CHAPTER II
LITERATURE SURVEY

2.1 Classification of Catalyst Deactivation Processes

General reviews of catalyst deactivation have been given by Oudar and Wise, 1985. They have laid the foundations of a better understanding of catalyst deactivation processes. Basically, three kinds of deactivation may occur: (1) sintering or thermal deactivation of catalyst; (2) poisoning; (3) fouling.

Sintering is a physical process associated with the loss of area of the catalyst when it operated above the normal range of temperature. 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 Al_2O_3, operating 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 platinum supported on alumina. Here sintering can occur not only by reduction of the supported area but by a "coalescence" or loss of dispersion of the metal crystallites. This loss of area causes a sharp drop in activity.

Poisoning in this topic will be used solely to describe catalyst deactivation due to small amounts of material, associated with the adsorption of the poison on the active sites of the catalyst. 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. In this particular case, selectivity enhancement is achieved by preferential blocking of certain sites on the catalyst.

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. The most typical of fouling processes is that of the carbonaceous deposit or "coke" that forms on most catalysts used in the processing of the petroleum fractions or other organic chemical feedstock. It is important to recognize that the coke deposit in this case originates from the reactions occurring and is not an impurity; 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.

2.2   Mechanism of the Promoter Action

The term promoter is defined as "a substance added to a catalyst during its preparation in small amounts (usually less than 10%) which by itself has a little activity but which imparts either better activity, stability or selectivity for the desired reaction than is realized without it" (Emmett, 1954).

The action of promoters may be judged from: (a) the mechanism by which the promoter acts; (b) the conditions for promotion, and (c) the interrelationship between the properties of the promoter and the catalyst specific to the particular type of reaction. Various explanations for the mechanism of the promoters have been made available, but not one as yet has been universally accepted. It was proposed that if the catalyst acts by virtue of its ability to form intermediate compounds, then the promoter functions as a secondary catalyst accelerating both formation and subsequent decomposition of the intermediate product formed between the catalyst and the reactants.

Further, the promoter may not only accelerate the actual velocity of the reaction, but it may function also as a "protector" of the catalyst. The protective action of the promoter may be expressed likewise in the restoration of the catalyst to its normal function.

The action of a promoter may be specific in the sense of altering the relative adsorption of the reacting components. One researcher suggested that a promoter action takes place when the main component adsorbs one reactant and the promoter another (Oudar and Wise, 1985). If the action of the promoter were the alteration of the relative adsorption of reacting substances then either an optimum ratio for the desired interaction would be obtained.

The mechanism of a promoter action may concern itself also with increase in the number of active atoms or their groups in the catalyst or be due to a specific change in the nature of active atoms so that a greater number of transformations per unit time may be effected (Berkman et al., 1940).

It has been also conceived that promoters may aid in the formation, as well as in the preservation, of active centers on the catalyst particles. By assuming that a promoter action is provided either through the existence of points of attachment for molecules different from those of the original catalyst, or is due to the fact that the active points are better spaced. The promoter acts then by orienting molecules to create a "space" effect in the sense of Langmuir's conceptions (Oudar and Wise, 1985).

If isolated molecular units have a higher reactivity than the substance as a whole, then the increase in reactivity of a promoted catalyst may be due to the fact that the promoter separates small parts of the catalyst mass. The mechanism by which a promoter acts has been connected with the nature of the interface between the catalyst and the promoter. The maximum promotion was assumed to occur when every molecule of the catalyst was separated from its

neighboring molecules by a definite number of single molecules of the promoter so as to prevent coalescence.

The advantage of the promoter was confirmed by Lieske et al., 1987, in the study of influence of tin, which acts as a promoter in platinum-tin catalysts. They reported that added tin increased the extent of coking by hexene but at the same time a larger part of platinum remains free of carbon. They explained this by a "drain-off" effect of the alloying tin: on $Pt-Sn/Al_2O_3$ the coke precursors are more easily transferred to the alumina support. Gault et al., 1981 converted C labeled hydrocarbons over catalysts containing 10 wt.% Pt and varying amount of tin (0.2 to 5 wt.%) on alumina catalysts at low (5.5 torr) or atmospheric pressure. The support was an inert alumina and, even though the catalysts contained 1 to 1.2 wt.% Cl, they did not consider the catalyst to have acidic character. They reported that the 10 wt.% Pt loaded catalyst, when loaded with small amounts of Sn, has the same catalytic properties as very highly dispersed Pt-alumina catalysts.

