CHAPTER II
LITERATURE SURVEY

2.1 n-Hexane Aromatization

The octane number of naphtha, or hydrocarbons derived from petroleum feedstocks having mostly 5 to 10 carbon atoms, is commonly increased by reforming reactions over Pt catalysts that produce high octane aromatic or branched paraffins. Therefore, aromatization of alkanes is an important process for upgrading motor fuels. Heavy naphthas containing hydrocarbons with 8 to 10 carbon atoms are effectively upgraded by bifunctional catalysts having both a Pt metal site and a surface acid site. Theses catalysts, however, are ineffective for upgrading light naphtha (C_5 to C_8) due to the poor selectivity to aromatics and the excessive cracking to light hydrocarbons.

A new catalyst, Pt supported on the potassium form of zeolite: (Pt/KL), was reported in 1980 to catalyze the aromatization of n-hexane with exceptionally high activity and selectivity (Davis, 1994). The nonacidic, L-zeolite reforming catalyst differs from conventional, bifunctional, having only a metal (platinum) function. The L-zeolite catalyst, therefore, benefits from the absence of acid-catalyzed hydrocracking resulting in higher liquid yields. Monofunctional reforming catalysts form aromatic products via one-six-ring closure and are unable to directly convert methylcyclopentane into benzene (Lane *et al.*, 1991).

Bernard (1980) reported the study that led to the development of an unusual monofunctional, nonacidic catalyst for cyclization of n-hexane

on zeolite L in the K-form, containing platinum. He found the very high activity and selectivity for aromatization of hexane over Pt/KL zeolite catalyst.

Hughes *et al.* (1986) showed that Ba incorporation can actually create acid sites as measured by IR spectroscopy of adsorbed pyridine inside the zeolite framework. However, calcination at 866 K was sufficient to remove all of the acid sites accessible to pyridine since Ba^{2+} cations migrated from open sites in the main channel of zeolite L to locked exchange sites behind the channel walls.

Mielczarski *et al.* (1992) also studied the effect of barium incorporation on the acidity and catalytic performance of Pt/L zeolites. Using ammonia adsorption and temperature-programmed desorption (TPD), they found two types of acid sites in uncalcined barium-exchanged zeolite L; one type was associated with strong acidity (high temperature NH_3 TPD peak) and one type was associated with weak acidity (low temperature NH_3 TPD peak) where the high strength sites were also presented on uncalcined KL zeolite. After calcination of BaKL and KL zeolites at 873 K, no peaks associated with the high strength acid sites were shown in either sample, and the KL sample adsorbed no ammonia which was consistent with the total lack of acidity of the KL zeolite. However, the low temperature peak associated with the weak acid sites on the BaKL sample was unaffected by calcination. Apparently, some of the Ba^{2+} cations remain in open sites in the main channels of zeolite L after thermal treatment and are still accessible to ammonia.

Tamm *et al.* (1987) elaborated on the mechanism on zeolite L which they found that the key step is the ring closure on a metal site of n-hexane to cyclohexane, which then rapidly dehydrogenates to benzene. Derouance and Vanderveken (1988) reviewed the literature and proposed a more specific confinement mechanism to interpret data on effects of the nature of paraffin carbon number and isomer structure on selectivity and activity.

Tauster and Steger (1990) discussed the idea that the linear channel structure of zeolite L collimated the diffusing flux of reagent n-hexane molecules. They also speculated that a linear orientation of the alkanes in the channels of zeolite L favored adsorption of n-hexane on a Pt cluster at a terminal carbon. They reasoned that if n-hexane preferentially adsorbed on the catalytically active Pt cluster at a terminal carbon, then 1,6 ring closure to form benzene must also be favored and the their results exhibited that Pt/KL catalyst gave both higher benzene selectivity and terminal hydrogenolysis than Pt/silica, which was consistent with the idea that terminal adsorption was enhanced on zeolite L catalysts as compared to non-acidic catalysts. They used the term 'molecular die catalysis' to describe the collimation effect that influenced the zeolite channels.

