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Influence of the Catalytic Coke Formation on Reactor Surfaces in Thermal Cracking Process

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Knowledge of diffusion properties and reactions that taking place in thermal cracking reactors can result in better operations and decoking procedures leading to extension of the lifetime of furnace tubes. Formation of carbon on metal surfaces and catalysts is a problem in most hydrocarbon conversion processes. In this paper, after investigating a model for catalytic coke formation in reactors, some of the effects of coke formation on coils surfaces, such as the amount of the carbon diffused onto the surface and descending of the active site as well as the rate of the catalytic coke production was surveyed. The model also showed that the fact the amount of the diffused carbon is more compared with that of the released sites, confirming that the crystal diffusion consists of the controller factor for the rate of the catalytic coke production.

Key Words: Catalytic coke, Modeling, Thermal cracking, Surface, Metal particle.

INTRODUCTION

The thermal cracking of hydrocarbons is one of the most considerable processes in the petrochemical industries, resulting in olefin products. Among them, ethylene is the most interesting product. The undesirable product of the thermal cracking process is coke, which causes several problems in the thermal cracking reactors and exits furnace from the process cycle. The coke deposits on the walls of the coil affects the operation of the pyrolysis coils with pressure drop increase, heat transfer reduction, hot spot and corrosion by carbonization. These phenomena have penalties such as reduced run length, selectivity reduction, production losses, high maintenance cost and increased utility cost. Several mechanisms participate in the coke production such as catalytic, homogeneous non-catalytic and heterogeneous non-catalytic mechanisms. The catalytic mechanism is the most significant mechanism in this production at the start-up period, provided that the reactor surface is clean.

Studies proved that metals, present on the reactor surface, can catalyze the coke formation[1,2]. Furthermore, researchers have employed a scanning-electron microscope equipped with EDAX to analyze the metal coke content[3]. Industrial cracking coils frequently contain different weight percentages of chromium, nickel and iron. In a review of Baker on the catalytic mechanism for the growth of carbon filaments, it was concluded that the available theories on this phenomenon failed to account for all the aspects of the experimental results[4]. Also, numerous experimental assessments, directed to the coke formation kinetics, have been published[5-7].

During the start-up of a furnace, the reacting gas mixture is in contact with the bare reactor walls. The filaments production mechanism includes the attraction of the hydrocarbon molecules on the surface and the production of carbon atoms. Initially, a hydrocarbon molecule is chemisorbed on the metal crystallite on the surface and by a surface reaction it is converted to coke. Carbon atoms, thus, are dissolved and diffused through the metal particles. By accumulation of these atoms in the metal crystals and by tension, the metal particles are plucked from the surface. In the next steps of the process, these particles may act as active sites in the catalytic coke production. As more carbon is deposited, a carbon filament is formed, carrying metal particles on it[8]. The carbon precipitation can give rise to structural deficiency in the carbon lattice, creating reactive carbon centers along the filament skin[9]. The hydrocarbon radicals and molecules from the gas phase are incorporated in these reactive sites, where lateral growth of the filaments occurs. As a consequence, a porous layer of interwoven filaments is formed. The resulting filamentous coke often contains 1-2 wt % metal. The filamentous coke is produced at temperature values from about 400 °C up to 1050 °C[10]. The properties of metal are very important in this mechanism. Coke formed on alloys surfaces often contained highly dispersed metal particles of nickel, chromium and especially iron[11]. These metal particles have apparently been extracted from the alloys surfaces. This mechanism explains the simultaneous formation of metal-catalyzed filamentous coke and corrosion, perhaps along with erosion of metal surface[12].

The objective of this study is the investigation of metal behaviour on the reactor surface during catalytic coke formation and it interpreting with catalytic coke formation introduction model.

EXPERIMENTAL

Catalytic coke formation modeling: The coke production rate through a catalytic and non-catalytic mechanism, in accordance with the process duration and with the combination of the two mechanisms, is stated by Albright[13] as follows:

$$r_c = \frac{dy}{dt} = A + BCe^{-ct} \tag{1}$$

The integration of the stated equation in the condition of y = 0 and t = 0 results in:

$$Y = At + B(1 - e^{-ct}) \tag{2}$$

In these equations: r_c is the coke production rate mg/m^2 h, A is the rate of non-catalytic coke production mg/m^2 h, Y is coke production in the time period of t mg/m^2, BC initial rate of catalytic coke production mg/m^2 h and c is reduction constant of catalytic coke h^{-1}.

