



CHAPTER II

THEORY

2.1 Porous materials

Porous materials are crystalline aluminosilicates that contain uniform pores and cavities with molecular dimensions. The structures of porous materials consist of an wide three-dimensional network of SiO_4 and AlO_4 tetrahedral. The tetrahedral are cross-linked by the sharing of oxygen atoms as shown in Figure 2.1.

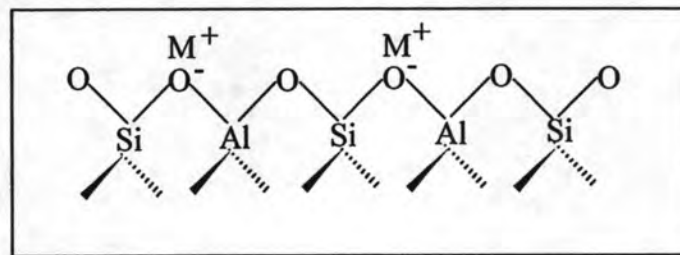
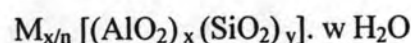


Figure 2.1 The structure of porous materials [28].

The AlO_2^- tetrahedral in the structure determines the framework charge. This is balanced by cations that occupy nonframework positions. The structure formula of porous material is the best expressed for the crystallographic unit cell as:



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 y/x usually has values of 1-5 depending upon the structure. The sum $(x+y)$ is the total number of tetrahedral in the unit cell. The portion [] represents the framework composition.

The magnificent importance of porous materials and related materials in a category of catalytic processes can be attributed to their superior properties in comparison with other types of materials. 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 hydrophobic or hydrophilic 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 selectivity

2.1.1 Porous material structures [28]

Porous materials are one of the molecular sieves with crystalline aluminosilicates of alkali and alkaline earth metals. The structure of porous materials consisted of a three-dimension framework of the tetrahedral primary building units when tetrahedral atoms are silicon or aluminum as shown in Figure 2.2.

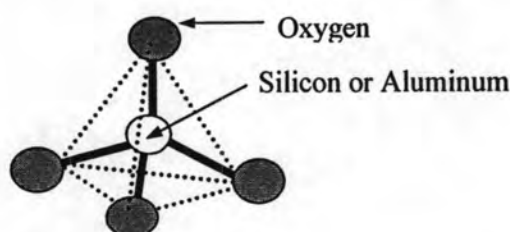


Figure 2.2 A primary building unit of porous materials [28].

Molecular sieves are porous materials that perform 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 porous molecular sieve	Pore size (Å)	Examples
Microporous materials	< 20	Zeolites, Activated carbon
Mesoporous materials	20 – 500	M41s, SBA-15, Pillared clays
Macroporous materials	> 500	Glasses

Porous materials have a common subunit of structure called primary building units of $(\text{Al},\text{Si})\text{O}_4$ tetrahedral, therein the Si or Al distribution is neglected. A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are sixteen such building units, which can be used to describe all of the known porous materials structures; for example, 4, 5, 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. The secondary building units (SBU) are shown in Figure 2.3. Most porous material framework can be generated from different SBU.

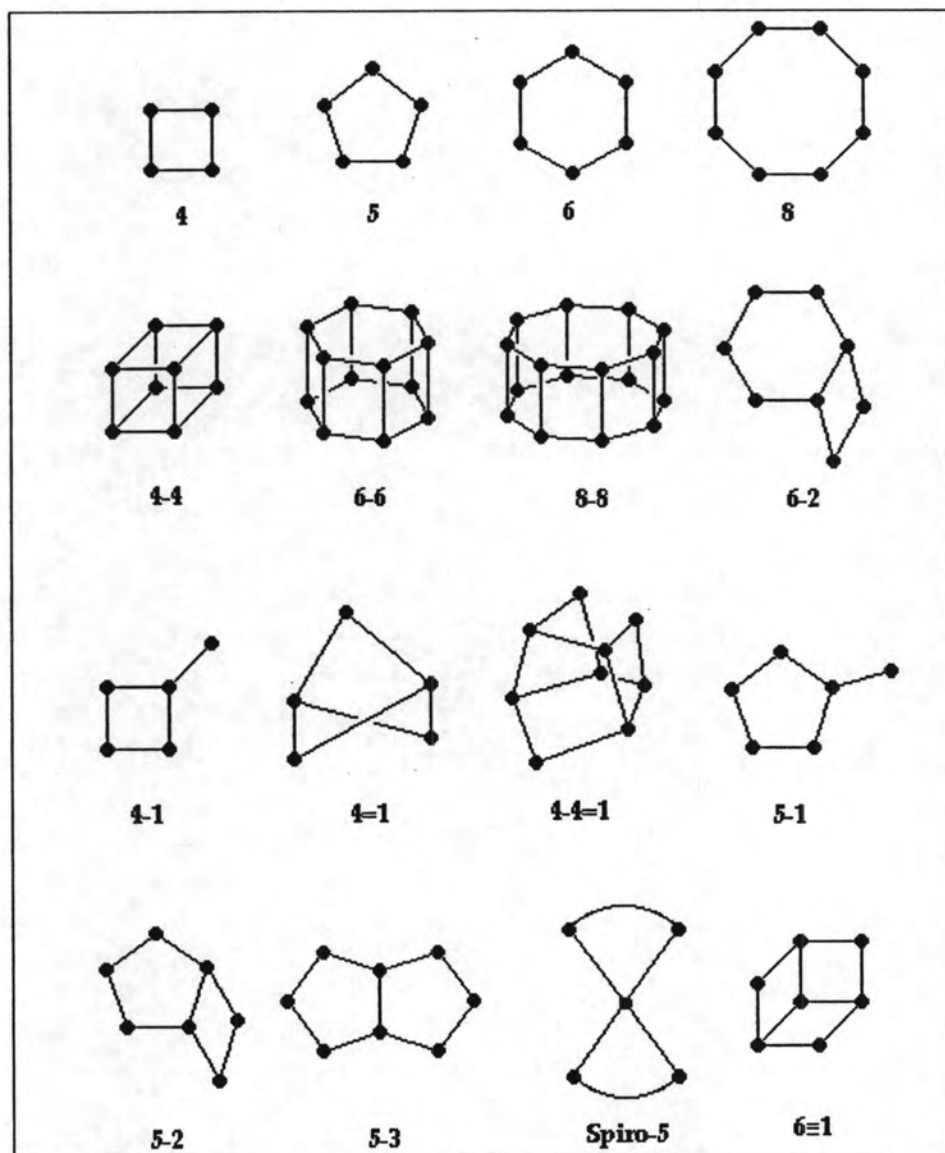


Figure 2.3 Secondary building units (SBU) in porous material structures [29].

