

## CHAPTER II

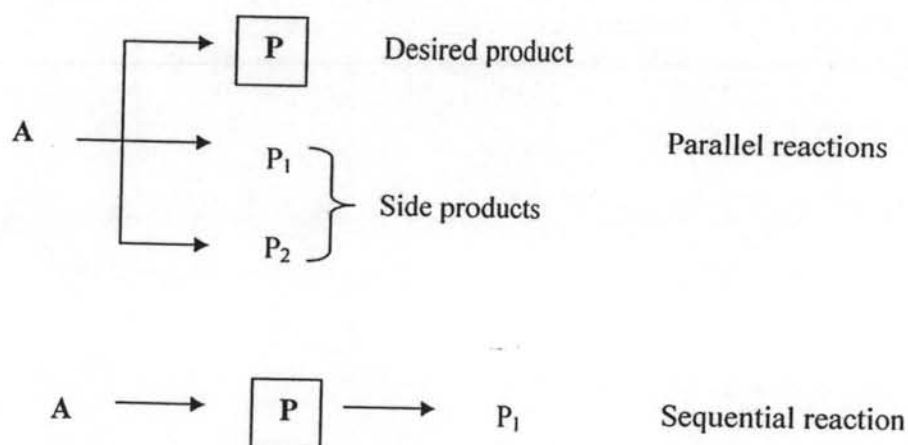
### THEORY

#### 2.1 Properties and characteristics of industrial catalysts

The suitability of a catalyst for an industrial process depends mainly on the following three properties [43].

- **Activity** is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor

- **Selectivity** of a reaction is the fraction of the starting material that is converted to the desired product. It is expressed by the ratio of the amount of desired product to the reacted quantity of reaction partner A and therefore gives information about the course of the reaction. In addition to the desired reaction, parallel and sequential reactions can also occur (Scheme 2.1)



Scheme 2.1 Parallel and sequential reactions.

- **Stability** (chemical, thermal and mechanical) of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking and poisoning. Catalyst deactivation can be followed by measuring

activity or selectivity as a function of time. Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of process.

Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority:

**Selectivity > Stability > Activity**

## 2.2 Types of catalysts

Catalysts can be divided into two main types: heterogeneous and homogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants. Heterogeneous catalysts, phase boundaries are always present between the catalyst and the reactants, in homogeneous catalysis, catalyst, starting materials, and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts only the surface atoms are active [43].

Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collision with substrate molecules. The reactant can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions. Table 2.1 summarizes the advantages and disadvantages of the two classes of catalyst. The major disadvantage of homogeneous catalysts is the difficulty of separating the catalyst from product. Heterogeneous catalysts are either automatically removed in the process (e.g. gas-phase reactions in fixed-bed reactions) or they can be separated by simple methods such as filtration or centrifugation. In the case of homogeneous catalysts, more complicated processes such as distillation, liquid-liquid extraction and ion exchange must often be used.

**Table 2.1 Comparison of homogeneous and heterogeneous catalyst**

	Homogeneous	Heterogeneous
Effective		
- Active centers	All metal atoms	Only surface atoms
- Concentration	Low	High
- Selectivity	High	Low
- Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction)
- Reaction conditions	Mild ( 50 - 200°C)	Severe (often > 250°C)
- Applicability	Limited	Wide
- Activity loss	Irreversible reaction with product (cluster formation); poisoning	Sintering of the metal crystallites; poisoning
Catalyst properties		
- Structure/Stoichiometry	Defined	Undefined
- Modification possibility	High	Low
- Thermal stability	Low	High
Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary Suspension: filtration
Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	High	Low

### 2.3 Zeolite molecular sieves

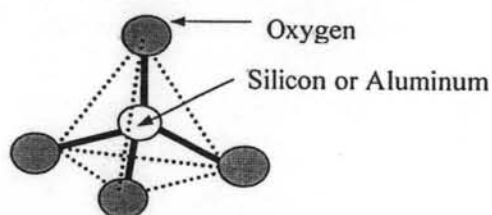
Molecular sieves are porous materials that exhibit selective adsorption properties which can be classified on the IUPAC definitions into three main types depending on their pore size that are microporous materials, mesoporous materials, and macroporous materials. Properties and examples of these materials are shown in Table 2.2.

**Table 2.2** 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

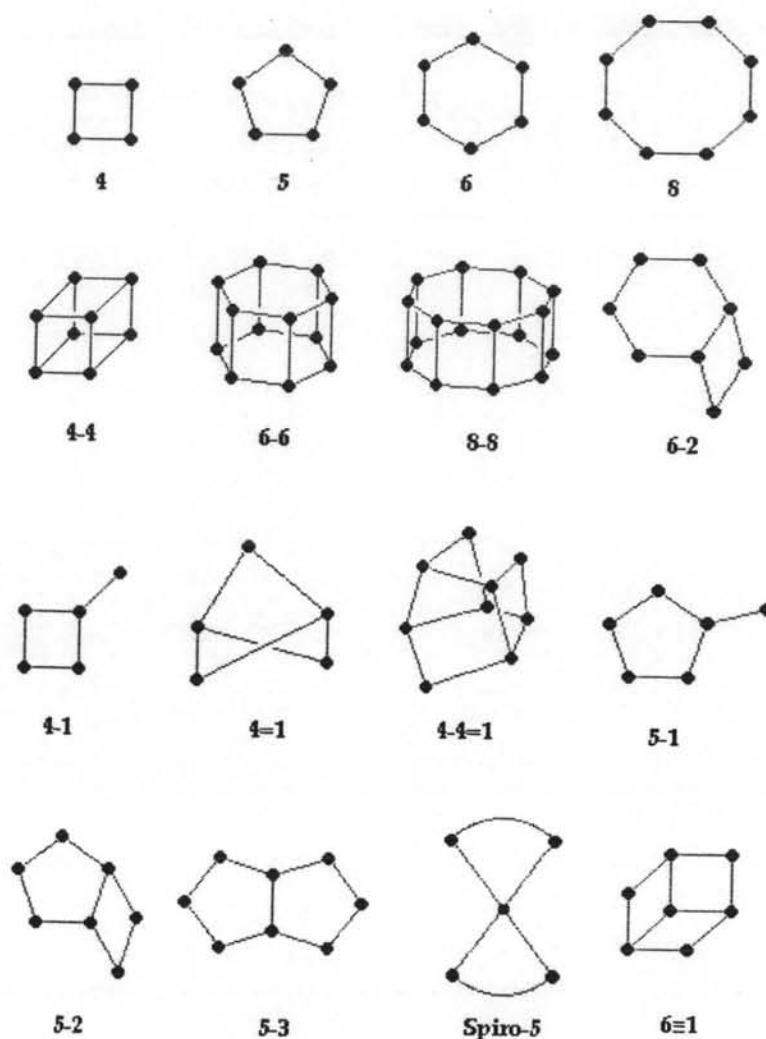
### 2.3.1 Zeolite structures [42]

Zeolites, a type of molecular sieves, are crystalline aluminosilicates of alkali and alkaline earth metals (such as sodium, potassium, magnesium, calcium, strontium, and barium). A zeolite has a three dimensional network structure of tetrahedral primary building units (PBU) which made of four oxygen anions with either silicon [ $\text{SiO}_4$ ] or aluminum cation [ $\text{AlO}_4$ ]<sup>-</sup> in the center as shown in Figure 2.1.



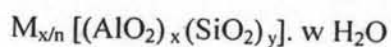
**Figure 2.1** Primary Building Unit (PBU) of zeolites.

A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are nine such building units, which can be described all of the known zeolite structures. The secondary building units (SBU's) 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 2.2



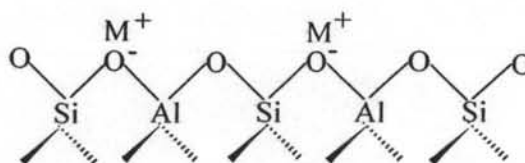
**Figure 2.2** Secondary Building Units (SBU's) in zeolites.

