

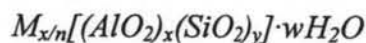
CHAPTER II

LITERATURE SURVEY

2.1 ZSM-5 Zeolite

The first zeolite mineral was discovered more than 200 years ago. In 1954, synthetic zeolites were first commercialized by Union Carbide as a new class of industrial materials for separation and purification purposes. In the past two decades, zeolite catalyst rapidly conquered additional processes in the field of hydrocracking of heavy petroleum distillates, octane number enhancement of light gasoline by isomerization, the synthesis of ethylbenzene (the precursor of styrene and polystyrene) from benzene and ethene after the Mobil-Badger process, the disproportionation of toluene into benzene and xylenes and the isomerization of xylenes (to produce *para*-xylene, the precursor chemical for terephthalic acid) (Weitkamp, 2000).

Zeolites are crystalline microporous hydrated aluminosilicate materials with framework structures composed of Si(Al)O₄ tetrahedral units. The structure is built by a three dimensional network of [AlO₄]⁵⁻ and [SiO₄]⁴⁻ tetrahedras. The tetrahedras are linked together by sharing oxygen atoms and thereby form a three dimensional framework. A representative formula of a general zeolite structure may be written as:



M is the cation of valence n , w is the number of water molecules y/x is the silicon/aluminum ratio for the zeolite. The counterion may either be a metal-, ammonium- or alkylammonium cation.

ZSM-5 zeolite is one of the most important zeolites used in petrochemical industry. The structure of ZSM-5 zeolite and its analogue silicalite-1, shown in Figure 2.1, has 10-membered oxygen ring and two types of channel systems with similar size: straight channels (5.3×5.6 Å) and sinusoidal channels (5.1×5.5 Å). These two different channels are perpendicular to each other and generate intersections with diameters of 8.9 Å. This 10-membered oxygen-ring-sized pore

system with uniform dimension as well as the absence of large cages with small windows leads to the special coke-resistant properties of HZSM-5 zeolites.

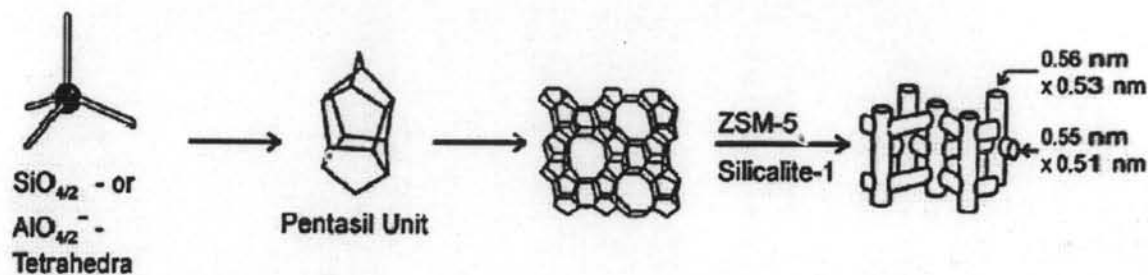


Figure 2.1 Structure of ZSM-5 zeolite.

Investigations by Viswanadham *et al.* (1997) suggested that:

- (1) Linear aliphatic molecules diffuse freely in ZSM-5 framework and can be adsorbed in both types of the channels.
- (2) *Iso*-aliphatic compounds experience steric hindrance effects, which may restrict their diffusion in sinusoidal channel system.
- (3) Aromatic compounds and methyl-substituted aliphatics have a strong preference for diffusion and/or adsorption in the linear elliptical channels. This implies that flat and large molecules prefer to diffuse in wider elliptical channels.

ZSM-5 zeolites in protonic type (HZSM-5) have been extensively used in acid catalyzed reactions. HZSM-5 zeolites can be synthesized with a broad range of Si-Al ratio from 6 to ∞ . The stability of ZSM-5 to steam was examined in the late 1960s. It was soon found that the highly siliceous nature and the structure of ZSM-5 provided both a very thermally and a very hydrothermally stable zeolite. The zeolite could be treated at temperatures as high as 1260 K before encountering any crystallinity loss. For ZSM-5 metals resistance, ZSM-5 had a much higher tolerance for vanadium than ultrastable Y (Degnan *et al.*, 2000).

