

AROMATIZATION OF LIGHT NAPHTHA FRACTIONS ON ZEOLITES 3. MODEL OF COKE FORMATION

In previous papers [1,2], we reported on the reaction kinetic and catalyst deactivation models for the Zeoforming process. The significant coking of a catalyst takes place, and two types of coke are formed. In this work the equations of coke accumulation are derived and its relations with relative activities are presented and discussed.

Key words: Zeoforming process, catalyst deactivation, model of coking.

In previous papers [1,2], we reported on the reaction kinetic and catalyst deactivation models for the Zeoforming process. This process is intended for a gasoline production by catalytic conversion of low-octane crude naphtha on zeolite catalysts and in hydrogen-free condition. In such a condition, the significant coking of catalyst takes place, and two types of coke are formed [3]. The first (low temperature, uncondensed or "polymeric" coke – C_P) is deposited in the intracrystalline volume of zeolite, and the second (high temperature, condensed coke – C_C) is formed on the outer crystalline surface.

These two types of coke are formed in different active centers. Rate deactivation equations for the centers located inside zeolite channels (r_P) and on the surface of zeolite crystallites (r_C) were proposed in [2]:

$$\frac{da_P}{dt} = -r_P = -k_P (\Theta_O^o)^2 a_P^2 \quad (1)$$

$$\frac{da_C}{dt} = -r_C = -k_C \Theta_O^o a_C \quad (2)$$

$$\Theta_O^o = b_O Y_O / (1 + b_O Y_O) \quad (3)$$

In this work the equations of the coke accumulation are derived, and its relations with relative activities are presented and discussed. The mechanism of monolayer deposition with partial self-regeneration is suggested for polymeric coke. In the case of condensed coke the polylayer deposition is proposed.

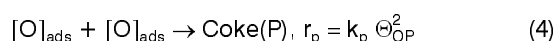
MODEL OF COKE FORMATION

It is worth to mentioning that rates of coke formation are proportional but not equal to the rates of deactivation. For example, in the case of polylayer

deposition only the first monolayer covers active centers, but others can increase the coke concentration without falling of the activity.

Polymeric coke

The "polymeric" coke formation inside zeolite channels can be presented as surface oligomerization of adsorbed olefins:



In the case of main reaction's linear mechanisms [4,5]:

$$\Theta_j = \Theta_j^o (1 - \Theta_P) \quad \text{and} \quad a_P = 1 - \Theta_P \quad (5)$$

Then $\Theta_{OP} = \Theta_{OP}^o a_P$, and Θ_{OP}^o can be expressed by equation (3) with corresponding b_{OP} .

Since this coke is considered as the uncondensed one [3], the partial self-regeneration by hydrogen is possible:



Then, using equations (4–6), the overall rate of "polymeric" coke accumulation can be expressed by the following equation:

$$\frac{1}{C_{max}^P} \frac{dC_P}{dt} = k_P (\Theta_{OP}^o)^2 a_P^2 - k_R Y_H (1 - a_P) \quad (7)$$

Formally, this equation corresponds to mechanism of monolayer coke deposition [6]. Meanwhile, because oligomers (as coke precursors) have a size closed to the size of zeolite channels, the coke accumulation is proportional to filling of channels volume [7]. In this case C_{max}^P is a maximum concentration of polymeric coke that is somewhat higher than monolayer C_{max}^P .

In order to derive the relation of coke concentration with the centers activity, equation (7) should be divided by equation (1):

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$$\frac{1}{C_{max}^p} \frac{dC_p}{da_p} = \frac{k_R Y_H}{k_F (\Theta_{OP}^o)^2} \frac{1 - a_p}{a_p^2} - 1 \quad (8)$$

After the integration of equation (8) we obtain:

$$\frac{C_p}{C_{max}^p} = 1 - a_p + \varphi_p \left(1 - \frac{1}{a_p} - \ln a_p \right) \quad (9)$$

$$\varphi_p = k_R Y_H / k_F (\Theta_{OP}^o)^2 \quad (10)$$

If the self-regeneration is negligible, $\varphi_p = 0$ and:

$$a_p = 1 - C_p / C_{max}^p \quad (11)$$

Graphics of dependency (9) are presented in Fig. 1. At low rate of self-regeneration ($a_p < 0.1$) the activity linearly decreases as the coke concentration rises. In the case of marked self-regeneration it influences only the coke content, but not the activity.

