CHAPTER III

THEORETICAL CONSIDERATIONS

As this study concerns the effect of coke formation on dispersed supported metallic catalysts surface, this chapter is devoted to some important aspects of metallic, especially noble metal (e.g., platinum), catalysts and coke deposited on their surface.

The details about catalytic dehydrogenation of gaseous paraffins is presented in section 3.1.

The catalysts selected to be studied is platinum-based catalysts which is widely used in industrial hydrocarbon processes. Catalytic surface is responsible for their activity, selectivity, and the extent of coke formation. Characteristics of this platinum-based catalyst are presented in part 3.2.

In the experiment, the dehydrogenation of propane to produce propylene is chosen an the test reaction. There are two reactions, dehydrogenation and hydrogenolysis, that have the very obvious effect on reaction products, and they are described in part 3.3.

Coking on noble metal catalysts is presented in part 3.4. In this part, there are three sections about the effect of coke on reaction products, the influence of the catalyst on coke formation,

and the mechanism of deactivation and coke formation.

3.1 Catalytic dehydrogenation of gaseous paraffins [19].

The dehydrogenation of the paraffin gases to the corresponding olefins is a problem of fundamental importance to the oil industry, because the technical problem of efficiently converting gaseous olefins into liquid motor fuel has been solved within recent years by both catalytic ("solid phosphoric", cold and hot sulfuric acids) and purely thermal processes. Therefore, a process for the conversion of paraffins into olefins would put to good use all the paraffin gases except methane. These gases are available in enormous quantities from such sources as natural gas and gasoline, petroleum distillation gas, gas from the cracking processes, coke-oven gas, and refinery gasoline.

A catalytic dehydrogenation process has been developed for converting normal and isobutane, propane, and ethane to the corresponding olefins. The first announcement of these successful results was made in 1935.

3.1.1 Principle of process and plant.

The process consists briefly in passing the preheated paraffin gases over a suitable catalyst. The outgoing gases contain olefins and hydrogen besides the unreacted original paraffins. The olefins are polymerized or used in alkylation, the hydrogen is separated, and the unreacted original paraffins are recycled.

The plant consists essentially of a furnace, banks of catalyst reactors, and a hydrogen separation unit. Automatic controls alternate the flow of paraffin gases first through the furnace and one section of reactors and then through another, while the catalyst is being regenerated in the first section. The regeneration consists in passing automatically controlled amounts of air mixed with combustion gases or steam, to burn off the carbon on the catalyst at a moderate combustion temperature (usually below 900°C.). A feature of the process is that the length of operating cycle is short, usually of the order of one hour.

The advantages of the catalytic process over purely thermal cracking are the much larger over-all yields of the corresponding olefins and a much higher reaction velocity. Even though the thermal results may be somewhat improved by the use of higher pressures and temperatures, the nonselectivity of the thermal reaction always causes them to lag behind those obtained with catalysts.

3.1.2 Catalysts.

A suitable catalyst for an economic process must fulfill the following requirements:

(1) It must have the ability to split off hydrogen selectively without cleavage of the carbon-to-carbon bond. This is a severe requirement since the energies of the bonds (Pauling's values)

Linkage	Cal./mol.	Electron volts
C-H	87,300	3.79
C-C	58,600	2.54

involved, favor the carbon-to-carbon cleavage. It is intensified by the fact that high temperatures of the order of 500-750°C. must be used, since at lower temperatures the equilibrium lies almost completely on the paraffin side and the reaction velocities are low.

(2) It must be easily regenerated when fouled by a corbon deposit.

(3) It must have a useful life of many hundreds of hours.

(4) It must be low priced.

These requirements are fulfilled by selected solid catalysts containing minor molar proportions of the platinum group component and a modifier metal component selected from the group consisting of a tin component, germanium component, rhenium component, and an alkali metal component, or an alkaline earth metal component, supported on carriers of relatively low catalytic activity (e.g. alumina) [20].

These catalysts are highly selective and direct the conversion in accordance with the general dehydrogenation equation,

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \qquad (3.1)$$

under proper operating conditions. The scission of the carbon-to-carbon bond, leading to the formation of carbon, methane, and other degradation products, has been almost completely

suppressed.

3.1.3 Thermodynamics.

According to empirical chemical knowledge, paraffins are dehydrogenated at high temperatures whereas olefins combine with hydrogen at low temperatures. In other words, the equilibrium of the reaction,

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2 \tag{3.2}$$

is shifted toward the right by temperature increase. In order to obtain industrially important concentrations of olefins, the temperatures employed must be rather high (above 500 °C).

3.2 Characteristics of supported metallic catalysts.

3.2.1 Structure and properties of dispersed metals.

Typical industrial metal catalysts have the metal dispersed on the surface of the support as small crystallites which are usually in the size range 8-50 Å in diameter. The crystallite size is controlled by calcination and reduction steps (Figure 3.1). A typical example is given by Guenin et al.[21], where reduction at low hydrogen pressure gives small crystallite sizes; calcining time and temperature also have an effect. Table 3.1 gives the fraction of total crystallite atoms which are surface atoms, the total number of atoms in the crystal, and the average coordination number (number of nearest-neighbor atoms) of surface atoms for octahedral crystallites of increasing size. Corner atoms have a coordination

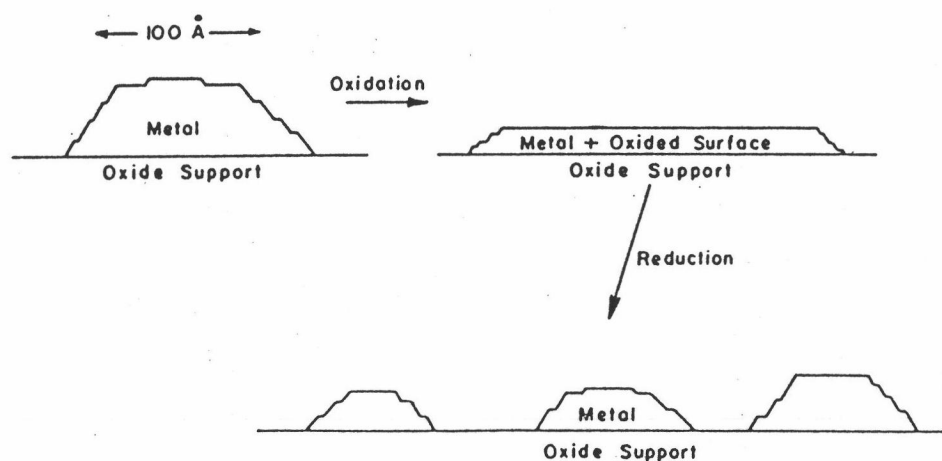number of 4; edge atoms, 6 or 7; and atoms on the face of the plane, 8 or 9.

Figure 3.1 Process of calcination and reduction causes formation of metallic crystallites.

Work by van Hardefeld and Hartog [22] demonstrated two important points :

(a) Low coordination surface atoms–corner atoms, edge atoms (i < 7) – are present in significant proportions only in crystallites of sizes d < 40 Å. Large crystals consist almost exclusively of face atoms.

