

CARBONACEOUS DEPOSITS ON NAPHTHA REFORMING CATALYSTS

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Carbonaceous deposits on naphtha reforming catalysts play a decisive role in limiting process performance. The deposits negatively affect catalyst activity, selectivity, and the production cycle of a semi regenerative reformer. The magnitude of negative effect of those deposits is directly proportional to their amount and complexity. Investigations on used reforming catalysts samples reveal that the amount and type (complexity of the chemical nature) of carbonaceous deposits are directly proportional to the catalyst life on stream and the severity of operating conditions. In addition, the combustibility behavior of carbonaceous deposits on the catalyst samples taken from different reformers are found to be different. Optimal carbon removal, for in situ catalyst regeneration, requires that specific conditions be developed, based on the results of well designed and properly performed investigations of the amount and type of carbonaceous deposits.

Key words: Carbonaceous, Naphtha, Reforming catalysts.

Introduction

Naphtha reforming for the enhancement of its octane number has become an integral part of modern petroleum refining processes. The importance of this process is not restricted to the enhancement of naphtha octane number. Moreover, it is also applied for the production of aromatic basic petrochemical feedstocks (Benzene, Toluene and Xylene, BTX). Modern naphtha reforming utilizes platinum based supported on partially chlorinated alumina catalysts the dual function properties (Anabtawi *et al* 1989).

Reforming catalysts supported on partially chlorinated possess both metallic and acidic functions. The metallic function catalyzes hydrogenation/dehydrogenation, while the acidic function is responsible for the hydrocracking, alkylation and isomerization reactions (Barron 1963; Anderson and Avery 1967; Lietz *et al* 1984; Anabtawi *et al* 1989; Redwan *et al* 1990). Smooth operation of a reforming process at its highest possible performance requires that the two functions be kept in balance during operation. This is achieved by supplying the feed with well calculated and controlled quantities of water and chlorinated hydrocarbons, such as chlorinated propane or carbon tetrachloride.

Other than inactive or neutral supports partially chlorinated alumina participates effectively to the catalyst performance and in the mechanism of chemical reactions (Barron 1963; Gates *et al* 1979; Querini and Trimm 1987).

Excessive Lewis acidity of the catalyst is not desired, however, alumina with high level concentration of Lewis sites is very active in cracking of *n*-alkanes, and it deactivates almost immediately (Bournonville and Frank 1987), through acceler-

ating undesired reforming reactions, among them carbon deposition.

A reaction mechanistic model, which has received increasing acceptance of naphtha reforming, assumes that the reaction proceeds via a surface precursor being 1,3-diadsorbed species with a double bond to the surface of the catalyst. Accordingly, the initial function of metal is to produce the required 1,3-diadsorbed species, and then to act as an electrophile for extracting electrons from the carbon skeleton of the hydrocarbons. If these functions are lost because of poisoning of the metallic part, or restriction of access to the catalyst surface through carbon deposition, the catalyst will lose its activity.

In the course of normal and trouble free operation the catalyst activity decreases gradually as coke deposition increases. Since naphtha reforming usually utilizes feed almost free of sulfur compounds, poisoning of the catalyst metallic part does not play a decisive role in catalyst deactivation. Therefore, coking of reforming catalyst is of high concern for the overall process performance. Restoration of catalyst activity is usually achieved by carefully removal of carbonaceous deposits and restoration of metal dispersion without negatively affecting the metal dispersion and physico chemical characteristics of the catalyst support. Regeneration processes are usually carried out according to recommendations of catalyst suppliers and/or manufacturers. Those instructions are of a general nature, and in most cases they do not result in a proper removal of carbonaceous deposit. To achieve complete removal of carbonaceous deposits on the catalyst surface it is necessary to know (a) the magnitude of carbon deposits and their various types, (b) the oxygen concentration level of the gas mixture

used for combustion, and (c) heating rate and regeneration temperature (Barbier 1980; Parera 1980; Barbier 1988).