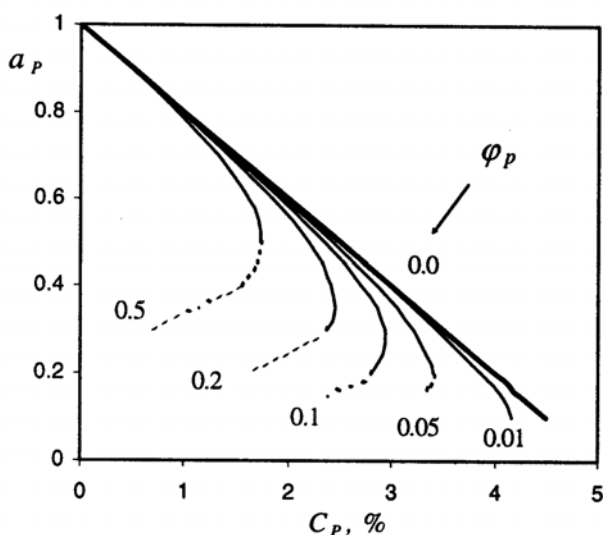


Figure 1. Dependence of the activity on polymeric coke concentration. $C_{max}^p = 5\%$.

Condensed coke

This type of coke is formed on the outer surface of zeolite crystallites due to hydrogen disproportionation in adsorbed oligomers:



Again, similar to equation (5):

$$\Theta_{OC} = \Theta_{OC}^o (1 - \Theta_C), \quad a_C = 1 - \Theta_C \quad (13)$$

The amount and the structure of the condensed coke [3] indicate the polylayer mechanism of this coke formation. According to such a mechanism $\Theta_C = \sum \Theta_{n-1}$, and the equation of coke accumulation has the following form [4,6]:

$$\frac{1}{C_m^c} \frac{dC_C}{dt} = k_C \Theta_{OC}^o (1 - \Theta_C) + k_N Y_O \sum_{n=2}^N \Theta_{n-1} \quad (14)$$

Because of $\Theta_{n-1} \propto (C_m - C_n)/C_m$ and

$$\sum_{n=2}^N C_m = C_{max} - C_m, \quad \sum_{n=2}^N C_n = C_C - C_1$$

equation (14) can be rearranged as follows [4,6]:

$$\frac{1}{C_m^c} \frac{dC_C}{dt} = (k_C \Theta_{OC}^o - k_N Y_O) (1 - \Theta_C) + k_N Y_O (C_{max}^c - C_C) / C_m^c \quad (15)$$

After dividing equation (15) by equation (2) and the integration we obtain:

$$\frac{C_C}{C_{max}^c} = 1 - \frac{C_m^c}{C_{max}^c} a_C - \left(1 - \frac{C_m^c}{C_{max}^c} \right) a_C^{\varphi_C} \quad (16)$$

$$\varphi_C = k_N Y_O / k_C \Theta_{OC}^o \quad (17)$$

Graphics of this dependency are presented in Fig. 2. It has two limiting cases. The first one (at $\varphi_C = 0$) corresponds to monolayer coke deposition:

$$a_C = 1 - C_C / C_m^c \quad (18)$$

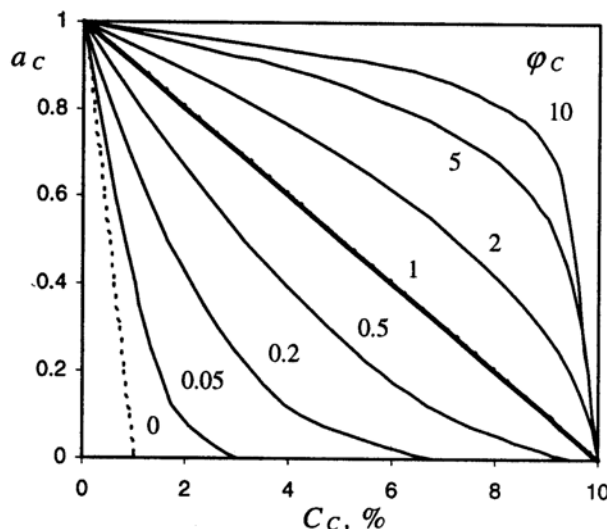


Figure 2. Dependence of the activity on the condensed coke concentration. $C_{max}^p = 10\%$, $C_m^c = 1\%$.