(b) Corner atoms predominate on the surface of extremely small crystallites (d < 10 Å).

Surface atoms differ from bulk atoms in that they have an incomplete set of neighbors. What has, however, only recently

Table 3.1 Properties of platinum crystals of different sizes with
regular faces.

Length of crystal edge		Fraction of atoms on surface	Total number of atoms in crystal	Average coordination number of surface atoms
Number	Å			
2	5.50	1	6	4.00
3	8.95	0.95	19	6.00
4	11.00	0.87	44	6.94
5	13.75	0.78	85	7.46
6	16.50	0.70	146	7.76
7	19.25	0.63	231	7.97
8	22.00	0.57	344	8.12
9	24.75	0.53	489	8.23
10	27.50	0.49	670	8.31
11	30.25	0.45	891	8.38
12	33.00	0.42	1156	8.44
13	35.75	0.39	1469	8.47
14	38.50	0.37	1834	8.53
15	41.25	0.35	2255	8.56
16	44.00	0.33	2736	8.59
17	46.75	0.31	3281	8.62
18	49.50	0.30	3894	8.64

been pointed out [23], but should have been clear at the outset, is
that crystallites are unlikely to be perfect in the sense of having
exactly the right number of atoms to form a regular geometric body,
and that the numbers of surface atoms having a given coordination
number make wild excursions from the values of the adjacent perfect
forms.

The extra valencies of these surface atoms are taken up
by adsorbates and reactants, and one can imagine that atoms in
different surroundings display distinct adsorption and reaction
properties. Somorjai [24] showed that the stereochemistry of corner
and edge atoms can be quite different from face atoms, therefore a
different "kind" of bonding is favored at these sites.   These

effects are amplified by the finding that corner and edge atoms are electron deficient compared to face atoms.

3.2.2 The role of catalyst surface morphology in activity and selectivity.

Some 30 years ago it was conventional to describe the differences in performance between similar catalysts in terms of "electronic" and " geometric" factors. Sachtler [25] has developed a convenient classification of crystallite requirements of relevance to catalyst selectivity.

Bond strength : The formation of chemical bonds between atoms of the substrate and the catalyst surface and their rupture at a later stage are essential steps in all heterogeneously catalyzed reactions; that is, if the bond is too weak, no chemisorption will take place, and if too strong, the desorption step will become too slow. For a given reactant, the main variables on the catalyst side that influence the bond strength are the chemical identity and the valence of the adsorbing atom(s). For a given metal atom and a given adsorbate, the bond strength is to some extent also influenced by the environment, in particular the chemical nature of the nearest neighbors. This is the essence of the ligand effect in catalysis, which is important in bimetallic catalysts or catalysts with adsorbed compounds such as sulfur or carbon.

Coordination : The coordination requirement of a reaction catalyzed by an isolated surface atom is defined as the minimum required number of coordination sites per surface atom. Blakely and Somorjai [26] showed with single metal crystals that

flat faces have a significantly lower activity than terraces, since atoms in step, kink, edge, and corner sites exhibit a higher degree of coordinative unsaturation. These effects are partly responsible for the fact that crystallite faces are efficient in C-C bond breakage, while C-H and H-H bond scissions are more effective on crystallite corners and edges.

Ensemble (site) : The ensemble requirement is the minimum required number of contiguous surface atoms of the element able to form bonds with the end adsorbate. This definition accepts the conjecture that for a specific reaction mechanism, the required active center on the catalyst surface can be either a single metal atom or an ensemble of several adjacent atoms. The ensemble requirement for a certain reaction can be studied by diluting the metal in an alloy with a chemically inert metal, thus reducing the concentration of large ensembles of the active metal. An example is that for Pt-Sn alloys. At low temperatures (< 450 °C), multiple site reactions such as isomerization, hydrogenolysis, and 1,5-dehydro-cyclization do not occur because the majority of ensembles comprise single atoms, hence the product aromatic content is low. But at higher temperatures (500 °C), 1,6-dehydrocyclization, which has a lower site requirement than the former reactions, occurs at a sufficiently fast rate, thus improving aromatic yields. Typical site requirements are shown in Table 3.2.

Template : This describes the stereochemical conditions a catalytic center must fulfill in order to render the reaction "stereospecific" or "shape selective," that is, capable of preferentially producing one of the several isomers. Although the coordination requirement is extremely important because different

Table 3.2 Reaction site requirements on platinum crystallites.

Reaction	Example compound	Generic reaction mechanism code	Crystallite size range (where mechanism dominant)	Effect of increasing dispersion on rate[a]	Minimum ensemble require- ment	Coordination requirement
Hydrogenolysis	1. Methylcyclo- pentane	Nonselective, cyclic	<20 Å	-	1	Corner/edge
		Bond shift	Full range	-	1	Corner/edge
		Selective, cyclic	>25 Å	-	2	Corner/edge and face
	2. Alkanes		Small	+	1	Corner/edge
			Large	-	3	Face
Isomerization	1. 3-Methyl- pentane	Nonselective, cyclic	<20 Å	+	1	Corner/edge
		Bond shift	Full range	-	1	Corner/edge
		Selective, cyclic	>25 Å	-	2	Corner/edge and face
	2. 2-Methyl- pentane	Nonselective, cyclic	12-200 Å	+	1	Corner/edge
		Bond shift	12-200 Å	-	1	Corner/edge
Dehydrocycliza- tion (with 1,5- closure)	Hexane	Nonselective, cyclic	Small	+	1	Corner/edge
		Bond shift	Small	+	1	Corner/edge
		Selective, cyclic	Large	-	2	Corner/edge and face
Ring (enlarge- ment (after 1,5-closure)	Methylcyclo- pentane		Full range	Negligible	1	Corner/edge and face
Dehydrocycliza- tion (with 1,6-closure)	Heptane		Full range	Negligible	1-2	Corner/edge and face (higher on corners)
Dehydrogena- tion	Alkanes Naphthene		Full range	Negligible	1	Corner/edge and face
Self-poisoning	Alkanes		>10 Å	-	2	Face

[a]+, increase of rate; -, decrease of rate.

reactions are favored on different parts of the crystallite surface (i.e., corner and edge of face atoms) - that is, at positions of minimum activation energy - the selective adsorption of poisons on these sites may have important effects on selectivity.

3.2.2.1 Structure sensitivity of reactions.

The term "structure sensitive" (or demanding) is applied to a reaction whose specific activity (same as turnover number) varies with the percentage exposed (dispersion/crystallite size) or, more generally, with the structure of active sites. These may be altered in other ways, as by alloying, introducting crystal imperfections, or poisoning. This is in contrast to structure-insensitive reactions (or facile reactions). A more general classification follows :

(a) Structure-insensitive reactions, for which the rate is proportional to the whole metallic area (in this case, any accessible superficial atom forms an active center whose properties are independent of its crystallographic site and environment).

(b) Structure-sensitive reactions, for which the rate is not proportional to metallic area but depends on the dispersion of the metal and, more generally, on the method of preparation of the catalyst. Such reactions must be carried out preferentially on specific parts of the surface.

