

CHAPTER II

LITERATURE

Coke deposition is a main reason for catalyst deactivation in hydrocarbon reaction and due to its importance it has been a subject matter for many works in recent years. Different areas have been focused such as kinetics of coke formation and analytical techniques of coked catalyst, development and characterization of catalysts and effect of reaction condition.

Carlos et. al.[3] 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 catalyst was 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 was burnt at 400°C, the residual coke showed 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 temperature, the burning was selective, the more hydrogenated and amorphous carbonaceous species were burnt first. At high temperature, the burning was nonselective and all species were 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 were formed.

Gallezot et al.[9] have studied the location and structure of carbonaceous deposits on Pt/Al₂O₃ coked catalyst. They found patches of amorphous coke covering the support surrounding each metal particle and the coke coverage could extend as far as 20 nm from a given particle. When compared electron energy loss spectroscopy (EELS) peak of deposited carbonaceous with the reference they could conclude that the local structure of coke was not graphitic or pregraphitic but may consist in a disordered arrangement of polyaromatic molecules.

Beltramini and Trimm[23] 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 originated from controlling of coke deposition on sites preferred for desired reactions. Comparison between Pt, Pt-Re, Pt-Ir, Pt-Sn and Pt-Ga / Al₂O₃ catalysts threw light on the importance of the difference catalytic functions in controlling activity, selectivity and coking.

Lin et al.[25] have studied carbon deposition on Pt and Pt-Sn catalysts for alkane dehydrogenation reaction. They found that carbon deposition was a dynamic process. The carbonaceous deposit may be converted to carbon through successive dehydrogenation on metal sites, or they may continuously migrate to the support with irreversible coke through condensation or hydrogen transfer reaction. The role of tin in Pt-Sn/Al₂O₃ reduced the strength of chemisorption of the hydrocarbon on the metal surface, so that the carbon precursors could migrate towards the support more easily. Thus, the result of tin was not only to decreased coke on metal sites, but increased coke on support.

Chen and Chen [26] have investigated the effect of alkali and alkaline-earth metals on the resistivity to coke formation and sintering over nickel-alumina catalysts. They have found that alkali and alkaline-earth metals improved resistivity to coke formation and sintering on nickel-alumina base catalyst. Furthermore, the promoters also helped in decreasing the coking rate of nickel catalyst.

Kunatippapong [27] has determined the irreversible coke deposition on platinum active site of propane dehydrogenation catalyst. It was 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 °C and irreversible coke on a metal active site was removed all by diluted oxygen at 500 °C.

Jaikaew [28] has studied the effect of alkali metals in dehydrogenation catalysts for reduction of coke. The work 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.

Lim [29] have studied the effects of promoters tin and potassium on coke formation on metal site of propane dehydrogenation reaction. It was found that addition of hydrogen to feed stream reduced low temperature coke. Promoter tin could reduce coke deposition on metal active sites because of the decreasing size of platinum ensemble. Finally addition of K to Pt-Sn/Al₂O₃ could decrease the amount of low temperature coke on metal active site. This effect of K may be due to hydrogen spillover to remove coke precursor or low temperature coke or both of them.

Beltramini et.al.[30] have studied the effects of paraffins, naphthenes and aromatics on coke formation in reforming reaction over a Pt/ γ -Al₂O₃ catalyst. They found that coke formation was not directly related to the molecular weight of hydrocarbons, but related to the structure of reactants and products formed from the reaction. For n-paraffin, coke deposit increased with the molecular weight of hydrocarbons except n-pentane because of main product of n-pentane was cyclopentane which was a very important coke precursor. For naphthenes, it was clear that the five carbon atom ring was the cause of higher coke depositions than others carbon atom rings. Finally, for aromatics, the structures and the position of the chains joined to the aromatic rings have an important influence on coke formation.

Furthermore, coke formation not only depended on different feeds and their products, but also depended on metallic and acidic functions of the catalyst used in reforming reaction.

Barbier et.al.[31] have studied the effect of metallic dispersion of Pt/Al₂O₃ 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.

Parera [32] found that the deactivation of Pt-Re/Al₂O₃ 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.

