

CHAPTER III

THEORY

In this chapter, the catalyst deactivation are briefly explained in section 3.1. The coke formation process on catalyst is reviewed in section 3.2. Section 3.3 gather the regeneration of deactivated catalysts.

3.1 Catalyst Deactivation. (Satterfield,1980)

A catalyst may lose its activity or its selectivity for a wide variety of reasons. The causes may be grouped loosely into

1. Poison
2. Fouling
3. Reduction of active area by sintering or migration
4. Loss of active species

A catalyst poison is an impurity present in the feed stream that reduces catalyst activity. In a complex reaction it may affect one reaction step more than another; hence the selectivity towards a desired reaction may be improved by deliberately adding a poison. It adsorbs on active sites of the catalyst, and if not adsorbed too strongly, it is gradually desorbed when the

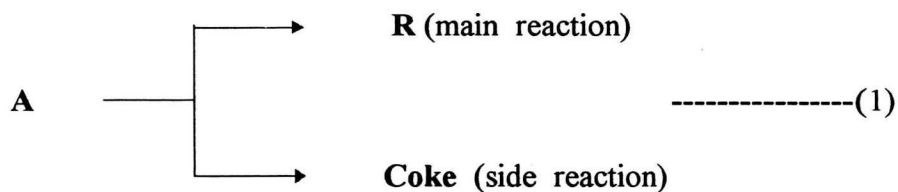
poison is eliminated from the feed stream. The phenomenon is then temporary. If adsorption is strong, the effect is permanent. The desorption may be enhanced by reaction with the fluid. Thus in a hydrogenation reaction a metallic catalyst may be poisoned by adsorption of a sulfur compound, but desorption may be enhanced by its conversion to H_2S by reaction with H_2 . If a reaction product is strongly adsorbed, the reaction may be termed self-poisoned or self-inhibited

The term fouling is generally used to describe a physical blockage such as the deposit of dust or fine powder or carbonaceous deposits (coke). In the latter case activity can usually be restored by removal of the coke by burning.

The fouling catalyst deactivation have been found by Butt (1972) and Levenspiel (1972) in Hughes (1984) and they have laid the foundations of a better understanding of fouling catalyst deactivation process. 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. Another class of fouling reactions is that of metal sulphide deposition arising from the organometallic constituents of petroleum which react with sulphur-containing molecules and deposit within the pores of the catalyst

during hydrotreating operation (Newson,1975). Liquid fuels derived from coals also give rise to similar deposits during hydrocracking of the resultant liquid (Davies,1978). These last two examples may be termed impurity fouling, and as such they are not typical of the more general type of fouling associated with coke formation on the catalyst surface. The formation of carbonaceous or coke deposits (containing, in addition to carbon, significant amounts of hydrogen plus traces of oxygen, sulphur, and nitrogen) during the processing of organic based chemical feedstocks is the more usual example of fouling. 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.

In general, coke can originate from the reactant or product by reaction (1) or (2). Reaction (1) is called parallel fouling while (2) is called series fouling or consecutive fouling. Fouling may (and indeed often does for complex system) also occur by a combination of reactions (1) and (2). The extent of coke formation will depend on the orders of reaction with respect to the formation of the desired product **R** and the coke, and on the magnitudes of the temperature coefficients for each reaction.



Sintering is an irreversible physical process leading to a reduction of effective catalytic area. It may consist of growth of metal crystallites on a support or of a decrease in area of a nonsupported catalyst.

The particular active species may also be converted to another form less active or selective, as is the case with certain complex metal oxides used in partial oxidation reactions. A complex metal oxide crystal may also decompose into other compounds, sometimes caused by loss of a particular element via volatilization of a compound. A somewhat amorphous catalyst may crystallize, or a compound active in one crystal habit may be converted into a less active crystalline form. A supported metal catalyst may be reduced in activity or selectivity by becoming alloyed with a metallic impurity or by reaction with the support; for example, a nickel / alumina catalyst may be converted to a nickel aluminate.

