



CHAPTER III

THEORY

The three most important aspects of the practical use of a heterogeneous catalyst are activity, selectivity and life time. The life time of a catalyst has been the subject of very few studies. In the oil refining and petrochemical industry, deactivation of the catalyst through the settling of carbonaceous residues originate from parallel and/or series reactions of hydrocarbon pose an important technological and economic problem. In practice, the plant has to be shut down at regular intervals to ensure the regeneration of the catalyst. It is obvious that reducing the rate of coke formation will represent an appreciable technical improvement, However, the remedies for deactivation, if any, can only be derived from an understanding of the mechanism of coke formation and of its effects on the activity and selectivity of the catalysts.

The intent of this chapter is to devoted to some important aspects of metallic, especially noble metal (e. g. platinum), catalysts and coke deposition on their surface. The first part gives the characteristic of supports metallic catalysts, the second part to the coking on noble metal catalysts.

CHARACTERISTICS OF SUPPORTED METALLIC CATALYSTS

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 Å⁰ in diameter. The crystallite size is controlled by calcination and reduction steps (Figure 3.1). A typical example is given by Guenin et al. (23) 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 of surface atoms for octahedral crystallites of increasing size (25). Corner atoms have a coordination number of 4, edge atom, 6 or 7 and atom on the face of the plane, 8 or 9. It is noticeable that the most pronounced change in average coordination number of surface atoms is in the crystallite size range 5-14 Å.

Work by van Hardefeld and Hartog (26) demonstrated two important points :

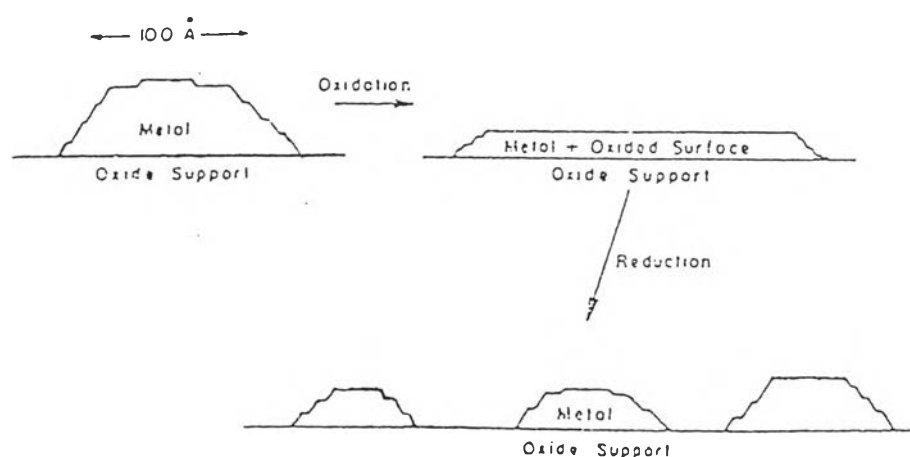


Figure 3.1 Process of calcination and reduction causes formation of metallic crystallites (24).

Table 3.1 Properties of platinum crystals of different sizes with regular faces (24).

Number	Length of	Fraction of atoms	Total number of	Average
	crystal edge			on surface
	A°			number of surface
				atoms
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	49.75	0.30	3894	8.64

(a). Low coordination surface atoms, corner atoms, edge atoms ($i < 7$) are present in significant proportions only in crystallites of sizes $d < 40 \text{ \AA}$. Large crystals consist almost exclusively of face atoms.

(b). Corner atoms predominate on the surface of extremely small crystallites ($d < 10 \text{ \AA}$).

Surface atoms differ from bulk atoms in that they have an incomplete set of neighbors; for example, a bulk atom in a fcc or hcp crystal is surrounded by 12 nearest neighbors, whereas atoms in the surface are bound by 3 to 11 neighbors. 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 (27) showed that the stereochemistry of corner and edge atoms can be quite different from face atoms, therefore a different kind of bonding is favoured at these sites. These effects are electron deficient compared to face atoms.

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

Some 35 years ago, it was conventional to describe the differences in performance between similar catalysts in terms of "electronic" and "geometric" factors. Sachtler (32) 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 reaction, if the bond is too weak, no chemisorption will take place and if too strong, the desorption will become too slow.

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 (29) 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 temperature (<450 °C), multiple site reactions such as isomerization, hydrogenolysis and 1,5 dehydrocyclization do not occur because the majority of ensembles comprise single atoms, hence the product aromatic content is low. But at higher temperature (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 describe the stereochemical conditions that a catalytic center must fulfil in order to render that reaction “ stereospecific “ or “ shape selective “ that is, capable of preferentially producing one of the several isomers.