For some reactions, the active site may be a single atom, but for others it may involve several surface atoms

whose arrangement relative to one another is critical. A considerable number of studies now indicate that simple hydrogenation reactions on various metals are structure insensitive, but those involving C-C bond breakage, such as hydrogenolysis and skeletal isomerization, are structure sensitive.

In a brief summary, Table 3.2. shows the ensemble requirements, coordination requirements, and structure sensitivity (effect of dispersion) of different metal site reforming reactions. This is a more detailed version of work by Clarke [27] and Ponec [28]. Important points to note are :

(a) The relative importance of bond shift and nonselective cyclic mechanisms in hydrogenolysis and isomerization is controlled by electronic effects, with the latter being more significant at dispersions approaching unity. On the other hand, the selective cyclic mechanism is important on larger crystallites because of the greater percentage of face atoms for the two-site mechanism (geometric effect), and because the electronic structure is more permissive.

(b) Alkane hydrogenolysis increases with decreasing particle size due to the simpler mechanism, compared to cyclopentane hydrogenolysis. Although cyclopentane hydrogenolysis is nonselective for small particles, it decreases with decreasing particle size since geometric requirements for the "multiple" mechanism require the molecule to lie parallel to the surface , even though only one metal atom is required for the reaction.

(c) The poisoning of the metal surface by

coke has been found to have the same minimum site requirement as hydrogenolysis due to the coordinative prerequisite of multiple bond formation.

(d) A reaction which has single- and multiple- site pathways occurs at a higher rate on multiple sites.

In the previous discussion the concentration is on the effects of crystallite structure and reaction mechanisms on the structure-sensitivity phenomenon. However, there are two other influential effects which have not been accounted for and these are briefly discussed below.

(1) Metal-support interactions (MSI).

The existence of a sequence of chemical bonds, either ionic or covalent in character, between the support and the metal, provides a mechanism for electron transport across the interface. The extent of this effect (charge transfer from metal to suppor) would be greater, the smaller the particle size; or the greater, the interfacial area of contact. Thus any electronic effects (which may result in modification of reaction selectivity) observed are inherently difficult to separate from those directly attributable to the size of the metal atom assembly, and MSI hence may show up as a structure-sensitivity phenomenon from a macroscopic viewpoint.

(2) Catalyst self-poisoning.

Hydrocarbon reactions on transition metals

are always accompanied by structure-sensitive side reactions which lead to self-poisoning of the catalyst by "carbon". A working surface is under steady-state conditions, almost alway covered by a monolayer of "carbon". Only the edges and corners, which are difficult to cover by a continuous layer keep their intrinsic high activity in the H-H and C-H bond breaking process, thus causing the preferential coking of the crystallite faces. The possibility that observed structure sensitivity could be by caused by self-poisoning has been discussed by Katzer and Manogue [29]. For example, the increase in alkane hydrogenolysis rate with dispersion (Table 3.2) could be due to the fact that smaller particles are more resistant to self-poisoning.

3.2.2.2 Effect of crystallite alloying on reaction selectivity.

In recent years there has been a tendency to replace monometallic catalysts (Pt) by a preparation which contains a combination of two or more metals. The attractiveness of this new generation of catalysts consists of their superior stability, as evidenced by a lower rate of decline of the catalyst performance and by selectivity. In particular, undesired reactions such as hydrogenolysis and formation of "coke" are suppressed, resulting in higher selectivites for the desired processes of dehydrogenation, isomerization, and dehydrocyclization. A rationalization of the typical effects of alloying on selectivity and activity will be described on the basis of the electronic and geometric factors referred to earlier in the present section.

(a)   Individual surface atom concept.

A renewed interest in a fundamental theory for heterogeneous alloy catalysis was due to the following important causes [30] :

(1)   The increase in observed activity of some bimetal systems due to changes in selectivity.

(2)   Selectivity of alloys often differs strongly from that of their components of any mechanical mixture of them. In particular, the reactions involving C-C fissions are often affected much more severely by alloying than reactions that leave the carbon number of the molecule unchanged.

(3)   Bimetallic catalysts have superior stability compared to monometallics under severe industrial conditions.

(4)   The ascertaining by modern methods that the surface composition of alloys can strongly deviate from the bulk composition.

(5)   Chemisorption data of highly diluted alloys of nickel or platinum in inert metals such as copper, silver, or gold showed that amounts of gas chemisorbed were roughly proportional to the concentration of the transition metal in the alloy surface.

These results led to the   "individual surface atom" concept, where the atoms retain their individuality when forming alloys, thus realizing the possibility of titrating selectively the surface atoms of one constituent [31]. In alloys of a group VIII (e.g., Pt) transition metal with a group IB metal (e.g.

, Cu, Ag, Au), only the transition metal atoms such as platinum are catalytically active. So when the electronic structure of individual atoms does not vary with alloying, the catalytic activity behavior can be explained by the dilution of active sites in an inert matrix and the relative preponderance of sites consisting of few active atoms over the larger sites.

If two catalytically active metals are blended, a new kind of site may be created, consisting of both types of atoms ($Pt-Ir/Al_2O_3$). The catalytic activity of these types of sites is expected to be intermediate between the activities of both constituents. Thus, as far as hydrogenolysis is concerned, one has to consider the possibility that a big ensemble can be formed by a mixture of A and B. If one of the constituents is selectively poisoned, the atoms of the other active sites are diluted in a more or less inactive matrix.

Apart from this ensemble effect, the alloy partner may also influence the electronic structure of the catalytically active metal. In this "ligand" effect, the strength of a chemical bond between an adsorbate atom and a surface atom is influenced by neighbors of that surface atom. For the Pt-Ir catalyst, there is an electron donation from the platinum to iridium.

(b) Factors influencing ensemble effect in bimetallic catalysts.

As discussed earlier, the catalyst activity, stability, and selectivity of some bimetallic catalysts

usually deviate from additive behavior predictable from the individual metal properties. Guczi [32] reviewed the factors controlling hydrocarbon reactions catalyzed by supported and unsupported alloys, emphasizing that ensemble effects are usually dominant, arising from the necessity to have a critical size of the assembly of atoms in the active "landing" site for the incoming and reacting molecules; thus alloying is the main controlling factor for the different reaction routes.

A classic example of the ensemble effect in alloy catalysis is given by Sachtler and Somorjai [33] who showed that cyclohexane dehydrogenation goes through a maximum at an intermediate composition of Au (inert) in Pt (active) under atmospheric conditions on a single crystal. For pure platinum the activity is low due to carbonaceous deposit formation, which, like hydrogenolysis, is fast due to the availability of ensembles for multiple bond formation. Addition of Au reduces the self-poisoning reactions, which cannot occur on small ensembles, thus causing an increase in reaction rate. At high Au compositions, the activity declines because ensembles become too few and too small to catalyze cyclohexane dehydrogenation. From a deactivation viewpoint, it has been suggested that the role of the second metal is to reduce ensemble sizes below that necessary for C-C bond fission and "deep hydrogenation," which produce coke precursors.