The second case (at $\varphi_C = 1$) corresponds to nonselective coke formation, with the same rate on active and coked centers:

$$a_C = 1 - C_C / C_{max}^c \quad (19)$$

Dependencies at $\varphi_C > 1$ are of special interest because of drastic deactivation after a long time operation at high activity.

ANALYSIS OF EXPERIMENTS

Equations derived above, coupling with the reaction and deactivation kinetic models [2], were used for the analysis of experiments on Zeofforming catalyst deactivation [3].

The model includes equations (1) and (2) for the activities, and equations (9) and (16) for the coke concentration. The mass balance equation for molar fractions of components has a form:

$$\sigma \frac{dY_i}{dt} + Y_i \frac{d\sigma}{dt} = \sum_{j=1}^R \nu_{ij} r_j, \quad r_j = r_j^o a_j \quad (20)$$

with corresponding reaction rates:

$$\begin{aligned} r_1 &= k_1 (1 - \Theta_O^o) Y_{n-P} a_C \\ r_2 &= k_2 (1 - \Theta_O^o) Y_{i-P+N} a_C \\ r_3 &= k_3 (1 - \Theta_O^o) Y_{n-P} [1 - Y_{i-P+N} / (K_P Y_{n-P})] a_C \quad (21) \\ r_4 &= k_4 (\Theta_O^o)^2 a_P \\ r_5 &= k_5 \Theta_O^o Y_H a_P \end{aligned}$$

where Θ_O^o is supposed to be the same for two types of centers and is expressed by equation (3); here O – olefins; n-P – normal paraffins; i-P+N – isoparaffins and naphthenes; A – aromatics; H – hydrogen; and G – gas.

Echevskii [3] carried out the experiments using catalyst IC-30-1 in an isothermal reactor, at WHSV = 2 h⁻¹ and the atmospheric pressure. The gas condensate of Kherson refinery was used as a feed, containing 33.2% wt. of n-paraffins, 46.3% wt. of i-paraffins and naphthenes, and 20.5% wt. of aromatics.

The results of modeling are presented in Fig. 3 and indicate a good model prediction of the product composition dynamics. It is worth mentioning that the values of the reaction rate constants in this case differ

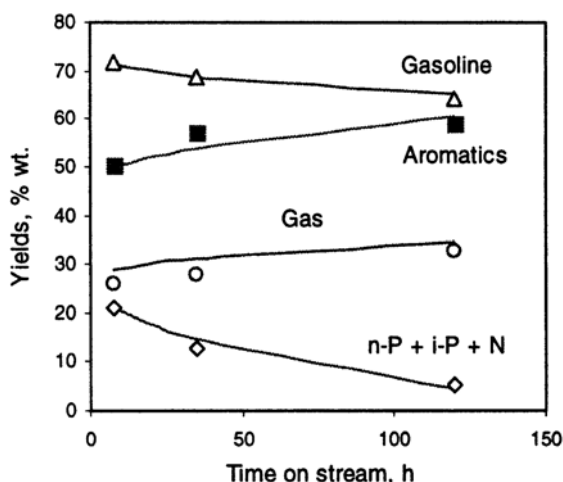


Figure 3. Product composition dynamics under catalyst deactivation. Points – experiments [3]; lines – model prediction

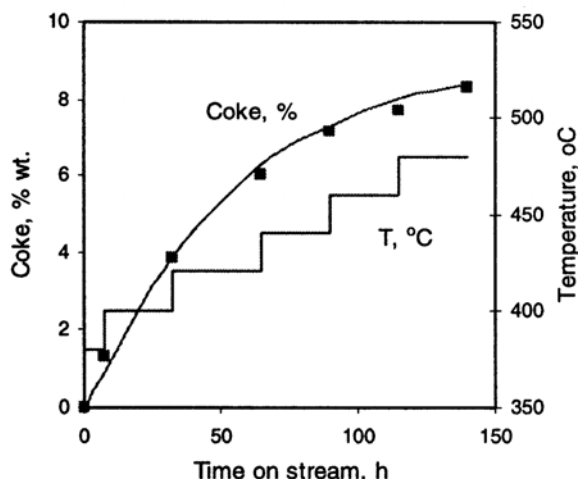


Figure 4. Dependence of coke concentration on time on stream. Points – experiments [3]; lines – model prediction

from those reported elsewhere [1,2] because different catalysts and the pressure were applied.

