CHAPTER II

THEORY

Porous materials can be classified based on the IUPAC definitions into three groups. Microporous materials have pore diameters less than 20 Å, mesoporous materials have pore diameters ranging from 20 to 500 Å and macroporous materials have pore diameters larger than 500 Å.

Microporous materials[38] embrace materials from amorphous silica and inorganic gels to crystalline materials such as zeolites (aluminosilicates), aluminophosphates, gallophosphates and related materials. The enormous interest in these materials, especially zeolites, is due to their wide catalytic applications within industrial areas such as oil refining, petrochemistry and synthesis of chemicals. The materials are also important as adsorbents.

2.1 Zeolites

Zeolites[39,40] are crystalline microporous materials containing hydrated aluminosilicates with a framework based on an extensive three-dimensional network of oxygen ions. The ions situated within the tetrahedral sites formed by the oxygen can be either as Si^{4+} or an Al^{3+} ion. The AlO_2^- tetrahedra in the structure determine the framework negative charge while the zero charge SiO_2 tetrahedra do not. This is balanced by alkaline and/or alkali earth cations that occupy non-framework positions. A representative empirical formula for a zeolite is written as:

$$M_{2/n}O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O$$

M represents the exchangeable cations, generally from the group I or II ions, although other metal, non-metal, and organic cations may also be used to balance the

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framework charge, and n represents the cation valency. The value of x is equal to or greater than 2 because Al^{3+} does not occupy adjacent tetrahedral sites, otherwise it results in the negatively charged units next to each other.

The different ring sizes found in zeolites, based on the different number of tetrahedral atoms defining the opening, are shown in Figure 2.1. The ring sizes are often mentioned as the number of oxygen atoms which are equal to the number of tetrahedral atoms.

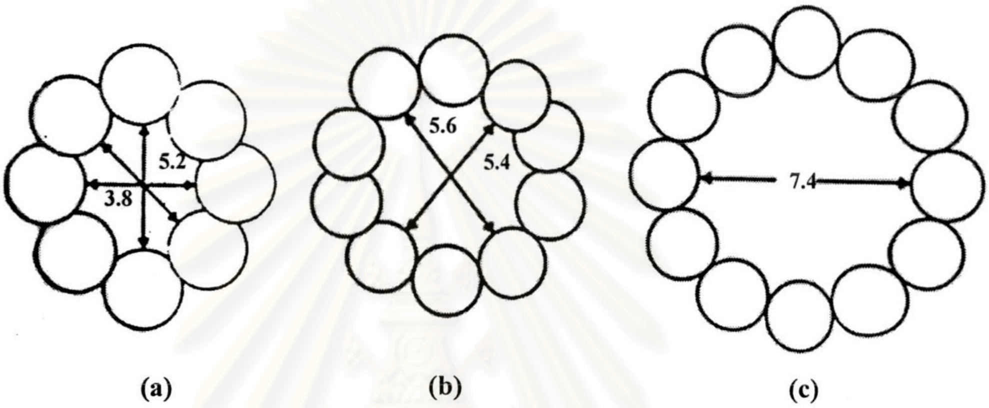


Figure 2.1 Examples of the three types of pore openings in the zeolite molecular sieves.[39] (a) an 8 ring pore opening

(b) a 10 ring pore opening

(c) a 12 ring pore opening

Moreover, zeolites can be classified by structural building units. These units are also used in efforts to understand the way that individual structures form from the starting mixtures used in their synthesis. The primary building unit of a zeolite structure is the individual tetrahedral TO_4 unit, where T is either Si or Al. A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedra. There are nine such building units, which can be used to describe all of the known zeolite structures. These secondary building units consists 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. Some topologies of these units are shown in Figure 2.2.

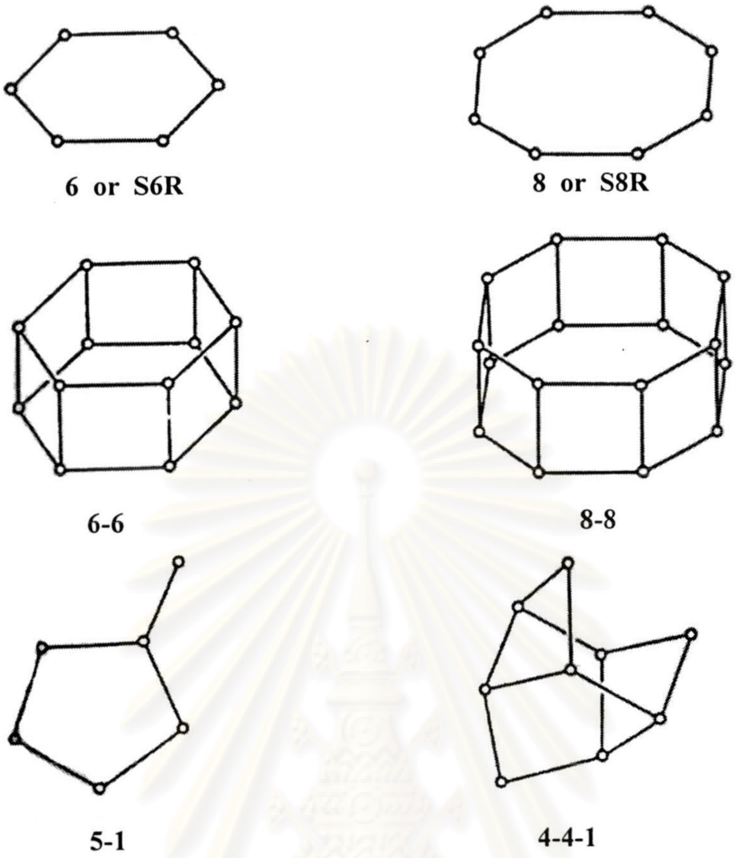
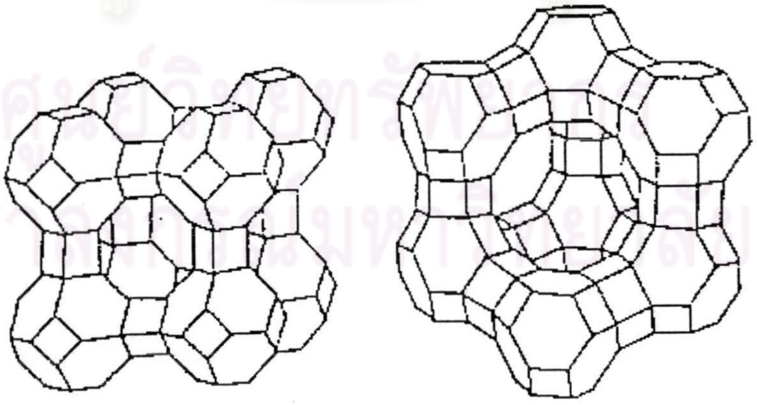


Figure 2.2 Secondary building units found in zeolite structures.[39]

Most zeolite frameworks can be generated from several different SBU. For example, the sodalite framework can be built from either the single 6-member ring and the single 4-member ring. Some of them are shown in Figure 2.3.



zeolite A
(a)

faujasite
(b)

Figure 2.3 Some zeolite structures (a) zeolite A and (b) faujasite.[39]

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2.1.1 Acidic Zeolites

If a zeolite structure contains only SiO_4 tetrahedra, it would be electrically neutral and no acidity would be developed on its surface. In fact, Brønsted acid sites are developed when Si^{4+} is isomorphically substituted by a trivalent metal cation, for instance Al^{3+}, and a negative charge is created in the lattice, which is compensated by a proton. The proton is attached to the bridged oxygen atom connected between nearby silicon and aluminum atoms, resulting in the so-called bridged hydroxyl group which is responsible for the Brønsted acid sizes of zeolites as shown in Figure 2.4.

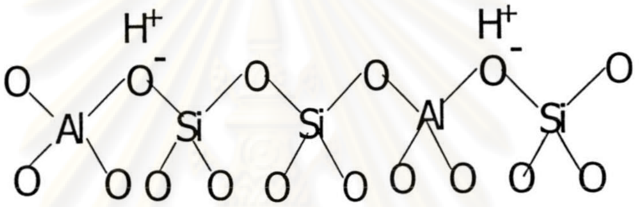

Figure 2.4 Brønsted acid sites of zeolite.

The reactivity and the selectivity of molecular sieve zeolites as catalysts are determined by active sites provided by an imbalance in charge between the silicon and the aluminum ions in the framework. Each aluminum atom contained within the framework structure induces a potential active acid site. Classical Brønsted and Lewis-acid models of acidity have been used to classify the acid sites on zeolites. Brønsted acid is a proton-donor and Lewis acid is an electron acceptor. The presence of both types of acid sites in zeolites is shown in Figure 2.5.

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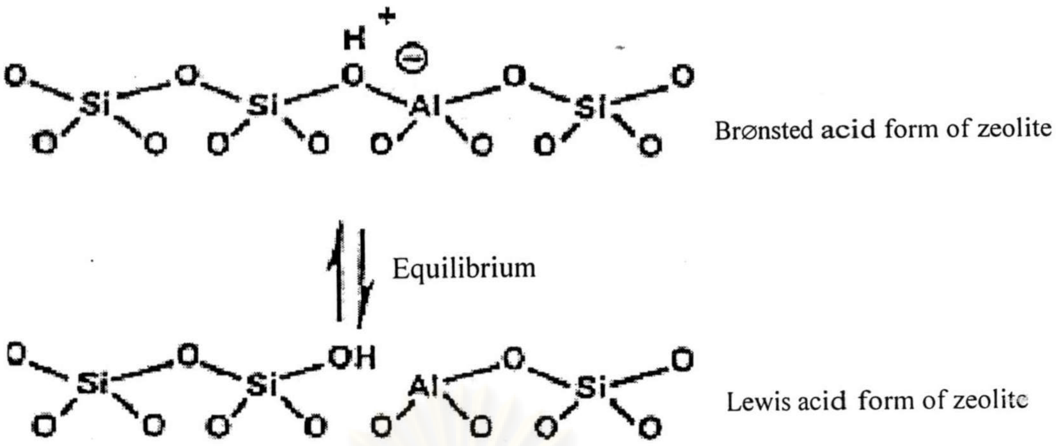

Figure 2.5 Brønsted and Lewis acid sites of zeolites.[39]

Hydrothermal syntheses of silica-rich zeolites generally consist of water as the solvent, a silicon source, an aluminum source, and a structure-directing agent. Better understanding of the effect of the structure-directing agent has long been aimed at. This will entail better control of the resulting structures, and even prediction of the specific structure could be possible. Some progress in the field has been made some general rules of correlation between the structure-directing agent and the structure of zeolites with a high silica content:

1. Hydrothermal silicate syntheses result in dense crystalline and layered materials when no structure-directing agent is present.
2. Linear structure-directing agents usually result in one-dimensional molecular sieves with 10-ring channels.
3. Branched structure-directing agents tend to form multi-dimensional zeolites with pore diameters of 4-7 Å.
4. One-dimensional, large pore zeolites often result from large polycyclic structure-directing agents.

