

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Heterogeneous catalysts

Over 80% of the molecules in the millions tons of crude oil processed annually throughout the world come into contact with a solid catalyst at one time or another in their trips through refineries.

Heterogeneously catalyzed reactions are composed of purely chemical and purely physical reaction steps. For the catalysis process to take place, the reactants must be transported to the catalyst surface. Thus, apart from the actual chemical reaction, diffusion, adsorption and desorption processes are of importance for the progress of the overall reaction. The total process may be divided into the following seven steps, any one of which can be rate determining.

1. Diffusion of the reactants through the boundary layer to the catalyst surface.
2. Diffusion of the reactants in to the pores (pore diffusion)
3. Adsorption of reactants on the surface of pores.
4. Chemical reaction on the catalyst surface.
5. Desorption of products from the catalyst surface.
6. Diffusion of the products out of the pores.
7. Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.

Diffusion limitation at the external surface of catalyst particles is recognized by the following characteristics.

1. The rate is proportional to catalyst weight (or to the concentration of active component) and raised to a power less than unity.

2. The rate is increased by improving the movement of the gas or liquid with respect to the catalyst.
3. The temperature coefficient and the apparent activation energy are low [2]

2.1.2 Promoter

Promoters are substances that they are not catalytically active, but increase the activity of the catalysts. The function of these substances, which are added in the catalyst in small amounts, has not been elucidated. There are four types of promoters; (a) structural promoters; (b) electronic promoters; (c) textural promoters; and (d) catalyst-poison-resistant promoters.

Structural promoters increase the selectivity by influencing the catalyst surface so that the number of possible reactions for the adsorbed molecules decreases and the favored reaction path dominates.

Electronic promoters influence the electronic character of the activity phase by dispersing in the phase and therefore chemically binding with the adsorbate.

Textural promoters inhibit the growth of catalyst particles to form larger and less active structures during the reaction. They prevent loss of active surface by sintering, increasing the thermal stability of the catalyst.

A catalyst may contain one active component and one or more promoters. Since the above four effects tend to overlap in practice, it is sometimes difficult to precisely define the function of a promoter [1].

2.1.3 Zeolites

Zeolites are crystalline hydrated aluminosilicates, possessing a rigid three-dimensional framework constituted by corner sharing of all the four oxygen atoms of SiO_4 and AlO_4^- tetrahedral primary building units. The framework contains channels or interconnected voids that are occupied by the cations and water. Each AlO_4^- unit in the framework bears a net negative charge, which is balanced by a cation. These

cations are mobile and can undergo ion exchange. Depending on the type of zeolites, the pore size and connectivity pattern varies. The crystallographic unit cell of a zeolite³ may be represented as $M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$, where M is the cation of valence n, x and y are the moles of AlO_2 and SiO_2 units respectively and z is the number of water molecules [3].

Zeolites have a well-defined pore structure with confined active sites responsible for catalysis. The pore size and shape of the zeolites are responsible for shape selectivity in different reactions. Shape selective catalysis provides specific, desired pathways leading to desired products in hydrocarbon processing and synthesis of chemicals.

2.1.4 Reactant shape selectivity

When the operative pore size of the zeolite is such that it excludes larger molecules present in the reactant and admits only certain smaller molecules, only such small molecule reacts within the pore. This preferential transformation of the smaller molecules is called reactant shape selectivity. This type of selectivity is observed during the dehydrogenation of mixed alcohols, cracking of n-butanes and branched butanes over small pore zeolites and the hydrogenation of cyclohexene and cyclodecene over a zeolite supported catalyst [4].

2.1.5 Product shape selectivity

This type of selectivity occurs when some of the compounds formed within the pores are too bulky to diffuse out as products. The bulky product molecules may undergo secondary reactions to smaller molecules or may block the catalyst pores resulting in the deactivation of the catalyst. The products formed in this case are due to restricted diffusivity of the products during the course of the reaction, thus creating selectivity towards the product of a certain dimension. A classical example of this type of selectivity is the preferential formation of p-xylene during the reaction of methylation of toluene and the monomolecular isomerization of alkyl aromatics over ZSM-5 catalysts [5-6].

2.1.6 Restricted transition state selectivity

When the reaction occurs inside a confined micropore of a catalyst, the geometry of the pore imposes a steric restriction on the transition state, which is too bulky to be accommodated within the pores/ cavities of the zeolites. In such cases, neither the reactants nor the products are restricted from diffusing through the pores of the zeolite. Examples of this type of selectivity are the trans-alkylation of dialkyl benzenes and alkylation of naphthalene over mordenite catalyst.

