

## **CHAPTER II**

### **HISTORICAL REVIEW**

Deactivation of catalysts with time on stream is a phenomenon involving the decrease in activity and selectivity of catalysts that invariably occurs in many industrial processes which in turn complicates the design and operation of the reactors. A catalyst may lose its activity or selectivity for a wide variety of reasons. The causes may be grouped loosely into:

1. Poisoning;
2. Sintering;
3. Fouling.

Poisoning occurs when there is an impurity present in the feed stream that reduces catalyst activity by occupying active sites. Sintering is a complicated phenomenon which varies with the nature of the metal, the chemical nature and morphology of the support, and the nature of various gases (Satterfield, 1991). Deposition of coke is one of those basic deactivation processes which is called 'Fouling' (Froment and Bischoff, 1990) and its main effect is the physical blocking of the catalyst surface (including its pores). 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).

Technically, catalysts are considered as chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction. Metal-based catalysts are used widely in industry to promote a variety of reactions involving

hydrocarbon feedstocks. As with any catalyst systems, activity, selectivity and life are important, the latter being dictated by the possibility of sintering, poisoning or coking. The latter problem which causes the partially or completely deactivation of catalysts will be considered. The important patents in this 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 amounts (usually less than 10%) which by itself has little activity but which imparts either better activity, stability or selectivity for the desired reaction than 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 or improved selectivity.

## 2.1 Type of Promoters

This term is used to cover a wide variety of phenomena, but most promoters can be classified as textural promoters or structural promoters. A textural promoter relates to the physical effect and a textural promoter is an inert substance which inhibits the sintering of microcrystals of the active catalyst by being present in the form of fine particles. These prevent the active catalyst particles from contacting with one another so they do not agglomerate which resulted in a minimum loss of active surface area. In contrast to a textural promoter, a structural promoter causes a chemical effect by changing the chemical composition of the catalyst. In many cases, the

effect of a structural promoter is clear although its mechanism is not. In other cases, it is not clear whether the effect of the promoter is primarily a physical or a chemical effect.

## 2.2 Mechanism of the Promoter Action

The action of promoters may be judged from: (a) the mechanism by which the promoter behaves; (b) the promotion conditions; and (c) the interrelationship between the properties of the promoter and the catalyst specific to the particular type of reaction. Many mechanisms of promoters' action have been explained in different ways but none has been universally accepted as yet. It is 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/or 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 also function as a *protector* of the catalyst. The protective action of the promoter may be exhibited in a restoration of the catalyst to its original 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 with another. If the action of a promoter was 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 an alteration 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 result from an increase in the active 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).

### **2.3 Effect of Alkali Doping on Catalyst Properties**

Alkalis in particular show a wide variety of effects (Mross, 1983) and are not restricted to a few specific types of reaction. Generally, the alkali can act in three different functions as shown below:

1. Increase the selectivity or specificity;
2. Increase the activity;
3. Prolong the effective lifetime of the catalyst.

As already mentioned, there are numerous factors which can lead to deactivation. Doping with alkali can be used in certain cases to retard the catalyst deactivation, especially the coke formation.

A review of Mross categorizes at least eight modes of action. These are listed below:

1. Intrinsic catalytic effect of the alkali;
2. Creation of basic sites for accelerating the base-catalyzed reactions;
3. Neutralization of acidic centers which can enhance the undesired side reactions;
4. Modification of the adsorption properties of the catalyst surface;
5. Auxiliary function during the preparation of the catalyst;
6. Modification of the physical properties of the melt active component;

7. Reduction of the volatility of the active component through compound formation;
8. Prevention or reduction of the rate of phase transformations.

The effect of alkali frequently increases with atomic weight, thus;



The effect of alkali doping upon a catalyst is frequently attributed to a neutralization of acidic centers.

