

CHAPTER II

THEORY

2.1 Zeolite

2.1.1 Zeolite structures

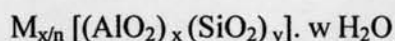
Molecular sieves are porous materials that exhibit selective adsorption properties which can be classified on the IUPAC definitions into three main types depending on their pore size that are microporous materials, mesoporous materials, and macroporous materials. Properties and examples of these materials are shown in Table 2.1

Table 2.1 IUPAC Classification of porous materials

Type of material	Pore size (Å)	Examples
Micropores	< 20	zeolites, activated carbon
Mesopores	20 – 500	M41s, SBA-15, pillared clays
Macropores	> 500	glasses

Zeolites, a type of molecular sieves, are crystalline aluminosilicates of alkali and alkaline earth metals. They both occurred in nature and archived from synthesis. The unique properties of zeolites i.e. high surface area, high sorption, ion exchange, and high acidity have been exploited for their catalytic applications such as oil refining (as cracking catalysts and as adsorbents), petrochemical industry, and synthesis of chemicals

Zeolites are porous aluminosilicate materials that can be described by the general formula:



Where M is the cation of valence n, generally from the group I or II ions, although other metals, nonmetals, and organic cations are also possible, w is the number of water molecules. Water molecules presented are located in the channels and cavities, as the

cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedral unit in the structure.

The extraframework cations usually serves as templates for synthesis and may also be readily exchanged. The framework in a zeolite structure refers to the connectivity of the Si or Al atoms. The ratio of Si/Al in a zeolite sample is important. The minimum Si/Al ratio is 1 due to the Loewenstein rule which states that there can be no Al-O-Al bonding in a zeolite sample. The open porous nature of the zeolite structure is one of its most important properties. Open pores and voids within the structure provide places for mobile cations and water to reside. A few examples of the open nature of the zeolite structure are shown in Figure 2.1.

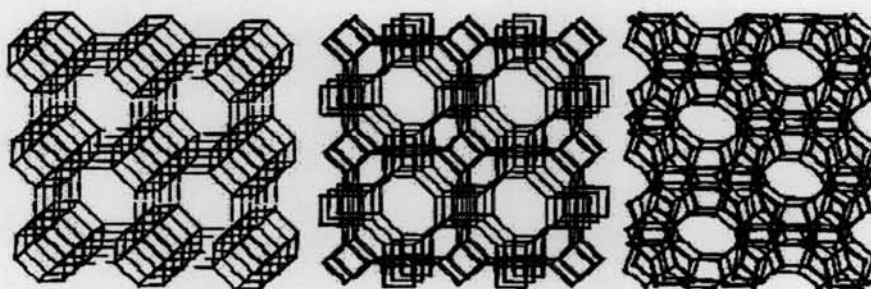


Figure 2.1 Crystal structures of ITA, CHA, and MFI from left to right.

The zeolite framework consists of cross-linked TO_4 tetrahedra where T is Al or Si. Each T atoms occupy four connected vertices of a three dimensional network and the oxygen occupy two connected positions between the four connected vertices. Having been derived from silicate type network structures, the O/T ratio in a zeolite structure is always equal to 2. The O-T-O bond angle (α in Figure 2.2) is close to the ideal tetrahedra bond angle of 109.5° . The T-O-T bond angle (β in Figure 2.2) is much more flexible than the O-T-O bond angle and is usually around 140° to 165° [14].

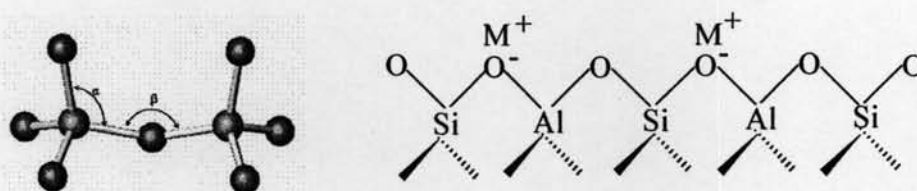


Figure 2.2 The structure of zeolites. [14]

The TO_4 tetrahedra are often referred to as the primary building units of zeolite structures. Primary building units are linked together to form secondary building units. The secondary building units consist of n-ring structures which can contain as many as 20 tetrahedra and as little as 4[15]. This is shown schematically in Figure 2.3 Each corner in the secondary building units represents the center of tetrahedra.