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

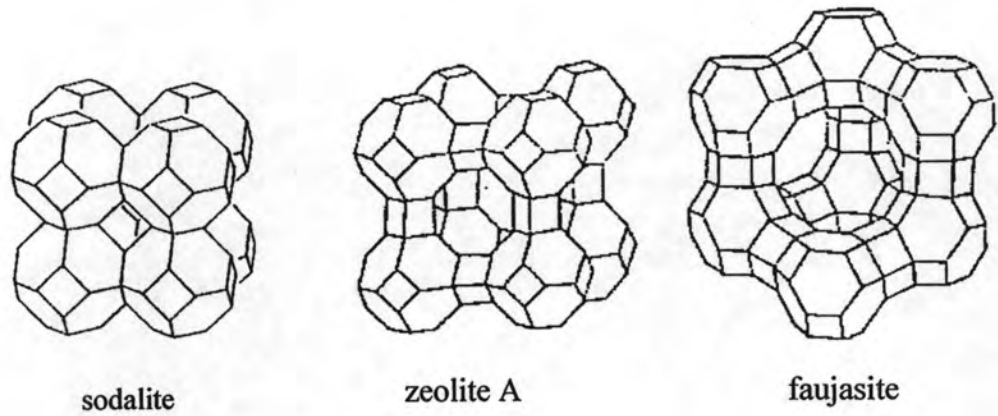


Figure 2.4 The structures of sodalite, zeolite A and faujasite-type porous material [30].

The different ring sizes found in porous materials, based on the different number of tetrahedral atoms defining the opening, are shown in Figure 2.5. The ring sizes are often mentioned as the number of oxygen atoms which are equal to the number of tetrahedral atoms.

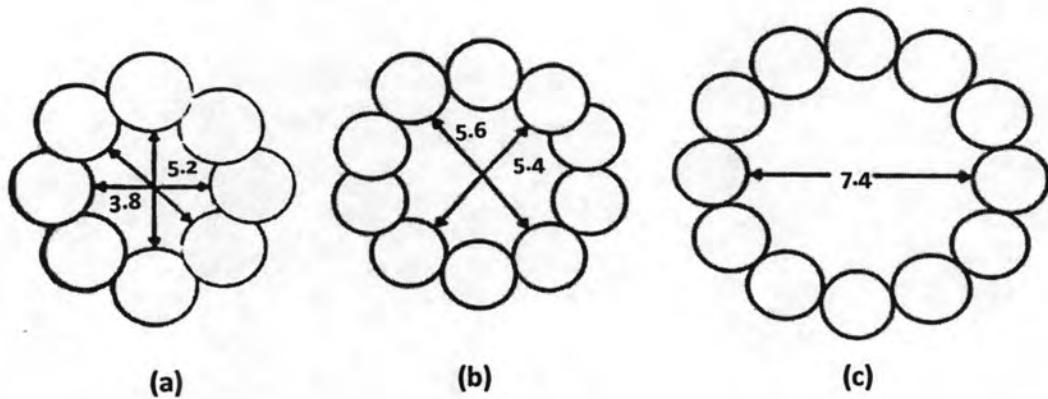


Figure 2.5 Examples of the three types of pore openings in the porous material molecular sieves (a) an 8 ring pore opening (small pore), (b) a 10 ring pore opening (medium pore) and (c) a 12 ring pore opening (large pore) [28].

A porous material has a three dimensional network structure of tetrahedral primary building units (PBU) which make of four oxygen anions with either silicon $[\text{SiO}_4]$ or aluminum $[\text{AlO}_4]^-$ cations in the center as shown in Figure 2.6(a). Then secondary building units (SBU) consist of selected geometric groupings of those tetrahedral by oxygen bridges as shown in Figure 2.6(b).

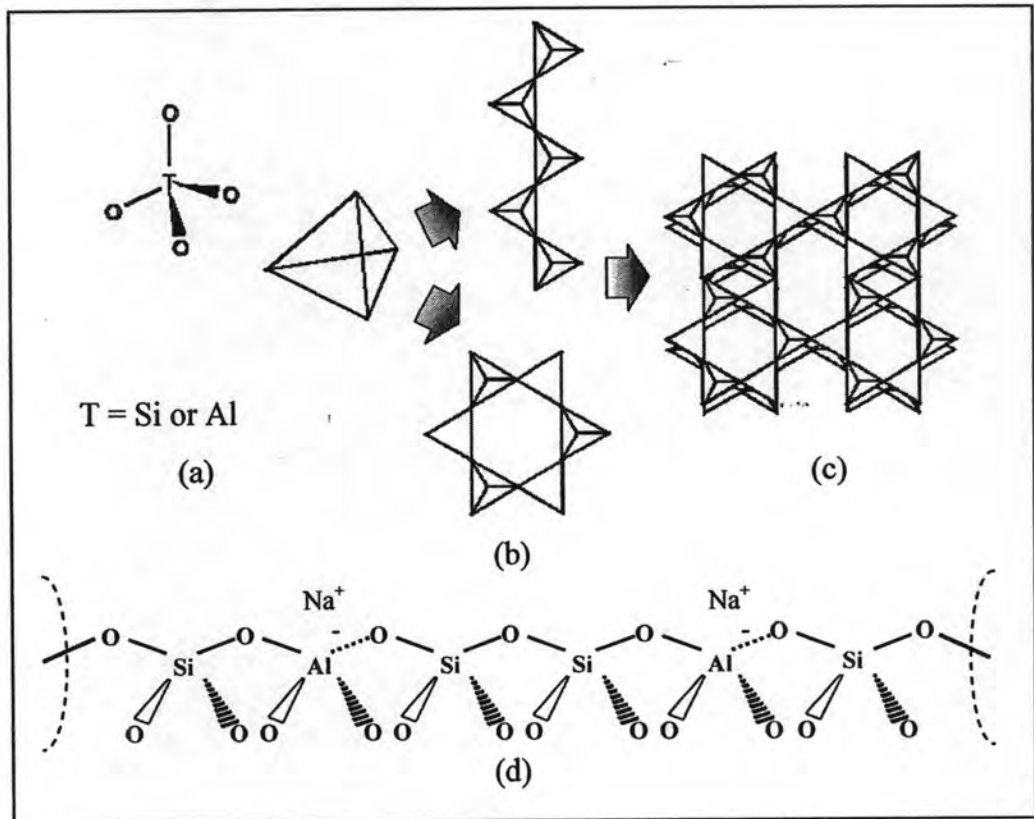


Figure 2.6 A primary building unit (a), secondary building unit (b), framework of a porous materials (c), and metal ions balancing the framework charges of a porous material (d) [28].

2.1.2 Acid sites of porous materials

Most industrial application of porous material is based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction [30-32]. This means that the activity required is based upon the production of Brønsted acid sites arising from the creating 'hydroxyls' within the pore structure. These hydroxyls are formed by ammonium exchange followed by a

calcination step. Porous materials as normally synthesized usually have 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 porous material is not stable in acid solution, it is common to use the ammonium, 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 2.7. The surfaces of porous materials can thus display either Brønsted or Lewis acid sites, or both, depending on how the porous material is prepared. Brønsted sites are converted into Lewis sites as the temperature is increased above 500°C , and water is driven off.