3.2 Coke Formation.

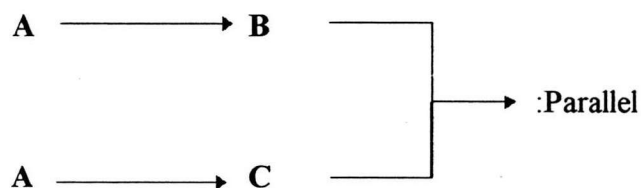
Microscopic examination by Haldeman and Botty (1959) has established that the coke consists of filmy aggregates of size less than 10 nm. X-Ray studies have also established that approximately 50% of the coke deposits are in the form of pseudo-graphitic structures with the residue probably existing as unorganized aromatic systems and of aliphatic and alicyclic appendages to polynuclear aromatic system. It is generally agreed that 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. Satterfield (1980) explained about carbon formation that carbonaceous deposits (coke) could be formed on catalysts under a wide variety of conditions in a reducing environment. The factors involved on nonmetallic substances such as acid catalysts are substantially different from those with metals. On nonmetallic catalysts the deposit may contain considerable hydrogen, represented by an empirical formula CH_x in which x may vary between about 0.5-1. Carbon deposits on metals generally contain little or no hydrogen, depending in part on the reaction temperature.

Hughes (1984) said that the precursor to the coke deposits was 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 immediate precursors. More recently, Wojciechowski et al. (1974) challenged this

and proposed that the immediate precursor are defines. They 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 inferred that coke formation was attributable of these.

There seems little doubt that it is difficult to ascribe coke formation to any single precursor. The nature of the feedstocks used in experiments has varied considerable and it is probable that many mechanistic proposals may be put forward to explain the development of coking under specified conditions. It should be noted that all hydrocarbons, from paraffins to aromatics, will yield coke under appropriate experimental conditions.

Hughes (1984) explained that the parallel and consecutive reactions for coking can be written as follow:



Thus, parallel fouling gives large coke deposits when the reaction concentration is high, since the reaction is the coke precursor. Therefore, when

coking occurs by a parallel mechanism, the greatest deposition of coke would be expected at the inlet of the reactor as was predicted by Froment and Bischoff (1961). Conversely, larger coke deposits are formed in series fouling, when the product B has a high concentration since this is the immediate precursor of the coke in this case. In normal operation the product concentration increases with distance along the reactor, and therefore the coke distribution should follow a similar pattern.

The work by Parera and Barbier et.al. (1979) has shown that the initial deposition is purely on the metal component of the catalyst. Further coking is seen to occur on the support, and finally increase in the rate of carbon deposit is explained by the conjunction of

- a) The high temperature needed at the time to ensure require performances.
- b) Decrease in the hydrogen purity of the recycle gas which brings about a drop in the hydrogen / hydrocarbon ratio at the inlet of the reactors.
- c) Pore plugging due to high of coke deposition. As has already been pointed out, this loss in activity is made up for by an increase in the operating temperature.