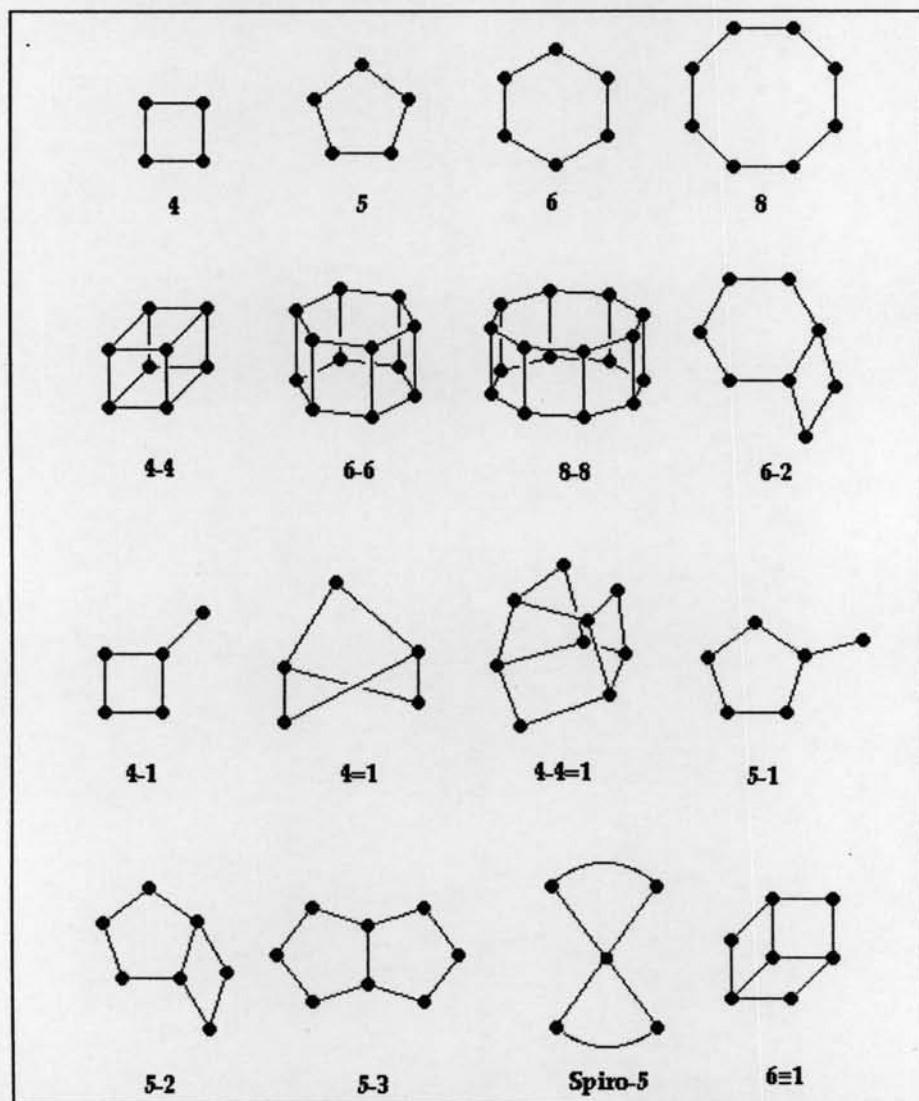


Figure 2.3 The secondary building units of zeolite structures. [15]

Most zeolite frameworks can be generated from several different SBUs. For example, the sodalite framework can be build from either the single 6-member ring or the single 4-member ring. Some of them are shown in Figure 2.4.

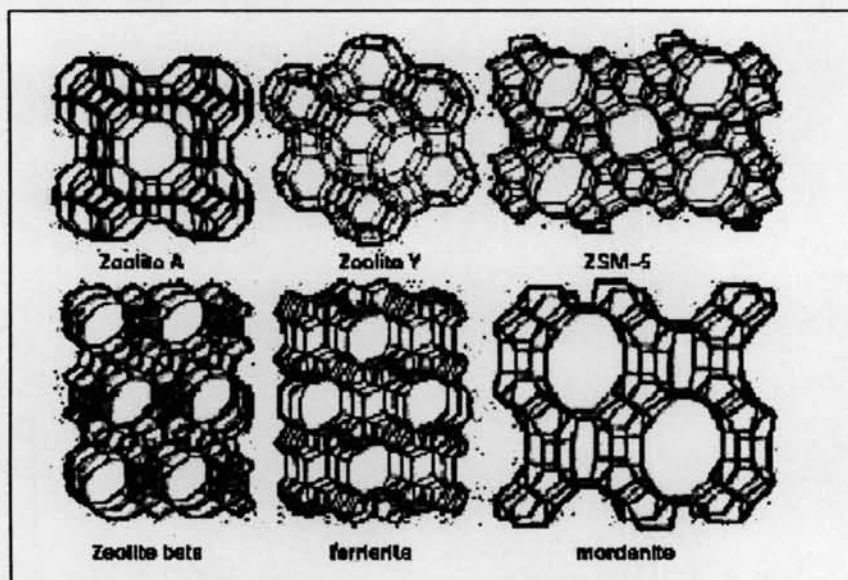


Figure 2.4 Framework topologies of various zeolites. [16]

2.1.2 Acid sites in zeolites

Zeolite acts as the acid catalyst due to the present of acid site. Brønsted acidity is at the proton donor site, and electron deficient atom that can accept an electron pair behaves a Lewis acid site. Both types of acid site of zeolite were shown in Figure 2.5.

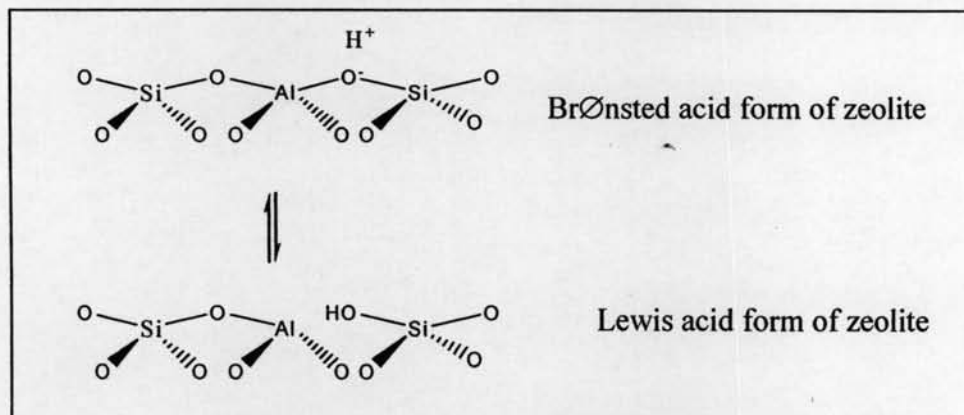


Figure 2.5 Brønsted and Lewis acid sites of zeolites.

2.1.3 Shape selective

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are nor fundamentally different with zeolites or with any acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes: reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 2.6.