3. Structure Sensitivity of reactions

The term "structure sensitive " (or demanding) is applied to a reaction whose specific activity (same as turn over 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 allowing, introducing crystal imperfection 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 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

Table 3.2 Reaction site requirements on platinum crystallites (24).

Reaction	Example compound	Generic reaction mechanism code	Crystallite size range (where mechanism dominate)	Effect of increasing dispersion on rate ^a	Minimum ensemble requirement	Coordination requirement
Hydrogenolysis	1. Methylcyclopentane	Nonselective, cyclic	< 20 Å	-	1	Corner/edge
		Bond shift	Full range	-	1	Corner/edge
	2. Alkanes	Selective, cyclic	> 25 Å	-	2	Corner/edge and face
				Small	+	1
Isomerization	1. 3-Methylpentane		Large	-	3	Face.
		Nonselective, cyclic	< 20 Å	+	1	Corner/edge
		Bond shift	Full range	-	1	Corner/edge
	2. 2-Methylpentane	Selective, cyclic	> 25 Å	-	2	Corner/edge and face
		Nonselective, cyclic	12-100 Å	+	1	Corner/edge
		Bond shift	12-200 Å	-	1	Corner/edge
Dehydrocyclization (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 (enlargement (after 1,5 closure)	Methylcyclopentane		Full range	Negligible	1	Corner/edge and face
Dehydrocyclization (with 1,6 - closure)	Heptane		Full range	Negligible	1-2	Corner/edge and face (higher on corners)
Dehydrogenation	Alkanes Naphthene		Full range	Negligible 1	1	Corner/edge and face
Self-poisoning	Alkanes		> 10 Å	-	2	face

^a+, increase of rate ; -, decrease of rate

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.

There are two other influential effects concern structure-sensitive reactions as follow.

(a). Metal - support interaction (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 support) would be greater, the smaller the particle size or the greater, the interfacial area of contact. Thus any electronic effect (which may result in modification of reaction selectivity) observed are inherently difficult to separate from directly attributable to the size of the metal atom assembly and MSI hence may show up as a structure-sensitive phenomenon from a macroscopic view point.

(b). 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 under steady-state conditions is almost always 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 sensitive could be caused by self-poisoning has been discussed by J.R. Katzer and W.H. Manogue (30). For example, the increase in alkane hydrogenolysis rate with dispersion (Table 3.2) could be due to the fact that smaller particles used are more

resistant to self - poisoning.

4. 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 selectivities for the desired processes of dehydrogenation, isomerization and dehydrocyclization. A rationalization of the typical effects of alloying on selectivity and activity is needed on the basis of the electronic and geometric factors.

4.1 Individual surface atom concept

A renewed interest in a functional theory for heterogeneous alloy catalysis was due to the following important causes (31) :

(a). The increase in observed activity of some bimetal systems due to change in selectivity.

(b). 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.

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

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

(e). 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 (32). 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. Therefore 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 (33).

If two catalytically active metals are blended, a new kind of site may be created, consisting of both types of atoms (Pt-Ir/Al₂O₃). 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 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.

4.2 Factors influencing ensemble effect in bimetallic catalysts

The catalyst activity, stability and selectivity of some bimetallic catalysts usually deviate from additive behavior predictable from the individual metal properties. Guzzi (34) 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 (35) 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 rate of hydrogenolysis and metal site coking drastically decrease.

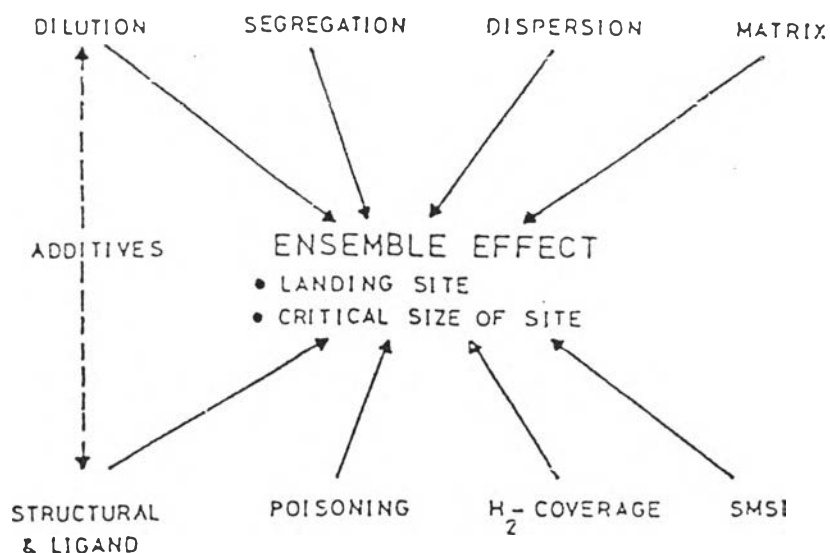


Figure 3.2 Factors affecting the ensemble effect in bimetallic catalysis (24).