The tetrahedrons are mutually connected by sharing oxygen atom as shown in Figure 2.3 which produces the framework of zeolite. The negative charge of the lattice is neutralized by the positive charge of the metal cations. In the basic zeolites these are usually cation of univalent and bivalent metals or their combination. The general formula for the composition of zeolites is



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  $\text{AlO}_2^-$  tetrahedral unit in the structure.



**Figure 2.3** The structure of zeolites [42]

### 2.3.2 Properties of zeolites

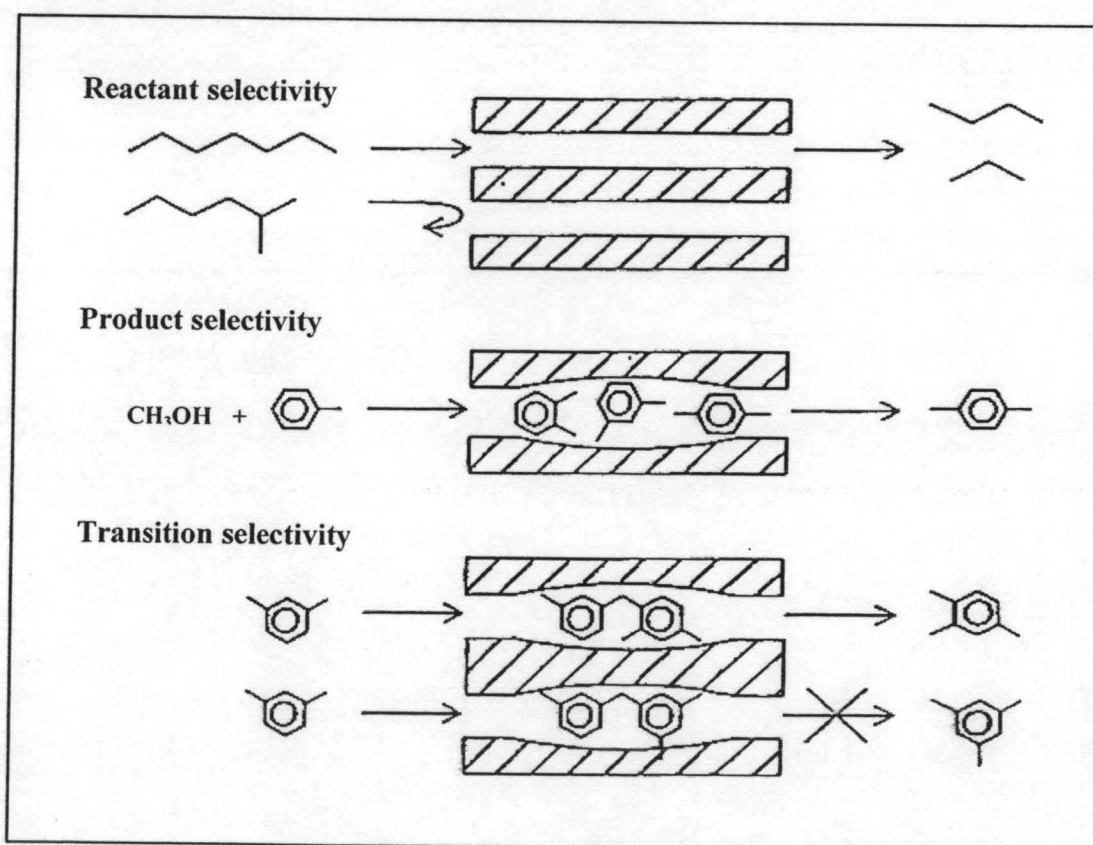
#### 2.3.2.1 Acid sites of zeolites

Most industrial application of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction [16, 44, 45]. 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 2.4. 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  $500\text{ }^\circ\text{C}$ , and water is driven off.



### 2.3.2.2 Shape selectivity

Shape selectivity plays a very important role in catalysis. Highly crystalline and regular channel structures are among the principal features that zeolite used as catalysts offer over other materials. Shape selectivity is divided into 3 types: reactant shape selectivity, product shape selectivity and transition-state shape selectivity effectively enter and diffuse inside the zeolites. These types of selectivities are shown in Figure 2.5. Reactant selectivity means that only starting materials of a certain size and shape can penetrate into the interior of the zeolite pores and undergo reaction at the catalytically active sites. Starting material molecules that are larger than the pore apertures can not react. Product selectivity arises when, corresponding to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment around the active site: the rate constant for a certain reaction mechanism is reduced if the necessary transition state is too bulky to form readily.



**Figure 2.5** Three types of selectivity in zeolites: reactant, product and transition-state shape selectivity [47].



Heterogeneous catalysis is important in fine-chemical and pharmaceutical manufacture and in petroleum refining. Many of the catalysts used by these industries are based on aluminosilicates, which combine high stability with excellent activity in acid-mediated reactions. Within this class of material, zeolites microporous crystalline aluminosilicates with three-dimensional framework structures have attracted particular attention: they are significantly more active than the layered structures (clays) and mesoporous structures.

#### 2.4 MCM-22 zeolite

MCM-22 is designed as MWW structure and has the same topology with PSH-3 [48], SSZ-25 [49], ERB-1 [50] and ITQ-1 [5]. MWW frameworks are shown in Figure 2.6. This type of zeolite has the large pocket (inner diameter = 0.71 nm) on the external surface and two independent pore systems with 10-membered ring (10MR): one is defined by the two-dimensional sinusoidal channel, and the other by the 12MR supercages, with dimensions  $0.71 \times 0.71 \times 18.1 \text{ nm}^3$ . There is the former micropore, which is designed as an interlayer micropore, in the layer possessing the MWW framework, whereas the latter one is an intralayer micropore which exists between the layers.

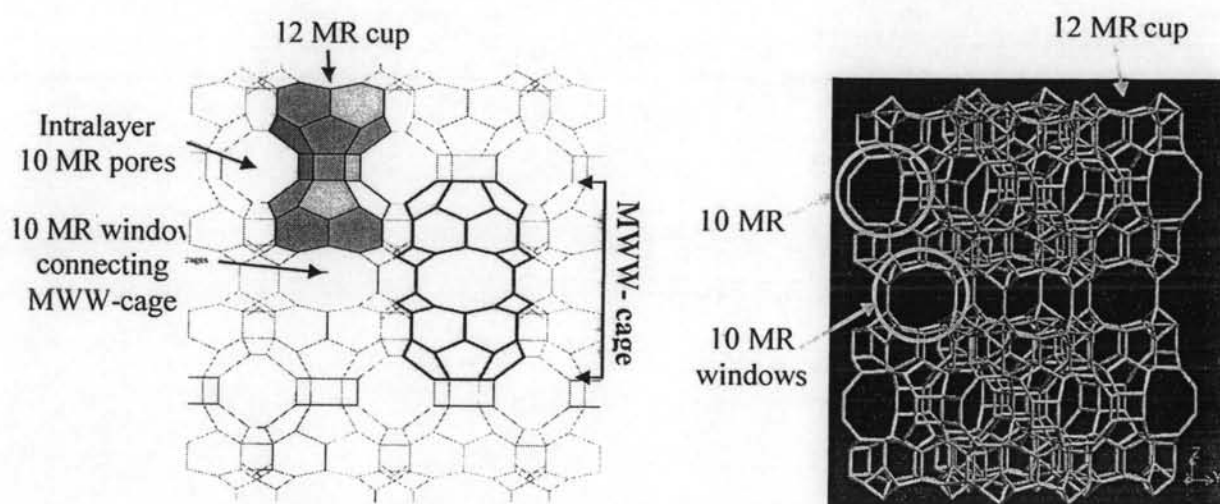


Figure 2.6 MWW frameworks [52]