Ensemble effects can be modulated by several other factors (Figure 3.2.). Surface segregation of one metal and site elimination by blocking are two well-known effects. Matrix and strong metal-support interaction effects (SMSI) influence the state of dispersion and stability of bimetallic catalysts under

reaction or rejuvenation conditions. The effects of dispersion and alloying are two of the more important factors. Ensemble sizes on single metal crystallites generally decrease with increasing dispersion; consequently the proportion of multiply bonded intermediates decreases. Due to the lower proportion of these intermediates (which can be coke precursors), the catalyst experiences lower metallic coking rates.

However, when alloying is performed, the surface will contain atoms of an inactive metal; hence the active metal ensemble size will diminish, sometimes without any serious change of the surface geometry, crystallite size, etc., and consequently the rates of hydrogenolysis and metal site coking drastically decrease.
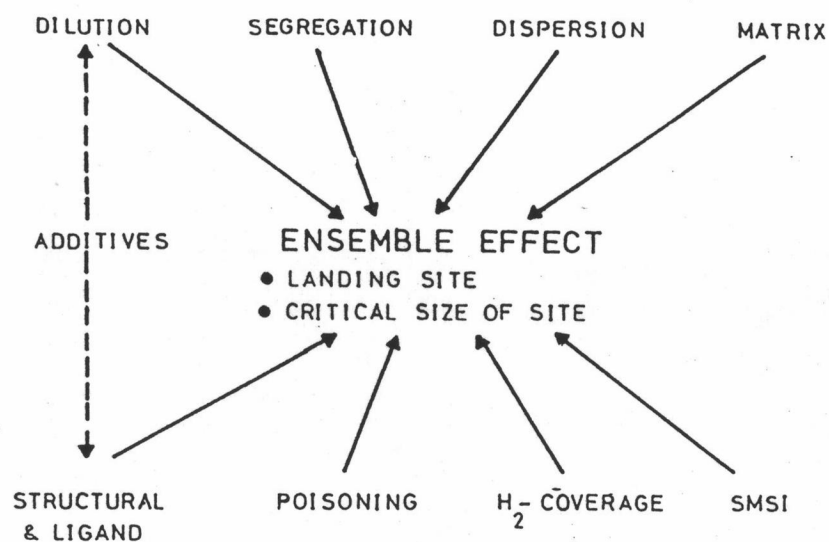
Figure 3.2 Factors affecting the ensemble effect in bimetallic catalysis.

The surface geometry of a Pt/Al₂O₃ catalyst is shown in Schemes A-C, to show the intimate relationship between ensemble size, selective poisoning by an additive, and deactivation by carbonaceous fragments. In each case, the result is a dilution in the number of large active ensembles of platinum. The advantageous hydrogenolysis suppression is used industrially on Pt-Re/Al₂O₃ catalysts (Figure. 3.3). Sulfur, firmly bound to Re, blocks the cracking power of Re and dramatically diminishes the size of platinum ensembles. This leads to an observed enhancement of all reactions running as and through dehydrogenation (e.g., single-site dehydrocyclization and isomerization); thus Pt-Re+S alloys behave similarly to Pt-Sn alloys because the sulfided rhenium acts as an inert diluent.
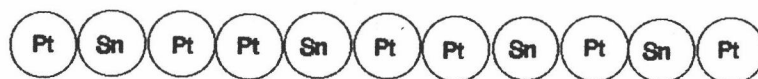
SCHEME A. Alloying with inactive metal (tin).
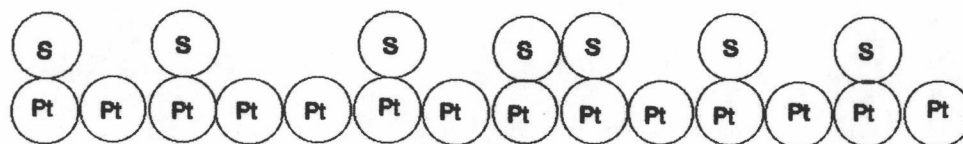
SCHEME B. Poisoned by sulfur.
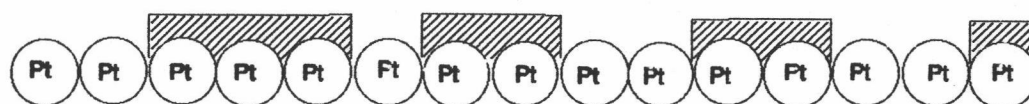
SCHEME C. Deposits of coke.
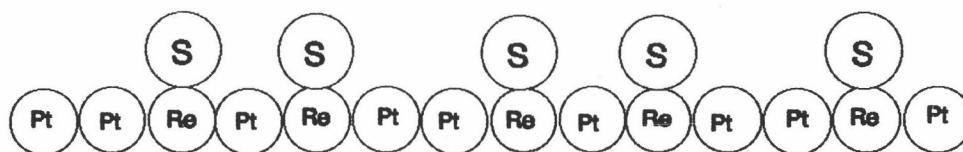
Figure 3.3   Schematic illustrating the stabilization of the
              catalytic activity of Pt-Re catalysts in the presence of
              sulfur.

In the case of Pt-Ir alloys, both
components are very active. The improved _activity_ (aromatic yield)
of these catalysts over the Pt-Sn or Pt-Re+S (sulfided Pt-Re) alloys
is due to the high dehydrocyclization activity of the iridium
component. The higher hydrogenolytic activity due to the iridium
component is controlled by continuous addition of sulfur in the feed
(0-10 ppm), thus reducing the Pt-Ir ensemble sizes on the catalyst,
but still improving the selectivity for the single-site
1,6-dehydrocyclization reactions.
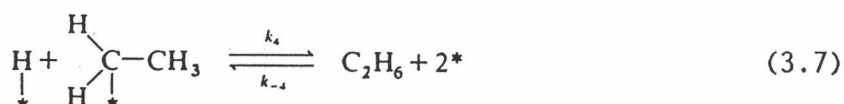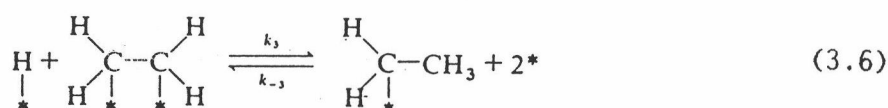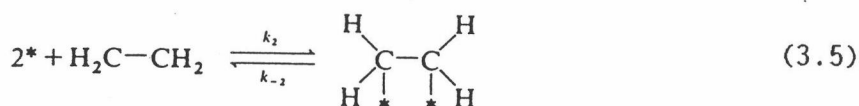
3.3   Important reactions.