Pieck et.al.[33] 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 a 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. They found that the main difference was 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 was richer in hydrogen, covered the metallic function in a higher proportion, and was burnt faster. The catalytic activity for the hydrogenation (metallic reaction) of the laboratory-coked catalyst decreased more, but it could be partially recovered by increasing the hydrogen pressure. The reduction on the acidic activity produced by coking was similar for both catalysts.

Beltramini [34] studied the catalytic activity, product selectivity, and coke deposition during methylcyclopentane(MCP) reforming on bifunctional Pt/Al₂O₃-Cl catalysts with different metal loadings, but constant metal dispersion as well as constant Cl loadings. Surprisingly, the overall conversion of MCP was found to decrease as the metal content of catalyst increased. Analysis of the coke by temperature programmed oxidation (TPO) revealed two distinct peaks, one associated with coke on the metallic function and the other associated with coke on the acidic function. The change of activity of the metal and acid functions with time was monitored by following the rate of hydrogenolysis and hydrocracking, respectively. The metallic function deactivated rapidly at first due to coking but then reached a steady state due to an equilibrium between the rates of coke formation and its removal. The acidic function exhibited a more gradual deactivation behavior with time as coke built up on the support.

Daisuke [35] have studied kinetic model reactions in the gas phase at the early stage of coke formation on the model reaction adopted for formation of cyclic compounds and growth of ring. In the temperature range below 600 °C, they concluded that :

1. Ring formation was greatly attributed to Diels-Alder type reaction where the adhesive fragment hydrocarbon such as butadiene of the allyl radical added to unsaturated hydrocarbons to produce a C₆ or C₅ cyclic compound.

2. Growth of the ring was also attributable to further cycloaddition of these fragment hydrocarbons to cyclic olefins produced.

3. Polymerization of pure aromatics accompanying dehydrogenation contributed a little to polycyclization. On the other hand, growth of ring formation by pure aromatics could proceed only at higher temperature.

4. Growth of the ring favored a cyclic olefin molecule that possess a nonconjugated double bond and a nearly planer structure.

Querini et.al.[36] 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, 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 spectra. Even though this simplified form of kinetic expression did not explicitly account for all the physical phenomena in a coke-burning process, it considered 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 provided kinetic parameters which could be used to predict TPO spectra of partial-coke-burn experiments. Difficulties in the predictive capability of this model arrived 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 could adequately account for these variations, if their characteristics and extent were known, e.g., they may be determined by electron microscopy.

Sergio Miguel et. al.[37] compared the characteristics of the metallic phase between Pt and Pt-Sn catalysts supported on Al₂O₃, K-doped Al₂O₃ and MgO by FTIR and XPS. The beneficial effects by addition of tin to platinum, both in the increase of selectivity to propene and the low coke formation, were related to the possible electronic modification of Pt by Sn, mainly for Al₂O₃ and MgO supported. On the other hand, the modification of Pt by Sn addition appeared to be of a minor importance on K-doped Al₂O₃ supported catalysts.

Jackson [38] have studied deactivation and regeneration of Pt/Al₂O₃ catalyst in propane dehydrogenation by using isotope carbon-13 of [2-¹³C]C₃H₈ and Hydrogen-2 of [²H]H₂ and [²H]C₃H₈. The result showed that initially the coke deposit was made up of C-1 fragments, which aged to form polycyclic aromatics. In other word, the overall carbon deposition reaction being represented by C₃H₈ → 3C + 4H₂, while the hydrogenolysis reaction, C₃H₈ → 2CH₄ + C, was only of importance in the early stages of the reaction cycle. Removal of isotopically labeled carbonaceous from the surface was revealed by treatment in oxygen at 600°C. There was surface mixing of carbon deposited at different times. However, some of the carbons could not be removed from the metal functions by treatment in oxygen at 600°C.

It was also observed that hydrogen and carbon could exchange with both the surface and gas phase in both the fresh and aged forms. With time on stream and with increasing reaction cycle, the catalyst became increasingly selective to propene, indicating that the carbonaceous deposit had a major role in defining the selectivity as well as the activity of these catalyst.