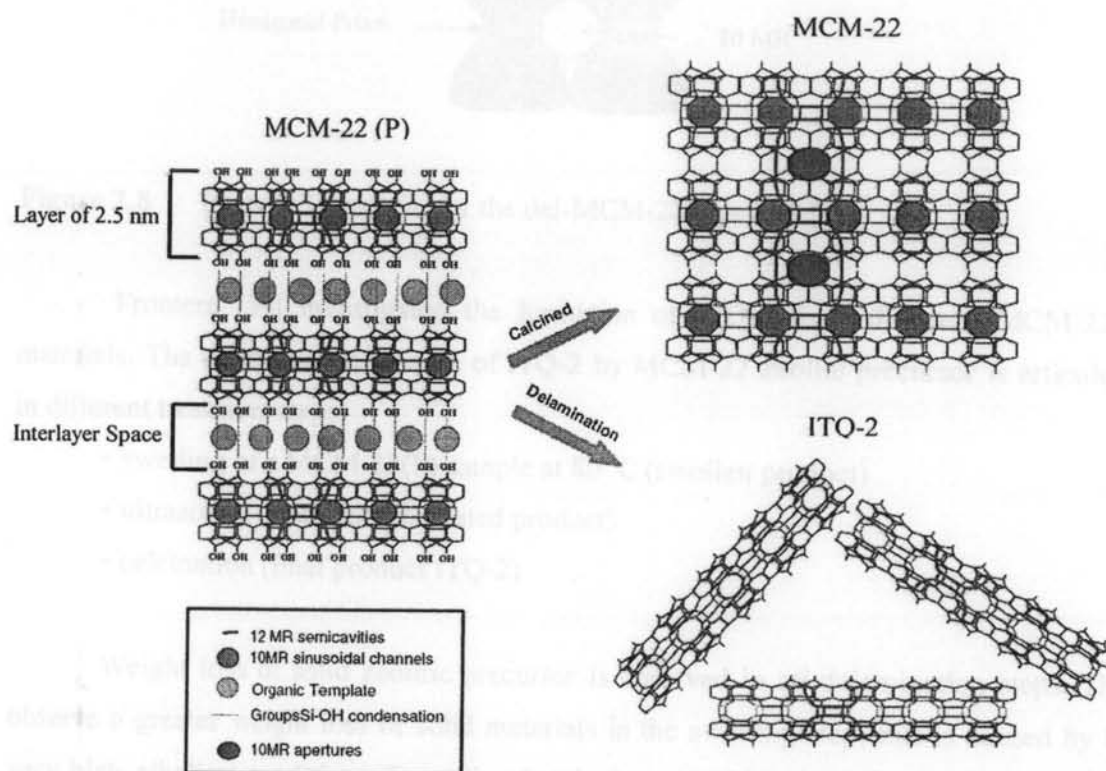
### 2.4.1 Synthesis of MCM-22 zeolite

The hydrothermal synthesis of MCM-22 zeolite has been studied in detail using HMI. In early reports, MCM-22 having  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios around 30 could be obtained as a pure phase for a relatively board range of  $\text{OH}/\text{SiO}_2$  ratios, whereas crystallization from a parent mixture with low aluminum contents (i.e.  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ) yielded a mixture of the MWW phase with the MFI or the FER phase. Mochida and co-workers [15] reported that the seeding in the hydrothermal synthesis of MCM-22 zeolite could avoid the formation of the undesired phase. These early reports as well as the original patent [1], indicate that stirring or rotating in hydrothermal crystallization is necessary to obtain a high quality MWW phase. Crystallization by using HMI under the static conditions yielded a pure phase of MCM-22 for narrow ranges of synthetic parameters, such as gel composition, crystallization period and temperature. The stirring/rotating crystallization yielded isolated hexagonal thin plates, which was around 1  $\mu\text{m}$  in width, of MCM-22 crystals, whereas the static crystallization gave crystals composed by the aggregation of the hexagonal thin plates. Much attention has been paid on the unique crystalline structure due to possibilities in application to many catalytic reactions.

However, zeolites present some limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the case in the synthesis of fine chemicals. Attempts to improve the diffusion of reactants to the catalytic sites have so far focused on increasing the zeolite pore sizes as well as decreasing zeolite crystal size. Recent work has described a new zeolitic material (del-MCM-22) in which a layered zeolite precursor is delaminated in much the same way as the layered structure of a clay may be unbound, resulting in an aluminosilicate whose zeolite-type catalytic sites are contained within thin, readily accessible sheets. Then the delamination process can improve the accessibility of the catalytic sites to large molecules [59].

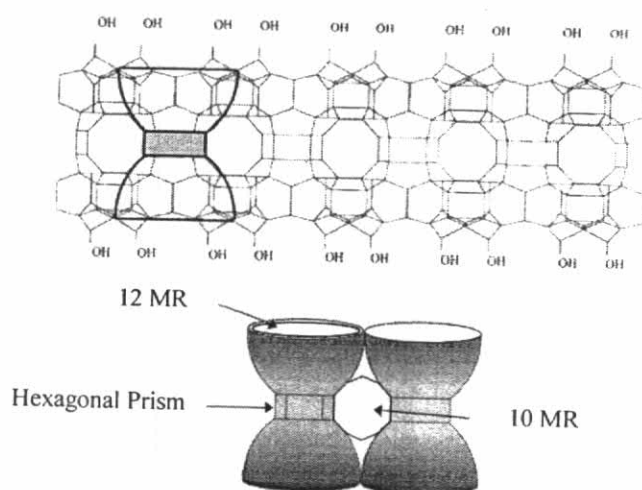
### 2.4.2 Preparation of del-MCM-22

The del-MCM-22 zeolite has been prepared by swelling and exfoliating the MCM-22 precursor, and consists of monolayers of a crystalline aluminosilicate with an extremely high external surface. The del-MCM-22 zeolite showed high catalytic activities in the reactions of large molecules inaccessible to the 10MR micropore system, if compared with MCM-22 zeolite. This is due to high external surface area of a structure, which gives a large amount of structurally accessible acid sites.



**Figure 2.7** Structural schematic representation of MWW-type zeolites and del-MCM-22 [60].

Corma *et. al.* [59] proposed structure of the del-MCM-22 layer from a high-resolution transmission electron microscopy (HRTEM) photograph. The delamination of the layered precursor of the MCM-22 zeolite (MWW structure) affords monolayers of a crystalline aluminosilicate with more than  $700 \text{ m}^2 \text{ g}^{-1}$  of a well defined external surface formed by cups of  $0.7 \times 0.7 \text{ nm}$ . In this layered structure the circular 10-member-ring microporous system is preserved, which is schematically shown in Figure. 2.8.



**Figure 2.8** Proposed structure for the del-MCM-22 layer [61].

Frontera [39] investigated the formation of ITQ-2 from different MCM-22(P) materials. The delamination process of ITQ-2 by MCM-22 zeolite precursor is articulated in different treatment steps:

- swelling of a MCM-22(P) sample at 80 °C (swollen product)
- ultrasound treatment (sonicated product)
- calcination (final product ITQ-2)

Weight loss of solid zeolitic precursor is observed in all delamination steps. They observe a greater weight loss of solid materials in the swelling step; this is caused by the very high alkaline condition of swelling batch that promotes the preferential leaching of silicon in the zeolite material, leading to a lower Si/Al ratio in the alkaline treated materials. The partial destruction of the zeolite framework caused by solubilization of the  $\text{SiO}_4^-$  species and the intercalation of surfactant agent in the layer of MCM-22(P) promote significant variation in the crystallinity of precursor, and due to the small thickness and disorder of the layer, the powder X-ray pattern consists of broad peaks of low intensity. However, the final solid ITQ-2 is formed by disordered individual sheets of crystalline layers. A relevant loss of ordered material is obtained after the swelling treatment, while the ultrasounds treatment does not promote relevant disorganization.