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2.1.2 Properties of Zeolites

The tremendous importance of zeolites and related materials in a variety 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 hydrophobicity or hydrophilicity of the materials.
3. The pore openings and cavities in the range of 5-12 Å. In addition, the electric field within the micropores will activate many reactants.
4. Insoluble materials and well defined pore structures.
5. Different types, different properties
6. The presence of shape and size selectivities depicted in Figure 2.6.

Shape selectivity plays a very important role in catalysis over zeolites. Highly crystalline and regular channel structures are among the principal features that zeolite catalysts offer over other materials. The capability of zeolites to organize and to discriminate molecules with high precision is responsible for their shape-selective properties. Reactant shape selectivity results from the limited diffusivity of some reactants, which cannot effectively enter and diffuse inside the zeolites. 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 constant for a certain reaction mechanism is reduced if the necessary transition state is too bulky to form readily.

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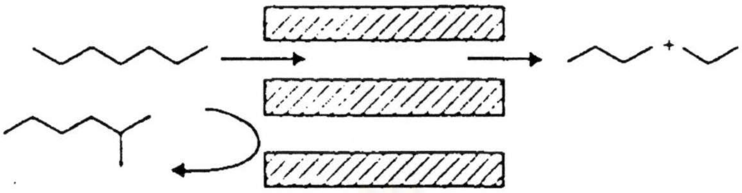
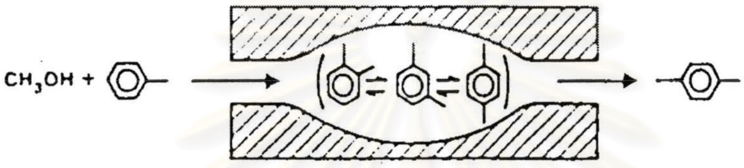
Reactant Selectivity



Product Selectivity



Transition-State Selectivity

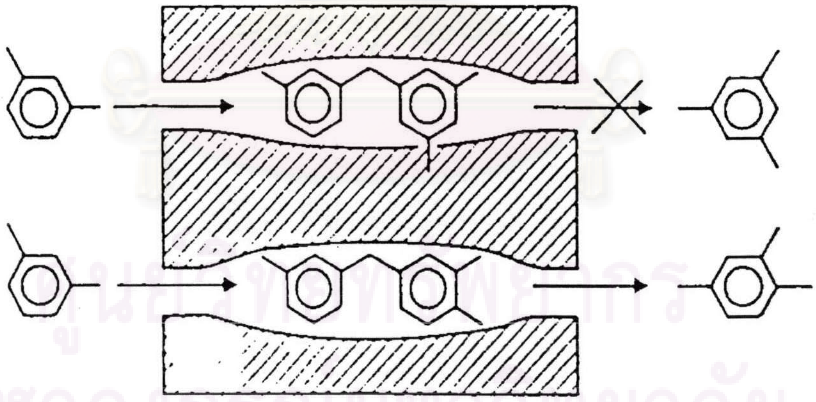


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Figure 2.6 Diagram depicting the three types of selectivity: reactant, product, and transition-state shape selectivity.[39]

All the properties mentioned above are dependent on the thermal and hydrothermal stability of the materials. Resistance towards heat, steam and chemical attacks is necessary if the materials are to be used as catalysts at all. Very stable zeolites are possible to produce, but they have one serious limitation: they are not able to efficiently process molecules that are larger than their pore diameters (maximum 13 Å). Consequently, it has been a long search for synthesis methods that will increase the pore size, and at the same time retain the crystalline framework.

The natural way to go would be to increase the size of the structure-directing agents, and thereby increase the pore structure of the materials. For zeolites this strategy has not been very successful until quite recently. In the early 1980s, however, researchers at Union Carbide discovered that the strategy was applicable to systems containing aluminum and phosphorous in the framework, the so-called $AlPO_4$ structures.[38] These materials have pore sizes in the range of 13-15 Å, and examples are cloverite, VPI-5 and $AlPO_4$-8. Soon after, related materials such as siliconaluminophosphates (SAPOs) and metal aluminophosphates (MeAPOs) were synthesized as well. Common for many of these materials is their lack of thermal or hydrothermal stability.

The most significant advance in the preparation of large pore crystalline materials is probably the synthesis of the high silicate zeolite UTD-1 a few years ago. UTD-1 has a one-dimensional pore system consisting of elliptical pores. UTD-1 is extremely stable compared to VPI-5, $AlPO_4$-8 and cloverite. It shows no loss of crystallinity at temperatures up to 1000° C, even in the presence of water. It also contains enough Brønsted acid sites to be used in the cracking of paraffins. A major drawback, however, is the structure-directing agent, which is a huge organometallic cobalt-complex. This must be removed, and remaining cobalt in the pores has to be acid leached. This will probably restrict the practical applications of this zeolite.

All in all it can be concluded that large pore crystalline materials are not yet very applicable in catalytic processes, even though large progress has been made.

Today the most promising materials in the mesoporous range seem to be those which were discovered in the late 1980s and early 1990s. In 1988 the syntheses of ordered mesoporous materials with narrow pore size distributions and large surface area were reported.[38] The materials were prepared from the layered polysilicate named kanemite, and a two-step formation mechanism was proposed.[38] First the Na^+ ions in the kanemite interlayers were ion-exchanged by alkyltrimethyl ammonium cations. Second, the flexible kanemite layers folded and cross-linked to each other, and in this way an inorganic framework was formed.

Another formation mechanism was proposed.[38] They agree in the first step mentioned above, but in the second step they suggested a reorganization of the kanemite layers under influence of the polar headgroups of the surfactants. The single kanemite layers were disrupted and the silicate species was locally rearranged. The driving force of this rearrangement was assumed to be the structural loss of kanemite and the ability of the surfactants to transform from bilayer structures to cylindrical micellar aggregates. The silicate species rearranged further around the micelles, and silanol condensation finally formed an inorganic network.

2.2 MCM-41

Mesoporous materials[38] are typically amorphous or paracrystalline solids, such as silicas or transitional aluminas or modified layered materials such as pillared clays and silicates. The pores in these materials are generally irregularly spaced and broadly distributed in size. Despite these efforts, mesoporous molecular sieves with regular, well-defined channel systems have remained elusive.

In 1992 researchers at Mobil Research and Development Corporation published the syntheses of a group of mesoporous materials, designated M41S.[33,34] These materials are also formed to have narrow pore size distributions, tunable from 15 to 100 Å, larger than the pore-size of microporous zeolites (≤14 Å). The extremely high surface areas (>1000 m^2/g) and the precise tuning of pore sizes are among the many desirable properties that have made such materials the focus of great interest.

The main groups of this family are MCM-48, which has a three-dimensional, cubic-ordered pore structure, MCM-41, which has a one-dimensional, hexagonally-ordered pore structure and MCM-50, which has an unstable lamellar structure. Figure 2.7 schematically shows the structure of these three phases. These materials are fundamentally different from zeolites by the fact that the pore walls are amorphous.[41,42]

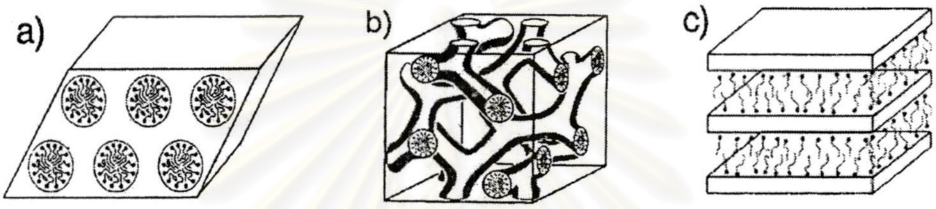

Figure 2.7 A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.[42]

2.2.1 Structure and Properties of MCM-41

MCM-41, one of the members of this extensive family of mesoporous sieves, possesses a hexagonal array of uniform mesopores. MCM-41 has been synthesized with uniform channels varying from approximately 15 to 100 Å in size. The larger pore materials typically have surface areas above 1000 m^2/g and hydrocarbon sorption capacities of 0.7 cm^3/g and greater.

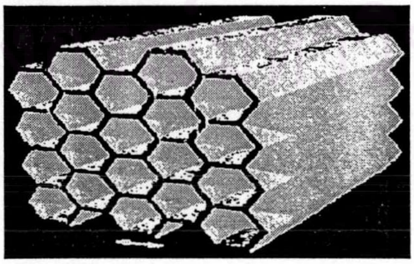

Figure 2.8 Hexagonal packing of unidimensional cylindrical pores.[43]

2.2.2 Structure and Properties of Al-MCM-41

Siliceous mesoporous materials have, for most purposes, not enough intrinsic acidity to be catalytically active. Catalytic activity is, however, enhanced by modification of the siliceous framework by other elements (often metals). The most studied of the modified MCM-41 materials are probably those containing aluminum. These materials are acidic, and the acid sites of Al-MCM-41 have been characterized. The general structure of Al-MCM-41 is similar to zeolite which is shown in Figure 2.4. It is generally accepted that tetrahedral aluminum is incorporated into the wall structure, while octahedral aluminum is regarded as extra-framework species. This may be done in several ways. One method is direct addition of the extra element precursors to the synthesis solution. Hence, the modifying elements are incorporated into the structure. Another possibility is to modify the materials after a desired structure has been formed. It was found that 26-30% of the silicon atoms were connected to hydroxyl groups. These are attractive anchor sites for attachment of elemental precursors, resulting in a monolayer of active sites. A third method is loading metals in the structure by the so-called incipient wetness impregnation technique.

2.2.3 Synthesis of Al-MCM-41

The preparation methods of Al-MCM-41 materials are reminiscent of the synthesis of zeolites. The main difference is that a surfactant is used as template. The preparation of MCM-41 materials takes place under mild conditions, typically under hydrothermal conditions at the temperature of 100-150°C, in the presence of anionic, cationic, gemini or neutral surfactants, under either basic or acidic conditions.

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The modification or expansion of synthesis conditions especially toward milder conditions is one of the main objectives of mesoporous materials synthesis for energy savings.[44] The synthesis routes of mesoporous materials are conveniently classified into the following six types according to the interaction between inorganic species (I) and surfactant (S):

- Electrostatic interactions with and without mediating anion (X^-) or cation (M^+), (S^+I^-), (S^-I^+), ($S^+X^-I^+$) and ($S^-M^+I^-$).
- Neutral templating through hydrogen-bonding using neutral primary amine (S^0I^0).
- Covalent bonding (S-I).