In principle, the acid strength and acid types are the key properties of zeolites, which play a crucial role in the activity and selectivity of the zeolites. The acid strength of zeolite is mainly dependent on the Si/Al ratio. The strongest Brønsted acid sites can be obtained upon completely isolated Al in framework due to the higher electro-negativity of Si compared to Al. If Si/Al ratio higher than 10, the strength of the acid sites keeps almost constant. However, the acid strength can be enhanced by the presence of extra-framework Al (EFAL), which is ascribed to the inductive effects relative to Lewis acid sites on the neighboring Brønsted acid sites. Activities of ZSM-5 zeolites with different Si/Al ratios have been studied (Buchanan, 1998). When the Al contents in the zeolite are low, the catalytic activity is proportional to the Al content of the zeolite, this relation is a linear function for a wide range of compositions. These results identify the proton donor sites for the cracking reaction. At higher concentrations of Al in the zeolite, the dependence is no longer linear.

In year 2000, he studied the effects of silica/alumina to reaction patterns over ZSM-5 catalysts with 55:1 and 450:1 Si/Al ratio. It was found that, for pure hexane and pure octane feeds, the propylene/butene ratio for the 450:1 ZSM-5 in cracking of a hexane/octane feed was significantly lower than for the 55:1 ZSM-5. For the degree of skeletal isomerization versus cracking for a 1-hexene feed over the two ZSM-5 catalysts. The hexene is more highly isomerized over the 450 : 1 catalyst. Isomerization is much faster here than cracking. These results suggest that the 55 : 1 catalyst may be more mass-transfer limited than the 450 : 1 catalyst.

ZSM-5 additive can be used to increase propylene yield at the expense of gasoline. ZSM-5 makes propylene by cracking the C₆ to C₁₂ gasoline molecules almost exclusively to light olefins but had little effect on the heavier components such as heavy fuel oil. This is not surprising, because the pores in ZSM-5 are only 5-6 Å wide, which is not large enough for these large molecules to enter (shape-selectivity). Results of numerous pilot plant and commercial studies show that adding ZSM-5 additives at levels of up to 6% by weight of catalyst can increase propylene yield by 80% to 100%. There are a number of different formulations of ZSM-5 additives and most of these will favor propylene production relative to C₄ olefins.

2.2 Mechanism of Catalytic Cracking over Zeolite

The mechanism of catalytic cracking of alkanes and olefins over solid acidic catalysts continues to generate a vigorous discussion even after 50 years of extensive research in this field. Three main questions remain unresolved: the nature of active sites on the catalyst surface, the nature of transient reaction intermediates formed in the reactions between the sites and substrates (linear and branched alkanes), and the chemical mechanism of the cracking reaction, the C-C bond fission. The modern mechanisms of heterogeneous acid catalyzed transformations of hydrocarbons on zeolites and other solid acids involve adsorbed carbocations as active intermediates. This mechanism involves three elementary steps: initiation, propagation, and termination. The initiation step is represented by the attack of an active site on the reactant molecule to produce the activated complex that, in the gas phase or when using liquid superacids, would correspond to the formation of a carbocation. The chain propagation is represented by the transfer of a hydride ion from a reactant molecule to an adsorbed carbenium ion. Finally, the termination step corresponds to desorption of the adsorbed carbenium ion to give an olefin whilst restoring the initial active site. In general, for components with equal carbon numbers, the rate of cracking decreases in the order: *i*-olefins > *n*-olefins > *i*-paraffins \approx naphthenes > *n*-paraffins > aromatics.

The mechanism of olefins cracking over zeolite has been summarized by Corma and Orchilles (2000). Firstly, the olefin corresponds to the attack of one Brønsted acid site from the carbenium ion. It can rearrange without increasing the branching of the chain or can generate a branched carbocation. The former process is believed to occur through a 1,2 hydrogen shift, whereas branching isomerization also occurs on zeolites, via a protonated cyclopropane ring and, this can play an important role during the cracking of linear paraffins and olefins. A third reaction, is the cracking of the C-C bond by β -scission (cleavage of the C-C bond located β to the trivalent positively charged carbon atom).