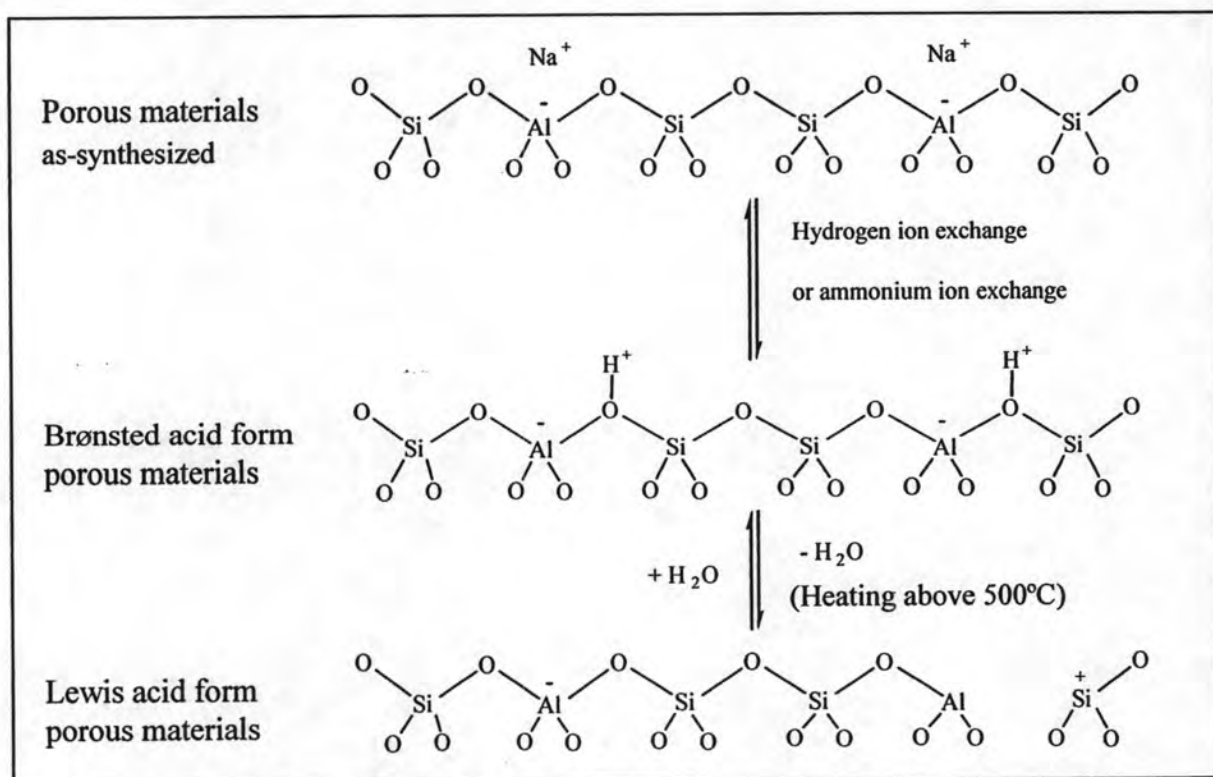


Figure 2.7 The generation of Brønsted and Lewis acid sites in porous materials [33].

2.1.3 Shape and size selectivity of porous materials

Shape and size selectivity presents a very important role in catalysis. Highly crystalline and regular channel structures are among the principal features that porous material 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. These types of selectivity are shown in Figure 2.8. Reactant shape selectivity results from the limited diffusivity of some reactants, which cannot effectively enter and diffuse inside the porous materials. Product shape selectivity occurs when diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment around the active site: the rate steady for a certain reaction mechanism is reduced if the necessary transition state is too bulky to form readily.

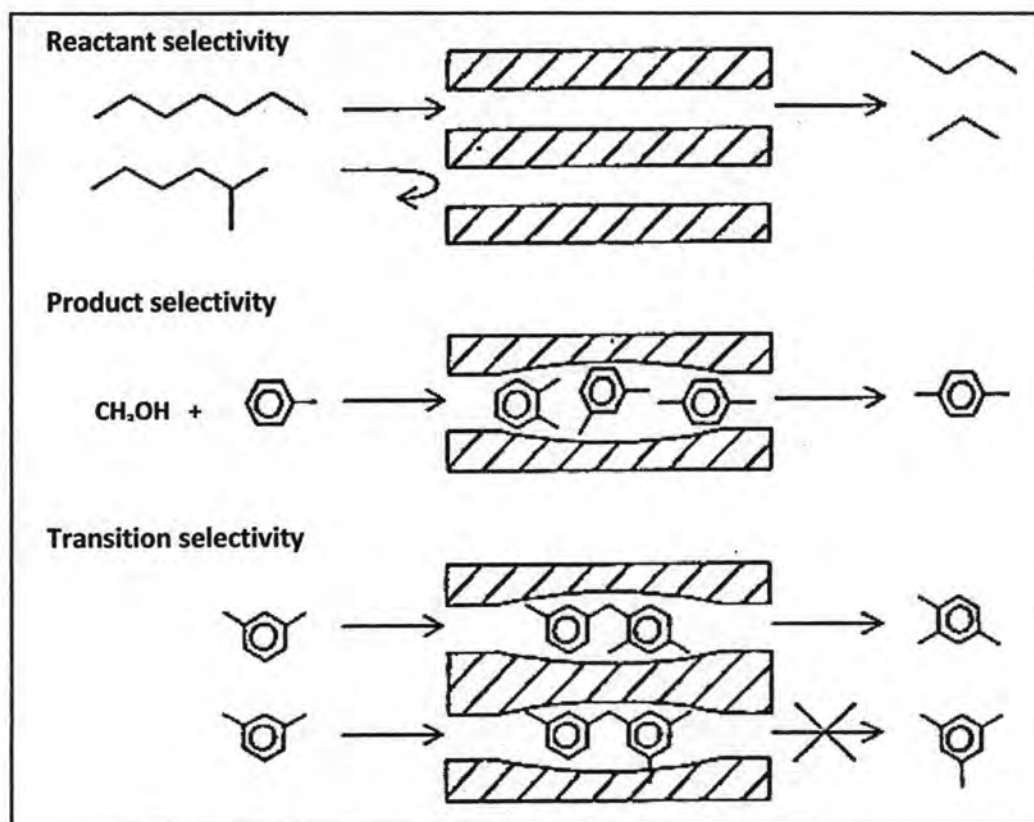


Figure 2.8 Three types of selectivity in porous materials: reactant, product and transition-state shape selectivity [34].

2.2 Mesoporous materials [35-37]

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.

Mesoporous materials are a type of molecular sieves, such as silicas or transitional aluminas or modified layered materials such as pillared clays and silicates. Mesoporous silica has uniform pore sizes from 2 to 50 nm and has found great utility as catalysts and sorption media because of the regular arrays of uniform channels. Larger surface area is desired for enhancing of the reactions.

2.2.1 Classification of mesoporous materials

Mesoporous materials can be classified by different synthetic methods. 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 types of interaction between templates and inorganic species

Materials	Template	Assembly	Solution
MCM-41	Quaternary ammonium salt	Electrostatic	base or acid
FSM-16	Quaternary ammonium salt	Electrostatic	base
SBA-15	Amphiphilic triblock copolymer	H- bonding	acid (pH<2)
HMS	Primary amine	H- 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 [38]

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

2.2.2 Synthesis schemes of mesoporous materials

Crystalline molecular sieves are generally obtained by hydrothermal crystallization. The reaction gel, usually, contains cations (e.g. Si^{4+} for silicate materials, Al^{3+} for aluminate materials) to form the framework; anionic species (e.g. OH^- and F^-); organic template and solvent (generally water). Typically, the nature of template can be considered into two parts that are hydrophobic tail on the alkyl chain side and hydrophilic head on the other side. The examples of templates used are primary, secondary tertiary and quaternary amines, alcohols, crown or linear ethers, and as well as polymers. An understanding of how organic molecules interact with each other and with the inorganic frameworks would increase the ability to design rational routes to molecular sieve materials. The organic templates are frequently occluded in the pores of the synthesized material, contributing to the stability of mineral backbone.

