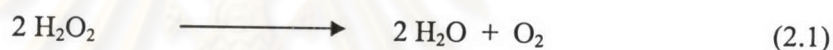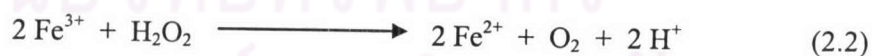# CHAPTER II

THEORY

2.1 Catalysis

2.1.1 Term of Catalysis

Catalysis was designated by Berzelius[35] more than 160 years ago when he studied the reaction of hydrogen peroxide that is shown in equation 2.1

$$2 H_2O_2 \longrightarrow 2 H_2O + O_2 \tag{2.1}$$

and found that several compounds greatly increased the rate of H_2O_2 decomposition. Catalyst was defined as a compound which increases the rate of a chemical reaction, but which is not consumed in the reaction. In the present, scientists know that the catalyst not only increases the reaction rate but also modifies the mechanism and reduces the activation energy barrier of reaction via decreasing in free energy.[36] The example shown in Figure 2.1[35] is the decomposition of H_2O_2 accelerated by Fe^{2+} and Fe^{3+}. H_2O_2 is catalyzed by both Fe^{2+} and Fe^{3+} and their reactions are shown in equation 2.2 and 2.3.

$$2 Fe^{3+} + H_2O_2 \longrightarrow 2 Fe^{2+} + O_2 + 2 H^+ \tag{2.2}$$

$$2 Fe^{2+} + H_2O_2 + 2 H^+ \longrightarrow 2 Fe^{3+} + 2 H_2O \tag{2.3}$$

Fe^{2+} and Fe^{3+} are interchanged each other. This example shows that the iron species enter the reaction mechanism step, but the net equation as shown in equation 2.1 does not give any iron species. Iron ions do not lose after end of the reaction, so they can be reused. The ability to reuse is an important property of catalysts that helps the industry to save the cost.
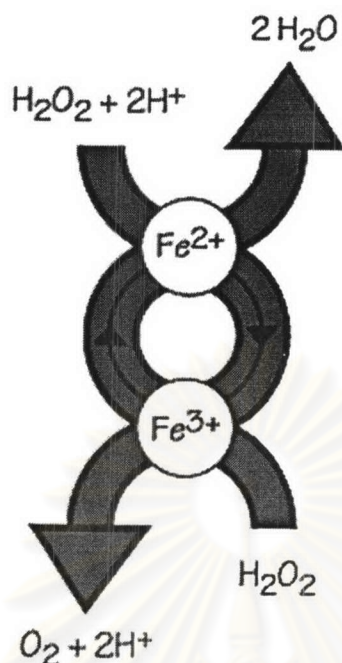
$$2\,H_2O$$

$$H_2O_2 + 2H^+$$

$$Fe^{2+}$$

$$Fe^{3+}$$

$$H_2O_2$$

$$O_2 + 2H^+$$

Figure 2.1 The decomposition of H_2O_2 catalyzed by Fe^{2+} and Fe^{3+}.[35]

2.1.2   The requirement of catalysts

Industrial catalysts are influenced not only by science but also by business, economics, and market. More efficient utilization of raw materials and improved yields with minimal energy required usually lead to greater profits.[4] In addition, the discovery of new catalysts and their application have led to major innovations in chemical processing. Market and business factors combine to encourage or require further improvements in catalyst technology.[36]

The use of catalyst provides a lower manufacturing cost which can come from any of the following:

(1)   reduced equipment costs,

(2)   reduced feedstock costs,

(3)   lowered utility costs,

and (4)   reduced by-product debits.

Figure 2.2 shows the example of beneficial utilization of catalysts. The desired product is 4-methylthiazole which in classical pathway is prepared with more steps (5 steps) than in catalytic pathway (2 steps).[37]
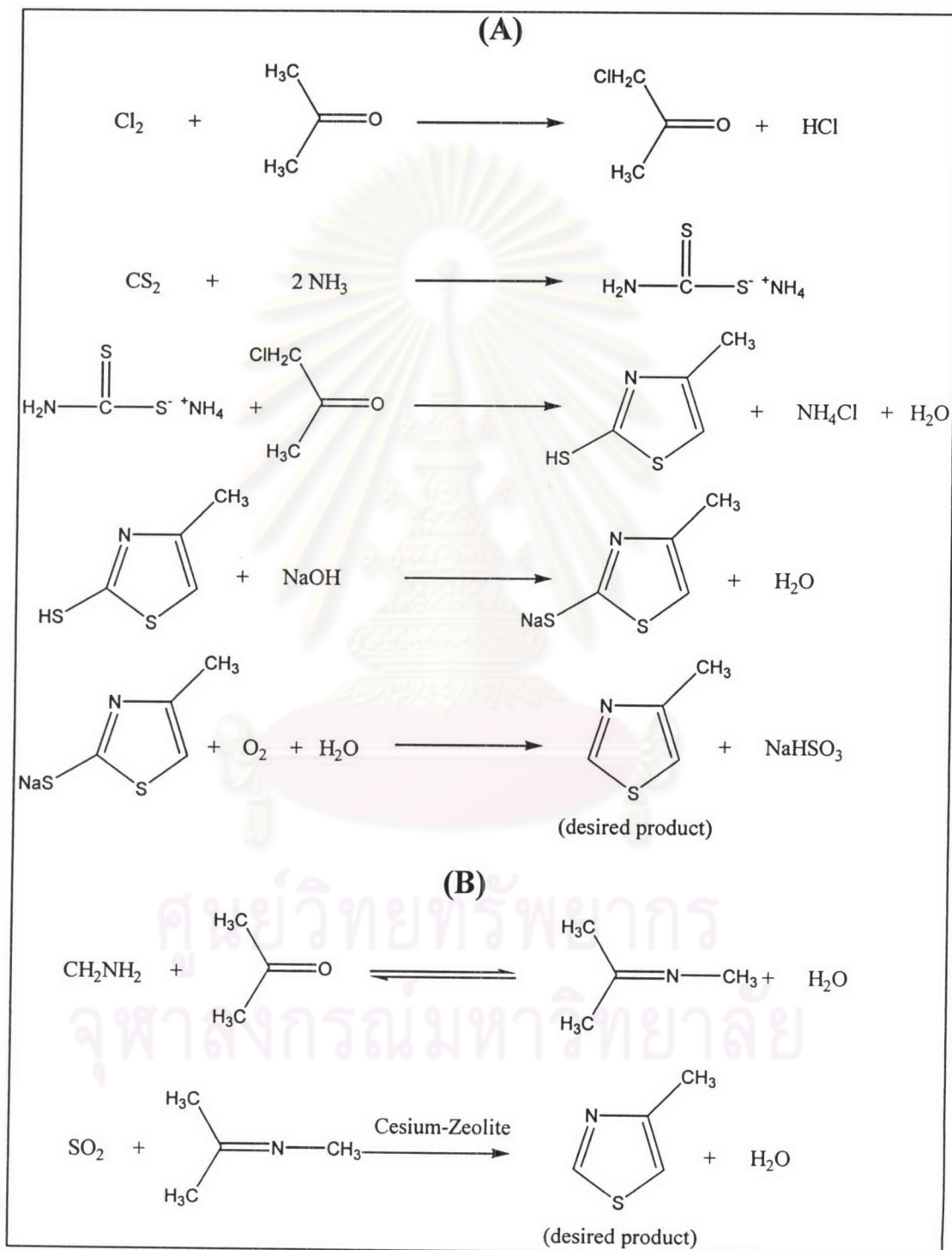

Figure 2.2 The pathways to synthesize of 4-methylthiazole via (A) classical method and (B) catalytic method.[37]

2.1.3   Types of catalysts

Catalysts are classified into 2 types:[5]

1)   Homogeneous catalysts

A homogeneous catalyst works in the single-phase reaction, typically liquid/liquid phase, that is usually stoichiometric and use mild reaction condition.[4] Most homogeneous catalysts concern with the transition metal complexes or organometallic compounds which are generally dissolved in the reaction medium.[7]

2)   Heterogeneous catalysts

A heterogeneous catalyst is found to be immiscible with the reactants; therefore, it is easy to be separated.

Table 2.1 lists the general properties of homogeneous and heterogeneous catalysts. More accessibility and usage at mild condition are the advantage of homogeneous catalysts, however; it is hard to separate them from remaining reactants or products. The operation at mild condition reduces the cost of energy for industry, yet it spends more expansive to separate and recover the homogeneous catalysts. The environment can be affected by the reaction waste if the waste contains the incompletely separated catalysts which are generally toxic.[7]

Table 2.1   Properties of homogeneous and heterogeneous catalysts

Homogeneous catalyst	Heterogeneous catalyst
High accessibility	Low accessibility
High selectivity	High selectivity
Mild condition	Severe condition
Difficulty of separation	Ease of separation
	Ease of regeneration

On the other hand, although the effectiveness and accessibility of heterogeneous catalysts are lower than homogeneous catalysts, the advantage of using the former is the facility to separate and regenerate because the reactant and/or product are different phase from the heterogeneous catalysts. They reduce the contamination of the hazardous catalysts to the surroundings.

Since the middle of the 20th century, the heterogeneous catalysts have been used worldwide about 10 billion dollars annually with 3% annual growth rate that mostly are used in petrochemical industry.[6,38] The development of the heterogeneous catalysts to rise its effectiveness becomes the attractive topic for the researchers.

2.2 Porous silicate materials

2.2.1 Basic silicate structure

The major component of silicate-base materials is silicon and oxygen atoms. Its fundamental unit, named primary building unit, is a tetrahedral complex (SiO_4^{4-}) consisting of a Si^{4+} in tetrahedral coordination with four oxygen atoms as shown in Figure 2.3. The complexity of silicate structures occurs because of the various ways in which the tetrahedral groups may link by the common sharing of oxygen ions to form polynuclear complexes. The connecting of the primary units in one, two, or three dimensions results in the different structures of materials. The structures of silicates can be classified into five main types:[39]

1) Island structure: the SiO_4^{4-} exists as discrete ions in compounds such as sodium calcium orthosilicate, Na_2CaSiO_4. The four oxygen atoms around silicon are not linked to any other silicon atoms, and their charges are balanced by sodium and calcium cations.

2) Isolated group structure: the two or more oxygen atoms at the tetrahedral corners were shared together to form polyanionic groups. The $Si_2O_7^{6-}$ in heminorphite ($Zn_4Si_2O_7(OH)_2$), $Si_3O_9^{6-}$ in benitoite ($BaTiSi_3O_9$), and $Si_6O_{18}^{12-}$ in beryl ($Be_3Al_2Si_6O_{18}$) are the examples of these group presented in Table 2.2.[40]

Silicon atom
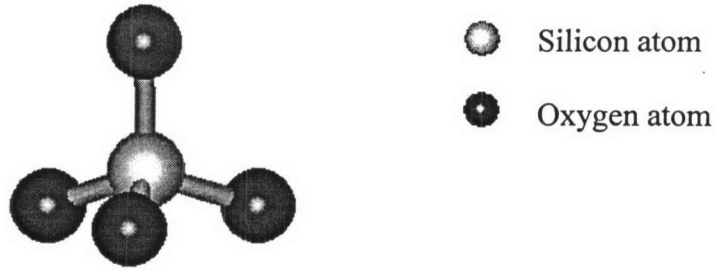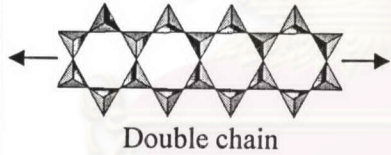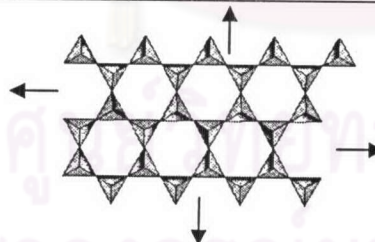
Oxygen atom

Figure 2.3 The Si^{4+} surrounded with four oxygen atoms which is basic unit of structure of silicate materials.

Table 2.2 Structure of silicate compounds[40]

		Formula of negatively charged ion group	Silicon to oxygen ratio	Example
Island		$(SiO_4)^{-4}$	1:4	Olivine
Continuous chains	Single chain	$(SiO_3)^{-2}$	1:3	Pyroxene group
	Double chain	$(Si_4O_{11})^{-6}$	4:11	Amphibole group
Continuous sheets		$(Si_4O_{10})^{-4}$	2:5	Micas
Three-dimensional networks	Too complex to be shown by a simple two-dimensional drawing	SiO_2	1:2	Quartz

3) Chain structure: silicates can also polymerize into infinite chain when two adjacent silicates are mutually joined with each oxygen atom, and are continually linked as linear.