3.3.1   Dehydrogenation reaction.

Dehydrogenation of hydrocarbons on metals is exemplified
by the reaction :

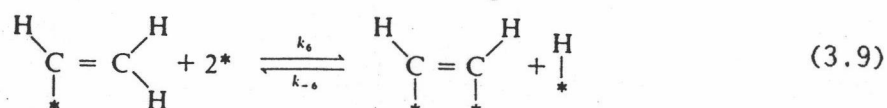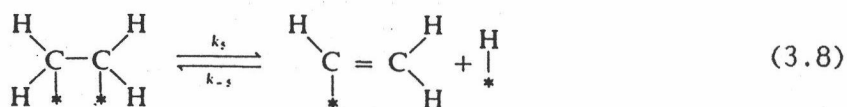$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \tag{3.3}$$

The reaction (3.3) did not go by the simple removal of two hydrogen

atoms to give propylene, since there was extensive H-D exchange between the hydrogen of C_3H_6 and D_2 from the research by Turkevich et al. [34]. This exchange indicates that the elementary reaction steps are reversible and forms the basis of the following proposed reaction mechanism (asterisks represent surface sites) :

$$H_2 + 2^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2 \overset{H}{\underset{*}{|}} \tag{3.4}$$

$$2^* + H_2C-CH_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overset{H}{\underset{H}{\underset{*}{|}}}C-C\overset{H}{\underset{*}{\underset{H}{|}}} \tag{3.5}$$

$$H + \overset{H}{\underset{*}{|}} \overset{H}{\underset{*}{|}}C\cdots C \overset{H}{\underset{*}{\underset{H}{|}}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \overset{H}{\underset{*}{|}}C-CH_3 + 2^* \tag{3.6}$$

$$H + \overset{H}{\underset{*}{|}} \overset{}{\underset{H}{\underset{*}{|}}}C-CH_3 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_2H_6 + 2^* \tag{3.7}$$

There is another type of dehydrogenation, illustrated by the surface-reaction steps :

$$\overset{H}{\underset{H}{\underset{*}{|}}}C-C\overset{H}{\underset{*}{\underset{H}{|}}} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \overset{H}{\underset{*}{|}}C=C\overset{H}{\underset{H}{}} + \overset{H}{\underset{*}{|}} \tag{3.8}$$

$$\overset{H}{\underset{*}{|}}C=C\overset{H}{\underset{H}{}} + 2^* \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \overset{H}{\underset{*}{|}}C=C\overset{H}{\underset{*}{|}} + \overset{H}{\underset{*}{|}} \tag{3.9}$$

Here there is furthur C-H bond scission, leading to what is essentially an adsorbed propyne molecule. This was shown to be the cause of a self-poisoning of the catalyst [35]. Since propyne is more strongly adsorbed than propylene, propylene formed on the surface would have a short residence time before desorbing because of competition with the more strongly adsorbed propyne. This would keep the surface concentration of propylene low, consequently

propylene will be produced under the dehydrogenation conditions.

3.3.2 Hydrogenolysis reactions.

At high temperatures, C-C bond formation and scission may also occur, leading to hydrogenolysis. The temperatures required and the relative importance of this reactions depend on the metal and the hydrocarbons.

A common form of C-C bond scission occurs with formation of CH_4 along with smaller amounts of C_2H_6. In its simplest form, hydrogenolysis proceeds as follows on metal surfaces :

$$CH_3CH_2(CH_2)_nCH_3 + H_2 \longrightarrow CH_4 + CH_3(CH_2)_nCH_3 \qquad (3.10)$$

$$CH_3CH_2(CH_2)_{n-1}CH_3 + H_2 \longrightarrow CH_4 + CH_3(CH_2)_{n-1}CH_3 \qquad (3.11)$$

The mechanism of hydrogenolysis appears to involve adsorption of adjacent carbon atoms on adjacent metal sites with breaking of C-H bonds. For the C-C bond rupture to occur, the carbons appear to have to undergo further dehydrogenation, forming multiple carbon-metal bonds and leading to almost complete dehydrogenation of the carbon atoms in some cases :

$$
\begin{array}{c}
-CH_2 \\
\diagdown \\
C\cdots C \\
\| \quad \| \\
M \quad M
\end{array}
$$
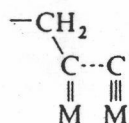
The strength of the metal-carbon bonds appears to be crucial to the rate of breaking the C-C bond. Once the C-C bond is broken, rehydrogenation of the fragments occurs, leading to CH_4 and a

paraffin from the other fragment.

Hydrogenolysis reactions require high temperatures and strong bonding of reactants to the catalyst and are therefore difficult to accomplish; they are demanding compared with dehydrogenation reactions, which occur much more readily. They appear to require at least a pair (and possibly a more complex ensemble) of metal atoms. Although the size of supported metal crystallites typically has little influence on the specific rates of dehydrogenation reactions, it strongly influences hydrogenolysis rates; the smaller crystallites are the more active by as much as a hundredfold. This result is consistent with the requirement for strong carbon-metal bonding to break the C-C bond and the fact that bonding is stronger to metal atoms with a lower number of neighboring atoms [36], i.e., atoms on corners, edges, and higher index planes, which are relatively abundant on small metal crystallites.

3.4 Coking on noble metal catalysts.

The coking of catalysts containing noble metals has long been of interest, primarily as a result of the industrial importance of reforming catalysts and their deactivation as a result of coke formation. Platinum, other noble metals, and binary and ternary alloys are of particular interest and have been studied in detail.

There are several unusual features associated with coking of noble metals and several differences from transition metals. Most studies have been carried out using a Pt/Al_2O_3 reforming catalyst and it is important to remember that both metal and support can coke

[5,37].

In these catalysts, it is well established that coke is deposited almost instantly as the reaction commences but deactivation as a result of coking takes many thousands of hours of operation. Coke deposited on the surface must, then, affect or be involved in the catalytic chemistry without significantly deactivation the catalyst. To go further than this, the initial coke deposits are considered to be desirable, in that they are formed on the most active catalytic sites, which if they were not deactivated, could produce unwanted excess hydrocracking. As a result, it is clear that some coking is desired but that excess coking should be avoided.

In contrast to the transition metals, it has also been established that carbon dissolution in bulk metal, although it can occur, is probably not important to the overall coking process. As a result, it seems likely that a dissolved carbon-platinum equilibrium is established, but that the catalytic properties of the metal are little affected and that coke accumulation involves a surface migration-nucleation process rather than a dissolution-precipitation sequence. The coking process is then described by Figure 3.4, where the possible factors influencing the process are the production and dehydrogenation of intermediates, the migration of these intermediates (or carbon) to a nucleation site, the nature of such sites and the growth and/or subsequent reactions of the deposits on these sites.

Not surprisingly, the amount of coke deposited on the metal depends on the hydrocarbon, but there is little evidence of an
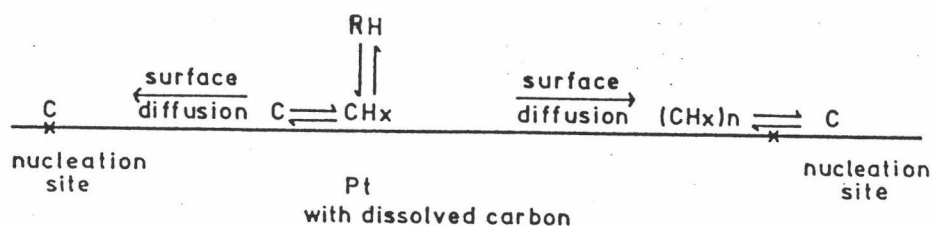
Figure 3.4 Model for the production of carbon and platinum [36].

active carbon intermediate being as important to the main reaction. Instead, it appears that partially hydrogenated species are produced and that these migrate across the surface. The evidence for this is good. The coke deposits are found to have, initially, a hydrogen content of about 1.0-1.5 hydrogen atoms per surface carbon atom and hydrogen transfer with species on the surface that produce gaseous products is easy. Large amounts of hydrogen can be stored on the deposits, but if hydrogen is completely removed, little if any of the gas can be introduced in a higher-energy binding state. At the same time, removal of hydrogen leads to restructuring of the deposits to a more graphitic form, a reorganization that can also be induced by increasing temperature. Hydrogen associated with this deposit is available for reaction, but as dehydrogenation a ordering occur, the deposits become more graphitelike.