Hollander *et al.* (2002) illustrated cracking mechanism by the reaction of *n*-heptene, the formation of carbenium ions from olefins can easily proceed by addition of the proton from a Brønsted acid site of the catalyst to the carbon-carbon double bond. Cracking of the adsorbed carbenium ion proceeds through the β -scission mechanism or through the protonated cyclopropane mechanism. An illustration is given in Figure 2.2.

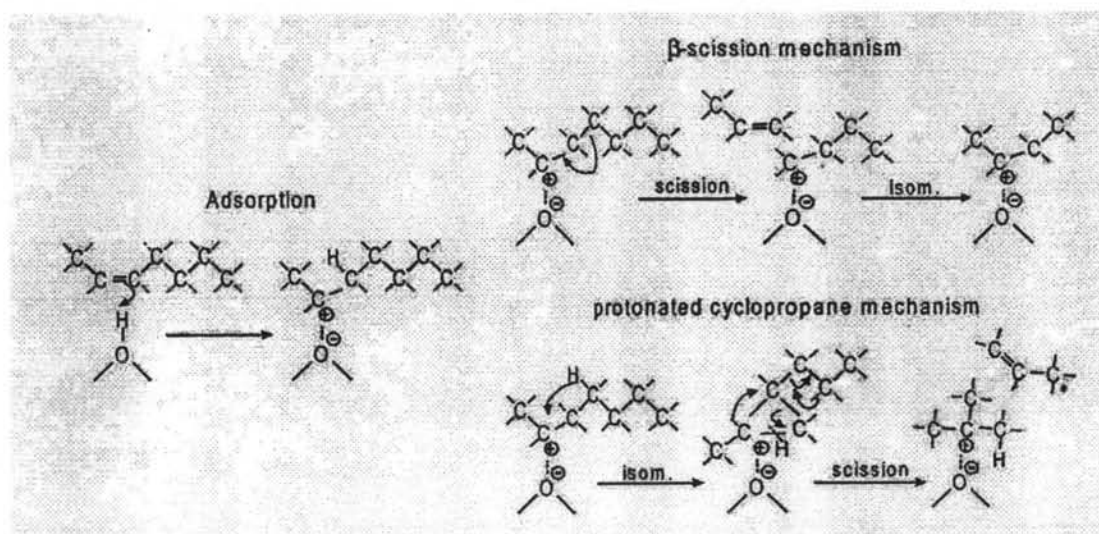


Figure 2.2 Cracking mechanisms illustrated by the reaction of *n*-heptene; adsorption at a Brønsted acid site.

The alkane cracking mechanism is now generally accepted that cracking via two different mechanisms (Anderson *et al.*, 2002). Classical catalytic cracking mechanism, also referred to as the carbenium ion or bimolecular catalytic cracking mechanism, takes place when branched secondary and tertiary alkylcarbenium ions derived from the feed molecule are cleaved by a single β -scission into smaller alkylcarbenium ions and alkenes. Products formed during the catalytic cracking of a C_nH_{2n+2} alkane via this mechanism trend to possess carbon numbers within the range 3 to $n - 3$. Hence, using *n*-heptane as an example, equal amounts of C_3 and C_4 hydrocarbons result. The formation of primary alkylcarbenium ions is unlikely and so ethylene, ethane and methane are not observed.

A second mechanism, proposed in 1984 by Haag and Dessau. The Haag-Dessau cracking mechanism, also known as the protolytic cracking, monomolecular cracking, and carbonium ion cracking mechanisms, is now also widely accepted. In this mechanism, alkanes are protonated to form carbonium ion transition states that can undergo either C–C bond cleavage yielding alkanes (including methane and ethane) or C–H bond cleavage yielding dihydrogen and carbenium ions. These carbenium ions subsequently form alkenes via back-donation of a proton to the zeolite, as illustrated in Figure 2.3. The formation of ethylene is possible via this mechanism.

