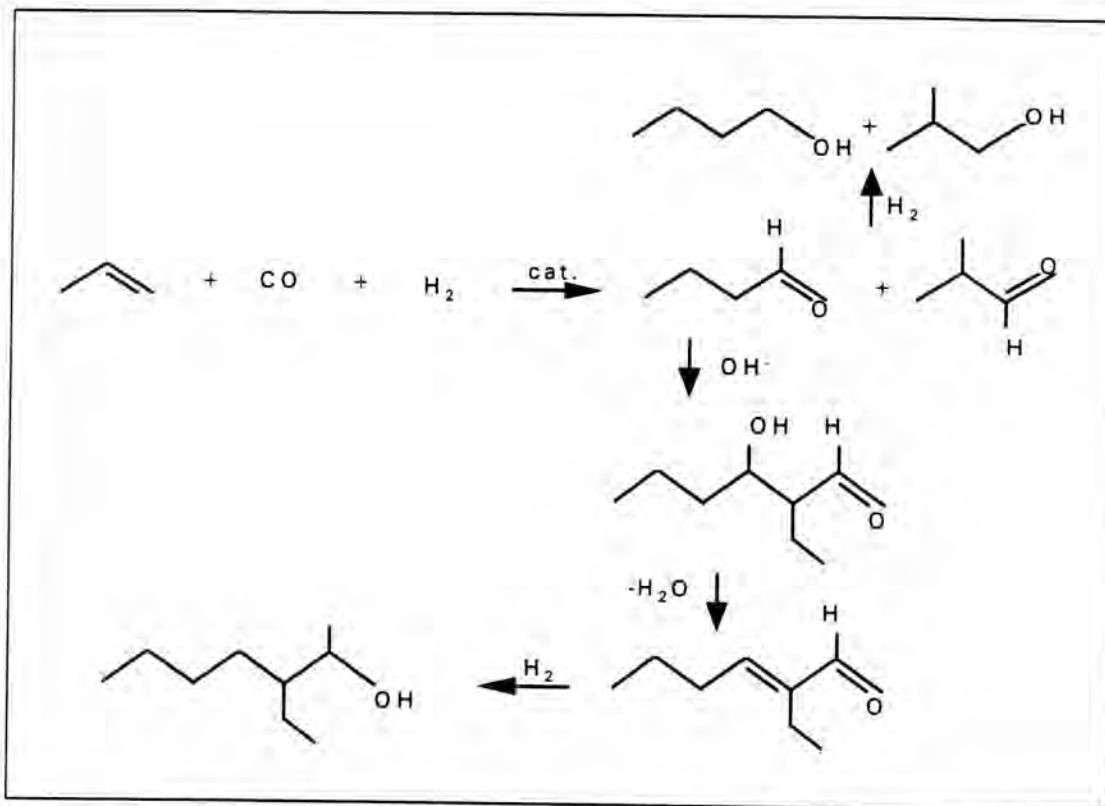

$$...(2.1)$$

Typically, it is the linear product that is of the greatest use. Side reactions include hydrogenation and isomerization of the 1-alkene, hydrogenation of aldehyde products, and aldol condensation of the aldehydes.

2.2.1 Application of Hydroformylation

Hydroformylation is one of the most industrially important homogeneously catalyzed reactions. The resulting primary product, the aldehyde, can be converted into a multitude of industrially important secondary products such as alcohols, acids, diols, amines, or esters.

Propylene[41] is used primarily as the olefin. The resulting n-butylaldehyde can be transformed either to n-butanol via hydrogenation

