

CHAPTER II

LITERATURE REVIEW

The most valuable product is pharmaceuticals, food, chemical feedstock and fuel, respectively. For petroleum perspective, aromatics is the most valuable product because it is widely used as chemical feedstock such as benzene, toluene, and xylenes which are well known as BTX. On the other hand, aromatic affects human health and environmental impact. Typically, toluene demand is less than industry supply but xylenes is opposite. It is interesting to enhance xylene production from low value feedstock such as *n*-pentane by catalytic process.

2.1 Aromatic Hydrocarbons

Hydrocarbons are chemical compounds containing only hydrogen and carbon. Aromatic hydrocarbons have at least a benzene ring. A benzene ring is a molecular structure that is created when six carbon atoms connect with each other in a linked ring. Each carbon atom has four electrons; two electrons link up with neighboring carbon atoms, while one goes to a hydrogen atom. It is well known that aromatics hydrocarbons are important industrial chemicals which find a wide variety of uses in petrochemical industry. The key industrial products of aromatics are benzene, toluene and xylene (BTX). Table 1 shows the global demand of benzene, toluene, xylene and *p*-xylene, significant growth rate of *p*-xylene is the highest among others.

Table 2.1 Global demand of benzene, toluene, xylene and *p*-xylene (million tons)

Global	Benzene	Toluene	Xylene	<i>p</i> -Xylene
2003	35.9	16.4	24.6	19.3
2009	45.9	21.3	34.7	30.3
Growth rate (%)	4.2	4.5	5.9	7.8

Xylene has three isomers; *o*-xylene, *m*-xylene and *p*-xylene, demand of *p*-xylene is the 80% among three isomers with only 24% of total xylenes production. *p*-Xylene is an aromatic hydrocarbon containing benzene ring and two methyl substituents at position one and four. Physical properties of *p*-xylene are colorless, flammable liquid or crystals and characteristic odor. *p*-Xylene vapor may explode when ignition is in an enclosed area and there is a potentially dangerous fire hazard from flashback. *p*-Xylene is the one of high demand for polyester manufacture such as terephthalic acid and dimethylterephthalate. Applications are fiber, medicine, pesticide, and pigment. Conventional *p*-xylene technology is based on the isomerization of mixed xylenes as shown in Figure 2.1.

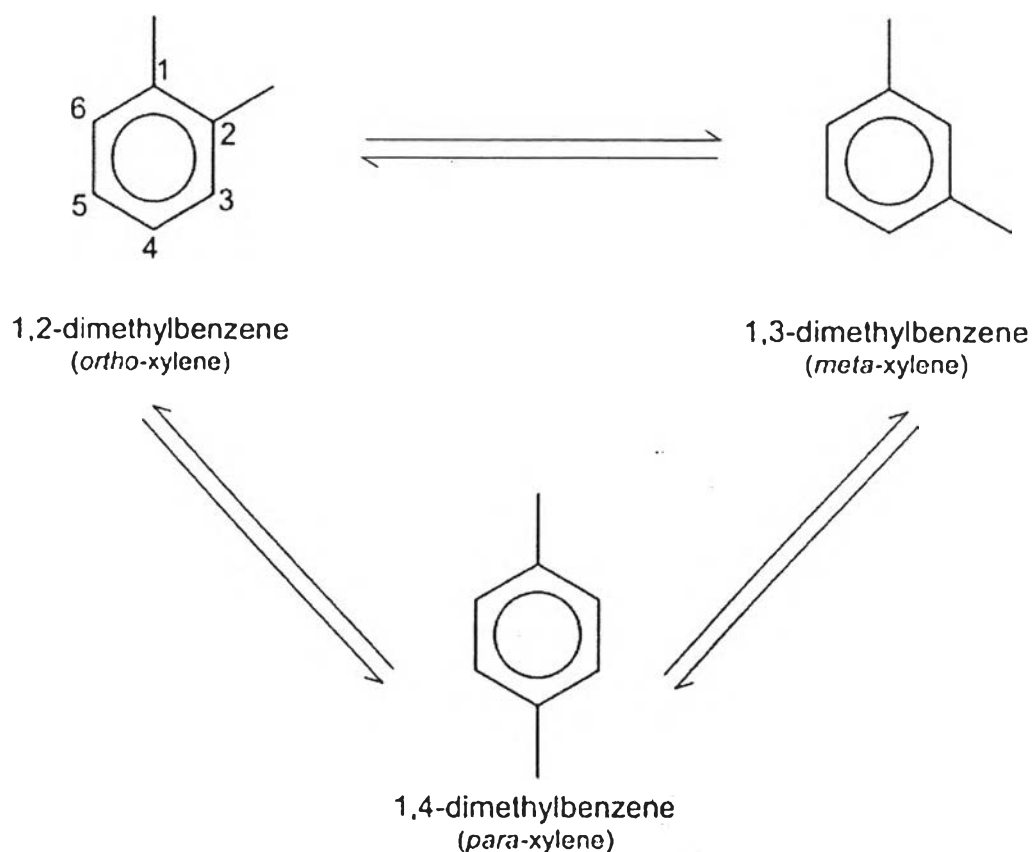


Figure 2.1 The isomerization of mixed xylenes.

The thermodynamic equilibrium data of xylene isomer is 23% *o*-xylene, 53% *m*-xylene and 24% *p*-xylene over unmodified ZSM-5 zeolite catalysts. Secondary isomerization of *p*-xylene on external acidic would cause quickly isomerize of *p*-xylene to *o*-xylene and *m*-xylene. Therefore, highly selective *p*-xylene production greatly reduces the separation cost and also reduces the production of less desired xylene isomers.

Light saturated hydrocarbon compounds, C₂-C₄ alkanes are used with ethane in natural gas in order to increase heating value. Ethane and propane can be refinery fuel. Liquefied petroleum gas (LPG) is propane alone or in mixture with butane. A large part of *n*-pentane is used as working medium in geothermal power stations because of low cost and low boiling point. Sometimes, it is added into some refrigerant blends as well. Thus, it is interesting to convert *n*-pentane to *p*-xylene, low-value to high-value products are the best alternative for investment completely.

