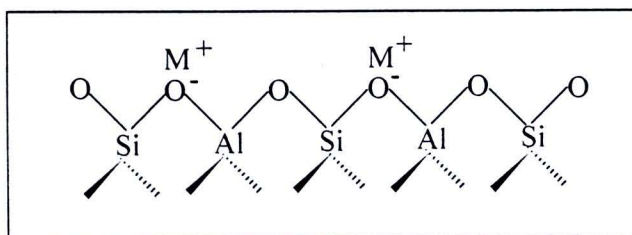


## CHAPTER II

### THEORY

#### 2.1 Zeolite

Zeolites are crystalline aluminosilicates that contain uniform pores and cavities with molecular dimensions. The structures of zeolites consist of an extensive three-dimensional network of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral. The tetrahedral are cross-linked by the sharing of oxygen atoms as shown in Figure 2.1



**Figure 2.1** The structure of zeolites [11].

The important role of zeolites and related materials in processes can be attributed to their superior properties. Some of their advantages are listed below:

1. Large surface area and adsorption capacity
2. The possibility of controlling the adsorption properties by tuning the hydrophobicity or hydrophilicity of the materials
3. The pore openings and cavities in the range of 5-12 Å
4. Insoluble materials and well defined pore structures
5. Different types, different properties
6. The presence of shape and size selectivities

##### 2.1.1 Zeolite structures

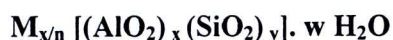
Molecular sieves are porous materials that exhibit selective adsorption properties. They can be classified into three main types depending on their pore size: and the IUPAC definitions: microporous materials, mesoporous materials, and

macroporous materials. Properties and examples of these materials are summarized in Table 2.1.

**Table 2.1** IUPAC Classification of porous materials

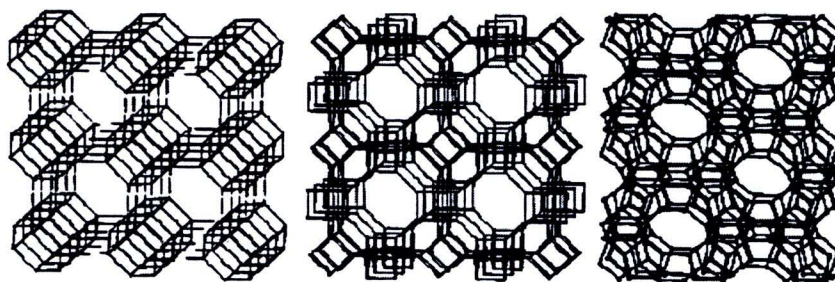
Type of material	Pore size (Å)	Examples
Micropores	< 20	zeolites, activated carbon
Mesopores	20 – 500	M41s, SBA-15, pillared clays
Macropores	> 500	Glasses

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 adsorbents), petrochemical industry, and synthesis of chemicals. Zeolites are porous aluminosilicate materials that can be described by the general formula:



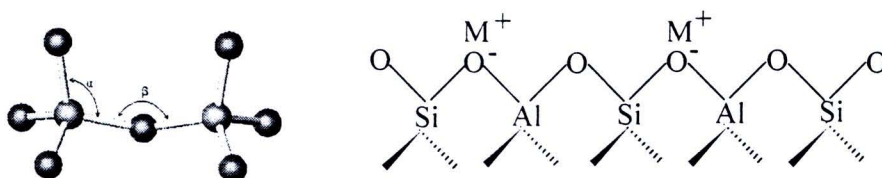
where M is the cation of valence n, generally from the group I or II ions, although other metals, nonmetals, and organic cations are also possible, w is the number of water molecules. Water molecules presented are located in the channels and cavities, as the cations that neutralize the negative charge created by the presence of the  $AlO_2^-$  tetrahedral unit in the structure.

The extra framework cations usually serve 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 2.2.