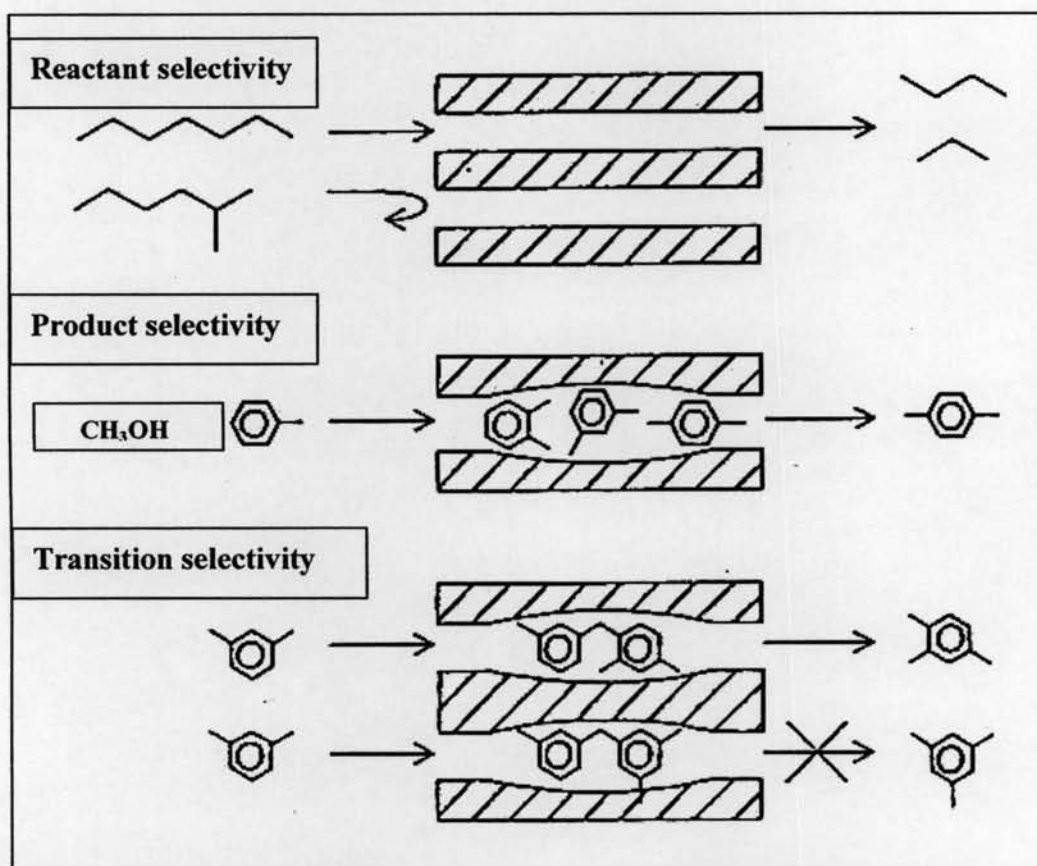


Figure 2.6 Diagram depicting the three types of selectivity. [17]

Reactants of charge selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reaction. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and pass through opening, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

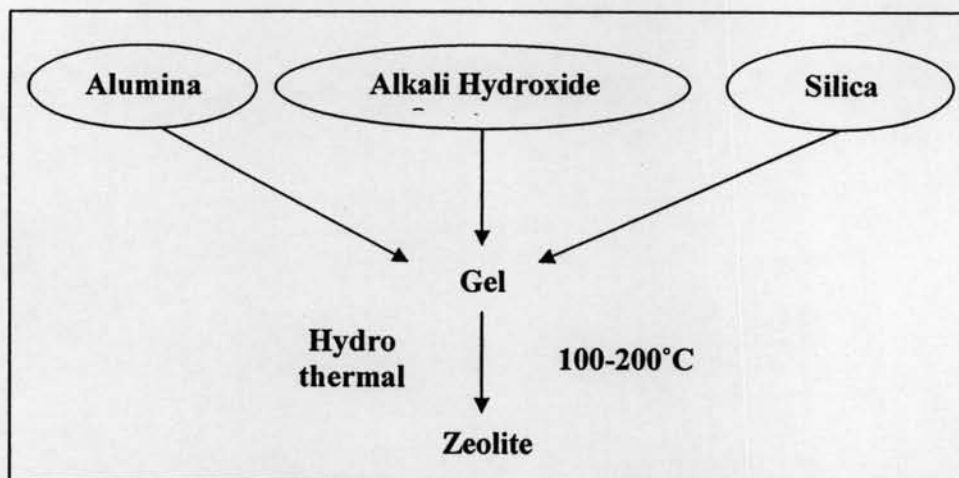
2.1.4 Zeolite synthesis

Zeolites are generally synthesized by a hydrothermal process from a source of alumina (e.g., sodium aluminate or aluminium sulfate) and of silica (e.g., a silica sol, fumed silica, or sodium water glass) and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession. Nucleation effects can be important, and an initial induction period at near ambient temperature may be followed by crystallization temperature that may range up to 200°C or higher. The pressure is equal to the saturated vapor pressure of the water present. The synthesis method is shown in Scheme 2.1.

The final product depends on a complex interplay between many variables including SiO₂/Al₂O₃ ratio in the starting medium, nucleating agents, temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic cations. Much remains to be learned about how the initial reaction mixture forms the precursor species and how these arrange into the final crystalline products. A key concept is that the cations present give rise to a templating action, but clearly the process is more complex.

After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about 550°C. Organic species are also thus removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolite this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. For other zeolites Na⁺ is replaced with NH₄⁺ via an ammonium compound such as NH₄OH, NH₄Cl or NH₄NO₃. Upon heating NH₃ is driven off, leaving the zeolite in the acid form. For some

reaction a hydrogenation component such platinum or nickel is introduced by impregnation or ion exchange.



Scheme 2.1 Representation of synthesis methods for zeolites.

2.2 Zeolite beta

2.2.1 Structure and properties of zeolite beta

Zeolite beta is an old zeolite discovered before Mobil began the “ZSM” naming sequence. Zeolite beta was initially synthesized by Wadlinger et al. [19] using tetraethylammonium hydroxide as the organic template. The structure of structure of zeolite beta was recently determined because the structure is very complex and interest was not high until it becomes important for some dewaxing process.

Beta is a high-silica 12-ring pore zeolite containing a three-dimensional pore system. Zeolite beta can be conceived as an intergrowth of two crystalline (hypothetical) polytypes A and B that are depicted in projection on the top section of Figure 2.7. In this drawing (the oxygen atoms have been omitted for clarity) one can observe that the pores in polytype A are arranged in an ABABAB. . . type configuration and in polytype B they are arranged in an ABCABC. . . type configuration. An identical set of pores to the ones depicted in Figure 2.7 also runs left-to-right in both polytypes, and a distinct third set runs vertically in both polytypes.