For the attainment of a mechanism with a catalytic coke production, several different kinetic models have been proposed and their equations have been written and solved. The results of each model were compared with the experimental data[5] and their rate constants together with their error percentages were calculated.

The experimental results, used for determining the reliability of the proposed kinetics, were taken from Kumar and Kunzru articles and the produced coke at the beginning of the coke production process was considered as the produced catalytic coke on the surface[5,6]. In the suggested kinetics, the X factor was the coke precursor in the coke production. For each case, the X factor calculation of the rate constants was performed. Moreover, the calculation of the activation energy and the other parameters was carried out. Regarding the Arrhenius equation, the k_o and E_o constants of each reaction were also calculated.

$$k = k_o e^{\frac{-E_o}{RT}} \tag{3}$$

After examination of four kinetic, the best results for catalytic coke formation achieved from this model[14]:

$$\begin{gathered} X + S \overset{k_1}{\rightleftharpoons} XS \\ XS \xrightarrow{K_2} C.S + n\,H_2 \\ CS \xrightarrow{K_3} eS + f\,C + g\,CS \end{gathered} \tag{4}$$

The equations of the fourth kinetic model are as follows:

$$\begin{aligned} r_S &= -k_1 C_x . C_S + k_1' C_{XS} + K_3 e C_{CS} \\ r_{XS} &= k_1 C_X . C_S - k_1' C_{XS} - K_2 C_{XS} \\ r_{CS} &= K_2 C_{XS} - K_3 C_{CS} \\ r_C &= K_3 f C_{CS} \\ r_{H_2} &= n K_2 C_{XS} \\ r_X &= -k_1 C_X . C_S + k_1' C_{XS} \end{aligned} \tag{5}$$

In these equations, X is hydrocarbon molecules, S is active sites, CS is the produced carbon amount on the surface and C is the carbon amount, which diffuses into the metal crystal. The rate of the catalytic coke production was regarded to be the rate of the CS production. Furthermore, the e, f, g coefficients were employed, due to the difference between the diffused carbon and the released sites.

The constant values and the calculated error for this model are depicted in Table-1. The conformity of the experimental results and the results of this kinetic model are displayed in Fig. 1.

The e and f calculated values were also reasonable. In detail, the e coefficient value was smaller than that of the f coefficient. This phenomenon could be attributed to two facts. Firstly, on the fact that the diffused carbon amount was greater compared with that of the released sites and secondly on the fact that the carbon initially occupied the crystal pores and, then, plucked by tension the metal particles from the surface.

TABLE-1
CALCULATED ERRORS AND PARAMETERS FOR THE KINETIC MODEL

Parameter	K				E				e	f	g	Error (%)
	k_{01}	k'_{01}	K_{02}	K_{03}	E_{01}	E'_{01}	E_{02}	E_{03}				
Value	2.14×10^3	2.60×10^{-11}	6.26×10^1	4.91×10^1	-1.16×10^3	1.32×10^4	7.48×10^{-3}	7.34×10^{-3}	1.07×10^{-1}	0.2	1.82×10^{-1}	3.8

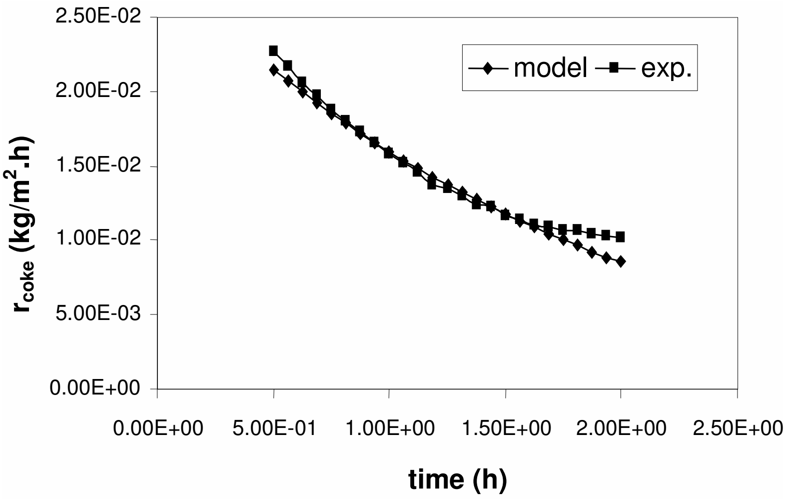

Fig. 1. Comparison of the results of the forth kinetic with experimental data

In this model, the calculated values for the activation energy were also found to be in a reasonable range. At first, E_{01}, which is associated to the absorption reaction, illustrated a negative value. Subsequently, the reaction rate would diminish, if the temperature increased. This observation is true for all surface absorption reactions. Secondly, the E_{01} value was positive, disclosing that in repulsive reactions if the temperature increased, the rate would increase, as well. Thirdly, the E_{02} value was also positive, revealing that during a temperature increase, the conversion of the attracted advanced factor into coke on the surface would raise. Eventually, the E_{03} positive value demonstrated that the carbon sedimentation in the crystal would increase by increasing the temperature[14].