Synthesis of silicate mesophases is possible through the (S^+I^-) pathway in basic media, the ($S^+X^-I^+$) in acidic media, and the (S^0I^0) in nearly neutral media as illustrated in Figure 2.9. The original Mobil's method under hydrothermal conditions was categorized into the (S^+I^-) type, and this type of synthesis was revealed to be possible even below 100°C. The other two methods, ($S^+X^-I^+$) and (S^0I^0), are carried out at room temperature. In the (S^+I^-) synthesis in basic media, siliceous mesophases could be formed from inorganic silicate sources such as sodium silicate and colloidal silica as well as monomeric (molecular) Si sources, especially alkoxides, while in the room-temperature ($S^+X^-I^+$) and (S^0I^0) synthesis, molecular Si sources, alkoxides and chloride were exclusively used. The acidic synthesis at room temperature has the advantage of shorter synthesis time and lower surfactant concentrations as compared with the basic high-temperature synthesis.[44] In order to expand the acidic room-temperature synthesis, it would be desirable to utilize inorganic silicate sorces which are easier in handling and cheaper than molecular Si sources.

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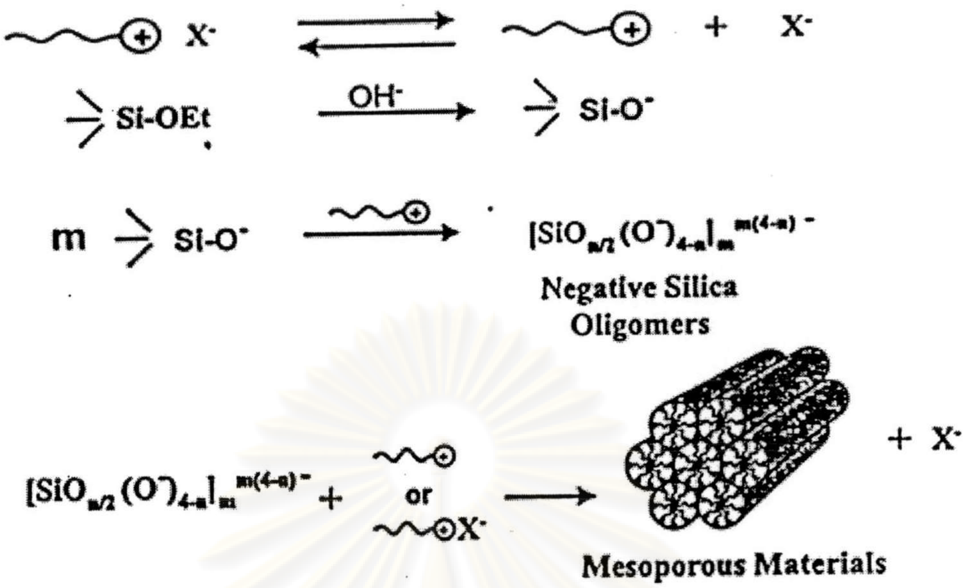
Basic Route



Acidic Route

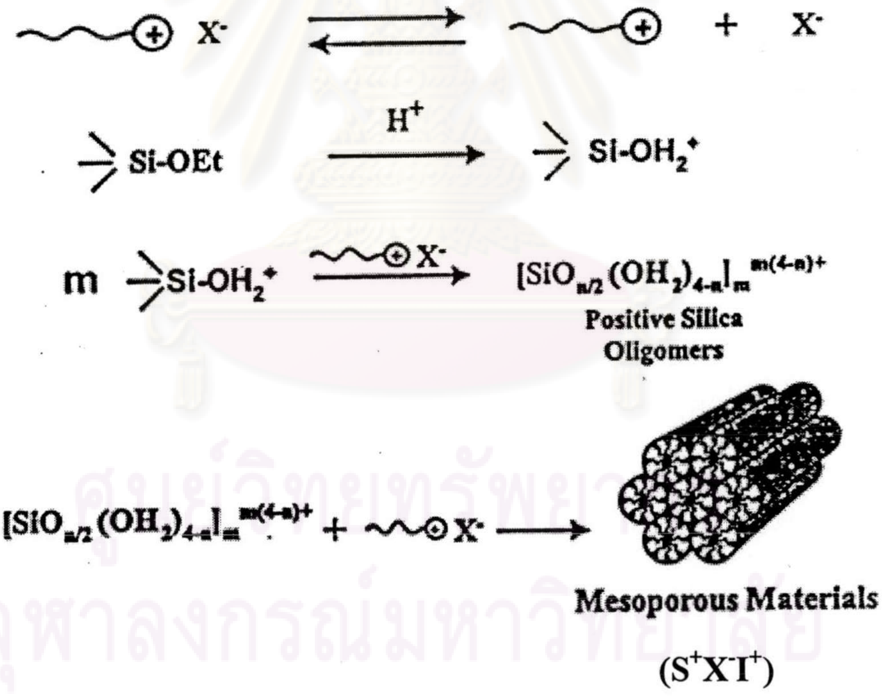


Figure 2.9 The comparison of the formation processes of the mesoporous materials in basic and acidic conditions.[45]

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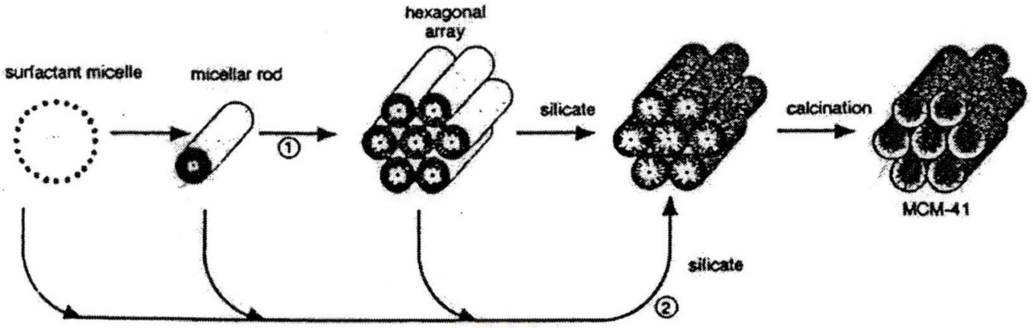
2.2.4 Mechanism of the Crystal Formation[46,47]

2.2.4.1 Liquid Crystal Templating Mechanism

The four main components in the M41S syntheses are structure-directing surfactants, a source of silica, a solvent and a catalyst (an acid or a base). In the pioneering work on the synthesis of M41S materials by the Mobil researchers alkyltrimethyl ammonium halides was used as the structure-directing surfactants and combinations of sodium silicate, tetraethoxy silicate (TEOS), fumed silica and Ludox as the silica source. Sodium hydroxide and tetraethyl ammonium hydroxide were used as basic additives to the aqueous synthesis solutions. In the cases of aluminosilicate materials, an aluminum source was added as well. The synthesis solutions were kept at temperatures ranging from 100 to 150°C for 24-144 h. Then the solid products were filtered, washed and dried. Finally, the materials were calcined at 540°C under a gas-flow of nitrogen and subsequently air, resulting in the mesoporous structures. It was found that the relative concentrations of the species present in the synthesis solutions were of great importance for the final pore structures. They also showed that the pore diameter of MCM-41 increased as the chain length of the surfactant increased. Furthermore, mesitylene was solubilized into the micelles. This made the micelles more voluminous, and materials with pore diameter as large as 120 Å were prepared, although the pore size is not irregular.

A "liquid crystal templating" (LCT) mechanism was proposed by the Mobil researchers, based on the similarity between liquid crystalline surfactant assemblies and M41S as shown in Scheme 2.1. The common traits were the mesostructure dependence on the hydrocarbon chain length of the surfactant tail group, the effect of variation of the surfactant concentrations, and the influence of organic swelling agents. With MCM-41, which has hexagonally packed cylindrical mesopores, as the representative M41S material, two mechanistic pathways were postulated (Scheme 2.1):



Scheme 2.1 Two possible pathways for the liquid crystal templating mechanism.[46]

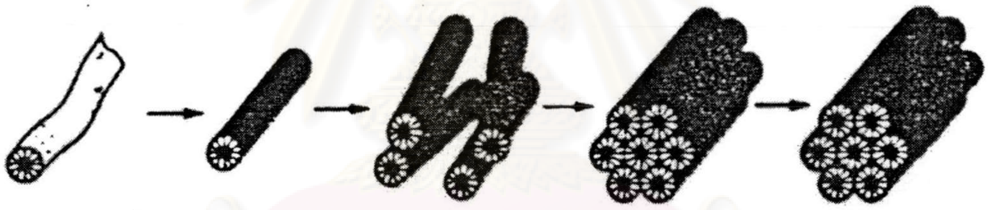
1. The silicate species occupied the space between a preexisting hexagonal lyotropic liquid crystal (LC) phase and deposited on the micellar rods of the LC phase.
2. The inorganics mediated, in some manner, the ordering of the surfactants into the hexagonal arrangement.

In either case, the inorganic components, which were negatively charged at the high pH values used, preferentially interacted with the positively charged ammonium head groups of the surfactants and condensed into a solid, continuous framework. The resulting organic-inorganic mesostructure could be alternatively viewed as a hexagonal array of surfactant micellar rods embedded in a silica matrix: removal of the surfactants produced the open, mesoporous MCM-41 framework. It is now known that pathway 1 did not take place[46] because the surfactant concentrations used were far below the critical micelle concentration (CMC) required for hexagonal LC formation. This mechanistic pathway was shown possible recently under different synthesis conditions.

The second mechanistic pathway of LCT was vaguely postulated as a cooperative self-assembly of the ammonium surfactant and the silicate precursor species below the CMC. It has been known that no preformed LC phase was necessary for MCM-41 formation. Several mechanistic models have been advanced and share the basic idea that the silicate species promoted LC phase formation below the CMC.

2.2.4.2 Silicate Rod Assembly

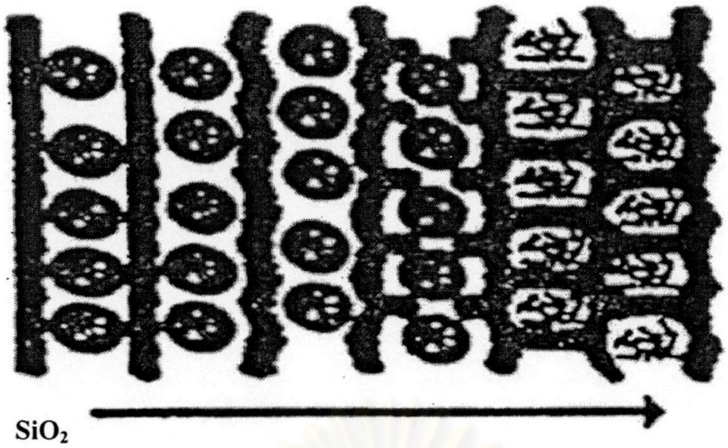
It was found that the hexagonal LC phase did not develop during MCM-41 synthesis, based on in situ ^{14}N-NMR spectroscopy.[46] It was then proposed that, under the synthesis conditions reported by Mobil, the formation of MCM-41 began with the deposition of two to three monolayer of the silicate precursor onto isolated surfactant micellar rods as illustrated in Scheme 2.2. The silicate-encapsulated rods were randomly ordered, eventually packing into a hexagonal mesostructure. Heating and aging then completed the condensation of the silicates into the as-synthesized MCM-41 mesostructure.