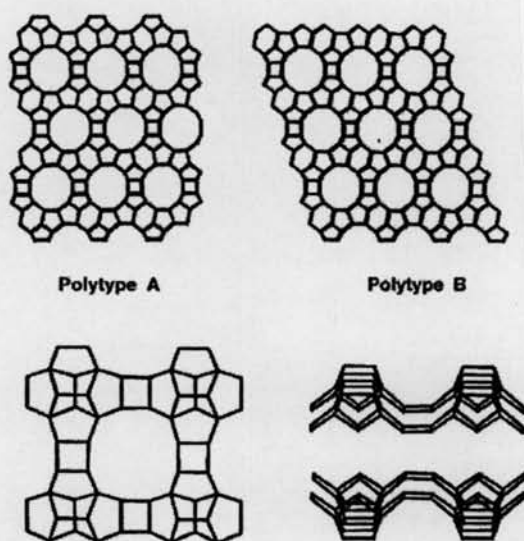


Figure 2.7 Frameworks of polytypes A and B of zeolite beta (top) and a layer or periodic building unit (PerBU) of zeolite beta (bottom). Only the T-atom positions are used for simplicity. [20]

The chemical composition of zeolite beta is:



The zeolite may offer interesting opportunities as a catalyst, since it combines three important characteristics: large pore (12 membered oxygen ring), high silica to alumina synthesis ratio, three dimension network or pores. In addition, the dimensions of on type of pores (5.5 \AA) can give a certain level of shape selectivity, high thermal and chemical stability. This has been suitable for isomerization of $\text{C}_4\text{-C}_7$ hydrocarbons to gasoline fraction with increasing octane number [21,22], to transalkylation of xylenes [23], and to condensation of benzene and formaldehyde [24].

2.2.2 Synthesis of zeolite beta

The synthesis of zeolite beta has been studied. Most synthetic zeolite are made by hydrothermal method using templating agent such as tetraethylammonium hydroxide (TEAOH). The crystal displayed truncated square bipyramidal morphology with diameter from 0.5 to $1.0 \mu\text{m}$ and Si/Al ratio from 14 to 72 in a wide range of crystallization

temperature and time. The intensity of the X-ray line was strongly influenced by the condition of calcinations the best results were obtained by calcinations under water vapor [25, 26]. The silicon content were increased in reaction mixture which led to a small enhancement of the Si/Al ratio in the crystal.

Wilma N.M. [27] studied the synthesis of zeolite beta with lower templating content and observed the influence in its crystallization and crystal size. The average crystallite sizes were increased when templating contents were decreased, especially, when temperature was increased from 130 to 150°C and longer crystallization time was set.

Nanocrystalline zeolite beta was first synthesized and characterized by Cambor et al. [28]. Without the presence of alkali metal cations, as small as 5 nm were obtained from zeolite beta. Later, Prokesova et al. [29] reported that zeolite beta with a crystal sizes ranging from 50 to 70 nm was successfully synthesized using different silica and aluminum sources. Laudau et al. [30] synthesized the colloidal zeolite beta crystals. The zeolite material in colloidal solution was in the range of 60–100 nm, which were aggregates of 10–20 nm small zeolite nanocrystals. Chica and Corma [31] reported that nanocrystalline zeolite beta is better catalyst than H-mordenite for n-heptane due to its large pore size (0.76 nm). They also observed that nanocrystalline zeolite beta has higher selectivity for isomerization than commercial beta zeolite due to its lower crystal size. Lucas *et al* [32] reported that beta zeolite yielded a higher extent of branched isomers due to its large pore size. The large pore size was facilitated rapid diffusion of branched products. Nanocrystalline catalyst had low unit cells. They provided more active sites for catalyzing the surface reactions. Selectivity were increased due to reduce diffusion limitations.

2.3 Mesoporous materials

Two classes of materials that are extensively as heterogeneous catalyst and adsorption media are microporous and mesoporous materials. Well-known members of the microporous class are zeolites, which provide excellent catalytic properties by the

larger pores have been made, but they were unsuccessful. Larger pores are present in porous glasses and porous gels, which were known as mesoporous materials.

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures, which has resulted in a worldwide resurgence in this area. The template agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially. Three different mesophases in this family have been identified, i.e., lamellar, hexagonal, and cubic phase. MCM-41 [33] has a hexagonally packed array of cylindrical pores. The structure of MCM-48 [34] has a three-dimensional, cubic-ordered pore structure and MCM-50 [35] contains a lamellar structure as illustrated in Figure 2.8.

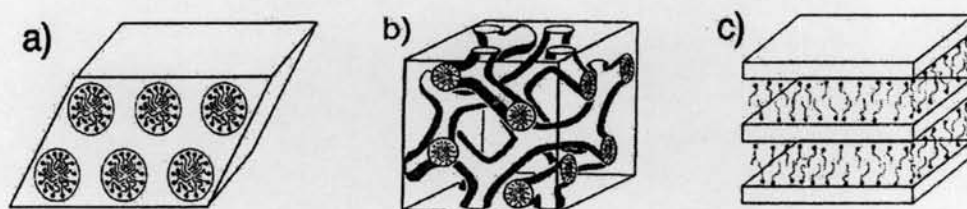


Figure 2.8 A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

Recently there are many families of mesoporous materials. Especially, new mesoporous member with hexagonal structure was discovered, such as HMS (Hexagonal Mesoporous Silica) [36], FSM-16 (Folded Sheets Mesoporous Materials) [37] and SBA-15 [38] with straight hexagonal structure. Because different types of templates can be used for synthesizing hexagonal mesoporous materials at various pH of gel, the new hexagonal materials can be obtained. The interaction of various types of template with inorganic species for assembling these materials are different as summarized in Table 2.2, together with the condition typically employed for a synthesis.

Table 2.2 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species.

Material	Template	Assembly	Media (pH)
MCM-41	Quaternary ammonium salt	Electrostatic	Basic or Acid
FSM-16	Quaternary ammonium salt	Electrostatic	Basic (pH = 8.5)
SBA-15	Amphiphilic triblock copolymer	Hydrogen bonding	Acid (pH = 1-2)
HMS	Primary amine	Hydrogen bonding	Neutral

MCM-41 and FSM-16 can be synthesized using quaternary ammonium salt as a template. In case of SBA-15, amphiphilic triblock copolymer can be modified as a template and must be synthesized in acid condition of hydrochloric acid. On the other hand, HMS can be prepared in neutral and environmentally benign condition using primary amine as a template. Although these materials have the same hexagonal structure, some properties are different as shown in Table 2.3.

Table 2.3 Properties of some hexagonal mesoporous materials [33,36,37,38].

Material	Pore size (Å)	Wall thickness (nm)	BET specific surface area (m ² /g)	Framework structure
MCM-41	15-100	1	>1000	Honey comb
FSM-16	15-32	-	680-1000	Folded sheet
SBA-15	46-300	3-6	630-1000	Rope-like
HMS	29-41	1-2	640-1000	Wormhole

2.3.1 Mechanism of mesostructure formation

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for the various synthesis routes [38]. On the most common level, these models are predicted upon the presence of surfactants in a solution

to direct the formation of inorganic mesostructure from stabilized inorganic precursors. The type of interaction between the surfactant and the inorganic species was significantly different depending on the various synthesis routes as shown in Table 2.4

Table 2.4 Example route for interaction between the surfactant and the inorganic soluble species.

