

## CHAPTER II

### DEACTIVATION BY COKING

One of the problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time-on-stream owing to deactivation. For catalytic reforming reactions involving hydrocarbons side reactions occur on the catalyst surface dealing to the formation of carbonaceous deposition. Coking process is both of chemical and physical nature and occurs simultaneously with the main reaction. Coke formation is inevitable, but it can be slowed or prevented and some of its consequences can be avoided. Thus, there are numerous investigations of the effect of coke deposition on the catalysts in hydrocarbon reactions. The present work contains papers concerned with the following topics of coking: general overviews of the problem, coking in specific catalytic processes, characterization of coke deposits and modeling of coke formation and catalyst deactivation.

Additionally, the knowledge of the chemical and physical aspects of catalyst deactivation is of importance for the design of deactivation-resistant catalysts, the operation of industrial chemical reactors, and the study of specific regenerating procedures. Coking and deactivation depend on the characteristics of the active sites and on the operating conditions such as reaction time, temperature, pressure and nature of reactant. They also depend on the mode of deactivation. Thus, these details will be introduced in theory of coke deposition.

#### 2.1 Literature reviews of coke deposition

##### 2.1.1 General overviews of the problem

In general, in many processes the gas mixture composition is kept as far as possible from conditions under which carbon formation is thermodynamically favored. The chemical nature of the carbonaceous deposits depends very much on how they are formed, the conditions of temperature and pressure, the age of the catalyst, the chemical nature of the feed and products formed [51, 71-75]. A further area discussed in the previous works [3, 7, 27, 76, 77] was the selection of the

appropriate system for regeneration of the catalyst and the coupling of the regenerator with the main catalytic reactor. Several authors pointed out a direct relationship between the amount of coke deposited and the aromatic and polynuclear aromatic content of the feed [62, 78-82]. However, with the decrease in the coking temperature, the coke nature was gradually changed from highly polyaromatics to low polyaromatics [4, 73]. Also the coke removal by oxidative treatment became easier [74]. Hydrogen decreased the deactivation rate and could even activate the catalyst by removing reversible coke [83, 84]. It has been reported that coke formation occurred more rapidly when a hydrogen acceptor, such as an olefin, was present, in line with the hypothesis of a carbonium ion chemistry for coke formation [85]. The other paper extended this industrial aspect for the specific case of steam reforming [24, 86]. The mechanism of coke formation was reviewed and different approaches to control coking were discussed. Control of coking by modification of the steam carbon ratio and its dependence on the kinetics of the intermediate reactions were emphasized. Minimization of coke deposition can be affected by addition of trace amounts of sulfur in the feed. Indications exist that the use of rare earth oxides as supports can also reduce coking.

Moreover, the catalyst composition also affected significantly the coke deposition. Promoters or additives enhanced the rate of gasification of adsorbed carbon or coke precursors and/or depressed the carbon-forming reactions. This minimizes the content of carbon on the catalyst surface [3, 4, 15, 87]. The first bimetallic naphtha reforming catalyst, Pt-Re/Al<sub>2</sub>O<sub>3</sub>, was introduced in the late 1960s and offered improved activity and stability compared to its monometallic Pt/Al<sub>2</sub>O<sub>3</sub> [15, 88]. A number of bimetallic systems have since been introduced including Pt-Ir, Pt-Sn and Pt-Ge, all of which have improved properties [3, 15, 88]. Tin and germanium were found to modify the properties of these catalysts mainly via a geometric effect. However, formation of bulk Pt-Sn and Pt-Ge alloys contributed to the overall rate of deactivation of these systems. The alloy particles formed in these systems were analyzed using transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). In the case of Pt-Ir and Pt-Re, metallic rhenium and iridium provided sites for the hydrogenolysis of coke deposits resulting in improved

resistance to deactivation [88]. According to the earlier work [32], 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 coke.

For the bimetallic system Pt-Sn, it has been much studied as a catalyst for reforming or dehydrogenation reactions. Several suggestions have been made to explain the effect of tin as a promoter [26, 29, 89-98]. Increased dispersion due to tin acting as a spacer or formation of ensembles of a favorable size was examples of explanations based on geometric effect [14]. It has also been suggested that tin leads to increased mobility of adsorbed hydrogen or poisons acidic sites on the alumina support [14, 26, 92]. Much recent work has been focused on the state of tin in these catalysts, particularly on the oxidation state of tin and the possibility of alloy formation after reduction. Mössbauer studies led to the identification of Pt-Sn alloys,  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$  [99, 100]. In summary of previous studies, it is again emphasized that on the basis of temperature-programmed reduction, tin remained in the Sn (II) state [101]. Moreover, it was reported that a Pt-Sn alloy was formed at high metal loadings but that their data were consistent with the presence of Sn (II) at low Pt loadings [102]. An ESCA sample holder was designed to establish the state of Sn and Pt in a reduced catalyst [103]. A general picture is that alloying is important on  $\text{SiO}_2$  and other supports with less interaction, whereas on  $\text{Al}_2\text{O}_3$  tin is stabilized in the +2 oxidation state [26]. However, some studies indicated the possibility of alloy formation also on  $\text{Al}_2\text{O}_3$  supports, particularly with high Sn loading. Bimetallic PtSn particles with tin as  $\text{Sn}^0$  was reported on  $\text{Al}_2\text{O}_3$  after specialized preparation routines. It was suggested that repeated coking regeneration cycles led to increased alloying and consequently to a reduced activity in dehydrogenation. The change in catalytic stability on both supports was paralleled by a dramatic change in the hydrogen adsorption properties, as seen from the TPD profiles after reduction [26, 93, 97, 104].

Along similar lines, alkali metal ions, e.g. potassium, were incorporated in several catalysts (e.g. Ni-based steam reforming catalysts, etc.) [31, 105-109]. Potassium had several effects; it neutralized acid sites which would catalyze coke deposition via the carbonium ion mechanism previously mentioned, and catalyzed the gasification of the adsorbed carbon deposits, thus providing an *in situ* route for

catalyst regeneration [105, 109]. The addition of potassium to Pt/SiO<sub>2</sub> and Pt/Sn/Al<sub>2</sub>O<sub>3</sub> also reduced the size of the surface platinum ensembles [110-112]. However, potassium increased the saturation extent of hydrogen adsorption and decreases the extent of carbon monoxide adsorption on Pt/SiO<sub>2</sub> and Pt/Sn/SiO<sub>2</sub>. The dehydrogenation rate increased upon addition of potassium to Pt/Sn/SiO<sub>2</sub> due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane. The increased dehydrogenation activity may also be due to the stabilization by potassium of molecularly adsorbed isobutane [109]. In addition, The diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) was employed to study the state of CO on the surface of these catalysts in published elsewhere [113]. Shifts and changes in the spectra obtained by infrared spectroscopy of adsorbed CO have been previously used in an argument to explain the electronic nature of any promotion mechanism. Along the way, several authors [114] said that the nature of the coke formed on Y zeolites with different rare earth content during the cracking of tridopropylbenzene was studied. Increasing rare earth contents decreases both total and insoluble coke build-up.