Different researchers have proposed various other types of shape selectivities. Derouane *et al.* [7] proposed shape selectivity, referred as molecular traffic control type, which occurred in zeolites containing intersecting channels of different diameters. In this type of selectivity the reactants enter preferentially through one set of channels and the products diffuse out through the other, thus minimizing counter diffusion.

Recently Guisnet *et al.* [8] reported tunnel type of shape selectivity. This type of selectivity is observed only in mono-dimensional molecular sieves like MCM-41 type. The reactant molecule before desorption undergoes various successive reactions in regular, non-connecting long channels.

2.1.7 Catalytic properties of zeolites

In the petrochemical industry zeolites are used for cracking, hydrocracking, isomerization and alkylation reactions. Most of the work in zeolite catalysis is concentrated on their acid and metal stabilizing properties.

Zeolite based catalysts, which are commonly used in acid catalyzed reactions, are also used in oxidation reactions. A titanium containing zeolite with the MFI structure (TS-1) was developed, which together with hydrogen peroxide replaced conventional stoichiometric oxidants in various oxidation processes. The potential of shape selective catalysis is further amplified by the added dimensions of isomorphous substitution and the availability of a large variety of AlPO_n , SAPO_n and MeAPO_n type compositions. They are very active and selective catalysts for a variety of

important hydrocarbon conversions. As acid catalysts they promote olefin isomerization and oligomerization.

In conventional catalytic dewaxing, zeolites typically crack the paraffin to lighter olefinic materials. Many excellent reviews are also available in the literature on the applications of zeolites and aluminophosphate molecular sieves in hydroprocessing and organic synthesis [8].

2.1.8 Brønsted acid sites

Pure siliceous zeolites are electrically neutral. By replacing silicon (tetrahedrally coordinated with oxygen atoms) having a formal charge of 4+ in the zeolite lattice with aluminium (formal charge 3^+) a negatively charged tetrahedron is created. Among others (NH_4^+ and alkali cations like Na^+ , K^+ etc.) the counterion H^+ compensates this negative charge. The protons are formally assigned to be bonded to the bridging oxygen of an Si-O-Al bond to form hydroxyl groups that act as strong Brønsted acids at the solid/gas interface. Brønsted acid sites will have acid strength, which depends on their environment, i.e. depending on chemical composition and the structure of the zeolite. The local environment of the acid site in a molecular sieve is determined by the structure, i.e. the coordination of the TO_4 tetrahedra in the framework (topology). This leads to different amounts of topologically inequivalent tetrahedral position. For example, mordenite (MOR) has four T sites while MFI has twelve non equivalent T sites [9].

2.1.9 Lewis acid sites

Lewis acid sites (electron pair acceptor sites) are related to the formation of positively charged oxide clusters or ions within the porous structures of the zeolites. These species are typically alumina or silica/alumina, formed by extraction of aluminum from the lattice, or metal ions exchanged for the protons of acid sites. Depending on the nature of the metal cation, these may contain hydroxyl groups (by partial hydrolysis of water). Note, that these metal cations together with the adjacent framework oxygens will act as Lewis acid/base pair and may polarize bonds in reacting molecules. The former type of Lewis acidity, i.e. aluminum oxide clusters

containing alumina in octahedral and tetrahedral coordination will usually be a stronger Lewis acid than exchangeable metal cations (“true” Lewis acids) [10].

2.1.10 Mordenite

Mordenite (MOR) is a zeolite with 12-membered (0.65, 0.70 nm) channels. They are in parallel to each other along the z direction and interconnected by 0.48-nm deep 8-membered pockets (Figure 2.1). Platinum-dispersed mordenite is a bifunctional catalyst, active for isomerization of n -alkanes and aromatization of paraffins. Activity of Pt samples depends on platinum distribution and dispersion, which are often affected by segregation and agglomeration of platinum during pretreatments, viz. calcination and reduction [11].