As in the previous model, the k_1, k'_1, K_2 and K_3 values were calculated: $k_1 = 3657$, $k'_1 = 5.7 \times 10^{-14}$, $K_2 = 62$ and $K_3 = 49$.

The k'_1 resulting value in contrast with the k_1 value is considerably smaller, exhibiting that the rate of the forward reaction is much higher than the rate of the reverse reaction. In fact, this result was expected from the first reaction, meaning that in the case of the advanced factor attraction of the coke production, the probability of its repulse from the surface was very low. Here, also the K_3 value was smaller than the K_2 and k_1 values, confirming that the crystal diffusion consisted of the controller factor for the rate of the catalytic coke production.

RESULTS AND DISCUSSION

After the examination of this kinetic model, the next step was to discover how this kinetic model could explain the changes of the other factors, involved in this reaction and their respective effects in this production.

This process was investigated in a longer period in order to observe the way that the developed model would change in a longer time frame and the way that it would predict each parameter. It was desirable to predict the attraction of the coke precursor on the surface. In Fig. 2, where these changes are summarized, the production rate constantly diminished until it reached the minimum level. At this point, the catalytic coke coverage was at the maximum surface. After the carbon diffusion into the surface, the tension application, the release of some metal atoms and their diffusion into the coke surface, the coke production gradually increased until it reached a constant level. Encapsulation of the metal particles reduces the rate of dehydrogenation of the chemisorbed hydrocarbon atoms. At this stage the catalytic activity of the metal particle diminishes and both carbon formation and CO production slow down. Thereby, some of the metallic atoms (even though in a small quantity) regularly approached the surface, creating active sites for the attraction of the advanced factors for the coke production.

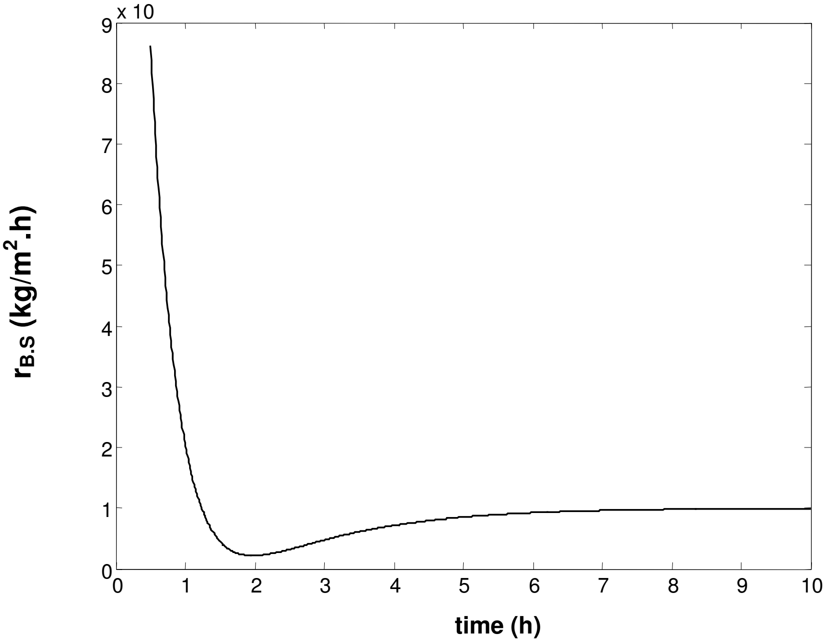

Fig. 2. Attraction rate of coke precursor for a longer period

Some investigations on the diffused carbon amount onto the surface were conducted. Fig. 3 presents that at the beginning of the coke production process, because of the crystal pores, the produced coke amount on the surface was partly diffused onto it. When the time elapsed, a higher carbon production took place on the surface and its sedimentation increased. However, when the pores were filled, the carbon diffusion into the crystal reduced and the curve declined towards zero.

