

CHAPTER III

THEORY

To well understand the nature of coke deposited on the catalysts, one needs some backgrounds of deactivation by coking. In this chapter, some basic information of coke concerning is briefly described which will help in understanding the nature of coke form specific reaction an deposition. Three sections are involved: Catalyst deactivation, coking on noble metal catalyst, and composition, structure and localization of carbon deposits.

3.1 Catalyst Deactivation

A catalyst may lose its activation or its selectivity for a wide variety of reasons. The caused may be grouped loosely into [48].

1. Poison
2. Fouling
3. Reduction of active area by sintering or migration
4. Loss of active species

One of these deactivation which was mainly focused on the present work is the deactivation by fouling. The term fouling is generally used to describe a physical blockage such as the deposit of dust of fine powder or carbonaceous deposits (coke). In the latter case activity can usually be restored by removal of the coke by burning.

The deactivation by fouling have been paid attention by many researchers for long times. Hughes[49] has mentioned that the catalyst deactivation by fouling usually involves significant amounts of deposits material. Amount up to 10-20% of the catalyst weight were frequently obtained. Basically, two types of fouling may occur, due to (1) the reaction system itself and (2) deposition by an impurity in the feed stream.

The first is typified by "coke" or carbon deposition on catalysts which occurs under certain conditions when hydrocarbon streams are processed. Since the deposit originates from a cracking type reaction either the feed stream or in the various products, it can not be completely eliminated. On the other hand, the latter is typified by poisoning so that the feed may, in principle, be purified to remove the impurities.

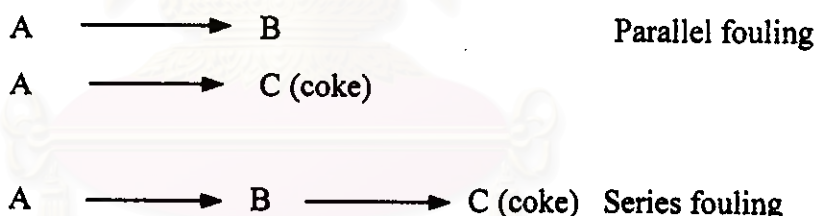
The fouling by coke deposition is always associated with the main reaction. Therefore, it is usually not possible to eliminate the coke deposition totally, but the process of coking can often be substantially reduced by modifying the catalyst so as to improve its selectivity. An example of this is the addition of small amounts of alkali to steam reforming and dehydrogenation catalysts. This reduces the acidity of the catalyst and tends to reduce the craking type reactions that may occur.

Examples of reactions that produce carbonaceous deposits are extremely numerous. Virtually any process having carbon atoms in the feed or product molucules can, under appropriate condition, gives rise to deposition of coke. Naturally, molecules with large numbers of carbon atoms and/or those with aromatic or naphthenic rings tend to produce coke deposits more easily. Both aromatics and olefins are the immediate coke precursors which readily yield coke deposits.

Butt[50] has stated that on the deactivation by fouling the strongly adsorbed carbonaceous deposits could form large polynuclear aromatic structures, apparently through polymerization and condensation. However, coke is not a well-defined substance; normally it has an empirical formula approximating CH , but the chemical

nature depends very much on how it is formed. For example, coke is known to develop in filamentous or whisker-like structures of encapsulating-type structures on metals and in pyrolytic-type structures on acidic surfaces. The coke also varies depending on reaction temperature and pressure. Moreover, these structures change as they age on the catalyst surface. Thus, it is apparent that there are great variations in the morphology of the coke depending on the catalyst and its history. Butt[50] has commented that industrial hydrocarbon feeds are complex mixtures of compounds and the amount and type of coke formed depend on the chemical nature of the feed and products formed. The activity of the catalyst depends on the number of active centers that are available to carry out the main reactions.

Hughes[49] has noted that coking would occur in a reaction either in parallel or consecutive to the main reaction. This coke profile would be descending in the case of a parallel mechanism but ascending for a consecutive (or series) mechanism. The parallel and consecutive reactions for coking can be written as follows:



Thus, parallel fouling gives large coke deposits when the reactant concentration is high, since the reactant is the coke precursor. Therefore, when coking occurs by a parallel mechanism, the greatest deposition of coke would be expected at the inlet of the reactor. Conversely, large coke deposits are formed in series fouling, when product B has a high concentration since this is the immediate precursor of the coke in this case. In normal operation the product concentration increases with distance along the reactor, and therefore the coke distribution should follow a similar pattern.

3.2. Coking on noble metal catalyst

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 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.