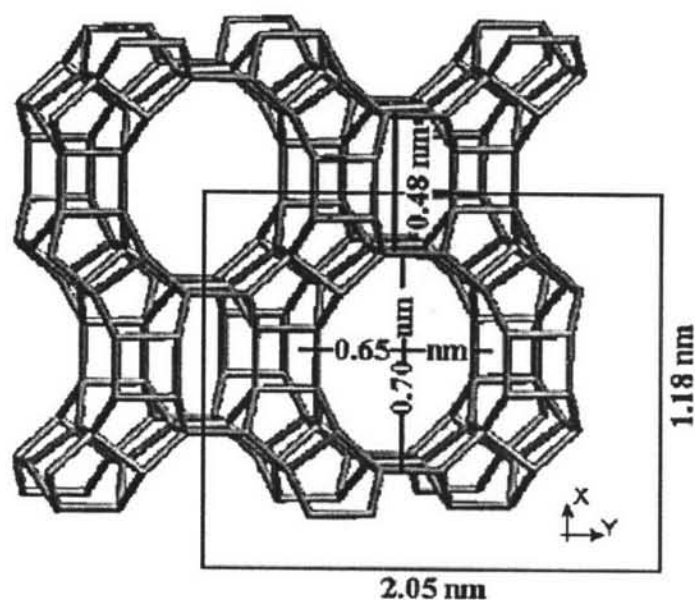
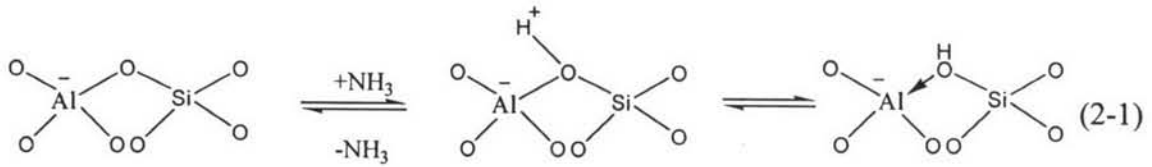


Figure 2.1 Structure of MOR showing parallel channels of ~ 0.7 nm size in z axis and the interconnecting pockets of 0.48 nm in y axis. [11]

2.1.11 Acidity of zeolite

Acid strength of zeolite can be varied by numerous preparation methods (ion exchange, partial dealumination, and substitution of the framework of Al and Si atoms). Direct replacement of the alkali metal ions with protons by treatment with

mineral acids is only possible in the exceptional cases (*e.g.*, mordenite and ZSM-5). The best method is exchanging of the alkali metal ions by NH_4^+ ions, followed by heating the resulting ammonium salts at 500°C to 600°C (deammonization; Equation 2-1)



Brønsted acid centers are generally the catalytically active sites of the H-zeolite. Weak to moderate strong acid sites can be generated in zeolite by ion exchange with multivalent cations. Owing to the polarizing effect of the metal cations, water is dissociatively adsorbed, and the equilibrium of Equation 2-2 is established.



The following order of Brønsted acidity is given for cation-exchanged zeolite: H-form \gg La form $>$ Mg form $>$ Ca form $>$ Sr form $>$ Ba form. Reason for the large differences in reactivity are the different charges on the ions, and the decreasing ionic radii from Na^+ to H^+ and the associated polarizing power of the ions. The incorporation of transition metal ions into zeolites leads to increasing bi-functional catalysts in which metal and acid centers can simultaneously.

Another major influence on the acidity of zeolites is the Si/Al ratio. The zeolite can be classified into three groups, according to the Si/Al ratio and the associated acid/base properties (Table 2.2). Since the ion exchange capacity corresponds to the Al^{3+} content of the zeolites, those with lower Si/Al ratios have higher concentrations of active centers.

Table 2.1: Classification of acidic zeolite according to Si/Al ratio [12]

Si/Al ratio	Zeolite	Acid/bases properties
1 to 1.5	A, X	low stability of lattice low stability in acids high stability in base high concentration of acid groups (medium strength)
2 to 5	Erionite, Chabazite, Chinoptilolite, Mordenite, Y	high stability of lattice high stability in acids low stability in base
10 to ∞	ZSM-5, Mordenite, Y	low concentration of acid groups (high strength)

Important factors influencing the reactions of bifunctional catalysts are the location of the metal, the particle size, and the metal-support interaction. The bifunctionality of the metal-doped zeolite catalysts is explained for the important of isomerization and hydrogenation. The metal content facilitates the hydrogenation and dehydrogenation steps, while the acid catalyzed isomerization step takes place under the restricted conditions of zeolite cavities [1].

2.1.12 Metal-doped zeolites [1]

Zeolites are especially suitable as support materials for active components such as metals. Suitable metals are effective catalysts toward hydrogenations and oxidations, whereby the shape selectivity of the carrier is retained.