### **2.1.2 Coking in specific catalytic processes**

The effect of coke deposition on the methanol to gasoline process using a HZSM5 catalyst was investigated by both experimental and modeling studies. Fixed and fluidized bed reactor performance under coking conditions was compared [115]. The paper cited in the literature [116] considered the combined effect of poisoning and coking using the cracking of cumene as a model reaction. An important conclusion resulting from this work was that some characterization of the number of coke entities could be established per active site. Furthermore, the effect of coking on the deactivation of spinel type nickel catalysts used for acetylene dehydrogenation has been considered [117]. Interesting effects were obtained by modification of the catalyst by ZnO and H<sub>2</sub>S pretreatment of the catalyst and addition of this to the feed. Changes in coke morphology occurred with H<sub>2</sub> addition while the sensitivity of the catalyst toward deactivation results from promotion action in the catalyst. The industrially important hydrotreating operation in the presence of nitrogen compounds has been studied as shown in the review [118]. Perhaps, it was found that the

presence of these compounds facilitates coke formation, yet for the same level of coke the nitrogen containing coked catalysts gave less deactivation than normal coked catalysts. This was due to strong adsorption of nitrogen compounds on non-active catalyst sites. Additionally, coke formation in the thermal cracking of hydrocarbons was studied in a pilot plant unit. A mathematical model describing the coke formation has been derived [36, 52, 53, 119, 120]. On a series of HY zeolites, the formation of coke from propene was investigated at 450°C [71]. The first mode occurs mainly for coke molecules trapped in supercages close to the outer surface of the zeolite crystallites or close to mesopores; the resulting highly polyaromatic molecules overflow onto the outer surface or into the mesopores. The second mode consists of coupling of coke or coke precursor molecules trapped in adjacent supercages.

Catalyst deactivation by coke formation can occur through a more or less reversible mechanism. In the literature [121], they have applied a transient approach to model the reversible behavior of the deactivation, and to separate the deactivation from the main reaction kinetics. The microriser was a laboratory-scale entrained flow reactor that can be operated in an ideal plug-flow regime when the gas velocity was high enough. The reactor can be used to study the kinetics of catalytic cracking and the coke deposition, even at a very short timescale, since the length of the reactor can be easily varied [122]. In some aspects on bimetallic Pt-Re/Al<sub>2</sub>O<sub>3</sub>-Cl reforming catalysts, the decrease in carbon deposition with increasing chlorine content could be explained by the preferential enhancement of reaction paths that do not allow the formation of some coke precursors [123]. In the aromatization of light hydrocarbons, hybrid catalysts containing Zn or Ga supported co-catalysts showed much better performance and on-stream stability than the parent ZSM-5 zeolite. It was observed that coke species formed were “light” coke having a paraffinic nature, in contrast with the more aromatic “heavy” coke produced by the parent zeolite [72]. The growth of carbon filaments was observed on the surface of high-temperature Pt/Al<sub>2</sub>O<sub>3</sub> catalysts used for the synthesis of hydrogen cyanide as well as, surprisingly, low temperature Pd/SiO<sub>2</sub> catalysts used in the vinyl chloride process if enhanced concentrations of Fe were present.

### 2.1.3 Characterization of coke deposits

Various analytical techniques have been used in order to characterize the nature, amount and distribution of coke deposits [37, 38]. The chemical identity of the carbonaceous deposits has been extensively investigated by IR. The aromatic band at  $1610\text{ cm}^{-1}$  in the IR spectrum indicates that the coke was highly aromatic in character. Supporting evidence was again provided by IR spectroscopy where a weak band at  $3080\text{ cm}^{-1}$  indicative of the C-H stretch of aromatics was observed with no evidence of paraffinic species [41, 124, 125]. The combination of CO adsorption experiments within a wide pressure range with CO desorption measurements at room temperature and elevated temperature provides valuable information on the location of Pt particles in KL zeolite and their electronic structure. A minor part of the particles locates on the outer surface of the zeolite microcrystals and in the near surface region. CO adsorption on these particles resulted in the appearance of a CO band at  $2050\text{ -}2020\text{ cm}^{-1}$ . The major part of the Pt metal clusters was engaged in the zeolite structure as very fine particles. The interaction of CO with these clusters was strongly perturbed by the zeolite matrix, which leads to the prominent shift of the adsorbed CO band down to  $1960\text{ -}1920\text{ cm}^{-1}$ . The development of the relative intensities of the bands in the spectra can be explained by the kinetics of the adsorption on the particles located within the zeolite channels [126-128].

Details of the proximity of coke to metal additives or the support and the nature of coke are often inferred from the shape of resultant TPO spectra. Therefore, for a complete interpretation of TPO spectra a fundamental understanding of the kinetics of coke combustion was required. Mechanisms of coke combustion were uncertain, although some investigations have been reported. In early work intracrystalline diffusion processes, under certain conditions, were shown to affect combustion rates [13, 20, 22, 48]. TPO experiments in earlier publication [129] have established that coke reaction order changes with catalyst morphology and that gasification of coke deposits with an inert gas yields carbon oxides - a consequence of reaction of coke with support surface hydroxyl groups. Several groups [13, 130] have also shown that hydrogen-rich coke is highly reactive. Coke was composed of two main types of carbonaceous deposits. Another researcher provided three types of

coke; 1) on the metal sites but does not completely cover the sites, 2) on metal sites and completely cover the sites and 3) on support [73, 131, 132]. For the more hydrogenated fraction located on the metal, activation energy for oxidation of 8.9 and 10.4 kcal.mol<sup>-1</sup> using slopes and Borchardt-Daniels methods was determined [13]. Regarding the more polymerized fraction located on the support, activation energy using slopes, Borchardt-Daniels and inflection methods was found to be 24.2-26.2 kcal mol<sup>-1</sup>. When the catalyst has been previously hydrogenated, a considerable decrease in the activation energy is noticed, thus a value of 3.2 kcal mol<sup>-1</sup> was obtained. This decrease is due to the favorable effect of the hydrogen adsorbed on the metal which plays an important role as igniter of the combustion. Optimized activation energies allow a comparison of soft and hard coke combustion reactivity. Measured temperature dependent H/C ratios indicate that low hydrogen content (hard) coke, forms from adsorbed hydrocarbon molecules (soft coke) via dehydration or dehydrogenation [48]. Soxhelt extraction of spent catalyst has been used with organic solvent. The soluble components of coke extracted were analyzed by GC/MS. Many compositions were proposed [47, 49, 50, 133].

However, there is still a lack of detailed mechanistic knowledge on coke formation, largely due to the problems associated with the structural characterization of the insoluble organic matter present in relatively low concentrations on hydrocarbon conversion catalysts. In principle, of all the spectroscopic techniques (FTIR, mass spectrometry, etc.) available to probe the organic structure of catalytic coke deposits that are insoluble in common organic solvent, solid-state <sup>13</sup>C-NMR has the unique ability to directly determine the distribution of aromatic, aliphatic and other carbon types present [19, 44, 134-138]. Such investigations had the advantage of being advantage able to identify intermediate species involved in the formation of insoluble coke. As reported in the previous work [134], they investigated cokes produced by FCC catalysts from industrial units and from laboratory studies. The resultant coke composition although mainly aromatic reflected the properties of the feed employed. Coke formation was investigated on zeolite USHY with 1-hexene as the feed in the literature [19]. They found that the irreversibly adsorbed surface species comprised both aromatic and aliphatic species at the lower reaction

temperature [135]. The  $^{13}\text{C}$ -NMR spectra of the adsorbed species indicated the presence of alkyl, allyl and aromatic carbons, together with allyl and alkyl carbocations [136-138]. The characterization of coke formed from cracking propylbenzene at 200°C and 280°C on USY and ZSM-5 zeolites. The  $^{129}\text{Xe}$ -NMR spectra indicated that the coke had formed within the supercages and the CP  $^{13}\text{C}$ -NMR spectra showed that the coke was highly aromatic [116]. As discussed in previous literature [44], they showed that initially the coke deposit was made up of  $\text{C}_1$  fragments, which aged to form polycyclic aromatics. Studying the adsorbed species derived from ethylene on supported Pt catalysts, the study indicated that  $\pi$ -adsorbed ethylene was the predominant species on the Pt catalyst at room temperature. Transformation of the adsorbed ethylene on Pt surfaces has been observed to occur by 513 K with formation of aromatic species and saturated carbon species. At higher temperatures, more coke precursors and coke in the form of strongly adsorbed polyaromatic species were formed along with light hydrocarbons such as methane and ethane as the reaction products. The coke deposited on surfaces of a platinum catalyst after that treatment at 673 K has been characterized as polyaromatics with an overall chemical formula of  $\text{C}_{2n}\text{H}_n$  ( $n \approx 12$ ) [44].