Collimating (geometric) effects were also found to be important during the hydrogenolysis of methylcyclopentane over Pt/L catalysts by Alverez and Resasco (1996). The statistical product ratio of 3-methylpentane to 2-methylpentane was 1/2 and values closed to this were found for hydrogenolysis reactions over Pt/silica. If molecules of methylcyclopentane were collimated by the zeolite so that the methyl group was parallel to the channel axis, then the production of 3-methylpentane and hexene should be favored. After eliminating cluster size effect, they found a strong preference for the formation of 3-methylpentane from methylcyclopentane over Pt/L catalyst compared to Pt/silica and this was interpreted as a confirmation that collimation effects were important for hydrocarbon reactions over Pt/L zeolites.

The mechanism of C_6 hydrocarbons on reforming catalysts; Pt/Mg(Al) O, Pt/K-L, Pd/Mg(Al)O, and Pt-Re/Al_2O_3 using the temporal analysis of products (TAP) reactor was investigated by Lafyatis et al. (1994). They used pulse experiments with several different of pure C_6 feeds in a continuous flow of H_2 at a pressure of 1 bar and temperature at 400 and 510°C. Under these

conditions, the reaction network for all of the catalysts appeared to occur by a monofunctional metal pathway: methylpentane, methylcyclopentane, n-hexane and benzene, respectively.

The influence of physico-chemical parameters such as crystallite size, nature of framework and extra-framework cation and extent of platinum loading on n-hexane dehydrocyclization over Pt/LTL zeolites was reported by Joshi *et al.* (1994). Catalysts with low crystallite size had higher selective transformation of n-hexane to benzene which can be attributed to the higher surface area and the smaller diffusional path length. Furthermore, the selective formation of benzene was favored by the framework cation having lower e/r (electric charge/radius) ratio due to suppressing of cracking reactions.

The effect of various additives to platinum catalysts was studied by Fukunaga and Ponec (1997). They found that the presence of K^+ or Mg^{2+} on various Pt supported catalysts increased the catalytic activity of n-hexane aromatization when compared to cation-free Pt catalyst. The role of the K^+ or Mg^{2+} was two-fold that were neutralization of acidic OH groups and influence on the reaction of platinum.

Jentoft *et al.* (1998) studied the influence of catalyst morphology on performance in n-hexane reforming. The morphology of the LTL zeolite support influenced the activity, selectivity and stability of LTL zeolite-supported platinum cluster catalyst, but the length of the zeolite crystallites (200-5000 Å) was found not to influence the catalyst performance. The study also showed that platinum in the intracrystalline zeolite pores and the platinum on the extracrystalline surfaces behaved differently. The platinum on the external surfaces was deactivated more rapidly than that in the zeolite pores because the platinum within the zeolite pores was protected from deactivation by coke formation by steric restrictions in the pores, whereas platinum on the extracrystalline surfaces was not.

2.2 Catalyst Preparation

The preparation of catalysts is frequently described as an art, and a catalyst recipe may specify detailed and arcane procedures that appear to be necessary in order to achieve reproducibility and the desired properties. Most catalysts are either finely divided metal supported on a carrier such as alumina or silica, or a compound, more or less complex, either on a carrier or unsupported (Satterfield, 1991).

2.2.1 Impregnation

This method is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metal salts. The catalysts that are made in this way may give a low dispersion of the metal on the carrier and can sinter more easily.

The method of Pt incorporation is also an important parameter in the synthesis of Pt/L aromatization catalysts. Ostgard *et al.* (1992) prepared Pt/KL catalysts by ion exchange (IE), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI+KCl) and the catalysts were characterized by dynamic techniques, chemisorption of H_2 and CO, Fourier transform-infrared spectroscopy (FT-IR) of adsorbed CO, and catalytic test using n-hexane and methylcyclopentane conversions as probe reaction. They found that size and location of Pt particles and their precursors in zeolite KL depended strongly on the method of introducing the precusor. Catalysts prepared by IWI contained, after calcination, predominantly Pt^{4+} ions with a minority of Pt^{2+} ions. In the calcined IWI+KCl catalyst virtually all Pt was present as Pt^{4+} ions. After reduction the Pt particles of the IWI catalysts (both with and without KCl) were located predominantly inside the channel, while in the IE sample part of the metal was located on the external zeolite surface. Moreover, the acidity of all Pt/KL catalysts was low. The order of increasing

acidity was IWI+KCl < IWI < IE. This confirmed that protons were formed in the reduction of Pt ions and that KCl reacted with protons to give HCl, which escaped.