Scheme 2.2 Assembly of silicate-encapsulated rods.[46]

2.2.4.3 Silicate Layer Puckering

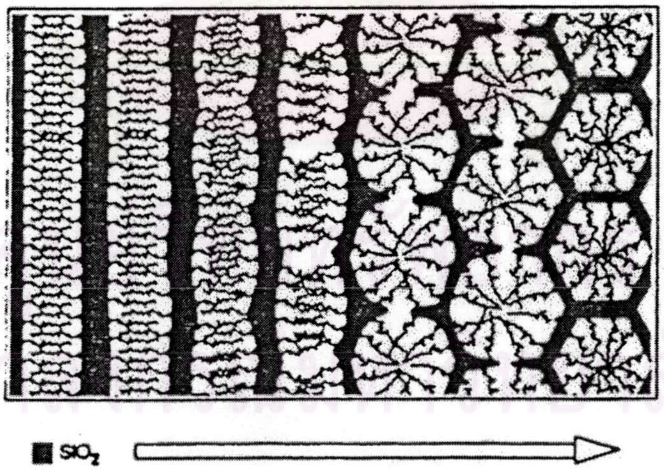
Instead of the formation of silicate-covered micellar rods, it was postulated that surfactant molecules assembled directly into the hexagonal LC phase upon addition of the silicate species, based on ^{14}N-NMR spectroscopy.[46] The silicates were organized into layers, with rows of the cylindrical rods intercalated between the layers as depicted in Scheme 2.3. Aging the mixture caused the layers to pucker and collapse around the rods, which then transformed into the surfactant-containing MCM-41 hexagonal-phase mesostructure.



Scheme 2.3 Puckering of silicate layers in the direction shown.[46]

2.2.4.4 Charge Density Matching

A charge density matching mechanistic model was proposed by Monnier *et al.*[48] It was suggested that MCM-41 could be derived from a lamellar phase. The initial phase of the synthesis mixture was layered as detected by X-ray diffractometry and was formed from the electrostatic attraction between the anionic silicates and the cationic surfactant head groups as shown in Scheme 2.4.

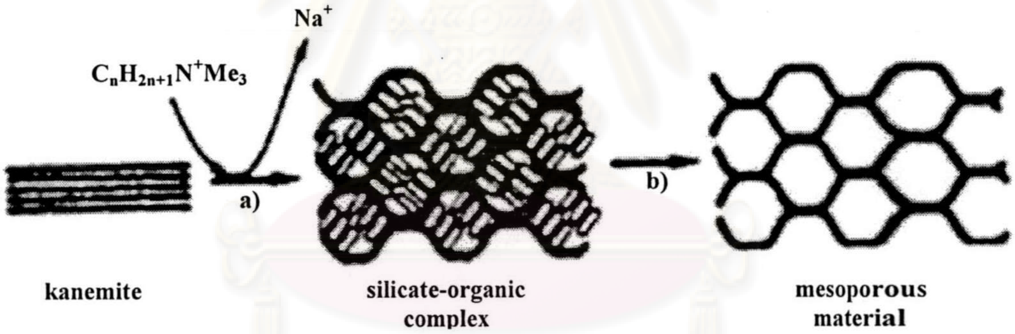


Scheme 2.4 Curvature induced by charge density matching mechanism. The arrow indicates the reaction coordinate.[46]

As the silicate species began to condense, the charge density was reduced. Accompanying this process, curvature was introduced into the layers to maintain the charge density balance with the surfactant head groups, which transformed the lamellar mesostructure into the hexagonal mesostructure.

2.2.4.5 Folding Sheets

The lamellar-to-hexagonal phase motif also appeared in materials called FSM prepared from the intercalation of the ammonium surfactant in kanemite, a type of hydrated sodium silicate composed of single-layered silica sheets. After the surfactants were ion-exchanged into the layered structure, the silicate sheets were thought to fold around the surfactants and condense into a hexagonal mesostructure as expressed in Scheme 2.5. The final product was claimed to be very similar to MCM-41, with no resemblance to the original kanemite structure. However, it was found that the layered structures were still retained in the kanemite-derived mesoporous materials.



Scheme 2.5 Folding of silicate sheets around intercalated surfactant molecules: a) Ion exchange. b) calcination.[46]

2.2.4.6 Silicatropic Liquid Crystals

Under synthesis conditions that prevented condensation of the silicate species, such as at low temperatures and high pH up to 14, a true cooperative self-assembly of the silicates and surfactants was found possible. ^{2}H-and ^{29}Si-NMR spectroscopy, and neutron scattering, that a micellar solution of CTAB transformed to a

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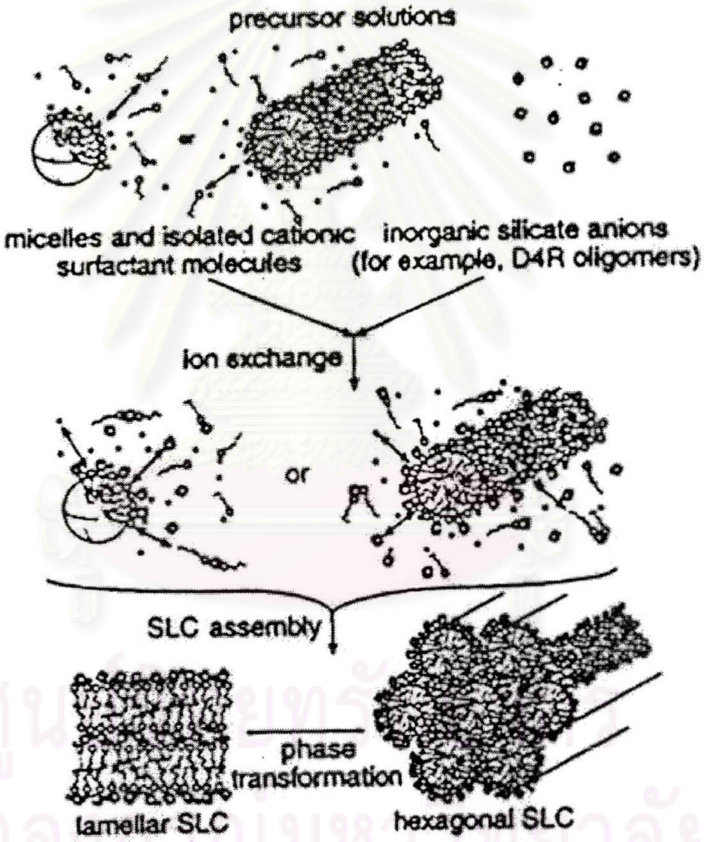
hexagonal phase in the presence of silicate anions were showed: this was consistent with the effect of electrolytes on micellar phase transitions.[46] The silicate anions ion-exchanged with the surfactant halide counterions, to form a silicatropic liquid crystal (SLC) phase that involved silicate-encrusted cylindrical micelles as shown in Scheme 2.6. The SLC phase exhibited behavior very similar to typical lyotropic systems, except that the surfactant concentrations were much lower and the silicate counterions were reactive. Heating the SLC phase caused the silicates to condense irreversibly into MCM-41



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Scheme 2.6 Formation of a silicatropic liquid crystal phase.[46]

It was also demonstrated that in addition to the charge balance requirement (i.e., electrostatic interaction) there was preferential bonding of the ammonium head group to multi-charged D4R (double four-ring, $[Si_8O_{20}]^{8-}$) silicate anions under the high pH conditions.[46] The interaction was so strong that an alkyltrimethylammonium surfactant solution forced a silicate solution that did not contain D4R oligomers to re-equilibrate and form D4R species. It was suggested that this behavior came from the closely matched projected areas of a D4R anion and an ammonium head group and the correct distribution of charges on the projected surfaces.

It was reported that mesostructured silicates with D4R silicates were prepare[46]. Combination of the D4R precursors with cetyltrimethylammonium chloride (CTAC) surfactants produced mesostructured precipitates by acidic vapor treatment led to the observation of cubic, lamellar, and hexagonal phases as intermediate transformation phases.

2.2.4.7 Silicate Rod Clusters

The previous theories have regarded the formation of MCM-41 as a series of events that occur homogeneously throughout an aqueous solution. Recent work[46] has showed that MCM-41 might be formed heterogeneously. Evidence was found for MCM-41 intermediate structures in the form of clusters of rodlike micelles "wrapped" by a coating of silicate through low-temperature transmission electron microscopy (TEM) and small-angle X-ray scattering. The clusters of elongated micelles were found before precipitation occurred. As the reaction progressed, the silicate species diffused to and deposited onto the individual surfaces of the micelles within the cluster: the clusters of elongated micelles eventually became clusters of silicate-covered micelles. Thus, the clusters of micelles served as nucleation sites for MCM-41 formation.

2.2.4.8 Generalized Liquid Crystal Templating Mechanism: Electrostatic Interaction

A generalized mechanism of formation based on the specific type of electrostatic interaction between a given inorganic precursor I and surfactant head group S was proposed by Huo and co-workers. Based on the nomenclature, pathway 2 of the original LCT mechanism as illustrated in Scheme 2.1, which involved anionic silicate species and cationic quaternary ammonium surfactant, could be categorized as the S^+I^- pathway. By extension, the other charge-interaction pathways are S^-I^+, $S^+X^-I^+$ (X^- is a counteranion), and $S^-M^+I^-$ (M^+ is a metal cation). This classification system is useful, especially when other types of inorganic-organic interactions are considered (Figure 2.10). The success of the cooperative templating model, referred to here as the generalized LCT mechanism (Scheme 2.7), was illustrated by the diverse compositions of organic-inorganic mesostructures found possible. As for silicate mesostructures, it was found that they were possible to be formed through the $S^+X^-I^+$ pathway. By operating below the isoelectric point of silica (pH ~ 2) under acidic conditions, the silicate species were cationic (I^-). The same ammonium surfactant S^- could be used as a templating agent but the halide counteranion X^- became involved through this pathway as it served to buffer the repulsion between the I^- and S^+ by means of weak hydrogen-bonding forces. The resulting materials are known as "acid-prepared mesostructures" or APM materials.

