CHAPTER II
BACKGROUND

2.1 Deactivation of Catalyst

The use of catalysts in the chemical and process industries is currently widespread. The nature of the catalytic process whereby a given reaction may be accomplished at a lower temperature than that required for the homogeneous reaction is likely to lead to the application of catalytic methods to even more processes as fuel costs continue to rise. Unfortunately most catalysts used in heterogeneous catalytic processes are subject to a decrease from the initial activity over a period of time. The time required for the activity of a catalyst to fall to an undesirable level varies with the severity of the process conditions and with the type of reaction being catalyzed.

General reviews of catalyst deactivation have been given by Butt and Levenspiel (1972) and they have laid the foundations for a better understanding of catalyst deactivation processes. Basically, three kinds of deactivation may occur: (i) sintering or thermal deactivation of the catalyst; (ii) poisoning; and (iii) fouling.

2.1.1 Catalyst Deactivation by Sintering

Sintering is a physical process associated with loss of area of the catalyst which occurs when the catalyst is operated above the normal range of temperature. Such temperatures may occur throughout the catalyst or may be localized at the individual areas where reaction occurs. Two different kinds of sintering may be distinguished depending on the type of catalyst employed.

If the catalyst is a normal high-area support type material, such as silica or the various forms of alumina or a silica-alumina cracking catalyst, operation at high temperatures will cause a loss of specific surface with associated changes in the pore structure, giving a corresponding loss in activity. The second type of catalyst is that where the active ingredient is usually a metal which is supported on a high-area oxide support. Examples are nickel and platinum catalysts supported on alumina or silica. Here sintering can occur not only by reduction of the support area but by a "coalescence" or loss of dispersion of the metal crystallites. This loss of area of the active constituent of the catalyst causes a sharp drop in activity. Furthermore this type of sintering generally occurs at temperatures below that at which the support material suffers loss of area. In the case of a bifunctional catalyst such as platinum on alumina reforming catalysts, temperature excursions may reduce the area of both components. In other cases where the support does not have a direct chemical role one of its main functions is to prevent aggregation of the metal crystallites.

2.1.2 Catalyst Deactivation by Poisoning

Poisoning is often associated with contaminants such as sulfur compounds in the feed stream of petroleum fractions; it is then termed impurity poisoning. Though this is the most well documented and best identified of poisoning processes, it is important to recognize that other forms of poisoning may occur. These include poisoning by a product of the desired reaction which may be preferentially adsorbed on the active sites of the catalyst, thus retarding the adsorption of reactant.

In principle it is always possible to remove impurity poisons from the feed stream by purifying the feedstock, but in practice the cost of purifying

the feedstock to achieve the very low impurity level often required may prove prohibitive, so it may often be preferable to tolerate some degree of poisoning.

In some cases selective poisoning may affect one reaction step more than another, thus the selectivity toward a desired reaction may be improved by adding a small amount of poison. Physical grinding in an agitated vessel is also reported as causing poison-like behavior.

2.1.3 Catalyst Deactivation by Fouling

The cause of catalyst fouling comes from the formation of carbonaceous deposits or "coke". The formation of coke deposits (containing, in addition to carbon, significant amounts of hydrogen plus traces of oxygen, sulfur, and nitrogen) during processing of organic based chemical feedstocks is the more usual example of fouling. As the coke builds up, the catalytic surface area is reduced and the pores of the support are increasingly restricted causing a loss in activity.

It is important to recognize that the coke deposit in this case originates from the reactions occurring and is not an impurity. Because of this intrinsic association with the main chemical reactions, fouling by coke cannot be eliminated by purification of the feed. If the reaction occurs, coke deposition must also necessarily occur according to the overall chemistry of the process. However, coke formation can be minimized by appropriate choice of reactor and operating conditions, and in some cases by modification of the catalyst.

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger amounts of material are responsible for deactivation in fouling processes than in poisoning.