The above results have been confirmed by Jacobs *et al.* (1998). TEM and EXAFS were used to characterize platinum particle resulting from IWI method and the results obtained from both techniques revealed that platinum particles were still small even were used to run the reaction.

2.2.2 Chemical Vapor Deposition

This method is widely used to control the pore size of zeolites and to improve the shape-selectivity of zeolite catalysts. It has been pointed out that CVD, which is the chemical adsorption of deposition reagent on the surface hydroxyl groups of zeolites, terminal silanols and acidic hydroxyl groups, played an important role in the deposition process. This kind of deposition might unavoidably causes the changes in both the geometric and electronic properties of the zeolite support (Zheng *et al.*, 1998). This method is sometimes called as vapor phase impregnation.

Metals loading by the vapor phase impregnation method has several advantages. First, it is possible to load metal into the molecular sieves with neutral frameworks as well as charged frameworks. Second, metal loading by this method could not change the acidic/base properties the molecular sieve whereas metal loading by ion exchange can change acidic properties of the support because of production of H^+. A novel Pt incorporation procedure involved sublimation of $Pt(AcAc)_2$ into dehydrated zeolite-L under controlled conditions (Hong *et al.*, 1992). The factors influenced metal loading were heating temperature, heating time and pressure inside the sealed tube containing the reaction mixture.

Jacobs *et al.* (1998) prepared Pt/KL zeolite catalysts by IWI (Incipient Wetness Impregnation) and CVD (Chemical Vapor Deposition) technique and

tested the activity of the catalysts on n-hexane aromatization. They found that CVD method resulted more homogeneous distributions of small Pt clusters inside the channels of the zeolite. These catalysts resulted in decreased hydrogenolysis activity and remarkably higher aromatization activity.

2.3 Catalyst Deactivation

It is necessary to know about the deactivation of the catalyst to be able to run an industrial process. While the topic of deactivation has received much attention in the last two decades, there still exist many unanswered questions. Deactivation of catalysts with time on stream is a phenomenon which occurs invariably in many industrial processes. Most catalysts used in heterogeneous catalytic processes are subjected to a decrease in the initial activity over a period of time. The time required for the activity of a catalyst to fall to an undesirable level varies with the severity of the process conditions and with the type of reaction being catalyzed.

Catalysts deactivate and must be regenerated or replaced. It can take less than a second, as in fluidized catalytic cracking, or several years, as in ammonia synthesis. Basically, three kinds of deactivation may occur: (1) sintering or thermal deactivation of the catalyst; (2) poisoning; (3) fouling or coking.

2.3.1 Catalyst Deactivation by Sintering

Sintering is a physical process associated with a loss of area of the catalyst which occurs when the catalyst is operated above the normal range of temperature. Such temperatures may occur throughout the catalyst or may be localized at the individual areas where reaction occurs. The sintering process may result in an overall loss of area of the support material or oxide base, or may cause a loss of dispersion of the metal crystallites in a supported

metal catalyst. Sintering may also be important in the reduction of the metal constituent of the catalyst.

Sintering is a complex phenomenon and despite much careful investigation it is still not possible to predict the rate at which the various structural characteristics (e.g. porosity and surface area) change for given operating conditions.

Treacy (1999) studied the role of Pt agglomeration and channel blockage in the deactivation of Pt/K-zeolite L aromatization catalysts by a transmission electron microscopy (TEM). A Z–contrast imaging study of Pt particle size distributions showed that there was an increase in the number of channel blockages by Pt with increasing catalyst reaction time. This problem was exacerbated by long zeolite L channel lengths while if the channels were too short, Pt seepage to the external surfaces became significant and the rate of coke production increased, again resulting in loss of accessible Pt.

2.3.2 Catalyst Deactivation by Poisoning

The most usual type of catalyst poisoning is caused by an impurity that is either present in the gas stream or is formed by some processes during the reaction. In both cases this poison becomes adsorbed on the active sites of the catalysts, causing a fall-off in the activity of the catalysts. The poisoning may be either temporary or permanent.

Most poisoning processes are effectively irreversible, so the catalysts have to be discarded ultimately but there is an important class of poisons that are reversible in action. In principle it is always possible to remove impurity poisons from the feed stream by purifying the feedstock or by using a guard catalyst, but to a level often required that may prove prohibitive. Therefore it may often be preferable for the catalyst to tolerate some degree of poisoning.