The deposits themselves grow across the surface unselectively, decreasing the metal surface available by a masking process. This is shown by the fact that the selectivity patterns of reforming reactions show little change as coking proceeds.

The thermodynamics of the reforming reactions are such that it is desirable to work at high temperatures and lower pressures, but these are the conditions that favor coke formation. In recent years, it has been found possible to use bi- or multimetallic catalysts supported on alumina to promote reforming, the catalysts producing less coke under the desired conditions. Combinations of Pt-Re, Pt-Ir, Pt-Sn, Pt-Ge, and a host of other bi- or multimetallic systems have been reported [39] and are now used widely in industry. As a result, it is necessary to ask how the formation of coke is changed by inclusion of other components.

By analogy with other systems, the second component could reduce coking by changing the geometry or nature of the catalyst or by enhancing the gasification of coke. A common feature of all catalysts is the presence of platinum [39] and other components are believed-at least in part-to alloy with platinum. As a result, geometric and electronic interactions would be expected and could be responsible for reducing coke formation.

Reforming catalysts probably show coking effects as a result of the presence of two catalytic functions most clearly. Coke produced on the metal can be shown to be different to coke produced on the oxide by temperature-programmed oxidation [7, 8]. Metallic coke is more easily gasified than support coke. It is produced early in the reforming reaction and is favored relative to acidic coke by operation under less severe conditions. Acidic coke is more polymeric and is more difficult to gasify. There is, at best, only a small reaction between acidic coke and hydrogen and coke production is favored relative to metallic coke by operation under more severe conditions.

The mobility of several carbonaceous species on the surface is well established, and their residence time is long. This fact, in itself, means that hydrogenation will be favored and coking reduced. On the acidic support, however, hydrogenation is essentially uncatalyzed, and polymerization/coking favored.

3.4.1 Effect of deposited coke on reactions.

Fig. 3.5 shows the evolution of the amount of carbon deposited on a monometallic catalyst. After a very rapid initial deposit – of the order of 2 wt% – the formation of carbon slows considerably, occurring at a regular rate, before finally increasing drastically. Work by Parera and Barbier et al. [40, 41] has shown that the initial deposition is purely on the metal component of the catalyst (first few hours of operation). Further coking is seen to occur on the alumina [7], and the final increase in the rate of carbon deposit is explained by the conjuction of :
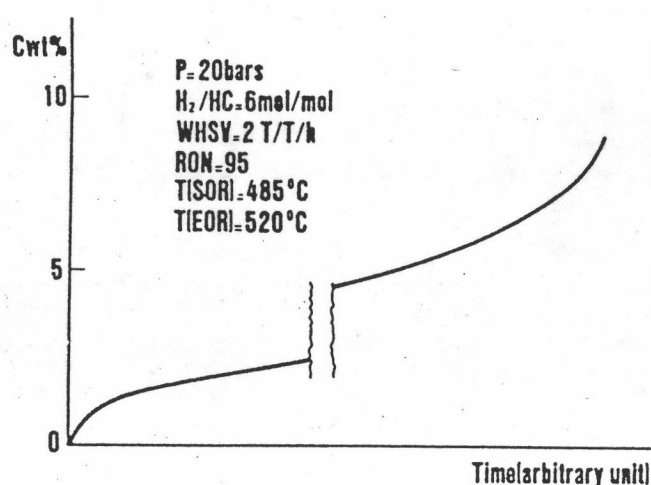
Figure 3.5 Typical evolution of carbon deposit on catalyst during reforming of naphtha.

(a) High temperatures needed at that time to ensure required 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 degrees of coke deposition.

As has already been pointed out, this loss in activity is made up for by increase in the operating temperature.

3.4.1.1 Dehydrogenation.

Dehydrogenation of paraffins and naphthenes is a fast reaction, and under reforming conditions, the corresponding thermodynamic equilibria are rather quickly achieved. Barbier et al. [42] have shown that for low carbon converage at atmospheric pressure, about 3 carbon atoms are needed to suppress the dehydrogenating activity of 2 platinum atoms. The result in Figure 3.6 showing the effect of coke on the dehydrogenating activity for cyclohexane verify the fact that the majority of coke is deposited on the alumina, since the activity of the catalyst for this metal site catalyzed reaction should be nil with coke contents of less than 0.1 weight percent, if all the carbon is deposited on the platinum. Unfortunately, with such high carbon amounts, there is on connection between residual activity and the carbon percentage.
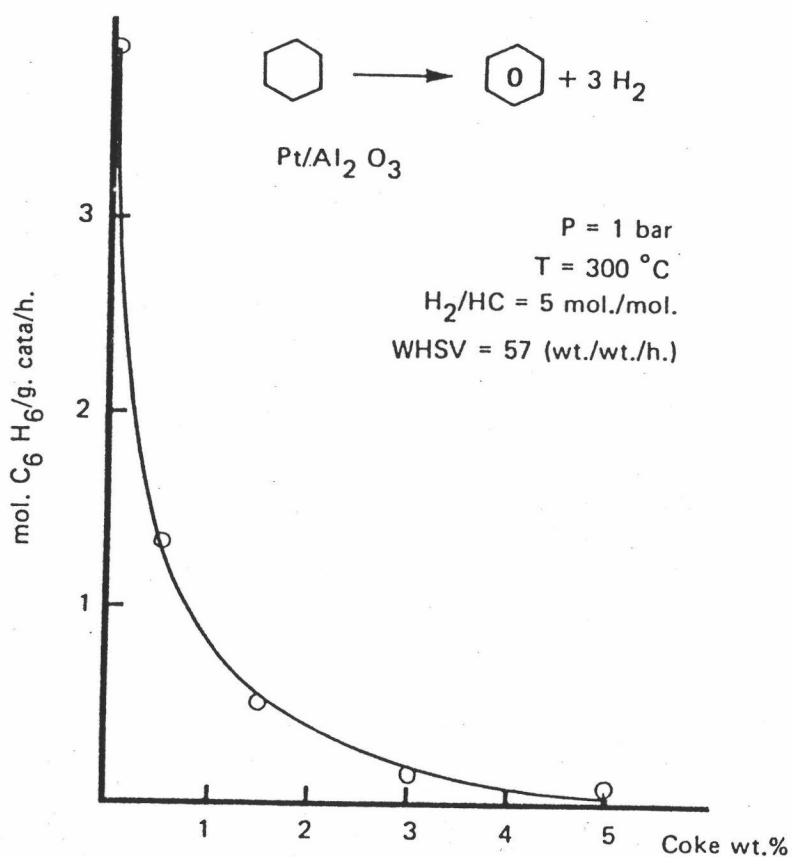
Figure 3.6   Effect of coke on dehydrogenation activity.