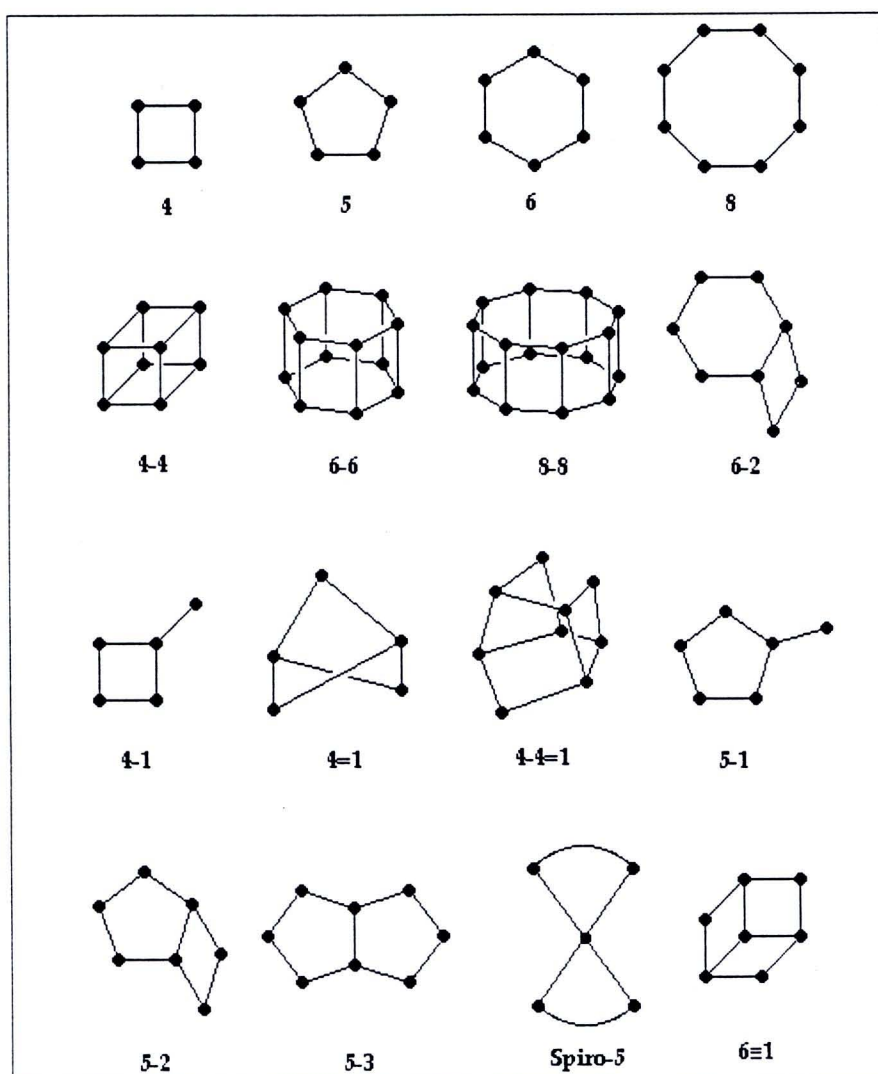
**Figure 2.2** Crystal structures of zeolites from left to right: ITA, CHA, and MFI.

The zeolite framework consists of cross-linked  $\text{TO}_4$  tetrahedra where T is Al or Si. Each T atom occupies four connected vertices of a three dimensional network and the oxygen occupies 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 ( $\alpha$  in Figure 2.2) is close to the ideal tetrahedra bond angle of  $109.5^\circ$ . The T-O-T bond angle ( $\beta$  in Figure 2.3) is much more flexible than the O-T-O bond angle and is usually around  $140^\circ$  to  $165^\circ$  [12].



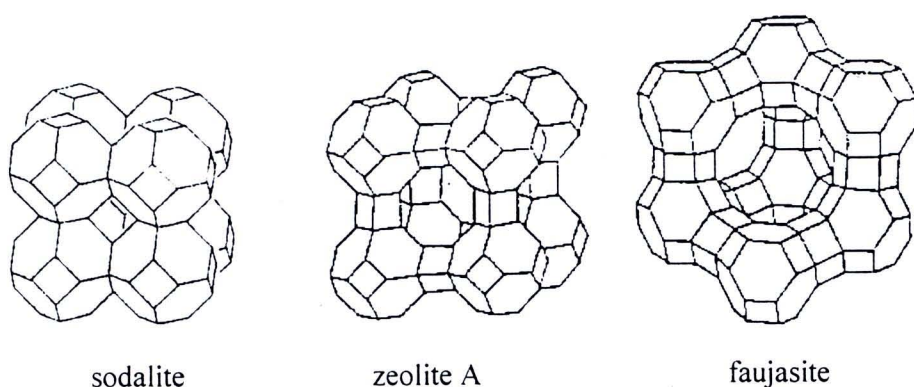
**Figure 2.3** The structure of zeolites [12].

The  $\text{TO}_4$  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 contain as many as 20 tetrahedra and as little as 4 [13]. This is shown schematically in Figure 2.4. Each corner in the secondary building units represents the center of tetrahedra.



**Figure 2.4** The secondary building units of zeolite structures [13].

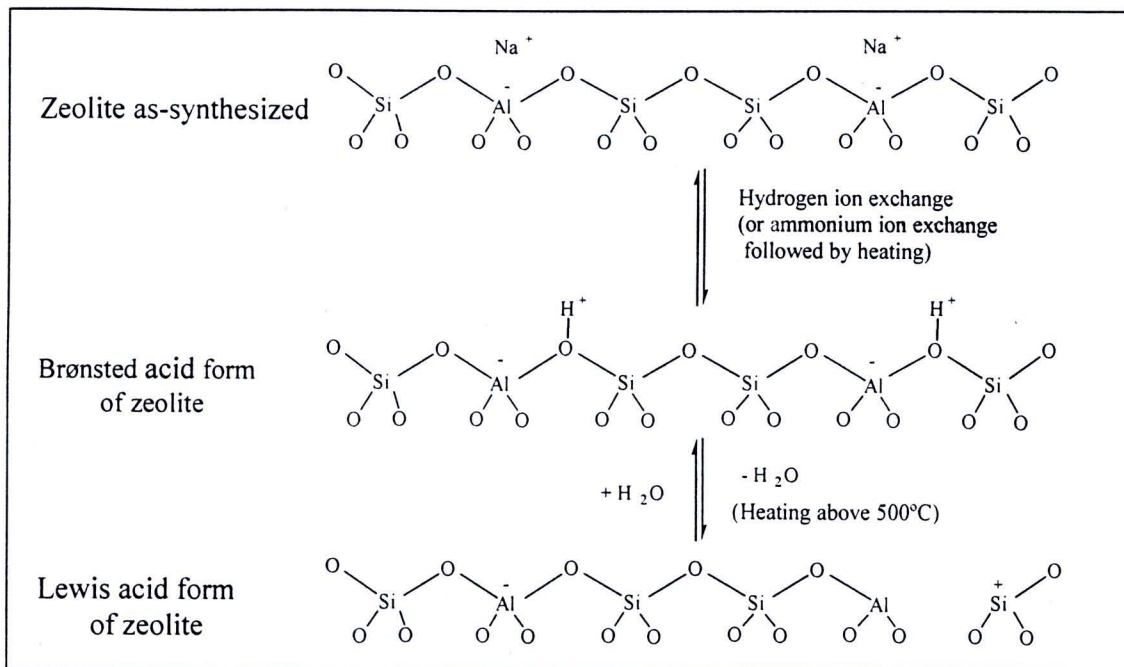
Most zeolite frameworks can be generated from several different secondary building units (SBUs). For example, the sodalite framework can be built from either the single 6-membered ring or the single 4-member ring. Some of them are shown in Figure 2.5.