3.2.1. Effects of operating conditions on coking deactivation

Operating conditions have an extremely important influence on the deactivation of reforming catalysts. Franck and Martino[51] and Figuli et.al.[15] give excellent summaries as follows:

3.2.1.1. 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 the catalysts are unstable under these conditions because of enhanced coking[52]. Figure 3.1 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 becomes very fast even under 10 bar of hydrogen pressure. It is noted that when H₂/HC ratio is below 10, the effect is extremely important.

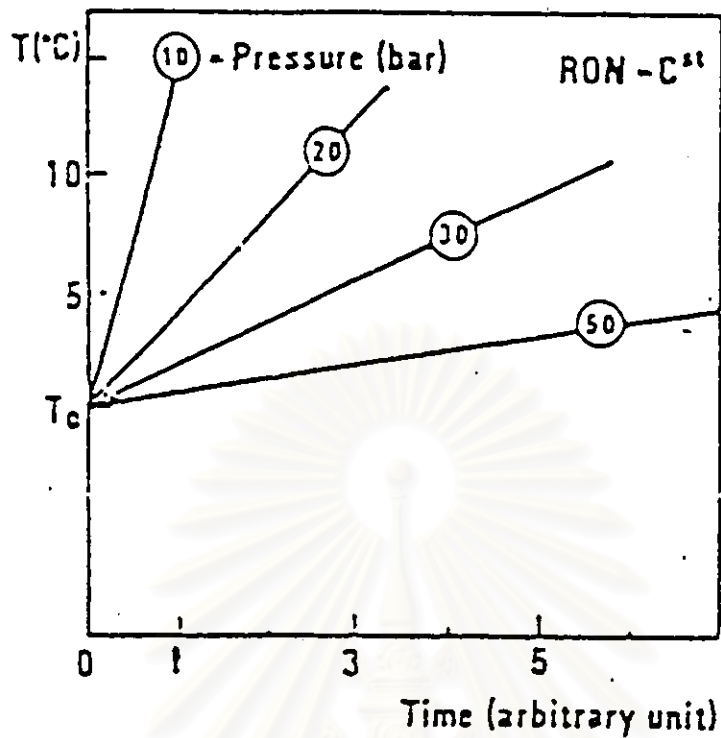


Figure 3.1 Typical influence of pressure on stability [52].

It is interesting to note that a decrease in hydrogen pressure not only promotes 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.

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3.2.1.2. Nature of hydrocarbons

Cooper and Trimm[53] showed that the coke evolution on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst for 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 3.2 that the rate of coke decreases in the following order for both metal an alumina sites:

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

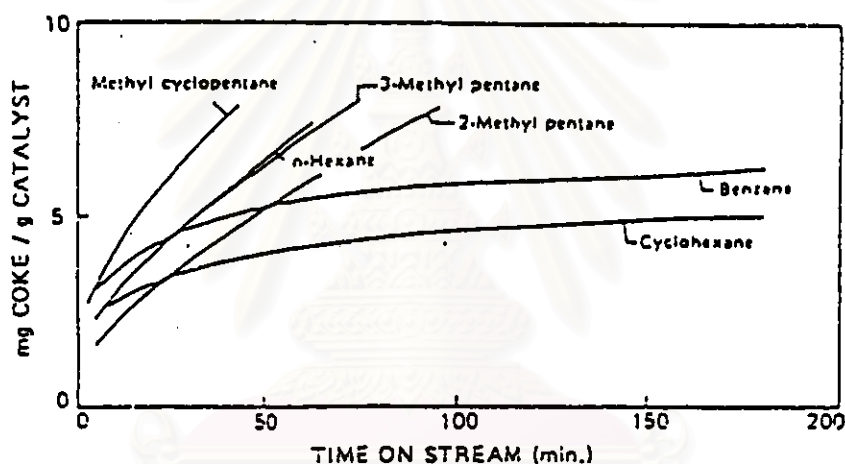


Figure 3.2 The deposition of coke on $\text{Pt}/\text{Al}_2\text{O}_3$ from various hydrocarbons ;
 $T = 500\text{ }^\circ\text{C}$ [53].

3.2.1.3 Temperature

Temperature is the only possible operating variable for activity maintenance in an industrial unit. Figure 3.3 shows the influence of temperature on the amount of coke contained with a bimetallic catalyst.