The surface geometry of a Pt/Al₂O₃ catalyst is shown in Figure 3.3, They show the intimate relationship between ensemble size, selective poisoning by an additive and deactivation by carbonaceous fragments (36). 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 catalyst (Figure 3.4). Sulfur, firmly bounded 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 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.

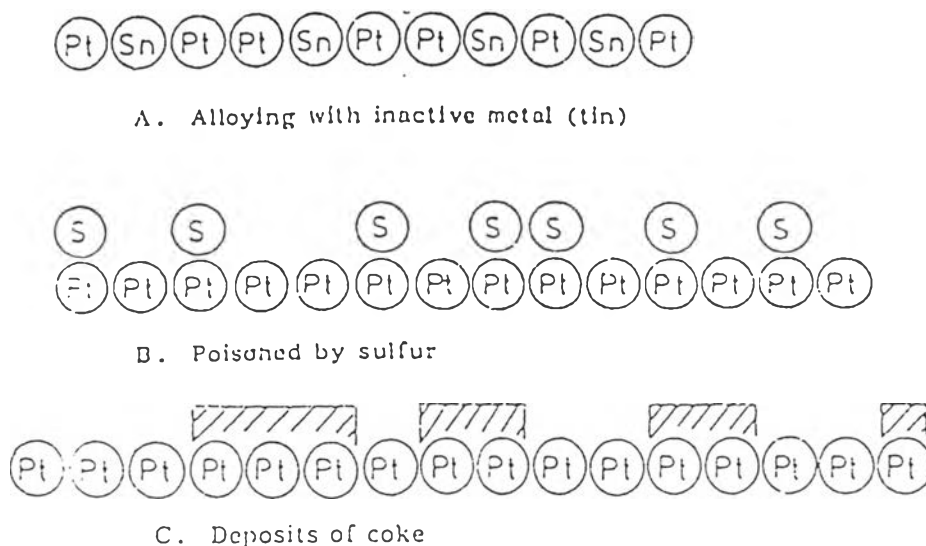


Figure 3.3 The surface geometry of a Pt/Al₂O₃ catalyst (24).

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-Sn) alloys is due to the high dehydrocyclization activity of the iridium component (37). The higher hydrogenolytic activity due to the iridium component is controlled by continuous addition of sulfur in the feed (0.10 ppm),

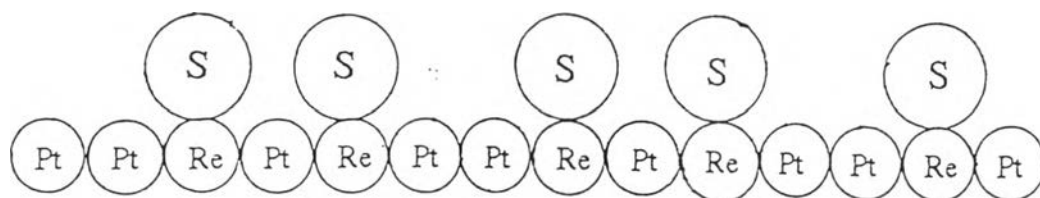


Figure 3.4 Schematic illustrating the stabilization of the catalytic activity of Pt-Re catalysts in the presence of sulfur (24).

thus reducing the Pt-Ir ensemble size on the catalyst (38). but still improving the selectivity for the single γ -site 1,6 dehydrocyclization reactions.

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, 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/Al₂O₃ catalyst and it is important to remember that both metal and support can coke (8, 39).

1. Effects of operating conditions on coking deactivation

Operating conditions have an extremely important influence on the deactivation of reforming catalysts. Franck and Martino (40) and Figuli et al (41). give excellent summaries as follows :

1.1 Hydrogen and hydrocarbon Pressures

From thermodynamics, dehydrogenation will be the best to operate at the lowest possible hydrogen pressure but it is well known that catalyst are unstable under these conditions because of enhanced coking (2). Figure 3.5 shows the evolution of the temperature needed at the inlet of the reactors in order to maintain a constant level of performance during operation according to different hydrogen pressure, it can be seen that although deactivation is relatively slow under 50 bar, it become very fast even under 10 bar of hydrogen pressure. It is noted that when H_2/HC ratio is below 10, the effect is extremely important.

It is interest to noted that a decrease in hydrogen pressure not only promote aging but also modified the reaction rate. At low hydrogen pressure, there are many highly unsaturated species on the surface of the catalyst which are precursors of coke, whereas at high hydrogen pressure there is less mobile coke but fewer of the intermediates which are needed for the reaction.

