CHAPTER II

LITERATURE REVIEWS

Every metal which catalyzes a reaction of hydrocarbon is covered by a layer of carbon compounds during a reaction. This carbonaceous deposit forms immediately when hydrocarbons are passed over the catalyst, leading to the deactivation of catalysts for hydrocarbon conversion. The behavior of carbon deposition has received a great deal of attention.

Reviewed Paper.

In this section, the relevant coke deposits paper are concluded for leading to raise the problem issue. The significant previous paper are as follows:

Barbier et.al.(1980) have studied the selective poisoning by coke formation on a Pt/Al_2O_3 catalyst. The result obtained from thermal programmed oxidation of coke by oxygen mixture in the temperature range of 0-500°C indicated two peaks as showed in figure 2.1. One could be ascribed to metal deactivation, the other to coke on alumina support. The effects on three test reactions by cyclopentane have differed due to the sites deposited by coke.

Salmeron and Somorjai (1982) have found that coke deposited on platinum is of two distinct types: one easily removed by hydrogen, the other more resistant to hydrogen removal. These cokes referred to as reversible and irreversible (graphitic) coke, respectively. The reversible coke is a hydrogenated surface species (H/C atomic ratio of 1.5-2.0) and the irreversible coke is graphitic in nature (H/C = 0.2)
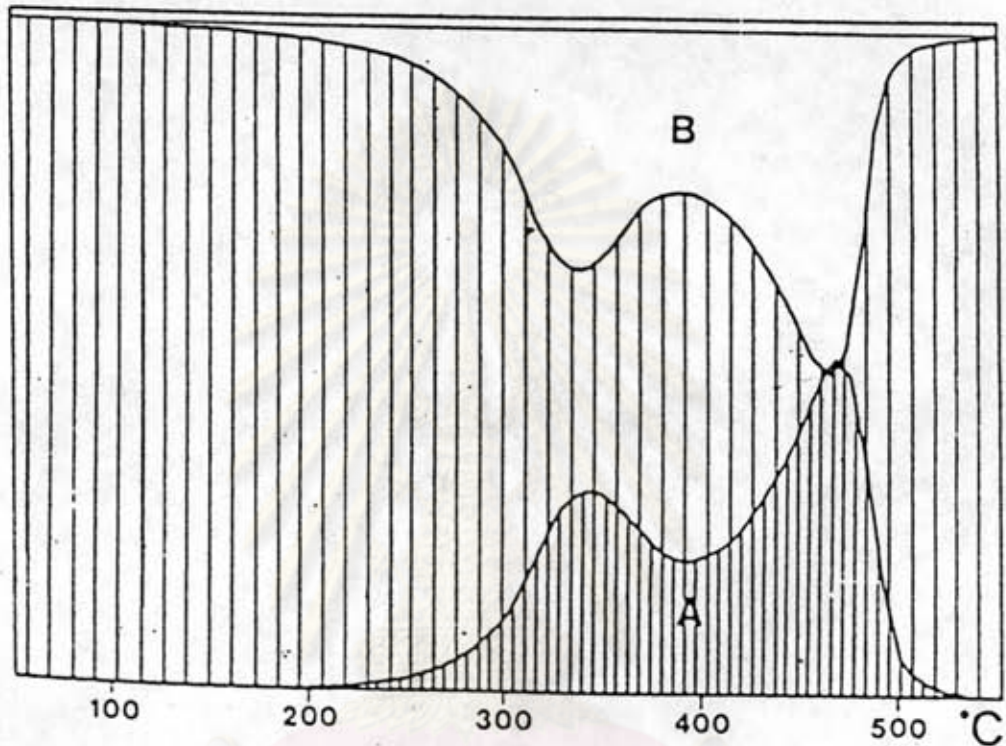
Figure 2.1 Temperature-Programmed Oxidation of coked Pt/Al_2O_3 catalyst

(A) CO_2 production   (B) O_2 consumptiopn   (Barbier, 1980)

Barbier et.al. (1985) have characterized the coke deposition on heterogeneous catalysts by Temperature-Programmed Oxidation. The comparison between the amount of CO_2 produced and the amount of O_2 consumed gives the ratio of H/C. For a Pt/Al_2O_3 catalyst it has been shown that coke deposited on the metal is less dehydrogenated than coke deposited on the support.

Barbier (1986) has reviewed coking of reforming catalysts. The review discussed about the relationship between the experimental working conditions of the catalysts and the quantity, the chemical nature, the location and the toxicity of deposited coke. A discussion of the effect of the metallic and acidic function brings out that coking is a balanced reaction between production and destruction of coke precursors, nucleation, growth and gasification of more ordered carbon deposits.

