

## CHAPTER II

### BACKGROUND

Deactivation of catalysts with time on stream is a phenomenon that occurs invariably in many industrial processes which in turn complicates the design and operation of the reactors. The fundamental causes of this phenomenon involving poisoning, sintering and fouling of catalysts. Deposition of coke is one of the those basic deactivation processes which is called 'Fouling' (Satterfield, 1991; and Froment and Bischoff, 1990) and its main effect is the physical blocking of the catalyst surface (including its pores). However, it has been reported that coke may have some poisoning effect on metallic and acidic sites. The form of carbon deposition (usually called 'coke') may vary from high molecular weight hydrocarbon species (polymeric carbon) to graphitized carbon. The nature of coke depends on the industrial conditions, the feedstock and the nature of the reaction (Hughes, 1984).

Basically, catalysts are considered as chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction, whose thermodynamic equilibrium they consequently cannot change. Metal-based catalysts are used widely in industry to promote a variety of reactions involving carbon-bearing feedstocks. As with any catalyst system, activity, selectivity and life are important, the latter being dictated by the possibility of sintering, poisoning, or coking. In this research attention is focused on the latter problem that may cause the catalyst deactivation partially or completely. The important patents in the field of catalysis are concerned with promoters and future progress in the field will probably be largely in this direction. The catalytic properties of

pure substances are generally well known but possibilities for improvement through the use of suitable promoter are great.

The term promoter is defined as 'a substance added to a catalyst during its preparation in small amount (usually less than 10%) which by itself has little activity but which imparts either better activity, stability or selectivity for the desired reaction than is realized without it' (Emmett, 1954). The possibility of choosing a promoter from theoretical considerations would permit one to obtain (a) desired catalytic reactions with the desired final products, (b) improvement of processes to insure better yields than those obtained with a catalyst alone, and (c) shifting of the reaction in a more favorable direction.

### 2.1 Mechanism of the Promoter Action

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 for the particular type of reaction. Various explanations for the mechanism of promoters have been made available, but not one as yet has been universally accepted. It was supposed that if the catalyst acts by virtue of its ability to form intermediate compounds, then the promoter functions as a secondary catalyst accelerating both the 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 a 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 reacting components. A promoter action takes place when the main component adsorbs one reactant

and the promoter another. If the action of a promoter were the alteration of the relative adsorption of reacting substances then either an optimum ratio for the desired interaction would be obtained, the ratio of adsorbed reactants being changed, or a rearrangement of chemical forces in the activated molecules would be effected where by the promoter would activate one of the interacting substances and the catalyst the other. The surface of a promoted catalyst may retain a large fraction of the total amount of gas absorbed in a reactive state as that of a non-promoted catalyst. The increased efficiency of a catalyst due to a promoter may be also the result of an increase in the internal area of the catalytic surface. The mechanism of a promoter action may concern itself also with an 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).

This advantage confirmed by Lieske et al., 1987 and Dautzenberg et al., 1980, in the study of influence of tin, which acts as a promoter in platinum-tin catalyst, on the coking of different hydrocarbons. They found that the addition of tin suppresses coke formation because of the ensemble effect. Tin may block platinum ensembles necessary for combination of  $C_1$  species into large structure. Moreover, it can change the configuration of adsorption into '*tilted position*'. So, initially coke deposits are formed very rapidly on the platinum sites. After that, the coke precursors are immediately transferred from platinum to acidic sites of the support by '*drain-off mechanism*'. Therefore the carbon coverage of the metal remains constant while coke is deposited on the support and platinum will free enough to be adsorbed by the other hydrocarbons. In addition, Burch and Garla, 1981, studied the conversion of n-hexane into aliphatic isomers which is catalyzed by platinum-tin catalysts. The results show that when tin is present the catalysts are much more stable and have

much higher selectivities for isomerization and aromatization reactions. They concluded that tin modified the acidity of the support and also modifies the properties of the platinum resulting in less self-poisoning.