As the catalyst activity and, hence, its selectivity deteriorates in the course of operation, operators increase operation severity. The rate of formation of carbonaceous deposits is a function of various interrelated factors. Increasing severity, unbalanced chloride and moisture content of the feed and low hydrogen-to-hydrocarbon ratio (H/HC) are the main reasons for increased rates of carbon deposition (Cooper and Trimm 1980; Redwan *et al* 1990). Small amounts of coke deposited on the surface of bimetallic Pt-Re/ Al_2O_3 -Cl catalysts has little effect on its acidic function, but it has negative impact on its metallic active sites. Carbonaceous deposits on the metal surface are less dehydrogenated than those deposited on the support, and hence removal of the metallic part coke is easier than that of the support (Barbier 1987). In addition, since the metal activates hydrogenation/dehydrogenation reactions, it has the possibility for self cleaning which causes the amount of coke deposition on the metal part to stay constant throughout the reforming process. Coke deposited on the support is highly dehydrogenated, and its amount increases steadily as the reforming process proceeds. Therefore, the long term deactivation of industrial Pt-Re/ Al_2O_3 -Cl reforming catalyst is due to the deactivation of the catalyst support.

The paper discusses this topic and presents results of detailed investigations on a series of reforming catalyst samples taken from semi regenerative reformers under actual operating conditions.

Experimental

Test samples were commercial Pt-Re/ Al_2O_3 -Cl catalyst used in a semi regenerative naphtha reforming unit. Samples were taken from the third reactor (RX-III) regularly on a monthly basis. Each test sample was ground to 125 mesh size, dried at 105°C for about 24 h then 0.15 g was subjected to thermal

analysis in the temperature range from room temperature up to 1000°C , while other part was analyzed for its carbon content.

The total carbon content of the samples was determined by the combustion method. The respective thermograms of the samples were recorded using the simultaneous thermal analyzer (STA - 429) at various heating rates and two oxygen concentrations (about 20 vol. % and 2.5 vol.%) of purge gas flowing over the sample. Representative thermograms of the samples' thermal analyses are shown in Figs 1 and 2. These figures present a set of three thermographs conducted for the same catalyst sample at different heating rates (2, 5 and $10^\circ\text{C}/\text{min}$), and oxygen concentrations of (2.5 and 20% v/v). Since combustion of carbonaceous deposits is exothermic the DTA curve (Temperature at which weight of the sample changed) of thermograms exhibit an exothermic peak starting at about 150°C and ending in the range between 500°C and 750°C depending on the heating rate of the sample and oxygen content of purge gas flowing over the sample (Figs 1 and 2).

Results and Discussion

The linear relationship of the weight loss and carbon content (wt. %) of the samples has been confirmed by plotting its total carbon content against its weight loss (wt. %), as shown in Fig 3. The curve of carbonaceous deposits removal (TG curve) tends to become almost linear (does not show well defined peaks) over the whole temperature range of the thermal analysis, at heating rates of both 5°C and $10^\circ\text{C}/\text{min}$. as the oxygen content of purge gas is reduced to about 2.5 vol. %, while at a heating rate of about $2^\circ\text{C}/\text{min}$. the TG curve exhibits a peak of carbonaceous deposits removal in the temperature range between 150°C and 750°C (Fig 2).

At oxygen concentration of about 20 vol. % the effect of samples' heating rates can be seen in the shifting of the end temperature of carbonaceous deposits removal. As the heating

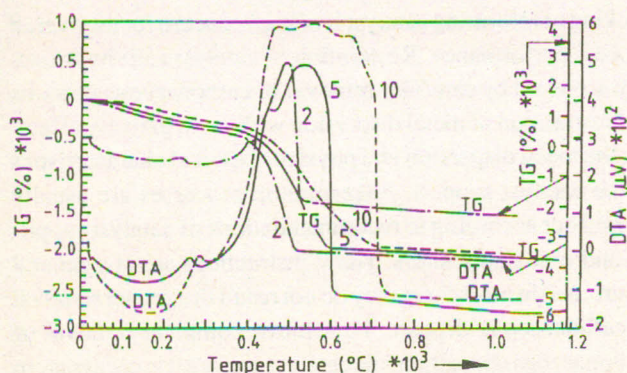


Fig 1. Representative thermograms of the analyzed samples recorded at different heating rates and oxygen concentration of about 20 vol % in the purge gas.