**Figure 2.5** Framework topologies of various zeolites [14].

### 2.1.2 Acid sites of zeolites

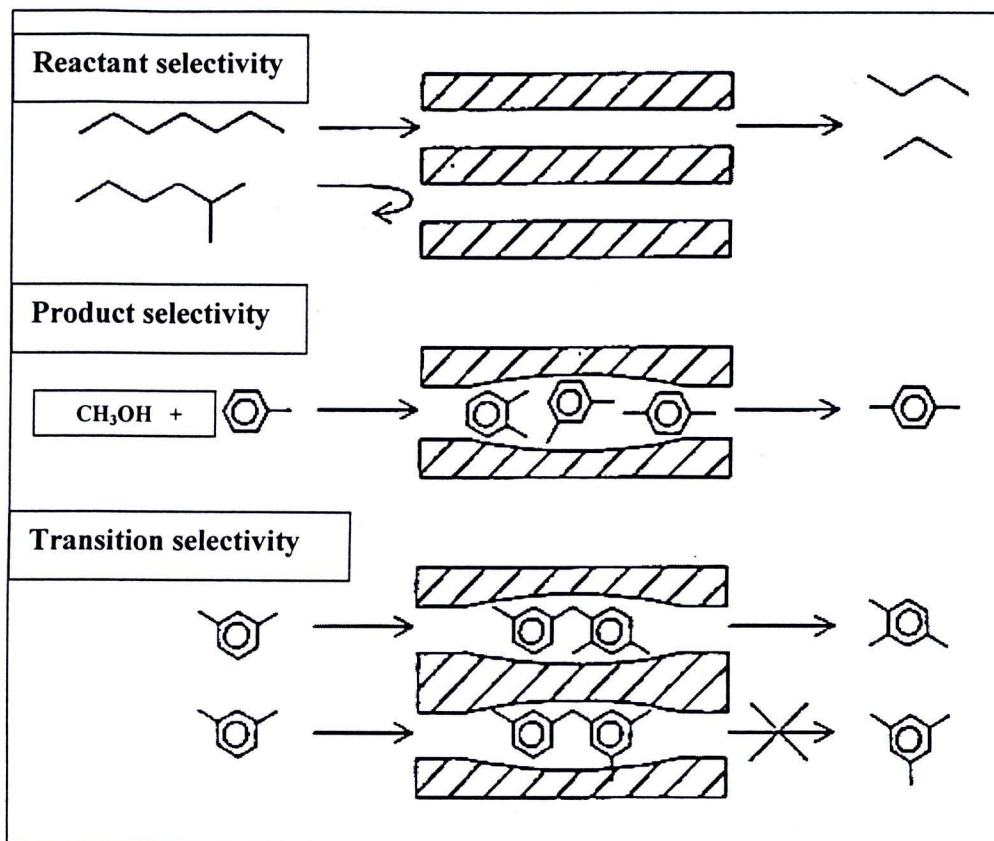
Most industrial application of zeolites is based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction [15-17]. This means that the activity required is based upon the production of Brønsted acid sites arising from the creating “hydroxyls” within the zeolites pore structure. These hydroxyls are formed by ammonium exchange followed by a calcination step. Zeolites as normally synthesized usually have  $\text{Na}^+$  balancing the framework charges, but these can be readily exchanged for protons by direct reaction with an acid, giving hydroxyl groups, the Brønsted acid sites. Alternatively, if the zeolite is not stable in acid solution, it is common to use the ammonium,  $\text{NH}_4^+$ , salt, and then heat it so that ammonia is driven off, leaving a proton. Further heating removes water from Brønsted site, exposing a tricoordinated Al ion, which has electron-pair acceptor properties; this is identified as a Lewis acid site. A scheme for the formation of these sites is shown in Figure 2.6. The surfaces of zeolites can thus display either Brønsted or Lewis acid sites, or both, depending on how the zeolite is prepared. Brønsted sites are converted into Lewis sites as the temperature is increased above  $500^\circ\text{C}$ , and water is driven off.