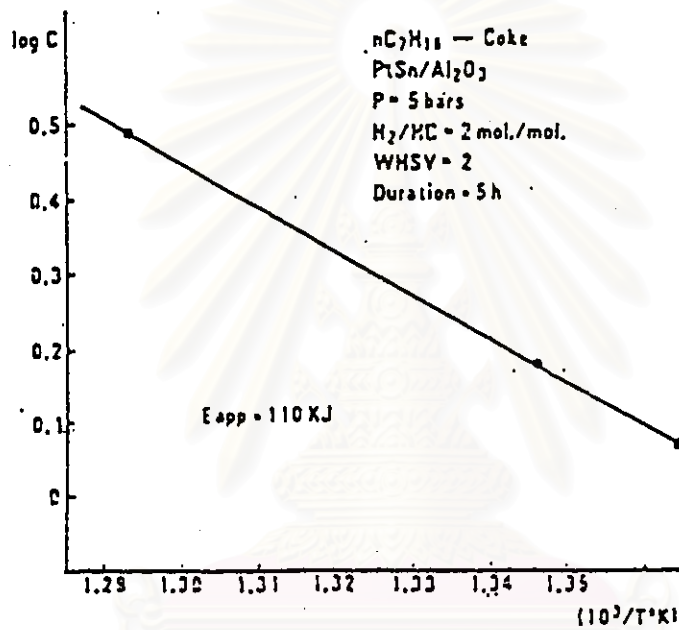


Figure 3.3 Influence of temperature on the rate of coke deposition[51].

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3.2.2. Influence of the catalyst

3.2.2.1 Dispersion

Guenin et.al.[54] 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.[55] 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 its 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[31].

3.2.2.2 Chloride Content

Chlorine has an important effect of both the initial dispersion of the platinum and the maintenance of its dispersion[51]. 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. According to Parera et al.[56-58] 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 [59].

3.2.2.3 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 3.4 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:

(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 the coking rate is at least equivalent, if not higher, than that observed with Pt alone.

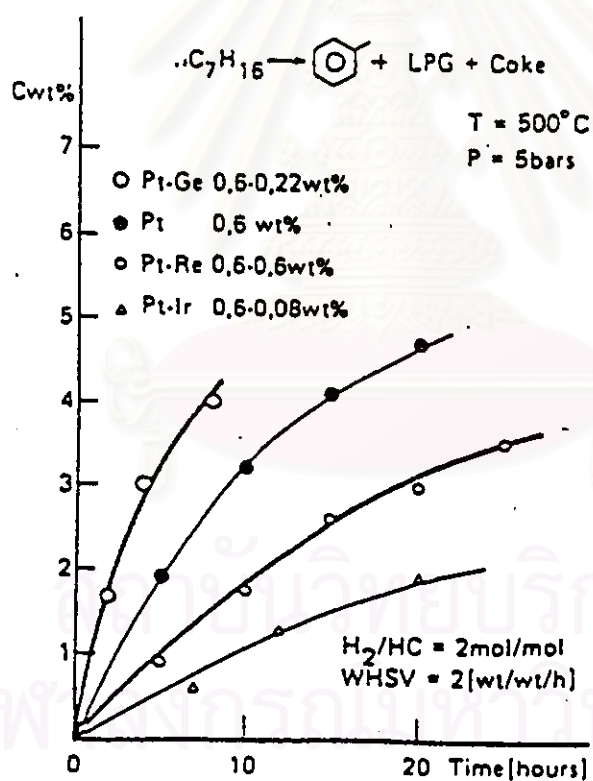


Figure 3.4 Rate of coke deposit for platinum and platinum-promoted catalysts.[51]

Even though the over all depositions are higher than $\text{Pt}/\text{Al}_2\text{O}_3$ for the second type of additives, the deactivation rate is less than $\text{Pt}/\text{Al}_2\text{O}_3$.

3.2.3. Effect of Deposited Coke on Reactions

3.2.3.1. 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. [60] have shown that for low carbon coverage at atmospheric pressure, about 3 carbon atoms are needed to suppress the dehydrogenation activity of 2 platinum atoms. The results in Figure 3.5 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 1 wt % if all the carbon is deposited on the platinum. Unfortunately, with such high carbon amounts, there is no connection between residual activity and the carbon percentage.