4) Sheet structure: by linking three corners of each tetrahedron to neighboring tetrahedra, structure types of a large group of silicates are found as a two-dimensional planar network of tetrahedra linked to form infinite anions of composition $(Si_2O_5)^{2-}_{\infty}$. Clay mineral, kaolinite $(Al_2Si_2O_5(OH)_4)$, is the well known sheeting silicate linked between two sheeting with Al^{3+} ions in the octahedral sites.

5) Framework structure: Continuous framework structures are resulted when all of the oxygen atoms in the tetrahedra are mutually shared between tetrahedral silicons in three dimensions. Between a pair of silicate, only oxygen can be joined. Molecular sieves are formed in this structure.

2.2.2 Aqueous chemistry of silicates

The outstanding feature of silicates is the spontaneous polymerization into three-dimensional structures out of aqueous solution. This evident depends on the pH, temperature, and silicate concentrations. At pH values less than 8, $Si(OH)_4$ is the dominant species in aqueous solutions of silica at low total Si concentrations ($< \sim 10^{-3}$ M). At higher concentrations the silanol (Si-O-H) groups spontaneously polymerize to yield higher oligomers linked by a disiloxy bond illustrated in Equation 2.4.

$$-Si-O-H + Si-O-H \longrightarrow -Si-O-Si- + H_2O \qquad (2.4)$$
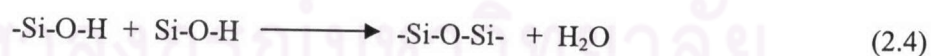
Reaction is the most favorable when one of the silanols is deprotonated to Si-O- group. These oligomers grow into colloid-sized silica particles, in which larger particles grow at the expense of smaller ones to form a sol. Ultimately these colloids themselves become crosslinked, and once the whole volume is crosslinked, the sol has become a gel. Water is still present, but only interstitially in an interconnected three-dimensional polymeric network. Gelation occurs most rapidly at moderately acidic pH about 5-6; it is slowest at the silica

isoelectric point (pH~2), probably because the $Si(OH)_4$ monomers are all fully protonated. At even l ower p H, p olymerization e vidently i s catalyzed by H^+. At higher pH (>8), however, much more concentrated silicate solutions are stable. In part this is because disiloxy bonds undergo nucleophilic attack by OH^- (shown in Equation 2.5) via a 5-coordinate intermediate.

$$-Si-O-Si- + \ OH^- \longrightarrow Si-O- + \ Si-OH \qquad (2.5)$$

This is also the mechanism by which silicates dissolve in basic solutions. In part, however, the sols are stabilized by mutual electrostatic repulsion; the colloidal particles acquire a negative charge through partial deprotonation because silanol groups on large polymeric units are much more acidic. From the study of Swaddle and co-workers[41], t he s ilicate s tructures i n alkaline solution could be classified into 25 forms as shown in Figure 2.4. The distribution of these species depended on pH, temperature, cation, and silica concentration. The formation of monomer and small oligomer was favored when the temperature or pH was increased and the silicon concentration was reduced.[42]
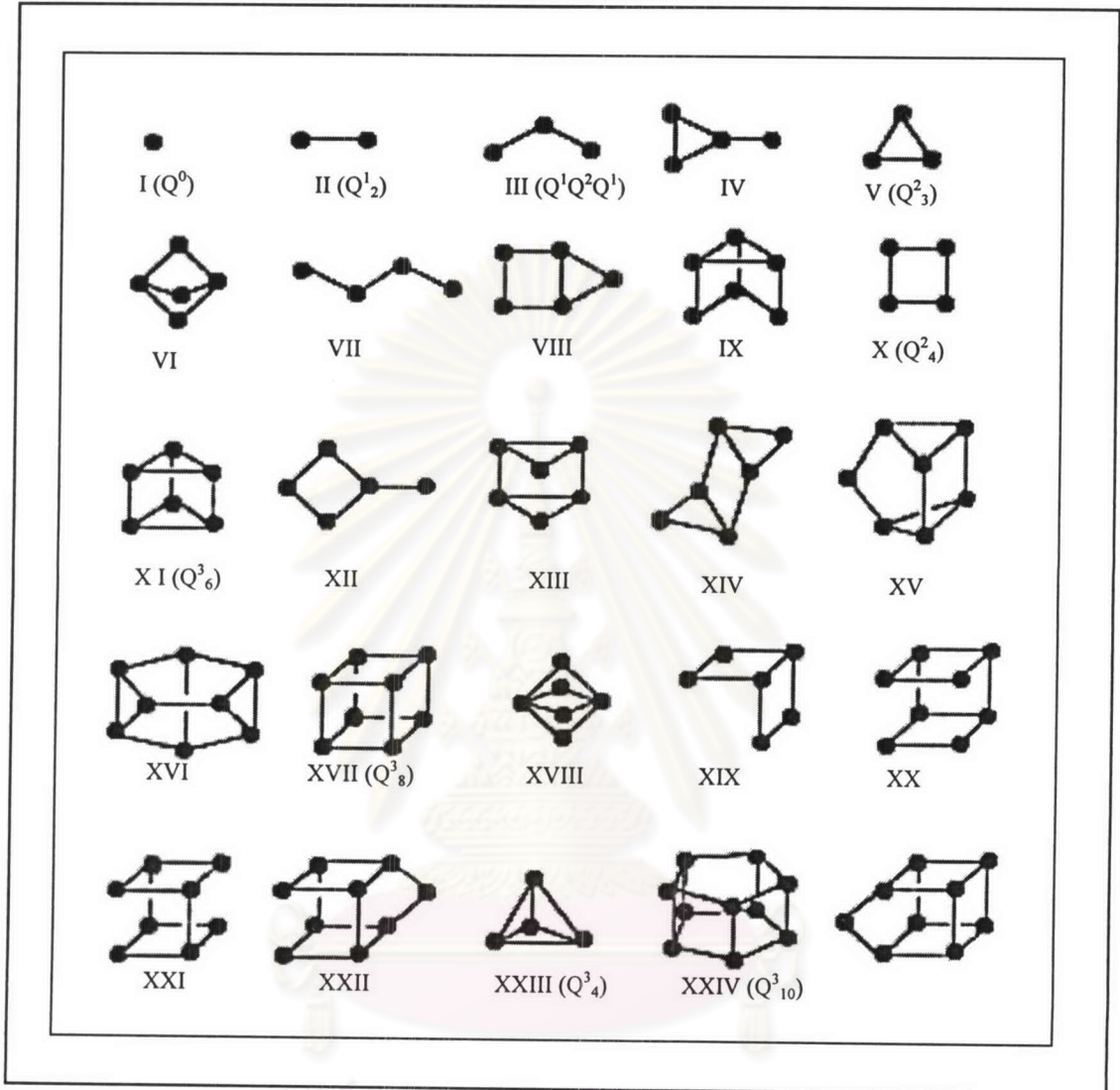
16

Figure 2.4 Silicate species identified by ^{29}Si NMR in alkaline aqueous solution: filled circles representing tetrahedral Si atoms and lines representing Si atoms linked through an oxygen atom.[41]

2.2.3   Zeolites

Zeolites are the most popular microporous molecular sieve. The first usage of zeolite as the catalysts occurred in 1953 when zeolite Y was used as an isomerization catalyst by Union Carbide, and then in 1962 zeolite X was used as a cracking catalyst by Plank and Rosinski.[43] At present, the billions of dollars per annum were saved from using the zeolites in the cracking of the cheaper crude oil to the higher value products.

The zeolites are the crystalline materials whose structure comprises of silicate frameworks in which aluminate is substituted partly. They are obtained by two methods.[43,44]

1)   Natural zeolites: Some are naturally occurring and are recovered by a mining operation, such as mordenite, chabazite, and stilbite. The natural zeolites usually form as spectacular crystals.[43] In early time, they were used as jewellery, particularly as earring, cuff links, and brooches. Next in 1891 Murray and Renard could recover the zeolites from red mud that was found at the bed of the Pacific Ocean.

2)   Synthetic zeolites: In 1938 Barrer[43] demonstrated that some zeolites could be synthesized in a form identical to their natural zeolites by imitating the natural volcanic conditions which are high temperatures, salt concentrations, and autogeneous pressures.[43] Until in 1949 the workers at Union Carbide, directed by Milton, developed a hydrothermal synthesis method using reactive alkali-metal aluminosilicate gels with autogeneous pressure. This method was performed at 373 K that is lower temperature than volcanic temperature. The examples of synthetic zeolites are ZSM-5 and MCM-22.

Both types of zeolites have economic importance. The natural zeolites are dispersed worldwide and cheaper; however, many researchers synthesized new synthetic zeolites that have different structures and properties from the natural zeolites. Some different properties are the desirability of industry, such as high acidity of ZSM-5.

The reasons for their success in catalysis are related to the following specific features of these materials[45]: (1) They have very high surface area and adsorption capacity. (2) The adsorption properties can be controlled. (3) Active sites, such as acid site, can be

generated for a particular application. (4) Their intricate channel structure allows the zeolites to present different types of shape selectivity, which can be used to direct a given catalytic reaction toward the desired product avoiding undesired side reaction. (5) Their structure presents the high thermal and hydrothermal stabilities.

2.2.3.1 Structure of zeolites

Zeolites, conventionally defined by Szostak[5] and Breck[39], are crystalline, hydrated aluminosilicates of group I and group II elements such as sodium, potassium, magnesium, and barium. The zeolites consisting of aluminate (AlO_4^{5-}) and silicate (SiO_4^{4-}) are defined as the framework structure with infinitely extending three-dimensional network. In the structure, the linking between alumina and silica or silica and silica is performed through sharing oxygen atom at the corner of each tetrahedral as shown in Figure 2.5.[5] The direct connection of two alumina units is forbidden in zeolites.
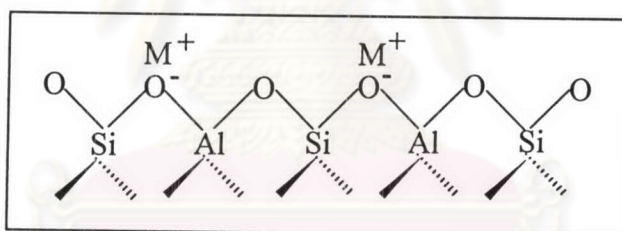
Figure 2.5 The framework structure of zeolites.[5]

As shown in Figure 2.5, when an aluminate is substituted in the framework of silica, it generates a negative charge that is balanced with cation at the nonframework position. Thus it can say that the amounts of AlO_2^- in framework determine the framework charge and the amounts of balancing cations. The general formula for the composition of zeolites is

$$M_{x/n} [(AlO_2)_x (SiO_2)_y] \cdot z\, H_2O$$
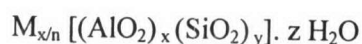
Where M is the balancing cation with n positive charges, commonly group I or group II ion and z is the number of water molecules in the channels and cavities of zeolites.