The currently accepted mechanism for the isomerization of a normal paraffin is a three-step process: adsorption of an *n*-paraffin molecule onto a dehydrogenation-hydrogenation site (metal site), followed by dehydrogenation into a *n*-olefin, desorption of *n*-olefin from the dehydrogenation-hydrogenation site (acid site), which convert *n*-olefin to branched-carbonation, and desorption of branched-carbonation ion from the skeletal rearranging site and diffusion to a hydrogenation-dehydrogenation

site (metal site) where it is finally hydrogenated into an iso-paraffin molecule as seen in figure 2.2.

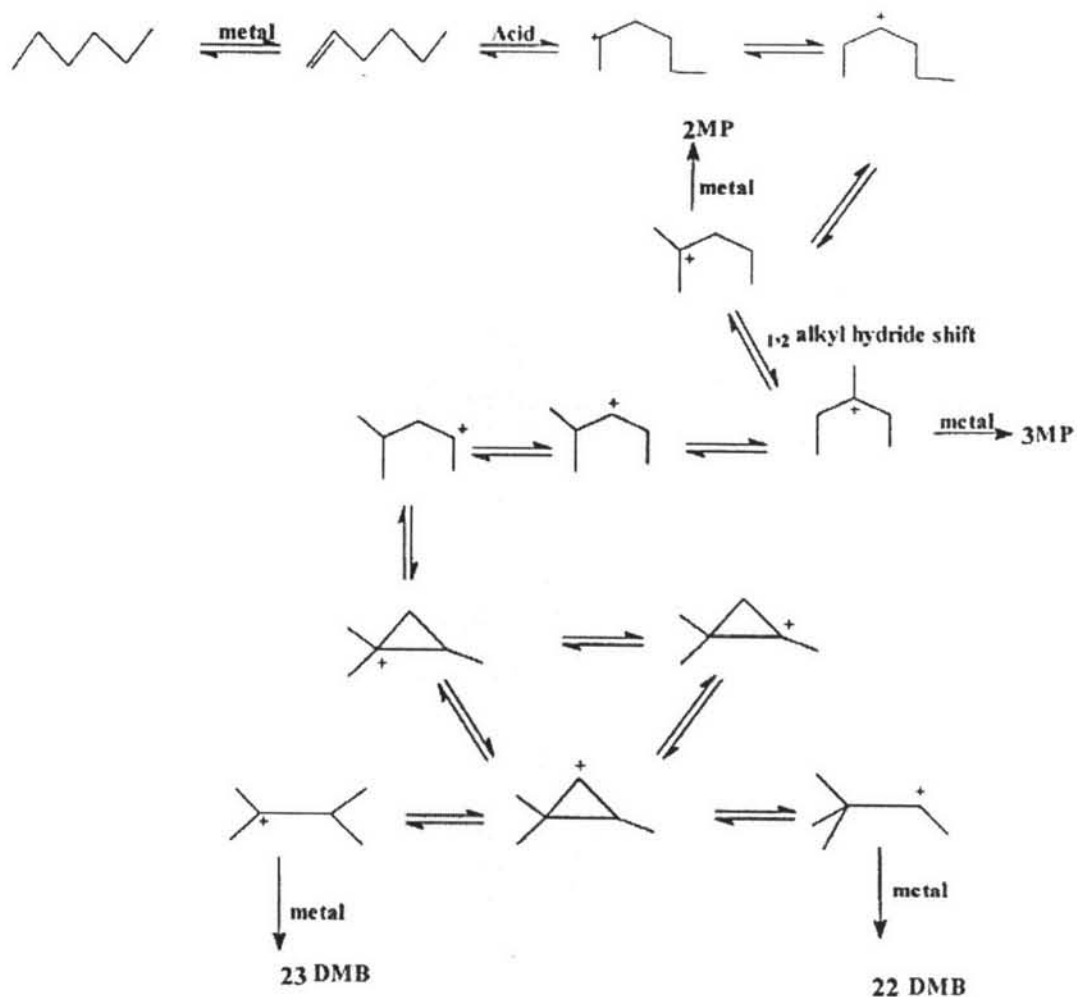


Figure 2.2 Bifunctionality of metal doped zeolites: isomerization and hydrogenation

Important factors influencing the reactions of bifunctional catalysts are the location of the metal, the particle size, and the metal-support interaction. The bifunctionality of the metal-doped zeolite catalysts is explained as for the important example of isomerization and hydrogenation. The metal content facilitates the hydrogenation and dehydrogenation steps, while the acid catalyzed isomerization step takes place under the restricted conditions of the zeolite cavities [1].

For industrial process, zeolite supported was used for several years to produce chemical and increase more octane number of fuel such as RZ-Platforming process, Alpha process.