The nature of the coke was also studied by X-ray diffraction. As outlined in the literatures. [17, 39], it was shown that existence of inter-layer structures separated by 3.46 Å and 3.44 Å in the samples coked in the plant and the laboratory, respectively. Selected features of the  $\text{C}1\text{s}$  XPS signals turned out to be suitable to characterize the graphiticity of the products of coke formation at a high temperature [139]. Secondary-ion mass spectrometry (SIMS) fragment ion ratios were utilized as rough qualitative probes for the microstructural properties of coke in comparison with well-defined grades of carbon. Filamentous carbon deposits were still an interesting phenomenon and their structure has been studied in the literature cited therein [38], using TPO of demineralised samples and SEM. Addition of hydrogen changed the structure of the filaments giving rise to different orientation of the graphitic platelets in the filaments [140]. Moreover, in the published earlier [42], they have studied the location and structure of carbonaceous deposits on  $\text{Pt}/\text{Al}_2\text{O}_3$  coked catalyst. They found patches of amorphous coke covering the support surrounding each metal



particle and the coke coverage could extend as far as 20 nm from a given particle. When compared electron energy loss spectroscopy (EELS) peak of deposited carbonaceous with the reference they could conclude that the local structure of coke was not graphitic or pregraphitic but may consist in a disordered arrangement of polyaromatic molecules. Coke deposits may not be uniformly distributed in the catalyst pellets, and attempts were made to measure the coke concentration profiles by several techniques, including controlled combustion, electron microscopy,  $^1\text{H}$ - and  $^{129}\text{Xe}$ -NMR, XPS, AES [141].

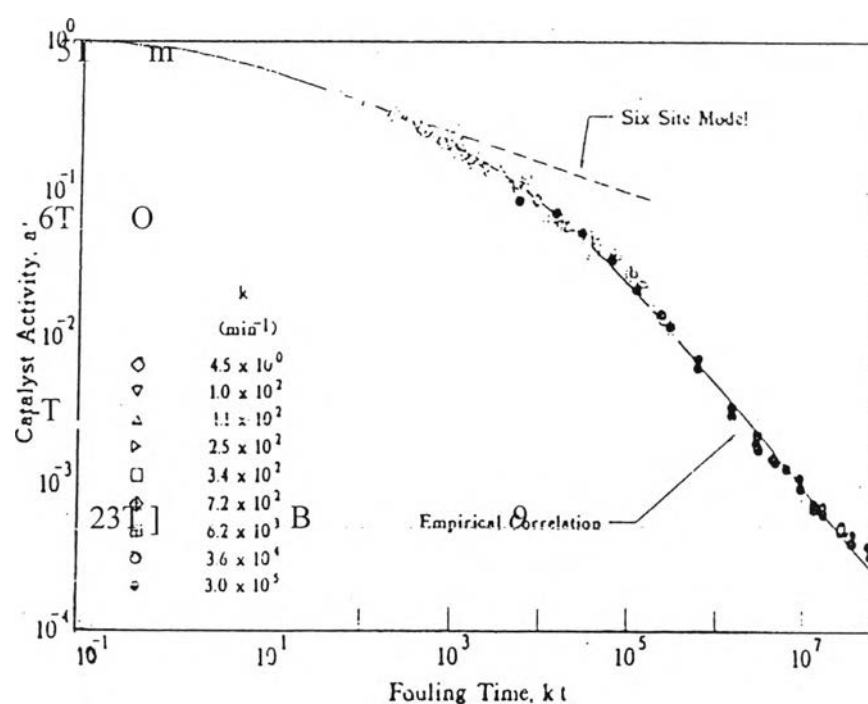
#### **2.1.4 Modelling of coke formation and catalyst deactivation**

The catalytic reforming of naphtha and the hydrocracking of heavy oil fractions were based on dual-function catalysts. These contained a metal component (Pt, Pt/Re, Pt/Sn in reforming, Pt, Pd, Ni/Mo in hydrocracking) and acidic component, (alumina in reforming, alumina or zeolite Y in hydrocracking). Dehydrogenation occurred on the metal component, while isomerizations and cracking occurred on the acid component. In dual-function catalysis species formed on one type of site have to move to the other before the next step of the reaction sequence can take place. The sites were covered by coke produced by side reactions [142-145] as the rate of reaction decreases. Mechanisms of carbon deposition on metal catalysts have been detailed in several reviews [5, 6, 16, 25, 54, 58, 146-151]. The formation of such species depended on the operating conditions, catalyst formulation, etc. Recently, a probabilistic model was developed for deactivation of a dual function catalyst by coke formation accounting for reaction and surface migration [6].

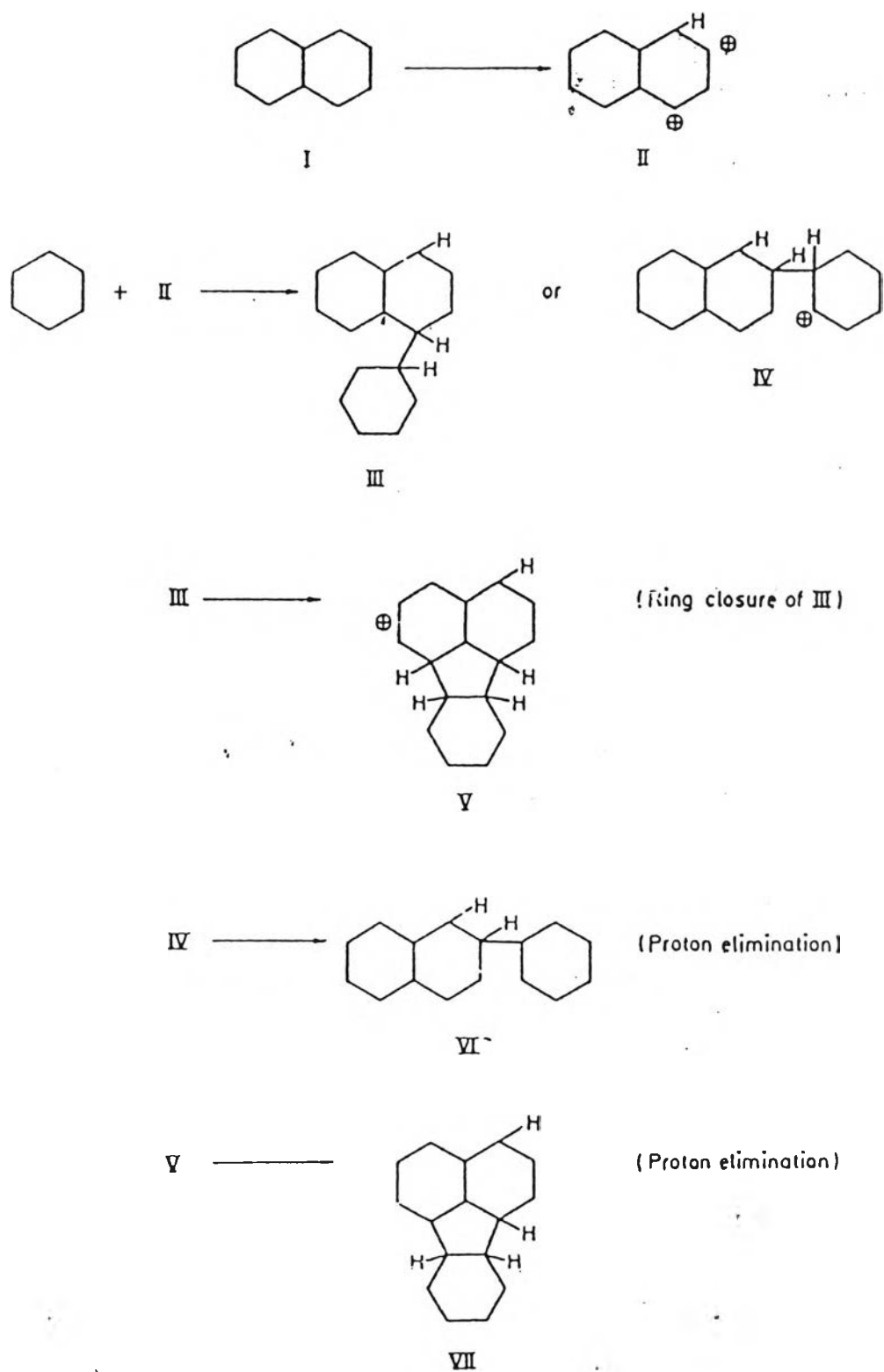
Gas phase coke forming reactions were free radical polymerization processes, and can be minimized by the introduction of a free radical trap. As described above, freshly deposited coke was not inert and growth was possible through polymerization or polycondensation [2, 152]. It has been shown that coke can easily reach a size sufficient to block mesopores. A single-ended pore became blocked all the sites located behind the blockage become inaccessible, so that a non linear relation was obtained between the deactivation function and the fractional site coverage, even for single site reactions. To deal with site coverage and pore blockage, a probabilistic