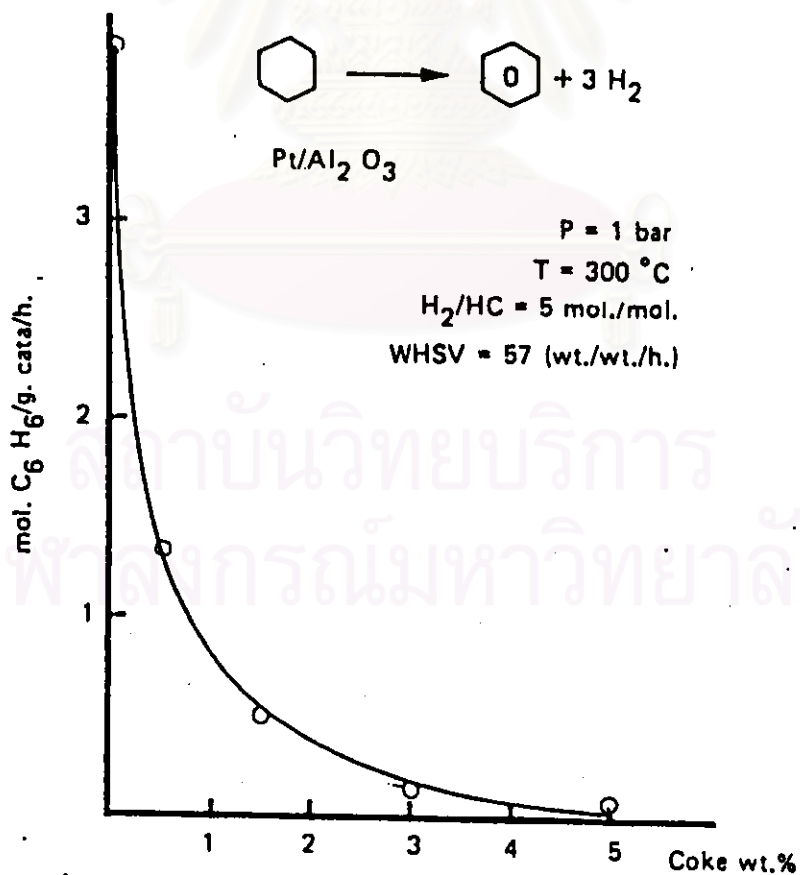


Figure 3.5 Effect of coke on dehydrogenation activity [61].

3.2.3.2. Dehydroisomerization and Isomerization

Transformation of methylcyclopentane into benzene (Fig.3.6) shows a gradual decrease in catalyst activity with coke formed, in the case of a fresh monometallic catalyst. Franck and Martino [68] suggested that the coke was less toxic for this reaction compared to dehydrogenation : this is related to the fact that the rate-limiting step occurs on the acid component, which is less sensitive to coke due to its immense surface area compared to platinum ($200 \text{ m}^2/\text{g}$ compared to $1 \text{ m}^2/\text{g}$ for Pt).

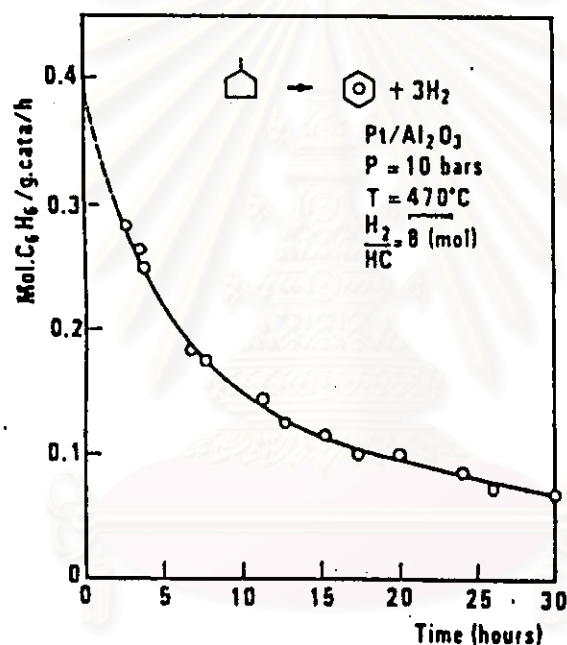


Figure 3.6 Methylcyclopentane dehydroisomerization on fresh catalyst [61].

Figure 3.7 shows the quantity of coke formed and the isoheptane yield under certain experimental conditions. It is noticeable that with 0.6 wt% carbon on the catalyst, the isomers' yield is multiplied by 0.3, whereas it is only halved when the carbon content goes from 0.6 up to 1.2 wt%. Since isomerization has monofunctional (Pt-catalyzed) and bifunctional (rate-limiting step on alumina) mechanisms, the initial deposition of coke on the metal component would explain this behavior, notion that acid site coke is not as toxic.