Surfactant type	Inorganic type	Interaction type	example materials
Cationic (S^+)	I^-	S^+I^-	MCM-41, MCM-48
	I^+X^-	$S^+X^-I^+$	SBA-1, SBA-2, zinc phosphate
	I^0F^-	$S^+F^-I^0$	silica
Anionic (S^-)	I^+	S^-I^+	Al, Mg, Mn, Ga
	IM^+	$S^-M^+I^-$	alumina, zinc oxide,
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0	HMS, MSU-X, aluminum oxide
	I^+X^-	$S^0X^-I^+$	SBA-15

Where S^x or N^x : surfactant with charge of X
 I^x : inorganic species with charge of X
 X^- : halogenide anions
 F^- : fluoride anion
 M^{n+} : with charge of X

In case of MCM-41 and FSM-16, the interaction between template and inorganic species is electrostatic interaction while hydrogen bonding interaction occurs in HMS and SBA-15 synthesis [44]. The pore diameter of these materials were controlled by alkyl chain length of surfactant. Mechanism of mesoporous formation were different depending on synthesis route for each material.

(a) Liquid crystal templating mechanism

A liquid crystal templating (LCT) mechanism was proposed by the Mobil researchers that firstly reported M41S material. The variation of surfactant concentration

plays a significant role to control the structure. Figure 2.9 shows two possible for the LCT mechanism for hexagonal MCM-41.

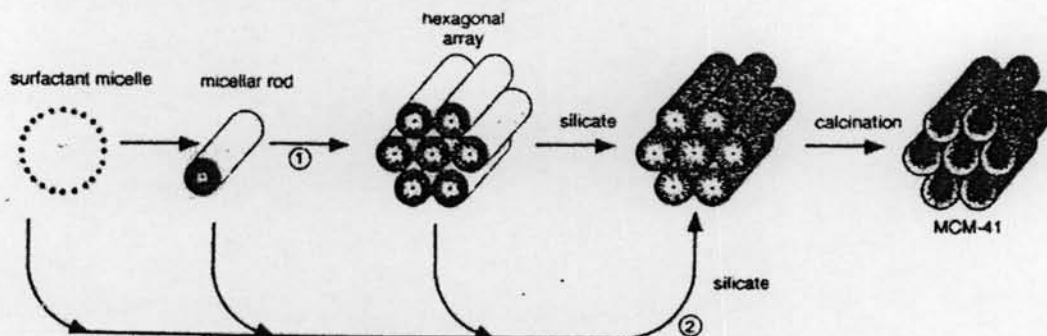


Figure 2.9 Two possible ways for the LCT mechanism.

There are two main pathways, in which either the liquid-crystal phase was intact before the silicate species were added (pathway 1), or the addition of the silicate results in the ordering of the subsequent silicate-encased surfactant micelles (pathway 2).

(b) Folding sheet formation

The intercalation of ammonium surfactant into hydrated sodium silicate, which composed of single-layered silica sheet call kanemite, produce the lamellar-to-hexagonal phase in FSM-16 material preparation. After the surfactants were ion-exchange into layered structure, the silicate sheets were thought to fold around the surfactants and condense into hexagonal mesostructure. The final product was claimed to be very similar to MCM-41. However, Vartuli *et al.* found that the layered structures were still retained in the kanemite-derived mesoporous materials [38]. Folding sheet formation is illustrated in Figure 2.10.

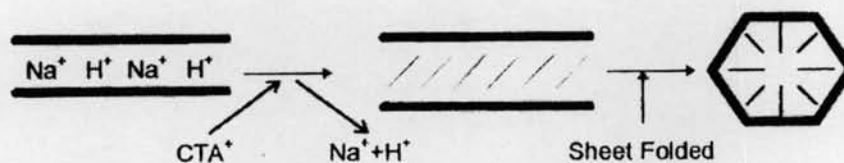


Figure 2.10 Schematic model representing "folding sheets" mechanism.

(c) Hydrogen bonding interaction

Tanev *et al* [39] showed that mesoporous silica could be prepared by the hydrogen-bonding interaction of alkylamine (S^0) head group and hydroxylated tetraethyl orthosilicate (I^0) as shown in Figure 2.11. The materials lacked long-range order of pore, but had higher amounts of interparticle mesoporosity, because the long-range effects of the electrostatic interaction that would normally control the packing of micellar rods were absent. This neutral templating synthesis route produced mesoporous silicates with thicker walls and higher thermal stability compared to the LCT-derived silicates. The silicate framework in the resulting mesophase was neutrally charged. From this reason, the surfactant can be easily removed by solvent extraction.