2.2.3 Interactions between inorganic species and surfactant micelles

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for synthesis routes [37]. 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 routes for interactions between the surfactants 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^+XI^+	SBA-1, SBA-2, zinc phosphate
	I^0F^-	S^+FI^0	silica
Anionic (S^-)	I^+	S^-I^+	Al, Mg, Mn, Ga
	IM^+	$S^-M^+I^-$	alumina, zinc oxide
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0	HMS, MSU-X, aluminum oxide
	I^+X^-	S^0XI^+	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

Using ionic surfactant (S^+ and S^-), the hydrophilic head mainly binds with inorganic species through electrostatic interactions. There are two possible formation routes. Firstly, direct pathway: surfactant and inorganic species of which charges are opposite interact together directly (S^+I^- and S^-I^+). Another is the indirect pathway, occurring when the charges of surfactant and inorganic species are the same, so the counter ions in solution get involved as charge compensating species for example the S^+XI^+ path takes place under acidic conditions, in the presence of halogenide anions ($X^- = Cl^-$ or Br^-) and the $S^-M^+I^-$ route is characteristic of basic media, in the existence of alkaline cation ($M^+ = Na^+$ or K^+). Figure 2.9 shows the possible hybrid inorganic-organic interfaces.

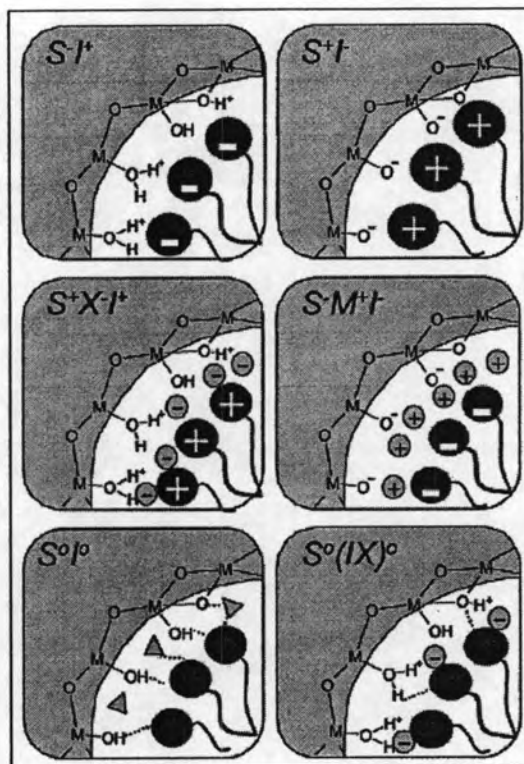


Figure 2.9 Schematic representation of the different types of silica-surfactant interfaces. Dashed line corresponded to H-bonding interactions [39].

In case of non-ionic surfactant (S^0 or N^0), the main interaction between template and inorganic species is hydrogen bonding or dipolar, which is called neutral path i.e. S^0I^0 and S^0FT^+ . Nowadays, non-ionic surfactants give important commercial advantages in comparison to ionic surfactants because they are easily removable, nontoxic, biodegradable and relatively cheap.

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.

2.2.4 Formation mechanism of mesoporous materials

2.2.4.1 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.

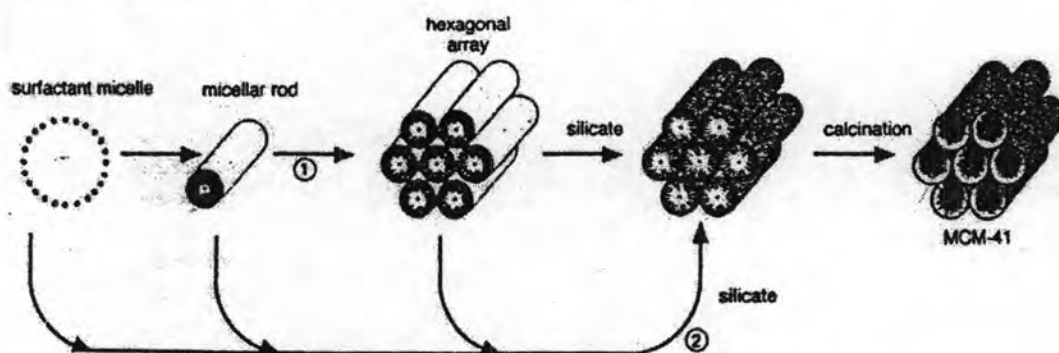


Figure 2.10 Two possible ways for the LCT mechanism [39].

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).

2.2.4.2 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 [37]. Folding sheet formation is illustrated in Figure 2.11.

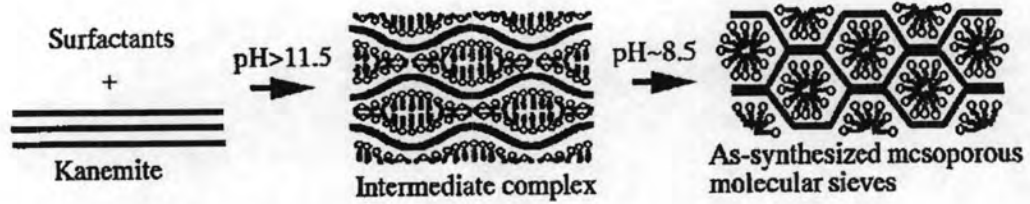


Figure 2.11 Schematic models representing “folding sheets” mechanism [39].

2.2.4.3 Hydrogen bonding interaction

Tanev *et al.* [40] showed that mesoporous silica could be prepared by the hydrogen-bonding interaction of alkylamine (S°) head group and hydroxylated tetraethyl orthosilicate (I°) 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.

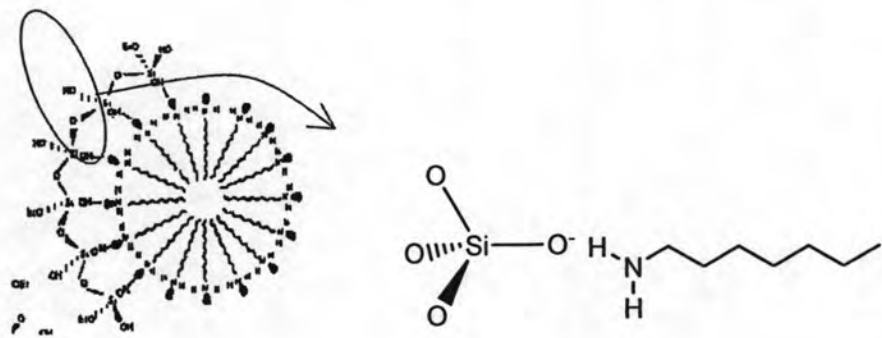


Figure 2.12 Schematic representation of the $S^{\circ} I^{\circ}$ templating mechanism of formation of HMS [37].