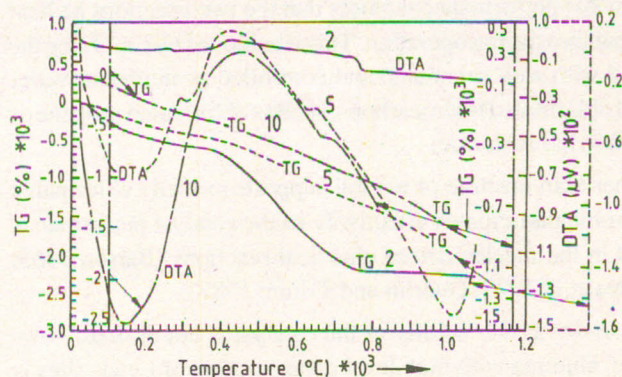


Fig 2. Representative thermograms of the analyzed samples recorded at different heating rates and oxygen concentration of about 2.5 vol % in the purge gas.

rate increases the end temperature increases (Fig 1). Both DTA curves at heating rates of $10^{\circ}\text{C min}^{-1}$ and oxygen content of 20 vol. %, and $5^{\circ}\text{C min}^{-1}$ and oxygen content of 2.5 vol. % exhibit several peaks in the range of the exothermic effect. Based on the thermal effects of the DTA curves of samples thermograms the weight losses of the samples for two consecutive production cycles were calculated in the temperature ranges 100 to 200°C , 200 to 350°C , 350 to 580°C and 580 to 900°C . Fig 4 presents samples total weight loss between 100°C and 900°C , as a function of heating rates at oxygen concentrations of about 2.5 vol. % and 20 vol. %, while both Fig 5 and 6 present the samples weight loss in the temperature

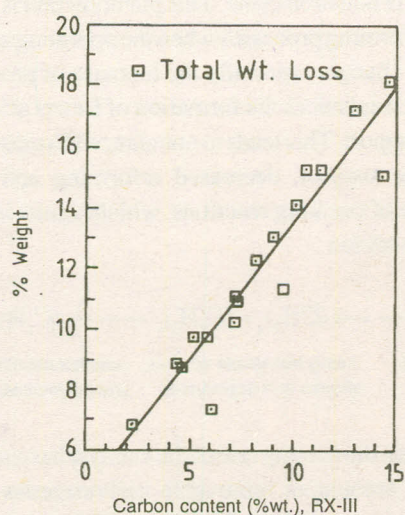


Fig 3. Samples total weight losses (wt %) in the temperature range 100 to 900°C as a function of their carbon contents (wt %).

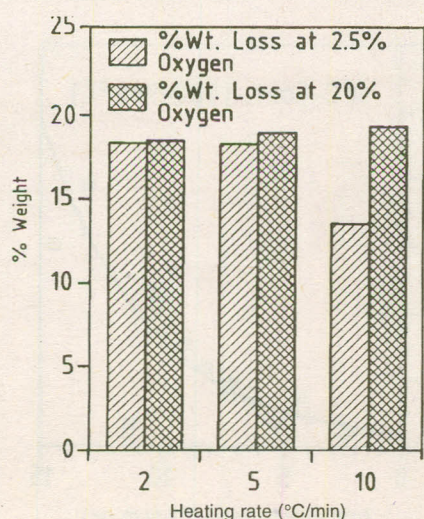


Fig 4. Samples total weight losses (wt %) in the temperature range 100 to 900°C as a function of heating rate, at oxygen concentration of about 2.5 and 20 vol. %.

ranges 200 to 400°C , 400 to 650°C , and above 650°C , at oxygen concentrations of both 2.5 vol. % and 20 vol. %.

The results suggest that, carbonaceous deposits on the catalyst surface are the main factors affecting catalyst weight loss when exposed to conditions of carbon removal (catalyst regeneration conditions). Therefore, the amounts of carbonaceous deposits that are removable in the afore mentioned temperature ranges are calculated and presented as a function of total carbon content of the samples in Figs 7 and 8.

It is well known that the amount of total amount of carbonaceous deposits on the catalyst surface is almost directly

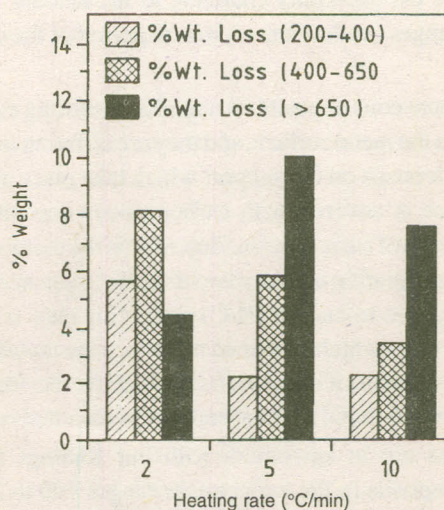


Fig 5. Samples total weight losses (wt %) in the temperature range 200 to 400°C , 400 to 650°C and above 650°C as a function of heating rate, at oxygen concentration of about 2.5 vol. %.

