CHAPTER II
LITERATURE SURVEY

2.1 Catalyst Deactivation

It is necessary to know about the deactivation of the catalyst to be able to run an industrial process. While the topic of deactivation has received much attention in the last two decades, there still exist many unanswered questions. Deactivation of catalysts with time on stream is a phenomenon which occur invariably in many industrial processes. Most catalysts used in heterogeneous catalytic processes are subject to a decrease in 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.

Catalysts deactivate and must be regenerated or replaced. It can take less than a second, as in fluidized catalytic cracking, or several years, as in ammonia synthesis. Basically, three kinds of deactivation may occur: (1) sintering or thermal deactivation of the catalyst; (2) poisoning; (3) fouling or coking.

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. The sintering process may result in an overall loss of area of the support material or oxide base, or

may cause a loss of dispersion of the metal crystallites in a supported metal catalyst. Sintering may also be of importance in the reduction of the metal constituent of the catalyst.

Sintering is a complex phenomenon and despite much careful investigation it is still not possible to predict the rate at which the various structural characteristics (e.g. porosity and surface area) change for given operating conditions.

2.1.2 Catalyst Deactivation by Poisoning

The most usual type of catalyst poisoning is caused by an impurity that is either present in the gas stream or is formed by some process during the reaction. In both cases this poison becomes adsorbed on the active sites of the catalyst, causing a fall-off in the activity of the catalyst. The poisoning may be either temporary or permanent.

Most poisoning processes are effectively irreversible, so the catalyst has to be discarded ultimately but there is an important class of poisons that are reversible in action. In principle it is always possible to remove impurity poisons from the feed stream by purifying the feedstock or by using a guard catalyst, but to a level often required that may prove prohibitive. So it may often be preferable to tolerate some degree of poisoning.

It should be emphasized that poisoning is not always undesirable. In some cases selective poisoning may be employed to enhance one reaction on a multifunctional catalyst whilst inhibiting a less desirable one.

2.1.3 Catalyst Deactivation by Fouling

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. The most typical of fouling processes is that of the carbonaceous deposit or "coke" that

forms on most catalysts used in the processing of petroleum fractions or other organic chemical feedstocks.

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 or use of a guard catalyst; if 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 associated with relatively large amounts of deposit and, if excessive, in addition to covering the active sites of the catalyst it may affect the diffusional properties of the porous catalyst pellet. In the limit, pore blocking may occur for both coke and metal deposition, and if allowed to continue the deposits will block the void spaces between the catalyst pellets, necessitating a complete shut down of the reactor.

2.2 Mechanisms of Coke Formation

The mechanism of coke deposition is a very complex multistep reaction sequence. The reaction path consists of adsorption, dehydrogenation, condensation-polymerization, and cyclization of hydrogen-deficient fragments, It is not possible to find a general coking mechanism. Different reaction schemes have been proposed for different systems.

A number of investigators have examined the nature of the coke deposit on catalysts. Microscopic examination by Haldeman and Botty (1959) has established that the coke consists of filmy aggregates of size less than 10 nm. This discrete nature of the coke deposits has been confirmed by many other

investigations. X-ray studies have also established that approximately 50% of the coke deposits are in the form of pseudo-graphitic structures with the residue probably existing as unorganized aromatic systems and of aliphatic appendages to polynuclear aromatic systems.

Hughes (1984) reviewed Froment and Bischoff (1961) work on a fixed bed reactor. By assuming that coking would occur in a reaction either in parallel or consecutive to the main reaction, it was shown that a profile of deposited coke would exist within the reactor. This coke profile would be descending in the case of a parallel mechanism, but ascending for a consecutive mechanism. When the reactant concentration is high, parallel fouling gives large coke deposits since the reactant is the coke precursor. Conversely, larger coke deposits are formed in series fouling, when the product has a high concentration. For propane dehydrogenation over Pt catalysts, multiple Pt atom "ensemble" sites are required for coke formation (Biloen et al., 1977).