2.2.5 Synthesis strategy of mesoporous material using block-copolymer as structure directing agent

In the synthesis of mesoporous materials such as MCM-41, FSM-16 ionic surfactant i.e. the cationic, alkyltrimethyl ammonium (C_nTA^+ , $8 < n < 18$), and anionic surfactant, tertiary amine ($C_nH_{2n+1}N^+(CH_3)_3$) are used as template, respectively. These syntheses were done in extreme (alkaline) pH condition and the obtained materials having pore size in the range of 15 to 100 Å only. However, by this mean, two limitations occurred:

- (1) The lower stability of the obtained materials: due to the thinner pore wall of materials (8-13 Å).
- (2) Difficult to expanding the pore size: the ionic surfactants give a limited pore size. The only way to expand the pore size is in employing swelling agents such as 1,3,5-trimethyl benzene, involving complicate synthesis.

Thus, the block copolymer has been used to solve these problems. Generally, amphiphilic block copolymer has been used in the field of surfactants, detergent manufacturing, emulsifying, coating, etc. The properties of block copolymer can be continuously tuned by adjusting solvent composition, molecular weight, or type of polymers. Figure 2.13 shows typical block copolymer used as templates.

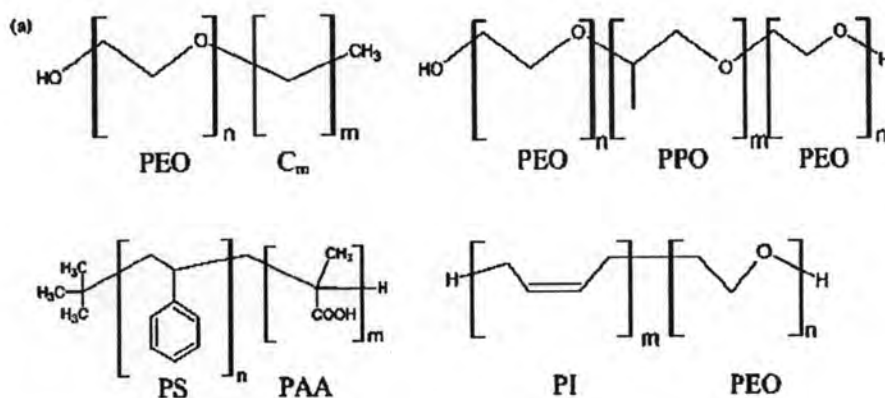


Figure 2.13 Block copolymer used in mesostructured generation [41].

Some advantages of using these block copolymer are:

- (1) *The thicker wall thickness* (about 15-40 Å), enhancing hydrothermal and thermal stability of materials.
- (2) *Pore diameter can be tuned easier* by varying type or concentration of polymer.
- (3) *Easier to remove from mineral framework* by thermal treatment or solvent extraction. Due to the hydrogen bonding interaction between template and inorganic framework, therefore, it should be easier to dissociate as compared to ionic templates (electrostatic interaction).

Interaction between block copolymer template and inorganic species, called hybrid interphase (HI), is particularly important, especially in PEO-PPO based one. Different possible interactions taking place at the HI are schematized in Figure 2.14. Most of the fine HI characterization has been performed on PEO-based (di or triblock) templates. Melosh *et al.* [41] determined that in F127-templated silica monoliths, organization arose for polymer weight fractions higher than 40%. For lower polymer:silica ratios, non-ordered gels were formed. This lack of order was due to a relatively strong interaction (probably of H-bonding type) of the (Si—O—Si) polymers forming the inorganic skeleton with both PEO and PPO blocks.

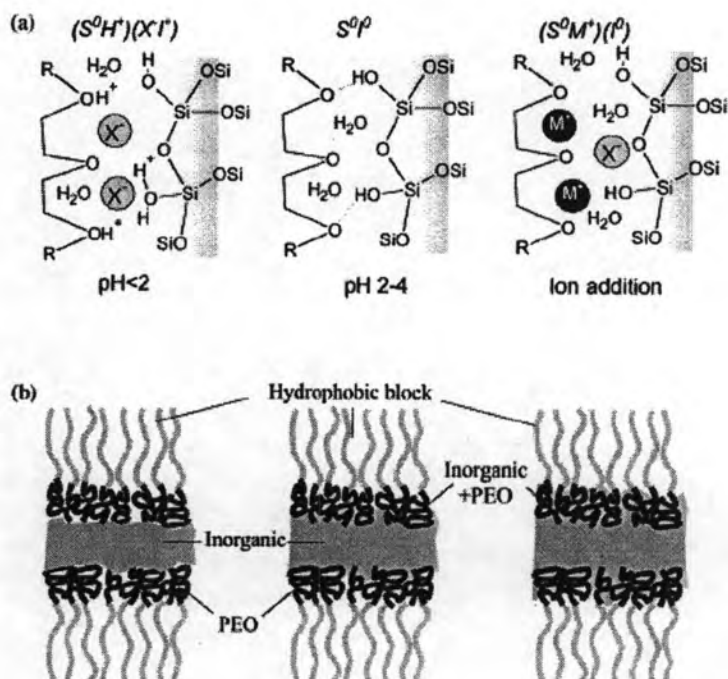


Figure 2.14 (a) Schematic view of the $(S^0H^+)(X^1-)$, S^0I^0 , and $(S^0M^+)(X^1-)$ hybrid interphases (HIs) (b) Three possible structures of a HI composed by a nonionic polymer and an inorganic framework [42].

2.3 SBA-15

2.3.1 Structure and properties of SBA-15

SBA-15 mesoporous material has been synthesized under acidic condition using triblock copolymer as a structure directing agent. This mesoporous material has shown higher hydrothermal stability as compared to MCM-41 due to its thicker pore walls (3.1-6.4 nm). They also possess uniform and hexagonal-structured channel similar to MCM-41 with larger pore size which make them more desirable to deal with bulky molecule. Some properties of MCM-41 and SBA-15, two well-known materials, are compared as described in Table 2.5. According to the properties listed in Table 2.5, SBA-15 shows a better performance than MCM-41 in almost of properties.

Table 2.5 Comparison of two well-known mesoporous materials, MCM-41 and SBA-15 in their characteristic properties [14, 43]

Properties	MCM-41	SBA-15
Pore size (Å)	20-100	46-300
Pore volume (mL/g)	>0.7	0.8-1.23
Surface area (m ² /g)	>1000	690-1040
Wall thickness (Å)	10-15	31-64

2.3.2 Synthesis of SBA-15 and formation mechanism

For SBA-15 materials, aging time and temperature are particularly important. Some research found that mesoporous SBA-15 prepared from calcination of an ‘as-prepared’ hybrid precursor contained a significant fraction of microporosity; further aging of the precursor in the mother liquors leads to an improvement on the pore size distribution (Figure 2.15), in agreement with the first work by Stucky *et al.* [14].