## **2.2 Concentration of Promoter**

The maximum active concentration of the promoter is rather small and varies. It is not the absolute value of the concentration but rather the definite ratio of the promoter to the catalyst which is of major significance in the change of the activity of the promoted catalyst. The necessity of a proper ratio of catalyst to promoter has been studied for many years. There is proper ratio that gives catalyst of high and persistent activity. When promoter was added in amount greater than that required to form the compound, the catalyst obtained lost its activity completely in tests of long duration (Berkman et al., 1940).

## **2.3 Effect of Promoter on Catalyst Properties**

For the dehydrogenation of lower alkanes on 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 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 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 the acidic and on the metal function. Corresponding to Burch and Garla, 1981 in the case of catalyst modified by tin. He proved that tin exists in a different form in each case. When tin is present in trace amounts of 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 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 the 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 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.

In industrial catalyst applications, a chloride content is deliberately maintained in the range of 0.8-1.1 wt%. Although some chlorine 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, in the effect of lithium and residual nitrate species on platinum dispersion in catalyst. They found a complete elimination of nitrate ion during the calcination at 773 K was not possible for catalyst 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 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).

## **2.5 Coking Formation on Catalyst**

Catalyst coking is a phenomenon that involved the deposition of carbonaceous species. Material deposited may include elemental carbon, high molecular weight polycyclic aromatics, high molecular weight polymers, and so on, any or all of which may originate in the gas phase, on the metallic catalyst, on the support or elsewhere in the system (Oudar and Wise, 1985). When the surface of a catalyst becomes deactivated by poisoning or fouling. Further reaction is inhibited by virtue of a foreign molecule being adsorbed in the porous structure of the catalyst and covering a fraction of its active surface. The reactant must then be transported to the non-deactivated parts of the catalyst before reaction can occur thus deactivation increase the average distance over which a reactant must diffuse through the porous structure. It can be expected that the deactivating species will travel deep into the particle, yielding a catalyst in which deactivation is evenly distributed. Catalyst

deactivation by fouling usually involves amounts of deposited material. Fouling by coke deposition is always associated with the main reaction. Therefore it is usually not possible to eliminate the coke deposition process entirely, but the process of coking can be substantially reduced by modifying the catalyst so as to improve its selectivity. Beltamini et al., 1985; Parera et al., 1983; Afonso et al., 1994; and Pieck and Parera, 1989, studied the coke formation in bifunctional metal-acid catalyst is a complex phenomenon involving both functions. Also the burning of the coke includes both functions. From the temperature programmed oxidation of the coke it showed two zones of burning: the first zone (lower temperature) is the burning of the coke deposited on platinum and the second one (higher temperature) to the coke on alumina. It is assumed that the coke formation starts on the metal because of the unsaturated products the metal produces. After a certain period of time, the coke on metal reaches an 'equilibrium' while the unsaturated products continue their condensation on the support.

The coke deposit in the form of thin filmy aggregates of size less than 10 nm. The molecular formula of coke deposits varies from  $C_1H_{0.4}$  to  $C_1H_1$ . Thus the coke corresponds to a hydrocarbon in composition but with only a small amount of hydrogen. For coking to low levels with fresh catalyst it found no significant change in surface area or pore volume. It seems that under these conditions for the particular catalyst used the pores are not sealed off by coke particles (Hughes, 1984).

The precursor to the coke deposits is still subject to some dispute. For sometime it was believed that because of the aromatic condensed ring form of many coke aggregates, aromatics were the intermediate precursors. More recently Afonso et al., 1994, proposed that the intermediate precursors are olefins. Their work focused on coke deposition on platinum-tin catalyst after the dehydrogenation reaction of n-alkanes to mono-olefins, under industrial

conditions in order to better understand the deactivation process of the catalyst. They found that olefins are primary precursors of the mechanism of coke formation. In analysis of the experiment obtained by cracking typical oil feedstock, it showed that coke was not a primary product of the reaction but was a product of secondary reactions arising from the primary products. Since the only primary products that were qualitatively different from the feed in the experiments were olefins, it was inferred that coke formation was attributable to these. It should be noted that all hydrocarbons from paraffins to aromatics, will yield coke under appropriate experimental conditions.