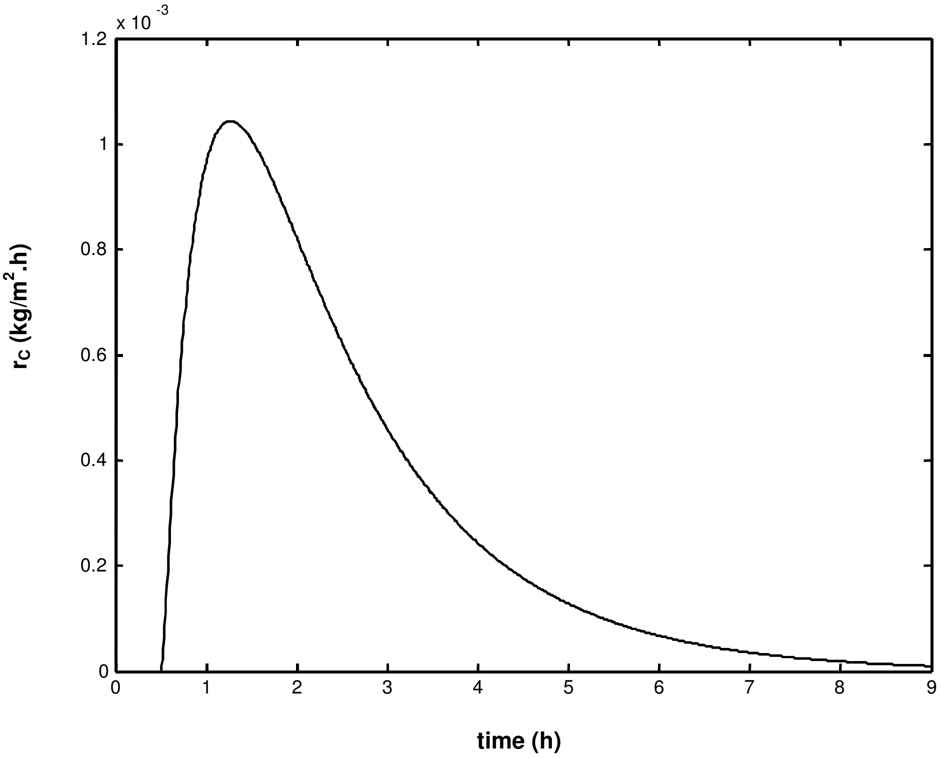

Fig. 3. Carbon diffusion rate into the surface

Also, the diffused carbon amount onto the surface was also examined and the associated curve is illustrated in Fig. 4. It is clear that when the coke production process begins the diffused carbon amount increases until the free space in the crystal is occupied. Eventually, this amount reaches a stable value.

This model was related to the time that the coke production process had not yet begun. As it was expected, with the passage of the time the active sites reduced on the surface because of the coke coverage. The amount of the active sites was descending as well as the rate of the catalytic coke production, which was descending exponentially and it showed that the descending progress of the active sites in the coke production (Fig. 5). Because of the hydrocarbons plurality, the coke was expected to be produced by other molecules under similar kinetic model.

