

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Pt/KL Catalyst

Platinum-containing KL (Pt/KL) zeolite is a world wide catalyst for commercial reactions due to its ability to induce aromatization of linear alkane. This interesting characteristics has generated many researchs on the catalyst. Many explanations have been introduced for its unique characteristic as far.

One of Pt/KL's interesting characteristics is collimating (geometric) effect discussed by Tauster and Steger (1990). Due to its geometric structure (*i.e.*, one-dimentional channel system with portholes of  $\sim 7.3\text{\AA}$ ), hexane molecules should enter Pt/KL's pore horizontally, leading to a terminal carbon molecule adsorption and therefore inducing 1,6-ring cllosure which further dehydrogenation to benzene. Terminal cracking of hydrogenolysis results evaluated from "Terminal Cracking Index", *e.g.*,  $C_5/C_4$  ratio, supports the above idea. For the case that the terminal carbon atom adsorption is favored, the terminal cracking should be favored either, resulting in high value of terminal cracking index. As a consequence, both aromatization selectivity and terminal cracking index are enhanced by the terminal adsorption of hexane on the platinum surface, which is the affect of the unique property of Pt/KL catalyst. In addition, methylcyclopentane (MCP) ring opening investigated by Alvarez and Resasco (1996) can demonstate the existence of collimating effects in Pt/KL catalyst. For this case, the steric effect of methyl branched group in MCP molecules caused the MCP molecules enter to the zeolite's pore horizontally. This is called collimating effect. According to the collimating effect, MCP molecules entered the zeolite pore and such molecules were not able to roll over, hence, resulting in the formation of 3-methylpentane (3MP)

molecules (Alvarez and Resasco, 1996). For Pt/Mg(Al)O, the 3-methylpentane (3MP)/2-methylpentane (2MP) ratios were significantly lower than those obtained from Pt/KL series. This may be explained by collimating effect. Besides, 3MP/2MP ratios for Pt/BaL showed the lower value than Pt/KL catalyst (Alvarez and Resasco, 1996). The explanation of this feature is a partial blocking of the zeolite channels by Ba<sup>2+</sup> cations, which does not occur on the KL zeolite treated under the same condition.

## 2.2 Catalyst Preparation

The purpose of the preparation technique is to disperse the catalytic components onto the support in order to maximize their availability to the adsorption of the reactants. The dispersion, the fraction of the metal atoms deposited on the surface, is well defined by Fogler (1999). Heck and Farrauto (1994) examined the dispersion equation as the fraction of catalytic sites on the surface to the total catalytic sites (See Equation 2.1).

$$\%Dispersion = \frac{\text{Number of catalytic sites on the surface}}{\text{Theoretical number of sites present}} \quad (2.1)$$

Although bifunctional catalysts (*i.e.*, catalysts with both metal sites and acid sites) can shift the reactions to the right direction, coke formation and side reactions can still occur. These undesired formations are enhanced by intermediate carbenium ions which are the affactation of the existance of acid sites on catalyst surface. Incipient Wetness Impregnation (IWI) method gives lower acidity of catalysts and smaller platinum partical size than Ion Exchange (IE) method. Electron micrograph results show evident of platinum particle outside the channels of the zeolite for Ion Exchange method, but no platinum particles larger than the size of the channels were observed for Incipient