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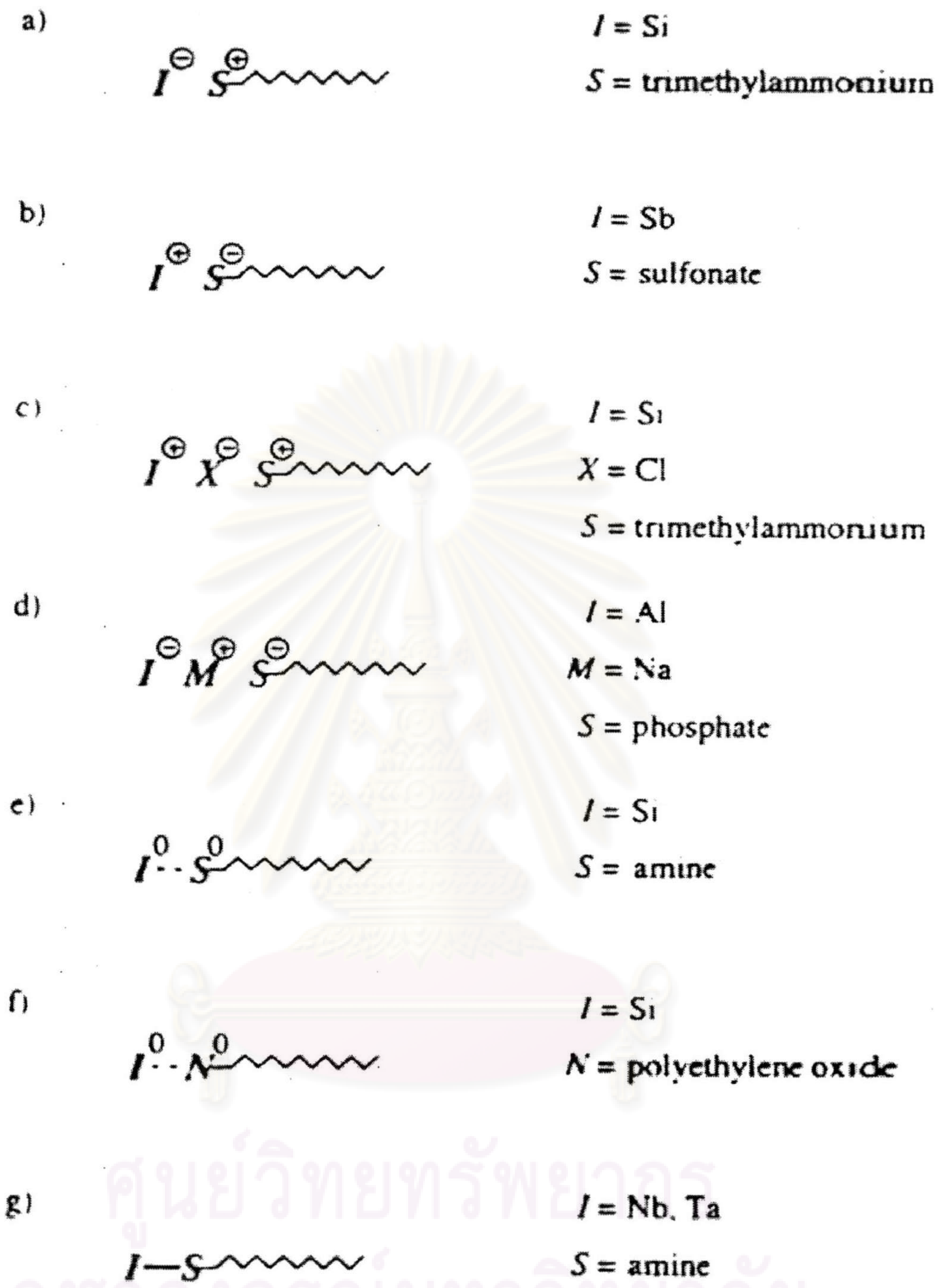

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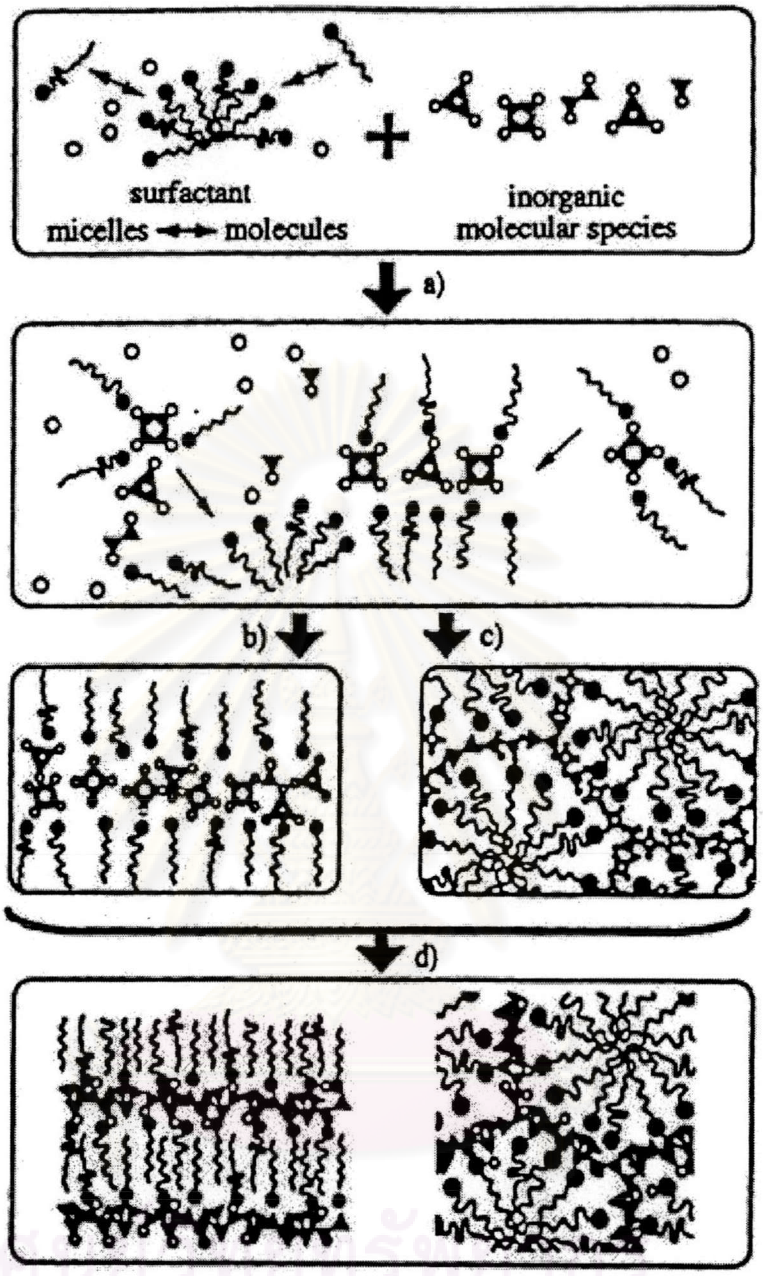
Figure 2.10 Schematic representation of the various types of inorganic-surfactant head group interactions : electrostatic: a)S^+I^-, b)S^-I^+, c)$S^+X^-I^+$, and d)$S^-M^+I^-$; hydrogen bonding : e) $S^{\circ}I^{\circ}$ and f) $N^{\circ}I^{\circ}$; and covalent bonding: g)S^-I.[46]



Scheme 2.7 Cooperative templating of the generalized LCT mechanism: a) cooperative nucleation; b), c) liquid crystal formation with molecular inorganic compounds; d) inorganic polymerization and condensation.[46]

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2.2.5 Parameters on the Crystal Formation

2.2.5.1 Effect of Template Concentration

The micellar solution can be considered as essentially made up of monomeric surfactant and of a single micellar species. Increasing the concentration of surfactant leads to sphere-to-rod shape transition of the micelle.[49] Moreover, temperature and ionic strength also affect the shape of micelles.[49] Generally, the spherical micellar shape is associated with low micellar size polydispersity, i.e. similar particle size. For more concentrated micellar solutions, the micelle fragmentation-coagulation equilibria are responsible for the process of continuous micelle formation and breakdown. CTAB forms spherical micelles at concentrations between the CMC (critical micelle concentration) about 0.1 wt% relative to water at 25°C and 0.5 M, while rod-shaped micelles are obtained at higher concentrations (>0.5 M).

During the synthesis of MCM-41, there are three types of nearest-neighbor assemblies: organic-organic, inorganic-organic and inorganic-inorganic species. Interactions among these assemblies contribute to the micellization, the formation of micelle-silicate composites and silicate condensation. The formation rate of micelle-silicate composites depends on the concentrations of surfactants and silicate, temperature and pH value. At constant temperature, pH and molar ratio of $[H_2O]/[Si]$, lowering the surfactant concentration is expected to slow down the formation rate of surfactant micelles and micelle-silicate composites (or nuclei), and to decrease the amounts of them and the subsequent silicate condensation between nuclei gives rise to the lower aggregation of MCM-41 crystals, such as Si-F with monodispersed particles of 0.5 μm. At a constant molar ratio of [CTAB]/[Si], increasing the water content will allow more monodispersed particles to be formed (e.g., Si-2 is more dispersed than Si-MCM-41). Therefore, the water content or surfactant concentration plays an important role in the degree of aggregation of the final products.

2.2.5.2 Effect of pH adjustment

The improvement of the structural and catalytic characteristics of MCM-41 type materials is of great importance in view of their applicability as catalysts and catalyst supports. A special post-synthesis treatment such as the extraction of the structure directing agent using acidic media prior to calcination has been shown to improve the thermal stability of Al-MCM-41. The variation of the synthesis parameters represents another possibility, since it was reported that the stability and characteristics of Al-MCM-41 are strongly affected by the synthesis conditions. The long-range order and stability of pure silica MCM-41 was improved through the intermediate pH adjustment of the synthesis gel.[50-51] Their results also suggested that this method could be extended to the synthesis of aluminum-containging MCM-41.[50] Subsequent studies of the pH-adjustment synthesis of pure silica MCM-41 suggested a significant influence of the acid used for pH adjustment on the sturcure of the product and that the optimum pH for silica MCM-41 was 10. The earlier ivestigations of Al-MCM-41 synthesis have shown that the pH adjustment improves the textural characteristics of these materials.

2.2.5.3 Effect of Temperature

Small crystal catalyst was synthesized by a two-stage varying-temperature technique[52], in which the reaction mixture was first kept at a relatively low temperature to ensure the largest nuclei population, then the temperature was swiftly raised to a higher value to achieve the fast crystal growth rate. It was found that the crystal size decreased with increasing first-stage duration and reached the minimum after the completion of nucleation. The second-stage temperature had no significant influence on the crystal size but mainly altered the crystal growth rate provided that the first-stage duration was long enough..

2.3 Characterization of Al-MCM-41

2.3.1 X-ray diffraction (XRD)

When one suspects that a mesoporous molecular sieve has been synthesized a well-established methodology must be followed to demonstrate that this is indeed the case. Many different experimental techniques have been utilized to characterize mesoporous materials. Often several techniques are used in combination, in order to provide unambiguous structural information. The procedure involves, first, the use of XRD.[53] It provides direct information of the pore architecture of the materials. For mesoporous materials, the diffraction patterns only have reflection peaks in the low-angle range, meaning 2θ less than 10. No reflections are seen at higher angles. It has thereby been concluded that the pore walls mainly are amorphous. The ordering lies in the pore structure, and the low-angle diffraction peaks can be indexed according to different lattices.