All of zeolites are constructed from the smallest part, named a primary building unit of silicate or aluminate tetrahedra. Then the tetrahedra are joined with oxygen sharing to generate the larger unit, called a secondary building unit, which is divided into nine types. They consist of 4, 6, and 8-member single rings, 4-4, 6-6, and 8-8 member double rings, and 4-1, 5-1, and 4-4-1 branched rings as illustrated in Figure 2.6. These units combine together in different arrangements resulting the various structures of zeolites and their properties. The related structure properties include:

1) High degree of hydration and the behavior of zeolite water

2) Low density and large void volume when dehydrated

3) Stability of the crystal structure of many zeolites when dehydrated and when as much as 50 vol% of the dehydrated crystals are void

4) Cation exchange properties

5) Uniform molecular-sized channels in the dehydrated crystals

6) Various physical properties such as electrical conductivity

7) Adsorption of gases and vapors

8) Catalytic properties.
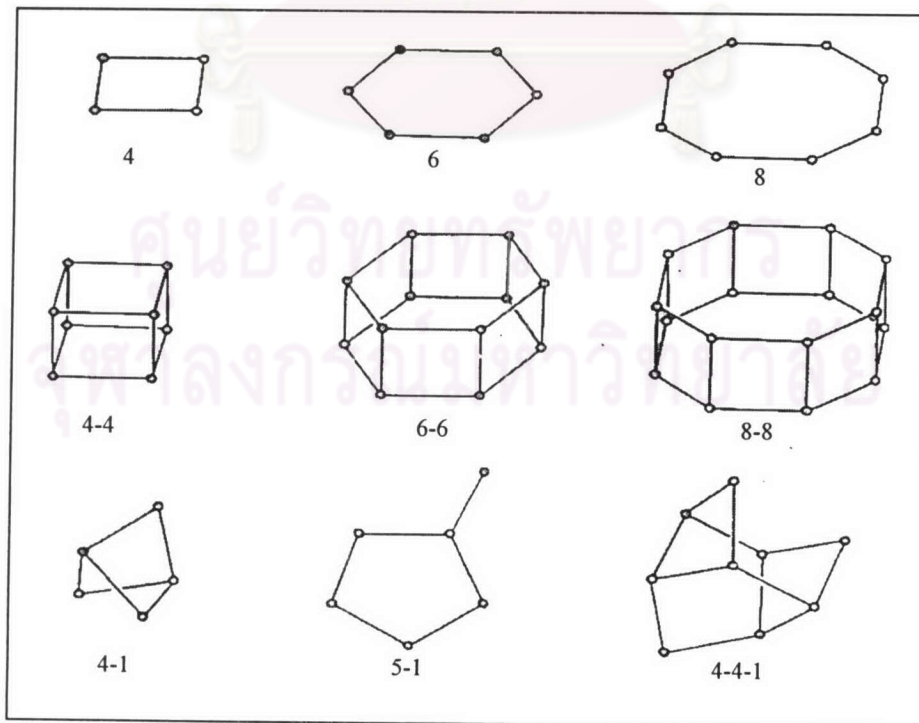
Figure 2.6 The nine types of secondary building unit found in zeolites.[5]

2.2.3.2 Internal channel structure in zeolites

The nature of the void spaces and the interconnecting channels in zeolites is important in determining the physical and chemical properties. Three types of channel systems are identified.

1. One-dimensional system: The channels do not intersect together that is found in analcime as shown in Figure 2.7.

2. Two-dimensional system: The main parallel channels are crossed by perpendicular channels, but between sheets are not linked such as mordenite.

3. Three-dimensional system: This system can be divided into two types. In one type, the channels are equidimensional; the free diameter of all the channels is equal, regardless of direction. The other type consists of three-dimensional intersecting channels, but the channels are not equidimensional; the diameter depends upon the crystallographic direction.

Figure 2.7 The examples of dimensional pore system: a) one-dimensional, b) two-dimensional, and c) three-dimensional pore system.[5]

2.2.3.3 Aperture sizes in dehydrated zeolites

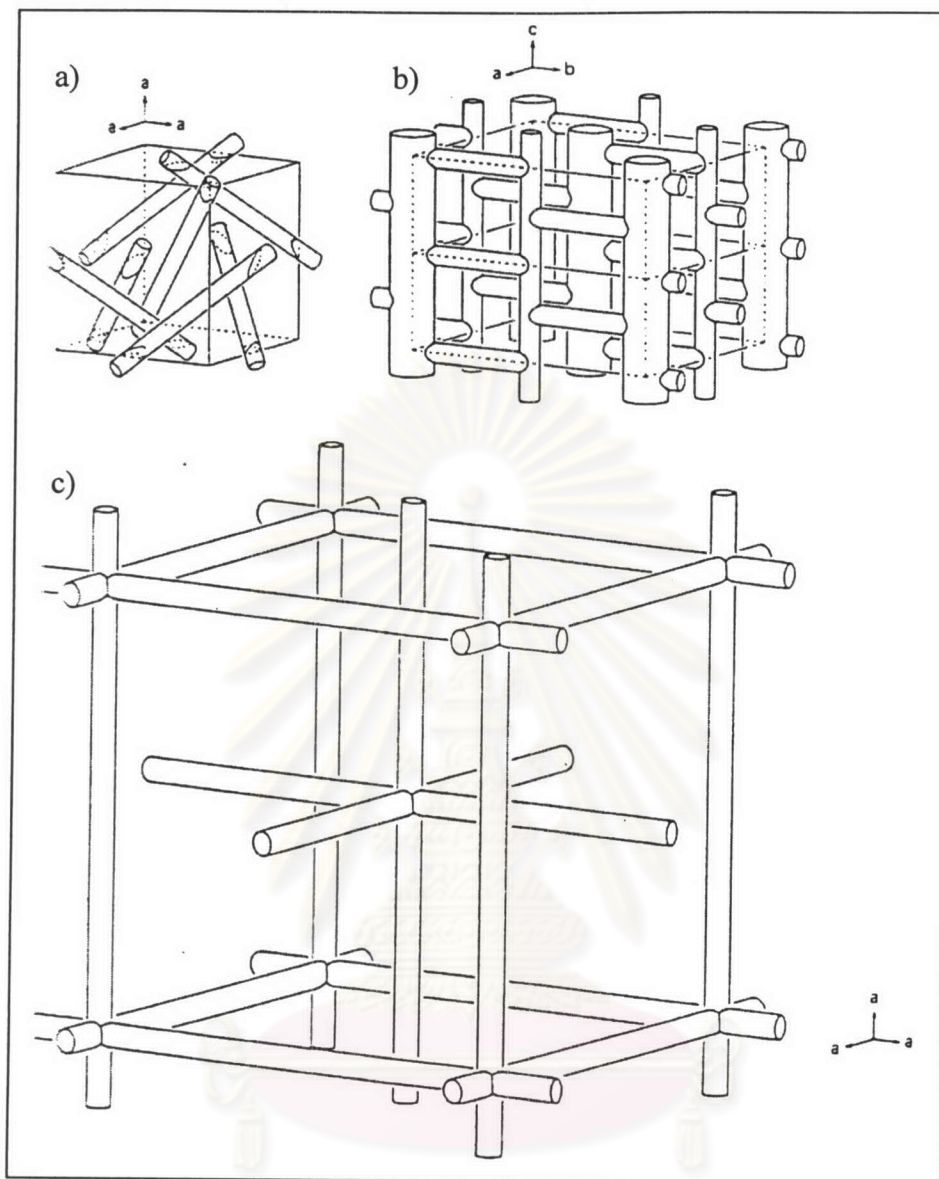The apertures of zeolites are bounded by oxygen atoms of connected tetrahedra and, in the first approximation the limiting size of the aperture is governed by the size of the ring. In general, these rings involve 6, 8, 10, or 12 oxygen atoms; the maximum opening is formed by regular rings as shown in Table 2.3[39] and the examples are presented in Figure 2.8.[5] The rings can be distorted to varying degrees; for example, in the zeolite A structure, the main aperture is formed by an 8-oxygen ring which is quite regular. The free diameter of 4.2-4.3 Å is based on the assumption that the oxygen ions are rigid hard spheres and is calculated from the interatomic distance of two opposing oxygens across the ring. The accepted diameter of the oxygen ion in general silicate structure is 2.7 Å. This is an oversimplification of the real situation since the electron distribution of the atom does not fall off abruptly at the limit of the ionic radius. To consider the interaction between molecules and the oxygen atoms in the aperture rings as hard spheres during adsorption is incorrect due to the importance of other factors such as the effect of temperature and thermal vibration of the oxygens in the aperture rings.

The restrict channel structures of zeolites create the shape and size selectivity which plays a very significant role in catalytic applications of zeolites. As shown in Figure 2.9[5], three types of selectivity are reactant selectivity, product selectivity, and transition-state selectivity. Reactant selectivity is required when the reactants in production process are contaminated or are not purified. The impurities in larger size or obstructive shape cannot access to the active sites inside zeolite's pores. For product selective, only some product species with proper dimensions can diffuse out of the pore. On the one hand, inside the restricted pore the undesired reaction can be limited by preventing of the formation of unwanted transition-state species.

Table 2.3 Apertures formed by rings of tetrahedra found in zeolite structures[39]

Number of tetrahedra in ring	Maximum free dimension (Å)
4	1.6
5	1.5
6	2.8
8	4.3
10	6.3
12	8.0
18	15
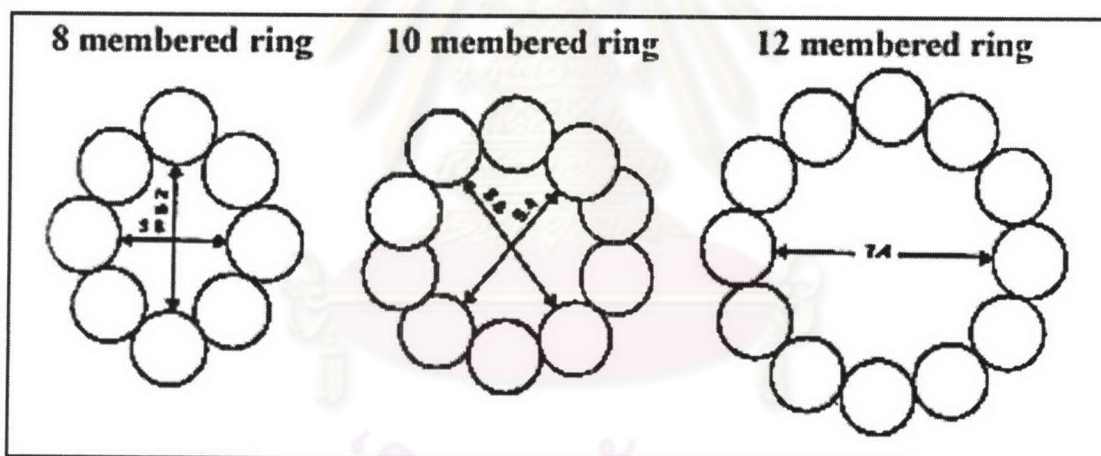
Figure 2.8 The example of relationship between numbers of rings and pore size.[5]
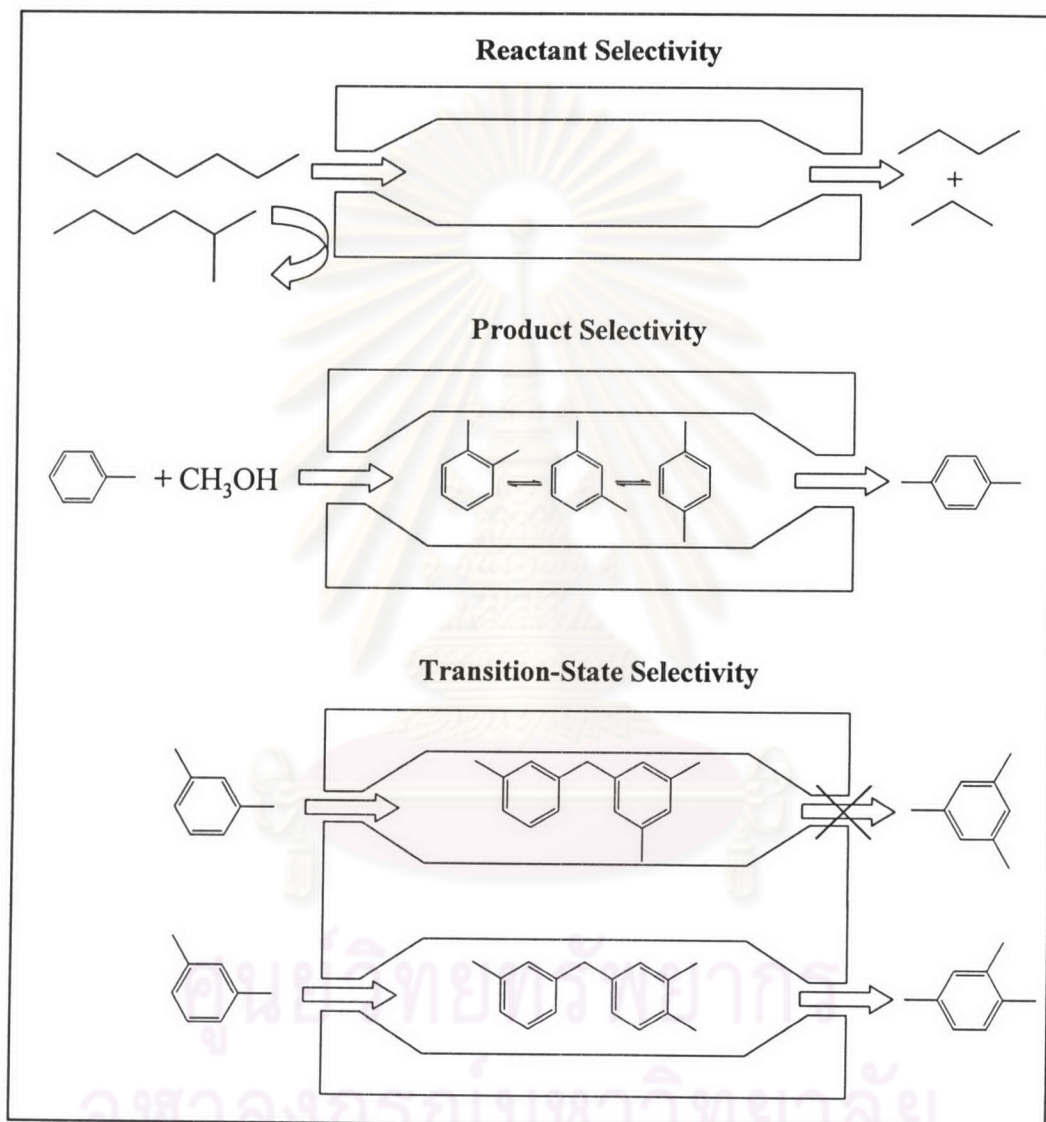
Figure 2.9 The size and shape selection of molecular sieves.[5]