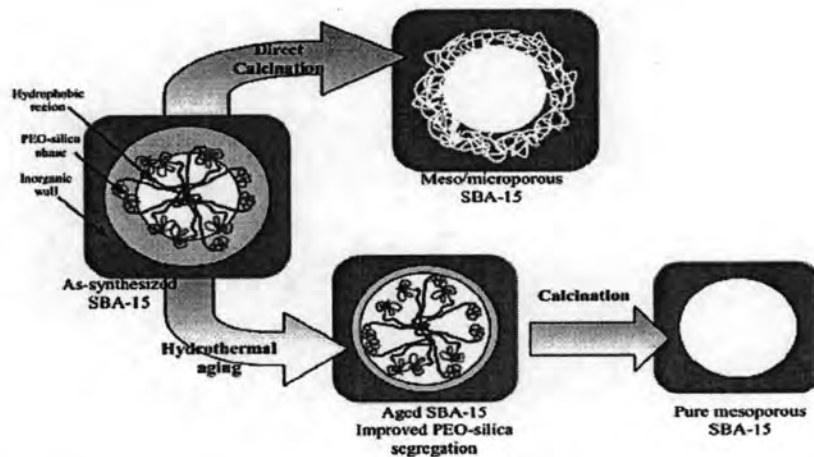
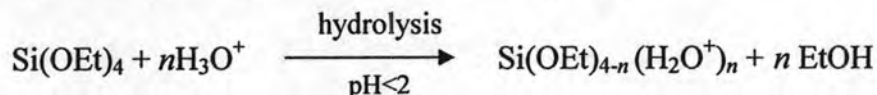


Figure 2.15 Pore evolution upon thermal treatment, depending on pre-treatment and aging [42].

Aging of an as-prepared precipitate at 80–100°C seems to help segregation of the PEO blocks and the inorganic framework, by promoting condensation of the latter. High temperatures also change the polymer behavior. It is known that for $T > 60^\circ\text{C}$, PEO blocks become less hydrophilic and expel water similar to PPO blocks when the temperature is higher than 40°C [42]. For a mechanism, firstly alkoxysilane species (TMOS or TEOS) are hydrolyzed as:



This is followed by partial oligomerization at the silica. Furthermore, at this condition, the PEO parts of surfactant associate with hydronium ions as followed:



Next, coordination sphere expansion around the silicon atom by anion coordination of the form X^-SiO_2^+ may play an important role. The hydrophilic PEO blocks are expected to interact with the protonated silica and thus be closely associated with the inorganic wall. During the hydrolysis and condensation of the silica species, intermediate mesophase is sometimes observed and further condensation of silica species and organization of the surfactant and inorganic species result in the formation of the lowest energy silica-surfactant mesophase structure allowed by solidifying network.

2.4 Modification of catalysts

2.4.1 Incorporation of aluminum into SBA-15

Among the metal-substituted mesoporous materials, aluminum-incorporated mesoporous materials have the great potential in moderating acid-catalyzed reactions for large molecules. However, it is very difficult to introduce the metal ions directly into SBA-15 due to the easy dissociation of metal-O-Si bonds under strong acidic conditions.

To date, only a few studies on the direct synthesis of Al-SBA-15 have been reported [44-46]. The comparison of direct and post syntheses of Al-SBA-15 is described in Table 2.6.

Table 2.6 Comparison of direct synthesis and post synthesis methods of Al-SBA-15 [44-48]

	Direct synthesis method	Post synthesis method
Synthesis condition	Require complicated procedure	Simple method
Aluminum form in materials	Most of samples have both tetrahedral and octahedral aluminum	Most of samples have only tetrahedral aluminum
Catalyst activity	Lower activity due to extra-framework aluminum	Higher activity due to aluminum in framework

The direct synthesis of Al-SBA-15 is difficult and often not stoichiometric. From this viewpoint, therefore, the development of a simple post synthesis method for the alumination of the mesoporous silicas that are synthesized under strongly acidic conditions becomes an appealing alternate choice.

Nowadays, several post synthesis method where aluminum was grafted onto the mesoporous wall with various aluminum sources such as $\text{Al}(\text{CH}_3)_3$, AlCl_3 have been developed without the mesoporous structure seriously destroyed [48]. In the case of zeolites, the introduction of Al into their framework will lead to the formation of bridging hydroxyl groups (Brønsted acid sites). However, whether the similar situation occurs in mesoporous materials still keeps argument. Some researchers assigned the hydroxyl vibration at about 3606 cm^{-1} in IR spectrum to the acidic bridging hydroxyl groups, while others disagreed with the assignment. For example, Trombetta *et al.* argued that the Brønsted acid sites in mesoporous materials or aluminosilicates resulted from terminal silanol groups in the vicinity of aluminum atoms [49]. After the

adsorption of a basic probe, such as pivalonitrile, the terminal silanol groups were induced to form the bridging hydroxyl groups (SiOHAl, shown in Figure 2.16).

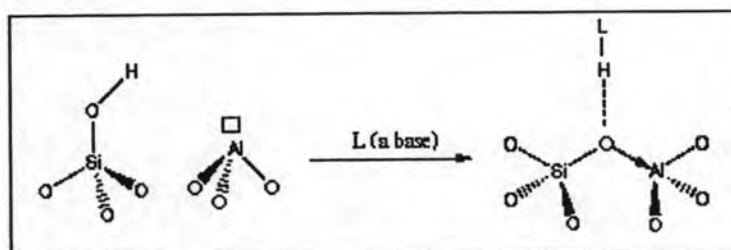


Figure 2.16 Aluminosilicates material using basic probe (L) inducing to form the bridging hydroxyl group [49].

2.4.2 Impregnation [50-51]

Supported metal catalysts may be prepared by three distinct methods (i) deposition, (ii) co-precipitation and (iii) impregnation. All of these, the last mentioned is the most important. It consists of soaking the carrier with a solution of a suitable metal salt, followed by evaporation to dryness. The supported salt is then either reduced or, in certain case, calcined in air to convert the salt to the oxide which is then reduced to the metal. The main functions of carrier are to provide a structural framework for the catalytic component and increase the surface area per unit weight of metal. Other desirable effects may include such factors as increased stability due to small crystallites of metal being sufficiently separated to prevent sintering and a greater resistance to poisoning. The choice of carrier depends to a large extent upon the purpose for which the catalyst is required.

2.4.2.1 Impregnation of metal on SBA-15 [52]

SBA-15 is a mesoporous ordered silica with promising properties as a catalyst support, for examples, high surface area, large mesoporous, lower acidity and so on. These benefits to the increase in dispersion of the active species, the internal diffusion of the reactant and product, where functionalization of the siliceous carrier with an active component can be achieved through a number of

methods. Properties of SBA-15 materials modified by the wet impregnation of metal; nickel, platinum, palladium and ruthenium the active metal precursor is dissolved in an aqueous or organic solution. Then the metal-containing solution is added to a SBA-15 support containing the same pore volume as the volume of solution that was added. Capillary action draws the solution into the pores. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface.

2.5 Characterization of mesoporous hexagonal structure

2.5.1 Powder x-ray diffraction (XRD) [53]

X-ray powder diffraction (XRD) is an instrumental technique used to identify 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.

XRD is a reliable technique that can be used to identify hexagonal mesoporous structure which performs five well-resolved peaks corresponding to lattice planes of Miller indices (100), (110), (200), (210), and (300). These XRD peaks appear at low angle (2θ angle between 0.5 and 3 degree) due to the materials are not crystalline at atomic level, diffraction at higher angles are not observed. Figure 2.17 shows a monochromatic beam of X-ray incident on the surface of crystal at an angle 2θ . The scattered intensity can be measured as a function of scattering angle 2θ . The resulting XRD pattern efficiently determines the different phases present in the sample.