1.2 Nature of hydrocarbons

Cooper and Trimm (42) showed that the coke evolution on Pt/Al_2O_3 catalyst for a number of different hydrocarbon have 6 carbon atoms. The initial deposition is on the metal site while that at latter times is on the alumina. It is obvious from figure 3.6 that the rate of coke decreases in the following order for both metal and alumina sites :

Methyl cyclopentane > 3-methylpentane > n-hexane > 2-methylpentane > benzene > cyclohexane.

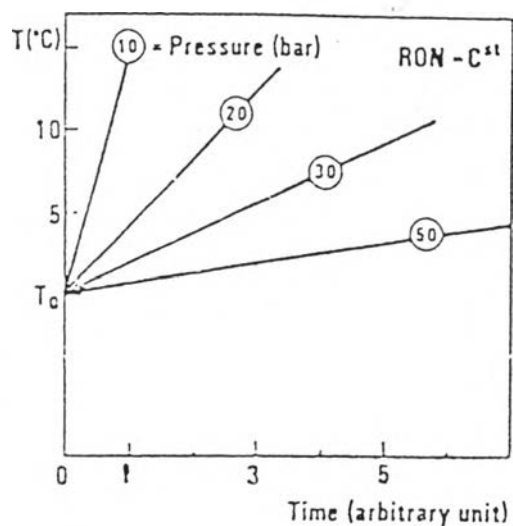


Figure 3.5 Typical influence of pressure on stability (43).

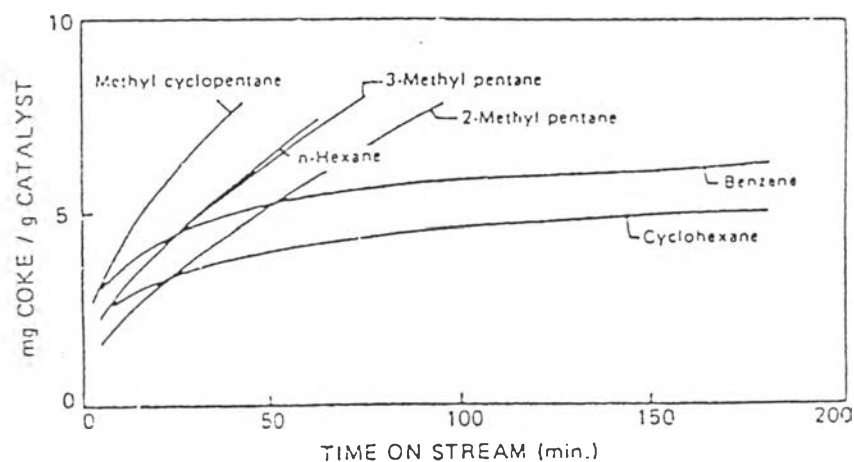


Figure 3.6 The deposition of coke on Pt/Al₂O₃ from various hydrocarbons ; T = 500 °C (42).

1.3 Temperature

Temperature is the only possible operating variable for activity maintenance in an industrial unit. Figure 3.7 shows the influence of

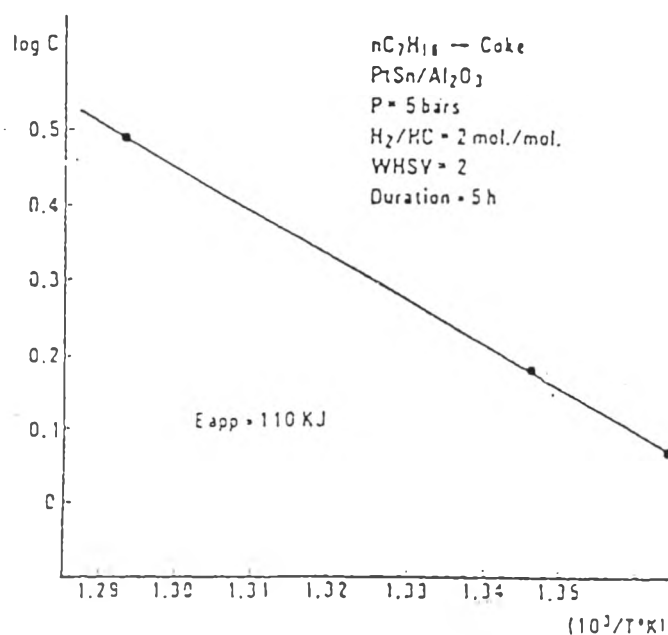


Figure 3.7 Influence of temperature on the rate of coke deposition (40).

temperature on the amount of coke contained with a bimetallic catalyst.