2.2.3.4 Active site in the zeolites

Pure silica compounds are inert in reaction, so the active sites in zeolites are influenced from the substitutions of aluminates that generate the negative charges balanced with the cations on the surface. When the cation is H^+, the zeolites can be used as the acid catalysts. The acid strength at the Brønsted acid varies with the zeolite's structure. Moreover an important property of zeolites is the ion-exchange ability that occurs at the balanced cation position as shown in Figure 2.3 where M is the metal cation. Several metal cations, which active to catalyze a reaction, can occupy this position. The examples are copper(II) in ZSM-5 for NO_x decomposition reaction[46] and molybdenum in Beta-zeolite for hydrotreating reactions.[47]

2.2.4 Mesoporous silicate materials

The main advantage of mesoporous silica materials, rather than zeolite is their ability to treat bulkier reactants and obtain larger products. Moreover they can be used as supports for grafting the large actual catalysts, such as enzymes.[48] Many materials were synthesized with various structures, such as MCM-41 with hexagonal structure and MCM-48 with cubic structure. FSM-16, HMS, and SBA-15 are the mesoporous silicate with a similar structure to MCM-41. Actually, these mesoporous materials are typically amorphous or paracrystalline solids in the atomic arrangement, but in channel arrangement they are crystallographically ordered.[49] MCM-41[50] was the first synthesized mesoporous silicate materials that many researchers studied its structure and properties, including usage as industrial catalysts.

2.2.4.1 MCM-41

MCM-41 is a member of mesoporous molecular sieves, which possesses a hexagonal array of uniform mesopores as illustrated in Figure 2.10. It has uniform channels varying from approximately 15 to 100 Å in diameter. The prominent properties,

which are important to be used as catalyst, are the large surface areas above 1000 m^2/g and the high volume capacity above 0.7 cm^3/g of hydrocarbon sorption.
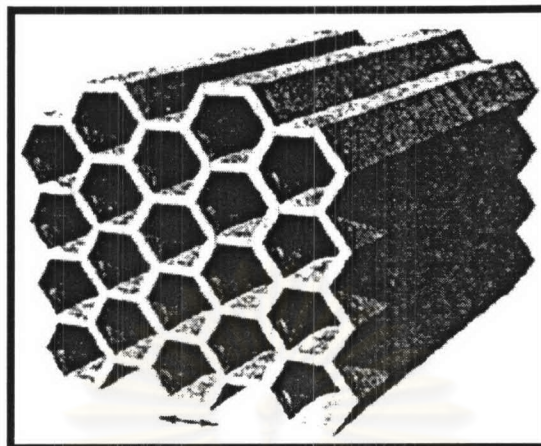
Figure 2.10   Hexagonal packing of unidimensional cylindrical pores.

Because the structure of MCM-41 is composed of only silica, it cannot be used directly as the catalyst. Thus several catalysts are coated on the surface of MCM-41, for example Cr/MCM-41[51] was useful catalyst in olefin oligomerization to produce lube oil additives and Ni and Mo deposit on the surface of MCM-41 for hydrodesulfurization and hydrodenitrogenation reaction.[52] Furthermore some metal atoms can be incorporated to the MCM-41's framework, likely the substitution of Al on the silicate framework of zeolites. The examples are Ti-MCM-41, W-MCM-41, Fe-MCM-41, and Al-MCM-41 used for oxidation of cyclohexanol, metathesis reaction, benzylation, and cracking of polymers, respectively. However the serious problem of these groups in industrial chemical reactions is the destruction of its structure because of the poor thermal, hydrothermal, and mechanical stabilities.[53-55] When the materials are used in the conditions that have moistures and high temperature, their structure is continuously collapsed that affects the lower desired properties, such as lower surface area, uniform pore size, and pore volume. On the one hand the pore wall of MCM-41 is also crash by mechanically pressing in the presence of adsorbed water.

There are many attempts to increase the hydrothermal stability of the hexagonal materials. Among those there are three successful methods as follows:

1)   The increase of the wall thickness and wall polymerization[56] by adjusting the pH during synthesis[57,58] and by restructuring method.[59,60]

2)   The decrease of number of silanol groups on the pore wall by reacting them with silanes, called the post-synthesis silylation, resulting in greater hydrophobicity against the moisture.[61,62]

3)   The salt effect[63,64] enhancing the hydrothermal stability via adding some salts such as sodium chloride, sodium ethylenediaminetetraacetate (Na_4EDTA), potassium chloride during synthesis or via ion exchanging with Na^+, K^+, Ca^{2+}, and Fe^{3+}.

These three techniques have disadvantages. The restructuring method consumes a long period, while the silylation agents are expensive. For addition of salt, although sodium and potassium salts or ions are cheap, it was poor in reproductibility.[57] Therefore, the use of unstable mesoporous materials was not complete.

2.2.4.2   SBA-15

In 1998, the world material science was incited by the discovery of a new mesoporous material, namely SBA-15, which have showed high thermal, hydrothermal, and mechanical stabilities.[11,12] These stabilities are influenced by the pore wall thickness in range of 35-64 Å, which is thicker than that of other mesoporous materials (less than 15 Å).[65,66] Like the structure of MCM-41, the mesoporous SBA-15 has long range order with the hexagonally arranged cylindrical structure and large one-dimensional mesopores up to 500 Å. The pore structure of SBA-15 is shown in Figure 2.11. The high hydrothermal stability of SBA-15 is an advantage over MCM-41. One of the advantages of the thicker walls is the ability to form stable crystal nuclei of the constitutive metal oxide within the walls or framework.[12,65,67]
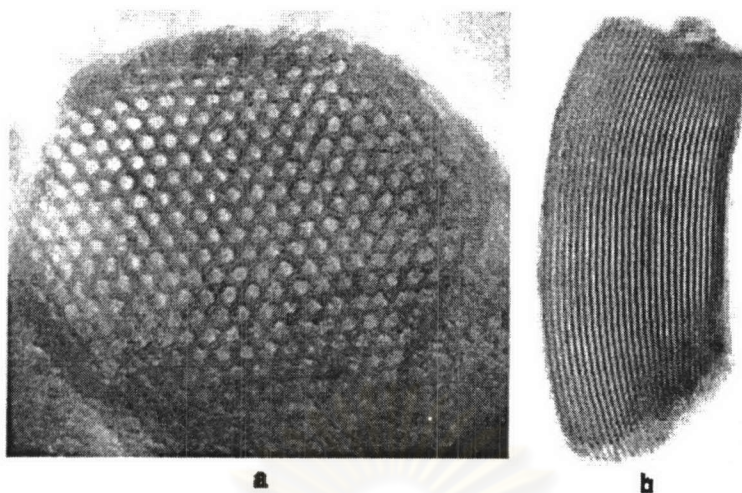
Figure 2.11 Transmission electron microscopy (TEM) images of hexagonal pores of SBA-15: a) along the C_6 axis and b) perpendicular to this axis.[68]

2.2.4.3 Characterization of hexagonal mesoporous structure

The most useful technique to investigate the hexagonal array structure, including all crystalline porous materials, is the x-ray diffraction (XRD) technique. Typically, the x-ray reflections are due to the ordered hexagonal array of parallel silica tubes and can be indexed assuming a hexagonal unit cell as (100), (110), (200), (210), and (300) at the low 2θ between 2° and 5°, as shown in Figure 2.12.[69] Since the materials are not crystalline at the atomic level, no reflections at higher angles are observed. When an X-ray beam strikes an atom on the surface at a specific angle, a portion of the beam is scattered as shown in Figure 2.13. The unscattered portion of the beam penetrates to the lower layer of atoms, where d is the interplanar distance of the crystal. Thus, constructive interference of the beam at angle θ is defined by the Bragg's equation as depicted in Equation 2.6.

$$n\lambda = 2d \sin\theta \tag{2.6}$$

For a hexagonal structure, the characteristics of d-spacing ratios are given as follows:

$$d_{100}/d_{110} = d_{200}/d_{220} = 1.732 = \sqrt{3} \tag{2.7}$$

$$d_{100}/d_{200} = d_{200}/d_{400} = 2.000 \tag{2.8}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{2.9}$$

Figure 2.12   X-ray diffraction pattern of hexagonal array MCM-41.[69]

Figure 2.13   Diffraction of X-ray by an atom on the surface.
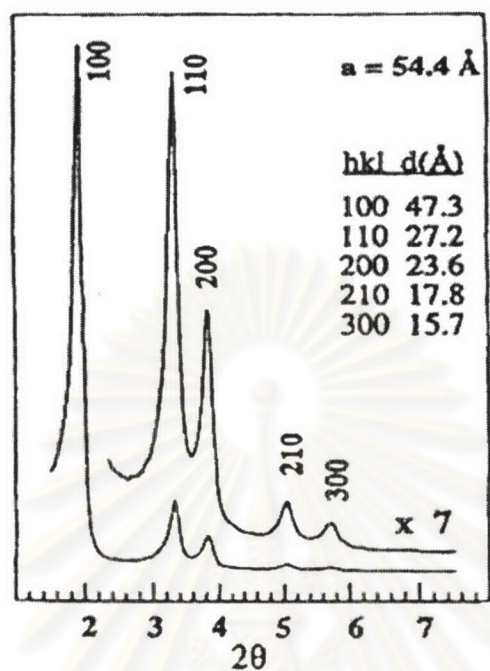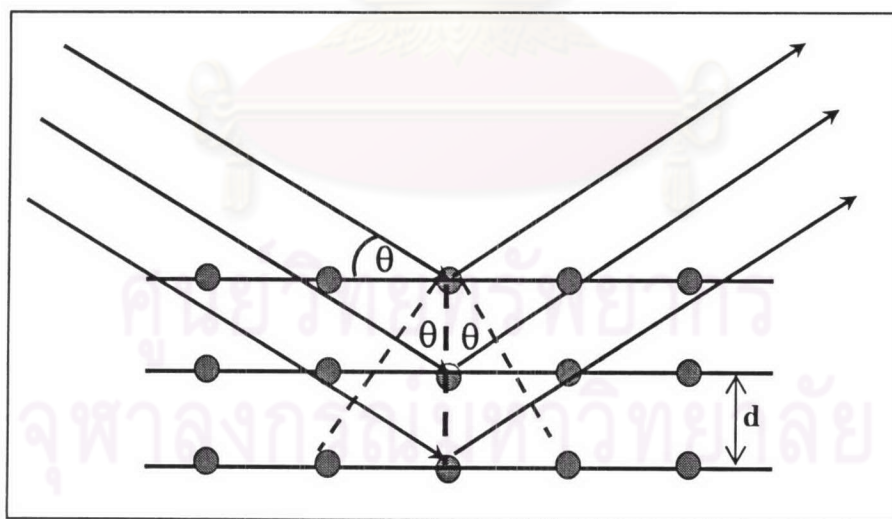
From Equation 2.7, 2.8, and 2.9, the unit cell parameter (a) can be calculated using Equation 2.11.

$$a = 2d_{100} / \sqrt{3}$$
(2.10)

2.3 Synthesis strategies

Crystalline molecular sieves are generally obtained by hydrothermal crystallization of a homogenized gel, which consists of both liquid and solid phases. The reaction gel, in principle, contains cations to form the framework (Si^{4+} for silicate materials and Al^{3+} for aluminate materials); anionic species (OH^- and F^-); organic templates and solvent (generally water).