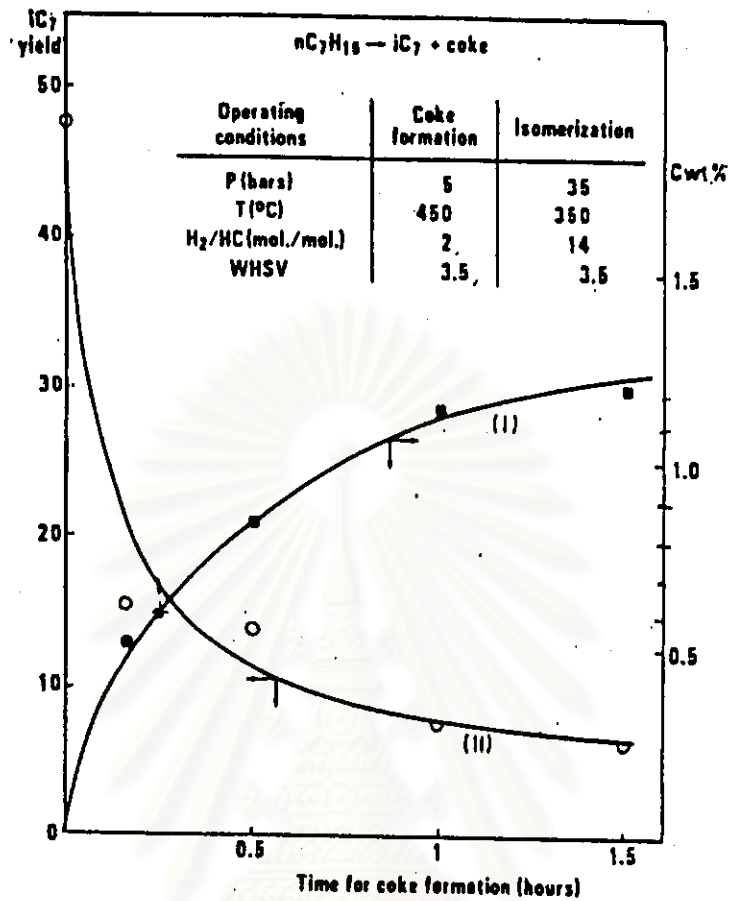


Figure 3.7. Coke deposit versus time(I) and n-Heptane isomerization versus coke deposit(II) [62].

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3.2.3.3. Dehydrocyclization

Dehydrocyclization of paraffins is uncontestedly the most complex and the most important of all the reforming reactions. Shum et al. [69] showed that under industrial conditions, the metal site pathways were controlling, contradictory to the previous philosophy of an additional acid site controlled bifunctional cyclization pathway [52].

When one examines the evolution of dehydrocyclization activity during the first hours of operation of a fresh catalyst (Fig.3.8), one can note a very high initial activity even under relatively high pressure. This activity decreases very quickly after a few hours of operation, levelling off to a "pseudoplateau" (lined-out catalyst) on which the evolution in time becomes much slower.

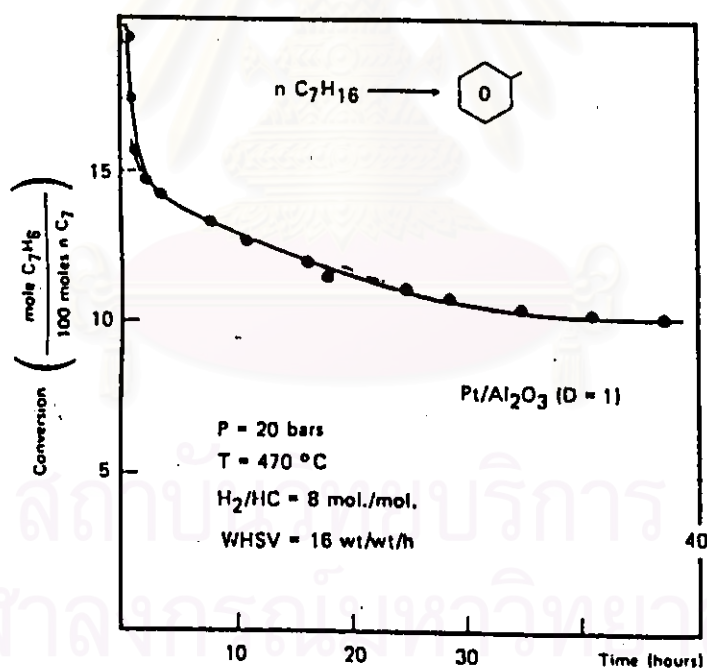


Figure 3.8 Initial activity and stabilization during n-heptane dehydrocyclization [63].

3.2.3.4. Hydrogenolysis

Figure 3.9 compares the toxicity of deposited coke on the metal sites of catalyst on the activities of dehydrogenation, exchange, and hydrogenolysis. The obvious catastrophic attenuation of the hydrogenolytic function agrees with work by Barbier et al. [31] and Trimm [70]. A number of authors suggested that the effect of coke on Pt/Al₂O₃ was similar to alloying of sulfur adsorption. Where there was a sharp decrease in hydrogenolysis activity compared to the other reactions [64-66]. The basic cause is the number of suitable ensembles for this 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 [67].