2.2 Mechanisms of Coking

Hughes (1984) reviewed Froment and Bischoff (1961) work on a fixed bed reactor. The profile of coke deposits suggests both parallel and series fouling paths. When the reactants have a high concentration, they act as coke precursor and follow the parallel path. When the product concentrations are high, a series fouling path becomes significant. For propane dehydrogenation over Pt catalysts, multiple Pt atom "ensemble" sites are required for coke formation (Biloen et al., 1977).

The thermograms of the Temperature-programmed oxidation (TPO) of coke on naphtha reforming catalysts (Pt/SiO$_2$ and Pt/Al$_2$O$_3$-Cl) were studied by Parera et al. (1983). Each type of catalyst shows only one peak, 123 to 369 °C for Pt/SiO$_2$ and 369 to 555 °C for Al$_2$O$_3$-Cl. This result corresponds to the results of Barbier et al. (1985) , the first combustion zone (lower temperature) belongs to the burning of the coke deposit on the metallic function (Pt). The second zone(higher temperature) is due to the coke deposited on acidic sites (Al$_2$O$_3$-Cl). The hydrogen to carbon ratio of coke on different coked catalysts and the coking time suggest that the carbon deposits on the metal are less dehydrogenated than coke deposited on the support and reach a constant amount in the first minute of the reaction and then remain constant while the overall coke is still accumulating.

Caruso et al. (1989) found a continuous decrease in coking rate for a reforming catalyst (Pt-Re/Al$_2$O$_3$) with increasing time on stream. The desired reaction and coking are both inhibited by the significant amount of coke on the catalyst surface.

Duprez et al. (1989) found an unidentifiable type of coke deposit on a catalyst that corresponded to TPO profiles at 380-440 °C in the same conditions as already described. Because this peak appears between the two

identified peaks (coke on metal and supports). Two different hypotheses were proposed to explain this phenomenon. One hypothesis states that it is coke deposited on a different type of acid center on alumina, based on the rapid appearance of the third peak and also due to different hydroxyl groups found by IR. Another compares the TPO profile with coke deposited on alumina that gave only the third peak. This new type of coke may be deposited on the support near the metal particles with carbon filaments that can migrate from metal sites.

2.2.1 Effect of Reaction Conditions

Trimm (1983) reviewed some methods to control coke deposits by modifying both the physical and chemical reaction conditions. Dilution and gasifying agents were introduced to the system. This decreased coke precursors and increased the carbon gasification pathway.

Barbier et al. (1985) studied the coke deposited on Pt/Al_2O_3-Cl during cyclopentane conversion. Both classical fixed bed and simple hydrogen/carbon analysis method was used. Smaller metal crystallites showed a resistance to higher coke deposits. This can be explained either by geometric or electronic transfer theories.

The effect of operating conditions on Pt/Al_2O_3 for cyclopentane conversion was investigated by Barbier et al. (1985). An increase in active metal dispersion can delay the coking reaction at high reaction temperatures. Low temperatures give the opposite result. An increase in pressure promotes the degree of graphitization of coke on the support and inhibits the catalyst activity of the platinum metallic phase. Steam can also inhibit coking on the support. The higher Pt content in Pt/Al_2O_3 catalysts for reforming, the higher conversion and coke formation. Increases in intermediate hydrocarbons (coke-precursors) were discussed by Pieck et al. (1989).

2.2.2 Effect of Promoters Loading

Addition of nonmetallic state tin to nonacidic alumina to form a dual function catalyst noticeably reduces the deactivation of the dehydrocyclization activity for benzene (Dautzenberg et al., 1980). Not only the stability but also the selectivity of the platinum function is modified by addition of tin. The formation of coke on the metal function is reduced by changing the adsorption properties of platinum by tin, the ensemble effect explanation. Platinum-tin reforming catalysts give a corresponding adsorption improvement but is explained by the electronic effect (Burch, 1981).

