Chapter 3

Theory

The purpose of the study is to better understand the nature of coke on metal site and it formation. But one should have some background of dehydrogenation reaction, catalyst deactivation and coking. Moreover, the effect of coking on dehydrogenation reaction and some parameters on coke formation on metal sites are also mentioned in this chapter.

In addition, this research used platinum supported on alumina as the catalyst and propane dehydrogenation as the test reaction. Coking on metal sites and its effect will be discussed in the later section.

3.1 Catalytic dehydrogenation of propane

The catalytic dehydrogenation process has been developed for converting normal and iso-butane, propane and ethane to olefins. The catalytic dehydrogenation of light alkanes has a great importance because it represents an alternative for obtaining alkenes for polymerization and other organic syntheses from low cost saturated hydrocarbon feed stocks.

Platinum supported on alumina catalyst and its series have been used for propane dehydrogenation. These catalyst are highly selectivity and conversion; however, it is easily deactivated by coking.

Propane dehydrogenation is illustrated by the simple reaction:

$$C_3H_8 \longleftrightarrow C_3H_6 + H_2 \qquad \Delta H_{298}^o = 124 \text{ KJ/mol.}$$

This reaction is highly endothermic and exentropic and is favored at high temperature (>700 ^{0}C) and low pressure (<100 kPa absolute).

Rising of temperature leads to the increase of side reactions such as cracking, hydrocracking, hydrogenolysis and dehydrogenation, therefore, methane ethylene, ethane, methylacetylene, allene, especially coke, etc. are occurred. Coke deposits is so rapidly formed that the catalyst activity can only be maintained by frequent regenerations, either cyclic or continuous. At the industrial stage, these two possibilities have led to two type of process, also employing catalyst of different types. The former is associated with the Air products (Houdry) Catofin and Phillips technologies. These processes employed chromium oxide/alumina system doped with potassium or sodium oxide as the catalyst. And the later process is the UOP Oleflex technique.

The UOP technology is very compact, and comparable to that of regenerative reforming. It features a series of three stacked reactors, through which the catalyst flow by gravity. Heat is provided by the passage of the feed, recycles of unconverted hydrocarbons and hydrogen gas and also of intermediate effluents, in the different compartments of the same furnace. At the bottom of the lower reaction stage, the catalyst system is picked up by a nitrogen lift to the top of the first reactor. The catalyst is based on precious metal deposited on alumina. Dehydrogenation takes place in a fixed bed reactor in the gas phase at a temperature of about 400-500 ^{0}C and low pressure 0.2-0.3 MPa. With propane, the process offers selectivity up to 85 percent of propylene. (Petro chemical processes,1989)
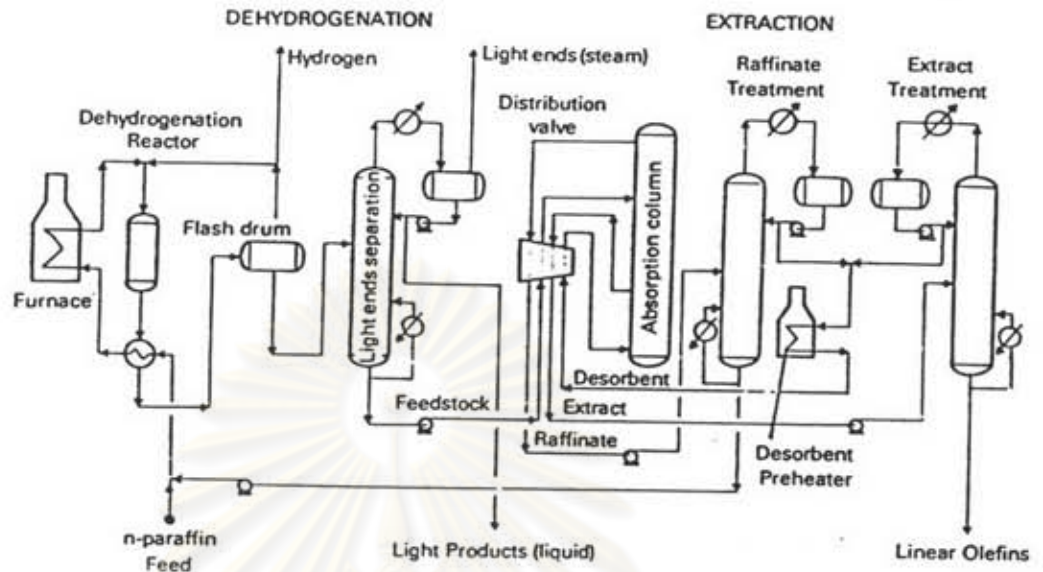
Figure 3.1 UOP Pacol/Olex process

3.2 Catalyst Deactivation

Catalyst deactivation is referred to the loss of catalyst activity or its selectivity. The causes may be grouped loosely into four groups (Satterfield, 1980)

3.2.1. <u>Poisoning.</u> A catalyst poison is the reduction of catalyst activity by an impurity which presents in the feed stream. The impurity absorbs on active site and inhibits the reactant to access active sites.