**Figure 2.6** The generation of Brønsted and Lewis acid sites in zeolite [18].

### 2.1.3 Shape selectivity

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to chemical standpoint the reaction mechanisms are fundamentally different with zeolites or with any acidic oxides. What zeolite adds 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 2.7.

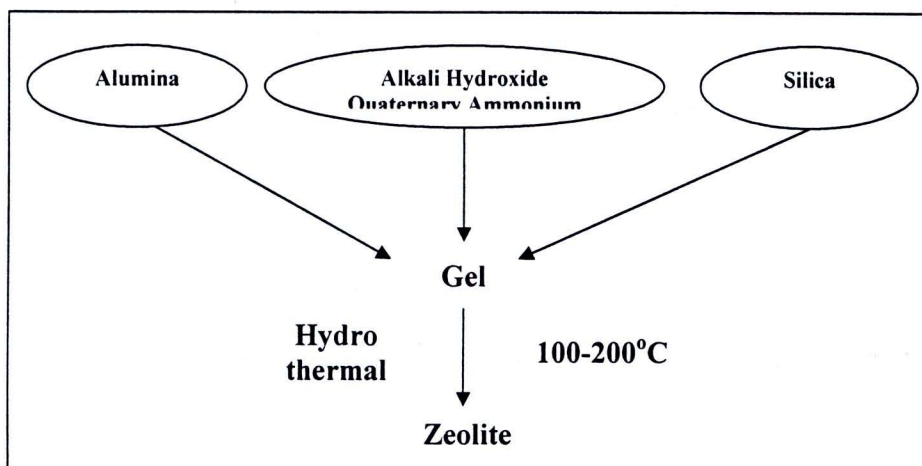


**Figure 2.7** Diagram depicting the three types of selectivity [19].

Reactants shape 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.

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 effect 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.



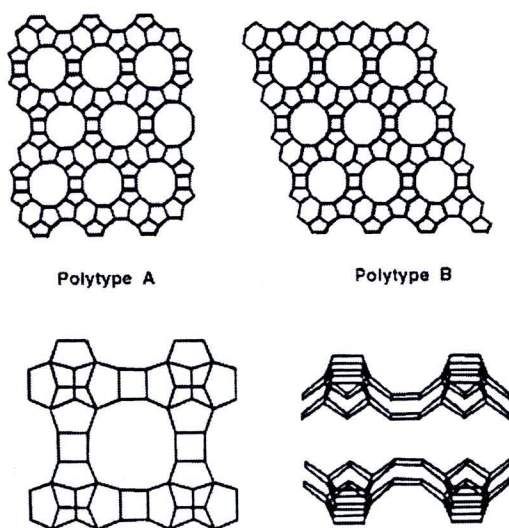
**Scheme 2.1** Synthesis method for zeolites.

The final product depends on a complex interplay between many variables including  $\text{SiO}_2/\text{Al}_2\text{O}_3$  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 they arrange into the final crystalline products. A key concept is that the cations give rise to a templating action, but the process mechanism is more complexed. After synthesis, the zeolites are washed, dried and heated to remove water of crystallization. Then, they are calcined in air, e.g., at about 550°C, to remove organic species. For catalytic purpose, zeolites must be converted into acidic form. For some zeolites this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. While, other zeolites can be achieved using ammonium compound such as  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ , for replacing  $\text{Na}^+$  with  $\text{NH}_4^+$ . Upon heating,  $\text{NH}_3$  is driven off and left the zeolite in the acidic form.

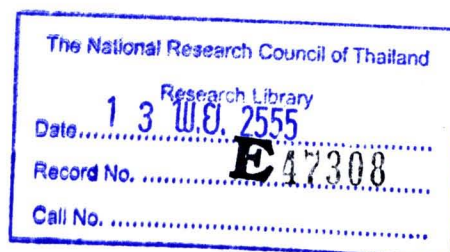
## 2.2 Zeolite beta

### 2.2.1 Structure and properties of zeolite beta

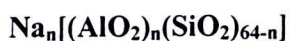
Zeolite beta is discovered in 1967 [20] was initially synthesized by Wadlinger et al. [21] using tetraethylammonium hydroxide as the organic template. The structure is very complicated and it was recently determined. Zeolite beta becomes importance in catalytic world for dewaxing process. Zeolite beta 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 2.8. 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 runs left-to-right in both polytypes, and a distinct third set runs vertically in both polytypes.



**Figure 2.8** 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 [22].



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 rings), high silica to alumina synthesis ratio, three dimension network or pores. In addition, the dimensions type of pores (5.5 Å) can give a certain level of shape selectivity, high thermal and chemical stability. This has been suitable for isomerization of C<sub>4</sub>-C<sub>7</sub> hydrocarbons to gasoline fraction with increasing octane number [23, 24], to transalkylation of xylenes [25], and to condensation of benzene and formaldehyde [26].