Lieske et al. (1987) compared the adsorption and coke formation from C_1 to C_6 between Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalyst. The ensemble effect was proposed to explain the results. Coke precursors transfer from platinum sites, where they formed, to the support. The reduction in the strength of chemisorption of ethylene on the platinum surface was reported by Liwu et al. (1990). With the same amount of coke, a platinum catalyst has less proportion of carbon deposited on the support than a platinum-tin catalyst. Afonso et al. (1994) studied the coke deposits on platinum-tin catalysts during dehydrogenation by solvent extraction and also found that more than one structure of carbonaceous materials occurs. These help explain the previous results on the components of coke deposits from TPO studied of $Pt-Ir/Al_2O_3$ and $Pt-Re/Al_2O_3$ (Barbier et al., 1989). All types are different in the amount of hydrogen they contain.

2.3 Catalyst Regeneration

The cracking catalyst must be regenerated to remove coke and restore activity after it has been used for a period of time. A regeneration is invariably effected by burning in a controlled fashion with oxygen-containing gas.

The major problem in regeneration is to burn off the coke without causing irreversible damage to the catalyst, and since a catalyst may be regenerated thousands of times in the course of a normal lifetime, permanent deactivation must be kept extremely small in any one regeneration. In spite of care there is a slow decline in prolonged use. The damage apparently comes from explosure to a very high temperature, and also from the presence of steam in the reaction, flushing, and regeneration gases, even at lower temperatures. The regeneration must be carried out with adequate provision for removal of heat, and steam should be maintained to a minimum.

The variables that influence a regeneration rate are as follows:

(1) Temperature;

(2) Oxygen content of regeneration gas;

(3) Initial coke content of catalyst;

(4) Fraction of initial carbon of catalyst;

(5) Type of catalyst (composition, activity, impurities present);

(6) Mode of formation of coke (feed stock, cracking conditions);

(7) Carbon/hydrogen ratio of coke (aging of coke);

(8) Efficiency of contacting of gas and catalyst;

(9) Pressure;

(10) Steam partial pressure.

The most influences of these variables are temperature, oxygen content of the gas, and amount of carbon on the catalyst.

The oxygen content of the regeneration gas is normally 0.5 to 2 percent. This presumably represents the gas throughout the regenerator. The temperature may range from 530 to 650 $^\circ$C although it is rarely above 600 $^\circ$C. Coke burning is an exothermic reaction and careful operations must always be practiced to avoid damaging a catalyst. The carbon in the effluent gases is

about equally divided between carbon dioxide and carbon monoxide; if anything the dioxide is in excess.

In certain commercial practice, catalysts are not burned clean, but are normally returned to the reactor when the carbon content reaches 0.3 to 0.7 percent by weight.

The way to decrease coke is to modify catalyst functions and reaction conditions. Various types of hydrocarbon reactions can produce coke under appropriate conditions. Generally the larger number of carbon atoms in molecules, such as aromatic and naphthenic rings, has higher potential to form coke. Reactions in which coking is important such as catalytic reforming, isomerization and various hydrogenation/dehydrogenations. In most cases the catalyst may be regenerated by burning off the coke in a diluted oxidizing gas stream. Then the catalyst activity returns to the initial value again.

2.3.1 Metal Redispersion

The physical process of redispersion of platinum atoms on the support by oxygen was concluded by Lieske et al. (1983). The effects of chloride ions are summarized below:

(i) There is no redispersion without oxidation of crystalline platinum and no oxidation without redispersion. Redispersion is accompanied by a proportional increase of the platinum oxidation state. This means that redispersion and oxidation of crystalline platinum are inseparably connected;

(ii) This "redispersing oxidation" of crystalline platinum is impossible with chloride-free catalysts;

(iii) The oxidized platinum must be movable and it can migrate on the surface of the alumina;

(iv)   A redispersion mechanism in 3 steps was proposed.

First step   Special localized surface atoms of platinum crystallites can be oxidized;

Second step   These oxidized sites are attacked by chloride ions coming from the alumina surface;

Third step   Oxidized species are mobile , migrate from platinum crystallites and may be trapped on appropriate centers of the alumina.

2.3.2   Mechanisms and Kinetics of Regeneration

It is well established that without secondary burning, carbon and graphite do not give 100% CO_2 but some CO, with the CO/CO_2 ratio increasing with temperature.