3.2.2. <u>Fouling.</u> The term fouling is generally used to describe a physical blockage such as the deposit of dust or fine powder or carbonaceous deposits (coke). In the latter case activity can usually be restore by removal of the coke by burning.

3.2.3. <u>Sintering.</u> This phenomenon is an irreversible physical process leading to a reduction of active surface.

3.2.4. <u>Loss of active species.</u> It is the loss of the compound of catalyst which associate in the reaction. In addition, the compound may be converted to another from less active (for example chlorine loss in regeneration step of dehydrogenation catalyst).

3.3 Coking on metal based catalyst.

Coke or carbonaceous compound is the compound of carbon and H_2 which contains little of H_2 or has H/C ratio less than one. All reaction concerning with hydrocarbon can cause coke deposits on catalyst such as dehydrogenation, reforming, catalytic cracking or oxidation reaction.

Basically, consideration of coking materials can infer two types of coke I) coke from reactant and ii) coke from impurities which contaminate in feed stream. (Hughes, 1984). The first type of coking occurs when the reaction concerned with hydrocarbon. Since coke deposition originates from cracking reaction either in the feed stream or in the products. In addition, coking from reactants can be provided into parallel coking formation or series coking formation which can be written as follow :

$$A \longrightarrow B \qquad \text{Parallel coking formation}$$
$$A \longrightarrow C$$
$$A \longrightarrow B \longrightarrow C \qquad \text{series coking formation}$$
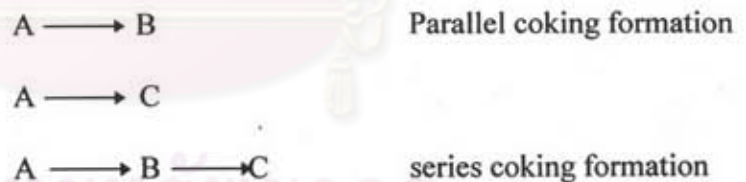
Thus, parallel coking gives large coke deposits when reactant concentration is high, because the reactant is the coke precursor. Therefore, when coking occurs by parallel mechanism, the greatest deposition of coke would be expected at the inlet of the reaction. Conversely, larger coke deposits are formed in series coking when product B has a high concentration because this is the intermediate precursor of the

coke in this case. In normal operation the product concentration increases with distance along the reaction, and therefore the coke distribution should follow a similar pattern.

The other type of coking does not involve the main reaction but coke forms on the catalyst by impurity.

$$A \longrightarrow B \qquad \text{main reaction}$$

$$I \longrightarrow C \qquad \text{side by side reaction}$$

Coking on the catalyst may occur by one feature or combination of all the three features.

3.3.1 composition, location and nature of coke on Catalyst.

Barbier and co-wokers (1987) used temperature program oxidation to burn coked catalyst and found two peaks at around 300 ^{0}C and the other around 450 ^{0}C. They defined the first peak as coke on metal sites and the second peak as coke on acidic support. Both cokes has formula CHx. but coke on metal is less dehydrogenated than coke deposited on the support. It means coke on metal has more hydrogen in molecules than coke on support.

Extraction of coke with solvent and analysis of extractable compound shows that coke is polyaromatic compound with possibly consisted of branched chain like metal on ethyl groups. Analysis of unextractable coke by x-ray diffraction shows that the carbon deposits are composed of pseudo-graphitic carbon. Most of coke on support is graphitic but coke deposit on metal consist of disordered arrangement polyaromatic. However, coke sometimes forms to be filamentous carbon by mean of metal carbides as the intermediate. P. Gallezot et. al. (1989) investigated coke on Pt metal site supported on alumina by electron energy loss spectroscopy. He found that filamentous carbon on Pt can extend as far as 20 nm.