Different features of a powder diffraction pattern can be exploited in the characterization of a material (see Table 2.1). Of course, powder diffraction data is most commonly used as a "fingerprint" in the identification of a material, but the other information that can be gleaned from a diffraction pattern should not be forgotten. If possible, the diffraction experiment should be adapted to optimize that feature which provides the information desired.

Although there are a number of different powder diffractometer geometries on the market each one with its positive and negative attributes, all have an X-ray source, a specimen holder and a detector, and almost all are capable of recording a respectable powder diffraction pattern. The difficulty arises when one wants to compare data from different instruments or even from the same instrument with different operators. The basic considerations and a few common sources of error will be discussed.

Table 2.1 Information contained in a powder diffraction pattern[53]

Feature	Information
Peak positions (2θ values)	Unit cell dimensions
Non-indexable lines	Presence of a crystalline impurity
Systematicallly absent reflections	Symmetry
Background	Presence (or absence) of amorphous material
Width of peaks	Crystallite (domain) size Stress/strain Stacking faults
Peak intensities	Crystal structure

The XRD pattern of MCM-41 shows typically three to five reflections of two theta. (2θ) between 2° and 5°. The reflections are due to the ordered hexagonal array of parallel silica tubes and can be indexed assuming a hexagonal unit cell as (100), (110), (200), (210) and (300). Since the materials are not crystalline at the atomic level, no reflections at higher angles are observed. The wall thickness can be calculated by determining the difference between the lattice parameter ($a = 2d_{100}/\sqrt{3}$). From Bragg's law, when an X-ray beam strikes a crystal surface at some angle θ, a portion is scattered by the layer of atoms at the surface. The unscattered portion of the beam penetrates to the second layer of atoms (Figure 2.11), where *d* is the interplanar distance of the crystal. Thus, the conditions for constructive interference of the beam at angle θ are called the Bragg equation as shown in Equation 2.1.

$$n\lambda = 2d\sin\theta \qquad (1)$$

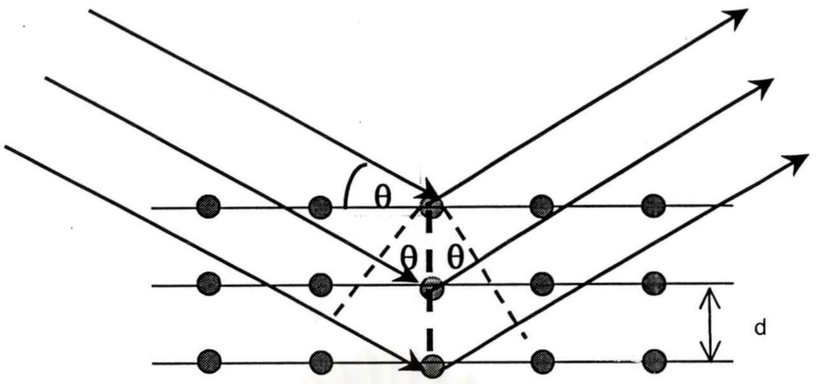

Figure 2.11 Diffraction of X-rays by a crystal.

Hexagonal structure have characteristics of d-spacing ratio as follows :

$$d_{100}/d_{110} = d_{200}/d_{220} = 1.732$$

$$d_{100}/d_{200} = d_{200}/d_{400} = 2.000$$

2.3.2 Nitrogen Adsorption

Adsorption techniques[38] are used to determine the porosity and specific surface area of materials. Different models for calculating the pore size distribution have been developed. The most common adsorbate is probably N_2 (at 77 K). According to the IUPAC definition, mesoporous materials exhibit a Type IV adsorption-desorption isotherm. At low relative pressures (P/P_0) the adsorption only occurs as a thin layer on the wall (monolayer coverage). Depending on the pore size, a sharp increase is seen at relative pressures from 0.25 to 0.5. This corresponds to capillary condensation of N_2 in the mesopores. The sharpness of the inflection reflects the uniformity of the pore sizes and the height indicates the pore volume. A hysteresis loop is often observed for N_2 adsorption-desorption isotherms when the pore diameter is larger than approximately 40 Å.

2.3.3 Solid State ^{27}Al-MAS-NMR

Another important characterization technique for mesoporous materials is solid state NMR. ^{27}Al-MAS-NMR spectroscopy[38] 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.

2.3.4 NH_3-TPD

Temperature-programmed desorption (TPD) of ammonia[54] is probably the most widely used method for characterizing acidity in zeolites and mesoporous materials. There are many variations on the method, but it typically involves saturation of the surface with ammonia under some set of adsorption conditions, followed by linear ramping of the temperature of the sample in a flowing inert gas stream. Ammonia concentration in the effluent gas may be followed by absorption/titration or mass spectroscopy. Alternatively, the experiment may be carried out in a microbalance and changes in sample mass may be followed continuously. The amount of ammonia desorbing above some characteristic temperature is taken as the acid-site concentration, and the peak desorption temperatures have been used to calculate heats of adsorption. The acidity of Al-MCM-41 samples has been measured[47] by adsorption-desorption of ammonia. The amount of Brønsted acidity increases with the aluminum content of the sample. When the acidity of Al-MCM-41 was compared with that of zeolite and an amorphous silica-alumina, it was found that the acid strength of the MCM-41 is weaker than in the zeolite and appears more similar to that of an amorphous silica-alumina.

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2.4 Cracking Reaction

2.4.1 Thermal Cracking

Simple alkenes are considered to be petroleum products, but they are not obtained directly from oil wells. Rather, they are produced industrially from alkanes in a process called cracking.[55] Cracking breaks larger alkanes into a mixture of smaller hydrocarbons, some of which are alkenes. This process yields predominantly ethylene (C_2H_4) together with other small molecules. The chemistry of the cracking process is of interest, not only because of its commercial significance, but also because it illustrates some additional chemistry of free radicals.

Ethylene, the alkene of greatest commercial importance, is produced by a process called thermal cracking. In this process, a mixture of alkanes from the distillation of petroleum is mixed with steam and heated in a furnace at 750-900°C for a short time, and is then quenched to prevent secondary reactions. The products of cracking are then separated. Steam cracking is of great importance in the production of hydrocarbons as chemicals, including ethylene, propylene, butadiene, isoprene, and cyclopentadiene.

In the United States, the hydrocarbon most often used to produce ethylene is ethane, a component of natural gas. In the cracking of ethane, ethylene and hydrogen are formed at very high temperature. In cracking, the temperatures used are so high that initiating radicals are formed by spontaneous bond rupture. Only two types of bonds in ethane can be broken: the C-C bond and the C-H bonds. The bond dissociation energies of the C-C bond requires somewhat less energy. Hence, fragmentation of a few ethane molecules into two methyl radicals takes place.

First initiation step:

$$\mathrm{CH_3{-}CH_3} \xrightarrow{\text{heat}} 2\,\bullet\mathrm{CH_3} \tag{2}$$

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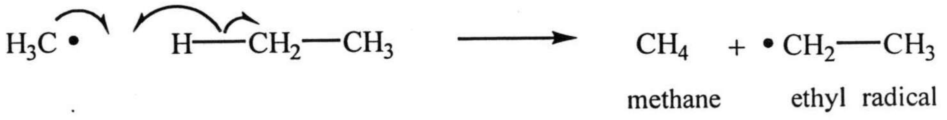
In a second initiation step, a methyl radical abstracts a hydrogen atom from another ethane molecule:

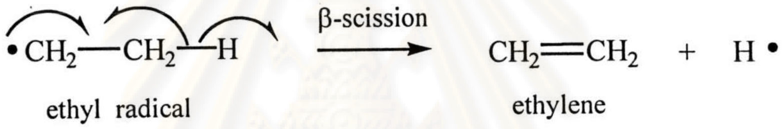
Second initiation step:



(3)

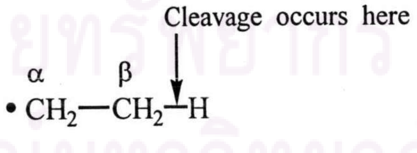
This step accounts for small amounts of methane formed in the cracking process. The ethyl radical is the chain-propagating radical. It first undergoes an interesting reaction in which it "unzips" to yield ethylene and a hydrogen atom in a process called β-scission:

First propagation step:



(4)

β-scission is another typical reaction of free radicals. The word "scission" means "cleavage" (it is derived from the same root as "scissors"). The Greek letter beta (β) refers to the fact that the cleavage occurs one carbon away from the radical site. (The Greek letters α, alpha; β, beta; γ, gramma; and so on are sometimes used to indicate the relative positions of groups on carbon chains.)



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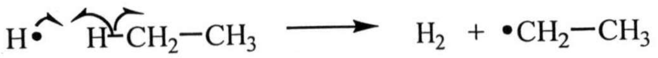
Although β-scission might look like a new reaction, actually it is simply the reverse of an addition; in this case it is the reverse of the addition of a hydrogen atom to ethylene.

The hydrogen atom produced in the first propagation step then abstracts a hydrogen atom from another molecule of ethane to give a new ethyl radical:

Second propagation step:



$$H\bullet \;\; H-CH_2-CH_3 \longrightarrow H_2 + \bullet CH_2-CH_3 \qquad (5)$$

The ethyl radical then enters into the first propagation reaction, Equation (4), thus continuing the free-radical chain. The hydrogen that is a by-product of Equation (5) is collected and used to produce ammonia by hydrogenation of nitrogen. The ammonia finds important use in agriculture as a fertilizer.

It can be seen that there are four types of reactions that free radicals can undergo. Three of these are reactions that produce other radicals:

1. Addition to a double bond
2. Atom abstraction
3. β-Scission.

The other reaction destroys free radicals:

4. Recombination of two free radicals to form a covalent bond.

These reactions constitute a "toolbox" of fundamental free-radical process. Most free-radical processes are examples of these reactions or combinations of them. The low-molecular-weight alkanes obtained from these cracking processes can be separated and purified, and are the most important raw materials for the large-scale synthesis of aliphatic compunds.[56]

2.4.2 Catalytic Cracking

Catalytic cracking[57] is probably the most important catalytic process economically. One of the most significant technical developments of the 20th century, it enables the efficient production of a larger fraction of premium fuels from each barrel of precious petroleum.

Thermal cracking of heavy feedstocks was first recognized as a refinery upgrading process around 1913. The more selective catalytic cracking process was introduced in 1928 after testing upgraded fuels in a Bugatti racing car.[57] The first commercial fixed-bed plant went into operation in 1936. The transition from the

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unwieldy, cyclical fixed-bed operation to the more efficient, continuous fluid-bed operation with continuous regeneration occurred in 1942. The introduction of zeolite cracking catalysts in 1962 enabled dramatic increases in catalytic activity and gasoline selectivity/yield. A significant recent development (1986) is the application of ZSM-5 as an octane enhancer.[57]

Most cracking, however, is directed toward the production of fuels, not chemicals, and for this catalytic cracking is the major process. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves carbocations, and yields alkanes and alkenes with the highly branched structures desirable in gasoline.