Walker et al. (1959) extensively reviewed the literature on the products of carbon combustion, and had drawn the following conclusions:

(a) Both carbon monoxide and carbon dioxide are the primary products of carbon combustion. The oxidation of carbon to carbon monoxide and carbon dioxide is not significantly restricted by equilibrium considerations even at a temperature of 4000 K;

(b) The CO/CO_2 ratio is relatively independent of the type of carbon source. The empirical relations used by various workers to predict this ratio give values between 0.3 and 0.9;

(c) The primary CO/CO_2 ratio increases with increasing reaction temperature;

(d) Lower gas velocities tend to increase the CO_2 content because of increased secondary oxidation of CO to CO_2. The presence of water vapor also increases this secondary oxidation.

The three rate controlling steps generally encountered in the burn-off of carbon from coked catalysts are

(1) control by intrinsic carbon burning kinetics;

(2) control by oxygen diffusion through the catalyst pores;

(3) control by both (1) and (2).

In the controlled region of "intrinsic" chemical kinetics, combustion is controlled by the intrinsic burning rate of carbon. The reacting oxygen diffuses to all coke particles throughout the pellet, and consequently combustion occurs throughout the pellet but when in the diffusion controlled region it is characterized by the "shell progressive" mechanism. The reaction zone in this process moves as a thin shell from the outer surface towards the center as reaction proceeds. The diffusion rate of oxygen, being significantly smaller than the reaction rate of coke, controls the combustion reaction. In general, however, the rate of regeneration is not wholly controlled by either mechanism since both steps have approximately equal importance; the burn-off is said to be under intermediate control.

Parera et al. (1983) investigated a coke burning function on bifunction metal-acid catalysts (Pt/Al_2O_3-Cl). According to the coke formation step of the previous section. The platinum function acts as a catalyst for combustion and coke deposits on platinum are richer in hydrogen. It causes the burning of coke to start from coke deposits on metal. An increase in burning temperature causes more O_2 spillover from platinum that can continue to burn the coke near the metal through the coke on the support. Treating the catalyst with hydrogen before burning the coke makes it is easier to remove the coke.

The aging of a coked catalyst on chromia-alumina catalysts before coke burning can change the less volatile hydrocarbon group to more aromatic

and dehydrogenated structures (Royo et al., 1994). These procedures can avoid high-temperature excursions in the regeneration step.

The $(Pt-Re-S/Al_2O_3-Cl)$ catalyst gives the same burning result (Pieck et al., 1992). At low temperature, the coke burning is selective, surface C=O and C-OH groups are formed as intermediates. At high temperature, the burning is nonselective, these groups rapidly complete the second oxidation to CO_2.

An increase in temperature results in a transition from the kinetic controlled region, through the intermediate control region to the mass transport dominated region. Weisz and Goodwin (1963) increased the regeneration temperature above about 500 °C. The intrinsic burning rate began to exceed the diffusion rate of O_2. The rate was more and more diffusion controlled as the temperature was increased further.

When the rate is diffusion controlled, some effects show up that are not present during intrinsic burning. The burning proceeds from the outside surface of the granule toward the center so that a partially regenerated granule has a clean outside layer and an unregenerated core.

The CO/CO_2 ratio decreases as burning proceeds toward the center of the granule. As oxygen diffuses through the pores to get to the burning interface, it has a chance to react with CO diffusing away from the burning. As the interface moves closer to the center of the granule, the probability of the exiting CO reacting with incoming oxygen increases, thus reducing the CO/CO_2 ratio.

Generally, catalysts which have no oxidizing-reducing activity give this type of burning. In contrast, oxidizing-reducing catalysts such as Cr_2O_3 on alumina, Cr_2O_3 on silica-alumina, or Pt on alumina give little or no CO when coke is burned off them.

2.3.3 Effect of Oxidizing-Reducing Activity

Oxidizing-reducing catalyst components, such as Cr_2O_3, Pd, Pt, etc., have a profound effect on the burning of coke deposits. They have high intrinsic catalytic burning rates. These "combustion" catalysts change the nature of the burning reaction in that the CO/CO_2 ratio is reduced and is usually zero.