However, coke deposits on metal sites can be divided into two distinct types : one is easily removed by hydrogen and the other one more resistant to be removed by hydrogen. Salmeron and Somorjai (1982) called these two types of coke deposited on metal as reversible coke and irreversible coke respectively. The irreversible coke is graphitic coke which has H/C ratio about 0.2

3.3.2 Effect of Pressure.

The reforming reaction as well as dehydrogenation is preferred to work at low pressure. At this condition it is easily for coke to deposit on the catalyst. Thus, the study of coke in laboratory usually accelerates coking by decreasing reaction pressure for obtaining more coke on the catalyst. However, alternation of pressure has the effect to the location and nature of coke. Increasing of pressure induces decreasing of coke on metal sites but increased coke on acidic support. Therefore, it changes the nature of coke deposited on the catalyst to be more dehydrogenated and be more graphitic coke or decreased H/C ratio of coke on the catalyst. Figure 3.2 showed the effect of pressure to the nature of coke
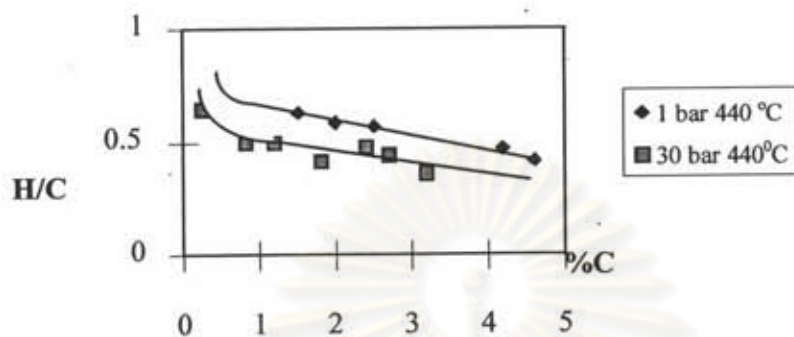
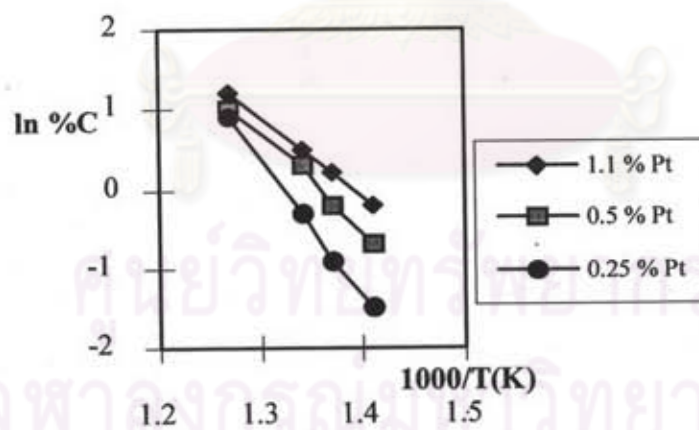**Figure 3.2 Effect of the coking pressure on the hydrogen content of coke deposit**

Figure 3.3 Arrhenius plot of the coking reaction on different Pt/Al$_2$O$_3$ catalysts

3.3.3 Effect of Temperature

Contrastly, effect of temperature reverse to the effect of pressure. At the low temperature coke coverages increases due to the increase of accessible metallic atoms. On the other hand, the increase of temperature lead to a decrease in coke deposits on the catalyst. Figure 3.3 showed the effect of temperature to coking reaction. However, the change of coking temperature do not alter the nature and location of coke on Pt/Al_2O_3 catalyst.

3.3.4 Effect of H_2/HC ratio

In industrial process of dehydrogenation hydrogen is added to feed stream to decrease coking on the catalyst. Hydrogen acts through a hydrogenolytic or by an inhibiting effect on the formation of highly dehydrogenated polymers.
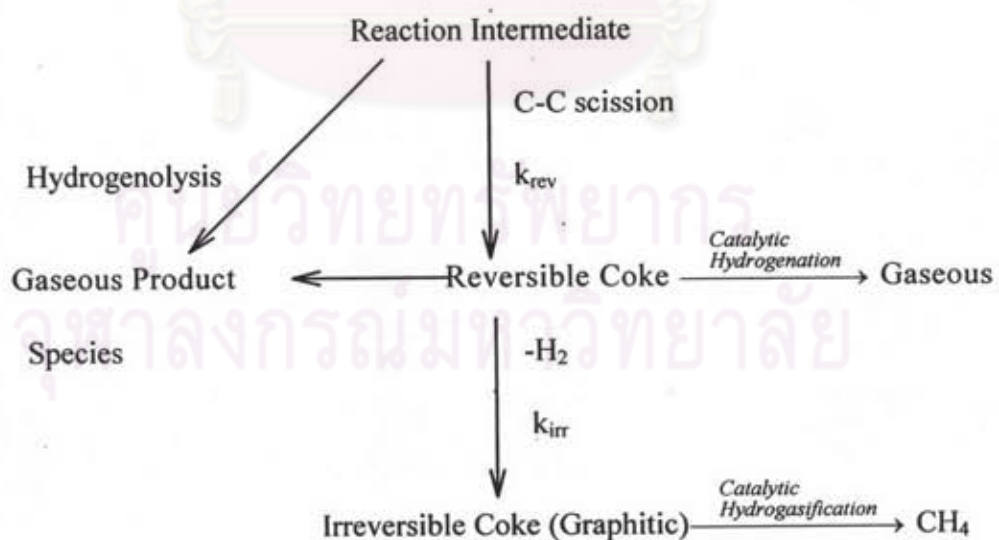
Figure 3.4 Mechanism of coking and hydrogen cleaning of a Pt crystallite(Biswas et.al.).