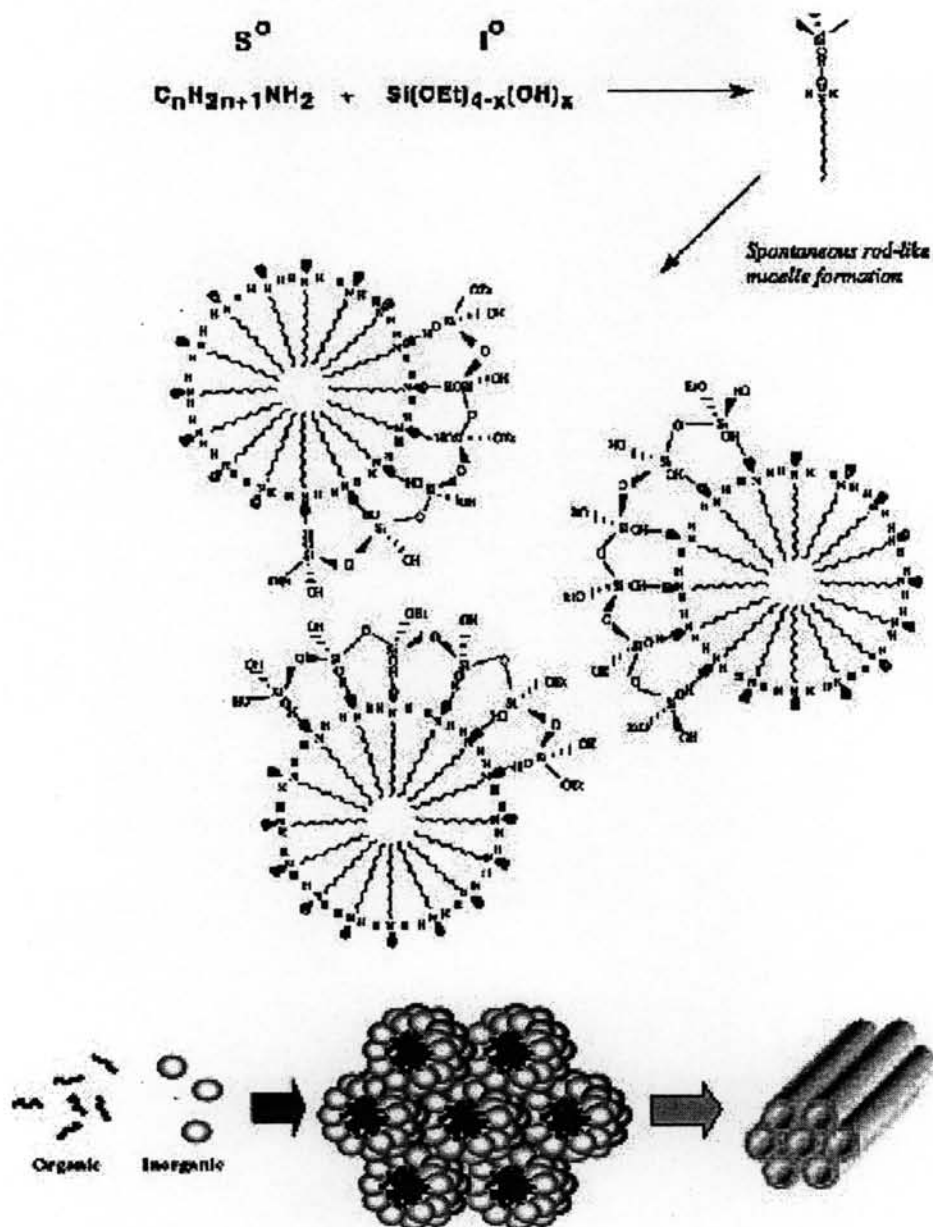


Figure 2.11 Schematic representation of the $S^{\circ}I^{\circ}$ templating mechanism of formation of HMS. [39]

2.4 Hexagonal mesoporous silica (HMS)

HMS was discovered in 1994 by Pinnavia *et al* [40]. This material can be synthesized at room temperature by neutral templating route. In this case, primary amine can be used as a template, alcohol such as ethanol or propanol was used as cosolvent

[39]. Although alcohol behaves as a cosolvent in HMS synthesis, it made a different of polarity of mixed solvent, which gave different hydrolysis rate and nucleation. Pinnavaia *et al.* revealed the different properties of HMS between the water rich system (water : ethanol = 90 : 10 v/v) and ethanol rich system (water : ethanol 35 : 65 v/v). Textural mesoporosity or the porosity arising from intraaggregate void and spaces formed by interparticle contacts of HMS using water rich system is higher. In the ethanol rich system, HMS with low textural porosity was obtained and the particles were composed of macroscale spheroid particles aggregated into the larger particles while water rich system yields mesoscale particle aggregated into larger particles [41].

The pore size of HMS can be controlled by alkyl chain length between C₈-C₁₈ in primary amine templates [39] and also modified with auxillary structure such as mesitylene to expand the pore of HMS [41]. The organic template of HMS can be totally removed from as-synthesized samples by solvent extraction, which is not possible in the case of the other pathways where strong electrostatic interactions exist between organic and inorganic phase. The solvent extraction can be prevented the partial degradation of the mesoporous structure that could occur during calcinations in air at a relatively high temperature. In addition, the environmentally synthesis condition make many researcher focused on HMS synthesis and its potential application [42]. Pure silica HMS was limited its application to catalysis, supports of adsorbents. In order to provide HMS with potential catalytic application, it was possible to modify the nature of framework by incorporation of heteroelement [42,43]. When trivalent metal cations like Al³⁺, B³⁺, Ga³⁺, Fe³⁺ were incorporated to framework of silica. The negative charges can be balanced with proton. These solid catalysts can be used as acid catalysts or acid support. Acidity adsorption of pyridine result on Al-HMS reported by Tuel *et al* [43] showed acidity of Al-HMS were weaker and their strength was approximately the same as that of amorphous silica-alumina. In addition, Mokaya and Jones found that directly calcined Al-HMS with Si/Al ratios 5 possessed acid sites very similar in strength to HY zeolite [44]. The incorporation of Al into mesoporous silicas is of particular interest as it gives rise to materials with solid acid and cation exchange properties. The acid and ion exchange sites are primarily associated with the presence of tetrahedrally coordinated Al in framework positions within the silica matrix. Al may be introduced into mesoporous silicas by direct

synthesis or by post-synthesis grafting methods. Both methods, however tend to result in (calcined) materials with a significant proportion of extra-framework (octahedrally coordinated)Al. It is desirable, with respect to acid catalysis and ion exchange properties, to maximize the proportion of Al in framework (tetrahedral) positions. So far no method has been described for modifying the sitting of Al in calcined mesoporous aluminosilicates so as to maximize the amount (or proportion) of Al in framework positions. Reinsertion of extra-framework Al (EFAL) into framework positions has been previously described for dealuminated Y zeolites *via* hydrothermal treatment of the zeolite in an aqueous solution of KOH. However, such treatment is not feasible for mesoporous aluminosilicates because it is too severe. The relatively fragile mesoporous frameworks would readily dissolve in the highly basic (pH = 13.5) KOH solution. Mokaya [46] reported a method *via* which virtually all octahedrally coordinated (extra-framework) Al in calcined Al-grafted MCM-41 materials can be inserted into (tetrahedral) framework positions. The method, which involves treatment of the mesoporous aluminosilicates with an aqueous solution of NH_4OH (pH \approx 11.1), can be performed either at room temperature (30 °C) or at a range of temperatures up to 80°C. NH_4OH was chosen due to the well known stability of Al grafted MCM-41 materials at pH = 11,10 and also because NH_4^+ is potentially an acid generating cation (and therefore no further ion exchange would be required to maintain Brønsted acidity).