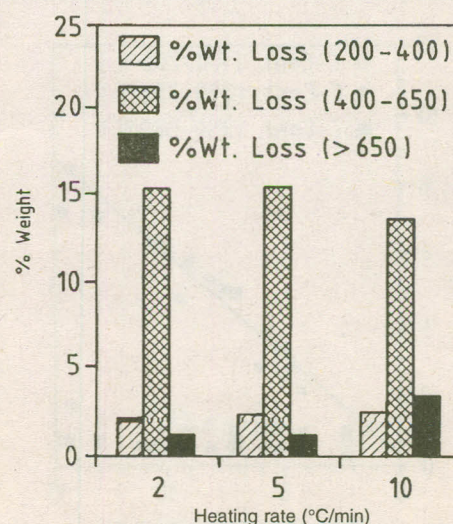


Fig 6. Samples total weight losses (wt %) in the temperature range 200 to 400°C , 400 to 650°C and above 650°C as a function of heating rate, at oxygen concentration of about 20 vol. %.

proportional and linearly increases as the catalyst time on stream increases (Parera *et al* 1980; Redwan and Alam 1991). Therefore, the total amount of carbonaceous deposits can be considered as an alternative variable of the catalyst time on stream. It is seen (Fig 7) that the amounts of removable carbonaceous deposits in the temperature ranges 100 to 200°C, and 200 to 350°C do not show measurable changes along the whole time on stream period of the catalyst, while the corresponding amounts of deposits in the temperature range 350 to 580°C are linearly proportional to the total amount of carbonaceous deposits and hence to the time on stream period of the catalyst. Carbonaceous deposits in the temperature range 580 to 900°C are exponentially changing as the amount of total deposits changes (as the time on stream period of the catalyst increases).

Initial carbonaceous deposits on naphtha reforming catalysts take place on the metal surface, and they are different in nature from those deposits on the support which take place after the metal surface is covered with carbonaceous deposits. The chemical nature of carbonaceous deposits on the metal surface permits differentiation between two different types according to their hydrogen-to-carbon (H/C) ratio. This ratio is 1.75 ± 0.25 for one type (which is formed mainly on the metallic part of the catalyst), while it is around 0.85 ± 0.25 for the other type (which is formed mainly on the support of the catalyst).

These results are in agreement with our findings for the amount of deposits in the temperature ranges 100 to 200°C, and 200 to 350°C. The amounts of these deposits are not increasing throughout the production period (time on stream) because this type of deposit can easily be hydrogenated and hence it is readily removable during the production run.

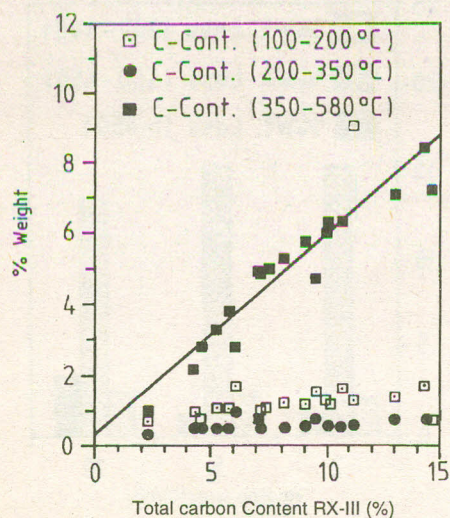
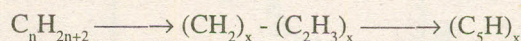


Fig 7. Samples contents of carbonaceous deposits (wt %) in the temperature ranges 100 to 200°C, 200 to 350°C and 350 to 580°C as a function of their total carbon contents.

On the other hand, carbonaceous deposits on the catalyst support have an H/C ratio below 0.1, which indicates the relative difficulty of their removal during the production period. Therefore, the amount of this type of carbonaceous deposits increases steadily and almost linearly with the time on stream of the catalyst, and hence with the total amount of deposits. The exponential increase of the carbonaceous deposits in the temperature range 580 to 900°C indicates that these types of deposits do not belong to the initially deposited carbonaceous products. These are rather formed as a result of secondary dehydrogenation and cracking reactions of the initially formed deposits which drastically increases against the end of the production cycle. This phenomenon is observed in naphtha reforming processes when the operating conditions considerably change, especially the increase of process temperature which enhances the formation of Lewis acid sites on the catalyst support. This leads to unbalanced Bronsted/Lewis acidity of the support, decreased reforming activity, and enhanced rate of cracking reactions, which results in accelerated coke deposition.