Beltramini and Trimm (1987) have studied the relationship between activity, selectivity and coke formation during a hydrocarbon reaction on a monometallic and several bimetallic catalysts. They found that the benefit of bimetallic catalysts originate from controlling of coke deposition on sites preferred for desired reactions. Comparison between Pt, Pt-Re, Pt-Ir, Pt-Sn and Pt-Ga/Al_2O_3 catalysts throw light on the importance of the different catalytic functions in controlling activity, selectivity, and coking.

Carlos et.al. (1989) have reviewed comparison of coke burning on catalysts coked in a commercial plant and in the laboratory. A commercial catalyst coked in a commercial naphtha reforming unit was compared with a laboratory catalyst and the fresh commercial one coked during laboratory experiments at pressure lower than the commercial. The carbon concentration on the catalyst and hydrogen/hydrocarbon ratio of the coke were measured. Temperature-programmed oxidation and test reaction for metallic and acidic functions of the coked catalysts were also performed. The main difference is in the coke composition and its distribution over the catalytic functions of the catalyst. Compared to the commercially coked catalyst, the coke on the laboratory coked catalysts is richer in hydrogen, covers the metallic function in a higher proportion, and is burnt faster. The catalytic activity for the hydrogenation (metallic reaction) of the laboratory-coked catalyst is decreased more, but it can be partially recovered by increasing the hydrogen pressure. The reduction on the acidic activity produced by coking is similar for both catalysts.

Biswas et.al. (1987) have proposed the role of catalyst surface morphology on activity and selectivity and the ensemble requirement. They have indicated that the coke deposition during long-term reformer operation is found to be on the alumina. Two types of coke are distinguished on the metal sites; they are labeled reversible and irreversible (graphitic) coke.

Liwu et.al. (1990) have investigated the process of carbon deposition on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalysts under different conditions in a multifunctional apparatus which could be used for hydrogen chemisorption, TPO and TPSR (Temperature-Programmed Surface Reaction) determinations. They have mentioned that carbon deposition was a dynamic process on both Pt and Pt-Sn catalysts. The carbonaceous materials which originated from the metal surface might be converted to carbon through successive dehydrogenation on metal sites, or they might continuously migrate to the support with irreversible coke formation through condensation or hydrogen transfer reactions. The incorporation of tin reduced the strength of chemisorption of the hydrocarbons on the metal surface, so that the carbon precursors could migrate toward the support more easily. The proportion of carbon deposited on the support of the platinum-tin catalyst was greater than that of the platinum catalysts.

Long term and short term deactivation on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalysts in n-hexane conversion have been studied by J. Margitfalvi et.al. (1987) at atmospheric pressure and low conversion. Both types of deactivation are very pronounced on catalysts, in which the acidic sites are not blocked by ionic forms of tin or lithium. Results obtained in this study were discussed in terms of a generalized reaction scheme, in which poisoning metallic and acidic sites and formation of a carbonaceous surface overlayer have their distinct contribution.

Zhang Tao et.al. (1991) have investigated the process of carbon deposition on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalysts under different conditions in a multi-function apparatus. They have found amorphous carbon and graphitic carbon by electron

microscopy. They mentioned that the first peak of the TPO profile disappears after partial oxidation of a coked catalyst, and the activity is completely recovered. The results of TEM (Transmission Electron Microscopy) and SAED (Selective Area Electron Diffraction) examination of the residual carbon on Pt-Sn catalysts after partial oxidation implies that the first peak of the TPO profile corresponds to carbon deposits located mainly on the metal surface, while the second one derives from the more graphite-like carbon located on the support.

Basso et.al. (1991) have studied the effects of metal-support interaction on coke deposition and oxidation on a Pt/Al_2O_3 reforming catalyst by pulse oxidation technique. They have found that platinum was partially oxidized before any carbon dioxide was detected; platinum oxidation, either to PtO or to a surface compound of Pt^{2+} with Al_2O_3, was completed in an early stage of coke oxidation. Coke oxidation to $T < 300°C$ was catalyzed by PtO or, though less efficiently, by the ternary Pt-Al-O compound; carbon dioxide evolution started at lower temperature for the high platinum load catalysts. Independent data showed that chemical interaction took place between platinum and Al_2O_3 at 600°C. It followed that coke formation was an ensemble-specific process.