approach was developed, since there was no preferential location of the coverage of a site and the subsequent blockage of the pore outlined in the reviews [9, 18]. Furthermore, several studies [5] first investigated the case of instantaneous growth of coke. This arises when the rate determining step in the sequence: site coverage, growth and blockage occurs as soon as a site was covered. All the coke had the same size, determined by the operating conditions and the pore diameter.

Additionally, an explanation of the decreasing slope of the deactivation curves derives directly from the interpretation of the slopes, that was, the number of sites involved in the deactivation process decreases with progressive deactivation. The deactivation process was envisioned as several reactions in parallel as shown in Fig.2.1 The precursor could become foulant by six-, five-, four-, three- and two-site mechanisms in parallel. To have an early, larger slope of  $-0.2$ , the six-site mechanism must be the fastest and then, as the deactivation proceeded, the other reactants-the three- and two-site mechanisms-prevail when surface coverage of the catalyst made six contiguous sites unlikely [130].



**Figure 2.1** Dimensionless fouling correlation [130]



**Figure 2.2** Carbonium ion mechanism for formation of higher aromatics from benzene and naphthalene [9]

Consequently, the mechanisms for carbon formation from carbon monoxide over Ni catalysts have been reviewed in [130]. In the case of the steam reforming of hydrocarbons on Ni-based catalysts, three different kinds of carbon or coke species were observed. Encapsulated like hydrocarbons was formed by slow polymerization of  $C_nH_m$  on Ni surface at temperatures lower than  $500^\circ\text{C}$ , filamentous or whisker-like carbon was produced by diffusion of C into Ni crystals, detachment of Ni from the support and growth of whiskers with Ni on top and pyrolytic-type carbon was obtained by cracking of  $C_nH_m$  species at temperatures above  $600^\circ\text{C}$ . The mechanism of coke formation on oxides and sulfides was rather complex but it could be roughly visualized as a kind of condensation-polymerization on the surface resulting in macromolecules having an empirical formula approaching  $CH_x$ , in which x may vary between 0.5 and 1 [9]. It has been suggested that the pathway to coke, starting from olefins or aromatics, may involve: (a) dehydrogenation to olefins; (b) olefin polymerization, (c) olefin cyclization to form substituted benzenes, and (d) formation of polynuclear aromatics from benzene. These mechanisms proceed via carbonium ions intermediates and accordingly they were catalyzed by Brønsted acid sites. The details of coke-forming reactions varied with the constituents of the reaction mixture, the operating conditions, and the catalyst used, but one could speculate that the reactive intermediates combined, rearranged and dehydrogenated into coke-type structures via carbonium ions-type reactions, as shown in Fig.2.2. Carbonium ions can also crack to form small fragment that can further participate in the coke-forming process as hydrogen transfer agents.

## 2.2 Theory of coke deposition

Coke is a term used to describe generally the carbonaceous materials which are formed and deposited on the surface of catalysts during catalytic reactions mainly of hydrocarbons. There is a wide range of different types of compounds lumped under the name “coke”. According to the review [130], it is a mixture of mono- and polycyclic aromatic rings connected by aliphatic and alicyclic fragments. The coke composition changes depending on the reactants, catalysts, reaction conditions, and reaction time.

## 2.2.1 The various factors on coking process

### 2.2.1.1 Influence of the operating conditions

Operating conditions have an extremely important influence on the deactivation of reforming catalyst [17, 153]. They are summarized as follows.

#### 1. Pressure

The reforming reaction as well as dehydrogenation is preferred to work at low pressure. At this condition, it is easy for coke to deposit on the catalyst. Thus, the study of coke in laboratory usually accelerates coking by decreasing reaction pressure for obtaining more coke on the catalyst. However, alternation of pressure has the effect to the location and nature of coke. Increasing of pressure induces decreasing of coke on metal sites but increase coke on acidic support. Therefore, it changes the nature of coke deposited on the catalyst to be more dehydrogenated and be more graphitic coke or decrease H/C ratio of coke on the catalyst. Figure 2.3 showed the effect of pressure on the nature of coke.

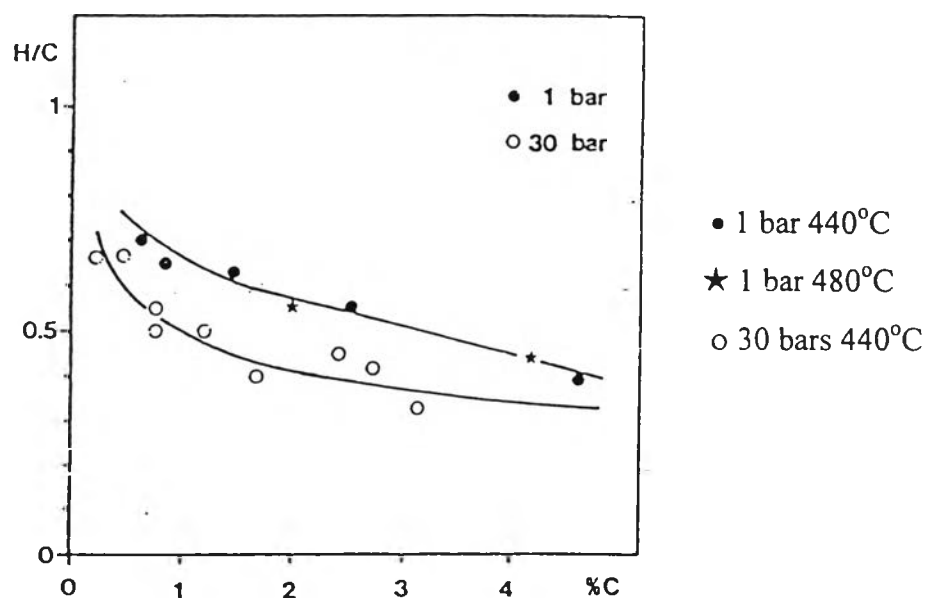


Figure 2.3 Effect of coking pressure on the hydrogen content of coke deposits [4]

Furthermore, it is interesting to note that a decrease in pressure not only promotes aging but also modifies the reaction rate. At low pressure, there are many highly unsaturated species on the surface of the catalyst, which are precursors of coke, whereas at high pressure there is less mobile coke but fewer of the intermediates that are needed for the reaction.