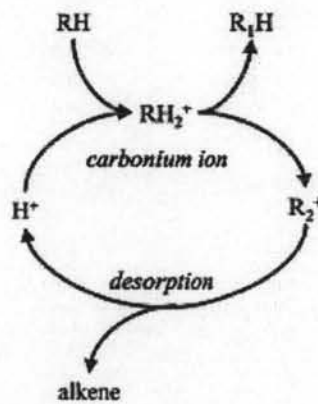


Figure 2.3 Haag-Dessau cracking mechanism for an alkane molecule (RH) proceeding via a carbonium ion transition state.

Kotrel *et al.* (2000) summarized the Haag-Dessau mechanism of protolytic cracking of alkanes, found that the data indicate protolytic cracking generally for C₃–C₆ alkanes at low conversions when the catalyst is HZSM-5. The product distributions closely approach those for pure protolytic cracking only for propane and *n*-butane with this catalyst, and only in the limit of zero conversion; otherwise, classical cracking accompanies protolytic cracking, being dominant when the alkene concentrations are more than minimal.

2.3 Role of ZSM-5 in Cracking Process

The fluid catalytic cracking unit (FCCU), which was originally designed as a conversion and gasoline producing unit, has now a new important objective: to enhance the *yield of the light olefins*, since these are important petrochemical feedstocks. The demand for propylene is increasing rapidly due to the expanding market for polypropylene and LPG-range olefins are used as feedstock for alkylation and isomerization units where clean, high octane gasoline components and other chemicals are produced. Another important application of the light olefins is in the production of oxygenates that are used as octane-boosting additives in gasoline. For example, *i*-butene and *i*-pentene are needed to produce methyl tertiary-butyl ether (MTBE). This can be achieved by introducing some operational changes in the unit, as for instance by increasing the reaction temperature and decreasing the riser contact time. However, the highest impact on short olefin production, and more specifically on the production of propylene in FCC units, has been achieved via catalyst modifications. The use of Y-zeolites with low unit cell size and, most important, the use of ZSM-5 as an additive have strongly increased the production of propylene in FCC.

Narbeshuber *et al.* (1995) studies the monomolecular conversion of light *n*-alkanes (propane to *n*-hexane) over HZSM-5 at temperature between 723 and 823 K. The results suggest that carbonium ions are intermediates for all primary reaction. Depending upon the nature of carbonium ion in the transition state, three parallel primary reactions were identified, leading to hydrogen exchange, dehydrogenation, and cracking. For all alkanes investigated, the rate of dehydrogenation was significantly smaller than the rate of cracking. With increasing size of the *n*-alkane, the rate of reaction increases due to the increase in the adsorption constant of hydrocarbon. The true energies of activation are independent of the hydrocarbon chain length and the position of the C-C bond to be cleaved.

Dehydrogenation-cracking double-stage (tandem) reaction of *n*-butane was investigated by Wakui *et al.* (2002). Using a Pt-Sn type dehydrogenation catalyst and a cracking catalyst (rare earth-load HZSM-5). In their experimental of *n*-butane cracking over HZSM-5 at low conversion (<ca. 30%) using a small-scale (short

contact time) reaction. The results are shown in Figure 2.4 (The cracking products obtained were hydrogen, methane, ethane, ethylene, propane, propylene, and butane), no aromatic products (BTX; benzene, toluene, xylene) were observed. Monomolecular cracking of *n*-butane tends to take place and the protonated *n*-butane is cracked in three paths: (1) to hydrogen and butene; (2) to methane and propylene; (3) to ethane and ethylene. According to this mechanism and the results, the occurrence probabilities of these three reactions were almost the same. With the use of rare earth (La)-modified HZSM-5, similar result was observed.