Finally, by the process of catalytic reforming enormous quantities of the aliphatic hydrocarbons of petroleum are converted into aromatic hydrocarbons which are used not only as superior fuels but as the starting materials in the synthesis of most aromatic compounds.

Catalytic cracking of any hydrocarbon very rarely results in the formation of a single product. Usually, a variety of products are formed in parallel. Their molecular weights can be the same as that of the substrate molecule, or either lower or higher. In addition, the carbon skeletons of the products, even the products with the same carbon atom number, can be either similar or different from that of the substrate. This variability makes classification of reaction products quite an involved issue. In this review, the following empirical classification[58] is adopted:

1. All products with the same carbon atom number as that of a substrate (both with the same or with different hydrogen atom numbers) are called primary products. The primary products may have the same carbon skeleton as that of the substrate (alkenes from alkanes) or isomerized skeletons.

2. All products which are formed in a single reaction, fission of a single C-C bond, or, in the case of alkenes, formation of a single C-C bond in dimerization reactions are called secondary products.

3. All products formed from secondary products rather than from substrates themselves are called tertiary products. Clearly, types of tertiary product can be very diverse.

Reaction products formed from any alkane or alkene under commercial conditions (high temperatures, contact times of several seconds) are nearly always mostly tertiary. This is the main reason for difficulties in determining reaction mechanisms of cracking. This review predominantly discusses research dealing with primary and secondary products.

2.5 Catalytic Cracking Mechanisms[58-61]

There are no major disputed issues about the mechanism of alkene cracking over solid acidic catalysts; it is generally agreed that the active centers in these reactions are protic acidic centers on the catalyst surface and that the reactive species are carbenium ions.

2.5.1 Formation of Carbenium Ions

The formation of carbenium ions from olefins can easily proceed by addition of the proton from a Brønsted acid sites of the catalyst to the carbon-carbon double bond. All hydrocarbon-cracking catalysts contain protic acidic center. Thomas first proposed their structure in one of the earliest articles dealing with the mechanism of catalytic cracking as [$HAlSiO_4$] with a positively charged hydrogen atom in the vicinity of a tetra-coordinated, negatively charged Al atom. Currently, a similar picture of such centers (traditionally called Brønsted centers) with the hydrogen atom attached to the oxygen atom bridging between Al and Si atoms is presented as the most plausible.

Generally, reactions of Brønsted acids with alkenes are well known in organic chemistry. The first stage is, most probably, the formation of a complex involving the double bond of an alkene. Such complexes, in the case of the propylene-alumina pair at room temperature, were observed by IR. The next stage is the formation of the carbenium ion in an equilibrium reaction:

$$H^+ \quad + \quad R^1R^2C{=}CR^3R^4 \rightleftharpoons R^1R^2C^+\text{-}CHR^3R^4 \qquad (6)$$

The direction of this reaction mostly obeys the stability rule of carbenium ions: primary << secondary << tertiary. For example, reaction of a 1-alkene with a linear chain produces the secondary carbenium ion, $CH_3\text{-}C^+H\text{-}R$. When carbenium ions are formed in superacids, they rapidly decompose/isomerize to tertiary carbocations such as $(CH_3)_3C^+$ and $(CH_3)_2(C_2H_5)C^+$. These carbenium ions remain stable in solution up to 130-150°C , whereas tertiary carbocations of lager sizes decompose with the formation of $(CH_3)_3C^+$ starting at 80°C.

As typical for all highly reactive organic intermediates in catalytic reactions, direct observations of carbenium ions derived from alkenes within solid acidic catalysts are difficult (although several attempts were made) and the formation of the ions is mostly inferred from their subsequent transformations to stable reaction products. Theoretical calculations suggest that the surface of acidic catalysts at high temperatures exerts a strong solvating effect and transforms carbenium ions R^+ into alkoxyaluminum moieties > Al-O-R with a low net positive charge on the carbon atom in the R group. C-O bonds in such alkoxy groups, when vibrationally excited, have an increased charge separation (but not full dissociation) and the R groups act as adsorbed carbenium ions.

2.5.2 Primary Products from Carbenium Ions

It is well known from organic chemistry that carbenium ions are prone to rearrangement reactions. The following reactions are known.

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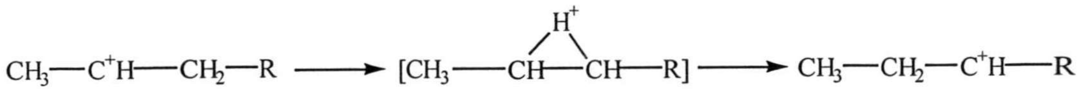
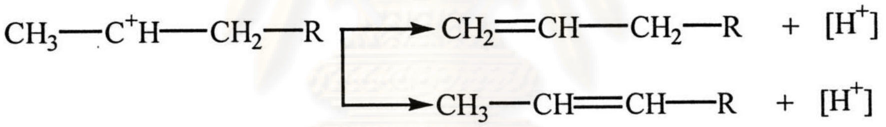
2.5.2.1 H-atom Shift



$$CH_3\text{—}C^+H\text{—}CH_2\text{—}R \longrightarrow [CH_3\text{—}\overset{H^+}{CH\text{—}CH}\text{—}R] \longrightarrow CH_3\text{—}CH_2\text{—}C^+H\text{—}R \qquad (7)$$

Under normal circumstances, reaction (7) is unobservable. However, if the catalyst center contains a D atom instead of an H atom, the D atom transferred to the carbenium ion rapidly migrates to any position in the chain. If the C=C bond in the alkene is two- or three-substituted, its steric isomerization takes place readily. For example, 1,2-phenyl-disubstituted ethylene with the isomerization of the *cis* to the *trans*-alkene. Reaction (7) is very fast and its exact mechanism remains uncertain, although, most probably, it involves the shown transition state (rather than an appreciably stable intermediate) in which two carbon atoms share one hydrogen atom and the vacant *p* orbital of C^+ and the sp^3 orbital of the migrating C-H bond are coplanar. Effectively, reaction (7) results in a very rapid scrambling of nearly all H atoms in carbenium ions.

Decomposition of the secondary carbenium ion formed in reaction (7) either regenerates the original alkene in reaction (8) or produces an alkene with an isomerized C=C bond in reaction (9):



$$CH_3—C^+H—CH_2—R \longrightarrow CH_2{=}CH—CH_2—R \;+\; [H^+] \qquad (8)$$

$$CH_3—C^+H—CH_2—R \longrightarrow CH_3—CH{=}CH—R \;+\; [H^+] \qquad (9)$$

2.5.2.2 Double-Bond Shift

Considering of reactions (6) to (9), the double-bond shift, is the most ubiquitous and the most easily observable process in catalytic reactions of alkenes over a variety of acidic catalysts (silica, alumina, aluminosilicates, zeolites) even under very mild conditions. For example[58], even at 100°C, contact of 1-hexene with zeolite Y for 0.02 s resulted in the isomerization of 1-hexene to the equilibrium mixture of 1-, 2-, and 3-hexenes. In the case of highly active catalysts, the double-bond shift reaction was investigated separately from other processes only if the reactions were carried out with aged catalysts at 150-200°C. All acidic solids, regardless of their cracking ability, isomerize alkenes. For example, nearly equilibrium mixtures were

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produced at 350°C from any linear alkene over dealuminated laponite, a very poor cracking catalyst.

In the case of linear alkenes, the distribution of double-bond shift products is usually governed by thermodynamic stabilities of respective compounds. They can be approximated by three empirical rules according to the literature[58]:

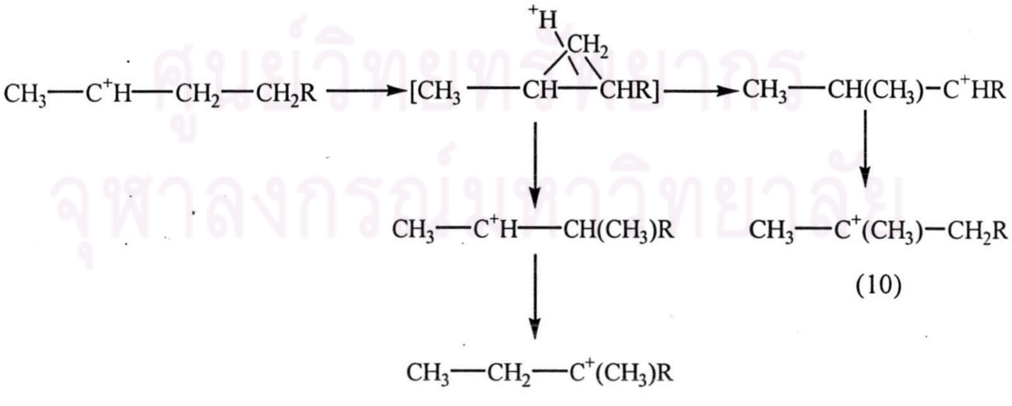
1. Populations of alkenes with internal double bonds (*trans* and *cis*) were determined by simple statistics: They were approximately reciprocal to the number of possible positions for the double bond in the chain.

2. *trans*-isomers constituted 68% of the sum of any alkene with the internal C=C bond. This ratio, however, depended on the type of the catalyst. For example, the *cis:trans* ratio in isomerization of 1- to 2-hexene at 200°C was close to the thermodynamic equilibrium ratio in the case of amorphous aluminosilicate, mordenite, and ZSM-5 zeolites, but it was significantly higher in the case of the H-Y zeolite.

3. 1-Alkene was formed in an 0.14:1 ratio with respect to any alkene with an internal C=C bond.

2.5.2.3 Alkyl-group Shifts via the Cyclopropane Transition State

The first of these reactions is shown for a substrate molecule with a linear skeleton, and it is followed by the H-atom shift:



(10)

(11)

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Such reactions are well known in organic chemistry; reactions (10) and (11) were used for many years to explain branching in hydrocarbons accompanying their cracking. They are often called the type-B skeleton rearrangement reactions. Catalytic transformations of alkenes produce very low yields of substituted cyclopropanes; therefore, the protonated cyclopropane structure in reaction (10) should be viewed as a transition state on the reaction coordinate from a linear to a branched carbenium ion rather than a true intermediate. Because reactions (10) and (11) result in thermodynamically favorable tertiary carbenium ions, they are usually invoked to explain the chain branching which accompanies alkene reactions over solid acidic catalysts. However, if a cracking catalyst contains only narrow micropores (ZSM-5), it favors the formation of linear structures at the expense of highly branched chains. As a result, stable carbenium ions produced in reactions (10) and (11) can apparently rearrange back to a more sterically favored linear carbenium ion. In such a case, reactions (10) and (11) may not result in any net chemical changes. Decomposition of stable carbenium ions such as that formed in reaction (10) should result in the formation of branched alkenes:

$$CH_3{-}C^+(CH_3){-}CH_2{-}R \longrightarrow CH_3{-}C(CH_3){=}CH{-}R + CH_2{=}C(CH_3){-}CH_2{-}R + H^+ \quad (12)$$

The first of the alkenes is more thermodynamically stable and is formed with a higher yield.