## 2. Nature of hydrocarbons

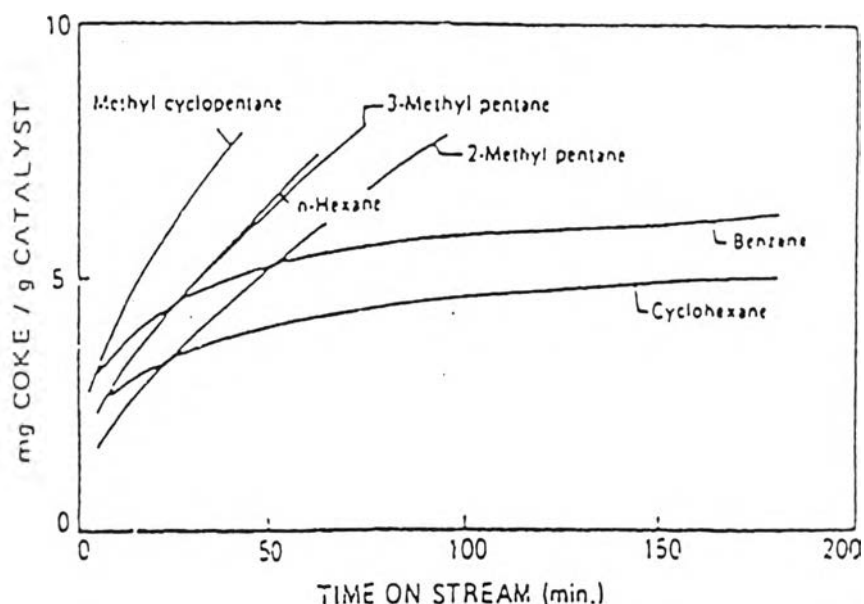
Several studies [154] noted that the coke evolution on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for a number of different hydrocarbons, each having 6 carbon atoms. The initial deposition is on the metal site while that at latter times is on the alumina. It is obvious from Figure 2.4 that the rate of coke decreases in the following order for both metal and alumina sites:

Methylcyclopentane > 3-methylpentane > N-hexane >  
2-methylpentane > benzene > cyclohexane

In addition, many properties also affect coking rate thus feed factor ( $F_f$ ) is suggested in Table 2.1 [155].

**Table 2.1** Feed factor on the relative coking rates under reforming condition of several pure hydrocarbon on alumina and used n-heptane as standard [155]

Hydrocarbon	$F_f$
n-heptane	1.0
toluene	1.5
n-Nonane	2.0
Cyclohexane	7.0
2-Me-Pentane	7.5
Me-Cyclopentane	43
1-Hexane	90
Cyclohexane	540



**Figure 2.4** The deposition of coke on Pt/Al<sub>2</sub>O<sub>3</sub> from various hydrocarbons; T= 500°C [154]

### 3. Temperature

Temperature is the only possible operating variable for activity maintenance in an industrial unit. Figure 2.5 shows the influence of temperature on the amount of coke containing in a bimetallic catalyst.

### 4. H<sub>2</sub>/HC ratio

In industrial process of dehydrogenation, hydrogen is added to feed stream to decrease coking on the catalyst. Hydrogen acts through a hydrogenolytic or by an inhibiting effect on the formation of highly dehydrogenated polymers. The coke cleaning mechanism is due to reaction with dissociated hydrogen as shown in Figure 2.6.

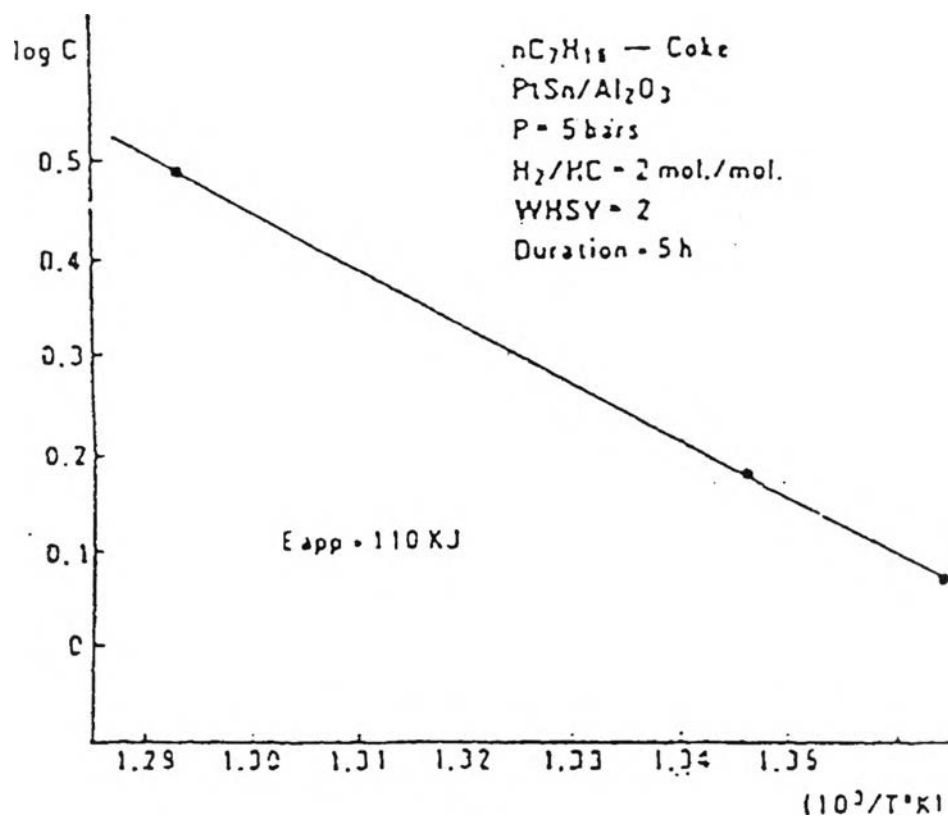


Figure 2.5 Influence of temperature on the rate of coke deposition [17]

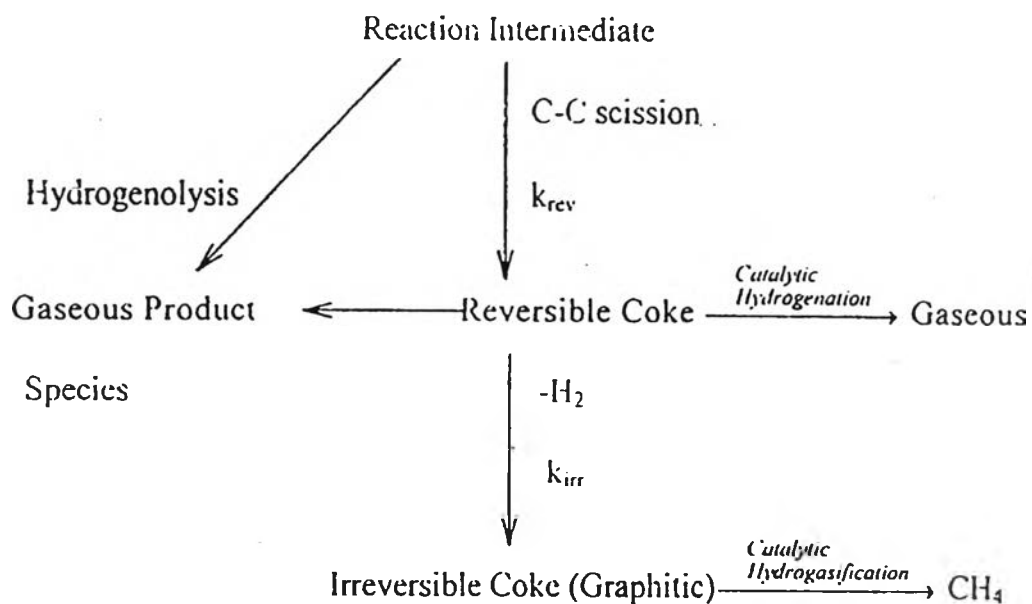


Figure 2.6 Mechanism of coking and hydrogen cleaning of a Pt crystallite [3]



### 2.2.1.2. Influence of the nature of the catalyst

#### 1. Dispersion

The small crystallite sites are very active in alkane hydrogenolysis, probably due to the lower self-poisoning of these crystallites. The multiple metal-carbon bond formation is necessary for carbon formation on metal crystallites and there is more likely in 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 its surface more attractive for multiple metal-carbon bond formation also.

Large metal crystallites also favor 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 C<sub>5</sub> ring coke precursors [1].