The different times of ultrasounds treatments show a progressive increase of total surface and mesoporous area increasing with sonication time. From MCM-22(P) precursor with  $\text{Si/Al} = 20$ , a longer ultrasound time promotes the undesired formation of MCM-41

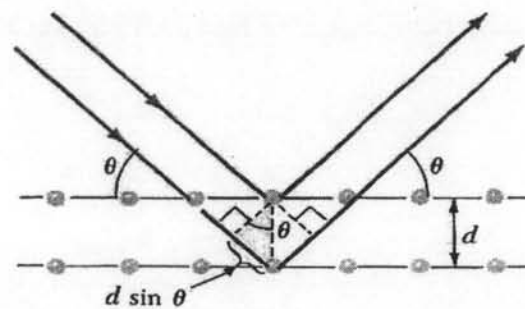
mesoporous materials, probably because the surfactant concentration and the pH of the suspension favour the silica polymerization, that in such conditions of reaction can occur also at room temperature. The preparation of material ITQ-2 is favoured by decreasing aluminium content of the precursor zeolite MCM-22(P). Moreover, the time of ultrasound treatment is a very important parameter to obtain a final product with good adsorption properties.

MCM-22 and del-MCM-22 has a specific surface area of approximately  $500 \text{ m}^2/\text{g}$ . Reliable characterization of the MWW structure requires the use of five techniques:

- (a) X-ray powder diffraction (XRD)
- (b) Scanning electron microscopy (SEM)
- (c) Nitrogen adsorption-desorption isotherm
- (d) Inductively coupled plasma – Atomic emission spectroscopy (ICP-AES)
- (e) Temperature-programmed desorption (TPD) of ammonia
- (f) Solid state  $^{27}\text{Al}$ -MAS-NMR

#### 2.4.3 X-ray powder diffraction (XRD) [53]

X-ray powder diffraction (XRD) is an instrumental technique used for identification of minerals, as well as other crystalline materials. XRD is a technique in which a collimated beams of nearly monochromatic X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other information obtained can include the degree of crystallinity of the minerals present, possible deviations of the minerals from their ideal compositions, the structural state of the minerals and the degree of hydration for minerals that contain water in their structure. For samples available as larger crystals or in a crystal morphology that favors a preferred orientation, it has to be assured that all individual crystallites are randomly oriented when analyzed, that can be achieved by, e.g., carefully sample grinding. Figure 2.9 shows a monochromatic beam of X-ray incident on the surface of crystal at an angle  $\theta$ . The scattered intensity can be measured as a function of scattering angle  $2\theta$ . The resulting XRD pattern efficiently determines the different phases present in the sample.



**Figure 2.9** Diffraction of X-ray by regular planes of atoms [54]

Using this method, Braggs' law is able to determine the interplanar spacing of the samples, from diffraction peak according to Bragg angle.

$$n\lambda = 2 d \sin\theta$$

Where the integer  $n$  is the order of the diffracted beam,  $\lambda$  is the wavelength;  $d$  is the distance between adjacent planes of atoms (the  $d$ -spacings) and  $\theta$  is the angle of between the incident beam and these planes.

#### 2.4.4 Scanning electron microscopy (SEM)

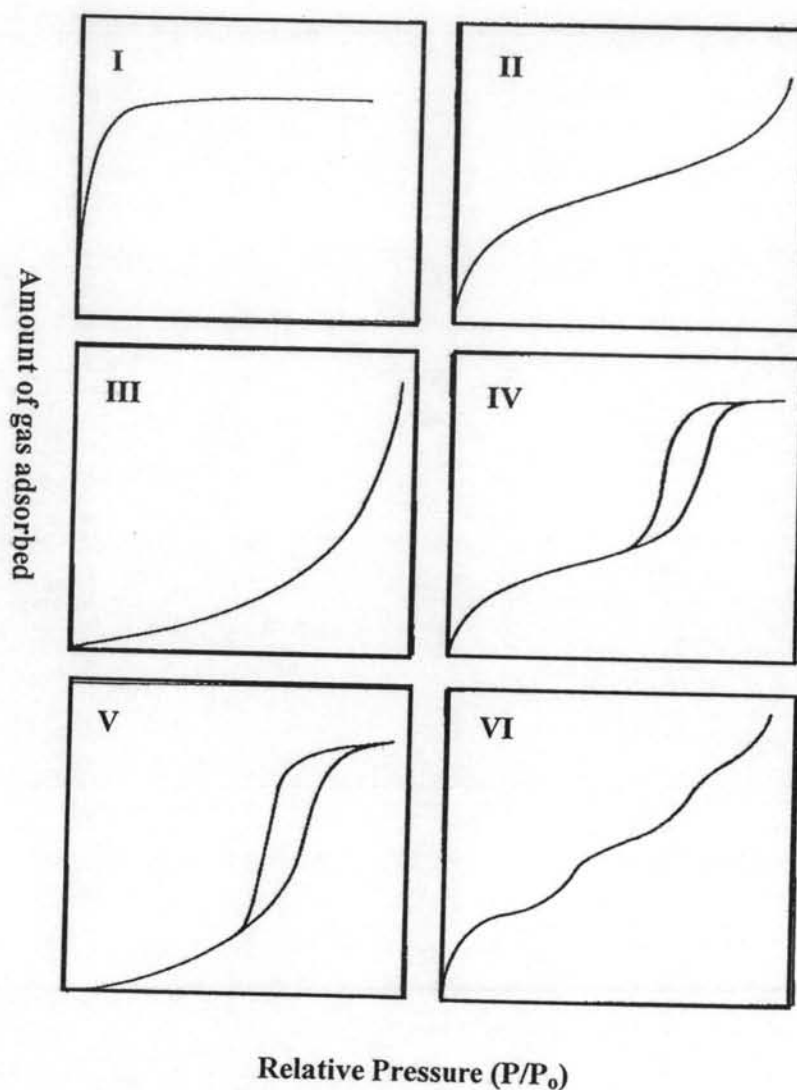
The scanning electron microscope (SEM) has unique capabilities for analyzing surfaces and morphology of materials. It is analogous to the reflected light microscope, although different radiation sources serve to produce the required illumination. Whereas the reflected light microscope forms an image from light reflected from a sample surface, the SEM uses electrons for image formation. The different wavelength of these radiation sources result in different resolution levels: electron have much shorter wavelength than light photons, and shorter wavelength are capable of generating the higher resolution information. Enhanced resolution in turn permits higher magnification without loss of detail. The maximum magnification of the light microscope is about 2,000 times; beyond this level is "empty magnification", or the point where increased magnification does not provide additional information. This upper magnification limit is a function of the wavelength of visible light, 2000 Å, which equal the theoretical maximum resolution of conventional light microscope. In comparison, the wavelength of electron is less than 0.5 Å, and theoretically the maximum magnification of electron beam instrument is beyond

800,000 times. Because of instrumental parameters, practical magnification and resolution limits are about 75,000 times and 40 Å in a conventional SEM. The SEM consists basically of four systems:

1. The *illuminating/imaging system* produces the electron beam and directs it onto the sample.
2. The *information system* includes the data released by the sample during electron bombardment and detectors which discriminate among analyze these information signals.
3. The *display system* consists of one or two cathode-ray tubes for observing and photographing the surface of interest.
4. The *vacuum system* removes gases from the microscope column which increases the mean free path of electron, hence the better image quality.

#### 2.4.5 Nitrogen adsorption-desorption isotherm

The N<sub>2</sub> adsorption technique is used for determination of the physical properties of mesoporous molecular sieves, such as the surface area, pore volume, pore diameter and pore-size distribution of solid catalysts. Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized in terms of pore sizes derived from gas sorption data. IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption. The IUPAC classification of adsorption isotherms is illustrated in Figure 2.12. Six types of isotherms are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III, and VI) or mesoporous (types IV and V).



**Figure 2.10** Types of sorption isotherms.

Adsorption isotherms are described as shown in Table 2.3 based on the strength of the interaction between the sample surface and gas adsorbate, and the existence or absence of pores. Pore types are classified as shown in Table 2.2.



**Table 2.3** Type and characteristics of sorption isotherms

Type of isotherm	Characteristics	Example
I	Adsorption in micropores	Benzene on zeolites
II	Multilayer adsorption on flat surfaces	N <sub>2</sub> on SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>
III	Weak gas-solid interactions	H <sub>2</sub> O on noble metals
IV	Multilayer adsorption and pore condensation	N <sub>2</sub> on MCM-41 type materials
V	Weak gas-solid interactions	H <sub>2</sub> O on noble metals
VI	Non porous adsorbent	Kr on graphite

Pore size distribution is measured by the use of nitrogen adsorption/desorption isotherm at liquid nitrogen temperature and relative pressures ( $P/P_0$ ) ranging from 0.05-0.1. The large uptake of nitrogen at low  $P/P_0$  indicates filling of the micropores ( $<20 \text{ \AA}$ ) in the adsorbent. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the sample, and the concave upward portion of the curve represents filling of mesopores and macropores.

