



## CHAPTER II

### LITERATURE SURVEY

A large percentage of catalytic reactions are effected by a deactivation phenomenon, which in turn complicates the design and operation of the reactors, as well as the study of reaction mechanisms. The fundamental causes of this phenomenon involving poisoning, coking and sintering of catalysts. As a result of the many facets of this problem, there have been a very large number of experimental and theoretical investigations of catalyst deactivation.

In the present work , the coke formation on the catalysts is considered. Therefore, these literature review may emphasize the above topics.

J. Barbier (8) et al. have studied the selective poisoning by coke formation on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The thermal programmed oxidation of coke by oxygen mixture was studied in the range of 0 °C - 500 °C. Two peaks were observed. One was ascribed to metal deactivation, the other to coke on alumina.

M. Salmeron and G.A. Somorjai (9) have found that coke deposits on platinum is of two distinct types : one easily removed by hydrogen, the other more resistant to hydrogen removal. These coke are referred to as reversible and irreversible (graphitic) coke, respectively. The reversible coke being a hydrogenated surface species (H/C atomic ratio of 1.5 - 2.0) and the irreversible coke being graphitic in nature (H/C ~ 0.2 ).

J. M. Parera (10) et al have studied the influence of coke deposition on the functions of a Pt/Al<sub>2</sub>O<sub>3</sub> - Cl bifunctional catalyst. Temperature programmed oxidation of the coked catalysts shows that the coke on the metal is oxidized at lower temperature than that on the acid function. Coke is mainly produced on the metal at the start of the run. At increasingly severe coking conditions, coke is produced on both functions and at higher severities on times, it is produced mainly on the acidic function. Coke on the metal is in equilibrium with gaseous hydrogen. On increasing the hydrogen pressure, the coke is eliminated more easily from the metal than from the acid.

N. S. Figoli (11) et al have studied the influences of pressure, H<sub>2</sub> to naphtha ratio, temperature, space velocity and time on stream for coke formation during naphtha reforming over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The decrease in octane number depends only on the amount of coke and does not depend on how the severity is achieved. The temperature programmed oxidation of the used catalysts shows two zones, one from 120 °C to 369 °C and the other from 369 °C to 555 °C. The second zone corresponds to the burning of a more polymerized deposit, the amount of which increased with severity of the operation much more than the first zone. The thermogram patterns were quite similar and independent of the operational conditions used to deposited the coke.

R. Burch and A.J. Mitchell (12) have studied the role of tin and rhenium in bimetallic reforming catalysts. They found that Sn is only effective in improving the stability of the Pt when it is co-deposited on the same alumina particles. Pt has a much higher activity than either Re or Sn for both hydrogenation and for hydrogenolysis. The role of Re is to improve the rate of hydrogenolysis of cyclopentadiene to paraffins. They suggested that one role of Re and also of Sn, may be to selectively hydrogenate dienes to alkenes.

J. Volter and U. Kurschner (13) have studied the conversion of methy cyclopentane and deactivation by coke formation on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. The coking inhibits the conversion in a nearly linear relationship, no distinct influence of tin on the amount of coke is observed. But with tin containing catalysts the benzene formation is increased and the hydrogenolytic splitting is decreased. The self - poisoning by coke varies the selectivities in a significant way. A similar change of selectivity was observed with increasing tin content also indicating a certain poisoning by tin. Tin inhibits the hydrogenolysis according to an ensemble effect and retards the deactivation of the catalyst by modifying the coke deposition.

The initial rate of carbon formation during cyclopentane reaction has been studied on different Pt/Al<sub>2</sub>O<sub>3</sub> catalysts of varying metal dispersity by J. Barbier (14) et al. It has been shown that coke deposition on the metal is a structure sensitive reaction which is preferably produced on large metallic particles. On the other hand , coke deposition on the whole catalyst is relevant to cyclopentadiene formation and is a structure insensitive reaction since the initial rate of coke deposition on the whole catalyst is proportional to the metallic surface area.