#### 2. Chloride Content

Chloride has an important effect of both the initial dispersion of the platinum and the maintenance of its dispersion [17, 123]. 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, and excess leads to excessive hydrocracking and coking activity. As stated in the earlier work [156], 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.

### 3. Composition of a metallic phase

The most remarkable progress made in improving reforming catalyst is the use of platinum with metal additives commonly called promoters. Figure 2.7 shows the evolution of coke on a number of alumina-supported bimetallic catalysts. The additives used can be grouped into the two types as follows: [4]

(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.

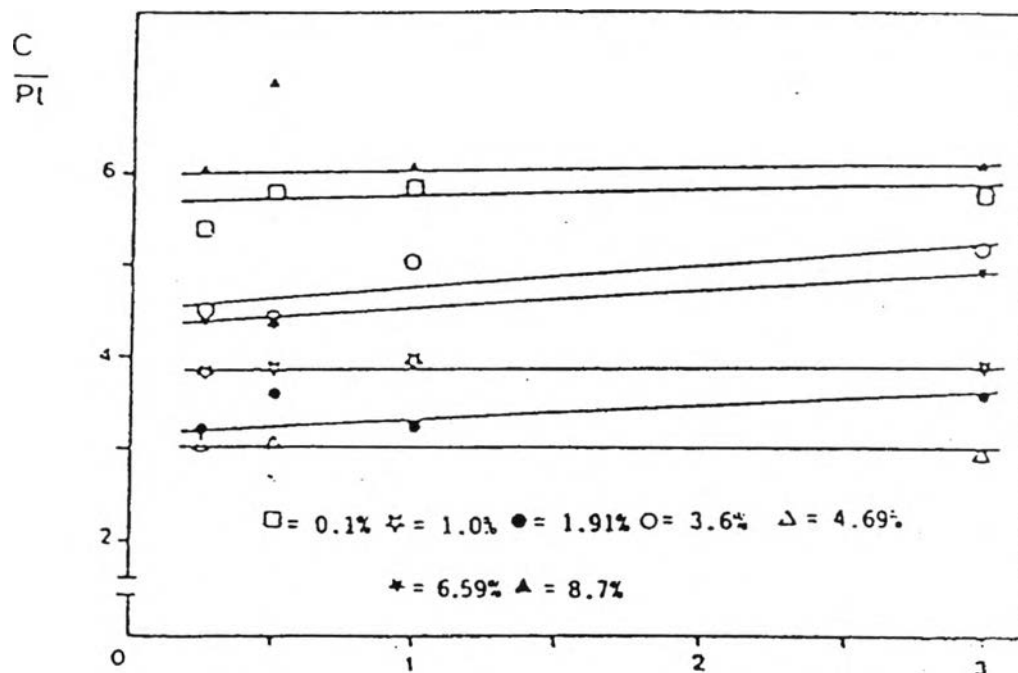
Even though the overall depositions are higher than Pt/Al<sub>2</sub>O<sub>3</sub> for the second type of additives, the deactivation rate is less than Pt/Al<sub>2</sub>O<sub>3</sub>.

### 4. Influence of the nature of the support

The nature of the support plays a large part in the rate of coking-reactions of supported metallic catalysts. Table 2.2 gives the amounts of coke accumulated on different platinum catalysts with comparable metallic dispersions but supported on various oxides. The amount of carbon deposited during the reaction of cyclopentane is more important as the acidity of the support is higher.

**Table 2.2** Influence of the nature of the support on the coking reaction of various Pt catalysts by cyclopentane [4]

Catalyst	Pt/Al <sub>2</sub> O <sub>3</sub>	Pt/SiO <sub>2</sub>	Pt/TiO <sub>2</sub>	Pt/MgO
Amount of C%	2.28	0.09	1.56	0.083



**Figure 2.7** Effect of the time on stream on the coke coverage of the metallic phase for different Pt/Al<sub>2</sub>O<sub>3</sub> catalysts at different metal dispersions [4]

### 2.2.2 Characterization of carbonaceous deposition

Characterization of coke on catalyst provides useful information on the nature of the coking processes. Structure and distribution of coke information on chemical structure of the coke can be characterized by advancements in analytical techniques. A possible approach to the study of an exhausted catalyst follows the following steps;

- (i) **Quantitative determination of organic deposits and their identification;**  
TPO, IR, ESR

The quantitative analysis of the organic material deposited on an exhausted catalyst can be performed by TPO. Analyzing the results, it must be considered that peaks are representative of several kinetic phenomena happening on solids to determine local characteristics. Particular attention must be paid to discriminate among irreversibly adsorbed materials and easily removable materials remained on the catalyst [20,22,129,156,157].

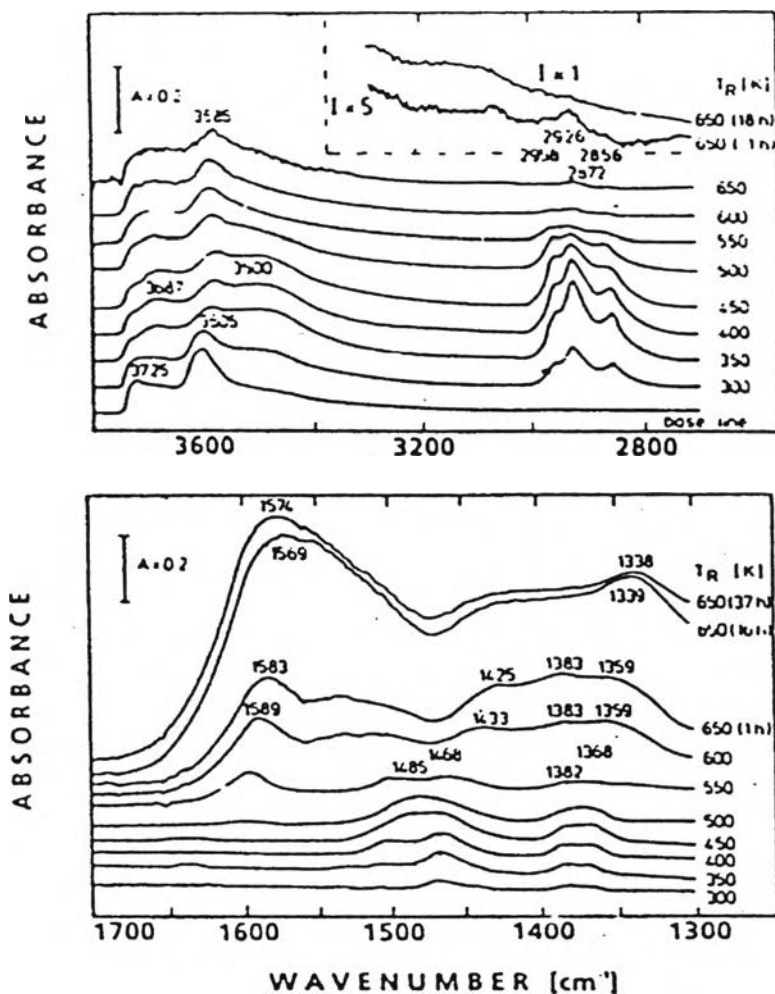


Figure 2.8 IR spectra of carbonaceous deposits [158]

IR studies give information concerning the chemical identity of the coke components such as olefinic, saturated or aromatic, the amount of coke through the intensity of the so-called coke band [49, 157, 158]. A set of spectra obtained during coke deposition is displayed in Figure 2.8. The absorbance of typical coke bands is at 1610, 1540 and 1490  $\text{cm}^{-1}$ . The band at 1610  $\text{cm}^{-1}$  is the so-called coke band. According to earlier investigations it originated from  $\delta(\text{C-H})$ -modes of a complex mixture of carbonaceous, hydrogen-deficient deposits, inter aromatics. The band around 1540  $\text{cm}^{-1}$  is ascribed to alkyl naphthalene or polyphenylene structures, whereas the one at 1490  $\text{cm}^{-1}$  is indicative of  $\delta_s\text{CH}_2$ ,  $\delta_{as}(\text{CH}_3)$ ,  $=\text{C}+\text{H}$ ,  $-\text{C}+\text{H}_2$  (deformations of primary or secondary carbocations or to CCC stretching of allylic carbocations. In the region of the C-H stretching modes between 2800  $\text{cm}^{-1}$  and

$2900\text{cm}^{-1}$ , the low-temperature coke exhibits pronounced bands which can be associated with  $\text{CH}_2$  and  $\text{CH}_3$  stretching modes [41].