Aromatization of light paraffin over ZSM-5 zeolite has studied (Bhat *et al.* 1995, Nakamura *et al.* 1996, and Viswanadham *et al.* 1996). Zeolite has different structural types; modenite, ZSM-5, ZSM-12, Erionite, etc. The ZSM-5 is widely used in chemical catalyst because it can resist formation of large hydrocarbon molecules so it can prevent coke deposits and enhance the catalytic stability (Kissin 1996).

Light paraffin aromatization process consists of many networks of reactions which are the following.

- 1) Olefin form through paraffin dehydrogenation and/or cracking.
- 2) Oligomerization of olefins and then oligomer cracking.
- 3) Olefin alkylation.
- 4) Oligomers cyclization into naphthenes.
- 5) Naphthene dehydrogenation into aromatics.

Conversion of *n*-pentane generally decreased with the increase SiO₂/Al₂O₃. It was known that the increased SiO₂/Al₂O₃ would result in the decrease of the acid site number, which facilitates the aromatization. Pentane aromatization on the shape-selective HZSM-5 catalyst is promoted by Brønsted acidic sites. Lewis acidic site supports alkene oligomerization compared to alkene cracking. Presently,

aromatization processes are commonly known, Reforming, Cyclar and Alpha Process are the important processes to produce aromatics from the light alkanes.

2.1.1 Reforming Process

The feed for reforming process is heavy naphtha (C₇-C₉) with bifunctional Pt/Cl-Al₂O₃ catalysts to produce aromatics. The use of catalytic naphtha reforming as a process to produce high-octane gasoline is as important now as it has been for about half century of its commercial use. The catalytic reformer occupies a key position in a refinery, providing high value-added reformate for the gasoline pool and frequently benzene, toluene, and xylene aromatics for petrochemical uses. This process involves reconstruction of low-octane hydrocarbons in the naphtha into more valuable high octane gasoline components without changing the boiling point range.

2.1.2 Cyclar Process

Cyclar process is based on a Ga/ZSM-5 catalyst which is developed by British Petroleum (BP) and UOP. Feedstock as LPG is converted into BTEX aromatics, hydrogen and light paraffins as Figure 2.2.

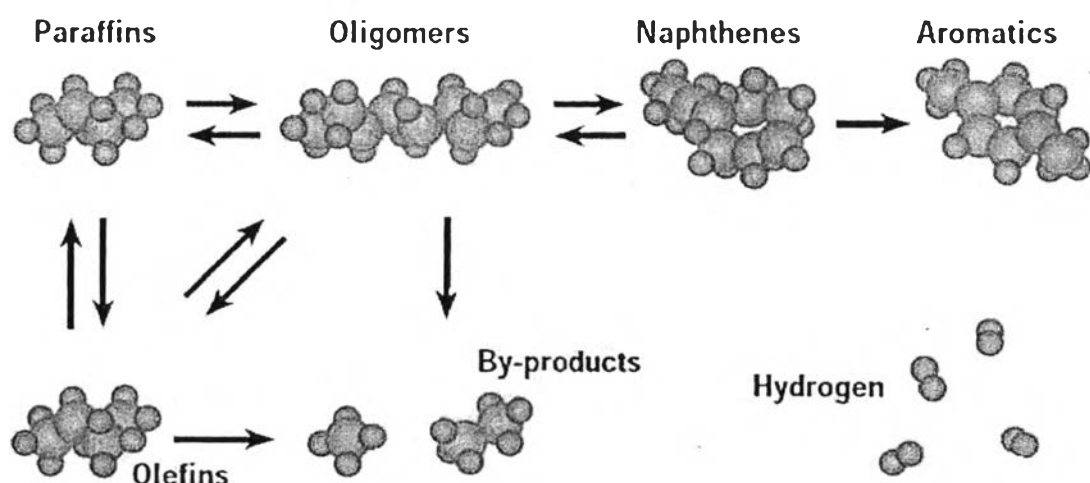


Figure 2.2 Schematic of the Cyclar process reaction.

(www.uop.com/wp-content/uploads/2013/09/cyclar-molecules-300x183.jpg)

The process is carried out in a number of vertically stacked moving-bed radial-flow reactors. Catalyst is withdrawn from the bottom reactor, regenerated and supplied to the top reactor without interrupting the process. Meanwhile, coke formation on aromatization catalysts becomes a dramatic criticism when olefin-rich feeds are employed (Blauhoff, 1999).

2.1.3 Alpha Process (Nagamori *et al.* 1998)

Alpha process is developed by Sanyo Petrochemical Company and now licensed by Stone & Webster. $Zn/\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$ catalyst is used to optimize by a hydrothermal treatment. Olefinic $\text{C}_3\text{-C}_8$ streams can be employed as feed. The Alpha process utilizes two identical fixed-bed reactors operated in a swing mode. First reactor is reaction and second reactor is catalyst regeneration. Benefit of this scheme makes the whole process continuously. This process has been operating satisfactorily without any major problems since July 1993. According to the simplified process flow diagram is shown in Figure 2.3.

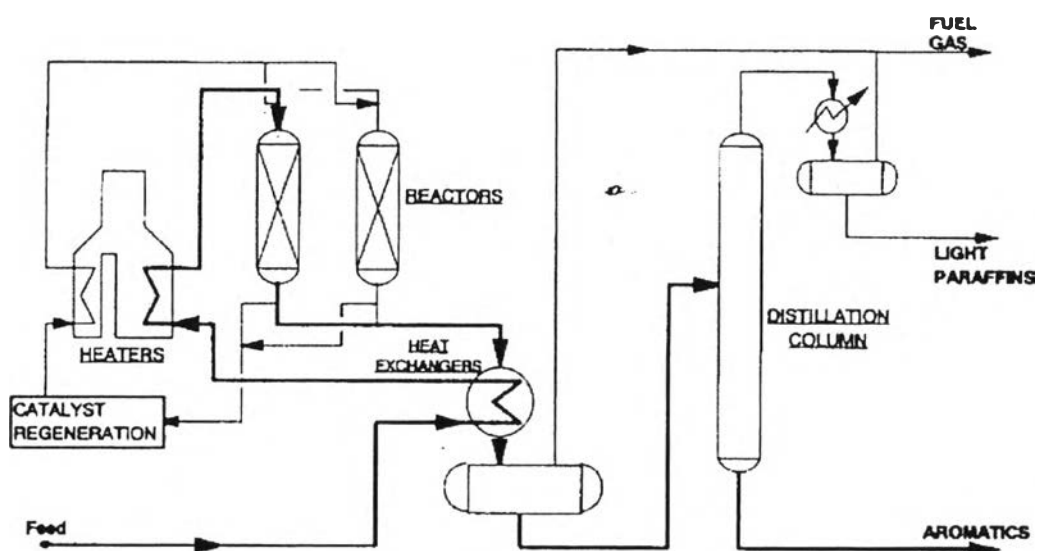


Figure 2.3 The reactor section in Alpha process.