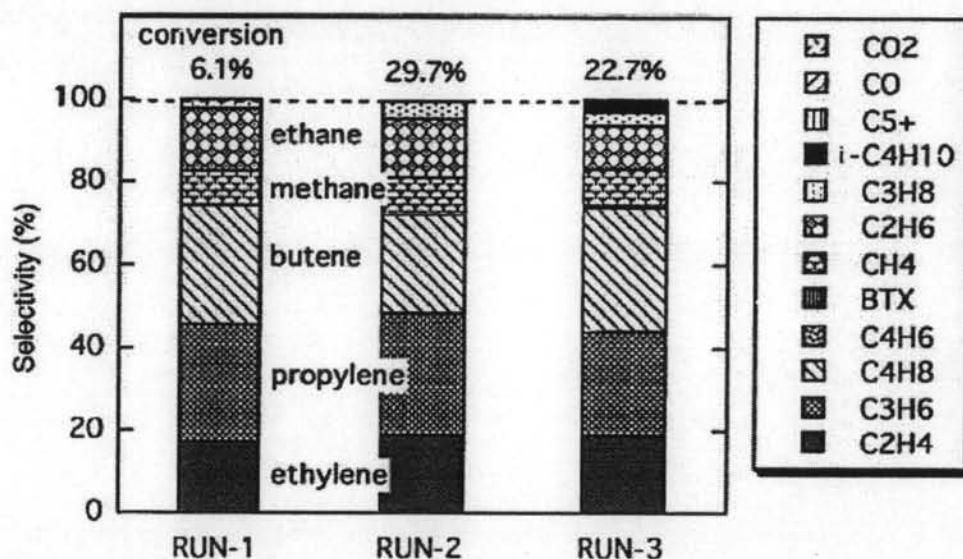


Figure 2.4 Distributions of products in cracking of *n*-butane catalyzed by HZSM-5. Catalyst: HZSM-5(69), 1.5 mg (RUN-1); 10 mg (RUN-2); HZSM-5(200), 60 mg (RUN-3). Reaction conditions: temperature, 600 °C; *n*-butane, 4.5 kPa; He, 77 kPa; N₂, balance; total flow rate, 10.8 cm³ min⁻¹ (RUN-1 and RUN-2); temperature, 650 °C; *n*-butane, 4.5 kPa; N₂, balance; total flow rate, 36.1 cm³ min⁻¹ (RUN-3).

At high conversion, considerable amounts of aromatic products and heavier hydrocarbon (C₅⁺) were observed. Ethylene and BTX were the major products in the case of HZSM-5 catalyst without modification and the yield of propylene and butane are lower when compare with low conversion because the products further reacted

bimolecularly to BTX. In the case of rare earth-loaded HZSM-5 (10%La/ZSM-5 or 10%Pr/ZSM-5), the yield of BTX was lowered and the yield of olefins was improved. The loading of rare earths on HZSM-5 had also been found to increase the hydrophilicity of the catalyst. As a result, the amount of steam introduced into the reactor had some positive effects for the suppression of BTX formation, whereas those effects of steam were not observed on HZSM-5 without rare earth-modification.

For dehydrogenation-cracking double-stage reaction, the results shown that the yield of light olefins (C_2+C_3) was higher than in the single cracking process and the yield of ethylene and propylene was much higher when *n*-butene was used as a substrate, but the concentration of the *n*-butene had to be lowered in order to yield aromatics in the same order.

2.4 Aromatization Reaction over Zeolite

The effectiveness of ZSM-5 additive to enhance lighter olefins in FCC unit shown that the concentration of aromatics is higher than over cracking catalysts free of ZSM-5. There have been seemed two alternative points on the origin of the aromatics. The mostly researchers suggested that the increment of aromatics observed in the cracked naphtha involving ZSM-5 is merely due to concentration effect, as a result of the selective cracking of various hydrocarbons and the absolute quantities of aromatics remained essentially unchanged. However, other researchers held that aromatics could be built up in the presence of ZSM-5 from the lower olefin and lower paraffin generated from the bulky hydrocarbon molecules.