2.3.1 The role of templates

The formation of molecular sieve materials, both microporous and mesoporous materials, concerns with the concepts of structural directing agents or templates. Templating was defined, in a general sense, as a process in which an organic species functions as a central structure about which oxide moieties organize into a crystalline lattice.[50] Structural direction requires that a specific framework is formed from a unique organic compound, however, this does not imply that the resulting oxide structure mimics identically the form of the organic molecule. Organic template molecules, mainly surfactants, exert a structure directing influence. Typically, the nature of template can be divided into two parts: hydrophobic tail on the alkyl chain side and hydrophilic head on the other side. The examples of templates used are primary, secondary, tertiary, and quaternary amines, alcohols, crown or linear ethers, and organometallic complexes as well as polymer. An understanding of how organic molecules interact with each other and with the inorganic frameworks would increase the ability to design rational routes to molecular sieve materials.

The organic templates are frequently occluded in the pores of the synthesized material, contributing to the stability of the mineral backbone. The framework stabilizing interactions can be of coulombic, van der Waals, or H-bonding type.

2.3.2   The behavior of surfactant molecules in an aqueous solution

In a simple binary system of water-surfactant, surfactant molecules, at a particular concentration, can aggregate to form micelles in various types. The shapes of micelles strongly depend on the concentrations as shown in Figure 2.14.[70] At low concentrations, they energetically exist as isolated molecules. With increasing concentration, surfactants aggregate together to form isotropic spherical and rod-shaped micelles by directing the hydrophobic tails to inside and turning the hydrophilic heads to outside in order to decrease the system entropy. The initial concentration threshold at which those molecules aggregate to form isotropic micelles is called critical micellization concentration (CMC).[71] The CMC determines thermodynamic stability of the micelles.[72] When the concentration is continuously increased, the micellar shape changes from sphere or rod-shape to hexagonal, lamellar, and reverse micelles.

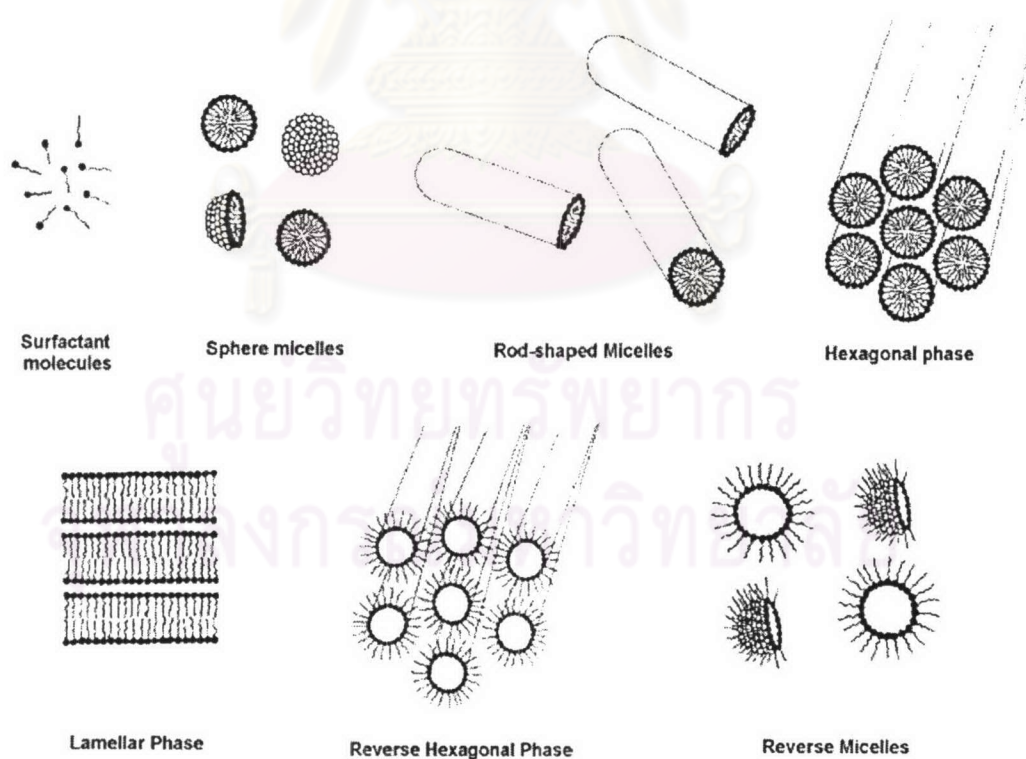

Surfactant molecules   Sphere micelles   Rod-shaped Micelles   Hexagonal phase

Lamellar Phase   Reverse Hexagonal Phase   Reverse Micelles

Figure 2.14   Phase sequence of the surfactant-water binary system.[70]

The particular phase present in a surfactant aqueous solution depends not only on the concentrations but also on the nature of surfactant molecules such as its length of the hydrophobic carbon chain, hydrophilic head group, and counterion. Moreover the pH, ionic strength, and temperature including other additives are the factors determining the shape of micelles. Generally the CMC decreases with increasing the chain length of a surfactant, the valence of the counterions, and the ionic strength in a solution. In contrast, it increases with increasing counterion radius, pH, and temperatures.

2.3.3   The interaction between inorganic species and surfactant micelles

The major components of framework structure, mainly silicate, present in aqueous solution as inorganic species. To acquire the desired structure, firstly the template forms the proper shape, and then the inorganic soluble species interact with the surfactant as shown in Table 2.4.[73] The hybrid solids formed are strongly dependent on the interaction between surfactants and the inorganic precursors.

In case of ionic surfactant (S^+ and S^-), the hydrophilic head binds with inorganic species through electrostatic interactions mainly. Two formation routes are possible. Firstly, direct pathway: surfactant and inorganic species of which charges are opposite interact together directly (S^+I^- and S^-I^+). The other one is indirect pathway occurring when the charges of surfactant and inorganic species are the same, so the counterions in solutions get involved as charge compensating species for example the $S^+X^-I^+$ path takes place under acidic conditions, in the presence of halogenide anions ($X^- = Cl^-$ or Br^-) and the $S^-M^+I^-$ route is characteristic of basic media, in the existence of alkaline cations ($M^+ = Na^+$ or K^+). Figure 2.15 shows the different possible hybrid inorganic-organic interfaces.[73]

Using nonionic surfactant (S^0 or N^0), the main interactions between the template and the inorganic species is hydrogen bonding or dipolar, giving birth to the so-called neutral path: S^0I^0 and $S^0F^-I^+$.

Table 2.4 The example routes for the interactions between the surfactant and the inorganic soluble species[73]

Surfactant type	Inorganic type	Interaction type
Cationic S^+	I^-	S^+I^-
	I^+X^-	$S^+X^-I^+$
	I^0F^-	$S^+F^-I^0$
Anionic S^-	I^+	S^-I^+
	I^-M^+	$S^-M^+I^-$
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0
	I^+X^-	$S^0X^-I^+$
	I^+F^-	$S^0F^-I^+$
	I^0 with M^{n+}	$S^0M^{n+}I^0$

Where S^x or N^x = surfactant with charge of x

I^x = inorganic species with charge of x

X^- = halogenide anions

M^{n+} = cation with charge n, normally alkaline cations

And F^- = fluoride anion
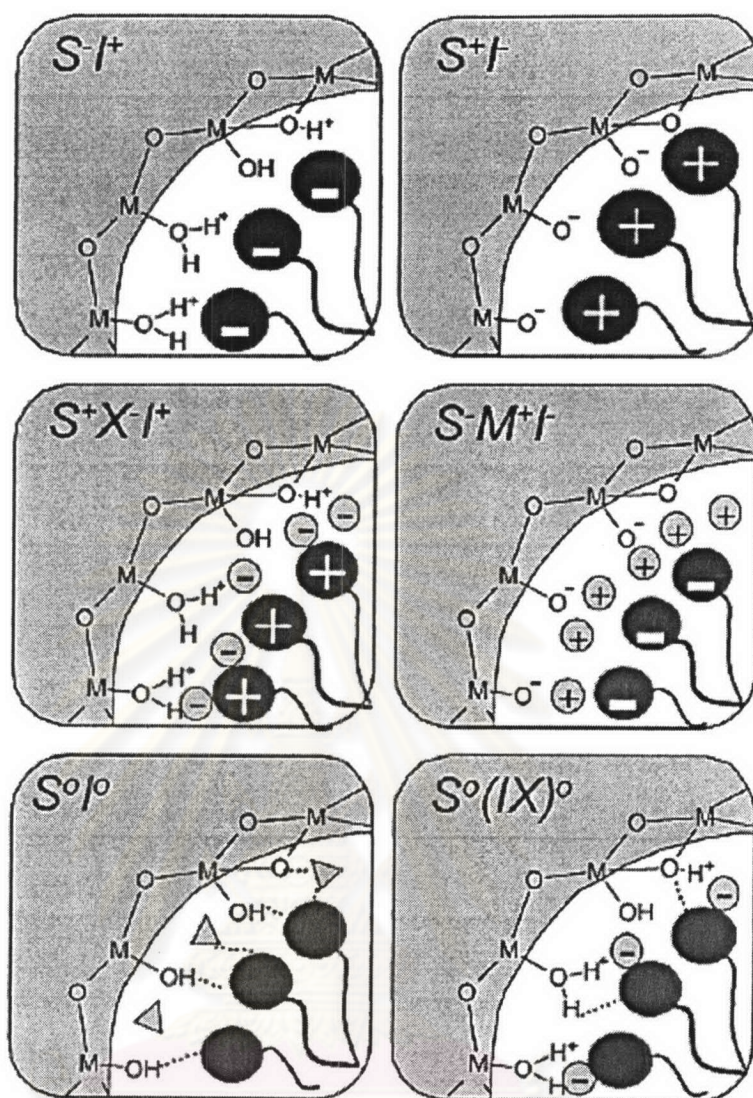
Figure 2.15 The different possible hybrid inorganic-organic interface.[73]

2.3.4 Mechanism of the crystallization process

The formation of porous silicate materials concerns with the condensation of silicate around the template. The mechanism is shown in Figure 2.16.[74] In step (A), the single-chain surfactant molecules react preferentially with silicate polyanions (e.g. dimmers, double three and four rings) which displace the original surfactants monoanions. Micelles serve as a surfactant molecule source or are rearranged according to the anion charge density and shape requirements. Next in step B and C, nucleation and rapid precipitation of organized arrays take place with configurations determined by the cooperative interactions of ion-pair charges,

geometries, and organic van der Waals forces. Silicate condensation, at this stage at low temperatures is minimal. The last step (D), condensation of the silicate phase now in turn becomes proceeding with increasing time and temperature. The silicate framework charge decreases during this process and may lead to liquid-crystal-like phase transitions as the surfactant phase tries to reorganize the changing interface charge density.
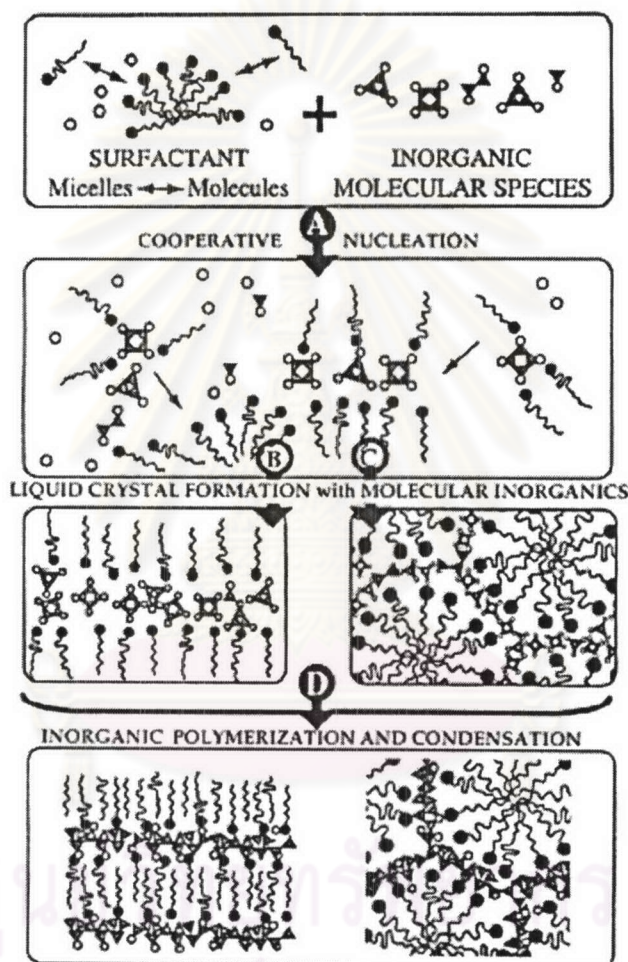
Figure 2.16   Cooperative templating model for biphase materials synthesis.[74]

