CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Catalyst for n-Octane Aromatization

Paál *et al.* (1980) discussed on aromatization of hydrocarbons with more than six carbon atoms. This reaction is thermodynamically even more favorable than the reaction of n-hexane because these hydrocarbons offer more than one way of cyclization. In case of n-octane, two octatriene intermediates may be formed, for which 1,3,5-octatriene would lead to ethylbenzene, and 2,4,6-octatriene would lead to *o*-xylene. The dehydrogenation of 2,4,6-octatriene will give octatetraene, which, in turn to styrene. The otho- xylene/ethylbenzene ratio increased, with increasing the hydrogen pressure. They also found effect of other variables, which can lead to increasing of *o*-xylene/ethylbenzene ratio, such as decreasing of Pt loading, increasing of tin addition, the poisoning of the catalyst with thiophene.

The conventional catalyst for octane aromatization is a bifunctional catalyst. Although the bifunctional catalyst showed an excellent activity for aromatization, hydrogenolysis occurred at the same time. This leads to the loss of aromatic selectivity. A monofunctional catalyst (has only metal site) has been considered as it can reduce this undesirable side reactions. Bernard *et al.* (1980) studied the Pt supported on the series of supports such as KL, NaX, NaY, NaOmega and NaMordenite for n-hexane aromatization. It was found that at 733 K and 1 atm, the most active catalysts were Pt/NaX and Pt/KL. These two catalysts had very high selectivity to aromatics. Thereafter many researchers have tried to investigate the differences in the aromatization performance of Pt/KL or Pt/support catalysts.

2.2 Catalyst Preparation

Supported-metal catalysts are usually prepared by ion exchange (IE), incipient wetness impregnation (IWI), and vapor phase impregnation (VPI) methods on a high surface area support. Each method results in different distribution size and location of metal. The catalyst prepared by these techniques has the metal dispersed

on the surface of the support as small crystallites. These crystallites are usually 8 to 100 Å in diameter, depending on the preparation method.

From previous studies, there are three methods for loading Pt on L-zeolite. Catalysts prepared by VPI method were found to be more active, selective, and stable for n-octane aromatization than IWI and IE catalysts.

Jacobs *et al.* (1999) synthesized Pt/KL catalysts by difference methods including IE, IWI and VPI, and investigated the effect of metal loading. The catalysts were pretreated at two different reduction temperatures; 400 and 500°C, in order to investigate the sensitivity of each catalyst to thermal treatment. All catalysts were characterized by using hydrogen chemisorption and high dispersion and FT-IR of adsorbed CO. The results showed that all catalysts exhibited high dispersion, and H/Pt ratio was greater than unity. FT-IR of adsorbed CO was used to characterize locations of Pt clusters. IE catalysts have a high fraction of Pt cluster located at external surface of L-zeolite, and were the most sensitive to thermal treatment. These catalysts were easily deactivated by coke formation. IWI and VPI catalysts showed a majority of Pt cluster located inside channel of L-zeolite. After thermal treatment, IWI catalysts were damaged by half of their activity, while the performance of VPI catalysts remained unchanged. In addition, different VPI methods were studied, including under moderate vacuum and a helium flow. Both of which showed similar results as when high vacuum was applied.

Jongpatiwut *et al.* (2002) studied the aromatization of n-octane on Pt/KL catalyst by VPI methods. It was found that the activity of Pt/KL catalyst for n-octane aromatization was low and it quickly dropped after a few hours on stream. The product distributions were mostly benzene and toluene with small quantities of ethylbenzene (EB) and *o*-xylene (OX), which are the expected products from the direct closure of the six-member ring. Benzene and toluene are secondary products resulting from the hydrogenolysis of ethylbenzene and o-xylene. Diffusional effect plays a significant role in determining this product distribution. Since ethylbenzene and *o*-xylene are produced inside the channels of zeolite, they are hydrogenolysed before they can escape. Because the C8 aromatics produce inside the zeolite diffuse out of the system with much greater difficulty than benzene (critical size of EB and OX are 6.7 A° and 7.4 A°) so it making longer resident time of OX inside the pore, it

is easier to be hydrogenolyzed and plug the pore. Therefore, they form coke and plug the pores to greater extent than benzene.