or, following aldol condensation and hydrogenation, to 2-ethylhexanol, the most important alcohol for plasticizers (see Scheme 2.3).
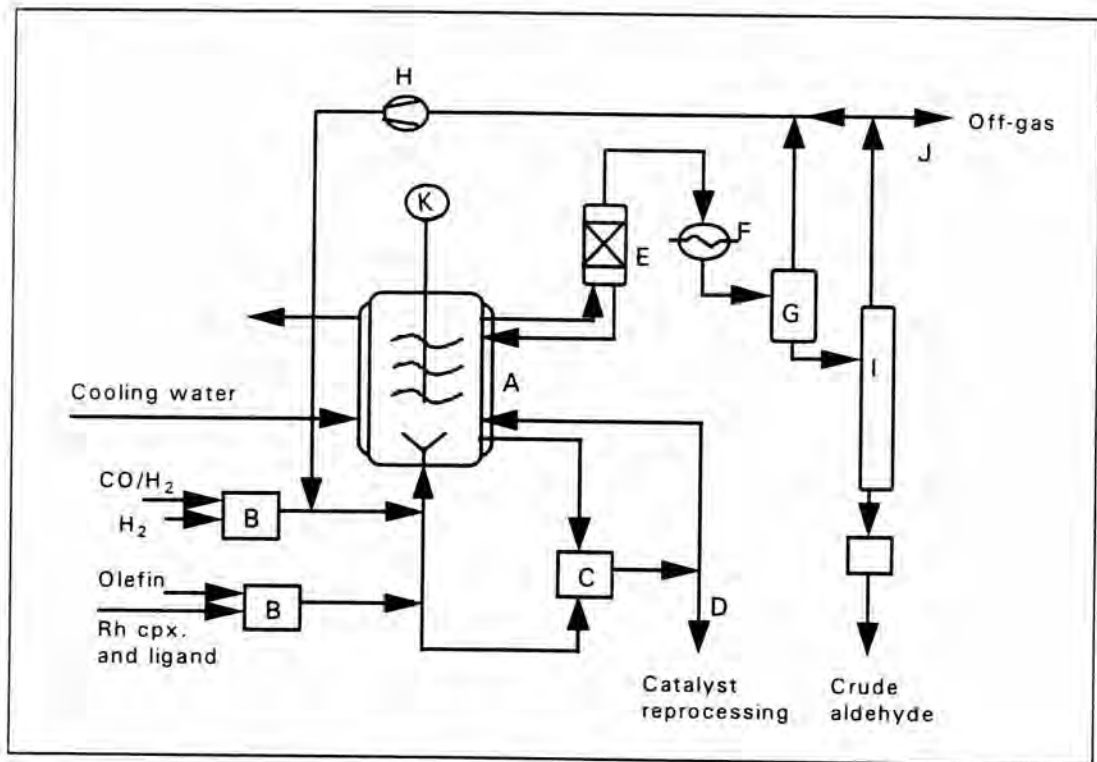

Scheme 2.3 : Hydroformylation and further other reactions.

Starting with higher olefins, one obtained alcohols and acids which are converted further to detergents, lubricating oils, plasticizers, and solvents. The large oxo plants are operated by companies such as BASF, ICI, Kuhlmann, Mitsubishi, Ruhrchemie, Shell, and Union Carbide Company.

2.2.2 Union Carbide Hydroformylation Process

Union Carbide began using tertiary phosphine hydrido rhodium carbonyl catalysts in a commercial hydroformylation process in 1976. Since then some other companies have modified this process. The most important of these, however, is the low-pressure oxo (LPO) process jointly developed by Union Carbide, Davy McKee, and Johnson Matthey. For example, with $HRh(CO)(PPh_3)_3$ as the catalyst precursor, hydroformylation of propene at 15-20 bar and 85-115 °C gives a high linear to branched aldehyde ratio (92:8). Figure 2.4 shows a schematic diagram of hydroformylation with the LPO process.[42]

The reaction mechanism of $HRh(CO)(PPh_3)_3$ catalyst precursor in the hydroformylation process[43-44] is shown in Scheme 2.4. The high selectivity for linear aldehyde shown by the higher stability of the square-planar intermediate formed in step ② with its trans-oriented phosphine ligands and a terminal alkyl group. As the alkyl group is being formed, the large cone angles of these phosphine ligands sterically favor the formation of the least bulky alkyl ligand which is linear rather than branched.