ESR spectroscopic studies of the radicals accompanying the formation of coke allow one to estimate the amount of coke and to obtain information concerning its nature. Olefinic and allylic radicals accompanied the formation of low temperature coke which was mainly composed of olefinic oligomers or polymers while polyaromatic radicals accompanied the formation of high-temperature coke which was mainly aromatic [49, 160].

**(ii) Comparison of the results with those obtained on the fresh catalyst; BET, SEM, TEM, XRD**

Another important useful information is the distribution of the deposit through and along the catalytic particle, especially when its concentration is very high. The morphological characterization is the most suitable technique because it allows to evaluate the variation of the size and volume of the pores compared the fresh catalyst by using  $\text{N}_2$  adsorption at 77 K (BET method) [86, 157].

It is imperative, in this type of approach understand if the morphological modification caused by the organic material deposit from structural modification of the solid. By microscopy, both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are investigated. When the accumulations of carbon on the surface become very large, the carbon can be observed directly by these techniques [139].

The final solid remains crystalline as shown by XRD in Figure 2.9. Curve I shows that the band corresponding to graphite (002) is very intense, whereas the other bands are not so clearly defined. By increasing the counting time (curve II), it has been possible to improve the resolution of bands (101) and (100), bands (102) and (004), as well as band (110). The coke particle measures about 4.5 nm along axis (002), which corresponds to a stacking of about a dozen graphitic planes. In the same

way, following axis (101), a size of about 2.0 nm was found, in other words, when  $d=2.09 \text{ \AA}$ , about 10 planes. These results confirm that this graphitic coke represents only a fraction of the total amount of coke and that its structure depends on the compounds treated during coking.

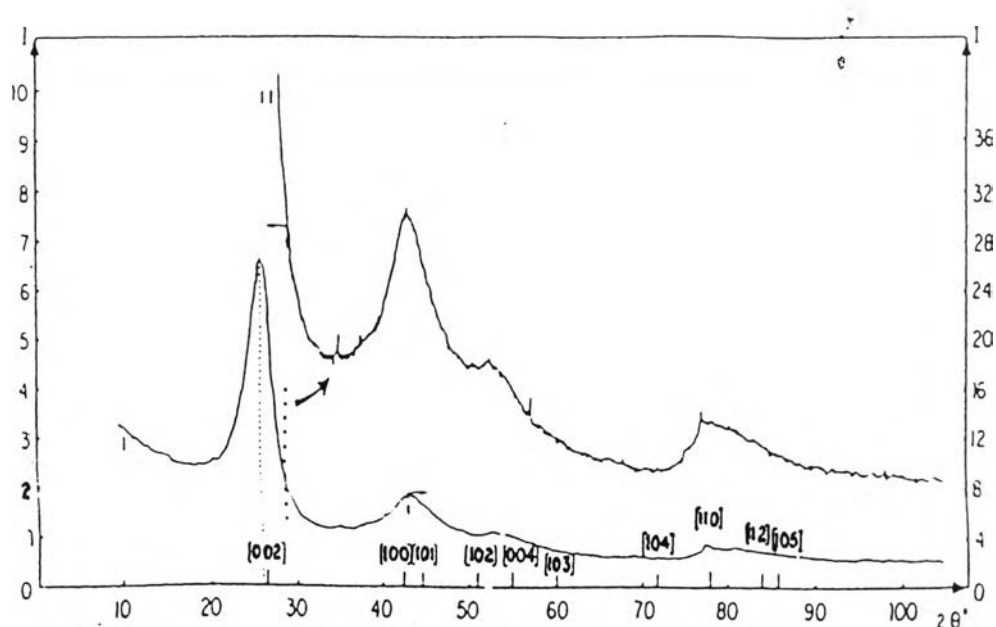


Figure 2.9 X-ray pattern of coke deposit [78]

- (iii) **Removal of deposits from the exhausted catalyst, followed by the determination of the main catalytic properties and comparison of the results with those obtained on the fresh catalyst; GC-MS**

The nature of irreversibly adsorbed or nonvolatile organic materials is, generally speaking, difficult to determine. However, an extraction with a solvent is made to study the solution with the methods of traditional analysis (GC-MS) [9, 161].

## 2.2.3. The Chemistry of Coke Deposition

### 2.2.3.1. Location

Coke may be removed by gasification with oxygen. The temperature programmed combustion of coked catalysts shows two oxidations. The low temperature combustion is due to the presence of coke on the metallic phase. Such a difference can be explained by assuming either that platinum catalyses the oxidation of carbon or that coke deposited on the metal is different than coke deposited on the alumina [4].

### 2.2.3.2. Composition

Measuring the oxygen consumed and the amount of carbon dioxide produced during temperature-programmed combustion indicates that the coke deposited on Pt/Al<sub>2</sub>O<sub>3</sub> corresponds to the formula CH<sub>x</sub> [4,133]. There are two distinct coke types on the platinum surface of a reforming catalyst. Single-crystal studies by a number of surface scientists have verified these coke 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). 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 of polyaromatic compounds with a H/C ratio in the range 0.05-0.1 [1].

### 2.2.3.3. Structure

Extraction of coke with various organic solvents, after dissolving the inorganic matrix, allows a chemical analysis of the extractable compounds. It was found that the extractable coke consists essentially of polyaromatic compounds with a possible branched structure like methyl, ethyl and uncommonly C<sub>3</sub> or more than C<sub>3</sub> groups [4].

The unextractable coke can be analyzed by X-ray diffraction. Table 2.3 shows that such deposits are composed of pseudo-graphitic phases with crystallographic characteristics very close to that of pure graphite.

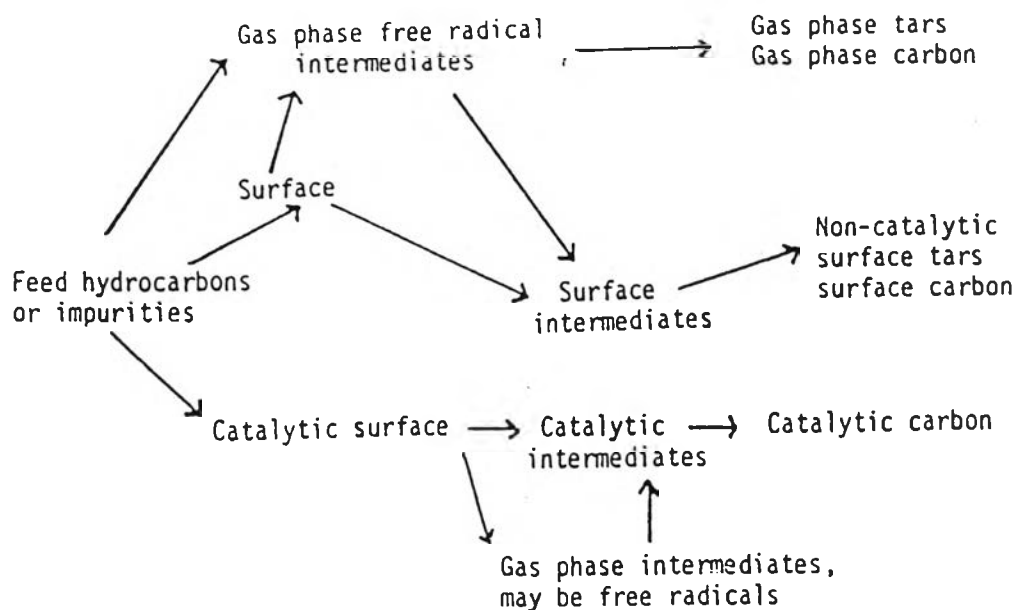
**Table 2.3** Characteristics of unextractable coke [4]

