CHAPTER 2

LITERATURE REVIEW

The main problem in hydrocarbon processing concerns the deactivation of catalyst by coking. Deposition of coke sometimes decreases the activity of catalyst more than 80 percents, thus, the catalyst must be regenerated to recover the active surface. Due to the great impact of coke on catalyst activity many researchers showed interest in these phenomena.

Therefore, this previous literature review is considered as follow.

Barbier et.al. (1980) have studied the selective poisoning by coke formation on Pt/Al_2O_3 . The thermal programmed oxidation of coke by oxygen mixture was studied in the $0\ ^{\circ}C$ - $500\ ^{\circ}C$ range. Two peaks were observed. One could be ascribed to metal deactivation, the other to coke on alumina support. The effect on three test reactions by cyclopentane have differed due to the sites deposited by coke.

L.W.Jossens and I.I. Petersen (1982) have studied fouling of a platinum reforming catalyst during the dehydrogenation of methylcyclohexane. They found that during early stage, the deactivation was totally reversible, that is, the initial activity of the catalyst was recoverable in a stream of hydrogen. More than 40 minutes on stream, the deactivation was only partially reversible and the rate of deactivation was proportional to the rate of dehydrogenation of methylcyclohexane.

Salmeron and Somorjai (1982) have found that coke deposited on platinum was of two distinct types : one easily removed by hydrogen, the other more resistant to hydrogen removal. These cokes were 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).

Barbier et.al. (1985) have studied the effect of metallic dispersion of Pt/Al_2O_3 series on coke formation from cyclopentane reactions. They observed that small metal crystallites presented a strong resistance to coke deposition while the large platinum crystallites showed a higher sensitivity to coke deposition. They explained these phenomena by mean of a higher stabilization of the adsorption of the cyclopentadiene produced during the reaction, by the large platinum crystallites than by the small ones which present an electron deficiency due to metal-support interactions.

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. The quantity of irreversible coke is increased by operation at high temperature or/and low pressures.

P. Gallezot et.al.(1989) have studied the location and structure of carbonaceous deposits on Pt/Al_2O_3 coked catalyst. They found patches of amorphous coke covering the support surrounding each metal particle and the coke coverage can extend as far as 20 nm. from given particle. When compared electron energy loss spectroscopy(EELS) peak of deposited carbonaceous with the reference they can concluded that the local structure of coke is not graphitic or pregraphitic but may consist in a disordered arrangement of polyaromatic molecules.

Lin Liwu et.al.(1990) found that coke deposit on metal surface first, may be converted to carbon through successive dehydrogenation on metal sites, or they may continuously migrate to the support with irreversible coke formation through condensation or hydrogen transfer reactions. The role of tin in $Pt-Sn/Al_2O_3$ is a reducing of the strength of hydrocarbons chemisorption on the metal surface, thus carbon precursors can migrate towards the support more easily. Hence, coke deposit on metal surface of $Pt-Sn/Al_2O_3$ is less than Pt/Al_2O_3 but coke on support of $Pt-Sn/Al_2O_3$ is greater than Pt/Al_2O_3 . They proposed that the high stability of $Pt-Sn/Al_2O_3$ is due to the larger bare metal surface under high temperature conditions.

P.Marecot et.al.(1990) have studied the effect of the nature of bifunctional catalysts on the regeneration by hydrogen. They found that the large platinum particles are less regenerated than small ones, although less coke remains on the catalyst. In addition less dehydrogenated coke is destroyed first by hydrogen treatment leaving on

the catalyst deposits with lower hydrogen-to carbon ratios.

J.M. Parera (1991) found that the deactivation of Pt-Re/Al$_2$O$_3$ catalyst by coking started on metal sites and then continued on the acid sites. During acid function deactivation, the coke on the metal and the catalytic activity for metal reactions remained constant. When the catalyst was regenerated, coke burning of the catalytic functions showed the same pattern. Coke on the metal function was burnt first, and followed by acid function.

J.N. Beltramini et.al.(1991) have studied coke deposition of Pt/Al$_2$O$_3$ with various dispersion. They observed that coke deposition on both metal and acid functions increased with Pt content. They postulated that it is due to Pt producing the coke precursors. Consequently, higher Pt loading provide lower conversions because of increased coke precursors which results greater amount of coke formed.