2. Influence of the catalyst

2.1 Dispersion

Guenin et al (23) showed that small crystallite sites are very active in alkane hydrogenolysis, probably due to the lower self-poisoning of these crystallites. Van Broekhoven et al. (44) found that multiple metal-carbon bond formation is necessary for carbon formation on metal crystallites and there is more likely on large crystallites where there is an abundance of high coordination number atoms and the increased possibility of larger ensembles. The lower effect of metal support interactions with larger crystallites would make the surface more attractive for multiple metal-carbon bond formation also.

Large metal crystallites also favour coke formation on the alumina, small crystallites present an electron-deficiency due to metal-support interaction, hence these crystallites cannot stabilize and catalyze the polymerization of the C5 ring coke precursors (45, 46).

2.2 Chloride Content

Chlorine has an important effect on both the initial dispersion of the platinum and the maintenance of its dispersion (40). It also modifies the acidity of the catalyst which controls the relative rates of isomerization and hydrocracking. Industrial catalysts work with a chloride content which is deliberately maintained in a range 0.8-1.1 wt % as although some chloride is needed, an excess leads to excessive hydrocracking and coking activity. According to Parera et al. (47, 48, 49) the amount of coke on a reforming catalyst is minimum when the catalyst's chloride content is in the range 0.7-0.9 wt %. With this chloride content, the deactivation rate is also a minimum and this has been attributed to a maximum in hydrogen spillover on the surface of the alumina, thus hydrogenating unsaturated substances which may subsequently have pursued alkylation and polymerization reactions to coke (50).

2.3 Composition of a metallic phase

The most remarkable progress made in improving reforming catalyst is due to the use of platinum with metal additives commonly called promoters. Figure 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 as follow :

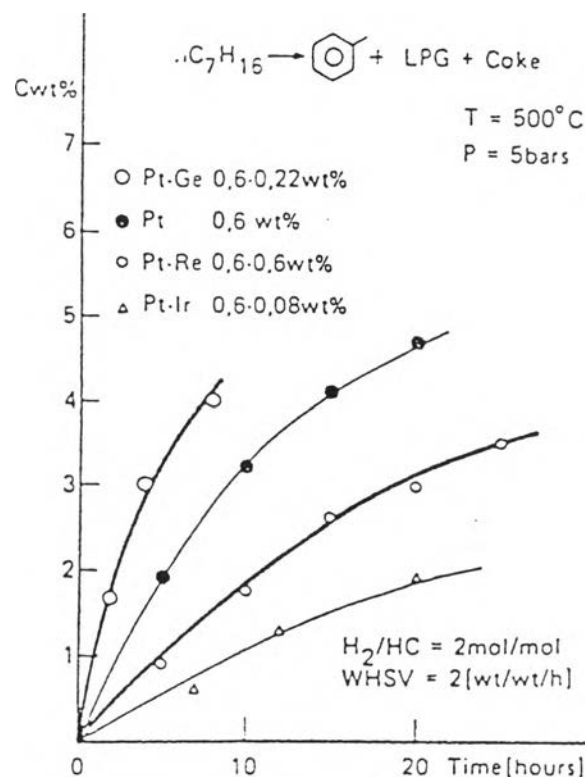


Figure 3.8 Rate of coke deposit for platinum and platinum-promoted catalysts (40).

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

(b). Additives such as germanium and tin for which thecoking rate is atleast equivalent, if not higher, than that oberved with Pt alone.

Even though the over all depositions are higher than Pt/Al_2O_3 for the second type of additives, the deactivation rate is less than Pt/Al_2O_3 .

3. 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.

A typical model for production of coke on platinum is shown in Figure 3.9 (51). A series of fragmentation 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 (52) and hydrogen transfer with species on the surface that produce gaseous products is easy. Removal of this hydrogen by successive fragmentation (hydrogenolysis) and dehydrogenation lead to a more graphitic form of coke (this also involves migration to a nucleation site where the irreversible deposit grows) reorganization can also be induced by increasing temperature (53). The fraction of the carbonaceous overlayer which is graphitic is shown in figure 3.10. Other mechanisms suggested in the literature for metal site coking are shown in Table 3.3.

4. The chemical nature of coke

It is shown that the metallic coke consists of two types: the reversible coke being hydrogenated surface species (atomic H/C ratio of 1.5-2.0) and the other being graphitic in nature (H/C ~ 0.2) (54, 55, 56).

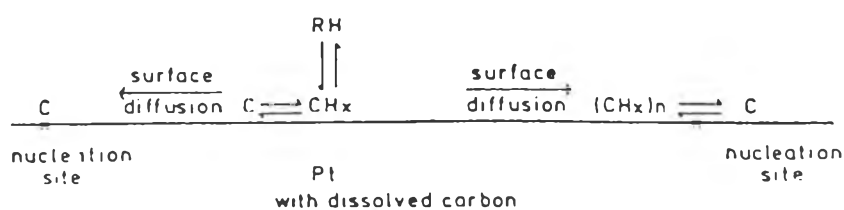


Figure 3.9 Model for the production of carbon on platinum (51).