Regeneration step is required because the catalysts activity need to be restored by burning off the coke. During burning coke, mainly concern is formation of the heavier products at external sites. Reaction caused the formation of coke are the same responsible for open-chain hydrocarbons aromatization. The stability against coking should be improved.

The formation of coke in hydrocarbon reactions over ZSM-5 zeolite inhibit further reaction either by competitive removal of acid sites or by blocking access of reactant molecules to the acid sites. To control the location of coke formation is very industrial interesting but it is unlikely that coke formation can be entirely eliminated in all reaction of interest. So, it makes some changes to improve the behavior by modified zeolite over thermal and hydrothermal pretreatment.

After the regeneration, temperature programmed desorption confirms Brønsted acid sites decreases significantly but Lewis acidity increases slightly. The amount framework of Al-OH group is suppressed after regeneration treatment in agreement with lowered Brønsted acid density (Tagliabue *et al.* 2004).

2.2 Naphtha Feedstock

Naphtha is a combination of a complex mixture of hydrocarbon molecules in C₅-C₁₂ range. It is typically divided into light and heavy naphtha. Light naphtha contains C₅-C₆ and boiling range is 30-90 °C. Heavy naphtha contains C₇-C₁₂ with boiling range of 90-200 °C. The naphtha feedstock consists of:

2.2.1 Paraffins or alkanes are saturated aliphatic hydrocarbons with the general formula C_nH_{2n+2}. They are either straight chain (*n*-paraffins) or branched structures (*i*-paraffins). The boiling point of an *n*-paraffin is always higher than that of the *i*-paraffin with the same carbon number. The density increases with increasing carbon number as well.

2.2.2 Olefins or alkenes are unsaturated aliphatic hydrocarbons which consist of straight chains and branched structures. They always contain one or more double bonds and a general formula C_nH_{2n}.

2.2.3 Naphthenes or cycloalkanes are saturated cyclic hydrocarbons that contain at least one ring structure. The general formula for mononaphthenes is C_nH_{2n} same as olefins. The most abundant naphthenes in petroleum have a ring of either five or six carbon atoms. The rings can have paraffinic side chains attached to them. The boiling point and the density are higher than paraffin at the same number of carbon atoms.

2.2.4 Aromatics contain one or more polyunsaturated rings (conjugated double bonds). These benzene rings can have paraffinic side chains or be coupled with other naphthenic or aromatic rings. The boiling points and the densities of these polyunsaturated compounds are higher than that of both paraffins and naphthenes with the same carbon number. At the beginning, aromatic is used as additive to boost octane numbers. The reactivity of the unsaturated bonds makes BTX which is essential building blocks for the petrochemical industry.

Naphtha is transformed into reformat which is BTX by catalytic reforming. Each products are controlled thermodynamically so improvement is using bifunctional zeolitic catalysts in order to adjust properly the zeolite pore opening similar to BTX molecules (Serra *et al.* 2005).

2.3 Catalysts for Aromatization of *n*-Alkanes

Converting light paraffins into aromatics was interested because one of the low-value petroleum feedstocks available in excess in petroleum refineries is light naphtha. Using bifunctional catalysts as metal oxide ZSM-5 zeolite catalysts, they found that gallium promoted aromatic selectivity (Nakamura *et al.* 1996). A large number of acid catalysts have been also applied in the aromatization processes of light hydrocarbon to chemicals and liquid fuels. Most petroleum-derived aromatics are obtained by catalytic reforming of naphtha, but classical Pt/ γ -Al₂O₃-based catalysts are unable to convert light hydrocarbons into aromatics. The shape selectivity and acidic properties of ZSM-5 zeolite can promote aromatization by reshuffling of hydrogen and carbon in a thermodynamically allowed sense at high temperature and relative low pressure (Tagliabue *et al.* 2004). ZSM-5 zeolites have

high selectivity due to their similar dimension of the pore openings to these of aromatic molecules and can be further enhanced by delicately adjusting the pore openings.

2.3.1 Zeolitic Materials

Zeolite can display different types of shape selectivity in organic reactions. For reactant selectivity, zeolite allows only part of the reacting molecules to enter the catalyst pores. In product selectivity, only compound with the correct dimensions can diffuse out of the pores. Only those reactions can take place where the transition state fits within the internal zeolite pores. It may be noted that transition state selectivity belongs to a family of reaction selectivities. They have in common that the surrounding zeolite affects the relative importance of parallel and/or consecutive reactions. Of particular importance in organic synthesis often is the so-called restricted growth type selectivity. The restriction causes the formation of higher addition, substitution or oligomerization products which are suppressed due to the dimensions of these products.

2.3.2 MFI (type material: ZSM-5)

The framework type of the high silica zeolite ZSM-5 (Figure 2.4), each sheet is linked by oxygen bridges to the next to form the 3-dimensional structure. Adjacent sheets are related to one another by an inversion center. This produces straight 10 ring channels parallel to the corrugations (along y), and sinusoidal 10-ring channels perpendicular to the sheets (along x). The latter channels link the straight channels to one another to form a 3-dimensional 10-ring channel system. According to the IUPAC classification, the diameter of micropores ranges from 0.3 to 2 nm, of mesopores from 2 to 50 nm and of macropores over 50 nm. ZSM-5 has found many applications in refinery and petrochemical processes. With 12 T-atoms in the asymmetric unit, MFI is one of the most complex zeolite framework types known.