The multipoint Brunauer, Emmett and Teller (BET) [55] method is commonly used to measure total surface area.

$$\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C} (P/P_0)$$

Where  $W$  is the weight of nitrogen adsorbed at a given  $P/P_0$ , and  $W_m$  is the weight of gas to give monolayer coverage, and  $C$  is a constant that is related to the heat of adsorption. A linear relationship between  $1/W [(P_0/P)-1]$  and  $P/P_0$  is required to obtain the quantity of nitrogen adsorbed. This linear portion of the curve is restricted to a limited portion of the isotherm, generally between 0.05-0.30. The slope and intercept are used for determination of the quantity of nitrogen adsorbed in the monolayer and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used for calculation for the surface area. The

surface area reported depends upon the method used, as well as the partial pressures at which the data are collected.

#### 2.4.6 Inductively coupled plasma - atomic emission spectroscopy (ICP-AES)

During catalyst preparation, the procedure is generally such that the obtained composition is very closed to the one wanted; but that does not eliminate the need to control the composition through analysis of the solid. The sample is dissolved in an has many inherent failings. It has only been appropriate solvent such as an aqueous solution of HF and the solution is subsequently analyzed by analytical methods such as AAS or ICP-AES. These methods require the complete dissolution of the solid sample and depend on an accurate chemical analysis of the solution.

#### 2.4.7 Temperature-programmed desorption (TPD) of ammonia [56]

Temperature-Programmed Desorption (TPD) is one of the most widely used and flexible techniques for characterizing the acid sites on oxide surfaces.

Determining the quantity and strength of the acid sites on alumina, amorphous silica-alumina, and zeolites is crucial to understanding and predicting the performance of a catalyst. For several significant commercial reactions (such as n-hexane cracking, xylene isomerization, propylene polymerization, methanol-to-olefins reaction, toluene disproportionation, and cumene cracking), all reaction rates increase linearly with Al content (acid sites) in H-ZSM-5. The activity depends on many factors, but the Brønsted acid site density is usually one of the most crucial parameters.

- **Preparation:** Samples are degassed at 100 °C for one hour in flowing helium to remove water vapour and to avoid pore damage from steaming which may alter the structure of zeolites. The samples are then temperature programmed to 500 °C at a ramp rate of 10 °C/minute and held at that temperature for two hours to remove strongly bound species and activate the sample. Finally the sample is cooled to 120 °C in a stream of flowing helium.

- **Adsorption:** Next the sample is saturated with the basic probe at 120°C; this temperature is minimized physisorption of the ammonia or organic amines. For ammonia, two techniques are available to saturate the sample: pulsing the ammonia using the loop or continuously flowing ammonia. Pulsing the ammonia allows the user to compare the quantity of ammonia adsorbed (via pulse adsorption) to the quantity desorbed for the

amine, the sample is purged for a minimum of one hour under a flow of helium to remove any of the physisorbed probes.

- **Desorption:** The temperature-programmed desorption is easily performed by ramping the sample temperature at 10°C/minute to 500°C. It is a good rule of thumb that the end temperature during the TPD not exceed the maximum temperature used in the preparation of the sample. Exceeding the maximum preparation temperature may liberate additional species from the solid unrelated to the probe molecule and cause spurious results.

During the TPD of ammonia or the non-reactive probes (pyridine or t-butyl amine), the built-in thermal conductivity detector (TCD) will monitor the concentration of the desorbed species. For the reactive probes (propyl amines), a mass spectrometer is required to quantify the density of acid sites. For these probes, several species may be desorbing simultaneously: amine, propylene, and ammonia.

#### 2.4.8 <sup>27</sup>Al-MAS-NMR [57]

Another important characterization technique for microporous materials is solid state NMR. <sup>27</sup>Al-MAS-NMR spectroscopy has been employed to distinguish between tetrahedrally and octahedrally coordinated aluminum in the framework at approximately 50 and 0 ppm, respectively. Hence, the amount of framework aluminum can be determined.

### 2.5 Cracking reaction

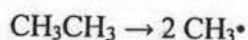
In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of any catalysts. Cracking, also referred to as pyrolysis, is the breakdown of large alkane into smaller, more useful alkenes and alkane.

#### 2.5.1 Thermal cracking [63]

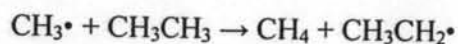
In thermal cracking elevated temperatures (~800 °C) and pressures (~700 kPa) are used, a process first developed by William Merriam Burton. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.

A large number of chemical reactions take place during steam cracking, most of them based on free radicals. Computer simulations aimed at modeling what takes place during steam cracking have included hundreds or even thousands of reactions in their models. The main reactions that take place include:

**1. Initiation reactions:** where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.



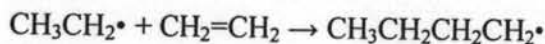
**2. Hydrogen abstraction:** where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.



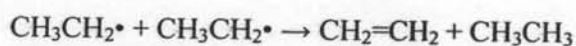
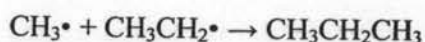
**3. Radical decomposition:** where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.



**4. Radical addition:** the reverse of radical decomposition, in which a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.



**5. Termination reactions:** which happen when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are recombination, where the two radicals combine to form one larger molecule, and disproportionation, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.



### 2.5.2 Catalytic cracking [64]

Catalytic cracking uses a solid acid catalyst (Most commonly Aluminium Oxide and Silicon Dioxide) and moderately-high temperatures (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. Such deposits need to be removed (usually by controlled burning) in order to restore catalyst activity.

The mechanisms of the reactions occurring during catalytic cracking are quite well understood, and can be summarized as follows. Small amounts of alkenes are formed by dehydrogenation, and this react with protons on the acidic catalyst to give *carbonium ions*. Now the sequence of stability of this ions is primary < secondary < tertiary; movement of a hydride ion (H<sup>-</sup>) changes a primary into a secondary ions, while methyl group migration forms tertiary ions. Long-chain carbonium ions are unstable with respect to small ones, and carbon-carbon bonds are broken by β-scission to give an alkene and primary carbonium ion. This and other unit steps are set out in Table 9.1. By a fortunate coincidence, a number of mechanistically related and useful reactions take place simultaneously at the surface of acidic cracking catalysts.

## 2.6 Catalytic cracking mechanisms

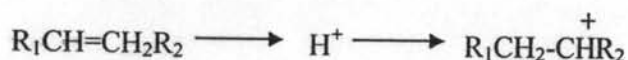
Zeolites are catalysts that offer the advantages of high densities of catalytic sites combined with stability at high temperatures; the latter is an advantage characterizing many inorganic solids and accounts for their wide applications as industrial catalysts. The industrial applications of zeolites involve acid-catalyzed reactions. Virtually all the reactions catalyzed by acids in solutions and in polymer matrices are catalyzed by zeolites incorporating acidic groups. The expectations involve reactants too large to enter the zeolite pore and products too large to form in, or leave, the pores.