3.4.1.2 Hydrogenolysis.

Fig. 3.7 compares the toxicity of deposited coke on the metal sites of a catalyst on the activities of dehydrogenation, H-D exchange, and hydrogenolysis.   the obvious catastrophic attenuation of the hydrogenolytic function agrees with work by Barbier et al. [41] and Trimm [43]. A number of authors suggest that the effect of coke on Pt/Al_2O_3 is similar to alloying or sulfur adsorption where there is a sharp decrease in hydrogenolysis activity compared to the other reactions. The basic cause is a decrease in the number of suitable ensembles for this
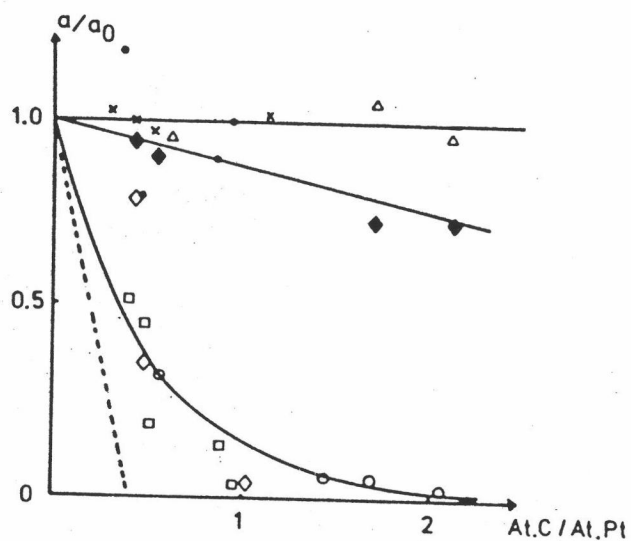
Figure 3.7   The evolution of the relative activity of 1 g. of
catalyst as a function of the number of metal site
carbon atoms deposited per platinum atom [42].
(a) Benzene exchange: Pt/Al_2O_3, 0-1%(A),♦ ;Pt/Al_2O_3, 1%
(C),● . (b) Cyclopentane hydrogenolysis: Pt/Al_2O_3, 13%
(D),◊ ; Pt/Al_2O_3, 1%(C), □ , Pt/Al_2O_3 (A),o .
(c) Benzene hydrogenation: Pt/Al_2O_3, 0.1% (A),× ;
Pt/Al_2O_3, 1%(C),△ .

reaction due to site blocking by coke, especially on the more active
high coordination number face atoms on crystallites. These results
agree with studies on single crystals by Somorjai [24].

3.4.2 Influence of the catalyst.

3.4.2.1. Composition of a metallic phase.

The most remarkable progress made in improving noble metallic catalysts is due to the use, with platinum, of metal additives commonly called "promoters". Since 1969 – when the first bimetallic catalyst was presented, using platinum, and rhenium – other combinations, based on iridium, germanium and tin, have been used. Fig. 3.8 shows the evolution of coke on a number of alumina-supported bimetallic catalysts. The additives used can be grouped into the two types listed here ; in each case, the result of the addition is an increase of the number of available Pt sites compared to monometallic Pt/Al$_2$O$_3$ [44] :
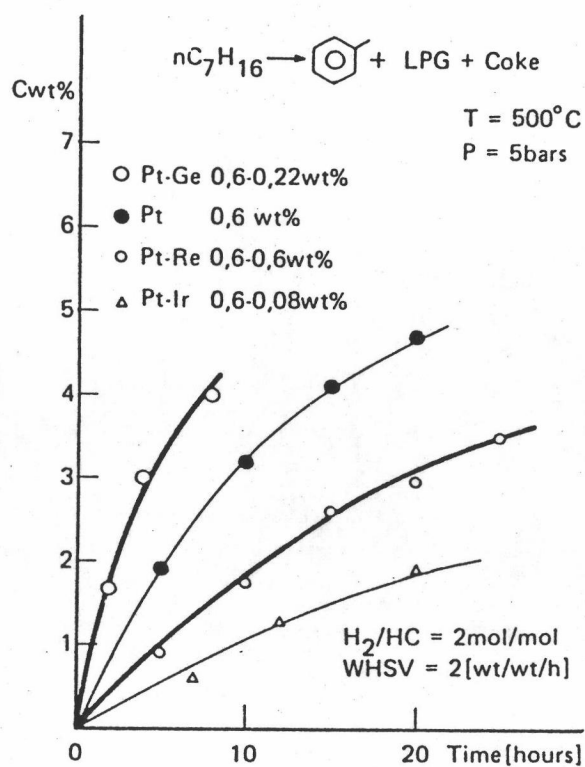
Figure 3.8 Rate of coke deposit for platinum and platinum-promoted catalysts.

(a) Additives such as rhenium and iridium, which diminish the overall coke deposit rate, and perhaps its organization.

(b) Additives such as germanium and tin, for which the coking rate is at least equivalent, if not higher, than that observed with Pt alone.

Even though the overall coke depositions are higher than Pt/Al₂O₃ for the second type of additives, the deactivation rate is less than Pt/Al₂O₃. This is due to the mechanism of deactivation, which involves graphitization of coke. Hence a distinction is made between coke deposition and deactivation mechanisms which are not necessarily interrelated.

As far as coke deposition on bimetallic metal sites is concerned, the ensemble effect lowers the probability of finding required ensembles for the coking (self-poisoning) reactions (Table 3.2). Hence, coke deposition on the metal decreases compared to Pt/Al₂O₃, even though the quantity deposited on the support is much higher.

3.4.3 Mechanism of deactivtion and coke formation.

3.4.3.1. Mechanism of catalyst deactivation.

A catalyst component which prolongs catalyst life (by modifecation of coke deposition) can be visualized in one of two ways : by reducing coke formation or by changing nature of the carbonaceous overlayer. Parera et al. [45] showed that the

total coke level of presulfided Pt-Re/Al₂O₃ is higher than presulfided Pt-Al₂O₃. Edgar [46] and Sinfelt [47] suggest that Pt-Re-S/Al₂O₃ is more "tolerant" to coke deposition, with operating coke levels of 20-25 wt.% being reported. Since, industrially, rhenium is in an inert sulfided state, Sachtler [48] dismissed an earlier theory that the activity improvement upon rhenium addition is due to the catalysis of the ring-opening reactions of cyclopentane cyclics, thus preventing the formation of cyclopentadiene and its dimers, which are very effective coke precursors on acid and metal sites. This earlier theory of reduced coke formation due to hydrogenolytic destruction of precursors is valid when the rhenium is unsulfided. Sachtler argued that the similar quantities of coke deposition for both catalysts, together with the fact that the important dehydrocyclization function of a catalyst is on the metal sites, suggest that the long-term deactivation of a reformer must be due to metal site deactivation which is somewhat less toxic on Pt-Re/Al₂O₃. Thus, the only possible explanation for this behavior is that the deactivation of the dehydrocyclization function of a catalyst is an alteration in the nature of metal site coke, which is usually deposited in the first few hours of operation. In conclusion, although the long-term coking of a reformer is on acid sites with a decrease in isomerization activity, the decrease in octane number observed industrially is due to deactivation of the metal function. Barbier et al. [14] suggests that this deactivation of the metal function is due to graphitization of the metal site coke which encapsulates the metal and makes the sites catalytically inert.