3.4 Coking Mechanism

Many researchers found that coking on reforming catalyst occurs in two stages :
(i) quasi-steady-state which coke initial rapid deposition on metal site with associated
changes in metal activity and selectivity (ii) slowly deposition of coke on acid sites.

J. Biswas et. al.(1987) inferred the mechanism of coke formation on reforming
catalyst as shown in the table 3.1

There are the other models which describe the coking kinetic of reforming
catalyst such as Fuentes (1985) or Froment (1985).

Fuentes used generalized power-low equation to describe catalyst deactivation
which include the steady-state activity.

$$\frac{-da}{dt} = f(T,C)(a - a_s)^n$$

where a_s is activity value of the catalyst at steady-state.

R.L. Mieville (1991) introduced the expression to describe the kinetic of coking
for reforming process as follow :

$$\frac{dC}{dt} = A.P_h^{-1}.P_{feed}^{0.75}.C^{-1}.\exp(-37000/RT)$$

where C = amount of coke, A = a pre-exponential term,

P_H = partial pressure of hydrogen, P_{feed} = partial pressure of feed.

T = temperature K. The derivative dC/dT is for value of C > 0.

Reference	Terminology	Mechanisms
Metal Site		
Sarkany et al. Trimm	Carbon	Fragmentation and successive dehydrogenation of C-C and C-H leads to carbon atom deposition on low index (high coordination number) planes of metal crystallites.
Luck et al. Sarkany et al.	Polyene	carbenes $\xrightarrow{\text{dimerization}}$ olefin $\downarrow$ polyolefin adsorb adsorbed polyolefin carbene polycyclic residues dehydrogenation graphitic coke
Masai et al.		precursors $\longrightarrow$ hydrogenated coke $\downarrow$ graphitic coke
Acid Site		
Trimm Parera et al. Gates et al. Zhorov et al.	Diels Alder	Coke arises from polymerization reactions involving carbonium ions. Metal sites catalyze dehydrogenation reactions in mechanism

Table 3.1 Mechanism of coke formation on reforming catalysts.

In addition, many properties also affect coking rate thus he suggested catalyst factor(Fc) and Feed factor (Ff) to compensate this effect. Tables 3.2 and 3.3 show F_f and F_c suggested by Mieville(1991) respectively.

Table 3.2 Feed factor on the relative coking rates under reforming condition of several pure hydrocarbon on alumina and used n-heptane as standard .

Hydrocarbon	Ff
n-heptane	1.0
toluene	1.5
n-Nonane	2.0
Cyclohexane	7.0
2-Me-Pentane	7.5
Me-Cyclopentane	43
Hexane-1	90
Cyclohexane	540

Table 3.3 Catalyst factor of Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ with the factor normalized to the standard Pt catalyst.

Catalyst	Fc
Pt	1.00
Pt-Re	1.44
Pt-Sn	0.60

3.5 Effect of promoter on coke formation

It is well known that some additives which are called promoter can increase the activity, selectivity or stability of catalyst. Most of the promoters are metals that are added simultaneously with the precursor to deposition on the surface of catalyst. Generally, promoter can be classified into two types : (i) textural promoter and (ii) structural promoter. (saterfield)

1) Textural promoter is an inert substance which inhibits the sintering of microcrytals of the active catalyst by being present in the form of very fine particles. These fine particles separate 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.

2) Structural promoter causes a chemical effect by changing the chemical composition of the catalyst. In many cases the effect of the structural promoter is clear but its mechanism of the action is not. In the other cases it is not clear whether the effect of the promoter is primarily a physical or chemical effect. Some possible mechanisms are :

2.1 There may be a dual-function action. The promoter may catalyze the formation of an intermediate. Thus the addition of a chloride to a platinum/alumina catalyst may be enhance its activity and be term "promotion", although the true mechanism is more clearly seen as an example of dual functionality.

2.2 The promoter may produce lattice defects or interstitial substitution.

2.3 The promoter may change the electronic structural of a catalyst, e.g., the ease of addition or removal of electron from a metal, and hence the strength of chemisorption.