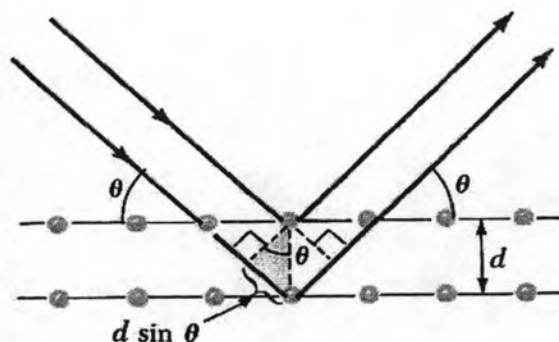


Figure 2.17 Diffraction of X-ray by regular planes of atoms [54].

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, λ is the wavelength; d is the distance between adjacent planes of atoms (the d -spacings) and θ is the angle between the incident beam and these planes.

2.5.2 Nitrogen adsorption-desorption technique [55-56]

The N_2 adsorption-desorption technique is used to determine the physical properties of mesoporous molecular sieves, that are 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. The IUPAC classification of adsorption isotherms is illustrated in Figure 2.18.

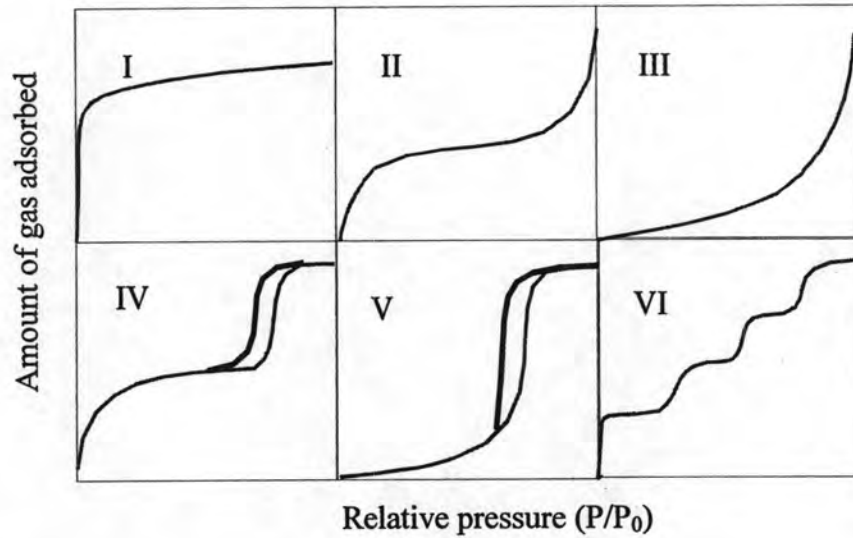


Figure 2.18 The IUPAC classification of adsorption isotherm [55].

Adsorption isotherms are described as shown in Table 2.10 based on the strength of the interaction between the sample surface and adsorptive. 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 mesoporous and macropores. The multipoint Brunauer, Emmett and Teller (BET) 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 slope and intercept are used to determine 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 to calculate the surface area. The surface area reported depend upon the method used, as well as the partial pressures at which the data are collected.

Table 2.7 Features of adsorption isotherms

Type	Interaction between sample surface and gas adsorbate	Porosity	Example of sample-adsorbate
I	relatively strong	Micropores	activated carbon-N ₂
II	relatively strong	Non porous	oxide-N ₂
III	weak	Non porous	carbon-water vapor
IV	relatively strong	Mesopore	silica-N ₂
V	weak	Micropores	
		Mesopore	activated carbon-water vapor
VI	relatively strong sample surface has an even distribution of energy	Nonporous	graphite-Kr

2.5.3 Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) [57]

It is essential to determine elemental composition to be assured that the composition of active elements in catalyst is close to what expected. It is also often used in explanation of the life time of catalyst by using the elemental composition of catalyst. To do these, chemical methods of analysis such as ICP-AES, XRF are still in use.

2.5.4 Solid state ²⁷Al-magic angle spinning-nuclear magnetic resonance (²⁷Al-MAS-NMR) [58]

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

2.5.5 Scanning electron microscope (SEM) [59]

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 increase the mean free path of electron, hence the better image quality.

2.5.6 Transmission electron microscope (TEM) [60]

TEM is a microscopy technique used for studying the size, size distribution and morphology of particles. TEM involves a beam of accelerated electron, 50-200 keV, emitted by a tungsten filament cathode in vacuum. These electrons are deflected in small angles by atoms in sample and transmitted through a thin sample. Then, these electrons are magnified by magnetic lenses and hitting a fluorescent screen coated with a phosphor to generate the bright field image. A schematic diagram of transmission electron microscope is shown in Figure 2.19. The images from electron microscopes indicate the shape of a sample crystallite which can be used to determine size and morphology of solid nanoparticles.

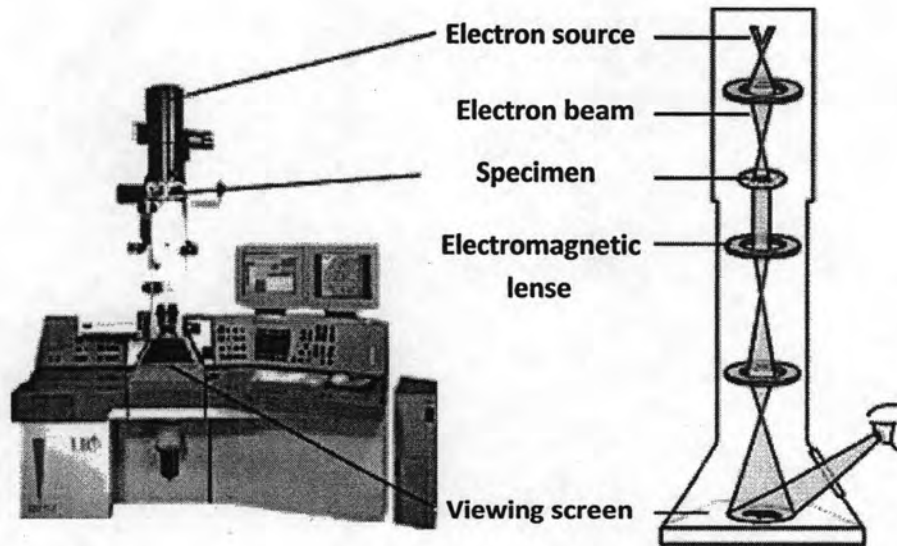


Figure 2.19 Schematic diagram of transmission electron microscope [60].

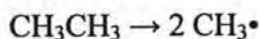
2.6 Cracking reaction

Cracking processes break down heavier hydrocarbon molecules (high boiling point oils) into lighter products such as petrol and diesel. These processes include thermal cracking, catalytic cracking and hydrocracking.

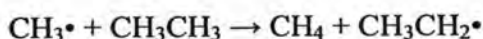
- **Thermal cracking** [61] elevated temperatures ($\sim 800^\circ\text{C}$) and pressures ($\sim 700\text{kPa}$) are used. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of 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:

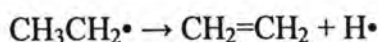
1. Initiation reactions, where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves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



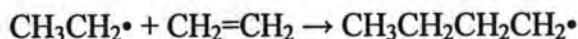
2. Hydrogen abstraction, where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.