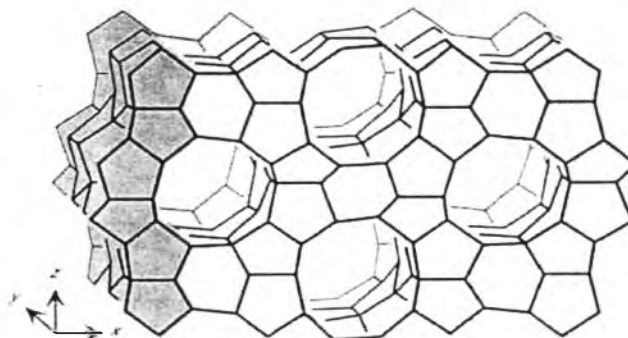


Figure 2.4 The MFI framework type.

IUPAC name:	MFI (ZSM-5)
Composition:	$\text{Na}_n(\text{Si}_{96-n}\text{Al}_n\text{O}_{192}) \cdot 16\text{H}_2\text{O}$ ($n \leq 8$)
Important structural isotypes:	<ul style="list-style-type: none"> - Silicalite-1 ($\text{Si}/\text{Al} = \infty$) - Boralite - (Si,Ge)-MFI
Channel system:	<ul style="list-style-type: none"> - 3-dimensional - straight 10-ring $5.2 \times 5.7 \text{ \AA}$ channels connected by sinudoidal $5.3 \times 5.6 \text{ \AA}$ channels - intersection cavities 9 \AA

2.3.3 Zeolite Framework Types (Jacobs *et al.* 2001)

Zeolite framework structures are fundamental to the understanding of zeolite chemistry. A framework type is opposite with framework structure. The framework type describes the connectivity of the tetrahedrally coordinated atoms (T-atoms) of the framework in the highest possible symmetry. The framework composition, the observed symmetry, and the actual unit cell dimensions are not considered. A three letter code (e.g. MFI) is assigned to confirmed framework types by the Structure Commission of the International Nomenclature. The codes are normally derived from name of the zeolite of type material, e.g. MFI from ZSM-5 (Zeolite Socony Mobil – five). ZSM-5 zeolite is a medium pore with channels

defined by ten membered rings that are much more favorable to the diffusion of *p*-xylene among *o*-xylene and *m*-xylene.

2.3.3.1 Sorption of Molecules with Varying Kinetic Diameter

The most direct way of assessing the distribution of the micropore size is to compare the sorption isotherms of molecules with different minimum kinetic diameters. For this purpose, the uptake of a series of sorbates with increasing minimal kinetic diameter on a solid is explored. The drop in the adsorbed amount with increasing size of the sorbate defines the minimum pore diameter of the tested solid. The minimum kinetic diameter of various probe molecules and the diameter of the zeolite pores are compared in the Figure 2.5.

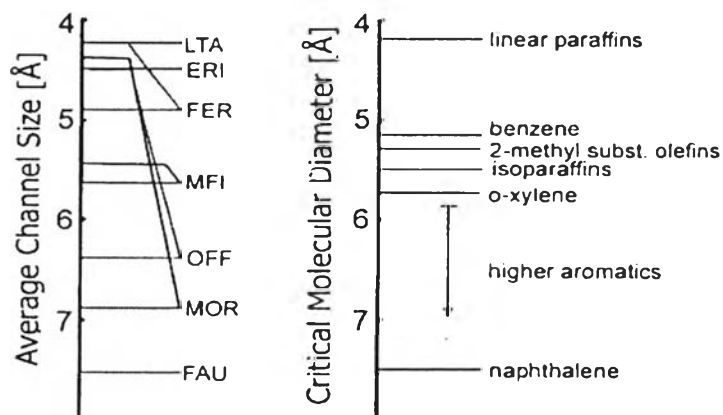


Figure 2.5 Pore diameters of zeolites and sizes of reactant molecules.

In the presence of distinct functional groups, the use of in situ spectroscopy can serve to evaluate the fraction of sites located inside and outside the particles of the microporous material. The natural limit of pore sizes to be probed depends on the size and the vapor pressure of the sorbate. Note that the interactions of molecules adsorbed in micropores can be very strong so relaxations of the lattice and changes in the effective pore diameter of the material can be observed, which also results in a strong temperature dependence of the accessibility.

2.3.3.2 Framework Composition

A number of the interesting properties of zeolites are based on the fact that the framework is anionic and the balancing cations exchangeable. Pure silica (SiO_2) framework is neutral but if some of the tetravalent Si are replaced by trivalent Al to produce an aluminosilicate, the framework becomes negative and counterions such as Na^+ are needed to balance its charge. The neutral aluminophosphate frameworks can be made anionic similar manner by inserting other elements into some of the T-sites. Even a small amount of a transition metal ion in the framework can make the material useful for catalysis applications. Many elements have now been incorporated into zeolite framework structures such as Pt, Ni, Zn, Ga, etc (Serra *et al.* 2005). The framework composition also affects the stability of a material. Namely, a high silica zeolite usually has a higher thermal stability than does the corresponding aluminosilicate. The framework Si/Al ratio is a reflection of the number of potential acidic sites and the acidic strength of ZSM-5.

2.3.3.4 Extra-framework Species

Channels and cages of a zeolite framework are usually filled with extra-framework species such as exchangeable cations, which balance the negative charge of the framework, removable water molecules, and/or organic species. These may come from the synthesis mixture or resulting of a post-synthesis treatment. Modern crystallographic techniques generally allow such information to be extracted from diffraction data, but there are some limitations that should be appreciated. The primary problem is the fact that extra-framework species do not generally follow the high symmetry of the framework, so they are called disordered.

Catalytic activity in zeolites is essentially governed by electronic transport between reactive components and local sites within the zeolite framework. In acid-based zeolite catalysts in Table 2, these sites are typically Brønsted acid sites, containing an H^+ ion localized near a bridging Si-O-Al cluster.