Characteristics of aggregates	coke	graphite
d(Å)	3.45	3.35
Lc(Å) Thickness of aggregates	17	-
La(Å) Diameter of aggregates	100	-
N (mean number of sheets)	6	-

#### 2.2.4. The mechanism of coke formation

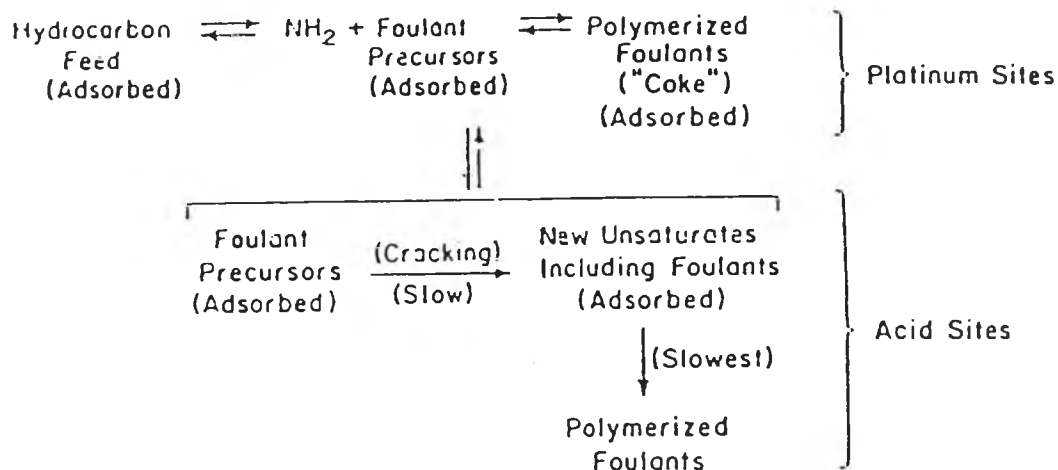
The mechanism of coke formation is complex with multi-step reaction sequences and greatly differs by catalyst-reactant system used. Dehydrogenation, isomerization, polymerization (condensation), hydrogen transfer, cyclization and aromatization are the reactions generally involved. A reaction scheme of coke formation from polycyclic model compounds was proposed by many researchers. Various routes of coke are summarized in Figure 2.10. It is seen that there are three major processes which are interconnected at many points. Gas phase reactions may lead to coke via free radical reactions which, in turn, may be influenced by the physical or chemical nature of the surface. Reactions may also occur on non-catalytic surfaces that lead to coke. Catalytic surfaces influence the nature of the intermediates, and, as a result, the nature of carbon. Gas phase coke forming reactions are free radical polymerization processes. Freshly deposited coke is not inert and growth is possible through polymerization [1, 2, 3, 6, 13, 23, 36, 54].





**Figure 2 10** Routes to coke formation; gasification of cokes or intermediates leading to coke can take pace at any point [2]

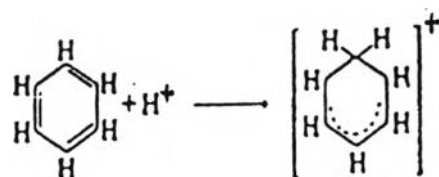
As cited therein the literature [130], they speculated on the mechanism and kinetics of fouling following experiments. Unsaturated reaction intermediates such as monocyclic diolefins are formed first, mainly at the platinum sites. These initial foulant precursors are then reversibly adsorbed on the platinum and can therefore migrate to the acid sites, where they are also reversibly adsorbed. Just how the migration occurs is not clear, but gas-phase transfer is suggested. These precursors can polymerize to form polycyclic compounds having several double bonds per molecule. This latter process is viewed as the rate-limiting step, being slower than the platinum-catalyzed reactions and also slower than the transferring the precursors to the acid sites. The mechanism is consistent with the observation that reactivation can occur in either nitrogen or hydrogen atmospheres and that the rate of reactivation is faster in hydrogen. The model is summarized in Figure 2.11.



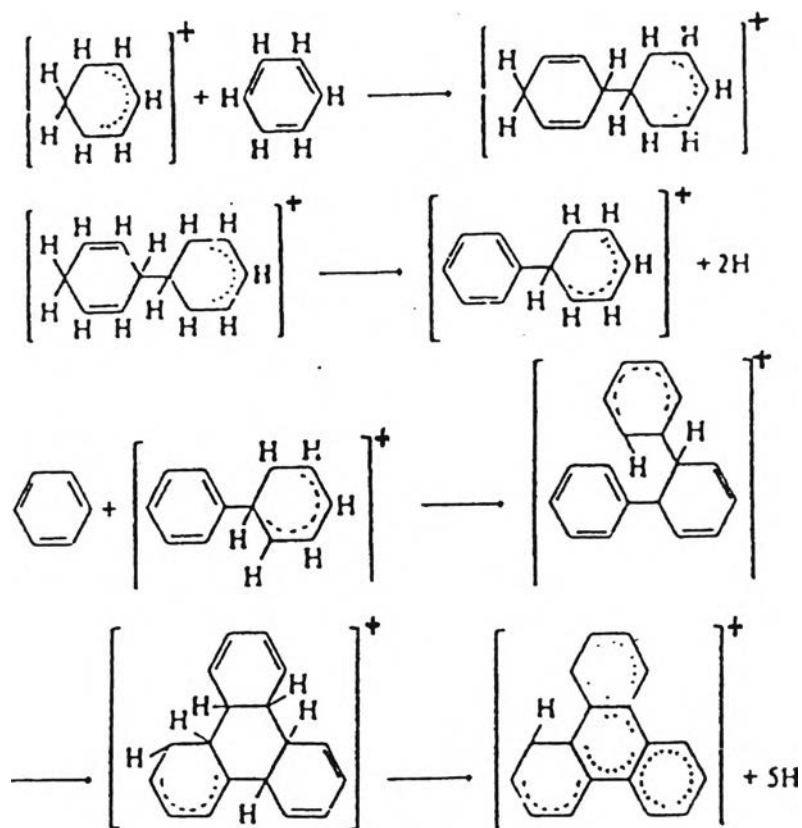
**Figure 2.11** Reversible reaction paths producing unsaturated foulants causing catalyst aging [130].

As stated before, carbonium ion chemistry has been valuable in explaining a number of aspects of coke formation, particularly in catalytic cracking. Because of the high stability of polynuclear carbonium ions, the intermediates can have a relatively long lifetime on the surface. One thus has a situation similar to addition polymerization, in which all propagation rate constants are the same. Presumably one could analyze the kinetics of this sequence using the pseudo-state hypothesis for the chain-growth molecules. The details of coke-forming reactions have been discussed in the literature [130]; simply stated, once aromatics are present they can react to higher hydrocarbons and coke, formed by polymerization. The reaction steps are as follows:

Step 1: initiation:

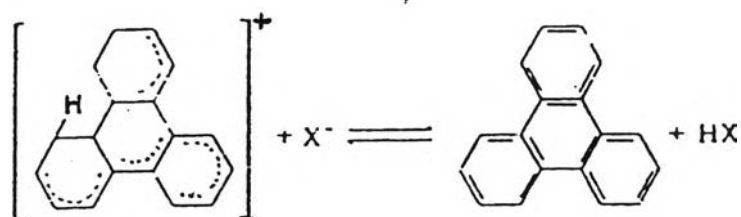


Step 2: propagation:



and so forth.

Step 3: termination



Consequently, coke deposition has been observed in relation to the carbon atom number of coke molecules deal with Schulz-Flory distribution ascribed in the more detailed in the next chapter.