## 2.6.1 Reactions occurring during catalytic cracking

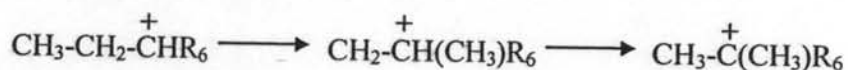
### 1. Dehydrogenation to alkene



### 2. Formation of carbonium ion



### 3. Methyl group migration



### 4. Hydride transfer

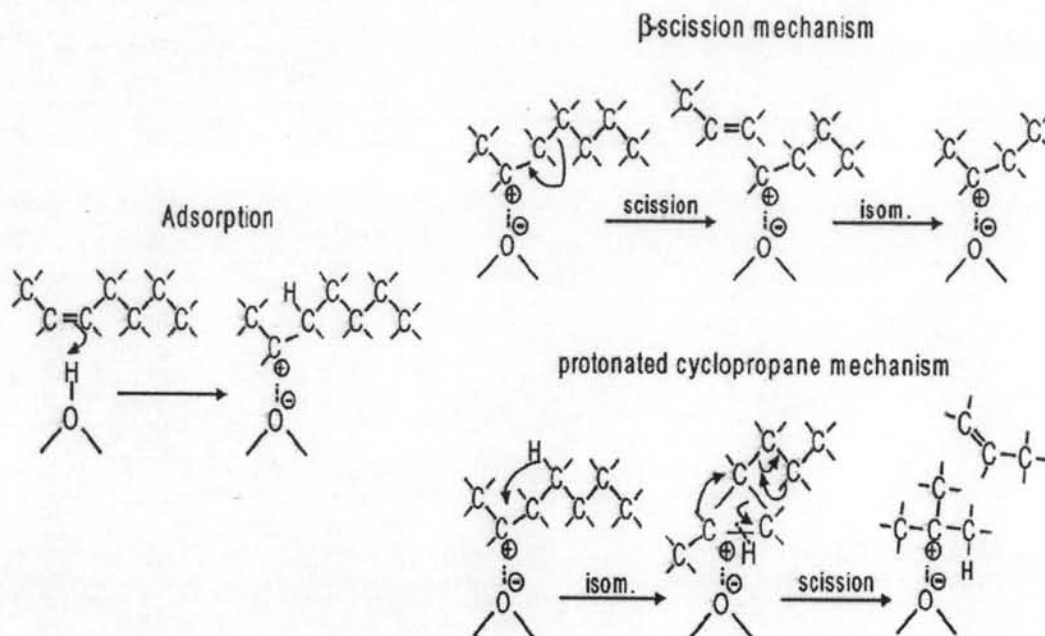


### 5. $\beta$ -scission



## 2.6.2 General cracking mechanisms [65]

Hollander *et al.* proposed mechanism of cracking. In general, for components with equal carbon numbers, the rate of cracking decreases in the order: *i*-olefins > *n*-olefins  $\approx$  *i*-naphthenes > *n*-paraffins > aromatics [5]. The cracking mechanism can be seen as a chain mechanism that involves the intermediate formation of carbocations, positively charged hydrocarbon species. Carbocations include both carbenium ions (e.g.  $R_1-CH_2-C^+H-R_2$ ,  $R_1-CH=C^+-R_2$ ) and carbonium ions (e.g.  $R_1-CH_2-C^+H_3-R_2$ ,  $R_1-CH=C^+H_2-R_2$ ). In carbenium ions, the charge carrying carbon atom can be di- or tri-coordinated, while in carbonium ions, the charge carrying carbon atom is tetra- or pentacoordinated. The stability of the carbocations decreases in the order tertiary > secondary > primary [5]. Cracking of hydrocarbons is primarily a reaction that proceeds through adsorbed carbenium ion intermediates.



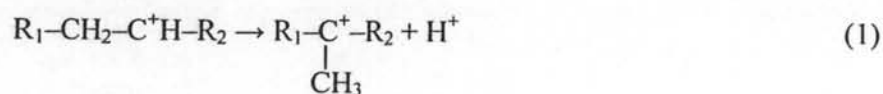
**Figure 2.11** Cracking mechanisms illustrated by the reaction of *n*-heptene; adsorption at a Brønsted acid site leads to formation of an adsorbed carbenium ion that can be cracked. Both the  $\beta$ -scission mechanism and the protonated cyclopropane mechanism are shown.

### 2.6.3 Reactions of olefins

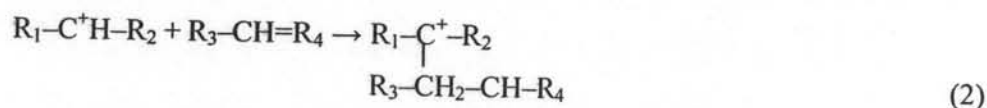
The formation of carbenium ions from olefins can easily proceed by addition of the proton from a Brønsted acid site of the catalyst to the carbon-carbon double bond. Cracking of the adsorbed carbenium ion proceeds through the  $\beta$ -scission mechanism or through the protonated cyclopropane mechanism [45,46]. An illustration is given in Figure 2.11.

Other reactions of the adsorbed carbenium ion are:

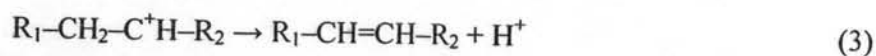
1. Isomerization to a more stable carbenium ion, for example, through a methyl shift:



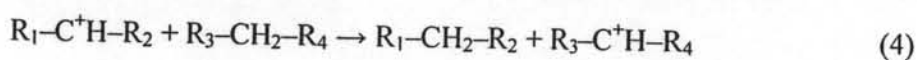
2. Oligomerization with olefin in a bimolecular reaction to form a larger adsorbed carbenium ion:



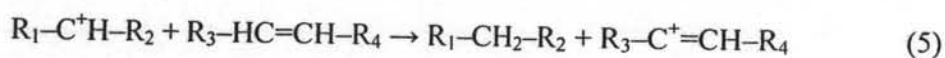
3. Desorption with deprotonation to form an olefin (the opposite of adsorption):



4. Desorption with hydride abstraction from a paraffin to form a 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 a paraffin and a more aromatic compound (H-transfer reaction):



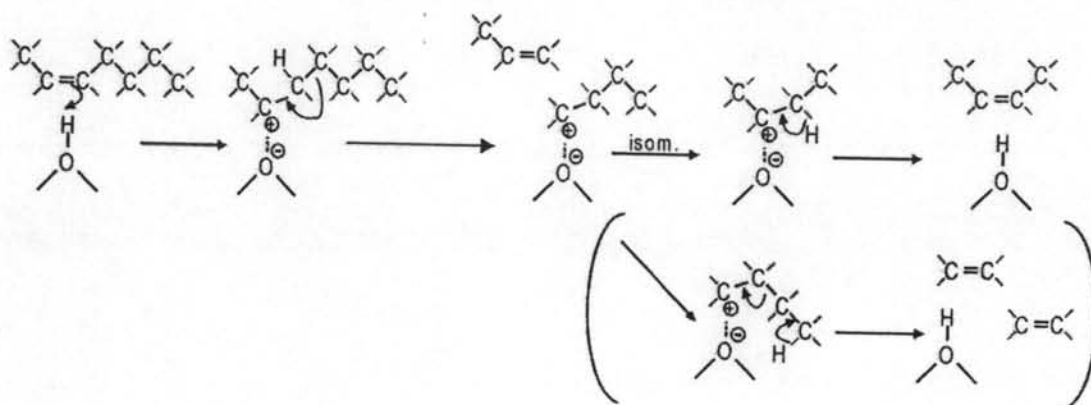
The bimolecular reactions (2), (4) and (5) can occur if the pore size of the catalyst is large enough to accommodate the reactive intermediates, or they should occur on the outer surface of the zeolite particles. If the pores are too small, as in the case of ZSM-5 (0.53 nm × 0.56 nm), these reactions cannot take place with the larger (gasoline) components, although oligomerization or dimerization of small (C<sub>2</sub>-C<sub>4</sub>) olefins could be possible.

With ZSM-5, cracking through dimeric intermediates has only been reported in the reactions of relatively small *n*-olefins (C<sub>4</sub>-C<sub>6</sub>). Abbot and Wojciechowski [29] have studied cracking of *n*-olefins from C<sub>5</sub> to C<sub>9</sub> at 678K with ZSM-5 and found that cracking of pentene solely took place through a dimeric/disproportionation mechanism [29, 55]. Cracking of heptene and larger molecules proceeded mainly through monomolecular cracking and at 678 K, hexene represented the transition case of the two mechanisms and was cracked by both monomolecular cracking and through dimeric intermediates [42].