2.3.5 Block copolymer as template

In the synthesis of SBA-15 materials, a triblock copolymer $PEO_{20}PPO_{20}PEO_{20}$ is used as the template. The triblock copolymer is classified to be amphiphilic copolymers with a strong application potential, mainly due to the high energetic and structural control that can be exerted on the material interfaces. The chemical structure of copolymer can be adjusted, like quaternary ammonium ion, as shown in Figure 2.17.[73] It was found that polymers are excellent templates for the structuring of inorganic networks; they have been also used for growth control of discrete mineral particles. In aqueous media, solubilization of nonionic block copolymer is due to the association of water molecules with the alkylene oxide moieties through hydrogen bonding, and should be enhanced in acid media where hydronium ions, instead of water molecules, are associated with the alkylene oxygen atoms.[12]

Figure 2.17 Main morphologies of block copolymer: spherical micelles (MIC), cylindrical micelles (CYL), lamellar structures (LAM), modulated lamellar (MLAM), hexagonal pinhole layers (HPL), gyroids (*Ia3d*), ordered cylinders (HEX), and body-centered cubic (BCC).[73]

In the each part of block copolymer, polyethylene oxide (PEO) part exhibits the hydrophilicity, while hydrophobicity belongs to the polypropylene oxide (PPO) part. The micelles are formed by aggregating with the dehydrated PPO blocks in their cores, surrounded by a corona formed by the hydrated PEO blocks as presented in Figure 2.18.[48] The CMC values of block copolymers vary as their structure and molecular weight.[75] The polymers with a larger hydrophobic domain form micelles at lower concentrations indicating that PPO units decrease the CMC values. On the other, the micelle formation becomes more difficult with the more hydrophilic PEO part. Polymer with higher molecular weight form micelles more readily.

Figure 2.18   The existence of a PEO corona surrounding a core PPO.[48]

Pinnavaia and co-workers[18,76] suggested that some advantages of using neutral non-ionic block copolymer over the ionic ones were immediately noticed: a) larger inorganic wall thickness 15-40 Å, enhancing the hydrothermal stability of the mesoporous materials; b) easier pore diameter tuning, by varying both the concentration of the surfactant and the addition of cosolvent; c) easier solvent removal, by solvent extraction and by calcination at low temperature (140 °C)[12] due to weakness of H-bonding interaction between the template and the inorganic framework.

2.3.6   SBA-15 synthesis mechanism

In SBA-15 synthesis, the acid was added into the aqueous media, so the assembly of inorganic species and surfactant might be expected to proceed through an intermediate of the form $S^0H^+X^-I^+$ where S^0 is triblock copolymer, H^+ is proton, X^- is generally anion of acid, and I^+ is inorganic species, mainly protonated silica.[12]

For the mechanism, firstly alkoxysilane species, tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS), are hydrolyzed as shown in Equation 2.11

$$Si(OEt)_4 + n\,H_3O^+ \xrightarrow[\text{pH} < 2]{\text{hydrolysis}} SiO(OEt)_{4-n}(OH_2^+)_n + n\text{EtOH} \quad (2.11)$$

which is followed by partial oligomerization at the silica. Furthermore, at this condition, the PEO parts of the surfactant associate with hydronium ions as depicted in Equation 2.12.

$$-PEO_m^- + y\,HX \xrightarrow{H_2O} -PEO_{m-y}\,[(EO).H_3O^+]_y......y\,X^- \quad (2.12)$$

Next, coordination sphere expansion around the silicon atom by anion coordination of the form $X^-\cdot Si\text{-}OH_2^+$ may play an important role. The hydrophilic PEO blocks are expected to interact with the protonated silica and thus be closely associated with the inorganic wall. During the hydrolysis and condensation of the silica species, intermediate mesophases are sometimes observed and further condensation of the silica species and organization of the surfactant and inorganic species result in the formation of the lowest energy silica –surfactant mesophases structure allowed by the solidifying inorganic network. Figure 2.19 shows the schematic model of formation that is based on the liquid crystal templating mechanism, proposed by Beck et al.[50] in 1992, explaining the formation of mesoporous structure that silicate condensation is not a dominant factor in the formation of mesoporous structure, but the whole process of two possible pathways is included. For the path way 1, hexagonal crystal mesophases form prior to addition of silicate species, while for the other pathway the silicate species added to the reaction mixture influence the order of isotropic rod like micelles of the desired liquid crystal phase, i.e. hexagonal mesophase. Therefore, the mesophase is structurally and morphologically directed by the existence of liquid crystal micelles and mesophases.
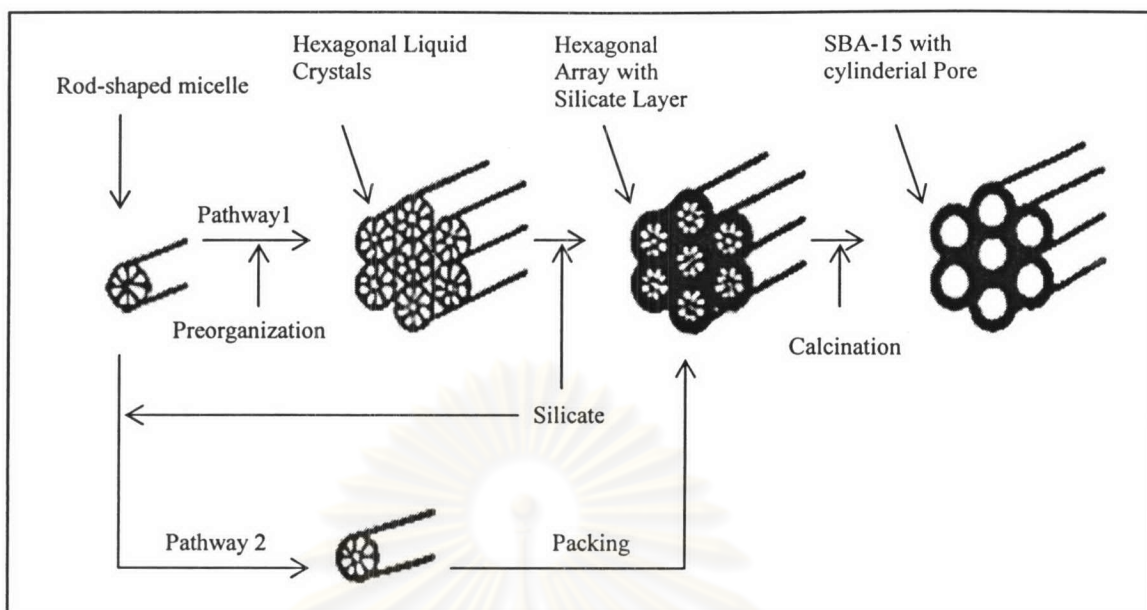
Figure 2.19 Schematic model of liquid crystal templating mechanism.

2.4   Chemistry of iron

The ionic radii of Si^{4+}, Al^{3+}, Fe^{3+}, and Fe^{2+} are 0.39, 0.57, 0.67, and 0.78 Å, respectively. From many reports[5,39], in case of zeolite structure, the substitution of Al^{3+} by other ions affects their structural properties such as stability, crystal lattice, acidity, catalytic activity, and so on. To understand these evidences, the study of iron nature is essential, and will be discussed below.

2.4.1   Aqueous chemistry of iron in aqueous solution

2.4.1.1   The structure of iron species

In aqueous solutions, iron mainly forms octahedral complexes with weakly coordinating anionic ligands such as H_2O, OH^-, and Cl^-. Oxygen donor ligands like phosphates, tartarates, oxalates, and EDTA tend to stabilize Fe(III) against reduction to Fe(II). These complexes are usually pale in color and the occurrence of mainly spin-forbidden bands in the visible region of the spectrum. In aqueous solution containing anions of low coordinating ability, the pale violet hexaquo ion undergoes the following hydrolytic equilibria

to give hydroxo species which are yellow because of a charge transfer absorption that extends into the visible region.

At the strongly acidic solution (pH below 1), the sole complex is $[Fe(H_2O)_6]^{3+}$. Between pH value of 1 and 2, the most predominant compound is $[Fe(H_2O)_5(OH)]^{2+}$ as shown in Equation 2.13. When the pH is raised above 2, the equilibrium in solution is shifted to precipitate the $Fe(H_2O)_3(OH)_3$ following Equation 2.14 and 2.15.

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad (2.13)$$

$$[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H_3O^+ \quad (2.14)$$

$$[Fe(H_2O)_4(OH)_2]^+ + H_2O \rightleftharpoons Fe(H_2O)_3(OH)_3 + H_3O^+ \quad (2.15)$$
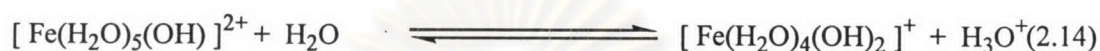
Further deprotonation of these ions can occur in the presence of added bases leading to larger and larger aggregates until eventually colloidal gels are formed and the iron hydroxide precipitates.

In acidic oxide environment, including aqueous solutions, Fe(III) is mainly octahedrally coordinated. However, tetrahedral coordination is known in basic environments.

2.4.1.2 Hydrolysis and precipitation of iron ions

The concentrations of the various Fe species were found as a function of pH. The pH values for $Fe(NO_3)_3$ solutions at 293-298 K in the absence of precipitation at 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} molar concentration are 1.5, 2.3, 3.0, 3.8, and 4.7, respectively. Such solutions are unstable to precipitation of amorphous hydrous oxide at concentrations greater than 10^{-2} molar. This may be seen from the pH values of the above solutions when saturated with fresh amorphous hydrous oxides. The values are 2.1, 2.5, 2.9, 3.4, and 4.3, respectively. Generally, it is observed that except at high concentrations, unacidified Fe(III) salt solutions are unstable with respect to precipitation of α-Fe_2O_3 or α-$FeO(OH)$. Such hydrolysis reactions of Fe(III) proceed along several well-defined stages. Initially, low molecular weight hydrolysis products like $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$ are present. When a base is added to a ferric salt (nitrate, chloride, sulfate, or perchlorate) in amounts insufficient to

precipitate the hydrous oxides, a red cation polymer is formed which is eventually converted to the oxide phase. The iron atoms in the cationic polymer have the coordination number 6. These octahedra are condensed most probably by sharing edges or vertices and consist of spheres of 20-40 Å in diameter, containing about 100 Fe ions. These polymers are not at equilibrium and are converted to iron oxides and hydrous oxides which are precipitated as solids at a rate which markedly increases with temperature. When base is added to the solution, the Fe ions in solution undergo directly precipitation without formation of the soluble polymer.

During the synthesis of ferrisilicate zeolites it is desirable to avoid the formation and further transformation of these polymers since the latter, once formed would inexorably lead to the formation of the insoluble oxides and hydrous oxide of Fe, especially at the higher temperatures above 100 °C used in zeolitic synthesis.