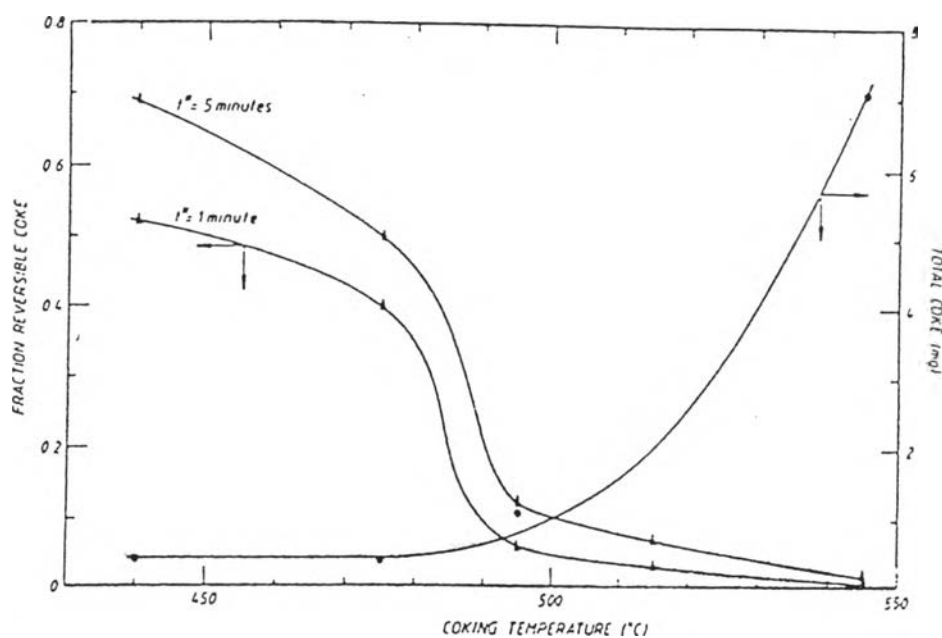


Figure 3.10 Fraction of irreversible coke on the metal sites at different temperature (17).

The chemical nature of the majority of coke (deposited on the alumina) may be analyzed after extraction by various organic solvents. The structure is typically that polyaromatic compounds with a H/C ratio in the range 0.05-0.1 (40).

5. Location of coke on metal crystallites

Figoli et al (63) showed that the initial deposition of coke is on the metal crystallites and the quantity does not change much with time (with in experimental error). Based on this fact, there are a few experimental results which give a hint to the location of coke on the metallic site of a heterogeneous crystallites.

Table 3.3 Mechanisms of coke formation on reforming catalysts (17).

Reference	Terminology	Mechanism
Metal Site		
Sarkany et al. (57) Trimm (58)	Carbon	Fragmentation and successive dehydrogenation of C-C and C-H leads to carbon atom deposition on low index (high coordination number) planes of metal crystallites.
Lockett et al. (59) Sarkany et al. (57)	Polyene	<pre> graph TD A[carbenes] --> B[olefin] A --> C[adsorbed polyolefin] B --> D[polyolefin] D -- adsorb --> C C -- carbene --> E[polycyclic residues] E -- dehydrogenation --> F[graphitic coke] </pre>
Masai et al. (60)		<pre> graph LR G[precursors] --> H[hydrogenated coke] H --> I[graphitic coke] </pre>
Acid site		
Trimm (58)	Diels Alder	Coke arises from polymerization
Parera et al (61)		reactions involving carbonium ions.
Gate et al (2)		Metal sites catalyze dehydrogenation
Zhorov et al (62)		reactions in mechanism

(a). Coke -forming reaction require the formation of multiply bond species similar to hydrogenolysis of cyclopentane (44) , thus requiring high coordination number metal atoms and large ensembles (>3).

(b). Small crystallites have greater coke resistance (44).

(c). Initial coke deposition causes a sharp decrease in the hydrogenolysis activity of a catalyst (13, 27, 51, 64, 65) which is caused by both ensemble and site selective effects.

These results suggest that the coke is partially deposited preferentially on the face atoms of metallic crystallites, although corner atoms are also partially covered by coke. This is in agreement with single crystal studies by Somorjai and Blakely (66) where they show the low coordination number corner sites are the longest surviving on platinum crystallites. Ponce (67) suggests a model of a working crystallite surface almost always covered by a continuous layer of coke with only the corner atoms of intrinsically high activity in H-H and C-H bond breaking serving as portholes for molecules arriving at the surface from the gas phase and for molecules desorbing from the surface.