Liu et.al.[41] proposed an experimental protocol that can provide a diagnostic tool for proving the state of catalyst coke and its influence on product composition in an operating reactor throughout the lifetime of the catalyst. The experimental equipment included a vibrational microbalance, a multi-outlet fixed bed reactor, and a temperature programmed oxidation. They illustrate its use by applying it to n-heptane reforming on a commercial Pt-Re/Al₂O₃ catalyst. Figure 2.2 showed the reactions $nC_7 \rightarrow iC_7$ and $nC_7 \rightarrow C_5N$ which were reversible. The constants determined were found to be consistent with the thermodynamic equilibrium constants estimate from two independent sources. By feeding toluene and hydrogen to the microbalance, they found that toluene was virtually unreactive, indicating that there was no reverse reactions from toluene to nC₇ and iC₇.

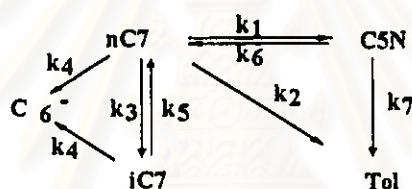


Figure 2.2. n-Heptane reforming network over Pt-Re/Al₂O₃. [41]

The model derived from the above procedure compares with experiment is showed in Figure 2.3. Figure 2.3 combines the model with the coking kinetic model to predict the observed changes in the reforming rate constants during the lifetime of catalyst. The results identified five-membered naphthenes(C₅N) as the key source of coke and provide the data needed to develop kinetic models for both reforming and coking.

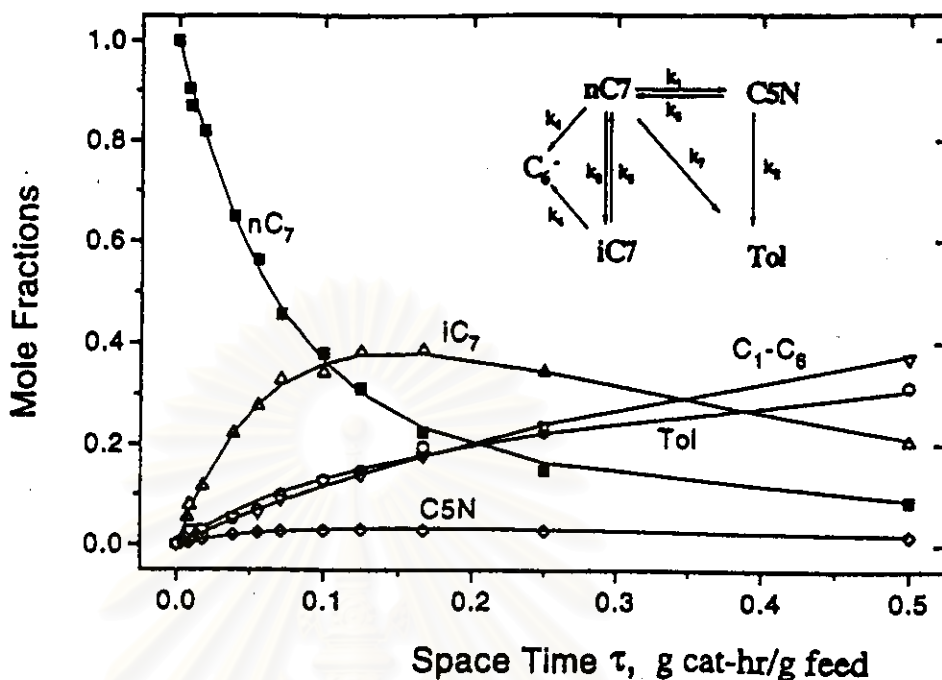


Figure 2.3. Model prediction vs. experimental data of Pt-Re/ Al_2O_3 at 750 °K and 517 k Pa.[41]

The research of coke formation on dehydrogenation catalyst has been investigated by Amornchanthanakorn [42]. 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/ Al_2O_3 , (0.3 wt%)Pt-(0.3 wt%)Sn/ Al_2O_3 , (0.3 wt%)Pt-(0.3 wt%)Re/ Al_2O_3 , (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6wt%)Li/ Al_2O_3 , (0.3 wt%)Pt-(0.3 wt%)Re-(0.6 wt%)Li/ Al_2O_3 . It was found that comparison to the base Pt/ Al_2O_3 catalyst, the Pt-Sn/ Al_2O_3 and Pt-Sn-Li/ Al_2O_3 had higher initial propane conversion. On the contrary Pt-Re/ Al_2O_3 and Pt-Re-Li/ Al_2O_3 had lower initial propane conversion than the Pt/ Al_2O_3 catalyst. An addition of tin to the base Pt/ Al_2O_3 promoted the propane, 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_2O_3 , Pt-Sn/ Al_2O_3 and Pt-Sn-Li/ Al_2O_3 catalysts. The amount of coke deposits could be arranged in the decreasing order as: Pt-Sn/ Al_2O_3 > Pt/ Al_2O_3 >

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 reviewed that addition of lithium decreased the formation of the irreversible coke.