Wetness Impregnation method. In the recent years, Vapor Phase Impregnation (VPI) method, a new technology, has shown good results in aromatization selectivity of benzene (Jacob *et al.*, 1998). The Extended X-ray Absorption Fine Structure (EXAFS) and Transmission Electron Microscopy (TEM) data observed by Jacob and his coworkers (1999) corroborates a very high degree of metal dispersion of Pt/KL series prepared by both IWI and VPI method. The advantage of VPI method over IWI method was reported by Jacobs *et al.* (1998). According to their TEM results, the IWI method gave a Pt/KL catalyst, with some larger platinum clusters outside the channels of the zeolite. The FT-IR of adsorbed CO can determine the morphology and location of platinum clusters on the catalysts, both inside and outside the channels of the zeolite. Stakheev *et al.* (1995) proposed that the different regions of wavenumber corresponding to the variations of morphology of platinum clusters. Regarding to this hypothesis, the low wavenumber bands (2050-1930  $\text{cm}^{-1}$ ) are assigned to Pt-CO species formed from the disruption of small platinum clusters inside the L-zeolite channels. The bands between 2050-2075  $\text{cm}^{-1}$  correspond to the larger platinum clusters in the near-surface region of the L-zeolite. The bands above 2075  $\text{cm}^{-1}$  are generally assigned to the larger platinum particles outside the zeolite channels. The FT-IR results of adsorbed CO on Pt/KL zeolite done by Sackamduang *et al.* (2001) showed the corresponding idea with Jacobs' work (1998). The wavenumbers shown by Pt/KL prepared by VPI method were associated with small platinum clusters located inside the channels of the zeolite, while the Pt/KL prepared by IWI method represented the bands at higher wavenumber which correspond to the larger platinum clusters (Sackamduang *et al.*, 2001). These studies indicated the advantage of VPI over IWI.

### 2.2.1 Incipient Wetness Impregnation (IWI) Method

IWI is one of many methods to achieve a loading of highly dispersed platinum particles onto the support. Besides, this method gives very small particle size of Pt loaded onto the support with low acidity leading to being monofunctional having only the metallic function. The detailed steps of this method will be described in Chapter 3. In order to get rid of many impurities and to clean the pores, KL zeolite has to be calcined prior to platinum impregnation. Deionized water was used as a medium to carry the platinum particles to impregnated on the zeolite, both inside and outside the pores. The last calcination reformed absorbed platinum to oxide form which is more stable and more appropriate to restore.

### 2.2.2 Vapor Phase Impregnation (VPI) Method

VPI, a new modified method, has been widely used over recent years. Impregnation of metal particles onto the support in vapor phase is the feature of this method. Due to the sublimation property of  $\text{Pt}(\text{AcAc})_2$ , platinum precursor in acetyl-acetonate form ( $\text{Pt}(\text{AcAc})_2$ ) is necessary for this method. After  $\text{Pt}(\text{AcAc})_2$  adsorbs onto zeolite surface, moisture and organic composites were removed from the sample by drying process. With the same objective as IWI mentioned above, the last calcination reformed Pt impregnated onto zeolite. Jacobs and his coworker (1998) suggested that VPI (by sublimation of  $\text{Pt}(\text{AcAc})_2$ ) achieved more uniform distribution of small particles located inside the channels of the zeolite. This may be a consequence of impregnation in vapor phase rather than that in liquid phase used for IWI.

## 2.3 Atomic Absorption Spectroscopy (AAS)

Atomic absorption is a procedure based on the principle that each particular element can absorb only one wavelength of light. In other words,

the light absorbed has to contain the equal same amount of energy as the energy which can excite the electron from ground state to the first excited state. Together with the fact that each element needs different amount of energy to excite its electron from ground state to the first excited state, AAS can be practically applied.

Under thermal equilibrium conditions, the number of the ground state atoms is related to the number of the excited state atoms as shows in Equation 2.2.

$$\frac{N_j}{N_0} = \frac{g_j}{g_0} e^{-\Delta E / kT} \quad (2.2)$$

where:

$N_j$  = the number of the excited state atoms

$N_0$  = the number of the ground state atoms

$g_j$  = statistical weight for excited state

$g_0$  = statistical weight for ground state

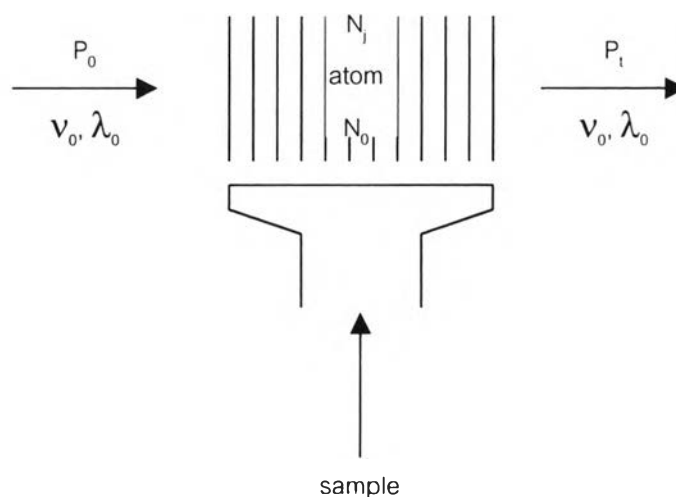
$\Delta E$  = differential energy of excited state and ground state ( $E_j - E_0$ )

$k$  = Boltzmann constant =  $1.38 \times 10^{-16}$  erg/deg

$T$  = temperature in Kelvin.

Normally,  $N_j$  is much less than  $N_0$ , which is very efficient for the use of AAS. The statistical weight can be found from  $g = 2J+1$ , and  $J = L + S$  or  $L - S$ , where  $J$  is Russell–Saunders coupling,  $L$  is total orbital angular momentum number ( $L = 0, 1, 2, 3$ ), and  $S$  is spin quantum number ( $S = \pm 1/2$ ).

When excited atom is back to the ground state, photon containing  $I_\nu$  intensity is emitted.



**Figure 2.1** Atomic absorption spectroscopy (AAS) system.

$$I_\nu = V \cdot A_{0j} h \nu N_0 (g_j/g_0) e^{-\Delta E/kT} \quad (2.3)$$

$$P_t = P_0 e^{-k_n \cdot b} \quad (2.4)$$

where:

$V$  = detected flame volume

$A_{0j}$  = Einstein probability coefficient

$P_0$  = initial radiant power

$P_t$  = remained radiant power

$k_n$  = absorption coefficient

$B$  = absorbing medium.

#### 2.4 Brunauer – Emmett – Teller (BET) Surface Area Analysis

This most commonly used method to determine the surface area of catalyst was developed by Brunauer, Emmett, and Teller in 1938. The adsorption data were calculated from the Brunauer – Emmett – Teller (BET) Equation, as shown in Equation 2.5.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1) P}{V_m C P_0} \quad (2.5)$$

where:

$V$  = volume of gas absorbed at pressure  $P$

$V_m$  = volume of gas absorbed in monolayer

$P_0$  = saturation pressure of adsorbate gas at the experimental temperature

$C$  = constant related exponentially to the heats of adsorption and liquefaction of the gas.

$$C = e^{(q_1 - q_L)/RT} \quad (2.6)$$

where:

$q_1$  = heat of adsorption on the first layer

$q_L$  = heat of liquefaction of adsorbed gas on all other layers

$R$  = gas constant.

BET concepts applied in BET Equation (See Equation 2.5) were well documented by Satterfield (1991). For the first layer, the rate of evaporation is considered to be equal to the rate of condensation, and the heat of adsorption is taken to be independent of coverage. For layer beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layer still vacant. The rate of desorption is taken to be proportional to the amount present in that layer. The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas.

At high  $P/P_0$  values, complexities associated with the realities of multilayer adsorption and/or pore condensation cause increasing deviation. The appropriate relative pressures  $P/P_0$  are in the range of 0.05 - 0.3. For

microporous substances such as zeolites, the linear region on a BET plot occurs at much lower values of  $P/P_0$ , typically around 0.01 or less. The surface area can be determined by using Equation 2.7.

$$S_g = \frac{V_m}{0.0224} (6.02 \times 10^{23}) (A) \quad (2.7)$$

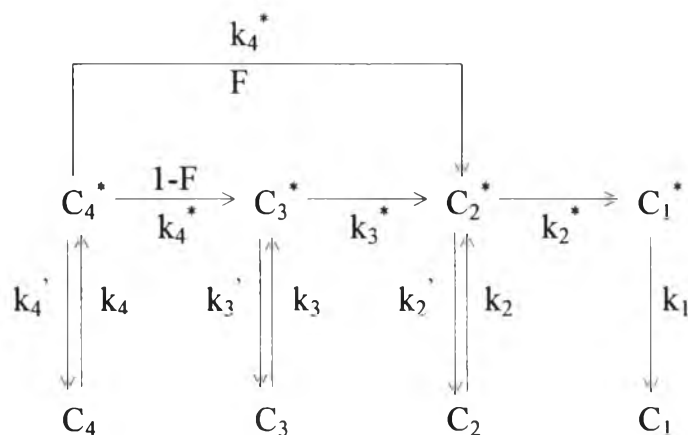
where:

$S_g$  = specific surface area

$A$  = area occupied by each adsorbate molecule.