The corresponding graphic of the coke accumulation is presented in Fig. 4 for the case of the rising temperature regime. For the simulation of this regime equations (1) and (2) were used for the activities and equations (7) and (15) were used for the coke concentrations, coupled with equations (20) and (21). The values of model parameters are listed in Table 1, where b_O , k_P , k_C and Q_O , E_P , E_C are equal to those reported elsewhere [2].

Table 1. Kinetic parameters of catalyst deactivation and coking

k_j (420°C), h ⁻¹		E_j , kJ/mole	
b_O	100	Q_O	60
k_P	0.01	E_P	40
k_C	0.005	E_C	60
k_N	0.17	E_N	27
$C_{max}^P = 6\%$, $C_m^C = 2\%$, $C_{max}^{ci} = 20\%$			

When a gradientless reactor is used for the study of catalyst deactivation, the analytical solutions of equations (1) and (2) become possible:

$$a_P = (1 + k_P (\Theta_O^o)^2 t) \quad (22)$$

$$a_C = \exp(-k_C \Theta_O^o t) \quad (23)$$

since Y_O in Q_O^o changes with contact time, but slightly depends on time on the stream [1,2]. Then equations (9) and (16) are valid for the coke concentrations.

The same model can be used for the analysis of the experiments carried out in an integral reactor at a constant temperature, and if Y_O gradient along the catalyst bed does not changes dramatically in time.

Such a case is presented in Fig. 5. These two experiments were carried out at constant temperatures,

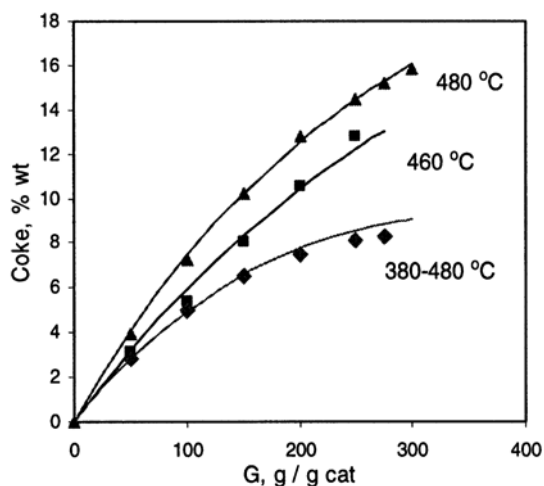


Figure 5. Dependence of coke concentration on feed to catalyst ratio. Points – experiments [3]; lines – model prediction

and the third experiment corresponds to that of Fig. 4. The simplified model (equations 9, 16, 22 and 23) was used for the analysis.

In this simple model the same values of kinetic parameters (listed in Table 1) are valid. Only the decrease of the olefins concentration with time was necessary for the fitting of the third experiment with rising temperature. It happens due to the complex evolution of the concentration gradients along the bed during deactivation with increasing temperature.

The equations of coking presented here, coupling with the kinetic and catalyst deactivation models published in [1,2], constitute the basis for simulation and optimization of the Zeoforming process in different types of reactors.

NOTATIONS

a_C, a_P – relative activities of centers covered by condensed and polymeric coke;

C_C, C_P – concentrations of condensed and polymeric coke;

C_m, C_{max} – monolayer and maximal coke concentration;

$G = Wt$ – feed to catalyst ratio;

k_C, k_P – formation rate constants of condensed and polymeric coke;

k_R, k_N – rate constants of self-regeneration and polylayers formation;

r_C, r_P – rates of coke formation;

r_j, k_j – reaction rate and corresponding constant;

K_P – equilibrium constant;

t – time on stream;

W – weight hourly space velocity (WHSV);

Y_O, Y_H – mole fractions of olefins and hydrogen;

$\sigma = \sum n_i / \sum n_i^0$ – coefficient of total mole number;

ν_{ij} – stoichiometric coefficient;

Θ_C, Θ_P – surface coverages by condensed and polymeric coke;

Θ_O^0, Θ_O – initial and current part of active centers occupied by adsorbed olefins;

τ – contact time;

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