J. Barbier (15) et al. have characterized the coke deposited on heterogeneous catalysts by temperature programmed oxidation. The comparison between the amount of CO<sub>2</sub> produced and the amount of O<sub>2</sub> consumed gives the ratio H/C. For Pt/Al<sub>2</sub>O<sub>3</sub> catalysts it has been shown that coke deposits on the metal is less dehydrogenated than coke deposits on the support.

Long term and short term deactivation on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts in n-hexane conversion have been studied by J. Margitfalvi (16) et al at atmospheric pressure and low conversion. Both types of deactivation are very

pronounced on catalysts, in which the acidic sites are not blocked by ionic forms of tin or lithium. Results obtained in this study were discussed in terms of a generalized reaction scheme, in which poisoning metallic and acidic sites and formation of a carbonaceous surface overlayer have their distinct contribution.

J. Biswas (17) et al have studied the transient kinetic behavior of a fresh or pre-sulphided catalyst brought on line which is term "lineout" , is found to be due to an initial deposition of coke on the metal sites of the catalyst ( $\sim 1$  wt %) , the quantity of this deposition being essentially constant over the length of reformer operation. The coke deposition during long term reformer operation ( $\sim 20$  wt %) is found to be on the alumina, however the observed deactivation in octane yields is due to the changes in nature of coke (gradual graphitization) on the metal sites of the catalyst. Thus two types of coke on the metal sites are distinguished, one being easily removed by hydrogen (reversible coke) and the other less readily removed (irreversible coke) . The quantity of irreversible coke is increased by operation at high temperature and/or low pressures. It is shown that catalyzed hydrogenation and hydrogasification limit metal site catalyst deactivation.

H. Lieshe (18) et al have studied coke formation from methane, n-hexane, 1-hexane and 1,5 - hexadiene. Coke precursors are formed on Pt sites and transfer to alumina. Two routes of coking were observed. Presence of tin decreases the adsorption bond strength of 1- hexane and at low concentrations increases the amount chemisorbed. This phenomenon is explained by the ensemble effect. A drain-off effect is proposed to explain the decrease of the coke coverage on the metallic sites upon addition of Sn.

P. Marecot (19) et al have studied the coke deposition on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts of varying dispersity during cyclopentane reaction. For all working

pressures the higher the metallic accessibility, the higher the amount of coke deposited on the catalyst. Nevertheless, coke deposited on the less dispersed catalysts is more toxic for the metallic function. An increasing metal accessibility improves the graphitization of coke on the support and so prevent the deactivation of the metal of a bifunctional catalyst.

J. Barbier (20) et al have studied deactivation by coking of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. The result showed that at low temperature when the destruction reaction (high apparent activation energy) is negligible, the coking rate is increased owing to increasing metal accessibility. In contrast, at high temperature the coking reaction is hindered by an increasing metal loading. A change in the coking temperature does not alter the chemical nature of the carbonaceous deposits and their distribution between the metallic and acidic phases of a bifunctional catalyst. On the other hand, an increase in coking pressure (with a constant hydrogen : hydrocarbon molar ratio) promotes the graphitization of coke on the support, protecting the catalytic activity of the metallic phase.

L. Liwu (21) et al have studied the dynamic process of coking on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts for alkane dehydrogenation. The results showed that on both Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, carbon deposition is a dynamic process. The carbonaceous materials which originate from the metal surface may be converted to carbon through successive dehydrogenation on metal site or they may continuously migrate to the support with irreversible coke formation through condensation or hydrogen transfer reactions. The results of chemisorption and thermal desorption of ethylene on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts showed that the incorporation of tin reduces the strength of chemisorption of the hydrocarbons on the metal surface so that the carbon precursors can migrate towards the support more easily.

Y. Weishen (22) et al have studied the dehydrogenation of propane on supported platinum - tin catalysts. They concluded that the activity is dependent on the types of supports, pressure and tin to platinum ratio. Sn have beneficial effects on the catalytic performance when it is present in the oxidized state.

Although there were many works studied on coke formation for Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. No detail was direct concerned about metal active site, therefore a study of coke deposition on metal active site by direct measurement of irreversible and reversible coke is proposed in order to characterize quantities and location of coke deposits on the metal active site.