Parera et al. (1983) studied the thermograms of the temperature programmed oxidation (TPO) of coke on naphtha reforming catalysts (Pt/SiO$_2$ and Pt/Al$_2$O$_3$-Cl). Each type of catalyst shows only one peak in the range 123 to 369°C for Pt/SiO$_2$ and 369 to 555°C for Pt/Al$_2$O$_3$-Cl. This result corresponds to the results of Beltramini et al. (1985), the first combustion peak that occurs at lower temperature is produced by the burning of the coke on the metallic sites (Pt). The second peak occurs at higher temperature is due to the burning of the coke on the acidic sites (Al$_2$O$_3$-Cl). Since with increasing Pt, coke increases, the area of the TPO diagram also increases. 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) studied the coke deposited on the Pt-Re/Al$_2$O$_3$-Cl catalyst during a commercial cycle of a naphtha reformer. At the beginning of

the operation cycle there is rapid coke formation on the catalyst and the hydrogen to carbon ratio of the coke decreases. After this short period and up to the end of the cycle, the rate of coke formation continuously decreases and the hydrogen to carbon ratio of the coke decreases very slowly. 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. This peak appears between the two identified peaks which can be ascribed to coke deposited on the metal and on the support. Two different hypotheses were proposed to explain this phenomenon. The first hypothesis states that it could be due to a carbon less graphitized than that which can burn at 500°C deposited on a different hydroxyl groups shown by IR spectrometry. Alternatively, it could also consist of carbon deposited on the support in the vicinity of the metal particles and resulting from a continuous slow migration of carbonaceous fragments from the metal to the support.

2.2.1 Effect of Reaction Conditions

Trimm (1983) reviewed some methods to minimize coke deposits by modifying both the physical and chemical reaction conditions. Dilution and gasifying agents were introduced to the system in order to reduce coking by controlling the ensemble size and promoting the gasification.

The coke deposited on different Pt/Al_2O_3 catalysts of varying metal dispersion during reaction of cyclopentane was studied by Barbier et al. (1985). It has been shown that well dispersed platinum catalysts present a strong resistance to coke deposition, the larger particles showing a higher initial rate of coking.

Barbier et al. (1985, 1988) studied the effect of operating conditions on Pt/Al_2O_3 for cyclopentane conversion. They found that an increase in active metal dispersion can delay the coking reaction at high reaction temperatures and give the opposite result at lower reaction temperatures. 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 the Pt content in Pt/Al_2O_3 catalysts for reforming, the higher is the conversion and coke formation. Increases in intermediate hydrocarbons or coke precursors were discussed by Pieck et al. (1989).

Larsson et al. (1996) studied the effect of reaction condition on the coke formed during propane dehydrogenation. They found that the amounts of the three different types of coke (coke on and in the vicinity of the metal, coke on the carrier, and graphitic coke on the carrier) were related to reaction conditions. The formation of the coke belonging to the first two types of coke increases with temperature and partial pressure of propylene while the third type increases with temperature and propane partial pressure.

2.2.2 Effect of Promoters Loading

Distinct selectivity changes have been observed in the conversion of n-hexane over platinum upon its being alloyed with tin (Dautzenberg et al., 1980). Addition of tin to nonacidic alumina supported platinum markedly reduces the deactivation of the dehydrocyclization activity that produces benzene. Not only the stability but also the selectivity of the platinum function are modified by addition of tin. The formation of coke deposits on the metal function is reduced by changing the intrinsic catalytic properties of platinum by tin, the ensemble effect explanation. Platinum-tin reforming catalysts give a corresponding adsorption improvement that 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 addition of tin to Pt/Al_2O_3 influences the adsorption of 1-hexene in a specific manner, the adsorbed amount increases whereas the adsorption bond strength is weakened. This can be explained by a steric adsorption model on the basis of an ensemble effect of alloyed tin. On $Pt-Sn/Al_2O_3$ the coke precursors are more easily transferred to alumina. 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 Pt catalyst has less proportion of carbon deposited on the support than a Pt-Sn catalyst. Afonso et al. (1994) studied the coke deposits from Pt-Sn catalysts during dehydrogenation by solvent extraction. They also found more than one structure of carbonaceous material occurring. 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 of the types of coke are different in their hydrogen content.