### 2.2.2 Synthesis of zeolite beta

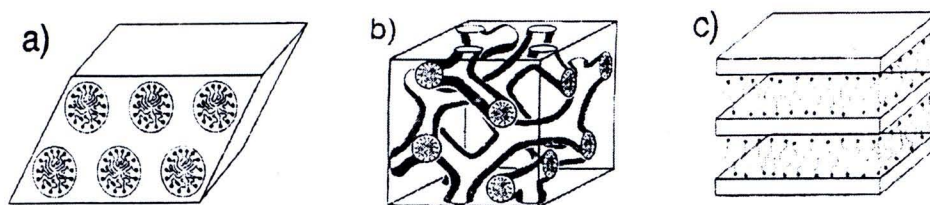
The synthesis of zeolite beta has been studied. Most synthetic zeolite are made by hydrothermal method using templating agent such as tetraethylammonium hydroxide (TEAOH). The crystal displayed truncated square bipyramidal morphology with diameter from 0.5 to 1.0 µm and Si/Al ratio from 14 to 72 in a wide range of crystallization temperature and time. The intensity of the X-ray line was strongly influenced by the condition of calcinations calcinations [27, 28]. The silicon content was increased in reaction mixture which led to a small enhancement of the Si/Al ratio in the crystal. Wilma N.M. [29] 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.* [30]. Without the presence of alkali metal cations, zeolite beta as small as 5 nm were obtained. Later, Prokesova *et al.* [31] 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.* [32] 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 [33] 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.* [34] 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 was increased due to reduce diffusion limitations.

### 2.3 Mesoporous materials

Two classes of materials that are extensively used 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 virtue of their crystalline aluminosilicate framework. However, their applications are limited by the relatively small pore openings. Many attempts to synthesize zeolites with 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 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 [35] has a hexagonally packed array of cylindrical pores. The structure of MCM-48 [36] is a three-dimensional, cubic-ordered pore structure and MCM-50 [37] contains a lamellar structure as illustrated in Figure 2.9.



**Figure 2.9** A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

Recently new members of mesoporous materials with hexagonal structure were discovered, such as HMS (Hexagonal Mesoporous Silica) [38], FSM-16 (Folded Sheets Mesoporous Materials) [39] and SBA-15 [40]. By varying different types of templates used and pH of gel for synthesizing hexagonal mesoporous materials 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

Materials	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 [35, 38-40]

Material	Pore size (Å)	Wall thickness (nm)	BET specific surface area (m <sup>2</sup> /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 synthesis routes [40]. On the 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
	$I^-M^+$	$S^-M^+I^-$	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

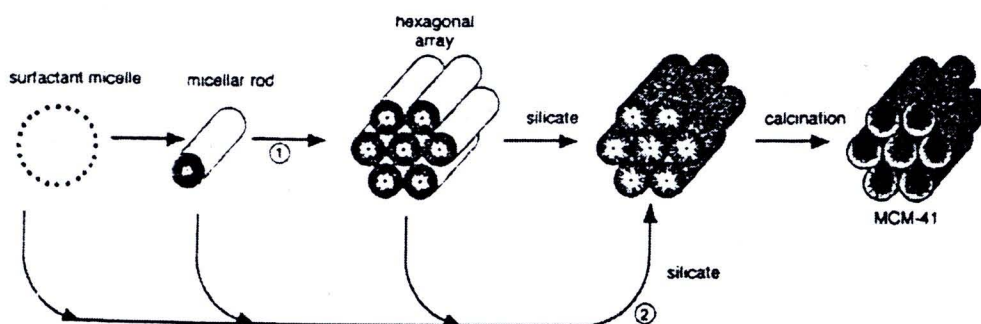
$F^-$  : fluoride anion

$M^{n+}$  : 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 [41]. The pore diameter of these materials was controlled by alkyl chain length of surfactant. Mechanism of mesoporous formation was different depending on synthesis route for each material.

### 2.3.1.1 Liquid crystal templating mechanism

A liquid crystal templating (LCT) mechanism was proposed by the Mobil researchers that firstly reported for M41S material. The variation of surfactant concentration plays a significant role to control the structure. Figure 2.10 shows two possible way of the LCT mechanism for hexagonal MCM-41.

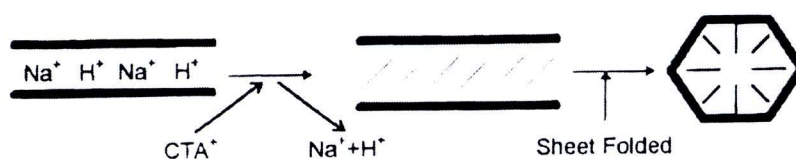


**Figure 2.10** Two possible ways for the LCT mechanism.

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).

### 2.3.1.2 Folding sheet formation

The intercalation of ammonium surfactant into hydrated sodium silicate, which composed of single-layered silica sheet called kanemite, produces the lamellar-to-hexagonal phase in FSM-16. After surfactants were ion-exchanged into the layered structure, the silicate sheets were folded around the surfactants and condensed 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 [40]. Folding sheet formation is illustrated in Figure 2.11.