Table 2.2 Acid and base systems

System	Acid	Base
Arrhenius	Form H^+	Form OH^-
Brønsted-Lowry	Donate H^+	Accept H^+
Solvent	Cation(+)	Anion(-)
Lewis	Accept electron pair	Donate electron pair

ZSM-5 zeolite catalyst usually have Brønsted acidic sites are related to aluminium located in the framework of the zeolite and Lewis acid sites are related to the extra-framework aluminum (EFAI).

2.3.3.4 Deactivated Catalysts

The different structure has individual lifetime of zeolitic catalysts. Catalyst deactivation takes place largely as a result of coke deposition. In general, zeolites with a three-dimensional structure will deactivate at a given amount of coke less rapidly than zeolite with a one-dimensional framework. In three-dimensional zeolites a channel which is blocked at one point can still be utilized for a catalytic reaction via interconnections.

2.4 Modification of Zeolites

It is known that monofunctional acid catalysts (ZSM-5) structure show good activity and selectivity for the conversion of light alkanes to aromatics. However, it is not the best dehydrogenating catalysts leading to limits the aromatics selectivity. Aromatization over HZSM-5 is accompanied by substantial cracking of C-C bond of alkanes with a production of 3 moles of small alkanes per one mole of aromatics (I.V. *et al.* 2009). However, the formation of aromatics is limited over HZSM-5 catalyst due to the following reasons. Firstly, thermodynamic data of alkane converts to aromatics more difficult over alkene to aromatic. Secondly, the kinetic of alkane aromatization is limited by the formation of olefinic compound which occurs through scission of carbonium ions into carbenium ions and hydrogen. Next, formation of

aromatics occurs by the hydride transfer from naphthenes to smaller olefins in the final step of the reaction. Lastly, steric constraints in the pore structure of ZSM-5 limits the hydrogen transfer from naphthenes to olefinic compounds (N. *et al.* 2004). To summary, the modification of ZSM-5 zeolite is necessary to improve the catalyst properties leads to obtain the high conversion of light alkane, high shape-selectivity for *p*-xylene products. Further studies have been report on several of modification methods such as, metal ion-exchange, dealumination and silylation with silica compounds.

2.4.1 Metal Ion-Exchange

Most ion exchange processes are carried out on an engineered form. The improvement of light paraffins conversion to aromatics has been studied to know the effect of various metal ions on the aromatization. The effect of Pt, Zn, and Ga loading ZSM-5 for pentane aromatization, it showed high aromatic selectivity because enriched dehydrogenation of alkanes (Meriaudeau *et al.* 1991). They found that Ga/ZSM-5 strongly promoted hydrogenation of olefins through hydrogen abstraction and enhanced dehydrogenation of alkanes as well. For Zn/ZSM-5, it had conversion lower than Pt/ZSM and Ga/ZSM-5. Typically, the price of Pt precursor is too expensive thus Ga ion-exchange is very interesting and is economical for further studied of modification of ZSM-5 zeolite (Kitagawa *et al.* 1986). Gallium ion strongly inhibited hydrogenation of olefin through hydrogen abstraction and enhance dehydrogenation of alkanes which increased aromatic selectivity (Gnep *et al.* 1988). Another support for Ga ion-exchange, XRD pattern showed thermal treatment after gallium impregnation had no changing of crystalline phase. Gallium dispersed well in the zeolite matrix TEM/EDS confirmed slight disappearance of Ga₂O₃ crystallites after thermal treatment (Tagliabue *et al.* 2004).

The *n*-pentane conversion to aromatics, Ga ion-exchange over HZSM-5 or Ga/ZSM-5 gave the higher aromatics yield and aromatics selectivity compared with HZSM-5. The presence of Ga³⁺ ion in ZSM-5 zeolites increases conversion of lower olefin into aromatics, but it does not affect the acidic property and cracking ability of the zeolite (Sirokman *et al.* 1986).

Choudhary and co-workers studied the influence of time-on-stream Ga/ZSM-5 zeolite in the aromatization of propane. They found that the strong acidity of zeolite is decreased with increasing the Ga-loading due to the replacement of some the zeolite protons by gallium ionic species (Ga^{3+} or GaO^+). Moreover, the coke deposited on the zeolite catalysts for a time-on-stream is increased with increasing the Ga-loading because of the increase in the dehydrogenation activity of the catalyst caused by the presence of Ga-oxide species in the zeolite channels. The enhancement of *p*-selectivity is also observed with increasing the Ga-loading 3 wt% in zeolite (Choudhary *et al.* 2000).

2.4.2 Silylated HZSM-5 Catalysts

One of many ways to improve zeolite for increasing the *p*-xylene selectivity is silylation which is deposition of an inert silica layer on the external surface of ZSM-5 zeolite. Generally, silylation is done by chemical vapor decomposition (CVD) or chemical liquid decomposition (CLD) has been demonstrated to be effective to obtain high *p*-xylene selectivity by eliminating the external acid sites as well as adjust the pore mouth of ZSM-5 zeolite. CLD is industrially significant because CVD is difficult to operate and poor reproducibility which hinder its practical application. In CLD process, solvent was required because the gradual diffusion of the CLD agent through the solvent on zeolite surface might result in a more uniform silylation at a less amount of deposition agent.

Lercher and co-workers studied CLD enhanced *p*-xylene selectivity with narrowing pore mouth so pore-opening controlled diffusion process. Small ZSM-5 crystal size had more acid sites on external surface and pore mouth region than big one. In summary, CLD had more effective big crystal size because it has lower acid site (Lercher *et al.* 2006). Another study compared CLD agent and observed shape-selective on modified ZSM-5. Hui and co-worker found that TEOS is the best solvent among phenylmethyl silicone (PMS), dimethyl silicone (DMS) and hexamethyl disiloxane(HMDS) because TEOS was the smallest and lowest viscosity so it was easily uniform silica layer. TEOS diameter is equal to 1.03 nm and larger than the micropore opening of ZSM-5 zeolites. Therefore, the diameter of TEOS is greater than the pore mouth of ZSM-5, only hydroxyl groups on the outer surface and close to the pore opening could react with the deposition agent to form

Si-O-Si or Si-O-Al bonds, which might result in the deactivation of the external non-selective acidic sites (Hui *et al.* 2011).