2.5 Plastic recycling method

Plastic recycling involves the transformation of plastic polymers by means of heating chemical agents to yield hydrocarbon products that may be used in the production of new polymers, refined chemicals or fuels. A variety of treatments may be category including chemical depolymerisation, gasification, thermal cracking and catalytic conversion.

2.5.1 Thermal cracking

Thermal cracking, or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500- 800°C and results in the formation of a carbonised char and a volatile fraction that may be separated into a condensable hydrocarbon oil and a non-condensable high calorific value gas. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions. In the case of polyolefins like polyethylene or polypropylene, thermal cracking has been reported to proceed through a random scission mechanism that generates a mixture of linear olefins and paraffins over a wide range of molecular weights [9]. In pyrolytic processes, a proportion of the species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter and intramolecular reactions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.

The Hydrocarbon cracking mechanism

A thorough study on the mechanism for the thermal decomposition of polymers are:

- (1) End-chain scission or unzipping: Cracking is targeted at chain ends first, and then successively works down the polymeric length. Unzipping results in the production of the monomer.
- (2) Random-chain scission: Random fragmentation of polymer along polymer length. Results in both monomers and oligomers.
- (3) Chain-stripping: Side chain reactions involving substituents on the polymer chain.
- (4) Cross-linking: Two adjacent 'stripped' polymer chains can form a bond resulting in a higher MW species. An example is char formation.

The thermal pyrolysis of PP and PE is known to follow the random chain scission route, resulting in mainly oligomers and dimers [46]. This mechanism is illustrated for

PE and PP in Figures 2.12 and 2.13, respectively. Peterson *et. al.* observed that PE decomposition by thermogravimetry yielded mainly 1-hexene and propene [47].

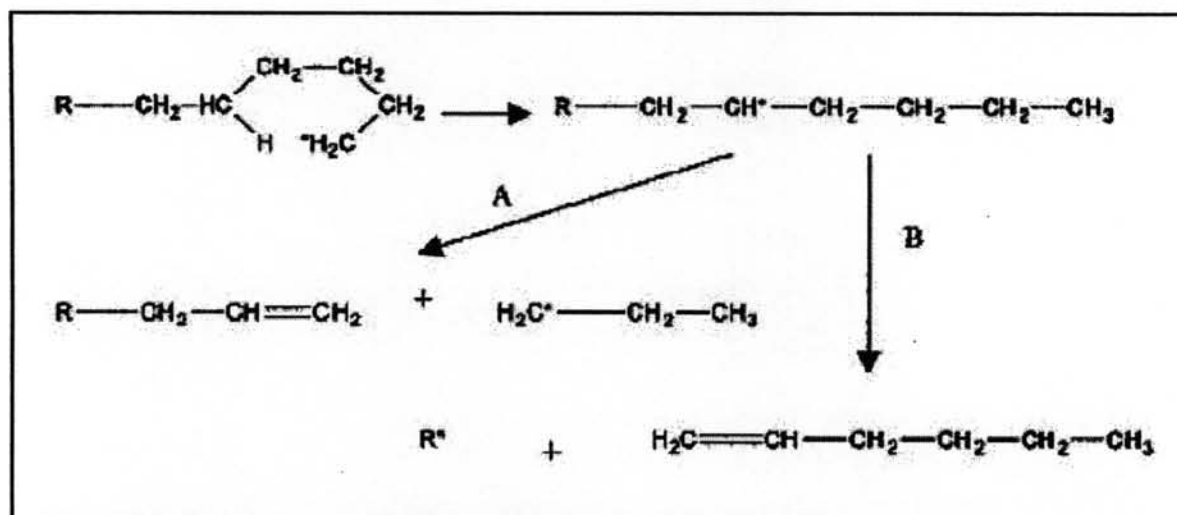


Figure 2.12 Random chain scission in polyethylene. [47]

Similarly Peterson *et. al.* observed that in the thermal pyrolysis of PP, the main products were pentane, 2-methyl-1-pentene and 2,4 dimethyl-1-heptene [47]. During degradation, methyl, primary and secondary alkyl radicals are formed, and by hydrogen abstractions and recombination of radical units, methane, olefins and monomers are produced.

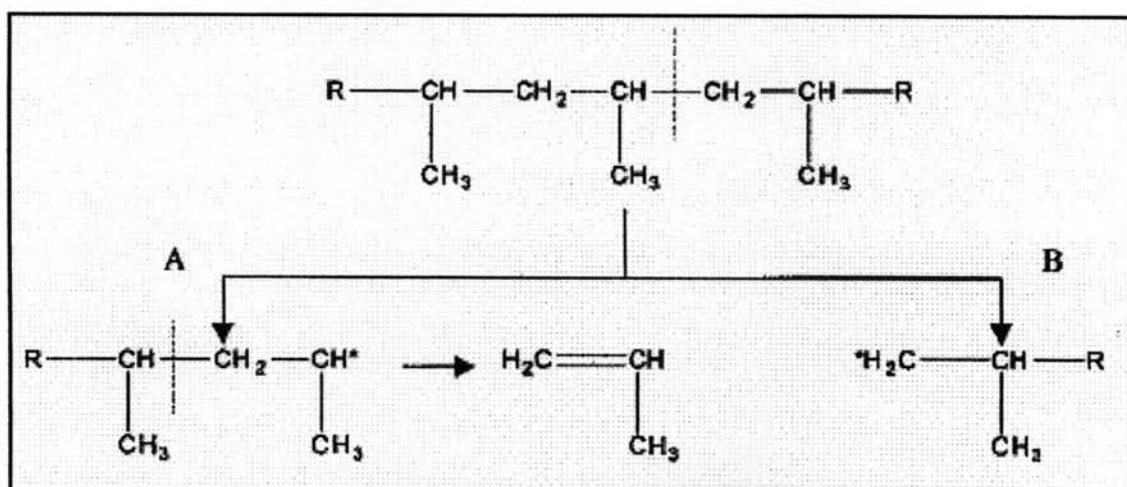


Figure 2.13 Random chain scission in polypropylene. [47]

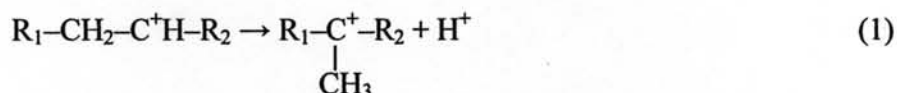
The polyolefin samples are typically degraded in a closed reactor/melting vessel and heated to a reaction temperature at which the polymer decomposes. A reaction time is allowed and over time, the degradation products (gaseous, liquids and solid) are collected and analyzed.