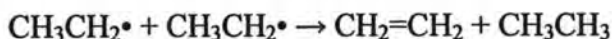
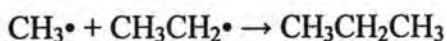
3. Radical decomposition, where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.



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.



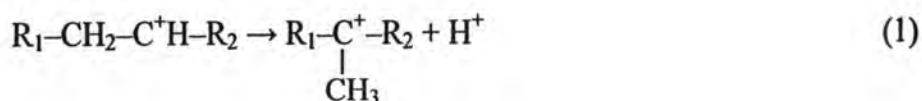
5. Termination reactions, which happen when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are *recombination*, where the two radicals combine to form one larger molecule, and *disproportionation*, where one radical transfers a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



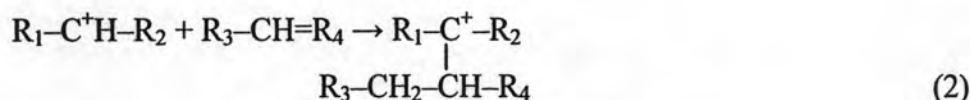
- **Catalytic cracking** uses a zeolite catalyst and moderately-high temperatures (400-500°C) to aid the process of breaking down large hydrocarbon molecules into smaller ones. During this process, less reactive, and therefore more stable and longer lived intermediate cations accumulate on the catalysts active sites generating deposits of carbonaceous products generally known as coke. The formation of 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 β -scission mechanism [62-63]

Reactions of the adsorbed carbonium ion are [64-65]:

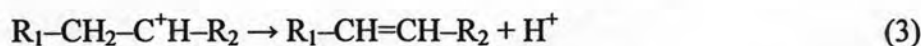
1. Isomerization to a more stable carbonium ion, for example, through a methyl shift:



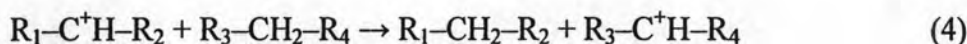
2. Oligomerization with olefin in a bimolecular reaction to form a larger adsorbed carbonium ion:



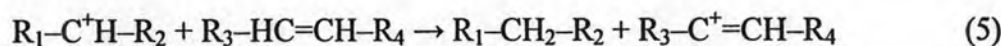
3. Desorption with deprotonation to form an olefin (the opposite of adsorption):



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 [66].

- **Hydrocracking** can increase the yield of petrol components, as well as being used to produce light distillates. It produces no residues, only light oils. Hydrocracking is catalytic cracking in the presence of hydrogen. The extra hydrogen saturates, or hydrogenates the chemical bonds of the cracked hydrocarbons and creates isomers with the desired characteristics. Hydrocracking is also a treating process, because the hydrogen combines with contaminants such as sulphur and nitrogen, allowing them to be removed.

2.7 Application of product from the glycerol waste cracking

After cracking reaction was complete, the gaseous product and the light liquid product were analyzed with GC. The major products of gas fraction were CO, CO₂ and 1,3-butadiene, whereas 2-cyclopenten-1-one and 2-propen-1-ol were the main light liquid products.

2.7.1 Synthesis gas (CO + H₂) [67]

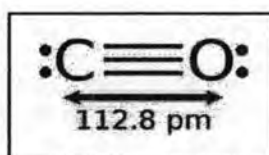


Figure 2.20 The structure of carbon monoxide [67].

This synthesis gas or syngas comprises of 85% of carbon monoxide and hydrogen and small amounts of methane and carbon dioxide. Syngas is the direct end-product of the gasification process. Though it can be used as a standalone fuel, the energy density of syngas is only about 50 percent that of natural gas and is therefore mostly suited for use in producing transportation fuels and other chemical products. As its unabbreviated name implies, synthesis gas is mainly used as an intermediate building block for many users in the petrochemical and refining industries, the final production (synthesis) of various fuels such as synthetic natural gas, methanol and synthetic petroleum fuel (dimethyl ether – synthesized gasoline and diesel fuel).

2.7.2 Carbon dioxide (CO₂) [68]

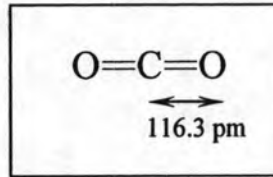


Figure 2.21 The structure of carbon dioxide [68].

Carbon dioxide is a by-product of glycerol waste cracking reaction. CO₂ is commonly used as a raw material for production of various chemicals as a working material in fire extinguishing systems; for freezing of food products; for enhancement of oil recovery from oil wells; and for treatment of alkaline water. In addition, it is used for photosynthesis and required for plant growth and development by plants.

2.7.3 1,3-Butadiene [69]

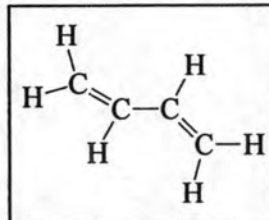


Figure 2.22 The structure of 1,3-butadiene [69].

Most butadiene is polymerized to produce synthetic rubber. While polybutadiene itself is a very soft, almost liquid material, polymers prepared from mixtures of butadiene with styrene or acrylonitrile, such as ABS, are both tough and elastic. Styrene-butadiene rubber is the material most commonly used for the production of automobile tires. Smaller amounts of butadiene are used to make nylon via the intermediate adiponitrile, other synthetic rubber materials such as chloroprene, and the solvent sulfolane. Butadiene is used in the industrial production of 4-vinylcyclohexene via a dimerization reaction and cyclododecatriene via a trimerization reaction.

2.7.4 2-Cyclopenten-1-one [70]

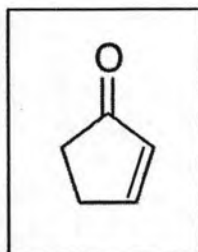


Figure 2.23 The structure of 2-cyclopenten-1-one [70].

Use of a 2-cyclopenten-1-one as a five-membered ring seems to be advantageous for intermediate of pharmaceutical such as 2-cyclopenten-1-one and its derivatives comprising the cyclopentenone nucleus as inhibitors of the NF- κ B factor, with anti-inflammatory, anti-proliferative, immunosuppressive, cytoprotective and antiviral activity, the substituents being selected among the ones which do not affect the NF- κ B inhibitory activity. Furthermore, 2-cyclopentenone is used in the industrial production for perfumes and agricultural chemical.

2.7.5 2-Propen-1-ol (allyl alcohol) [71]

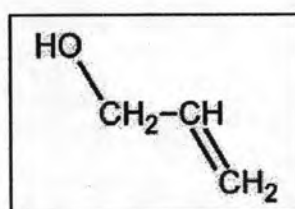


Figure 2.24 The structure of 2-propen-1-ol [71].

2-Propen-1-ol is used as a chemical intermediate in the production of epichlorohydrin, 1,4-butanediol and certain pharmaceuticals and as a raw material for production of glycerol and diethylene glycol bis(allyl carbonate) (for plastic optical lenses). It is also used in the manufacture of flavorings, perfumes, resins, plasticizers and fire retardants. Other uses are as herbicide and militar.