Jongpatiwut *et al.* (2004) studied the n-octane aromatization on Pt catalysts supported on the potassium form of different large-pore zeolites (K-LTL, K-BEA, K-MAZ, and K-FAU). All catalysts were prepared by VPI method. It was found that the Pt/K-LTL catalyst exhibit a better aromatization performance than the other zeolite catalysts. However, due to secondary hydrogenolysis, The C8 aromatics produced inside the zeolite are converted to benzene and toluene.

From these two previous work, we observed that the hydrogenolysis become a factor to the C8 aromatics produced inside the zeolite are converted to benzene and toluene so, the idea of reducing hydrogenolysis, enhancing life, activity, and selectivity of catalyst in n-octane aromatization has been discussed. One of them is the bimetallic Pt-Sn catalyst which the second element (Sn) acts as the metal promoter.

Various preparation procedures have been used for supported platinum-tin catalysts. The preparing methods that have been used for Pt-Sn catalyst are incipient wetness impregnation method and using the bimetallic complex precursor, e.g. $[Pt(NH_3)_4][SnCl_6]$, prepared on the support such as alumina, SiO2 and zeolite. It has been found that the methodology followed in the preparation of Pt-Sn catalyst may lead to different metallic phase and therefore such methodology plays an important role in determining the nature of the solid and its catalytic performance.

Coloma *et al.* (1996) contrasted the properties of several catalysts supported over carbon black, prepared by both co- and sequential impregnations and found the presence of tin in both metallic and oxidized states in the reduced catalysts with different relative amounts depending on the preparation method.

Chantaravitoon *et al.* (2004) found that coimpregnation of Al_2O_3 support with small amounts of tin facilitates high Pt dispersions, while sequential impregnation of the support with Sn first followed by Pt leads to much lower Pt dispersion.

Baronetti *et al.* (1985) used three different methods to make the Pt-Sn/Al_2O_3 catalyst: (A) coimpregnation of H_2PtCl_6 and $SnCl_2$; (B) two-step impregnation of alumina, first by Pt, then drying and impregnation of Sn; (C) two-step impregnation,

the same as B but in the reverse order. The TPR profiles for the catalysts A and B were about the same, but differed from C. They concluded that the interaction between the metals in the latter catalyst is weaker compared to the former two. The same research group has continued to study the bimetallic catalyst. They conclude that repeated oxidation and reduction, as in regeneration, will contribute to more Pt-Sn alloy formation.

As mentioned above, the order of metal loading plays an important role in catalytic properties and their performances. This research will emphasized on loading Pt and Sn via coimpregnation and two-step impregnation method in order to compare their surface characteristics and catalytic behaviors.

2.3 Promoter

The term *promoter* is used in a rather general sense to refer to a substance that, when added in relatively small amounts in the preparation of a catalyst, imparts better activity, selectivity, or stability. In some cases the promoter may be added to the reactant in small amounts and it acts by being adsorbed onto the catalyst. The increased performance is greater than that attributable to the promoter acting independently, which in many cases has no activity by itself for the specific reaction. The term is used to cover a wide variety of phenomena, but most promoters can be classified as textural promoters or structural promoters. A textural promoter acts by a physical effect and a structural promoter acts by a chemical effect (Gates *et al.*, 1991).

A *textural promoter* is an inert substance that inhibits the sintering of microcrystal of the active catalyst by being present in the form of very fine particles. These separated the true catalyst particles from contact with one another so they do not coalesce, thus preventing or minimizing loss of active catalyst area during service. To be effective, the textural promoter must be of somewhat smaller particle size than that of active species it must be well dispersed, and it must not react with or form a solid solution with the active catalyst. As a minimum, it must have a relatively high melting point (Gates *et al.*, 1991).

In contrast to a textural promoter, a *structural promoter* causes a chemical effect it changes the chemical composition of the catalyst. In many cases the effect of structure promoter is clear, but its mechanism of action is not. In other cases, it is not clear whether the effect of promoter is primarily a physical or chemical effect.