### 2.6.4 Proposed cracking mechanisms of polymer [62, 65]

ZSM-5 the cracking reactions of larger  $C_7^+$  olefins are restricted to simple  $\beta$ -scission reactions. The relatively straight chains (or parts of it) can enter the pores of ZSM-5, are adsorbed, split-off small olefins, and desorb. For example, the reaction of n-heptene over ZSM-5 (for simplicity only the  $\beta$ -scission mechanism) is shown in Figure 2.12. The adsorbed  $C_7$ -carbenium ion is cracked to propene and  $C_4$ -carbenium ion. Then  $C_4$ -carbenium ion isomerizes to butene or is cracked to two ethene molecules.

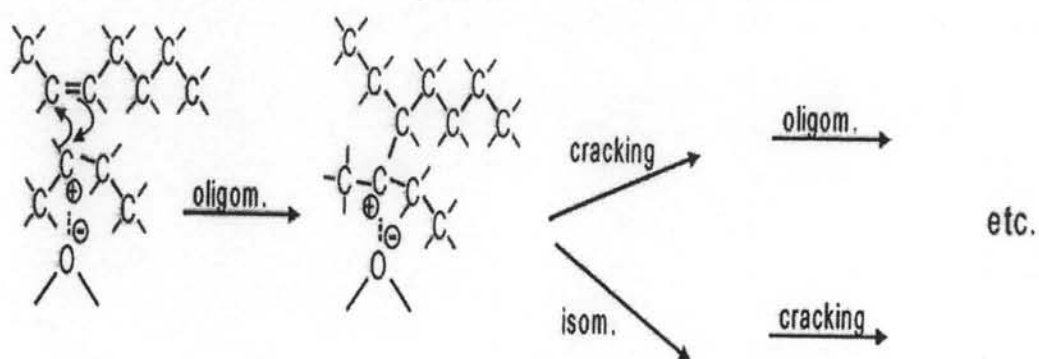


**Figure 2.12** Monomolecular cracking mechanisms (only mechanism possible with ZSM-5).

Generally, the second reaction, formation of ethene, is energetically less favorable because it involves the formation of two primary carbenium ions. However, due to the small pores of ZSM-5, the electrical field in the pores is larger and a relatively large interaction between the catalyst and the adsorbed carbenium ions shall exist. It is believed that the oxygen atoms of a zeolite structure play a role in solvating carbocations, delocalizing the positive charge into the framework. The smaller the size of the pores of the zeolite, the closer the different oxygen atoms are to the adsorbed reaction intermediates and the higher the possible interaction. So possibly, as a result of increased stabilization of the intermediates, the formation of ethene is enhanced when small pore-zeolites such as ZSM-5 are involved.

On the base catalyst, with zeolite Y as active species (pore size 0.74 nm) adsorbed  $C_4$ -carbenium species and new heptene molecule to form an adsorbed  $C_{11}$ -carbenium ion. The  $C_{11}$ -carbenium ion is cracked to hexane and  $C_5$ -carbenium ion. This bimolecular

cracking mechanism proposed by Williams *et al.* [66] is illustrated in Figure 2.13. Also, the adsorbed heptene carbenium ion could oligomerize before cracking.



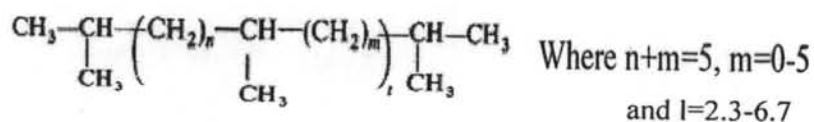
**Figure 2.13** Bimolecular cracking mechanism that can occur on zeolite Y in addition to the monomolecular mechanism.

Because of the larger adsorption strength of larger hydrocarbons, the bimolecular mechanism can have an important contribution in the cracking mechanism of the heavier gasoline-range olefins, provided that the catalyst pore size is large enough to accommodate the reaction intermediates. Aromatics and highly branched components, therefore, are too large to react through bimolecular mechanisms. Linear components are the most likely ones to react through this mechanism.

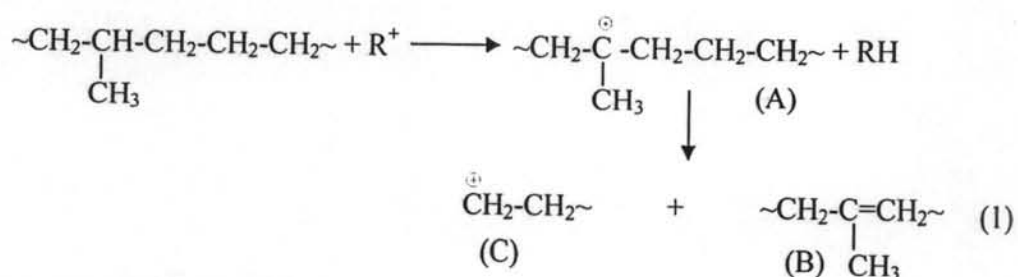
According to this proposed mechanism, the active site of ZSM-5 is the acid site itself, while the active site in zeolite Y can be represented by the adsorbed carbenium ion. The reaction intermediates with ZSM-5 contain the number of carbon atoms (C<sub>5</sub>-C<sub>11</sub>), while the (surface) intermediates with the base catalyst can be much larger. As a result, the cracking products from ZSM-5 will be mainly C<sub>3</sub>, C<sub>4</sub>, and to some extent also C<sub>2</sub> olefins, while with the zeolite Y base catalyst larger fragments can be formed.

This agrees with the results that can be found in literature; the main products from *n*-olefins and *i*-olefins cracking on ZSM-5 are light olefins with a high selectivity for propene, *i*-butene, and in some cases the increased yields of ethene are reported.

A mechanism for the catalytic cracking of PE and PP using Al-MCM-41 as catalyst is proposed by Ishihara *et al.* [71, 72]. As described, branched polyethylene components have short chains consisted of mainly of methyl groups.

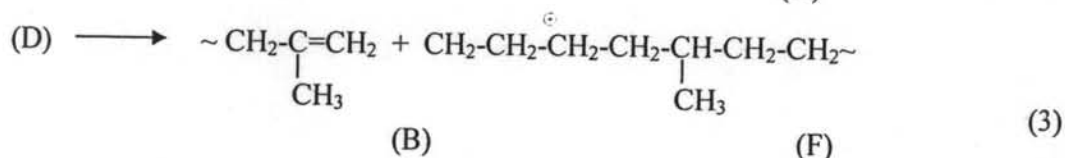
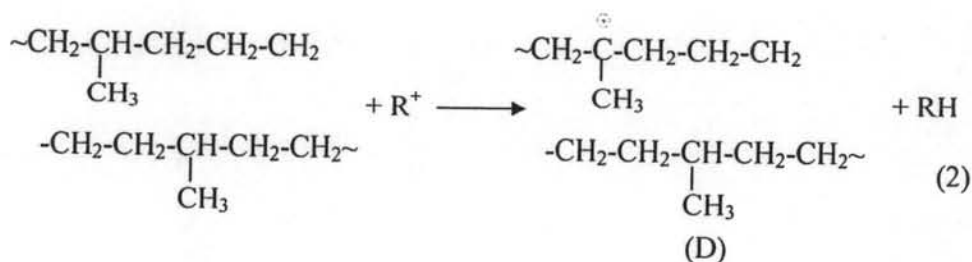


Branching of the main fraction was at a frequency of one branch per three ethylene monomer units. The typical oligomer structure was found to be virtually the same as that of polyisooheptyl based on branching frequency. Moreover, oligomer chains showed random branching in an ethylene sequence in regular structures of polyisooheptyl. The catalytic cracking of PE is initiated by attack of low molecular weight carbonium ion ( $\text{R}^+$ ) on a very small number of on-chain hydrogen atoms attached to tertiary carbon atoms in polymer chains. The initial reaction of molecular weight reduction is shown in equations (1).  $\beta$ -scission of on-chain carbonium ions (A) occurs to produce chain-ends (B) and (C):



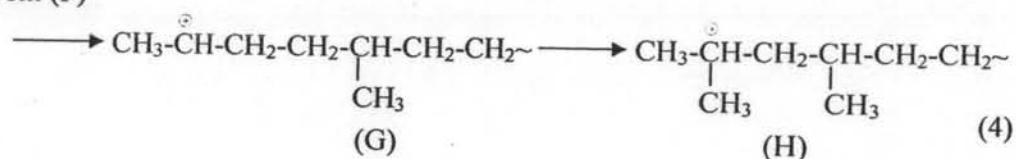
#### Mechanism of gas formation.