Basso et.al. (1991) have studied the effects of metal-support interaction on coke deposition and oxidation on a Pt/Al$_2$O$_3$ reforming catalyst by pulse-oxidation technique. They 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$_2$O$_3$, 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 loading catalyst. Reduction temperature was the important parameter to

coke oxidation and activity of the catalyst. Independent data showed that chemical interaction take place between platinum and Al_2O_3 at 600 ^oC. It followed that coke formation was an ensemble-specific process.

Y.Fan et.al. (1993) found that after repeated regeneration cycle of $Pt-Sn/Al_2O_3$ catalyst the interaction between metallic components and support was destructed, which leaded to structure degradation. When doping with rare-earth oxide such as Sm_2O_3 or CeO_2 the structure of Pt-Sn catalyst can be stabilized but did not change tin surface properties or catalytic properties of Pt-Sn catalyst.

The effect of tin oxide on $\gamma-Al_2O_3$ has been studied by Jianyi Shen et.al(1993). They found that additions of SnO_2 and SnO to $\gamma-Al_2O_3$ have different effects on the surface acid/base properties. SnO_2 decreased the number of strong acid sites, increased the number of weaker acid sites, and has little effect on types of acid and base sites. On the other hand, SnO was postulated to neutralize support properties because SnO on $\gamma-Al_2O_3$ decreased the strength and number of acid sites, weakened Lewis acid sites associated with aluminum cations, and eliminated the basicity of the support.

Odd A. Barias et.al. (1995) have studied the effect of tin as the promoter on platinum catalyst which supported on $\gamma-Al_2O_3$ and SiO_2 of dehydrogenation of propane. They found that without tin platinum showed the same initial specific activity (TOF) on both supports, but deactivated rapidly due to coking. Addition of tin

to γ-Al$_2$O$_3$ produced the interaction of tin and the γ-Al$_2$O$_3$ and tin was stabilized in an oxidation state > 0. Thus, adding tin lead to increasing platinum dispersion and reducing the deactivation without any change in the initial specific activity in dehydrogenation. The selectivity to propylene was strongly enhanced by tin, particularly due to blocking or poisoning of acid sites on the support. Tin on SiO$_2$ support was more readily reduced and formed alloy with platinum which resulted a large loss in the intrinsic activity of platinum.

Bualom J. (1995) has studied the effect of alkali metals in dehydrogenation catalysts for reduction of coke. She attributed that the role of alkali metals on the increase of active sites strength is reflected by the enhancement of free electron on the catalyst surface based on conductivity unit..

Siripoln K.(1995) has determined the irreversible coke deposition on platinum active site of propane dehydrogenation catalyst. He found that increase of platinum loading enhanced catalyst performance and increased total coke deposits on the catalyst. The presence of tin increased coke deposited on the catalyst but larger vacant sites of platinum on metal active sites remained free. The presence of alkali reduced coke deposited on catalyst and metal active site, due to hydrogen spill over. He also proposed a model for regeneration metal active sites that reversible coke on metal active site was removed all by diluted oxygen at 250 $^{\circ}$C and irreversible coke on a metal active site was removed all by diluted oxygen at 500 $^{\circ}$C.

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 $110\ ^oC$, 2) on metal sites and completely cover the sites which can be burnt at temperatures around $450\ ^oC$ and 3) on support that can be removed at the temperature around $550\ ^oC$. Additionally, experimental evidences suggested that changing temperature of dehydrogenation reaction in the range of $550\text{-}650^oC$ 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 reported reaction order of coke combustion with respect to the concentration of coke was 0.5.

Sergio de Miguel et.al. (1996) have studied the effect on tin and potassium on Pt-Sn catalyst for light paraffins dehydrogenation. They found the increase of selectivity and the decrease of coke formation when adding tin. They proposed that this may be related with the possible electronic modifications of platinum by tin which produce a weakness of the interaction strength between the olefins and metal surface. On the other hand, the modification of electronic state of platinum by tin addition

appears to be of a minor importance in bimetallic catalysts supported on K-doped Al_2O_3.

Although there were many researches studied about the effect of promoter on the properties of platinum series, the role of Sn and K on the relation between activity and active sites of the catalyst has never been investigated. Further more, this study will also identify type of on metal active sites of platinum catalyst.