



Chapter II

LITERATURE REVIEWS

Majority of catalytic reactions are affected 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 involve 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, this literature review will emphasize the above topics.

J. Barbier [5] et al. have studied the selective poisoning by coke formation on Pt/Al₂O₃. The thermal programmed oxidation of coke by oxygen mixture was studied in the 0°C - 500°C range. Two peaks were observed. One could be ascribed to metal deactivation, the other to coke on alumina. The effects on three test reactions by cyclopentane have differed due to the sites deposited by coke.

The coking of Pt/Al₂O₃ catalysts by C₆ hydrocarbons have been studied by B.J. Cooper and D.L. Trimm [6] tendency to coke formation decreases in the order methylcyclopentane >

3-methylpentane ~ n-hexane > 2-methylpentane > benzene > cyclohexane. The prediction of mathematical models have shown that coking by benzene and cyclohexane appears to involve a bimolecular condensations on metal function of the catalyst. Coking by the other C₆ hydrocarbons appears to be a polymerization reaction involving acid sites on the catalyst.

N.S. Figoli [7] et al. have studied the influences of pressure, H₂ to naphtha ratio, temperature, space velocity and time on coke formation during naphtha reforming over Pt/Al₂O₃. The decrease in octane number depended only on the amount of coke and did not depend on how the severity was achieved. The temperature programmed oxidation (obtained by differential thermal analysis) of the used catalysts showed two zones, one from 396 to 642 K and the other from 642 to 828 K. The second zone corresponded 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 deposit the coke.

J.M. Parera [8] et al. have studied the influence of coke deposition on the functions of a Pt/Al₂O₃-Cl bifunctional catalyst. Temperature programmed oxidation of the coked catalysts shows that the coke on the metal is oxidised at lower temperatures than that on the acid function. According to C₁/C₃ (metal to acid), 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 .

R. Burch and A.J. Mitchell [9] 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.N. Beltramini [10] et al. have studied the deactivating effect of different paraffins, naphthenes and aromatics during their reforming over a Pt/Al₂O₃ catalyst. They found that coke formation is not directly related to the molecular weight of those hydrocarbons, but to their structure or to those of their principal products. n-Pentane produces more coke than n-hexane or n-heptane, but coke deposition increases with the molecular weight of higher n-paraffin. The five carbon atom ring is the most important coke precursor for naphthenes. For aromatics, the structure and position of the chains joined to the aromatic ring have an important influence on coke formation. The deactivation effect of coke does not only depend on its amount because it affects in different ways the metallic and the acid functions of the catalyst. The reactions that occur with different feeds are diversely affected according to their particular mechanisms of reforming.

J. Volter and U. Kurschner [11] have studied the conversion of methylcyclopentane and the deactivation by coke formation on

Pt/Al₂O₃ and Pt-Sn/Al₂O₃ catalysts. The coking inhibits the conversion in a nearly linear relationship, no distinct influence of tin on the amount of coke was 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/Al₂O₃ catalysts of varying metal dispersity by J. Barbier [12] 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 [13] et al. have characterized the coke deposited on heterogeneous catalysts by temperature programmed oxidation. The comparison between the amount of CO₂ produced and the amount of O₂ consumed gives the ratio H/C. For Pt/Al₂O₃ catalysts it has been shown that coke deposited on the metal is less dehydrogenated than coke deposited on the support.

J. Barbier [14] et al. have studied the coke deposition during the reaction of cyclopentane on Pt-Re/Al₂O₃ and Pt-Ir/Al₂O₃

catalysts. They found that the amount of coke deposited on the catalyst is lowered by the addition of Ir or Re to Pt. On the other hand, the amount of coke oxidizable at low temperature (deposited on the metal) decreases in the order Pt-Re > Pt > Re > Pt-Ir > Ir. Nevertheless, toxicities of those carbonaceous deposits for catalytic hydrogenation reaction are the lowest on Pt-Re and the highest on Pt-Ir. These results can be explained by a ligand effect which can stabilize the adsorption of coke precursor or by a change in the nature of the coke.

J.M. Parera [3] et al. have studied the coking on bifunctional catalysts. They found that the coke formation is a bifunctional process. The metallic function is necessary to dehydrogenate the cyclopentanic ring to a cyclopentadienic ring and the acidic function is necessary to condense the cyclopentadienic ring producing polyring compounds. The monometallic catalyst has a greater coke formation capacity than the bimetallics due to its greater dehydrogenation capacity.

Long term and short term deactivation on Pt/Al₂O₃ and Pt-Sn/Al₂O₃ catalysts in n-hexane conversion have been studied by J. Margitfalvi et al. [15] at atmospheric pressure and low conversion. Both types of deactivation were very pronounced on catalysts, in which the acidic sites were not blocked by ionic forms of tin or lithium. Results obtained in this study are 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.

F. Frusteri [16] et al. have studied the deactivation and

subsequent self-regeneration of several Pt/Al₂O₃/honeycomb catalysts in the dehydrogenation of methylcyclohexane at 400 °C. They investigated the role of surface chlorine during the H₂ self-regeneration of catalysts. A regeneration mechanism, involving the spillover of residual hydrogen, is proposed.

P. Marecot [17] et al. have studied the coke deposition on Pt/Al₂O₃ 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.

M. Salmeron and G.A. Somorjai [18] have found that coke deposited on platinum is of two distinct types : one easily removed by hydrogen, the other more resistant to hydrogen removal. These cokes 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).