Cortright and Dumesic (1995) studied the effects of potassium on silica supported Pt and Pt/Sn catalysts for isobutane dehydrogenation and found that the addition of tin to Pt/SiO_2 enhances the selectivity for dehydrogenation of isobutane to isobutylene but also decreases the dehydrogenation rate over the exposed platinum. However, the addition of potassium to $Pt/Sn/SiO_2$ enhances the isobutane dehydrogenation activity, improves the dehydrogenation selectivity, and decreases the rate of catalyst deactivation.

2.3 Catalyst Regeneration

The cracking catalyst must be regenerated to remove coke and return the catalyst to acceptable activity after it has been used for a period of time. The oxidative regeneration is the most commonly used, involving the combustion of the coke deposits with oxygen-containing streams.

The main problem in the regeneration of coked catalyst is to burn off the coke without creating irreversible damage to the catalyst, since a catalyst may be expected to be regenerated more than one hundred times in its normal lifetime. Temperature, oxygen content of the gas and amount of carbon on the catalyst are the major variables that influence regeneration rate. In general, the oxygen content of the regeneration gas is 0.5 to 2 percent and the temperature may range from 530 to 650°C although it is rarely above 600°C. Coke burning is an exothermic reaction and careful operations must always be practiced to avoid damaging a catalyst.

2.3.1 Redispersion of Platinum

The physical process of redispersion of Pt in oxygen has attracted special interest because of its importance for the regeneration of the catalysts (Lieske et al., 1983). The effects of chloride ions are summarized below:

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

(ii) The redispersion is unachievable with chloride free catalyst. The almost unchanged chlorine percentage in the spent catalyst has been reported by Parera et al. (1989).

(iii) The oxidized Pt must be movable and migrates on the surface of the alumina.

On the basis of these conclusions, a new model of redispersion was proposed. In the first step special localized surface atoms of the Pt crystallite can be oxidized by oxygen. In the second step these oxidized sites are attacked by chloride ions coming from the alumina surface. The oxidized species are mobile and migrate on the surface of the alumina, and may be trapped on appropriate centers of the alumina. As a result, Pt is removed from the Pt crystallite and dispersed on the carrier.

2.3.2 Mechanisms and Kinetics of Regeneration

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

(i) The combustion products give carbon dioxide and carbon monoxide as major products. This combustion is not significantly restricted by equilibrium considerations even at temperatures of 4000 K.

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

(iii) The primary CO/CO_2 ratio increases with reaction temperature.

(iv) Lower gas velocities tend to increase the CO_2 content because of increases 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, or (3) control by both (1) and (2).

In the intrinsic controlled region, the reacting oxygen diffuses to all coke particles throughout the pellet and consequently combustion occurs throughout the pellet whereas in the diffusion controlled region it is characterized by the "shell progressive" mechanisms. The reaction zone in this

process moves as a thin shell from the outer surface towards the center as reaction proceeds. In general, the rate of regeneration is not wholly controlled by either mechanism since both steps are operating with varying degrees of importance. When both steps have approximately equal importance the burn-off is said to be under intermediate control.

Parera et al. (1985, 1989) investigated the coke burning function on bifunction metal-acid catalyst (Pt/Al_2O_3-Cl). According to the coke formation step on the previous section, the Pt function acts as a catalyst for combustion and coke deposits on Pt are richer in hydrogen. It causes the burning of coke to start from coke deposits on metal. An increase in burning temperature causes more oxygen spillover from Pt that can continue burning the coke near the metal through the coke on the support. Treating the catalyst with hydrogen before burning the coke makes it easier for removal of coke. On Chromia-Alumina catalysts (Royo et al., 1994), these procedures can avoid high temperature excursions in the regeneration step. The aging of a coked catalyst before coke burning can change the less volatile hydrocarbon group to more aromatic and dehydrogenated structures.

The Pt-Re/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.

2.3.3 Effect of Oxidizing-Reducing Activity

Oxidizing-reducing catalysts (such as Cr_2O_3, Pd, Pt, etc.) can change the nature of the burning rate because of its catalytic properties, reducing the CO/CO_2 ratio to close to zero (Weisz et al., 1966) as reviewed by Bond et al., (1995).