## 2.5 n-Butane Hydrogenolysis

Hydrogenolysis of n-butane is defined as the rupture of C-C bonds in the presence of hydrogen. The initial steps in such reaction are hydrogen dissociation and dissociation of C-H bond. Bond and Hui (1992) proposed the mechanism of n-butane hydrogenolysis as shown in Figure 2.2.



**Figure 2.2** n-Butane hydrogenolysis mechanism.

The reaction scheme (See Figure 2.2) allows fission of  $C_4^*$  to occur at either the center or a terminal C-C bond. The same mechanism was originally proposed by Kempling and Anderson (1972). They determined the rate of



disappearance of n-butane from the appearance of products in the effluent stream, as illustrated in Equation 2.8.

$$r = M \frac{(0.75 Y_3 + 0.5 Y_2 + 0.25 Y_1)}{W} \quad (2.8)$$

$$A = \frac{1}{4} \sum_{j=1}^3 j Y_j \quad (2.9)$$

where:

$r$  = rate of disappearance of butane

$M$  = effluent flow rate

$Y_3$  = mole fraction of propane

$Y_2$  = mole fraction of ethane

$Y_1$  = mole fraction of methane

$W$  = weight of catalyst in reactor

$A$  = mole of butane reacted

$Y_j$  = mole fraction of products containing  $j$  carbon atoms ( $j < 4$ ).

The selectivity for a reaction product was defined as the moles of that product formed divided by the moles of butane reacted.

$$S_j = \frac{Y_j}{A} \quad (2.10)$$

$$X = \frac{A}{A + Y_4} \quad (2.11)$$

where:

$S_j$  = selectivity of product  $j$

$X$  = fractional conversion

$Y_4$  = mole fraction of n-butane in the effluent stream.

Further complex variables were developed for more understanding in such reaction (Bond and Cunningham, 1996, 1997; Bond and Lin, 1997).

$$T_j = \frac{k_j'}{(k_j' + k_j^*)} \quad (2.12)$$

where:

$T_j$  = probability of an intermediate in either reaction containing  $j$  carbon atoms returning to the gas phase as the corresponding alkane rather than suffering further cracking

$k_j'$  = rate constant for desorption

$k_j^*$  = rate constant for further bond breaking.

At low conversion;