A reaction similar to reaction (10) but involving a carbenium ion derived from a branched alkene results in the methyl group shift along a hydrocarbon chain:

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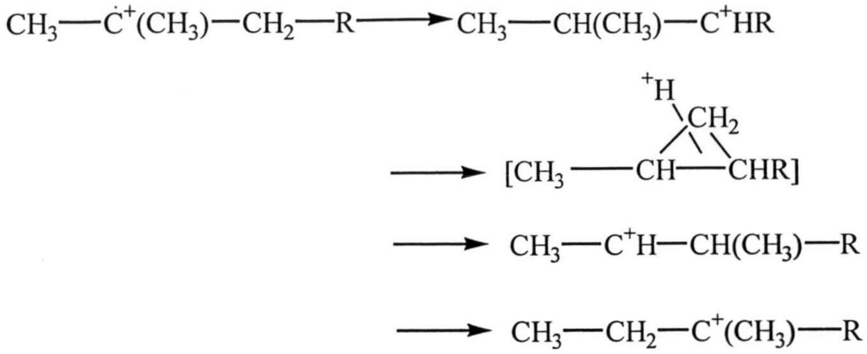

$$CH_3—\dot{C}^+(CH_3)—CH_2—R \longrightarrow CH_3—CH(CH_3)—C^+HR \longrightarrow [CH_3—\overset{{}^+H\ CH_2}{CH—CHR}] \longrightarrow CH_3—C^+H—CH(CH_3)—R \longrightarrow CH_3—CH_2—C^+(CH_3)—R \quad (13)$$

This reaction is called the type-A skeleton rearrangement; it is the principal reaction responsible for the isomerization of branched alkenes without a change in the number of branches. Reactions similar to reaction (13) also explain the transformation of geminally substituted alkenes into their vicinally substituted analogs:

$$(CH_3)_3C—CH{=}CH_2 \longrightarrow (CH_3)_3C—C^+H—CH_3 \longrightarrow (CH_3)_2CH—C^+(CH_3)—CH_3 \longrightarrow (CH_3)_2C{=}C(CH_3)_2 \quad (14)$$

2.5.2.4 Formation of Saturated Products from Alkenes

Reactions of alkenes over acidic catalysts are often accompanied by the formation of alkanes with the same skeleton:

$$CH_2{=}CH—CH_2—CH_2—R \longrightarrow CH_3—CH_2—CH_2—CH_2—R \quad (15)$$

$$CH_2{=}C(CH_3)—CH_2—R \longrightarrow CH_3—CH(CH_3)—CH_2—R \quad (16)$$

Such alkanes are produced, in parallel with isomerized alkenes, relatively easily. The source of hydrogen in reactions (15) and (16) is not yet known in detail. Analysis of model reactions of diaryl-substituted ethylenes over zeolite Ca-Y showed that the first hydrogen atom [reaction (6)] came from OH groups in the catalyst, whereas the second hydrogen atom, H^-, was abstracted from a suitable hydrocarbon substrate (an aromatic solvent, for example). At increased temperatures, extensive hydrogen redistribution reactions took place in which the formation of

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alkanes was balanced by the parallel generation of a variety of hydrogen deficient compounds, including aromatic compounds.

2.5.3 Secondary Cracked Products from Alkenes

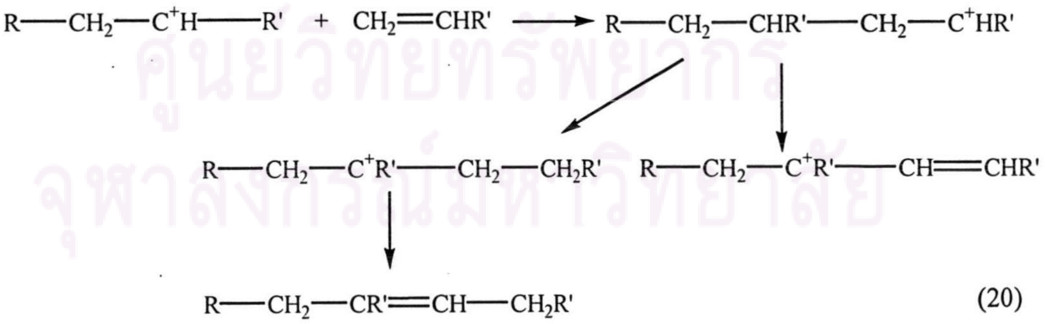
2.5.3.1 Alkene Oligomerization

All alkenes with vinyl and vinylidene double bonds easily oligomerize in the presence of Brønsted acids. This reaction is widely practiced on a commercial scale: synthesis of polyisobutene, synthesis of isobutene dimers (synthetic gasoline), synthesis of basestocks for synthetic lubricants, and so on. Polymerization of alkenes with vinylidene double bonds represents the simplest example. It proceeds through stable tertiary carbenium ions and usually results in the formation of regularly branched polymer chains:

$$R^+ + CH_2{=}CR'R'' \longrightarrow R{-}CH_2{-}C^+R'R''{-}(+CH_2{=}CR'R'') \longrightarrow R{-}CH_2{-}CR'R''{-}CH_2{-}C^+R'R'') \quad (17)$$

In the case of alkenes with vinyl double bonds, the oligomerization reactions involve formation of secondary carbenium ions. Due to the tendency of such ions to isomerize, the reaction usually produces irregularly branched polymer molecules:

$$R^+ + CH_2{=}CHR' \longrightarrow R{-}CH_2{-}C^+H{-}R' \quad (18)$$



$$R{-}CH_2{-}C^+H{-}R' + CH_2{=}CHR' \longrightarrow R{-}CH_2{-}CHR'{-}CH_2{-}C^+HR'$$

$$R{-}CH_2{-}C^+R'{-}CH_2{-}CH_2R' \qquad R{-}CH_2{-}C^+R'{-}CH{=}CHR' \quad (19)$$

$$R{-}CH_2{-}CR'{=}CH{-}CH_2R' \quad (20)$$

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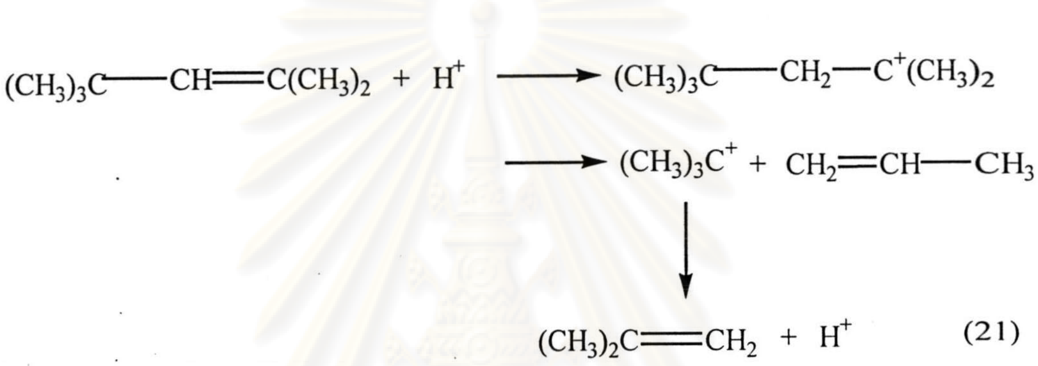
2.5.3.2 C-C Bond Scission Reactions

The C-C bond scission reactions in alkenes, which are the principal reactions of all cracking processes, also proceed easily. However, the competition between alkene oligomerization and cracking makes elucidation of alkene cracking patterns unusually difficult. The reaction proceeds via the well-known β-C-C bond scission mechanism: The C-C bond in the β-position to the charge dissociates and the charge migrates to one of its carbon atoms with a parallel formation of a double bond:



$$\begin{aligned}(CH_3)_3C{-}CH{=}C(CH_3)_2 + H^+ &\longrightarrow (CH_3)_3C{-}CH_2{-}C^+(CH_3)_2\\ &\longrightarrow (CH_3)_3C^+ + CH_2{=}CH{-}CH_3\\ (CH_3)_3C^+ &\longrightarrow (CH_3)_2C{=}CH_2 + H^+\end{aligned} \tag{21}$$

Similar results were produced in cracking of 2,4,4-trimethyl-1-pentene over a variety of metal-Y and metal-X zeolites; the main product also was isobutene. Reaction (21) is, in effect, a depolymerization reaction; it represents the detailed reversal of the isobutene dimerization reaction. It is thermodynamically favorable because it proceeds exclusively through tertiary carbenium ions. Formation of most minor light products (propylene, 1-methyl-2-butene, 2-butenes) can also be explained by this mechanism if the β-C-C scission is preceded by isomerization of the 2,4,2-trimethylpentenium ion formed in reaction(16). The isomerization reaction is evident from the formation of substrate isomerization products which proceeds according to the alkene isomerization.

2.5.4 Tertiary Products from Alkenes

In general, tertiary products can be defined as hydrocarbons which formation required more than one step of the C-C bond fission or the C-C bond formation:

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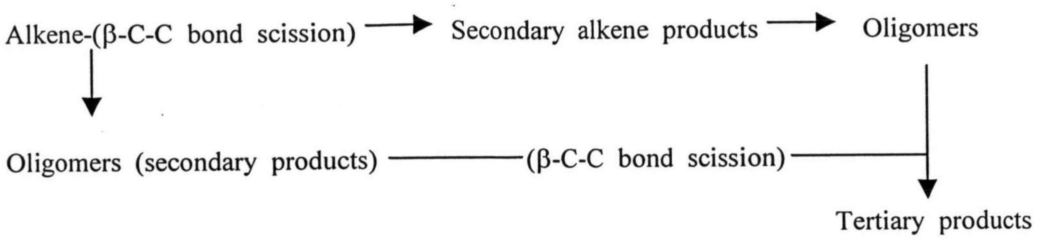

Several general conclusions about the structure of tertiary products from alkenes can be drawn from the results shown below[58]:

1. Each C_n alkene produced tertiary light products in the range from C_4 to C_{n-1}. No methane, C_2, or C_3 products were usually observed under mild conditions, whereas they became quite prominent at higher temperatures.

2. Irrespective of skeleton structures of the substrates, all linear and branched alkenes produced the same three light olefinic products with quite high yields: isobutene, 2-methyl-2-butene, and 2-methyl-2-pentene. Alkenes with the same skeletons but with differently positioned double bonds (2-methyl-1-butene, 2-methyl-1-pentene, and 4-methyl-2-pentene) as well as isoalkanes (isobutane, isopentane, and 2-methylpentane) were also usually formed.

3. Alkenes with the same skeletons but with different positions of double bonds produced the same light products but with different yields.

4. A temperature increased above 200°C rapidly brings a complete generation in the product distributions.

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