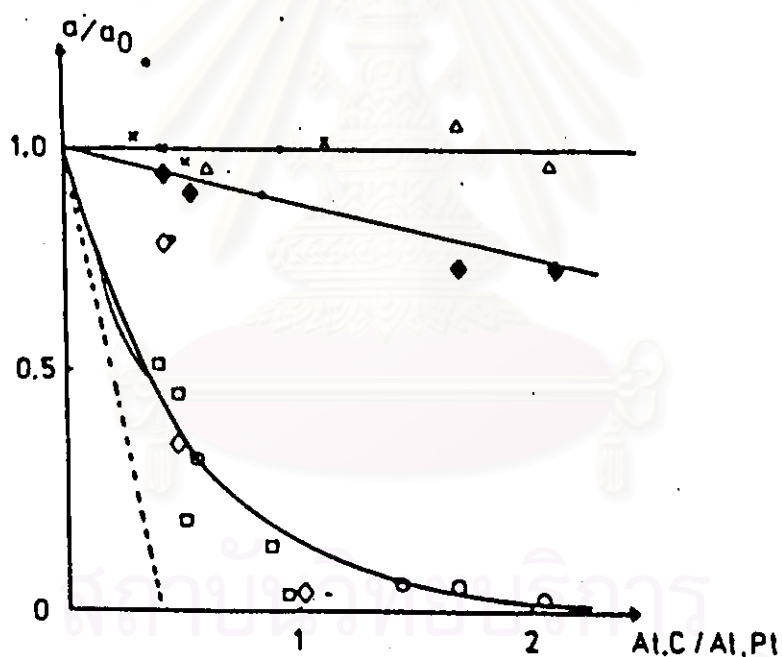


Figure 3.9 The evolution of the relative activity of 1 g of catalyst as function of the number of metal site carbon atoms deposited per platinum atom [60].

- (a) Benzene exchange : Pt/Al₂O₃ 0-1% (A), ; Pt/Al₂O₃, 1% (C),
 (b) Cyclopentane hydrogenolysis : Pt/Al₂O₃, 13% (D), ; Pt/Al₂O₃, 1%
 (C), ; Pt/Al₂O₃ (A), . (c) Benzene hydrogenation : Pt/Al₂O₃, 0.1% (A),
 ; Pt/Al₂O₃, 1% (C),

3.3 Composition, Structure, and Location of Carbon Deposits

3.3.1 Composition

Franck and martino [68] stated that carbon deposits were formed from hydrocarbons which almost never have more than 12 carbon atoms and usually have fewer than 10. On the average, a naphtha treated in reforming has at least two hydrogen atoms for each carbon atom, and if recycled hydrogen is taken into account, the hydrogen/carbon atomic ratio in the reactive phase is between 3 and 4. The combined feedstock of naphtha plus recycle gas is therefore rich in hydrogen when compared with various hydrocarbons (methane, paraffins, or aromatics), with different petroleum cuts, and especially with crude oils or coals, as shown in Table 3.1

Table 3.1 H/C Ratio of Various Hydrocarbons, Petroleum Cuts, Coal Liquids, and Coals.[68]

Compound	H/C (wt%)	H/C (atomic)
CH ₄	0.33	4.0
Paraffins	0.17	2.0
Benzene	0.083	1.0
Naphthalene	0.067	0.8
Straight-run naphtha	0.16	1.9
Coal liquid naphtha	0.13	1.56
Crude oil	0.09-0.13	1.08-1.56
Syncrude	0.07-0.10	0.84-1.56
Coal	0.05-0.07	0.60-0.84
Reformer combined feed	0.22-0.366	2.64-4.32

*Naphtha + hydrogen with $3 < H_2/HC < 10$

They remarked about techniques for determining carbon and hydrogen composition. The consolidated carbon deposits may occur when the coke are determined after stripping at high temperature. On the other hand, the coke which are more or less mobile, formed by the heavy aromatic hydrocarbons which are always present under operating conditions and which remain adsorbed on the catalyst when the catalytic bed is cooled down. Then therefore distinguished between deposits whose concentration can be determined by combustion after having taken the necessary precautions and those, on the other hand, which are precursors of such deposits and whose presence can be determined either by kinetic methods or by means of extraction using solvents.

Table 3.2 shows some H/C ratios measured for different carbon deposits; it may be noted that the data concerning reforming are rather rare. In the case of cracking or dehydrogenation reactions occurring without hydrogen, the figures are low, usually lower than those obtained for most coals. As far as reforming is concerned, the two figures given are very different. The first is an average of a few hundred results obtained on industrial samples treated for 24 hr at 100 °C, while the second was obtained after various solvent extraction treatments and high-temperature calcination, which probably left only the most refractory of those deposits on the catalyst. These differences show that even the carbon deposits which are called "consolidated" can be partially dissolved, which admit that there is, on the surface of the catalyst, a very wide spectrum of "carbon deposits" from those which are still soluble to products which are very close to inertinite.