Liu *et al.* (2004) studies on the model catalyst containing ZSM-5 (Si/Al = 50, 500), Zn-ZSM-5 (Si/Al = 50) and USY to examine the possible aromatics generation and the aromatization mechanism stimulated in catalytic cracking reaction with different hydrogen transfer characteristics. The results suggest that the presence of ZSM-5 and USY causes a tremendous decrease in olefins of gasoline fraction, leading to an enrichment of the aromatics in liquid product. It is evidently that aromatics are generated from lower olefins. So, they proposed the mechanism which is a hydrogen transfer reaction takes place on the Brønsted sites of the zeolite and the

lighter olefins undergo cyclization and dehydrogenation to form aromatics. The property of lower silica-to-alumina ratio of ZSM-5 enhance the aromatization process, resulting in less *i*-paraffins and more aromatics. This can be explained by the fact that both the amounts of Lewis sites and Brønsted sites of the high Si/Al ratio are much smaller than those of the low Si/Al ratio, indicating that the higher Si/Al ratio reduces the cracking reactivity of the ZSM-5 catalyst. After the Zn modification (Zn-ZSM-5) the density of Brønsted sites drops and the amount of Lewis sites increases obviously. Therefore, the Zn modification decreases the crackability of ZSM-5 and enhances its dehydrogenation, leading to higher concentration of aromatics in liquid product.

Furthermore, they suggested reaction pathways over ZSM-5 zeolite contained FCC catalyst, as show in Figure 2.5. More or less, there is the pseudo-equilibrium between a cyclization of carbenium ions and a protonation of naphthenes on the Brønsted sites of ZSM-5, and in the meantime the carbeniums can also undergo β -scission to obtain light olefins. If the base catalyst has higher hydrogen transfer activity, it can quickly seize the hydride ions that are released by the dehydrogenation of naphthenes, resulting finally in formation of aromatics and paraffins. On the other hand, if the hydrogen transfer activity of the base catalyst is very low, it cannot easily capture the hydride ions, resulting in β -scission of carbeniums to the formation of lighter olefins.

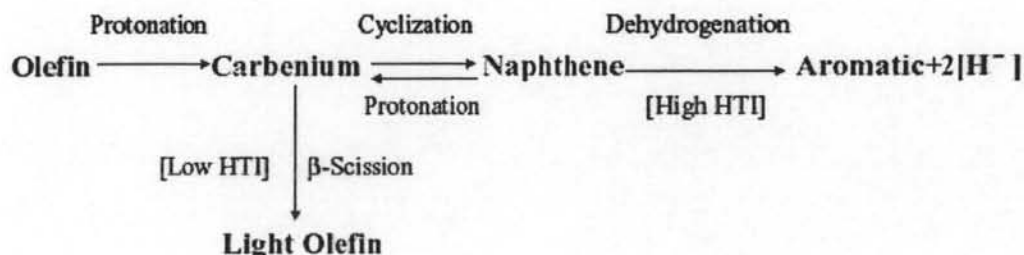


Figure 2.5 Reaction pathways over ZSM-5 zeolite contained FCC catalyst.

The effect of variations in acid properties of HZSM-5 on the coking behavior in butane aromatization were investigated by Song *et al.* (2005). The butane aromatization reaction was carried out in a continuous flow fixed-bed reactor with reaction conditions: $T = 350\text{ }^{\circ}\text{C}$, $P = 0.5\text{ MPa}$, $\text{WHSV} = 2\text{ h}^{-1}$. The ZSM-5 zeolite with Si/Al ratio = 50 was used as a basically catalyst. In this work, they varied the acidity by using hydrothermal treatment technique (to remove of aluminum in zeolite framework) at 450, 490, 520 and 620°C and K addition. The results suggested that the stronger acid sites on a catalyst are more favorable for the butene conversion although the weak acid sites can also catalyze the butene conversion. In the presence of suitably stronger acid sites, the oligomers formed via alkene oligomerizing could be transformed into alkanes, aromatics or other molecules by hydro-transfer, dehydrocyclization.

However, further enhancement in the steamed temperature caused a distinct decline of the content of benzene and toluene in the aromatics, accompanied by an increase in that of the bulkier aromatics; i.e. C_9^+ aromatics. This verified that small aromatic molecules such as benzene and toluene may not be the primary products of aromatization reaction, but maybe formed by dealkylation or transalkylation of poly-alkyl aromatics, which was favored on strong acid sites.