Kirszensztejn et.al. (1992) have found that the carbonaceous deposit enlarge the cumulative pore volume V_{cum}, cumulative pore surface S_{cum}, and specific surface area S_{BET}. As a result of a comparison of the nitrogen isotherms as well as pore size distribution curves of the samples before and after coke deposition, coke was found to have its own porous structure which was developed on the basis of the catalyst porous system.

Somsak Amornchanthanakorn (1992) has been investigated the research of coke formation on dehydrogenation catalyst. The work concerned the deactivation in propane dehydrogenation reaction on 3 types of catalyst and to characterize the coke deposited on these catalysts. The catalysts studied were (0.3 wt.%)Pt/Al_2O_3 ,

(0.3 wt.%)Pt-(0.3 wt.%)Sn/Al$_2$O$_3$, (0.3 wt.%)Pt-(0.3 wt.%)Re/Al$_2$O$_3$, (0.3 wt.%)Pt-(0.3 wt.%)Sn-(0.6 wt.%)Li , (0.3 wt.%)Pt-(0.3 wt.%)Re-(0.6 wt.%)Li . He found that comparison to the base Pt/Al$_2$O$_3$ catalyst, the Pt-Sn/Al$_2$O$_3$ and Pt-Sn-Li/Al$_2$O$_3$ have higher initial propane conversion. On the contrary Pt-Re/Al$_2$O$_3$ and Pt-Re-Li/Al$_2$O$_3$ have lower initial propane conversion than the Pt/Al$_2$O$_3$ catalyst. An addition of tin to the base Pt/Al$_2$O$_3$ catalyst enhances the propylene selectivity. And addition of rhenium to Pt/Al$_2$O$_3$ promoted the methane, ethane and ethylene selectivity of catalyst. The comparison of irreversible coke responsible for long term deactivation of metal active sites, was carried out among the set of Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$ and Pt-Sn-Li/Al$_2$O$_3$ catalysts. The amount of coke deposits could be arranged in the decreasing order as: Pt-Sn/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ > Pt-Sn-Li/Al$_2$O$_3$. The amounts of irreversible coke deposited on the metal active sites of the catalyst were higher for the catalyst that had the higher amounts of the total irreversible coke. The results also reviewed that addition of lithium decreased the formation of the irreversible coke.

Querini et al. (1994) used temperature-programmed oxidation technique: to study the kinetics of coke-O$_2$ reaction on supported metal catalysts. Coke oxidation rates on supported metal catalysts were studied by Temperature-Programmed Oxidation (TPO). The TPO data were successfully modeled with a linear combination of power-law kinetic expressions. The validity and limitations of the model, for carbon oxidation on metal containing catalysts, coke particle size and number, catalyst mass and oxygen concentration on TPO spectra predicted by the model agreed well with their experimental results. They also reported that coke particle size and mophology have a great influence on a TPO spectra. Even though this simplified form of kinetic expression does not explicitly account for all the physical phenomena in a coke-burn process, it considers some of the most important factors: the effect of carbon surface area and the promotional effect of supported metal on coke-burn kinetics. Deconvolution of a complex TPO spectra by the above model provides kinetic parameters which can be used to predict TPO spectra of partial-coke-burn experiments. Difficulties in the predictive capability of this model arrive if other factors

such as large variations in coke morphology and coke particle size exist and there is no information relating them to a particular feature in the TPO spectrum. However, the model can adequately account for these variations, if their characteristics and extent are known, e.g., they may be determined by electron microscopy.

Atchara Saengpoo (1995) has estimated the kinetic parameters of coke burning on Pt/Al_2O_3 dehydrogenation catalyst by TPO and constant temperature oxidation techniques. The results revealed that coke can deposit on the catalyst in three forms: 1) on metal sites but does not completely cover the sites which can be eliminated at a temperature around $110^{\circ}C$, 2) on metal sites and completely cover the sites which can be burnt at a temperature around $450^{\circ}C$ and 3) on support that can be removed at the temperature around $550^{\circ}C$. Additionally, experimental evidences suggested that changing temperature of dehydrogenation reaction in the range of 550-650$^{\circ}C$ and variation of hydrogen/hydrocarbon mole ratio between 0 and 3, though can significantly affect area of TPO curve, only affects the amount of coke. Characteristic of coke burning emerge from this research is that the combustion should be in series, i.e. coke 1, coke 2 followed by coke 3. The calculation gave values of activation energy/gas constant (Ea/R); for coke 2 about 11100 K. and for coke 3 about 4560 K. respectively. The reaction order with respect to the concentration of coke was 0.5.