Saengpoo [43] has estimated the kinetic parameters of coke burning on Pt/Al₂O₃ 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 °C, 2) on metal sites and completely cover the sites which can be burnt at temperatures around 450 °C and 3) on support that can be removed at the temperature around 550 °C. Additionally, experimental evidences suggested that changing temperature of dehydrogenation reaction in the range of 550-650°C and variation of hydrogen/hydrocarbon mole ratio between 0 and 3, though can significantly affect area of TPO curve, only affected 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.

Pieck et al.[44] studied the burning of coke on Pt-Re/Al₂O₃ catalyst. The activation energy and reaction order with respect to oxygen for the coke burning of a Pt-Re/Al₂O₃ naphtha reforming catalyst were evaluated by three different methods. Data were obtained by 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 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.

Odd et. al. [45] studied the catalytic dehydrogenation of propane over Pt and Pt-Sn catalysts supported on γ -Al₂O₃ and SiO₂. Without the promoter Pt showed the same initial specific activity (TOF) on both supports, but deactivated rapidly due to coking. The effect of Sn as a promoter depended on the support. On γ -Al₂O₃ tin interacted with the support and was stabilized in an oxidation state > 0 . The result was an increase in Pt dispersion and reduced deactivation without any change in the initial specific activity in dehydrogenation. The selectivity to propene was strongly enhanced by tin, particularly due to blocking or poisoning of acid sites on the support. On SiO₂ the Sn was more readily reduced, and alloy formation was possible. This led to similar increase in Pt dispersion and improved catalytic stability, but also to a strong reduction in the specific activity. The change in catalytic stability on both supports was paralleled by a dramatic change in the hydrogen adsorption properties, as seen from the TPD profiles after reduction.

Larsson, M. et.al. [46] have examined the coke deposit during propane dehydrogenation on Pt/Al₂O₃ and Pt-Sn/Al₂O₃ by using TPO. Time on stream, temperature and reaction gas composition have been varied. Three different peaks were identified from the TPO profiles on the Pt-Sn catalyst and attributed to different types of coke; coke and on in the vicinity of the metal, coke on the carrier, and graphitic coke on the carrier. The formation of the coke belonging to the first two peaks in the TPO profiles increases with temperature and propane partial pressure. A model was discussed where a minor part of the coke deactivated the catalysts. This coke was formed in parallel with the coke that was seen in the first two peaks in the TPO experiments. The graphitic coke formed on the carrier was not formed through this route. The experiments with different time on stream revealed that the first peak reached a constant level after about 15 h, while the second one still increased.

Minh et.al. [47] has investigated the kinetic of catalytic coke combustion by analyzing evolution of CO, CO₂ and H₂O during the temperature programmed oxidation (TPO) of coked cracking catalysts. Structure in the TPO spectra was affected by variations in the rate-determining oxidation step. An assumed oxidation

mechanism formed the basis for calculating rate parameters for carbon oxides evolution from industrial spent, cyclohexane coked and 1-hexane coked cracking catalysts. Optimized activation energies allow a comparison of “soft” and “hard” coke combustion reactivity. Measured temperature-dependent H/C ratios indicated that low hydrogen content (“hard”) coke, formed from adsorbed hydrocarbon molecules while high hydrogen content (“soft”) coke formed via dehydration or dehydrogenation.

From all of the above reviews, one can see that the function of the promoter in the catalyst was only to reduce the coke formation. But coke deposit remain an important problem in the deactivation of catalyst. Subsequently, this thesis studied the effect of reactants, alkanes and alkenes, on coke formation. This may be useful for understand the mechanism of coke formation in advance.



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