2.5.2 Catalytic cracking

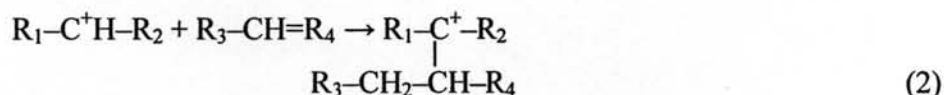
Catalytic cracking uses a zeolite catalyst and moderately-high temperatures (400–500 °C) to aid the process of breaking down large hydrocarbon molecules into smaller ones. During this process, less reactive, and therefore more stable and longer lived intermediate cations accumulate on the catalysts active sites generating deposits of carbonaceous products generally known as coke. The formation of carbenium ions from olefins can easily proceed by addition of the proton from a Brønsted acid site of the catalyst to the carbon–carbon double bond. Cracking of the adsorbed carbenium ion proceeds through the β -scission mechanism [48, 49].

Reactions of the adsorbed carbenium ion are [50, 51]:

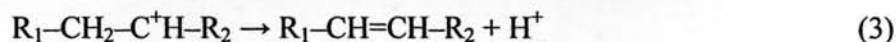
1. Isomerization to a more stable carbenium ion, for example, through a methyl shift:



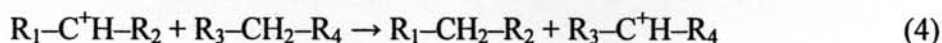
2. Oligomerization with olefin in a bimolecular reaction to form a larger adsorbed carbenium ion:



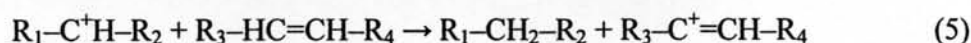
3. Desorption with deprotonation to form an olefin (the opposite of adsorption):



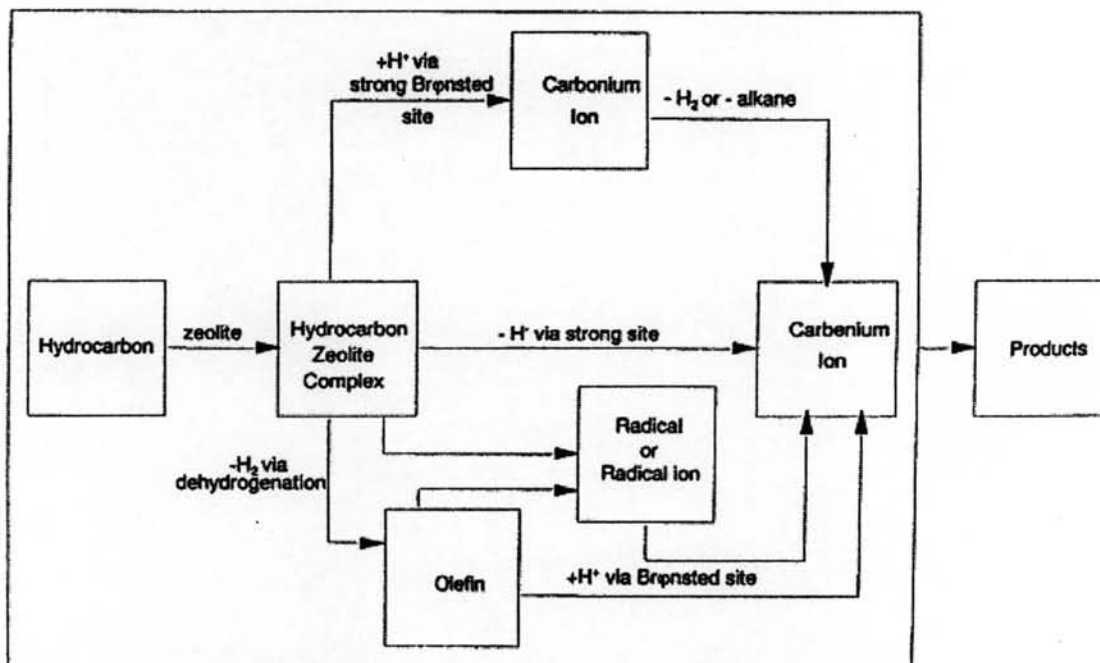
4. Desorption with hydride abstraction from a paraffin to form new paraffin from the carbenium ion and new carbenium ion from the paraffin (H-transfer reaction):



5. Desorption with hydride abstraction from (cyclic) olefins or coke (precursors) to form paraffin and a more aromatic compound (H-transfer reaction):



The bimolecular reactions (2), (4) and (5) can occur if the pore size of the catalyst is large enough to accommodate the reactive intermediates, or they should occur on the outer surface of the zeolite particles. A general mechanistic reaction scheme involving the discussion of the carbenium ion of catalytic cracking chemistry for the degradation of hydrocarbon has been proposed previously [52].



Scheme 2.2 Representation general mechanistic hydrocarbon degradation in zeolites.

This representation is simplified regarding the formation of carbenium ions in that it concentrates on reaction paths rather than on surface species. Theoretical studies suggest that, for the conversion of hydrocarbons on active zeolites, reactions proceed via carbenium ions as transition states (rather than as intermediates) and product distributions

are also generally in agreement with carbenium ion studies, although there is still debate about the actual mode of scission . The model uses the following assumptions.

1. The liquid-phase polymer. Initially, solid polymer is freely dropped into the reactor and immediately melts to disperse around the catalysts. The molten polymer, in contact with the catalyst particle forms a polymer/catalyst complex, reaction commencing at the surface. Polymer melting and spread times are negligible.

2. Evolution of intermediates. Scission reactions generate intermediates which include long-chain olefins and intermediate precursors for carbenium ions. The carbenium ions rapidly reach a steady-state concentration. Alkanes may be generated, via hydrogen transfer, and initially will be largely long-chain products. In general, the number of active sites limits the number of carbenium ion precursors.

3. Evolution of products. Once the intermediates are produced, further reactions could be expected to produce smaller chain olefins in equilibrium with surface carbenium ions, as well as alkanes, benzene, toluene and xylene (BTX) and coke. The equilibrium mixture of olefins and carbenium ions subsequently reacts further to produce the final products[52].