For the coke formation, they concluded that a large amount of acid sites, especially strong acid sites (i.e. high acid density) on the HZSM-5 catalyst will result in the formation of a large quantity of coke and serious channel blockage, which will accelerate the catalyst deactivation. The hydrothermal treatment to HZSM-5 catalyst can properly reduce the number of strong and weak acid sites to achieve a suitable acid site distribution; and this will improve the reaction stability on-stream by prohibiting coke formation and improving the channel blockage during olefin aromatization.

2.5 The Deactivation of Zeolite

In most industrial processes the cost of catalyst deactivation is very high, and mastering catalyst stability has become at least as important as controlling the activity and the selectivity. The deactivation of zeolites observed during the cracking reaction can be due to different causes:

- (1) Poisoning of the active sites either by feed components and impurities (i.e. Metal and nitrogen-based compounds), or by non-desorbed heavy products (coke).
- (2) Blockage of the access of the reactant to the active sites by coke.
- (3) Structure alterations.
- (4) Collapse of the zeolite framework during high-temperature steam treatment.

Coke formation is the main case of temporary catalyst deactivation during the transformation of organic compounds. Generally, coke is the formation of carbonaceous residues or can be defined as the by-products that are retained inside the zeolite pores or on the outer surface of the crystallites after the reaction. Deactivation by coke is reversible, coke being removed by oxidative treatment at high temperature.

In any case, the carbonaceous deposit on ZSM-5 zeolite would decrease catalytic activity, and even cause a complete loss of catalytic activity by covering the acid sites or by blocking the access of reactant molecules to the acid sites. How to overcome the barrier of the catalyst deactivation by coking and how to prolong the life of the catalyst are very important and interesting topics

Li and Stair (1997) used Ultraviolet (UV) Raman spectroscopy to characterize coke formation in ZSM-5 and USY zeolites under propylene at temperature from 300 K to 773 K. UV Raman spectra was completely avoided the strong fluorescence background that always present with conventional Raman spectroscopy. The spectra from this experimental confirms that the coke species formed in ZSM-5 are mainly olefin (1635 cm^{-1}) and aromatic species (1615 cm^{-1}) and the major portion of coke species in ZSM-5 can be removed even by He purging

at 773 K. For USY zeolite, coke species are polyaromatic and pregraphite, theirs are very stable and can only be removed in O₂ flow at temperatures above 773 K.

The deactivation behaviors of ZSM-5 zeolite channels were studied by Viswanadham *et al.* (1997). The experimentals were carried out with *n*-heptane aromatization in microcatalytic reactor containing 5 g of catalyst, which is a mixture of ZSM-5 and alumina in a 60:40 ratio. The fresh ZSM-5 and spent catalysts (12 h time-on-stream) were examined for pore size distribution using argon adsorption and the Horvath & Kawazoe method. The results suggested that the alumina binder protected the ZSM-5 catalyst by accommodating most of the coke. Moreover, analysis of the zeolitic part of the pores showed that the total pore volume of the fresh and used ZSM-5 are unchanged. In the fresh catalyst, pore volume of straight channels is higher than the sinusoidal channels but the reverse is observed in the case of the used catalyst. This indicated that most of the sinusoidal pores are still open even after deactivation due to the majority of straight channels are blocked by coke, so the total gas enters through sinusoidal channels and fills up the poremouth blocked straight channels through intersection and this keeps the total pore volume unchanged.

Guisnet and Magnoux (1997) summarized the effect of coking rate in zeolite catalyst, which used in hydrocarbon transformation processes.

The effects of coking rate are :

- (1) *Nature of the reactant*, coking occurs rapidly from alkenes and polyaromatics but slowly from linear alkanes or monoaromatics whose transformation into alkenes or polyaromatics is slow.
- (2) *Pore structure*, the selectivity to coke is equal to about 1 with large pore, 0.1 with medium pore and 0.05 with small pore zeolite due to steric constraints limit.
- (3) *Acidity*, lowest density and weakest strength of the acid are sites necessary for the selective formation of the desired products.
- (4) *Operating conditions*, the rate of coking increases generally with the reactant pressure or on the reaction temperature. Use of the hydrogen can reduce the concentration of coke precursors.