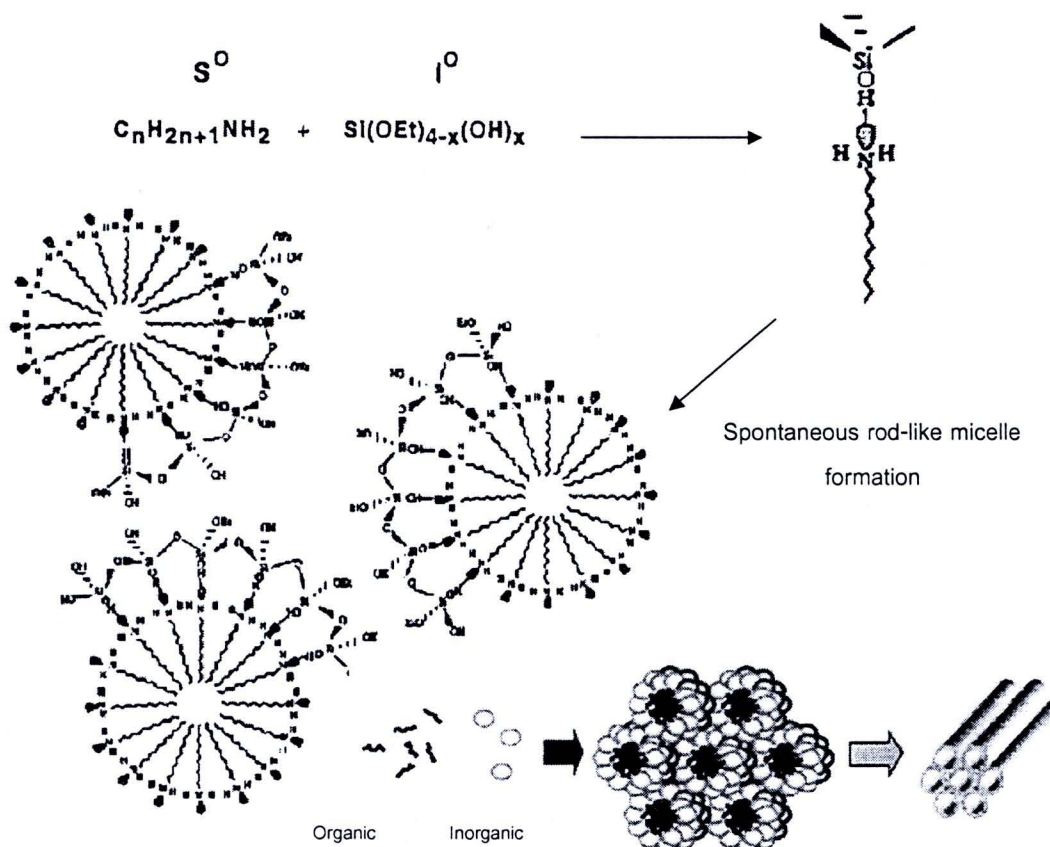


**Figure 2.11** Schematic models representing “folding sheets” mechanism.

### 2.3.1.3 Hydrogen bonding interaction

Tanev *et al.* [42] showed that mesoporous silica could be prepared by the hydrogen-bonding interaction of alkylamine ( $S^o$ ) head group and hydroxylated

tetraethyl orthosilicate ( $I^0$ ) as shown in Figure 2.12. The materials lacked long-range order of pore, but had higher amounts of interparticle of 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 2.12** Schematic representation of the  $S^0I^0$  templating mechanism of formation of HMS [42].

## 2.4 Hexagonal mesoporous silica (HMS)

HMS was discovered in 1994 by Pinnavia *et al.* [43]. 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 [42]. Although alcohol behaved as a cosolvent in HMS synthesis, it made a

difference in 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). The textural mesoporosity, the porosity arising from intraaggregate void and spaces by interparticle contacts of HMS using water rich system was higher than that in the ethanol rich system. The particles in the ethanol rich system were composed of macroscale spheroid particles aggregated into the larger particles, while the water rich system yields mesoscale particles aggregated into larger particles [44].

The pore size of HMS can be controlled by alkyl chain length between C<sub>8</sub>-C<sub>18</sub> in primary amine templates [42] and also modified with auxiliary structure such as mesitylene to expand the pore of HMS [44]. 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 prevent the partial degradation of mesoporous structure that could occur during calcination in air at relatively high temperature. In addition, the environmental friendly on synthesis condition make many researcher focusing on HMS synthesis and its potential application [45]. Pure silica HMS was limited in its application on catalysis and 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 [45, 46]. When trivalent metal cations like Al<sup>3+</sup>, B<sup>3+</sup>, Ga<sup>3+</sup> and Fe<sup>3+</sup> 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. The adsorption of pyridine result on Al-HMS reported by Tuel *et al.* [46] showed that the acidity of Al-HMS was weak and their strength was approximately the same as that of amorphous silica-alumina. In addition, Mokaya and Jones found that calcined Al-HMS with Si/Al ratio of 5 possessed the strength of acid sites similar to HY zeolite [41]. 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 position 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 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 [47] 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  $\text{NH}_4\text{OH}$  (pH  $\approx$  11.1), could be performed either at room temperature (30°C) or at a range of temperatures up to 80°C.  $\text{NH}_4\text{OH}$  was chosen due to the well known stability of Al grafted MCM-41 materials at pH = 11, 10 and also because  $\text{NH}_4^+$  was potentially an acid generating cation (and therefore no further ion exchange would be required to maintain Brønsted acidity).