However, in reforming process or dehydrogenation reaction with used Pt-based catalyst usually added some metal such as Sn, Re, Ir or alkali metal for increasing lifetime of the catalyst. Moreover, the promoter can affect the selectivity and activity or deactivation by suppressing coking of the catalyst.

Tin is widely used as a promoter in dehydrogenation reaction. There are a lot of researches about the effect of tin which is postulated to the geometry effect. Tin is added to Pt supported on alumina for segregating platinum particles, hence, the dispersion of platinum is increased. The enhancement of activity of the catalyst with added tin is attributed to the present of Sn^{2+} on the catalyst. (Odd.etal 1995) The small amount of platinum-tin alloy can be found on γ-Al_2O_3 but the main part of tin is Sn^{2+}. On the contrary, platinum-tin on silica support prefer to form alloy than on alumina support. This point out that the effect of tin as a promoter depend on the support. (Odd et al. 1996).

Lin Liwu et al (1990) studied the effect of tin to coke formation on platinum based catalyst. They found that although the amount of coke deposition on platinum-tin catalyst approached to Pt catalyst, the metal surface of Platinum-tin catalyst is covered less than platinum catalyst.

Trimetallic catalyst is used for obtaining higher dehydrogenation selectivity and great resistance to coke deposit. The third metal which is added to Platinum-tin catalyst usually be alkali metal such as lithium or potassium. R.D. cortright and J.A. Dumesic (1995) study the effect of potassium on silica-support Pt and Pt-Sn for isobutane dehydrogenation. They found that addition of potassium to Pt/SiO_2 did not affect heat of adsorption but increases the adsorption of saturate hydrogen. Furthermore, addition of potassium enhances the resistivity to coke formation.

Silipoln (1995) investigated coke formation on Pt/Al_2O_3, Pt-Sn/Al_2O_3. He found that adding tin to Pt/Al_2O_3 reduces coke deposition metal sites but increases total coke on the catalyst. On the other hand, addition of Na to Pt-Sn/Al_2O_3 reduces the amount of coke on both metal sites and acid support.

3.6 Regeneration of coked catalyst.

Since the catalyst is expensive. Catalyst which used in dehydrogenation or reforming process must be regenerated because of its activities by coke deposition. Many researchers tried to study regeneration phenomenon.

J.M. Parera (1989) found that coke on metallic function of Pt-Re-S/γ-Al$_2$O$_3$ is burned at low temperature with a rapid treatment. Thus he concluded that coke on metallic function is burned first and then continued on the acidic sites. Coke composition also has the effect to coke burning. Coke with hydrogen rich in molecules is easier to remove than graphitic coke. At high regeneration temperature the burning is nonselective and all species are simultaneously burned (Carlos et.al. 1992). Infrared spectroscopy has shown that there are C = O and C-OH occurred while burning coke. From that results, Carlos et al. proposed the following coke burning mechanism :

$$\text{coke} + O_2 \longleftrightarrow \text{oxidized coke} \longleftrightarrow CO_2 + H_2O$$
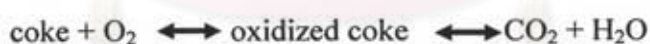
There are also other methods which can be used to regenerate coke catalyst such as using hydrogen or steam as a substance for regeneration. Regeneration by hydrogen obtains only methane as a gaseous product: Jacob A. Moulign et.al.(1992)studied the gasification of carbonaceous material on the catalyst and found that at low temperature the functional groups are hydropyrolyzed whereas at high temperature uncatalyzed gasification of the remain coke take place. The important research about regeneration coked catalyst by hydrogen was performed by Salmeron and Sormorjai(1987). They

found that coke on platinum catalyst can distinct into two types by the ability of coke removal by hydrogen, defined as reversible coke and irreversible coke.

In addition, some process used steam to regenerate the catalyst. D.Duprez(1991) The effect of steam on oxidizing all the coke deposited on the metal. However, introduction of steam during coking decreases the amount of coke deposited on the support.

The greatest problem in regeneration coked catalyst is sintering. Sintering occurs at high temperature in oxidizing condition and leads to metal active sites agglomeration. This phenomenon maybe due to hot spots produced by the metal catalyzed exothermic coke burning. Thus, low oxygen pressure is used to avoid an excessive increase in temperature. The amount of chloride in catalyst also affects sintering and redispersion of the catalyst. Loss of chloride during regeneration leads to catalyst agglomeration and decreases active surface. However, the sintered catalyst sometimes can be redispersion by treatment in gaseous mixture containing HCl to formed chloride compound on the catalyst surface.