2.4 Effect of Tin on the Catalyst

A number of promoter metals (e.g., Re, Sn, Ir) have been used as additives for naphtha reforming Pt catalysts to increase catalyst lifetime by hampering coking and/or to improve selectivity of desired product. Some of the additives have catalytic properties on their own (Re, Ir) while others are catalytically inactive (Sn). Tin added to Pt catalysts for naphtha reforming may be a good candidate for shifting the reforming selectivity toward non-degradative products, in particular, isomerization, rather than to the production of aromatics, which become undesirable components in commercial naphtha (Ponec *et al.*, 1995).

Tin can modify the stability and selectivity of the Pt function in two ways:

1. By an *ensemble effect*: Tin decreases the number of contiguous platinum atoms, tin atoms dividing the platinum surface into smaller ensembles. By doing that multipoint adsorption of hydrocarbon molecules on the surface is hampered; thus, hydrogenolysis and deactivation by coke deposition can be reduced (Guczi *et al.*, 1994).

2. By an *electronic effect*: Tin changes the electronic environment of Pt atoms. This type of interaction between Pt and the additive results in more electron deficient Pt atoms, which influence markedly the adsorption-desorption steps of the catalytic reaction (Parera *et al.*, 1986).

2.5 Pt-Sn Catalyst

The modified catalytic properties of Pt have been investigated by many researchers. The modified catalytic behavior of Pt-Sn catalysts exhibiting improved reforming selectivity and reduced deactivation by coking has been explained by many as an ensemble or ligand effect. Dautzenberg *et al.* (1980) and Biloenl *et al.*

(1980) suggested that the effect of tin was to divide the Pt surface into a smaller number of contiguous platinum atoms and that this arrangement brings about the beneficial effects on the selectivity and stability of the catalysts (ensemble effect). However, Burch and Garla et al. (1981) proposed that the role of tin was to modify the electronic properties of the small platinum particles (ligand effect). Another question under discussion is whether the state of the tin atom in platinum-tin catalysts is in zero valence or in an oxidation state. Although some researchers reported that tin was present in an oxidized state in platinum-tin catalysts and that the interaction between Pt and Sn^{+2} or Sn^{+4} may be the cause of an increased selectivity and better activity maintenance (Yang et al., 1992), Srinivasan et al. (1992) reported that part of tin was present in a metallic state and alloyed with platinum and the alloy was responsible for a higher selectivity and increased stability. Much progress has been made in understanding such a system, but some issues on the effect of Sn on supported Pt-Sn catalysts are still a matter of debate. The reactions of hydrocarbons on supported catalysts in general are quite complex because of the nature of the interaction of the various components in this system.

2.6 n-Octane Aromatization over Pt-Sn Catalyst

Pt-Sn bimetallic catalysts lead to pronounced changes in properties of catalytic activity and selectivity. In 1999, Rangel et al. studied Pt, Pt-Sn and Pt-W supported on γ-Al_2O_3 catalyst with reactions of n-octane reforming, cyclohexane dehydrogenation, and n-pentane isomerization. They found that Pt was completely reduced to Pt° metal, but only a small fraction of Sn of W oxides were reduced to metal. The second element decreased the metallic properties of Pt (H_2 chemisorption and dehydrogenation activity) but increased dehydrocyclization and stability. In spite of the large decrease in dehydrogenation activity of Pt in the bimetallics, the metallic function was not the controlling function of the bifuctional mechanisms of dehydrocyclization. Pt-Sn/Al_2O_3 was the best catalyst with the highest acid to metallic functions ratio (due to its lower metallic activity) presenting a xylenes distribution different from the other catalysts. The acid function of Pt-Sn/Al_2O_3 is

tuned in order to increase isomerization and cyclization and to decrease cracking as compared to Pt and Pt-W catalysts.

Lee S.H. and Lee H. *et al.* (1994) studied the dehydrogenation of n-octane over Pt-Sn/γ-Al$_2$O$_3$, the bimetallic Pt-Sn catalyst prepared by simultaneous impregnation as a complex showed higher activity than the catalyst prepared by successive impregnation with SnCl$_2$ and H$_2$PtCl$_6$, and the suspended Pt-Sn catalyst showed more enhanced catalytic behaviors in C$_8$-aromatics formation than the normal one. The geometric factor was an important parameter for the positive effect on catalytic activity in n-octane conversion, while the electronic factor, the electron density of the metal, was that in the aromatization of n-hexane.