A = Stirred-tank reactor   G = Separator

B = Reactant purification system   H = Compressor

C = Reprocessing   I = Stripping column
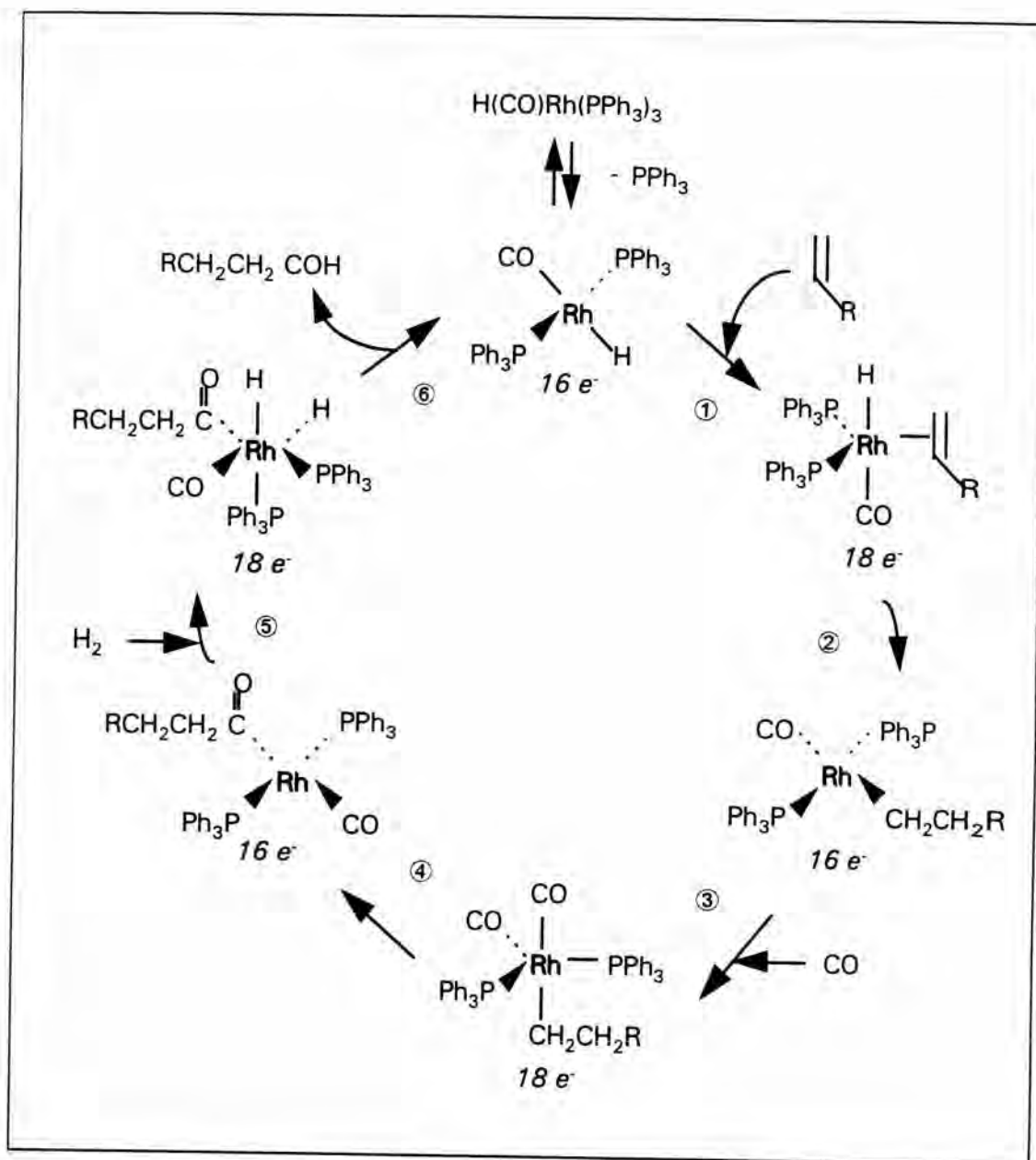
D = To catalyst reprocessing   J = Outlet

E = Demister   K = Motor

F = Condenser

Figure 2.4 : Diagram for LPO process.

Scheme 2.4 : Reaction mechanism for Union Carbide hydroformylation process.

The replacement of cobalt catalyst in the older processes by the modified rhodium catalysts markedly increases the linear/branched product ratio. Linear aldehydes are produced in high yield with very little by-product formation. Reaction temperature and pressure are also lower for the rhodium processes. Although rhodium is about twice more expensive than cobalt, these rhodium catalysts are 100 to 1000 times more reactive than the cobalt catalysts, and their use means cost savings on plant construction and reduced energy consumption because of the milder reaction conditions of the rhodium process. Efficient catalyst recovery will make rhodium-based processes attractive for commercial utilization.