$$\frac{S_2}{T_2} = 1 + F - S_3 \quad (2.13)$$

$$\frac{S_3}{T_3} = 1 - F \quad (2.14)$$

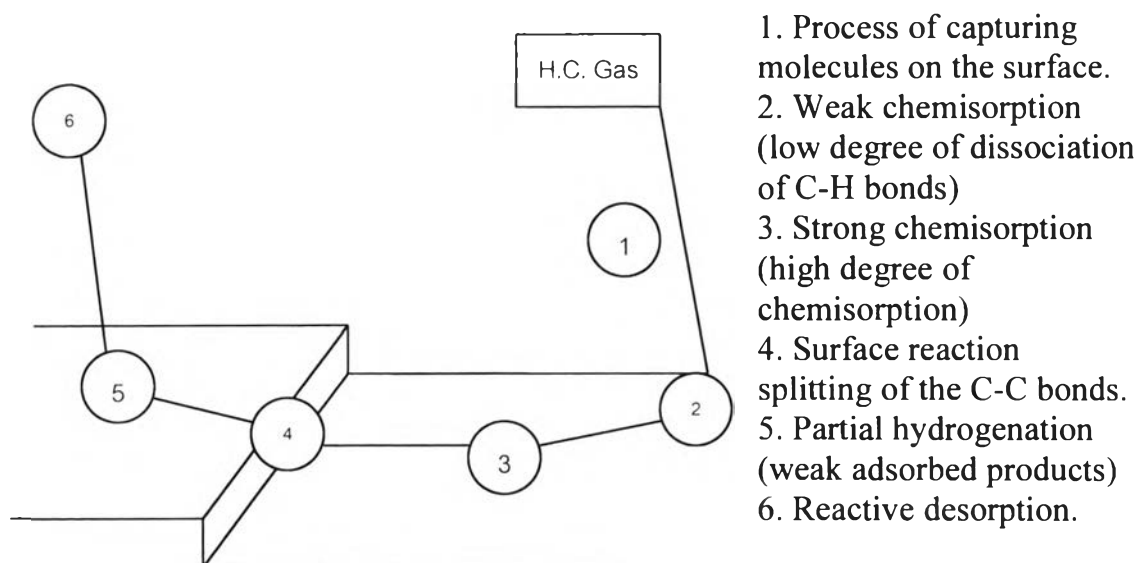
$F$  represents the probability of breaking the central C-C bond in n-butane. If the central and terminal C-C bonds have the same chances of breaking,  $F$  will be 0.33; higher values imply preferential breaking of the central bond and vice versa (See appendix A for detailed calculations).

Guczi *et al.* (1983) summarized very good hypothesis described as follows. When a power rate is used to correlate the rate of hydrogenolysis with the reactant pressure, e.g., rate =  $kP_{CH}^n P_{H_2}^m$ , it is usually found that:

- $n$  is positive and  $m$  is negative at pressure between 1.3 and 100 kPa.

- $m$  increase with increasing temperature and  $n$  approaches zero at high temperature.
- A maximum in the rate may be found in the system with a fixed hydrocarbon pressure and varying hydrogen pressure from very low to high values, but this occurs less frequently in the system with varying hydrocarbon pressure.
- The maximum in the rate is shifted to a higher value of hydrogen pressure if
  - The carbon number in the hydrocarbon increases
  - The temperature of the reaction increases
  - The metallic dispersion of supported metal catalysts increases.
- Normally the location of the maximum in the curves of rate versus hydrogen pressure is different for hydrogenolysis and isomerization.
- The maximum rate occurring with varying hydrogen pressure is not found at the same hydrogen pressure when different metals are used.

Figure 2.3 shows the general hydrogenolysis process.



**Figure 2.3** Elementary steps in the mechanism of hydrogenolysis.

Kempling and Anderson (1972) investigated n-butane comparing with i-butane hydrogenolysis on supported ruthenium. One interesting discussion of this work is that the pre-exponential factor for the hydrogenolysis of i-butane was lower than that of n-butane. They suggested that this significant value may be due to the steric effect of the branched group which may have interfered with the adsorption of the hydrocarbon or with the interaction of the adsorbed species and hydrogen. Therefore n-butane was more reactive than i-butane. Besides, they found that i-butane was as reactive as propane, and ethane has the least reactivity. In addition, they mentioned that the rupture of the carbon-carbon bond is the slowest step of the reaction sequence. In their paper, they also mentioned about an  $\alpha$ - $\beta$  diadsorption, with two adjacent atoms completely devoid of hydrogen, of ethane and propane hydrogenolysis on ruthenium. This argument can be extended to n-butane hydrogenolysis. n-Butane reacts in different ways on ruthenium and nickel. On ruthenium all C-C bonds have about the same probability to be broken, while only terminal bonds broke on nickel.

The mechanism of n-butane hydrogenolysis was early proposed by Kempling and Anderson (1972), which involved reversible dissociative chemisorption of n-butane and hydrogenolysis products, and irreversible splitting of the carbon-carbon bonds of the adsorbed species. The connection between isomerization and central carbon-carbon bond fission was postulated as a 2,3-diadsorption mechanism (Bond and Lin, 1997). In this work, many parameters were calculated based on the previous mechanism.