As far as "mobile deposits" are concerned, it has been possible to detect unnegligible amounts of heavy hydrocarbons, under special conditions, in reforming effluents both from n-heptane and from butylbenzene or from a real feedstock. They concluded that the deposits found on coked catalysts can be anything from polyaromatic hydrocarbons to coals which cannot be dissolved in organic solvents.

Table 3.2 H/C Ratio (wt. %) of Coke Deposits Obtained in Various Processes.[68]

Process	Feed	Catalysts	H/C
Cat-cracking	Midcontinent G.O.	SiO ₂ /Al ₂ O ₃	0.03-0.04
Dehydrogenation	Isopentane	Cr ₂ O ₃ /Al ₂ O ₃	0.005-0.013
Cat-cracking	Aromatics	SiO ₂ -Al ₂ O ₃	0.03-0.07
Cat-reforming	Straight-run naphtha	Pt/Al ₂ O ₃	0.05-0.10 ^a
Cat-reforming	Pure-hydrocarbos	Pt/Al ₂ O ₃	< 0.01 ^b

^a Measured after stripping with air during 24 hr at 110 °C and removal of adsorbed water.

^b Measured after washing with C₂H₅OH-C₆H₆, dissolution of alumina, and air treatment at 110 °C

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3.3.2. Structure

Franck and Martino[68] assumed that the carbon deposits were uniformly spread out on the surface of the catalyst. In the case of reforming catalyst, specific surface area $200 \text{ m}^2/\text{g}$, there would be a carbon monolayer for consolidated coke concentrations on the order of 10 wt%. Observations made during catalytic cracking showed that rather large aggregates were involved. These aggregators have, moreover, been studied with different techniques, such as thermal analysis, X-rays, electron microscopy, and various kinds of spectroscopy (infrared and Auger). However, some detailed characterizations of deposits obtained in reforming still remain relatively rare; in Espinat's [62] study, different techniques were used and compared for characterizing carbon deposits on reforming catalysts.

X-ray diffraction

The use of x-ray diffraction for characterizing carbon deposits on a used catalyst has made it possible to show the presence of three-dimensional aggregates which are well crystallized. However, in order to have a more sensitive analysis, the alumina must be previously dissolved with hydrofluoric acid, and an x-ray diffraction spectrum such as the one shown in Figure 3.10 is thus obtained. 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).

They found that 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.

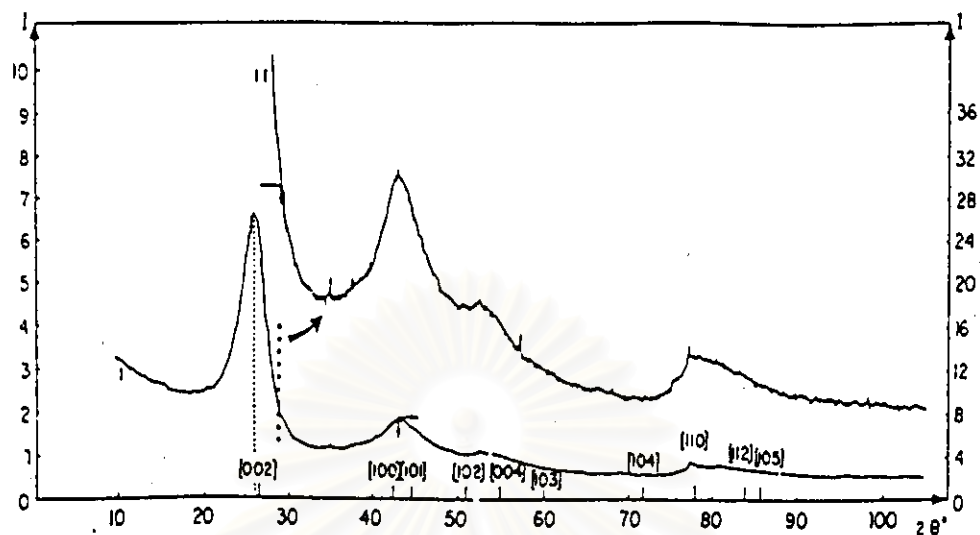


Figure 3.10 X-ray pattern of coke deposit. [68]

Raman spectroscopy

In Espinet's [62] study, alongside a fluorescence related to the presence of nondesorbed heavy polyaromatic hydrocarbons, two intense bands are detected on the coked catalysts in the region $1300-1650\text{ cm}^{-1}$, and these are characteristic of graphitic carbons. This technique, which as the advantage of being applicable even with low percentages of coke, has made it possible to demonstrate that, with 0.3 wt% carbon, coke are already organized structures, thus proving that the formation of localized carbonaceous aggregates takes place from the very beginning of the reaction.