In addition, the combination of the effect metal ion-exchanged and silylation on the aromatization of light alkanes over ZSM-5 catalyst and the effect of TEOS loading with different TEOS concentrations on Ga/ZSM-5 catalyst. Nitipan revealed that the *p*-xylene selectivity was quickly enhanced with increasing the amount of TEOS and reached to the highest *p*-xylene selectivity 99.7% at TEOS 20 vol. %. On the other hand, the conversion of *n*-pentane decreased with the increase of TEOS. These results were due to deactivation of external acid sites and also reducing surface areas of zeolite, which affects the diffusion of *m*- and *o*-xylene. Both *m*- and *o*-xylene are transformed to *p*-xylene by isomerization before escaping pores (Nitipan *et al.* 2012).

2.4.3 Dealumination

ZSM-5 zeolite are widely used for the conversion of variety of hydrocarbon feeds due to its excellent catalytic properties such as shape-selective medium- pore zeolite and higher resistance to deactivation by coke deposition than other commercial zeolite types. The formation of coke in hydrocarbon reactions over ZSM-5 zeolite inhibits further reaction either by competitive removal of acid sites or by blocking access of reactant molecules to the acid sites. To control the location of coke formation is very industrial interesting. Aukett and co-workers studied the dealumination reaction can be explained by aluminosilicate framework was partially rearranged. The positive charge sited on the extra framework AlO^+ species will be partially neutralized by electron donation from the hydroxyls oxygens and oxygens of water molecules. Results, decreasing in the number of Brønsted acid sites and increasing in Lewis sites corresponding to AlO^+ species will confirm in steamed catalysts (Aukett *et al.* 1986).

2.4.3.1 Dealumination by Acid Treatment

Dealumination is removal of framework aluminum atoms without destroying the micropore structure. It is one of the most useful and widely used modifications of catalysts. It can be achieved by hydrolysis of the Al-O-Si bonds by acid leaching. During dealumination, aluminium could be removed from the framework but not from the crystallite or the extra-framework aluminum (EFAI).

Muller and co-workers were studied the effect of acid treatment for external dealumination by oxalic acid with CLD over ZSM-5 has high the conversion and *p*-xylene selectivity in disproportionation of toluene (Hui *et al.* 2011). For same oxalic acid leaching, they found that different zeolite structure types; zeolite beta, mordenite, ZSM-5 and ferrierite. XRD confirmed that ZSM-5 is dealuminated without destroying structure. Furthermore, the enhancement of dealumination increased number of Brønsted acid site (Muller *et al.* 2000).

2.4.3.2 Dealumination by Steaming Treatment

To improve the behavior by modified zeolite over thermal and hydrothermal pretreatment. The influence of steam treatment on the properties of zeolite is particularly interesting for preparing catalysts for industrial application with high activity, selectivity, and stability. Factors were the severity of steaming treatment, the treatment temperature, the water vapor pressure, time on the treatment, and contact time.

The effect of steaming on acidity and aromatization activity was studied. Lucas and co-workers found decreasing in initial aromatization activity when increasing in temperature during the steaming pretreatment because it dealuminated in the tetrahedral to octahedral positions. For catalyst stability, the ZSM-5 was dealuminated at different temperature and WHSV^{-1} . The results showed low WHSV^{-1} leading better stability but high WHSV^{-1} produced sensitive improvement in catalysts deactivation behavior. The best aromatization stability, steamed at 550 C and WHSV^{-1} of 0.5 h, shows a less loss of aromatic products after 5 h. They summarized that weaker new active sites after steaming treatment extent aromatization stability and resistance coking formation (Lucas *et al.* 1997).

For the optimized studies condition of dealuminated ZSM-5 by steaming be still further needed, the effect of synthesis methods and modification treatments of ZSM-5 on light alkane aromatization and Viswanadham found that acidity decreased with an increasing steaming temperature because of the framework dealumination. So, the conversion of feed is decreased with an increasing steaming temperature. However, the aromatics yields followed the strong acidity, and the mildly steamed catalyst at 673 K having very strong acid sites exhibited the maximum aromatic yield. After mild hydrothermal treatment created strong acid sites

that showed the highest of acid-insoluble extra framework aluminium may be due to the chemical interaction of some EFAl species with the acid sites of normal strength. The modified HZSM-5 obtained by mild dealumination of steam at 673 K also exhibited the highest aromatic yields in the conversion of several feedstocks such as *n*-hexane, *n*-octane, and light naphtha (Viswanadham *et al.* 2006).

At mild hydrothermal condition supports, pore volume is higher than unmodified catalyst which showed opposite results from severe steaming (650 °C) that pore volume decreased. Steaming removed framework-Al to be EFAl which led pore volume decreased because bond length of Si-O (0.165 nm) is shorter than Al-O (0.175 nm). Zhang and co-workers summarized that non-framework Al species can be clean itself under mild condition (Zhang *et al.* 2006).

Furthermore, Kumar and co-workers considered mild steaming of ZSM-5 which water vapor is less than 0.2 bar. Although, mild steaming decreased the number of Brønsted acid site, but enhanced the strength by increasing the partial pressure of water vapor. XRD showed no any changing composition and crystal structure by steaming. Generally, mild steaming produced mesopore in ZSM-5 (Niwa *et al.* 2012). The consistent results, they revealed that amount of Brønsted sites decreased with hydrothermal treatment as well because of lowering in amount of acidic bridging hydroxyl (Si-OH-Al) group (Kumar *et al.* 2000).