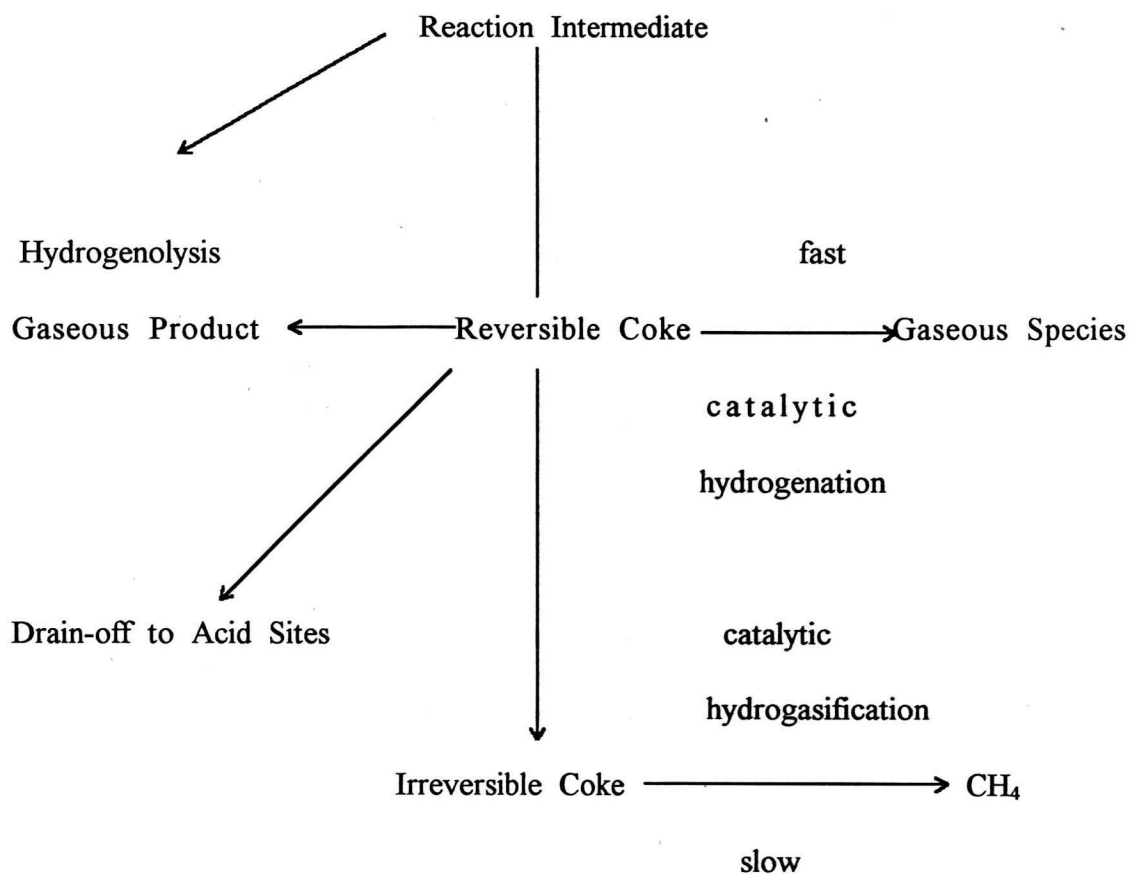


Figure 3.1 Role of hydrogen in controlling the deactivated of a catalyst.

(Bigwas,1987)

Figure 3.1 shown the role of hydrogen in controlling the deactivated of a catalyst:

- a) Controlling the amount of reversible coke by “catalyst hydrogenation”.
- b) Slow removal of graphitic coke by catalytic hydrogasification.
- c) Lower coking rates at high hydrogen pressure due to reduce concentration of coke precursors.

d) Restricting the irreversible reaction from reversible to irreversible coke by lowering the probability that a reversible coke will be able to migrate to a nucleation site where the graphitic deposit will grow.

3.3 Regeneration of Deactivated Catalysts.

This section is devoted to some important point of coke regeneration which described to detail in "Deactivation of catalyst" by Hughes(1984).

Fouling may be represented one main case is the deposition of carbonaceous material or "coke" on the catalyst. In many hydrocarbon and related reactions, such as various dehydrogenations, coke is gradually formed on the surface of the catalyst. The continuing accumulation of these deposits reduces the activity of the catalyst to the point that it must be regenerated. This build up of coke may become significant in a few seconds, as only over a period of many months, as in some catalytic dehydrogenation processes. The usual technique of regenerating a coked catalyst is by combustion with diluted oxygen, although steam or steam plus air is sometimes used. The coke combustion is treated in considerable detail by Hughes (1984) who presented "the catalyst may be taken off stream and heated to a moderate temperature in an atmosphere containing some oxygen so that oxidation or "burn-off" of the coke is achieved." He said that the main problem in the regeneration of coke catalyst particles was the minimization of the temperature rise caused by the

exothermic oxidation reaction when the coke was converted into CO_2 , CO and water. The usual procedure was to admit only a very low concentration of oxygen into the reactor in the early stages of regeneration: with complete oxidation of the coke deposit was achieved.

Thus the only current deactivation process that lends itself to facile catalyst regeneration is that which occurs when deposits are formed on the active catalyst surface. Since this is one of the main areas of catalyst deactivation, extensive studies have been undertaken to determine the optimum conditions for regeneration.

On the other hand, regeneration of coked catalyst in practice was presented by Satterfield (1980) that a considerable variety of regeneration procedures may be used depending on circumstances and, in particular, on catalyst composition. If regeneration is required often, a continuous process must provide a facility for continuously burn off separate from the reactor. If regeneration is required only at intervals of several months or longer, the reactor can be shut down for the period of the time required for regeneration and then put back on stream. If this interruption is too lengthy, or if regeneration is difficult to achieve in the reactor vessel, the coked catalyst may be quickly replaced with fresh catalyst and the regeneration carried out elsewhere.

For regeneration, temperatures through out the bed are held within a fairly moderate range, sufficiently high to secure an adequate rate of coke removal but not so high as to damage the catalyst.

3.3.1 Kinetics of Regeneration (Hughes,1984)

Weisz and Goodwin (1966) found that burn-off of coke was remarkably independent of the nature and method of deposition, they may not have noted the effects of different hydrogen concentration since their studies were concentrated on the overall combustion behavior.

Walker et al. (1959) was reviewed in Hughes (1984) about the literature on the products of carbon combustion, and have 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 temperature of 4000 K.