3.3.3. Location

Concentration in the grain

Scanning microprobe studies of catalysts coked under conditions approximating industrial operation reveal that the coke is distributed homogeneously in the catalyst grain: concentrations on the periphery and in the core of the grain are completely comparable.

Closer analysis by ionic microprobe confirms this overall homogeneous distribution, with, however, variations in local concentration of 0.5-2.7 wt% for an average coke content of 1.15 % as shown in Figure 3.11. For reference purposes, this figure also contains recording of the alumina, platinum, and chlorine signals.

Local concentration

By use of electron microscopy, it is possible to localize the coke on the micrograin level. Thus it was noted that alongside clearly organized aggregates, there do exist zones which are little coked. Furthermore, spectroscopic analysis of electron energy loss shows that alongside zones which are rich in well-organized coke, there are zones which are just as rich but in which the coke has an amorphous structure.

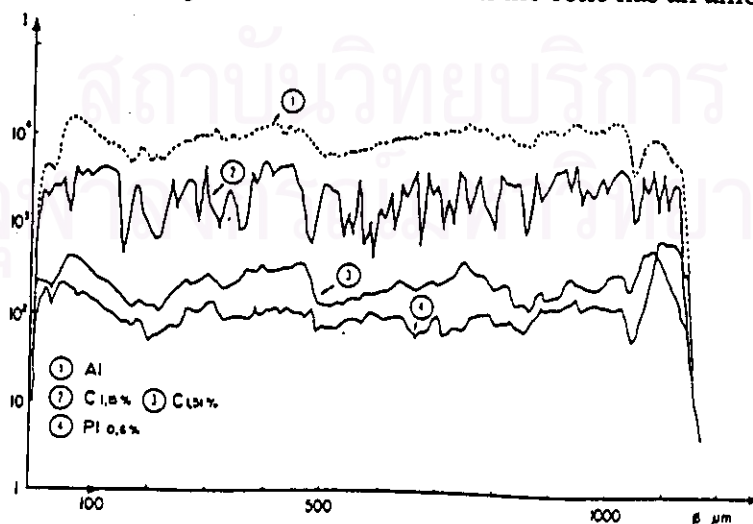


Figure 3.11 Ionic microprobe analysis of a coked catalyst [68].

The formation of three-dimensional carbonaceous aggregates, whatever their structure might be, logically leads us to suppose that the alumina pores are blocked. The results given in Figure 3.12 show that whereas the total porous volume decreases linearly according to carbon content, the BET surface area diminishes very quickly with the first few percent of carbon, and much more slowly thereafter. These observations correspond to rapid plugging of the smallest pores, even with very low coke concentrations.

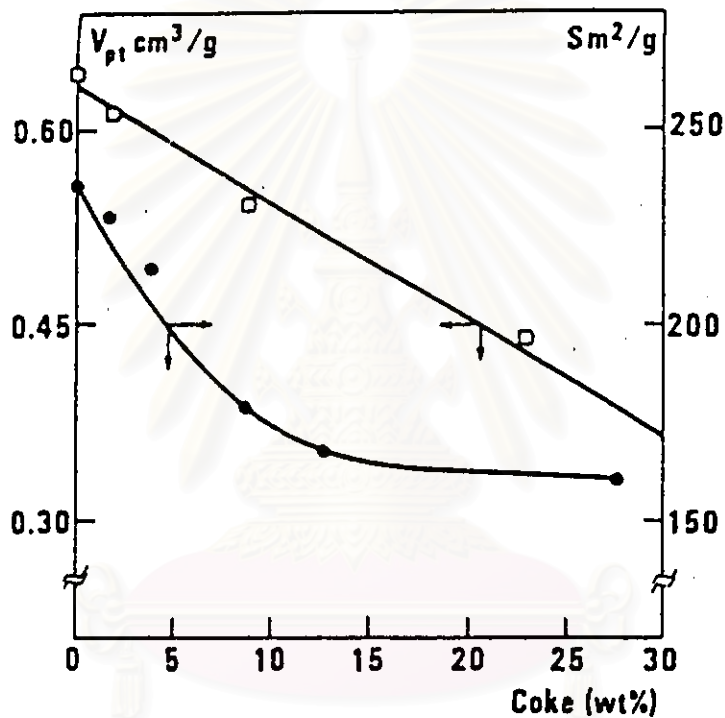


Figure 3.12 Effect of coke deposit on specific area and pore volume.[68]

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