2.1.13 RZ-Platforming process [13]

The RZ-Platforming process selectively reforms naphtha feed (C_6 and C_7 paraffins and naphthenes) to aromatics (BTX) by zeolite catalysts. Four major reactions occur in platforming reactors to produce the desired products:

1. Dehydrocyclization
2. Isomerization of 5-membered to 6-membered rings
3. Dehydrogenation of 6-membered rings to aromatics
4. Hydrocracking of large hydrocarbons to smaller hydrocarbons

The RZ-100 catalyst offers constant aromatic selectivity, in the range of 80% or higher, even when processing the most difficult C_6 and C_7 paraffin feed components.

2.1.14 Alpha process [14]

The alpha process converts olefin-rich carbons (C_4 or C_5 raffinate from ethylene plant) into aromatics (BTX) by using a zeolite-type catalyst. The catalyst developed is Zn-doped HZSM-5 zeolite, followed by hydrothermal treatment. The shows high aromatic selectivity (14% benzene, 44% toluene, 3% ethylbenzene, 26% xylene, and 13% C_{9+} aromatics).

2.2 Literature reviews

In 1992, Inui *et al.* has developed H-Ga-silicate catalysts with different gallium contents and used them for propylene-to-aromatics conversion. On H-Ga-silicate catalysts with high gallium contents, the selectivity to aromatic hydrocarbon and the concentration of hydrogen gas evolved were high. This must be attributed to the strong dehydrogenation action of gallium. On the platinum-loaded H-Ga-silicate catalyst, hydrogen gas evolved with aromatization was used for the hydrogenation of

lower olefins and for the hydrocracking of oligomers over platinum, and therefore, the selectivity to aromatic hydrocarbons and concentration of hydrogen gas in products was lower than that on non-platinum-loaded H-gallium-silicate catalyst [14].

In 1994 Dai *et al.* reported the influence of the loading method of platinum precursor and KCl, on the activity and selectivity of Pt/KL catalysts for hexane reforming reaction. The catalyst preparation methods involve ion exchange (IE), incipient wetness impregnation (IWI), and co-impregnation with KCl (IWI-KCl). The Pt/KL catalysts prepared by ion exchange with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ followed by impregnation with KCl (IE-KCl) gave much higher activity and selectivity for benzene formation than the catalysts prepared by other methods. It showed 100.0% conversion of hexane and 89.3% yield of benzene at 743 K and 0.2 MPa. In the IWI-KCl catalysts, the activity for benzene production was highly sensitive to the calcinations at high temperature. The Cl species on the IE-KCl catalysts may have existed in the state of KCl [15].

In 1996, Mao *et al.* reported the aromatization of *n*-butane. Hybrid catalysts containing irreducible oxides (silica and alumina) as co-catalysts provide aromatic yields which are almost twice that obtained with ZSM-5 zeolite. The addition of Ga_2O_3 to these co-catalysts enhances further the aromatizing performance of the hybrid catalysts. It is believed that such an additional improvement is due to the gallium species located in the interface between the two types of particles, and the Ga containing regions of the zeolite crystallinities near the pore openings. These gallium oxide sites appear more active than the normal ones because of their location near the zeolite pore openings [16].

In 1996, Yahima and co-workers reported the isomerization of *n*-hexane over Pt loaded $\text{H}\beta$, HZSM-5, and H-dealuminated mordenite. They found that Pt loaded $\text{H}\beta$ showed the highest activity and selectivity among the three catalysts. The conversion of *n*-hexane was 76% and selectivity to dimethylbutanes, and cracking product were 19.4, 76.2 and 4.4% respectively, at reaction temperature 275°C; W/F, 5 g h mol⁻¹; molar ratio of hydrogen to *n*-hexane [17].

In 1997, Corma *et al.* studied the transformation of propane into aromatics in the presence of oxygen, on a combined catalyst (MgO-supported vanadium oxide catalyst and H-ZSM-5 or Ga/H-ZSM-5. When the two functions are in close proximity, the yield to aromatics and selectivity to alkylbenzenes increase [18].

In 1998, Jacobs *et al.* studied the *n*-hexane aromatization on Pt/KL, Pt/Mg(Al)O, and Pt/SiO₂ catalysts at 773 K. The formation of benzene is preceded by the formation of hexenes. In contrast with previous reports, it has been found that the Pt/KL catalyst exhibits much higher aromatization activity than the Pt/Mg(Al)O catalyst. On Pt/KL the main product is benzene with hexenes and lighter compounds as principal by-products. By contrast, on the Pt/Mg(Al)O, the main products were hexenes [19].