Alkanes(naphtha) heavy but simple alkenes, complex naphthenes
alkynes and naphthenes and polynuclear aromatics

Fig 4 shows that the heating rate of the catalyst has a negligible effect on the amount of removable carbonaceous deposits when oxygen concentration is high (about 20 vol %), since the relative ratio at heating rates of 2°C min⁻¹, 5°C min⁻¹ and 10°C min⁻¹ is in the order 1 : 1.02 : 1.03, respectively. However, as oxygen concentration is reduced to about 2.5 vol %, the ratio

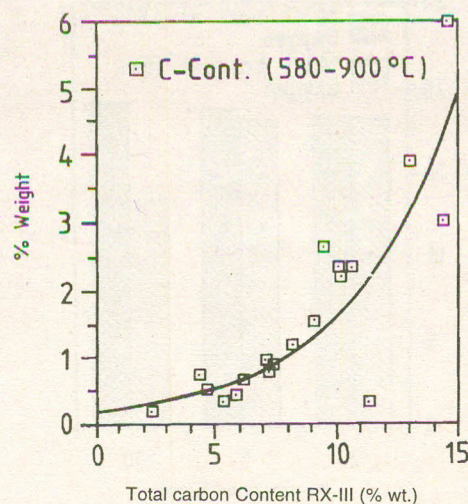


Fig 8. Samples contents of carbonaceous deposits (wt %) in the temperature ranges 580 to 900°C as a function of their total carbon contents.

order of total removable deposits at the same heating rates becomes 1 : 1 : 0.74, respectively.

Fig 5 indicates that at oxygen concentration of about 2.5 vol % the ratio of total removable deposits at heating rates of $2^{\circ}\text{C min}^{-1}$, $5^{\circ}\text{C min}^{-1}$ and $10^{\circ}\text{C min}^{-1}$ is in the order 1 : 1 : 0.74. Same figure shows that the ratios of removable deposits in the temperature ranges 200 to 350°C (low), 350 to 580°C (medium) and 580 to 900°C (high) are in the order 1 : 1.42 : 0.81, 1 : 2.5 : 4.36 and 1 : 1.5 : 3.19 at heating rates of $2^{\circ}\text{C min}^{-1}$, $5^{\circ}\text{C min}^{-1}$ and $10^{\circ}\text{C min}^{-1}$ respectively. This figure shows that, the effect of heating rate is not limited to the total amount of removable deposits, but also causes different distribution of removable deposits in various temperature ranges. Although the main part of removable deposits is in the medium temperature range at a heating rate of $2^{\circ}\text{C min}^{-1}$, it is in the high temperature ranges for both heating rates $5^{\circ}\text{C min}^{-1}$ and $10^{\circ}\text{C min}^{-1}$.

However, when the oxygen concentration is about 20 vol %, as shown in Fig 6 the ratio of total removable deposits at the heating rates of $2^{\circ}\text{C min}^{-1}$, $5^{\circ}\text{C min}^{-1}$ and $10^{\circ}\text{C min}^{-1}$ is in the order 1 : 1.04 : 1.04, and the relative distribution ratio in the temperature ranges (low, medium and high) is 1 : 7.75 : 0.7, 1 : 6.3 : 0.56 and 1 : 5.5 : 1.4, respectively, which clearly indicates that the main part of removable deposits is the part burnt out in the medium temperature range at all heating rates.

Conclusion

The obtained results permit the following conclusions:

1. Carbonaceous deposits on the metal part of the naphtha reforming catalyst are the initial deposits that are formed, however, quantity and quality of the deposits do not change with the time on stream of the catalyst, and the deposits can be easily removed in the relatively low temperature range. These deposits consist mainly of heavy, but simple alkenes, alkynes and naphthenes.
2. Carbonaceous deposits on the catalyst support are the main reasons for activity loss of the catalyst. They are formed mainly of heavy polynuclear aromatic and naphthenic compounds through a secondary reaction of the initially formed deposits. They increase continuously with the time on stream and their rate becomes faster against the end of the production cycle when the operating temperature is getting high.
3. Removal of carbonaceous deposits from the surface of naphtha reforming catalysts at a heating rate of $2^{\circ}\text{C min}^{-1}$ and 2.5 vol % oxygen concentration of the purge gas is desired. However, it is not efficient because complete removal of carbonaceous deposits is not possible at this oxygen level. The catalyst bed is exposed to a higher oxygen concentration for a short period of time, at the end of carbon removal process, to

ensure maximum removal of carbonaceous deposits that are removable only in the high temperature range.

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