2.4.3.3 Dealumination Combined by Acid and Steaming Treatment

Effect of steaming-HCl acid treatment on the aromatization stability, it showed that Al at external surface, after HCl leaching, decreases and has a lower total acidity than the parent and steamed catalysts because of removal part of external framework aluminium species at external surface. These results in the medium/strong sites of steamed-acid leaching are very close to unity and weak acid sites are also lower in number. In addition, the mesopore area increase in both of dealumination by steaming and steam-HCl treatment as a consequence of aluminium extraction in dealuminated zeolites that act positively in catalysts deactivation behavior, as it can reduce diffusional limitations in the zeolitic channel. Finally, Lucas concluded that steam-HCl treatment has the best deactivation behavior due to lower toxic coke on external deposition leading to blocking of zeolitic channels

There are some related work reported about dealumination of ZSM-5 by steaming and/or acid leaching showed a preferential adjustment of acidity and medium/strong sites ratio. The treatment of ZSM-5 zeolite is combined steaming and citric leaching for enhancing on-stream stability of FCC gasoline. They found that the modified by steam-citric acid leaching catalyst has a higher aromatic products and a lower of coke deposition than only steaming catalyst alone. Fan and co-workers claimed that after steaming of parent zeolite produces EFAl species, leading to blockage to the micropores of zeolite and results in the decrease of aromatization selectivity of corresponding catalysts. Optimization, the treatment combined with steaming at suitable temperature and citric acid leaching of HZSM-5 zeolite can finely adjust the strength of acid sites and increase the ratio of medium and strong Lewis acidity to medium and strong Brønsted acidity (Fan *et al.* 2007).

2.5 Catalytic Shaping

Zeolitic materials have to be shaped to meet the mechanical and mass transfer requirements of an industrial application; small spherical particles for fluidized bed, small granules for powdered detergents, beads and extruded pellets with different cross-sectional shapes. Solid catalysts have insufficient crush and attrition strength. The scale up of the process using powder catalyst is not recommended because of the high pressure drop associated with the high flow rates. Generally, mechanical strength is provided through adhesive forces and hydroxyl group between binder particles. The ceramics (Xu *et al.* 2000) and metals (Chu *et al.* 2013) have been successfully matrixes for zeolites. Mechanical stability of extrudates strongly decreased with increasing macropore volume. The oxide binders have the significant defects of blocking catalytic active sites and limit the diffusion of reactants in the zeolitic channels. Acidic binders can also cause rapid catalyst deactivation (Gu *et al.* 2010).

2.5.1 Bound Zeolite Forms

Bonding of zeolite powders typically is extrusion, bead forming and spray-drying. Extrusion is simple method to shape zeolite powder due to significant

pressure drop. Zeolite powder combines with binders to be dough for extrusion. Shaped catalyst consist of two part active phase is zeolite and binder. Extrusion zeolite particles with a non-zeolitic binder is followed by solvent removal and heating to relatively low temperatures. The risk of temperature induced structural changes, e.g. phase transformations and pore collapse typically limit the maximum temperature. However, the strength and attrition resistance of the pellets may be rather low and the use of non-zeolitic additives will reduce the surface area and may even result in unwanted side reactions (C.N. *et al.* 1996). High surface area, low pressure drop and a high strength, which calls for hierarchically porous materials (Freiding *et al.* 2007). The effect of ZSM-5 zeolite extrusion, the peptized agent is diluted acetic acid. Bhat and co-workers found alumina binder do not present any catalytic activity. *p*-Xylene is formed and isomerized to *m*-xylene on the external surface sites (Bhat *et al.* 1995).

For the peptized pseudoboehmite binders of ZSM-5 zeolite catalyst, Lee and co-workers in 2010 studied effect of binder, which is pseudoboehmite, on shaping ZSM-5 extrudates. The zeolite to binder ratio is 80:20 by wt%. The peptizing agent is diluted nitric acid and phosphoric acid for P-free and P-containing extrudates in shaping of ZSM-5 zeolite catalysts, respectively. They found that additional P in pseudoboehmite binder has completely removed the mesopore structure enriching the mechanical strength of the extrudates. They also revealed that the presence of P in the binder depress strong acidity and amount of coking formation. According to 40 wt% addition of P to the pseudoboehmite can increase mechanical strength of the extrudates at 8.2 MPa from 3.1 MPa of P-free containing extrudates (Lee *et al.* 2010).

Another, Kim and co-workers in 2006 studied an effect of γ -alumina content on catalytic performance of modified ZSM-5 for dehydration of crude methanol to dimethyl ether. They discovered that pseudoboehmite was used as binder for the preparation of zeolite extrudates. Adding binder can lower catalytic activity but extent stability against coke formation and water (Kim *et al.* 2006). After adding binder, the strength of acid sites were weaken. After extrusion, if the γ - Al_2O_3 content increased, intensities of weak acid sites were promoted. Therefore, strong and medium acid sites were diluted by γ - Al_2O_3 .

Later, Zhang and co-worker in 2015 investigated topic of hydrothermal treatment on ZSM-5 extrudates catalyst for methanol to propylene reaction: Finely tuning the acidic property. They found framework and extraframework alumina species of γ - Al_2O_3 binder. Mainly, weak acid site increased due to the addition of gamma- Al_2O_3 because it had only Lewis acid sites. This result was consistent with Kim and co-worker in 2006.

Traditional peptized boehmite and aluminophosphate binders had various studies. Gaspar and co-workers compared binders for shaping alumina powder peptized with boehmite and aluminophosphate. During calcination, boehmite is converted into porous alumina but aluminophosphate will be densified to non-porous phase such as alphacristobalite-like and tridymite-like. Results showed mesoporosity of peptized boehmite as binder is $0.47 \text{ cm}^3/\text{g}$ which is higher than $0.2 \text{ cm}^3/\text{g}$ of aluminophosphate binding. Moreover, the mechanical strength of aluminophosphate binder of 2.1 MPa is greater than boehmite of 0.7 MPa (Cassiano *et al.* 2014).

Combination of binder to reach properly properties were discovered many works. Marturano and co-workers discovered the influence of bentonite, aluminium phosphate and alumina gel as binder agents of a calcined α - Al_2O_3 . They summarized that the mechanical strength of chemical bond (aluminium phosphate) was higher than the ceramic bond (bentonite and alumina gel). The combinations of both bonds present the highest strength (Marturano *et al.* 1997). Holdrich studied shaping catalyst by extruding a mixture of 60% ZSM-5 and 40% binder consisting of boehmite, amorphous aluminium silicate and silica (Holdrich *et al.* 1984).