Gaseous products are produced from the liquid fraction produced by decomposition of oilgomers and reaction with typical oilgomers is shown in the following scheme. (where  $\text{R}^+$  represents the volatile carbonium ion,  $\sim\text{CH}_2-\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}_2$ )

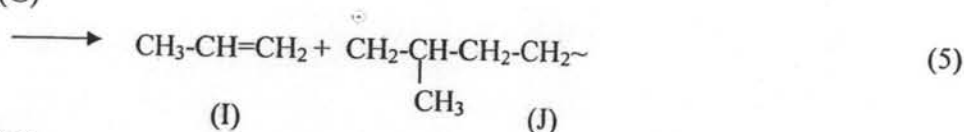


Gas formation takes place by way of the decomposition of these fractions. The unstable reaction intermediate (F) isomerized to secondary (G) or tertiary carbonium ions (H) as shown by equation (4).

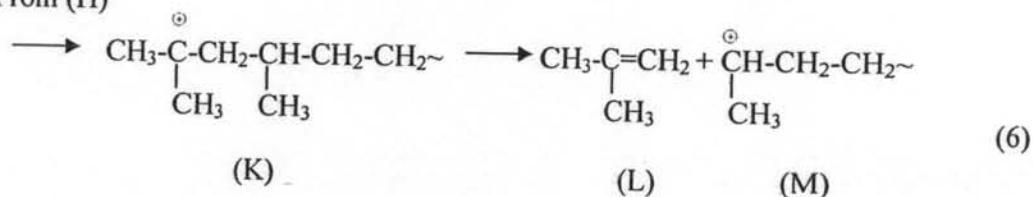
From (F)



From (G)



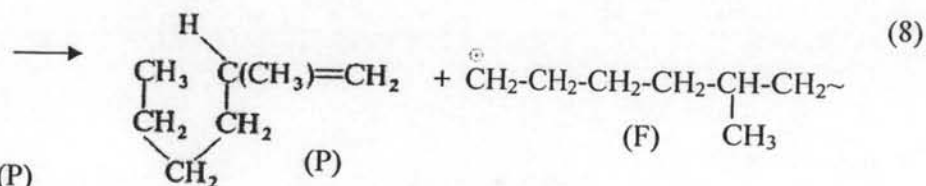
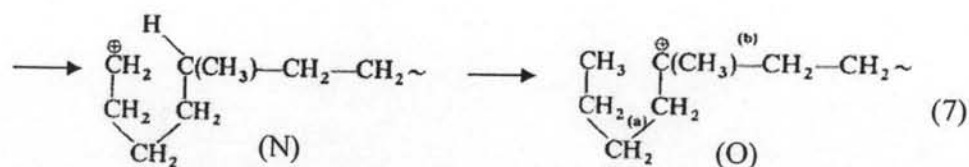
From (H)



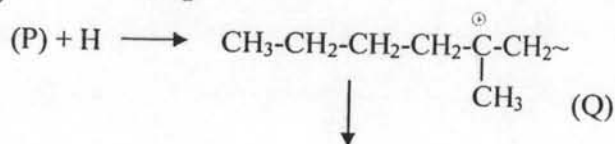
Ions (G) and (H) are essential to gaseous product formation and are mainly produced by  $\beta$ -scission of these carbonium ions (H). Isobutene is converted to isobutane through hydrogen transfer by the catalyst so that its yield is remarkably high. Propylene is produced in high yield by direct  $\beta$ -scission of other important ions (G) at high temperature.

The propane component is independent of propylene yield and is not produced by hydrogenation of propylene. The propane component is probably produced from propyl carbonium ions produced by  $\beta$ -scission of volatile tertiary carbonium ions without hydrogenation of propylene. For instance, stabilization of (F) ions takes place with lower activation energy of isomerization and thus intramolecular rearrangement to inner tertiary carbon atoms occurs. (F) ions cause intermolecular rearrangement by back biting reactions:

From (G)



From (P)





**Two types of constructions are imposed by the zeolite pores:**

1. Transport of reactants or products may be affected strongly by the pores and, in the limiting case, one kind of molecule may be too large to fit through the pores, although another may fit. This is the idea of molecular sieving whereby, for example, small molecules in a mixture may enter the pores and be catalytically converted whereas larger molecules pass through the reactor unconverted.
2. A different kind of restriction related to the steric requirements of the catalysis rather than to the transport of reactants and products: If there is not sufficient space in the zeolite pores to allow formation of the transition state for step in a catalytic cycle, then that cycle is suppressed. If it is suppressed at the expense of another cycle, the term restricted transition state selectivity is applied.

These ideas of shape-selective catalysis are developed that follow. Consider a mixture of two reactants, one small enough to enter the pores of zeolite catalyst and the other too large to enter. A classic example is n-butanol in a mixture with isobutanol in the presence of zeolite A incorporating  $\text{Ca}^{2+}$  ions. The straight-chain alcohol fits into the zeolite pores and undergoes catalytic dehydration much faster than the branched-chain homologue, which does not fit.

Another example involves cracking of the straight- and branched-chain paraffins. The data shown in the Table 2.5 demonstrate that straight-chain reactant is selectively converted in the presence of the small-pore zeolite A, whereas the intrinsic reactivity of the branched-chain reactant is greater, as is confirmed by the data obtained with the amorphous catalyst  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . These two examples are extreme cases demonstrating molecular sieving in catalysis. The selectivity pattern expected on the basis of solution chemistry alone is reversed by the zeolite. The limiting case of no reaction of the larger reactant is not quite reached because some reaction occurs on the small external surface of the zeolite crystallites.

**Table 2.4** Demonstration of shape-selective cracking of paraffins by zeolite A

Reactant	Conversion, % <sup>a</sup>			
	No Catalyst <sup>b</sup>	4A Zeolite	5A Zeolite	Silica-alumina
<i>n</i> -Hexane	1.1	1.4		12.2
3-Methylpentane	<1.0	<1.0	<1.0	28.0

<sup>a</sup> Reaction condition: 500°C, contact time = 7 s.

<sup>b</sup> Conversion determined with reactor packed with quartz chips.

## 2.7 Catalyst deactivation and regeneration [43]

Catalysts have only a limited lifetime. Some lose their activity after a few minutes, others last for more than ten years. The maintenance of catalyst activity for as long as possible is of major economic importance in industry. A decline in activity during the process can be the result of various physical and chemical factors, for example:

- Blocking of the catalytically active sites
- Loss of catalytically active sites due to chemical, thermal, or mechanical processes

The most common causes of catalyst deactivation in catalytic cracking is deposits on the catalyst surface block the active centers and change the pore structure (e.g. coking). The blocking of catalyst pores by polymeric components, especially coke, is another widely encountered cause of catalyst deactivation. In many reaction of hydrocarbons, side reactions lead to formation of polymers. If these are deposited near the pore openings, catalyst activity and selectivity can be influenced due to impaired mass transport into and out of pores.

At high temperature (above 200°C) these polymers are dehydrogenated to carbon, a process known as coking. Especially catalysts with acidic or hydrogenating/dehydrogenating properties cause coking. Coking on acid centers is observed with zeolite and aluminosilicate catalysts and with acidic supports. The extent of coke formation depends directly on the acidity. The precursors for coke formation are mainly aromatic and olefinic hydrocarbons, which are either contained in the starting materials or are formed as intermediate products in the process. In some processes, 5-10% zeolite is added to

amorphous cracking catalysts. This increases the activity by several orders to magnitude and drastically reduces coke formation. This is another example of shape-selectivity catalysis by zeolites, in which the coke-forming intermediates are restricted by the zeolite pores.