2.3   Effect of Promoter on Catalyst Properties

For the dehydrogenation of lower alkanes on the metal catalysts, many studies have shown that a platinum catalyst is a good dehydrogenation catalyst (Cortright and Dumesic, 1994) due to its high activity for C-H bonds rupture coupled with its poor ability to cleave C-C bonds. However, the selectivity and stability of platinum catalysts can be improved by the addition of a second metal which in this case plays the role of a promoter (Resasco et al., 1994). One of the factors which has renewed interest in the catalysts by alloys was the finding that for various hydrocarbon conversion processes by Dautzenberg et al., 1980. He found that the platinum catalysts could be substantially improved

by addition of certain metals, such as rhenium, germanium and tin. A significant observation is the fact that the steady state activity of these bimetallic catalysts is superior to that of monometallic catalysts. This also holds for tin modified supported platinum catalysts. For dual function catalysts it is assumed that the initial intermediate (i.e., a dehydrogenated species such as an olefin) involved in the formation of the carbonaceous deposits is catalytically created by the metal function. Addition of tin can inhibit the formation of initial intermediate which leads to reduced carbon deposition both on acidic and on the metal functions. This agrees with the experiment of Burch and Garla, 1981 in the case of catalyst modified by tin. They showed that tin exists in a different form in each case. When tin is present in the trace amounts as metallic tin, it will poison a platinum surface. When present in a nonmetallic state it acts as a promoter. The special properties of platinum-tin catalysts must be due to a change in the electronic properties of small platinum crystallites either by interaction with a tin (II) ion stabilized on the alumina to give electron deficient platinum, or by incorporation of a few percent metallic tin as a solid solution in platinum to give electron rich platinum.

2.4 Effect of Poisoning on Catalyst Selectivity

It is well known that diffusional resistances affect the yield of catalytic process. In general the effect is an adverse one, in that the yield of the desired product is reduced by diffusional limitation and therefore minimization of this effect is desirable. However, it is also well known that, industrially, the selectivity of a number of processes can be enhanced by the addition of small amounts of poisons, e.g., CO and H_2S, which act as selectivity moderators.

There are two ways in which a poison may affect the selectivity of a catalyst. The first is the preferential blocking of catalyst sites in the manner described above. An alternative is that the poison reduces the deterious effect of the diffusional limitation on the catalyst selectivity. Under the latter conditions, addition of a poison to a diffusion limited reaction may be advantageous since the increased selectivity may more than compensate for the reduced catalytic activity occasioned by the presence of poison.

Thus the effect of poisons on the selectivity enhancement appears to be significant. Further work is required so that this beneficial effect of poisoning can be exploited to the full in many other processes.

2.5 Effect of Alkali Treatment

The chloride which is found on any catalyst acts in different ways. Chloride has an effect on both the initial dispersion (Lieske et al., 1983) of platinum and on maintenance of this dispersion. It also modifies the acidity of the catalyst and reduces the cracking reactions that may occur. The action of alkali can manifest itself in such various different ways as the following.

(a) The selectivity of the catalyst passes through a maximum as the alkali content is increased.

(b) The activity of catalyst can be increased by promoting it with small quantities of an alkali metal.

(c) Doping with alkali can be employed in certain cases to delay catalyst deactivation when it is due to coking, sintering, or reorganization of the surface.

For industrial catalyst applications, a chloride content is deliberately maintained in the range of 0.8-1.1 wt.%. Although some chloride is necessary,

an excess of it leads to excessive cracking and coking activity (Oudar and Wise, 1985). According to the studies of Passos and Martin, 1992, on the effect of lithium and residual nitrate species on platinum dispersion in catalyst, they found that a complete elimination of nitrate ion during the calcination at 773 K was not possible for catalysts modified by high lithium content but residual nitrate ion can be eliminated during the reduction step. The residual nitrate ions cause an important drop in the metal dispersion . The drop in the dispersion is due to the simultaneous reduction of nitrate ion with the platinum precursor. Moreover, redispersion of platinum in oxygen is possible only in the presence of chloride which gives a mobile oxidation product. As a result platinum is removed from the platinum crystallites and further disperses on the carrier (Lieske et al., 1983).