The addition of potassium to bimetallic Pt-Sn supported on SiO<sub>2</sub> catalysts increases the selectivity and improves resistance of the catalyst to deactivation. This result suggests that potassium may act like tin by reducing the ensembles of surface Pt atoms. The larger ensemble sites of Pt are favored by the unwanted side reactions such as coking which requires at least 3 contiguous sites of Pt (Margitfalvi et al., 1985). Addition of potassium to Pt-Sn/SiO<sub>2</sub> catalyst has been used to study the influence of alkali metal on a catalyst and shows an increase in activity. It has also found that the isobutane dehydrogenation reaction has a negative order with respect to hydrogen over Pt-Sn-K/SiO<sub>2</sub> catalyst, indicating a higher coverage of hydrogen on the active sites. The increased dehydrogenation rate over this catalyst may be attributed to the increased number of sites available for removal of hydrogen from adsorbed isobutane (Cortright and Dumesic, 1995).

#### **2.4 Concentration of Promoters**

The maximum effective concentration of the promoter is rather small and varies. It is not the absolute value of the concentration but rather the specific ratio of the promoter to the active component which is of major significance in the change of the activity of a promoted catalyst. The necessity of a proper ratio of catalyst to promoter has been studied for many years.

There is always an optimal ratio that gives a catalyst high and persistent activity (Berkman et al., 1940).

The positive effect of alkali can be observed at the certain amount of added alkali. It is noteworthy that the selectivity of a catalyst passes through a maximum as the quantity of added alkali increases. After that, addition of more alkali reveals a negative effect by changing the surface structure of catalyst. There is evidence that adding too much lithium resulted in lowering conversion and selectivity of catalyst. This is because of the simultaneous reduction of residual nitrate ions with platinum during the reductive treatment of catalyst. Usually, this residual nitrate ions which come from the  $\text{LiNO}_3$  precursor in the impregnation step can be decomposed while calcining the catalyst. This simultaneous reduction induces the important drop in the metal dispersion because platinum is not reduced to the active or metallic state (Passos and Martin, 1992).

## 2.5 Coke Formation on Catalyst

Catalyst coking is a phenomenon that involves 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).

Coke formation on catalysts may take several forms and be caused by different mechanisms. If the temperature is high enough, pyrolysis reactions may occur in the gas phase and deposition of *gas-phase carbon* may occur on the catalyst. At lower temperatures carbon or coke is usually formed directly on the catalyst surface by means of catalytic processes. In its simplest form this may occur by a parallel or series reaction along with the main reaction (Hughes, 1984).

When the surface of catalyst is deactivated by fouling or poisoning, further reaction is inhibited by virtue of a foreign molecule being adsorbed in the porous structure of catalyst and covering some parts of its active surface. The distance that a reactant must diffuse through the porous structure may increase, and it is harder for a reactant to reach the surface active site where the reaction can occur. It seems to be expected that the deactivating species will penetrate deeper and deeper into the particle over time, yielding a catalyst in which deactivation is evenly distributed. Although deactivation and coking are often observed to occur simultaneously, a simple and direct relationship between the two observations has not been found. This also indicates that the catalyst activity and coke content have a complex relationship. The activity of the catalyst depends on the number of active centers that are available for carrying out the main reaction. Sometimes, coke is not formed on the active centers of the main reaction and deactivation may not occur. For example, reforming catalysts have shown a substantial activity even the coke content is equivalent to monolayer of surface coverage. Not only the position where coke is formed but also the distribution of coke within the pellets has an effect on the activity of catalyst. It is clear that for a given coke level, the coke concentrated near the pore mouths is more effective as a barrier of diffusing reactant than the same amount uniformly distributed (Butt and Petersen, 1988).

Fouling by coke deposition is always associated with the main reaction. Therefore, it is usually not possible to eliminate the coke deposition process entirely. However, the process of coking can be substantially reduced by modifying the catalyst so as to improve its selectivity. For example, the small amount of alkalis is added to dehydrogenation catalysts. This reduces the acidity of the catalyst and tends to reduce the cracking type reactions that may occur on available acid sites.

Addition of tin can also modify the characteristics of coke. Basically, there are two zones of coke burning off during temperature-

programmed oxidation. The first zone (lower temperature) is the burning of coke deposited on metal sites and the other one (higher temperature) is the burning of coke on the support (Parera et al., 1983; Beltramini et al., 1985; Afonso et al., 1994). It is assumed that the coke formation begins on the support because of the unsaturated products on which 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. Tin can behave like a surface species which promotes the mobility of coke precursor to diffuse from metal sites to the support.