It should be emphasized that poisoning is not always undesirable. In some cases selective poisoning may be employed to enhance one reaction on a multifunctional catalyst whilst inhibiting a less desirable one.

Vaarkamp *et al.* (1992) studied the effect of sulfur poisoning on a working Pt/KL aromatization catalyst that contained Ba. The fresh and spent catalysts were characterized by EXAFS and H_2 chemisorption. The results showed the agglomeration of Pt metal after exposed to sulfur, leading to pore blockage. Furthermore, the activity of catalysts to aromatization was greatly diminished.

The effect of sulfur poisoning on the microstructure of Pt/KL aromatization catalysts was also studied by McVicker *et al.* (1993). They examined the poisoned catalysts by high-resolution transmission electron microscopy and found that the Pt agglomerates actually formed near the pore mouth, rendering the Pt clusters in the channel interior essentially inaccessible and, therefore, inactive for hydrocarbon reactions.

The addition of heavy rare earth metals as promoters to increase sulfur resistance was studied by Fang *et al.* (1997). They have examined a series of Pt-RE-KL catalysts containing 0.2 wt % of different kinds of rare earth (RE) (Gd, Tb, Dy, Tm, Yb and Lu) and sighted the surface behavior and catalytic properties of the catalysts. It appeared that addition of a suitable amount of some heavy rare earth elements to Pt-KL catalyst was very beneficial to the aromatic selectivity of Pt-RE-KL catalysts as well as beneficial to decrease the hydrocracking selectivity in aromatization of C_6 feedstock. In addition, the adding of heavy RE elements into KL catalyst also gave rise to an increase in the active site number, that was, an increase in the dispersity of active Pt particles, therefore, the sulfur sensitivities of the Pt-RE-KL catalysts were decreased.

In another study, Tm containing Pt/KL catalysts were prepared by a variety of techniques, including incipient wetness impregnation, ion exchange, and vapor phase impregnation methods and the catalysts were tested for n-hexane aromatization using sulfur free and sulfur-containing feed (Jacobs *et al.*, 2000). The results showed that the addition of Tm and Pt using the VPI method was found to yield the greatest enhancement to the aromatization performance of the Pt/KL catalysts studied. Tm was also found to act as a getter for sulfur, so it delayed the poisoning of Pt by sulfur-containing feeds. Therefore they suggested that Tm may directly modify Pt or even participate in accelerating the aromatization reaction.

2.3.3   Catalyst Deactivation by Fouling

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger amounts of material are responsible for deactivation in fouling processes than in poisoning. The most typical of fouling processes is that of the carbonaceous deposit or coke that forms on most catalysts used in processing of petroleum fractions or other organic chemical feedstocks.

Fouling is associated with relatively large amounts of deposit and, if excessive, in addition to covering the active sites of the catalyst it may affect the diffusional properties of the porous catalyst pellet. In the limit, pore blocking may occur from both coke and metal deposition, and if allowed to continue the deposits will block the void spaces between the catalyst pellets, necessitating a complete shut down of the reactor.

Iglesia and Baumgartner (1993) speculated that the geometric constraints imposed by the zeolite channels in the vicinity of an active Pt site inhibited bimolecular reactions that led to catalyst deactivation. Therefore the uniqueness of the Pt/KL catalysts may not result from the ability of zeolite L to stabilize small metal clusters or to promote some metal-suppport

interaction, but instead may be due to the unidimensional channel structure of zeolite L protecting the Pt clusters from side reactions that deposited unreactive carbon, which lowers both activity and selectivity.

Jacobs *et al.* (1998) tested the aromatization activity of Pt loaded on different supports and they found that the sulfided Pt/KL catalyst behaved like Pt/Mg(Al)O and Pt/SiO$_2$. This can be explained as in the case of migration of the metal particles from the interior of the zeolite channels to the outer surface. The outer-Pt particles were not protected from coking and thus lost their ability to aromatize the hexene. One can see that, in the first run, the effect of coke alone resulted in a relatively rapid increase in hexene production. These coked particles would remain active only for hexene production while those inside continued making hexenes, which were rapidly converted to benzene.