

CHAPTER II

LITERATURE REVIEWS

Deactivation by the deposition of some carbonaceous compounds (commonly called " coke ") is a basic phenomenon when a catalyst is used with a hydrocarbon feed stock. The problem of catalyst deactivation by coking attracted increasingly numerous attention in recent years.

In this chapter, literature review is gathered in section 2.1. Section 2.2 is some comments on the previous work. Finally, the objectives in this research are described in section 2.3.

2.1 Reviewed Paper.

This work does not intend to review all published papers concerning coke. Rather, it would concentrate on those relate to the formation and /or combustion of coke on dehydrogenation catalysts.

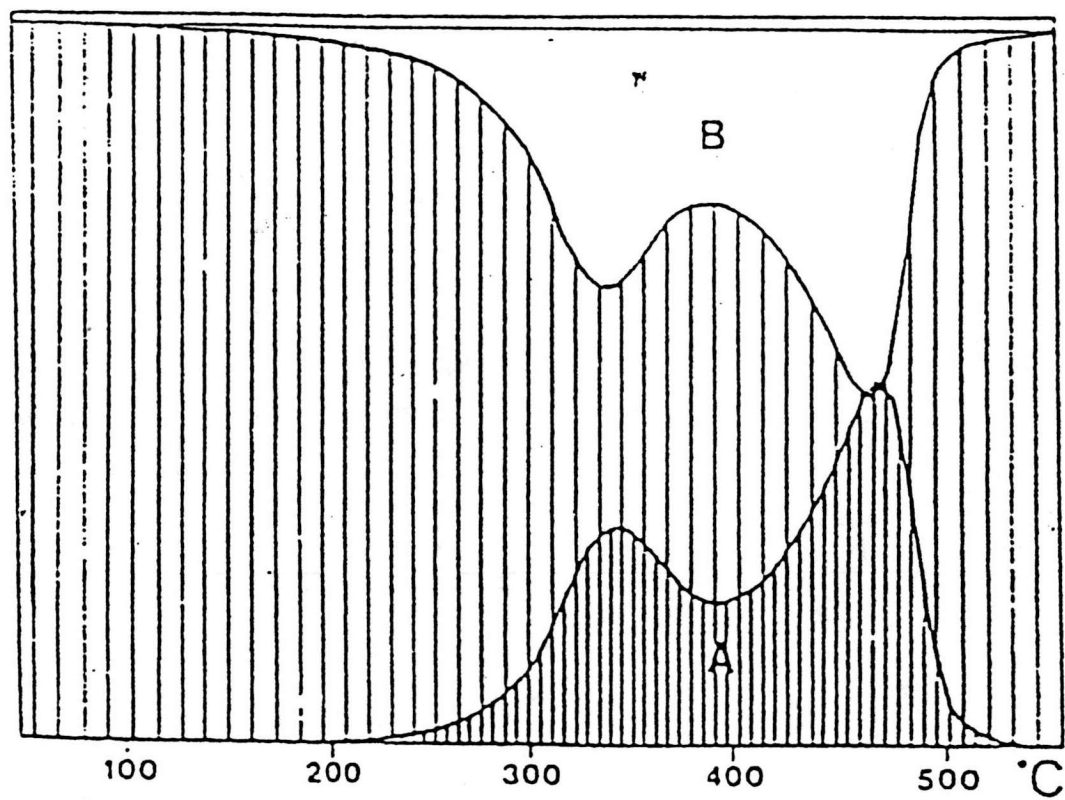
Barbier et.al.(1980) have studied the selective poisoning by coke formation on a Pt/Al₂O₃ catalyst. The results obtained from thermal programmed oxidation of coke by oxygen mixture in the temperature range of 0-500 °C

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 \approx 0.2)

Barbier et.al.(1985) have characterized the coke deposited on heterogeneous catalysts by Temperature - Programmed Oxidation. The comparison between the amount of CO₂ produced and the amount of O₂ consumed gives the ratio of H/C. For Pt/Al₂O₃ catalysts it has been shown that coke deposited on the metal is less dehydrogenated than coke deposited on the support.

For the hydrocarbon dehydrogenation system, coking on the catalyst, especially on the metal (generally platinum as the main component), is one of the most important problems need to be investigated to reduce the cost of regeneration and replacement of the catalyst. Deactivation of platinum catalysts is now relatively well documented and has recently been review by Barbier et.al. (1986,1987,1989).



(A) CO₂ production

(B) O₂ consumption

Figure 2.1 Temperature-Programmed Oxidation of coked Pt/Al₂O₃ catalyst.

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.

Pieck et al.(1989) studied the burning of coke on Pt-Re / Al_2O_3 catalyst. The activation energy and reaction order with respect to oxygen for the coke burning of a Pt-Re / Al_2O_3 naphtha reforming catalyst were evaluated by three different methods. Data were obtained by analysing a commercially coked catalyst using Temperature - Programmed Oxidation (TPO.), using an oxidative mixture containing 1.9% (v/v) oxygen in nitrogen. The methods gave similar

values of activation energy; for less polymerized coke about 10 kcal./mol. and for more polymerized coke about 25 kcal./mol. When the catalyst had been previously hydrogenated, the activation energy was 3.2 kcal./mol. The reaction order with respect to oxygen was 0.5.

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 coke 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 decrease on the acidic activity produced by coking is similar for both catalysts.

In 1992, Carlos et al. presented the results of the characterization of coke, deposited on a commercial reforming catalyst, during a burning process.