2.4.2 Iron-silicate species in aqueous solution

The first step in the synthesis of the ferrisilicate molecular sieves is, usually, the mixing of solutions containing Fe and Si at a low pH. In a normal procedure, the silicate solution is added dropwise into an acidic solution of Fe. During synthesis, monomeric silicic acid dissociates according to Equation 2.16.

$$Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+ \qquad (2.16)$$

The silanol groups of silica gel have a pK_a value of about 7 indicating an increase in acidity with increasing polymerization. When Fe ions interact with silicic acid in dilute acidic aqueous solutions, the stable $FeSiO(OH)_3^{2+}$ complexes are formed followed Equation 2.17.

$$Fe^{3+} + Si(OH)_4 \rightleftharpoons FeSiO(OH)_3^{2+} + H^+ \qquad (2.17)$$

Polynuclear complexes of ferrisilicates are formed when the concentration of Fe ions in solution exceeded 5×10^{-5} M as shown in Equation 2.18.

$$Fe(H_2O_6)^{3+} + Si(OH)_4 \rightleftharpoons [Fe(OSi(OH)_3)(H_2O)_5^{2+}] + H_3O^+ \qquad (2.18)$$

Next the monomeric ferrisilicate species formed can condense with a second molecule of Si(OH)$_4$ forming polynuclear ferrisilicate species presented in Equation 2.19 and 2.20.

$$[Fe(OSi(OH)_3)(H_2O)_5{}^{2+}] + Si(OH) \rightleftharpoons [Fe(OSi(OH)_3)_2(H_2O)_4{}^+] + H_3O^+ \quad (2.19)$$

$$[Fe(OSi(OH)_3)_2(H_2O)_4{}^+] + Si(OH) \rightleftharpoons [Fe(OSi(OH)_3)_3(H_2O)_3] + H_3O^+ \quad (2.20)$$

The interaction of iron(III) with dissolved silica as a function of the degree of polymerization of the concentration of Si(OH)$_4$ monomer, but not the concentration of Fe species. At pH greater than 2, the polymeric silica is still tying up an amount of iron comparable to that complexed by an equivalent amount of monomeric silicic acid. Since there are a smaller number of free silanol groups in polymeric silica, the higher acidity of the silanol groups in polymeric silica must be playing a compensating role on enhancing the formation of complexes with the iron ions.

While silicate groups are attached to the iron ion, the silanol groups in the polynuclear ferrisilicate species, $Fe(OSi(OH)_3)_n(H_2O)_{6-n}]^{3-n}$, can condense with other such silanol groups to give larger complexes as depicted in Figure 2.20. This complex will undergo to form silicate framework structure. The amount of silica needed to react with all the iron is dependent on the extent of polymerization within that silica source. Three factors critical in the consistent and successful preparation of ferrisilicate molecular sieves over a wide range of SiO$_2$/Fe$_2$O$_3$ ratio are the avoidance of iron hydroxide preparation, the necessity of using low molecular weight silica sources, and the need to suppress the formation of iron complexes with the organic templates. To prevent the formation of iron hydroxide, the silica source should be slowly added into an aqueous acidic iron containing solution, on the other hand, the iron hydroxides are precipitated when iron solution is added into the silica solution.
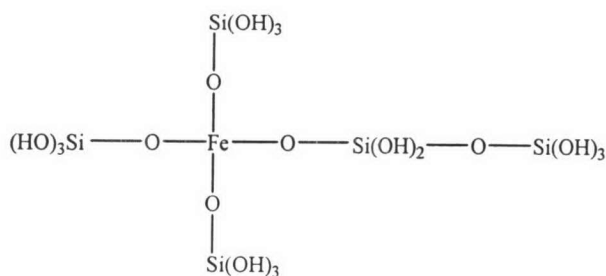

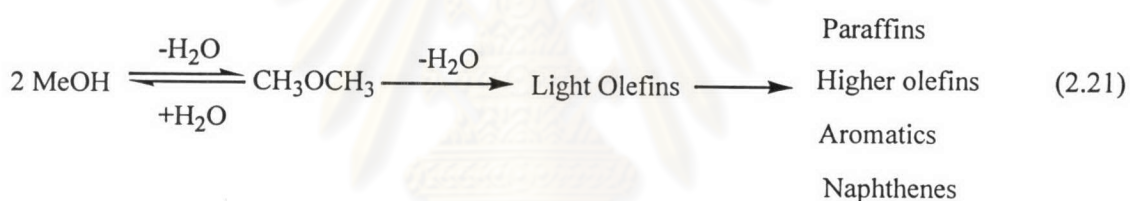**Figure 2.20** The higher polynuclear ferrisilicate species.

2.4.3 Characterization of Iron in Ferrisilicates by ESR Spectroscopy

Although the ferrisilicates can be synthesized from either Fe^{2+} or Fe^{3+}, all Fe species are changed to Fe^{3+} when the materials are calcined at high temperature presenting O_2 to remove organic templates. Since Fe^{3+} ions is paramagnetic in both the low-spin and high-spin electronic configurations,[77] ESR spectroscopy should be used to identify the status of chemical combination of iron sites in materials where the weak ligand field of the possible ligands (water, hydroxide, framework oxygen) results in high-spin ferric states. In this case, the interpretation of the ESR spectra is difficult due to complications associated with inhomogeneous broadening arising from the zero field splitting (ZFS) and overlapping signals. The X-band ESR spectrum of zeolites containing Fe^{3+} usually consists of three major signals at $g \approx 4.3$, $g \approx 2.2\text{-}2.3$, and $g \approx 2.0$. The commonly accepted assignment of these signals has been as follows: framework iron, iron in interstitial oxide or hydroxide phases, and iron in cation-exchange sites or extraframework sites, respectively.[78-82] The appearance of a signal at $g \approx 4.3$ has often been used as evidence for framework substitution.

Fe(III) has five unpaired electrons in the low-field, high spin state and only on in high-fields. For the perfect tetrahedral (T_d) or octahedral (O_h) symmetries, only one signal would be observed at $g_{eff} = 2.0023$. At lower symmetries the situation is complicated, for example in distorted tetrahedral (C_{3v}) or distorted octahedral symmetries (D_{4h}), the powder spectrum can display signals with g_{eff} from 2 to 6. When the symmetry is lower than D_{2h} or orthorhombic, one can observe an isotropic signal at g_{eff} of 4.29. To summarize, one may state that the signal in the range g_{eff} of 4.2 to 4.4 may indicate the presence of Fe(III) in a distorted tetrahedral environment. Similarly, the signals at g_{eff} of 2.0 and 2.3 were assigned to non-lattice Fe.[31]

2.5 Methanol conversion

The conversion from less valuable methanol to higher valuable products, particularly olefins, is the interesting topic. The reaction of methanol started from the success in preparation of gasoline from methanol (methanol-to-gasoline, MTG) using ZSM-5 zeolite as a catalyst operated at temperature around 400 °C and at a methanol partial pressure of several bars. In the reaction, the intermediates are olefins formed within the catalyst channels continuously converted to paraffins and aromatics. To inhibit the conversion of olefin to paraffins or aromatics, the development of catalysts were studied. For example, the medium-pore zeolites were used to prevent the formations of large hydrocarbon and the decrease of acid strength in catalysts such as the substitution of Al in framework by Fe due to the higher acidity generated higher amounts of gasoline. The main reaction of methanol conversion can be summarized as follows:

$$2\ MeOH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} Light\ Olefins \longrightarrow \begin{array}{l} Paraffins \\ Higher\ olefins \\ Aromatics \\ Naphthenes \end{array} \qquad (2.21)$$

2.5.1 Mechanisms of methanol conversion

Three steps for methanol conversion are 1) the formation of dimethyl ether, 2) the formation of C-C bond, and 3) the subsequent conversion of the primary light olefins into larger molecules. The main active site to stimulate the reaction is BrØnsted acid on the surface of catalysts, while the conjugate Lewis basic site would be responsible for the initial C-C bond formations.

2.5.1.1 Formation of dimethyl ether

The dimethyl ether, the first intermediate generated in the methanol conversion, can be formed by (a) interacting with catalyst surface resulting methoxy groups or by (b) directly condensing of two methanol molecules as illustrated in Scheme 2.1.[83,84] In the pathway (a), after reacting with H^+, the $[CH_3(OH_2)]^+$ complex continuously bounds with a framework to form methoxy species by nucleophilic attack of catalyst framework. Then the

complex was reacted with the second methanol molecule to generate dimethyl ether. For the second pathway (b), the $[CH_3(OH_2)]^+$ complex directly condensed with the methanol, not reacted with the framework. According to the study of Hirao *et al*[85], they indicated that the direct condensation in pathway (b) was preferred to path (a). Besides, the investigations from the magic-angle-spinning (MAS) NMR[84] supported the theory of pathway (b).
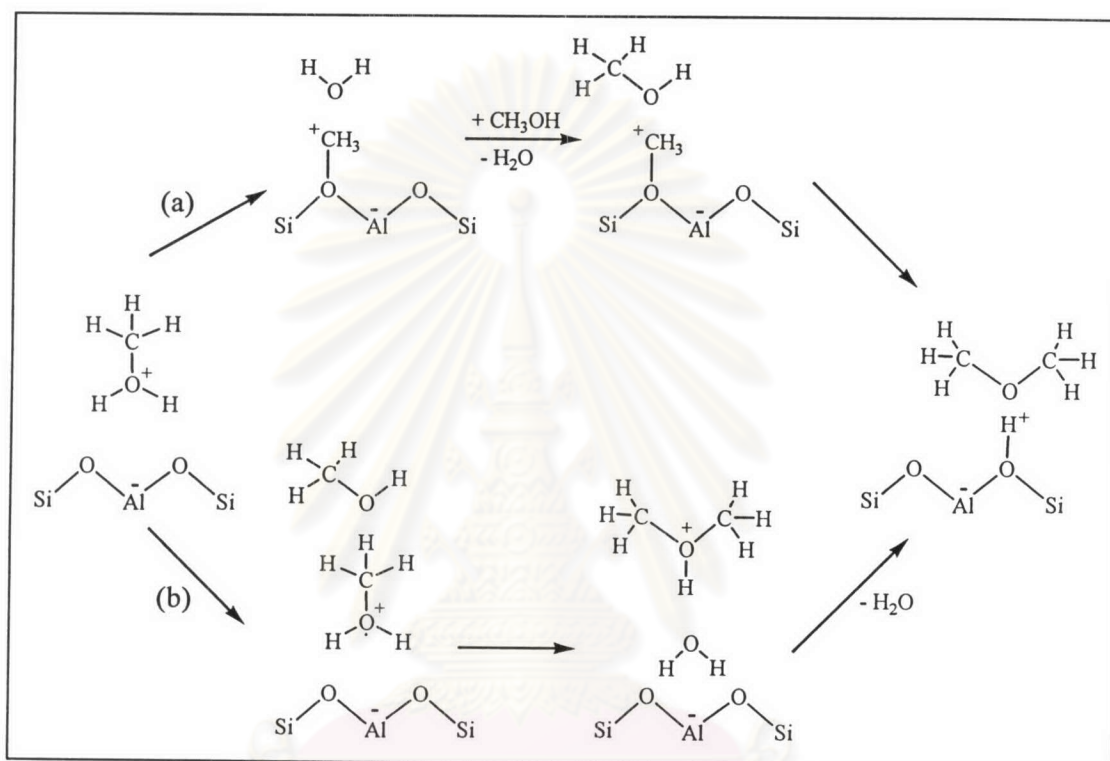
Scheme 2.1 Two pathways for the formation of dimethyl ether in the present of an aluminosilicate catalyst for methanol conversion process.[84]

2.5.1.2 Formation of C-C bond

There were many reaction mechanisms proposed for the formation of carbon- carbon bond, which was regarded as a step producing primary hydrocarbon products. These mechanisms are 1) oxonium ylide, 2) carbene, 3) free radical, and 4) hydrocarbon chain mechanisms which are different in term of intermediates.