## 2.5 Composite material

A composite material is composed of at least two elements working together to produce a material whose properties are different from the original material. In order to overcome the limitations of single element (micro- or mesoporous materials) and to combine the advantages of these two types of molecular sieves, a new type of materials containing both types porosity is expected to offer attractive features. The type of composite can be divided into physical composite and chemical composite. Recently, the higher catalytic activity of micro/mesoporous composite materials in comparison to conventional Al-MCM-41 was demonstrated in cumene cracking reaction.[48] The better catalytic behaviour of these composite materials have arisen from zeolite-like connectivity of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedral in the framework walls, and the high thermal stability of the resulted mesostructures.

For example, Kloetstra *et al.* [49] prepared zeolite faujasite overgrown the with a thin layer of mesoporous MCM-41, by adding FAU crystals to MCM-41 synthetic gel. The composite MCM-41/FAU showed good results in cracking of vacuum gasoil. Karlsson *et al.* [50] also prepared composite materials by simultaneous synthesis of MFI/MCM-41 phases using a two-template approach [ $\text{C}_6\text{H}_{13}(\text{CH}_3)_3\text{NBr}$  and  $\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{NBr}$ ] at optimal template concentrations and reaction temperatures. Bhatia *et al.* [51] reported that physical composite Beta/MCM-41 showed a higher conversion in the cracking of used palm oil for the production of liquid hydrocarbons compared to the chemical composite.

## 2.6 Recycling method

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.

### 2.6.1 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 the 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 [52]. In pyrolytic process, 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, that is primarily affected by the reactor design.

**The hydrocarbon cracking mechanism;** Thorough studies on the mechanism for thermal decomposition of polymers are:

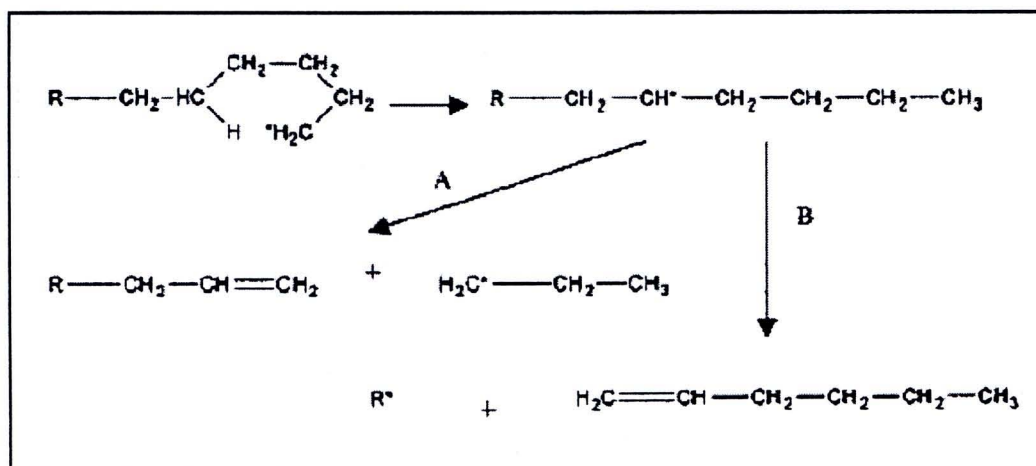
(1) End-chain scission or unzipping: Cracking is targeted at chain ends first, and then successively works down the polymeric length. Unzipping results in the production of the monomer.

(2) Random-chain scission: Random fragmentization 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.

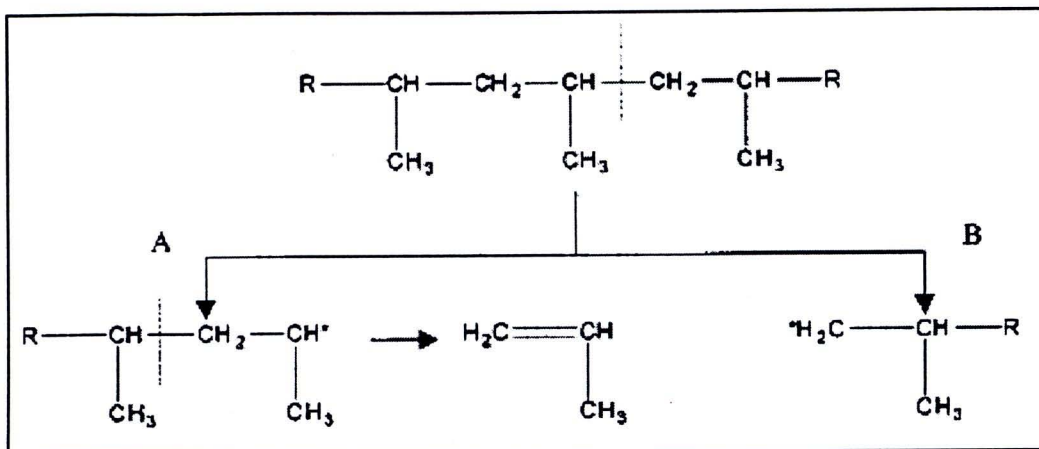
The thermal pyrolysis of PP and PE is known to follow the random chain scission route, resulting in mainly oligomers and dimers [53]. This mechanism is illustrated for PE and PP in Figures 2.13 and 2.14, respectively. Peterson *et al.* observed that PE decomposition by thermogravimetry yielded mainly 1-hexene and propene [54].