6. The drain -off effect

Volter al al (18, 68) have shown that coke transport from the metal to alumina is one mechanism for a reduction in metal-site coking reactions. On addition of a bimetallic component to Pt/Al₂O₃, polymeric and aromatic coke precursors are adsorbed less strongly due to an ensemble effect, they are more mobile and can more easily migrate to the alumina. This drain-off effect guarantees that a larger portion of active Pt sites will remain free from blocking precursors

compared to Pt/Al₂O₃.

7. Control of deactivation by hydrogen

Since hydrogen is such an important component of the working platinum catalyst, the following roles can be identified.

(a). High hydrogen pressures lower the concentration of coke precursors, thus keeping the coking rates low.

(b). The strong dehydrogenation reactions involved in coking are restricted by hydrogen.

(c). Hinders the reaction from reversible to irreversible coke by an ensemble effect (35, 69).

(d). Coke levels on the metal component are controlled by hydrogen cleaning.

The role for hydrogen in controlling the deactivation of a catalyst is shown in figure 3.11.

The phenomenon of reversible and irreversible coke has been proposed by a number of authors. Figure 3.11 shows the hydrogen cleansing of coke from a commercial Pt/Al₂O₃ catalyst, verifying the two-stage fast removal of reversible coke followed by the slower gasification of graphitic coke. The coke weight continues to increase with no steady level being reached. Hence, noting that the initial deposition (in hydrogen atmosphere) is reversible in nature, the

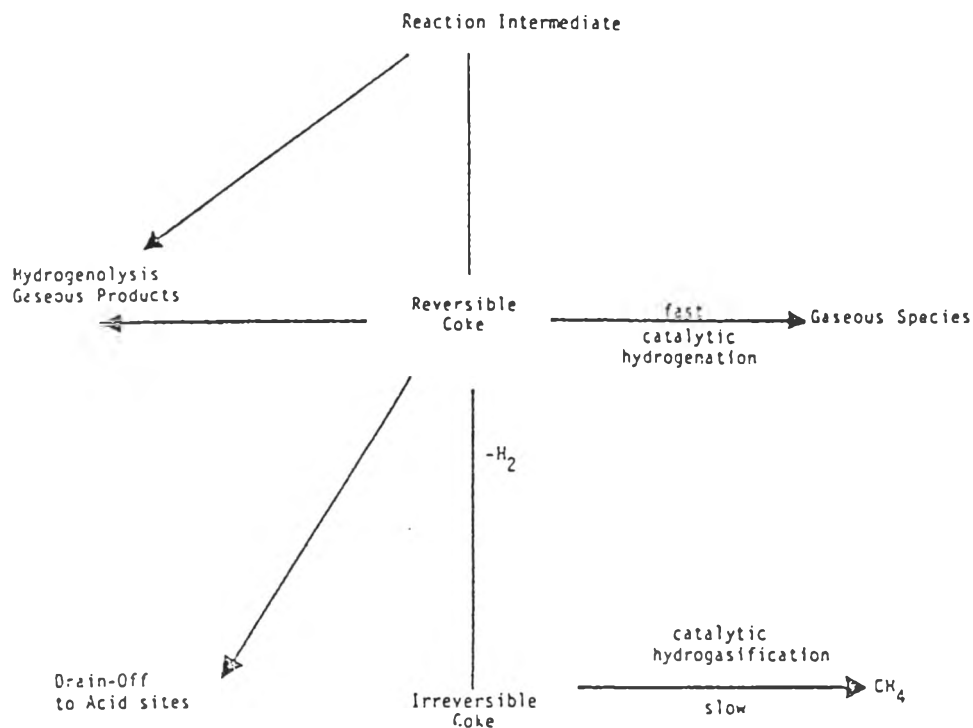


Figure 3.11 Mechanism of coking and hydrogen cleaning of a Pt crystallite (17).

attainment of a steady level of coke on the metal sites must be due to

Rate of reversible coking on metal = Rate of cleansing of
reversible coke by hydrogen

noting that the rate of reversible coke has decreased exponentially with degree of coking (Figure 3.12). In addition, during long-term deactivation.

Rate of change of metal > Rate of cleaning of
site coke to graphite graphitic coke by hydrogen.