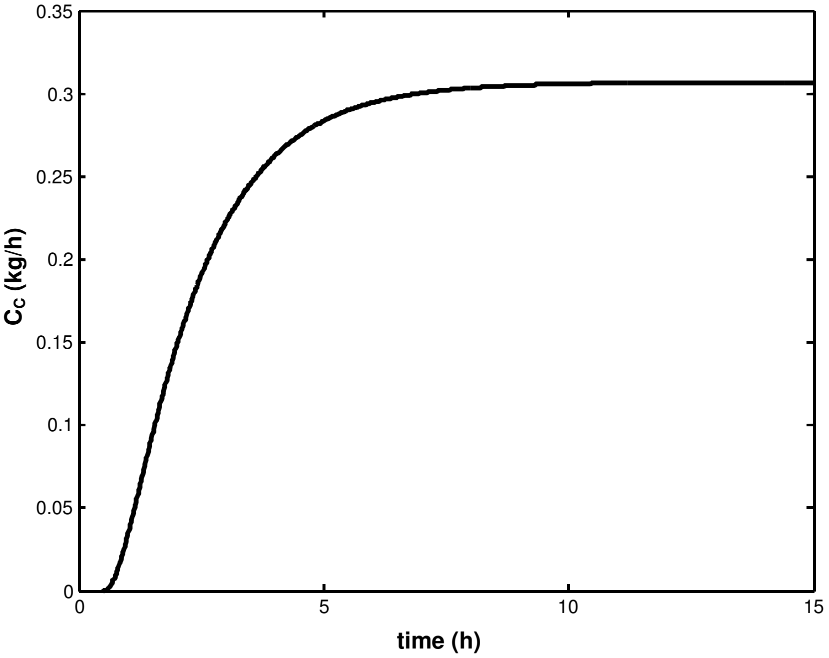

Fig. 4. Amount of diffused carbon into the surface

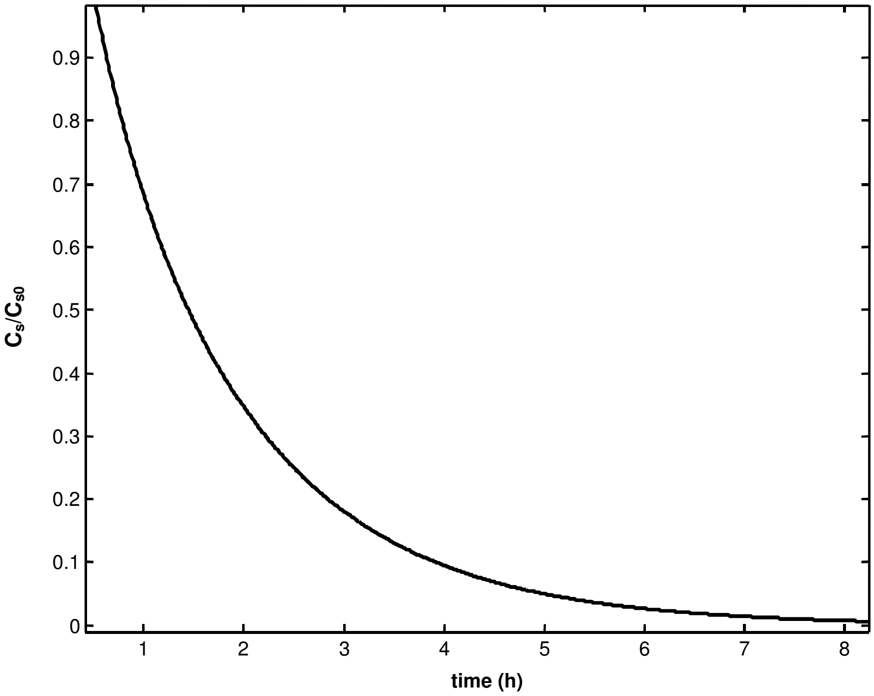

Fig. 5. Density of the active sites in comparison to the first mode

$$
\begin{gathered}
X + S \xrightleftharpoons{k_{1_1}} XS \\
X + S \xrightleftharpoons{k_{1_2}} XS \\
\vdots \\
X + S \xrightleftharpoons{k_{1_n}} XS \\[1ex]
X_1S \xrightarrow{K_{2_1}} C_1S + nH_2 \\
X_1S \xrightarrow{K_{2_2}} C_2S + nH_2 \\
\vdots \\
X_nS \xrightarrow{K_{2_n}} C_nS + nH_2 \\[1ex]
C_1S \xrightarrow{K_{3_1}} e_1S + f_1C + g_1S \\
C_1S \xrightarrow{K_{3_2}} e_2S + f_2C + g_2S \\
\vdots \\
C_nS \xrightarrow{K_{3_n}} e_nS + f_nC + g_nS
\end{gathered}
\qquad (6)
$$

Here each X_1, X_2 and … X_n may symbolize one of the coke precursors in the catalytic coke production.

Conclusion

Owing to the carbon coverage on the surface and the pores of the metallic crystals, the amount of metals reaching the surface would be lower than the diffused carbon. Eventually, with the passage of time the coke production was reduced.

- At the beginning of the coke production process, because of the crystal pores, some of the produced coke amount on the surface was diffused into it. Afterwards, a greater carbon production took place on the surface and its sedimentation increased. In the end, when the pores were filled, the carbon diffusion into the crystal diminished.
- The rate of the catalytic coke production constantly reduced until it reached its minimum value. After the carbon diffusion into the surface and the tension application, some of the released metal atoms were diffused into the coke surface, consisting of active sites. In this way, the coke production process again gradually increased up to a constant value. At this point, a small metal quantity could regularly approach the surface, creating active sites for the coke precursor attraction and the catalytic coke production.

Nomenclature

A : Rate of non-catalytic coke production (mg/m^2 h)
X : Hydrocarbon molecules
BC : Initial rate of catalytic coke production (mg/m^2 h)
c : Reduction constant of catalytic coke (h^{-1})
C : Carbon which diffuses into the metal crystal

CS : Catalytic coke on the surface
E : Activation energy
e, f, g : Constants
K : Rate constant
r_c : Rate of coke formation (mg/m^2 h)
S : Active sites
t : Time (h)
Y : Value of coke which remain on the surface in t duration (mg/m^2)

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