In 1998, Carnuzares *et al.* synthesized metal/HM catalysts for isomerization of *n*-butane. They found that different Ni loading method, ion exchange or impregnation did not affect the activity of the catalysts. At low Ni contents an increase in conversion and selectivity to isobutane was obtained when the Ni content was raised. However, at high Ni content, the hydrogenolytic activity of the catalyst was enhanced, which led to a decrease in its selectivity to isobutane. A different behavior was found with Pd/HM catalysts. Pd is present as small particles in the ion-exchange catalysts, but forms clusters in the impregnated catalysts. Higher conversion and isobutane selectivity were obtained for the impregnated catalysts [20].

In 2001, Laila and co-workers reported the hydroconversion activities of 0.35 wt% of Pt/Al₂O₃ promoted by addition of a second metal (0.35 wt%) such as Ir, Rh, Re, or U, in the conversion of *n*-pentane and *n*-hexane at temperatures of 300 to 500°C. They also investigated the reaction by the addition of 3.0 wt% F into the mono- and bimetallic catalysts. Incorporation of second metal and fluorination improved the activity of Pt/Al₂O₃. The orders of selectivities of fluorinated bimetallic catalysts were: PtRe (15.4 wt%) > PtU (9.6 wt%) > PtIr (4.7 wt%) > PtRh (0.2 wt%) for hydroisomerization; PtRh (54.6 wt%) > PtIr (30.0 wt%) > PtU (27.1 wt%) > PtIr (0.9 wt%) > PtRh (0.07 wt%) for dehydrocyclization of *n*-pentane at 500°C [21].

In 2002 Lubango and Scurrall investigated the aromatization of propane over Zn- and Fe-ZSM-5 based catalysts (Si/Al ratio = 35). Metal was loaded using solid state ion exchange method. The Brønsted acid was lost by Zn substitution as evidenced by temperature programmed desorption [22].

In 2002, Nicolaidis *et al.* reported a comparative study of H-NAS, Zn-NAS and Ga-NAS catalysts (NAS = novel aluminosilicates, comprising ZSM-5-based structures having XRD crystallinities ranging from the substantially amorphous to the partially crystalline). Zinc or gallium was introduced by solid-state ion-exchange. Zinc appears to enhance both activity and BTX (benzene, toluene and xylenes) selectivity, relative to the zeolitic parent solid, in contrast to gallium, which affects only BTX selectivity [23].

In 2003 Suwanprasop *et al.* studied a continuous process for the production of aromatic hydrocarbons from *n*-hexane and C₅₊ natural gas liquid over Pd-loaded ZSM-5 zeolite (0.5%Pd content). *n*-Hexane conversion and aromatic contents were found to be 99.7% and 92.3%, respectively. Under the same reaction conditions, C₅₊ natural gas liquid gave 94.3% conversion and 92.6% aromatic [24].

In 2003, Jongpatiwut *et al.* studied the aromatization of *n*-octane on a Pt/KL catalyst prepared by vapor phase impregnation (VPI). The catalyst exhibited optimum performance for the *n*-hexane aromatization, the activity for *n*-octane aromatization at 500°C and 1 atm was low and it quickly dropped after a few hours on stream. The product distribution obtained from the *n*-octane conversion showed benzene and toluene as the dominant aromatic compounds, with small quantities of ethylbenzene and *o*-xylene. By contrast, on the Pt/SiO₂ catalyst used for comparison, ethylbenzene and *o*-xylene were the dominant aromatic products, although the overall aromatization activity was much lower than on the Pt/KL catalyst. The rapid deactivation found in the aromatization of *n*-octane on Pt/KL compared to that of *n*-hexane can also be explained in terms of the diffusional effects. The C₈-aromatics produced inside the zeolite diffuse out of the system with much greater difficulty than benzene. Therefore, they form coke and plug the pores to a greater extent than benzene [25].

In 2004, Agáta *et al.* studied the role of zinc in Zn/ZSM-5 in a batch aromatization of *n*-hexane, the conversion of 47.6% with 50.2% aromatic selectivity was obtained. Moreover, they also studied the Zn loading method into ZSM-5, which are ion exchange, mechanical mixing, and impregnation methods. They found that incorporation of Zn by ion exchange causes acid site strength redistribution and generation of new relatively Lewis acid sites in zeolite, thus increasing the selectivity of *n*-hexane aromatization in comparison with the parent NH₄-ZSM-5 zeolite [26].