The latter relation causes the long-term deactivation of the catalyst (Figure 3.13) and is inhibited by high hydrogen pressure but is accelerated by high

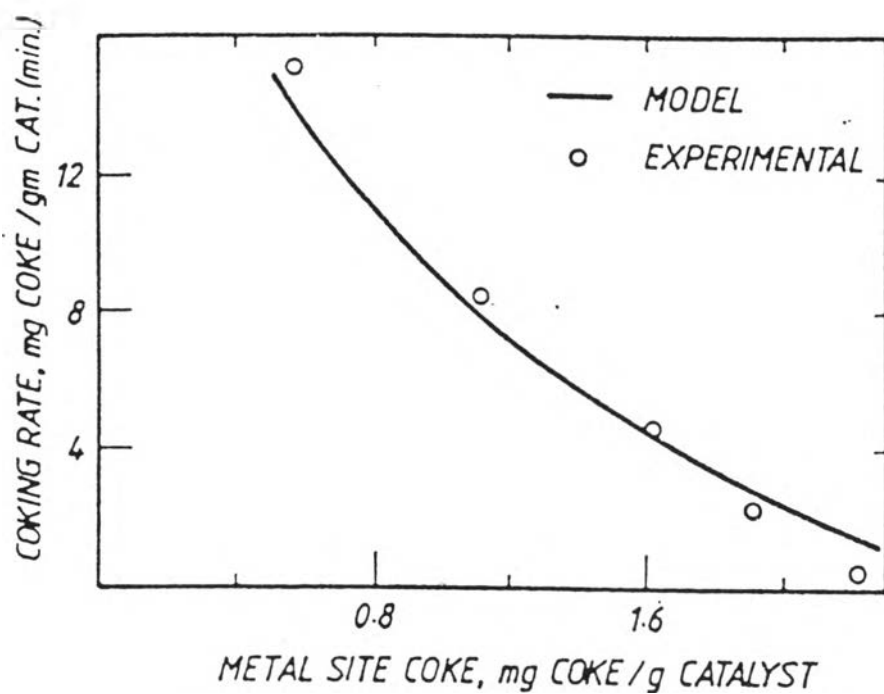


Figure 3.12 Comparison of deactivation model with experimental observation for cyclohexane reversible coking on $\text{Pt}/\text{Al}_2\text{O}_3$. Time frame is 20 seconds of coking so coke is reversible in nature (17).

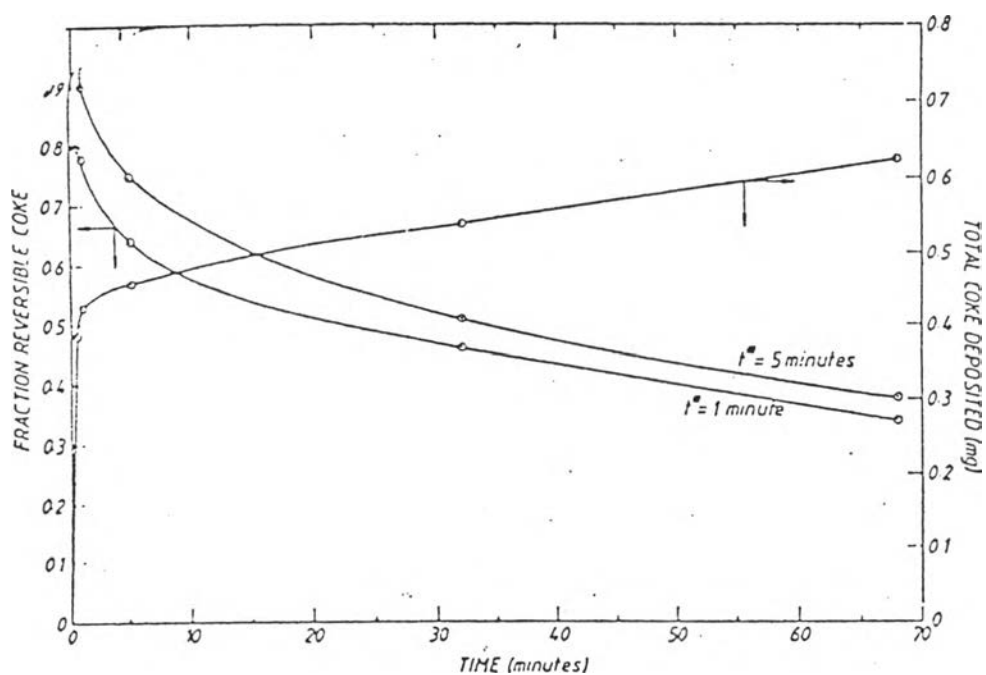


Figure 3.13 Effect of time of operation on reversible fraction on a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (17).

temperature.

8. Deactivation resistance for bimetallic catalysts

The deactivation study for Pt/Al₂O₃ showed that

(a). Observed deactivation in aromatic yield is due to graphitization of the initial coke deposition on the metal component of the catalyst, rather than the large coke deposit on alumina.

(b). Hydrogen acts as a cleaning reagent where it cleans the metallic reversible and graphitic cokes by catalytic hydrogenation and hydrogasification, respectively.

(c). The graphitization process is accelerated by high temperature but is inhibited by high pressures.

(d). The drain-off effect reduces the effective concentration of reversible coke.