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

c) The primary CO/CO_2 ratio increase with 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 vapour also increase this secondary oxidation.

The three rate controlling steps generally in the burn - off of carbon from catalysts are (1) control by intrinsic carbon burning kinetics, (2) control by oxygen diffusion through the catalyst pores, and (3) control by both (1) and (2)

In the kinetic control 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, and consequently combustion occurs throughout the pellet but at different rate at different radial positions. The mass transport or diffusion controlled region is characterized by the "shell progressive" mechanism already referred to. The reaction zone in this process moves as a thin shell from the outer surface towards the centre 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 are operating with varying degrees of importance. When both steps have approximately equal importance the burn-off is said to be under intermediate control.

Increase of temperature results in a transition from the kinetic controlled region, through the intermediate control region to the mass transport dominated region.

The intrinsic carbon burning rate is the rate of burn-off of coke in the absence of appreciable diffusional restrictions, and it has generally been observed to be proportional to oxygen concentration, but the dependence of the reaction rate on the carbon concentration shows some variation according to the individual investigations. One possible reason for this variation is that in some cases there may have been ageing, effect causing a decrease in carbon activity (Johnson and Maylnd, 1955 review in Hughes 1984). Massoth (1967) claimed that the reaction was not first order in carbon but was surface reaction controlled. Hughes and Shettigar (1971), using a statistical analysis of their rate data, concluded that the surface reaction expression gave a better fit than the first order process. The reaction of the hydrogen constituent of the coke appears not to have been investigated in detail. Massoth (1967) observed that the concentration of water vapour was initially very high, decreasing rapidly however as reaction proceeded. Consequently, Massoth suggested that the initial temperature peak observed could be attributed largely to the hydrogen content of the coke. He therefore proposed a model in which the coke was oxidized rapidly leaving a residue of hydrogen free carbon which reacted at a lower rate. A model was proposed but Massoth was not able to fit this to his results.

The activation energies reported for the oxidation of coke catalyst particles exhibit a wide variation as table 3.1 shows. The very low values are probably caused by diffusional restrictions and are not true activation energies as such. It seems that a value of 150 kJ/mol. is representative of the rate coefficient for the oxidation of carbon.

Table 3.1 Activation energy of the regeneration reaction. (Hughes,1984)

Temp. range (°C)	Ea (kJ/mol.)	Reference
≤ 480	167	Massoth (1967)
420-544	134	Hughes and Shettigar(1971)
450-600	157	Weisz and Goodwin (1966)
450-600	171	Johnson and Mayland(1955)
455-600	111	Dart et.al.(1949)
600-900	77	Mickley et.al.(1965)
430-550	151	Parvinian (1977)

3.3.2 Regeneration of Coked Catalyst Pellets.

The regeneration process is a special case of combustion in which the coke is deposited within a porous matrix by the reaction process and is subsequently removed from the matrix by oxidation to combustion gases. Thus the catalyst pore structure exists as a reservoir into which coke is deposited and removed, and in ideal operation the pore structure should remain invariant. When catalysts are being regenerated by burning off the coke, in addition to the conversion rate (time required for regeneration) it is important to establish the maximum temperature during the process in order to guard against catalyst sintering.

In general, the mechanism of regeneration of single catalyst pellets depends very much on the temperature range. At low temperatures oxygen is accessible to all the coke deposits throughout the particle. At the other extreme, at high temperatures, the oxidation rate becomes very fast, so the reaction becomes limited by mass transport of oxygen through the pores.

Early work on pellets was concerned mainly with the isothermal problem and in estimating the time required to remove all coke from the pellet. Hughes (1984) concluded the Ausmanan and Watson's work (1962) again that they identified two distinct rate periods called the constant rate and falling rate periods. The former was identified with burn-off of the surface

coke, and Ausman and Watson obtained oxygen concentration profiles for this period. The falling rate period is related to the burn-off of coke within the pellet, and oxygen profiles were obtained for this case also, but the rate expression for this period is a complex function of the fraction of oxygen remaining.

In addition, Hughes (1984) concluded Dobychn and Klibanova's studying (1959) that they also proposed a two-stage model based on a similar distribution of coke deposits between the surface and the interior. In fact, however, both sets of authors have used a rather complicated two-stage mechanism to explain results which could be explained more simply in terms of a general diffusion controlled model for coke burn-off, and the elaboration required in suggesting a change in mechanism from "surface" reaction to "interior" reaction is not justified.