3.4.3.2. Mechanism of coke formation.

Many mechanisms of coke formation all involve an initial step of dehydrogenation and formation of unsaturated species which are able to migrate, either in the gaseous phase or in the adsorbed phase, and to form dimeric or polymeric species on the acid sites of the catalyst.

Fig. 3.4 shows a typical model for production of coke on platinum. A series of fragmantation reactions and successive dehydrogenation reactions leads to the formation of carbon atoms and these atoms (or partially hydrogenated intermediates) may combine to form more toxic coke deposits. The coke deposits are found to have, initially, a hydrogen content of about 1.0 - 1.5 hydrogen atoms per surface carbon atom, and hydrogen transfer wiht species on the surface that produce gaseous products is easy. Removal of this hydrogen by successive fragmentation (hydrogenalysis) and dehydrogenation leads to a more graphitic form of coke (this also involves the migration to a nucleation site where the irreversible deposit grows) ; a reorganization can also by included by increasing temperature. The fraction of the carbonaceous overlayer which is a graphitic is shown in Fig. 3.9 for cyclohexane conversion on a Pt/Al_2O_3 catalyst. This discussion introduces the concept of reversible (partially hydrogenated) and irreversible coke (graphitic).
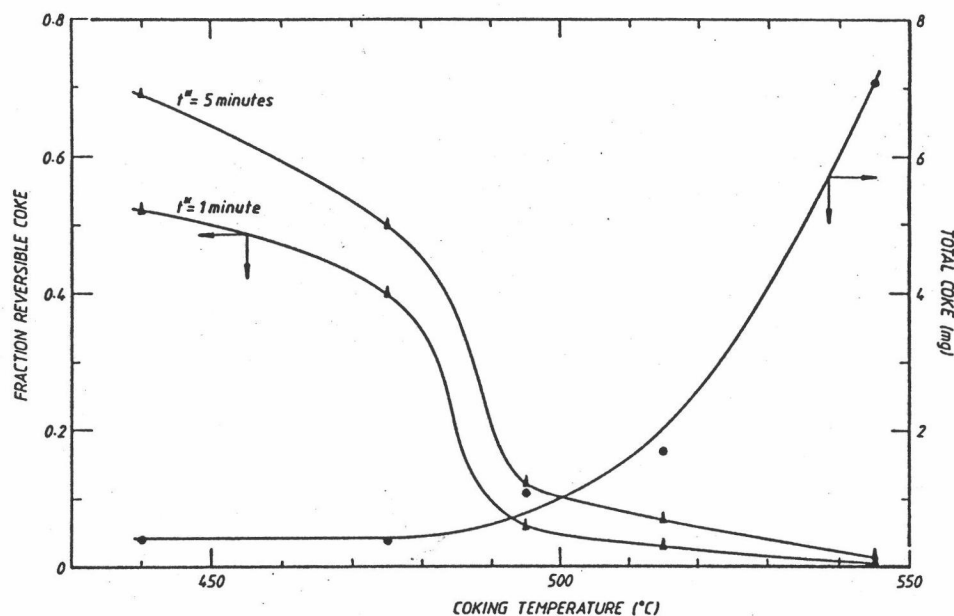
Figure 3.9 Fraction of irreversible (graphitic) coke on the metal sites of a Pt/Al₂O₃ catalyst at different temperatures.

3.4.3.3. <u>Control of deactivation by hydrogen reversible and irreversible Coke</u>.

Fig. 3.10 shows the activity recovery for cyclohexane dehydrogenation after a helium/hydrogen stream cycle was introduced. It is obvious that :

(a) Even an instantaneous loss in hydrogen causes the activity to disappear.

(b) The lower recovery of activity when the helium is passed over the catalyst for a longer time shows that the loss of hydrogen enhances the graphitization of coke.

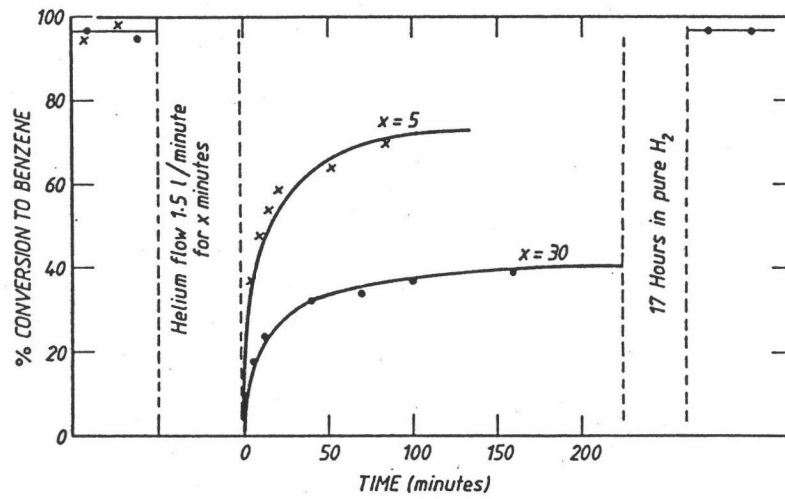Thus we see a role for hydrogen in controlling

Figure 3.10   Effect of pure helium cycle (time = x min.) on activity
recovery   of Pt/Al₂O₃ (feed = cyclohexane, T =   480 °C,
H₂/H.C. = 5, WHSV = 30, P = 1 atm).

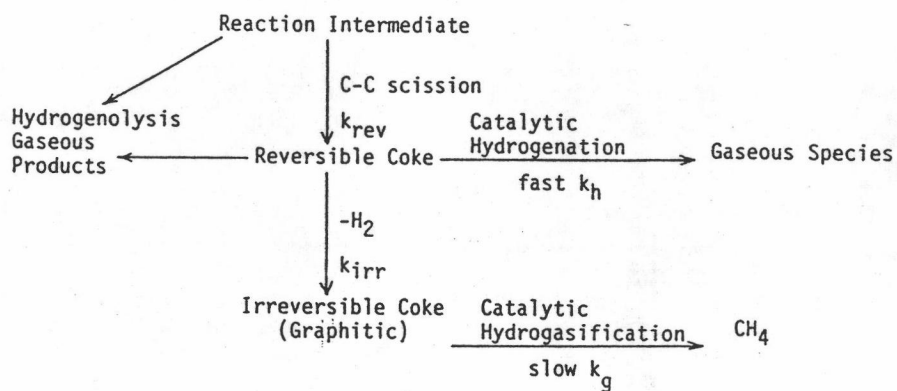the deactivation of a catalyst (Fig. 3.11) :

Figure 3.11   Mechanism of coking and hydrogen cleaning of a Pt
crystallite.

(a) Controlling the amount of reversible coke by "catalytic" hydrogenation.

(b) 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.

(c) Slow removal of graphitic coke by catalytic hydrogasification.

(d) Lower coking rates at high hydrogen pressures due to reduced concentration of coke precursors.