1) Oxonium ylide mechanism

This mechanism was proposed by Van den Berg and co-worker.[86] The dimethyl ether interacted with a Brønsted acid site on the solid catalysts to form a dimethyl oxonium ion, which reacted further with another dimethyl ether to form a trimethyl oxonium ion. Next the trimethyl oxonium ion was subsequently deprotonated by a basic site to form a surface associated dimethyl oxonium methyl ylide species. And then two possible pathways were the intramolecular rearrangement resulting the formation of methylethyl ether and the intermolecular methylation leading to the formation of the ethyldimethyl oxonium ion as shown in Scheme 2.2.[86] Both cases resulted the ethylene molecule as a product.
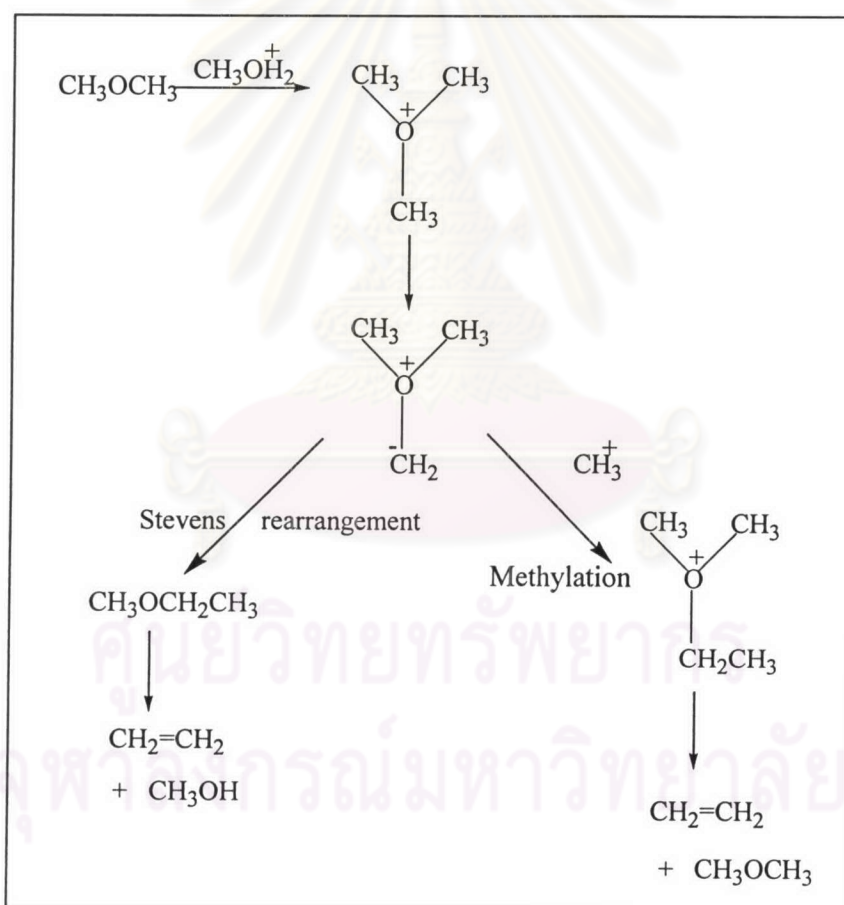
Scheme 2.2   A proposed oxonium ylide mechanism in the methanol conversion.[86]

2) Carbene mechanism

The carbene mechanism[86] involved the α-elimination of water from methanol followed by either polymerization of the resultant carbene to olefins or by concurrent sp^3 insertion of carbene into methanol or dimethyl ether. The formation of olefins via the carbene mechanism can be summarized in Scheme 2.3. The initial reaction step started from the protonation of methanol by Brønsted acid site and then the loss of water molecule occurred via α-elimination to generate carbene following the polymerization of carbene molecules.
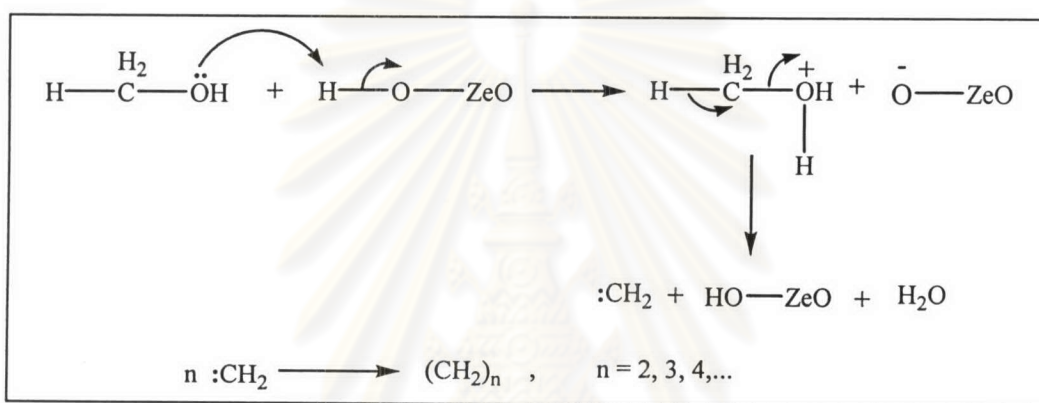
Scheme 2.3   The carbene formation from methanol adsorbed on the zeolite surface.[86]

3) Free radical mechanism

The free radical mechanism was introduced to be the alternative mechanism. Since the dimethyl ether could be the source of methyl radicals, detected by ESR spectroscopy, in the reaction of dimethyl ether over H-ZSM-5 catalyst.[86] The radicals are initially formed by interaction of dimethyl ether with paramagnetic centers in the catalyst framework, and consequently the C-C bond formation results from direct coupling of radicals. This mechanism was supported by the addition of NO, a well-known radical scavenger, into the methanol conversion resulting the complete inhibition of reaction. A detail of mechanism is shown in Scheme 2.4.

$$CH_3OH + H\text{-Catalyst} \longrightarrow CH_3O\text{-Catalyst} + H_2O$$

$$CH_3O\text{-Catalyst} + R^\bullet \longrightarrow {}^\bullet CH_2O\text{-Catalyst} + RH$$

$$^\bullet CH_3O\text{-Catalyst} + O\text{-Catalyst} \longrightarrow : O\text{-Catalyst} + : CH_2$$

$$\Updownarrow \qquad + \text{Catalyst-O}^\bullet$$

$$^- CH_2\text{-O-Catalyst}$$

$$RH + {}^\bullet O\text{-Catalyst} \longrightarrow {}^\bullet R + \text{Catalyst-OH}$$

Scheme 2.4   The free radical mechanism in methanol conversion.

4) Hydrocarbon chain mechanism

The growth of hydrocarbon products from one carbon atom in methanol, starting material, to the hydrocarbon containing several carbon atoms can be taken place by the addition of methanol or cracking of intermediates as shown in Scheme 2.5

$$2C_1 \longrightarrow C_2H_4 + H_2O$$

$$C_2H_4 + C_1 \longrightarrow C_3H_6$$

$$C_3H_6 + C_1 \longrightarrow C_4H_8 \;....$$

Scheme 2.5   The consecutive-type mechanism of the hydrocarbon chain reactions.[86]

The same type mechanism was known as hydrocarbon pool mechanism proposed by Dahl et al.[87,88] who studied the methanol conversion to hydrocarbons using SAPO-34 as a catalyst, and ^{13}C-labeled methanol and ^{12}C-ethylene made *in situ* from ethanol in the reaction (Scheme 2.6).

In Scheme 2.6, $(CH_2)_n$ represents the hydrocarbon pool, an adsorbate which may have characteristic in common with ordinary coke, and might contain less hydrogen than indicated so it would be represented by $(CH_x)_n$ with $0 < x < 2$. From the isotope labeling data, it was shown that the consecutive mechanism, as far as propylene

formation was concerned, did not turn out to be valid. Only a minor part of the propylene molecules might have been formed by addition of methanol to ethylene since this would imply a $^{12}C/^{13}C$ ratio larger than one. In fact, the ratio seemed to be lower, thus the majority of the propylene molecules should be formed directly from methanol. Moreover the Hungar *et al.* supported this mechanism in methanol conversion by studying *in situ* MAS NMR spectroscopy on H-ZSM-5[89], SAPO-18, and SAPO-34[90] under continuous flow conditions coupled with a simultaneous analysis of the reaction products by on-line GC. This new technique allowed the investigation of intermediates occurring on the catalyst surface in the steady state of a reaction. A preferential formation of ethylene and propylene was observed. Simultaneously recorded in situ ^{13}C NMR spectra showed signal at 12-25 ppm and 125-131 ppm for HZSM-5 and at 126-135 ppm for SAPO-18 and SAPO-34 indicating that the presence of adsorbed C_4-C_6 olefins. No hint for the presence of ethoxy, propoxy, or butoxy groups and the formation of alkyl oxonium ions were found.
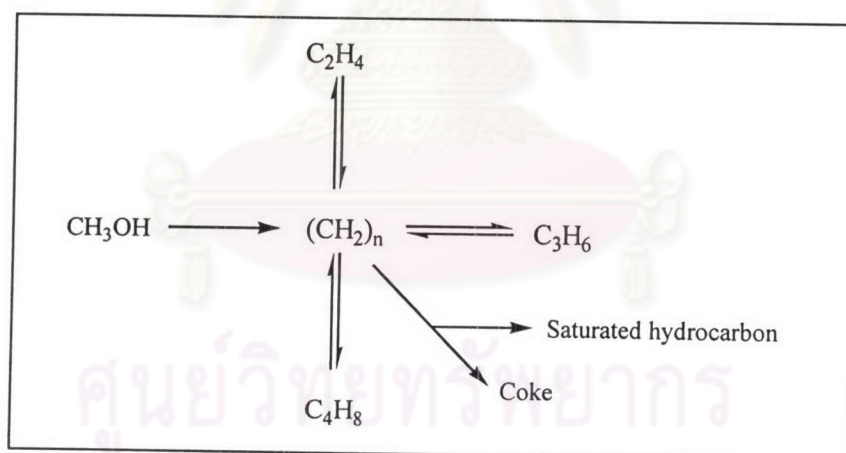
Scheme 2.6 The hydrocarbon pool mechanism paralleling the hydrocarbon chain reaction.

2.5.2 Coke Formation on the catalysts in methanol conversion

When the catalysts were used in the methanol conversion, a serious problem occurring was the deactivation of them caused the formation of carbonaceous deposits called coke on the catalyst surface. Coke is the generic name given to nonvolatile and undesirable organic compounds which should be considered as a mixture of hydrogen deficient residues. The coke is formed in or on catalysts during operation and blocks access to the catalyst active sites. Scheme 2.7[91] reveals that coke originates mainly from aromatic compounds. In methanol conversion, coke would already be formed at early stages of methanol conversion and would cover the acid sites of catalysts. Schulz *et al.*[92] studied the reaction of coke formation from methanol on ZSM-5 catalysts and displayed that the main constitutions of the coke were two ring aromatic compounds such as dimethyl- and trimethyl- naphthalenes like alkyl biphenyl and alkylate biphenyl methane.
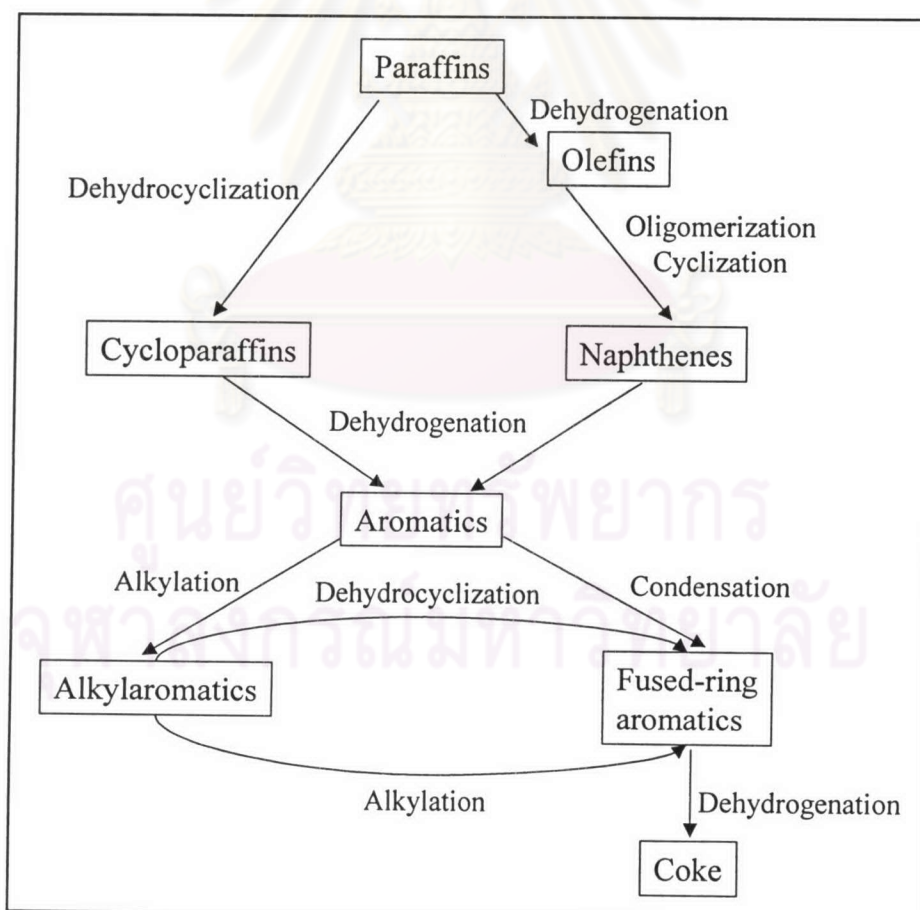
Scheme 2.7 The origin of coke deposition.[91]