Another, binders are compared including pseudoboehmite, silica gel and AlPO_4 hydrate. During calcination, they formed porous matrices γ - Al_2O_3 , SiO_2 and the crystal structure of tridymite AlPO_4 . In case of pore size, alumina- and silica-bound extrudates exhibit mesopore, however, the AlPO_4 -bound extrudates are macroporous enriching the internal mass transport. Comparison AlPO_4 among others at the same Si/Al ratio, they found non-coking deposited on $\text{AlPO}_4/\text{ZSM-5}$. In case of binder stability, AlPO_4 is better Al_2O_3 or SiO_2 because bonding forces of the sinter necks are much greater than van der Waals force. They also found γ - Al_2O_3 binder show the slowest deactivation among AlPO_4 and SiO_2 binder (Freiding *et al.* 2011).

Furthermore, γ -Al₂O₃ generates mesopores facilitating bulky hydrogen transfer responsible for aromatization (Saxena *et al.* 2013). In case, AlPO₄ is used as binder instead of conventional Al₂O₃ and SiO₂ due to easy coke deposition. Benefits of AlPO₄ as binder are maintaining Si/Al ratio because zeolite is not aluminated during the shaping process (Menges *et al.* 2012). Zeolite acidity decreases in HZSM-5 zeolite using SiO₂ as binder (Devadas *et al.* 1998).

In contrast, anhydrous AlPO₄ binder is well extruded but the mechanical strength is very weak (Freiding *et al.* 2007). Thus, the crush and attrition strengths are too low to use in reactor. In case of aluminum as binder used for extrusion or spray-drying can migrate into the zeolite framework. The additional aluminum promoted uncontrolled decrease in initial Si/Al ratio due to form extra acid sites (Shihabi *et al.* 1985). Therefore, it is preferred that the binder is an aluminium compound. Non-limiting examples for an aluminium compound are boehmite, pseudoboehmite and mixtures. The shaping occurs by processes essentially known extrusion, strand pressing, compression molding. According to various supported studies, they extruded mixture of power modified ZSM-5 and pseudoboehmite as binder (Saxena *et al.* 2013 and Viswanadham *et al.* 2013).

2.5.2 Peptization

It is a method to form colloids which are mixtures substance existing in a dispersed state in another substance. Colloids may exist as a gel, emulsion, aerosol, solid, foam or a solid aerosol. Peptization is a method in which aggregates disperse to give colloids.

The stability of a colloidal system is defined by particles remaining suspended in solution at equilibrium and shown in Figure 2.6. Stability is hindered by aggregation and sedimentation phenomena, which are driven by the colloids tendency to reduce surface energy. Reducing the interfacial tension will stabilize the colloidal system by reducing this driving force.

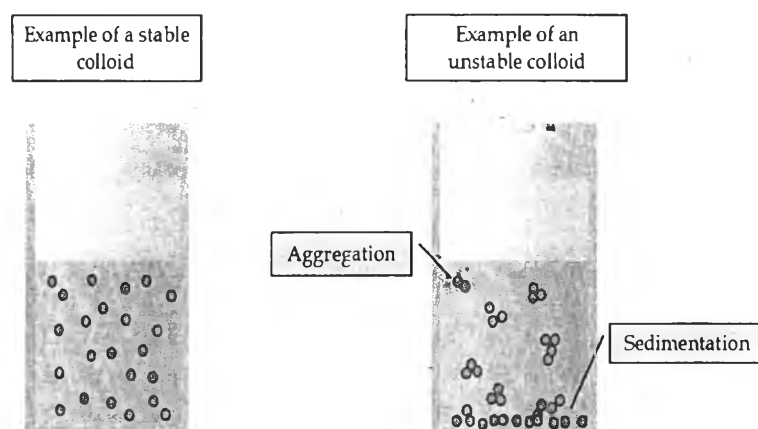


Figure 2.6 Examples of a stable and of an unstable colloidal dispersion.

In general, peptization is used in nanoparticle synthesis to make a large grouping of particles split into many primary particles. This is done by changing the surface properties, applying a charge, or by adding a surfactant.

The term's flocculation and coagulation have often been used interchangeably. Usually coagulation is irreversible whereas flocculation can be reversed by the process of deflocculation. The following Figure 2.7 schematically represents some of these processes (Vadakayil 2012).

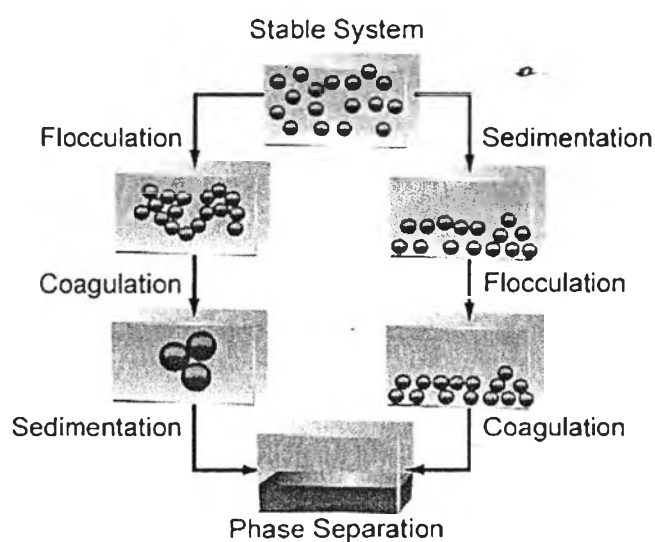


Figure 2.7 Cycle process of deflocculation.

Aggregation is due to the sum of the interaction forces between particles (Elimelech *et al.* 1998). If attractive forces such as van der Waals forces prevail over the repulsive ones (such as the electrostatic ones) particles aggregate in clusters. Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.

2.5.2.1 Electrostatic Stabilization

It is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase.

2.5.2.2 Steric Stabilization

It consists in covering the particles in polymers which prevents the particle to get close in the range of attractive forces. A combination of the two mechanisms is also possible as electrosteric stabilization. All the above mentioned mechanisms for minimizing particle aggregation rely on the enhancement of the repulsive interaction forces.