**Figure 2.13** Random chain scission in polyethylene [54].

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 [54]. 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



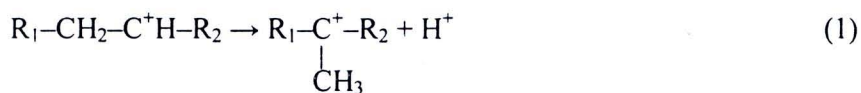
**Figure 2.14** Random chain scission in polypropylene [54].

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.

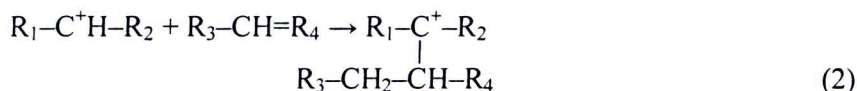
### 2.6.2 Catalytic cracking

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 carbonaceous products generally known as coke. The formation of carbonium 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 carbonium ion proceeds through the  $\beta$ -scission mechanism [55, 56]. Reactions of the adsorbed carbonium ion are [57, 58]:

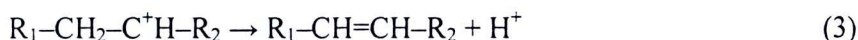
1. Isomerization to a more stable carbonium ion, for example, through a methyl shift:



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



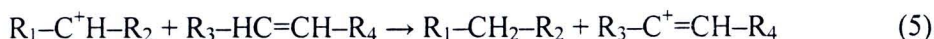
3. Desorption with deprotonation to form an olefin (the opposite of adsorption):



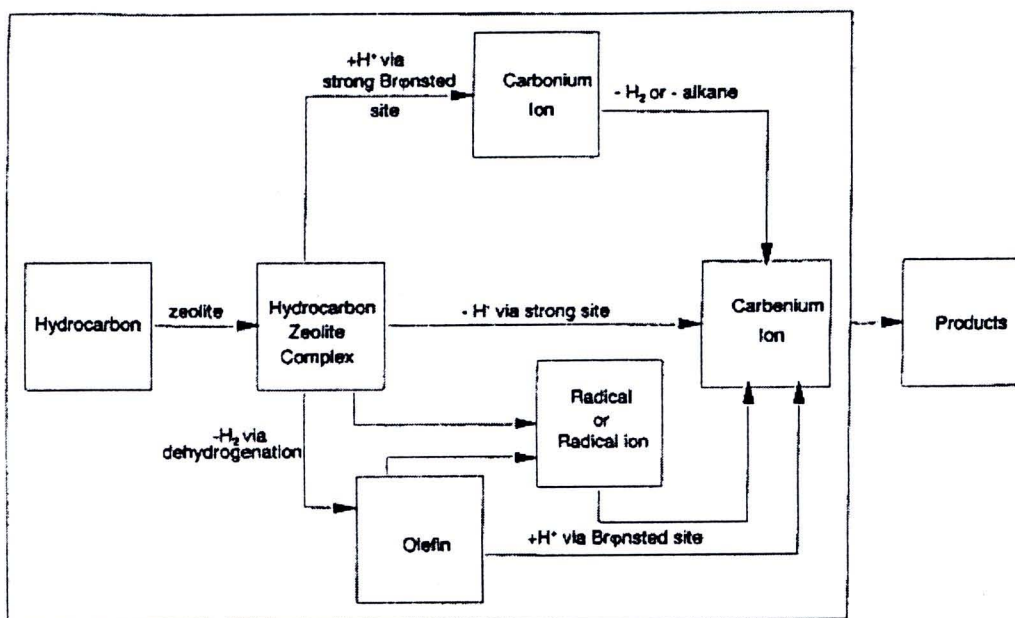
4. Desorption with hydride abstraction from a paraffin to form new paraffin from the carbonium ion and new carbonium ion from the paraffin (H-transfer reaction):



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 carbonium ion of catalytic cracking chemistry for the degradation of hydrocarbon has been proposed previously [59].



**Scheme 2.2** Representation general mechanistic hydrocarbon degradation in zeolites.

This representation is simplified regarding the formation of carbonium ions in that it concentrates on reaction paths rather than on surface species. Theoretical studies suggest that, for the conversions of hydrocarbons on active zeolites, reactions proceed via carbenium ions as transition states (rather than as intermediates). The product distributions are generally in agreement with carbonium ion studies, even though there is still debated about the actual mode of scission. The assumption has been made as follows:

1. The liquid-phase polymer. Initially, solid polymer is freely dropped into the reactor and immediately melted around the catalysts. The molten polymer, which is in contact with the catalyst particle, forms a polymer/catalyst complex and commences at the reaction surface. Polymers melt and spread times are negligible.

2. Evolution of intermediates. Scission reactions generate intermediates which include long-chain olefins and intermediate precursors for carbonium ions. The carbonium 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 carbonium 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 carbonium ions, as well as alkanes, BTX (benzene, toluene and xylene) and coke. The equilibrium mixture of olefins and carbonium ions subsequently reacts further to produce the final products [59].