The catalyst used was a Pt-Re/Al₂O₃ catalyst. The catalysts were burnt between 350-650 °C, and the remaining coke was characterized by temperature programmed oxidation, X-ray diffraction, electron diffraction, IR, ¹³C CP-MAS NMR, electron spectroscopy for chemical analysis, electron paramagnetic resonance and chemical analysis. After the coke is burnt at 673 K, the residual coke shows the minimum value in the H/C ratio and the maximum in the thickness of the aromatic layers, degree with the model of coke burning: at low temperatures, the burning is selective; the more hydrogenated and amorphous carbonaceous species are burnt first. At high temperatures, the burning is nonselective and all species are simultaneously burnt off. They also suggested that the coke was partially oxidized during the burning process and intermediate species having C=O and C-OH groups are formed.

The research of coke formation on dehydrogenation catalyst has been investigated by Somsak Amornchanthanakorn (1992). The work concerned about studying 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/Al₂O₃, (0.3 wt%) Pt-(0.3 wt%) Sn /Al₂O₃, (0.3 wt%) Pt-(0.3 wt%) Re /Al₂O₃, (0.3 wt%) Pt-(0.3 wt%) Sn-(0.6 wt%) Li / Al₂O₃, (0.3 wt%) Pt-(0.3 wt%) Re-(0.6 wt%) Li /Al₂O₃. He found that comparison to the base Pt/Al₂O₃ catalyst, the Pt-Sn / Al₂O₃ and Pt-Sn-Li / Al₂O₃ have higher initial propane conversion. On the contrary Pt-Re / Al₂O₃ and Pt-Re-Li / Al₂O₃ have lower initial propane conversion than the Pt/Al₂O₃ catalyst.

An addition of tin to the base Pt/Al₂O₃ catalyst enhances the propylene selectivity. And addition of rhenium to Pt/Al₂O₃ 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 / Al₂O₃, Pt-Sn / Al₂O₃, and Pt-Sn-Li / Al₂O₃ catalysts. The amount of coke deposits could be arranged in the decreasing order as: Pt-Sn /Al₂O₃ > Pt/Al₂O₃> Pt-Sn-Li / Al₂O₃. The amounts of irreversible coke deposited on the metal active sites of the catalyst was higher for the catalyst that had the higher amounts of the total irreversible coke. The results also revealed that addition of lithium decreased the formation of the irreversible coke.

Liu, (1994) presented about chemical characteristics and kinetics in regeneration of Pt-Sn /Al₂O₃ reforming catalyst. The work investigated the kinetics of coke combustion, platinum sintering in a non-hydrogen atmosphere and redispersion on Pt-Sn reforming catalyst. By using the kinetic results mathematical simulation on coke burning in a radial continuous regenerator was established. Good agreement was obtained between temperatures obtained from simulation measurement. The oxygen in the gas may enhance resistance against sintering at high temperatures and in the presence of water. The platinum sintered on the catalyst without decrease in support surface area can be completely redispersed through chlorination and oxidation.

Querini C.A. et al.(1994) used temperature-programmed oxidation technique: to study the kinetics of coke-O₂ 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, were analyzed in detail. The influence of heating rate, coke concentration, 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 morphology have a great influence on a TPO spectrum. 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 spectrum 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 arise 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.

2.2 Comments on Previous Work.

Type of deposited coke on catalysts was investigated by Barbier et al. . It has been stated that coke consists basically of two types of carbonaceous deposits: one deposited on the metal which can be oxidized to carbondioxide at about 300 °C and the other deposited on the support which can be oxidized to carbondioxide at about 450 °C .

The later , Somsak Amornchanthanakorn (1992) and Liu (1994) present that there are three types of coke deposited on catalyst : the first type deposited on metal but do no cover the total metal surface , the second type deposited on metal sites and cover the total metal surface and the last type deposited on support.

An interesting point is position of the first type coke combustion . Liu, reported that the temperature of this first type coke that it can be oxidized is at about 350 °C and this temperature was similar to temperature of Barbier. While Somsak Amornchanthanakorn studied the Temperature- Programmed Oxidation between 50 - 700 °C, and found that the burning of the first type coke can observe at the temperature as low as 100 °C . Liu commented to Somsak Amornchathanakorn 's work that the compound that was oxidized at this low temperature (100 °C) was remained reactant on catalyst and was not eliminated before carrying out Temperature- Programmed Oxidation. The coke formed on

the catalysts, how it burnt to regenerate and the combustion of the coke deposited over catalyst surfaces depend upon the catalyst characteristics and also upon type of coke. In addition, it has been suggested that the second type and the last type are likely to have the same composition but there are differ the temperature of combustion (Liu). For this reason, the difference in combustion temperature is possibly caused by different mechanism of combustion. In the other hand, it was also suggested that this difference in combustion temperature of both coke is caused by the difference in coke composition.

From the examples given above, it can be concluded that various types of catalyst with different composition were used. Hence, the variation of coke formed in each reaction was likely depened upon types of catalyst and reaction severity. Only a few studies have been done on the coke combustion and evaluation of kinetic parameters of coke buring on dehydrogenation catalyst. Most of the coke combustion studies were focused on cracking and reforming catalyst.

2.3 Purposes of This Research.

From the above mentioned reasons, the type of coke formed and coke combustion characteristic on a dehydrogenation catalyst were selected to be the subjects of study to enable a better understanding of regeneration process of this type of catalyst.