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=== **ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY** ===

New Models of Catalyst Deactivation by Coke:
I. Multilayer Coke Formation via the Consecutive Mechanism

N. M. Ostrovskii

Boreskov Institute of Catalysis (Omsk Branch), Siberian Division, Russian Academy of Sciences, Omsk, Russia

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Abstract—The equations for deactivation during multilayer coke formation occurring via consecutive addition are derived. This mechanism is true for many oxide acid catalysts. The available linear and exponential relations between the activity and the coke concentration are the specific cases of these equations. The models were experimentally supported for dehydrogenation, isomerization, and reforming.

INTRODUCTION

Catalyst coking is the most common reason for their deactivation.

The necessity of preventing catalyst coking largely determines the technology, instrumentation, and economics of many large-scale processes, such as cracking, reforming, dehydrogenation, etc.

In catalytic cracking, ~3–6% of a raw material is converted into coke and burnt off during catalyst regeneration. In the United States alone, this makes up 10–15 million tons of vacuum gas oil a year and is nearly identical to the capacity of all cracking plants in Russia. The regenerator comprises 60–70% of a reactor unit, and the expense for catalyst coking and regeneration is more than 80% of all operating costs of the process.

Catalyst coking in gasoline reforming makes it necessary to conduct the process under high pressures and in an excess of hydrogen, that is, under thermodynamically non-optimal conditions. For the same reason, reactors were packed with a 20–50-fold excess of a catalyst to allow its operation for 0.5–1 year before regeneration.

Coke formation on catalysts occurs via different mechanisms [1–6], including consecutive addition or a consecutive mechanism [3], the carbide-cycle mechanism [1, 7], and the compensated decomposition mechanism [8, 9].

However, the mechanism of active site deactivation by coke is much more important for catalysis than the mechanism of its formation. Taking this into account, we consider here mainly how the activity of catalysts changes during their coking.

AVAILABLE MODELS

Voorhies [10] was the first to quantitatively describe catalyst coking for catalytic cracking based on the theory of topochemical reactions:

$$C_C = At^n, \qquad (1)$$

where C_C is the coke concentration, g/g; t is time; and A and n are the formal parameters.

Froment and Bischoff [11, 12] introduced the activity parameter ($\Phi = k/k_0$) that related the reaction rate constants on deactivated (k) and fresh (k_0) catalysts and considered it as a function of the coke concentration. The Φ function can be

linear: $\quad \Phi_1(C_C) = 1 - \gamma C_C, \qquad (2)$

exponential: $\quad \Phi_2(C_C) = \exp(-\gamma C_C), \qquad (3)$

hyperbolic: $\quad \Phi_3(C_C) = 1/1(1 + \gamma C_C), \qquad (4)$

where γ is the experimental parameter.

These relations were used later in many studies to describe dehydrogenation, cracking, etc. The first two functions were subsequently verified in terms of coke formation mechanisms.

The linear dependence follows from the model [13] for formal one-layer coke deposition (independently of the layer thickness). In this case, $\Phi_1 = 1 - C_C/(C_C)_\infty$, where $(C_C)_\infty$ is the maximal coke concentration.

Exponential relation (3) can be obtained from the multilayer scheme of coke formation upon certain assumptions [14, 15].

These relations are often used to estimate the catalyst activity as a function of its service life. For exam-

ple, the irreversible deactivation of cracking catalysts is sometimes calculated by the equations [16]

$$A_t = A_0 \exp(-k_A t), \quad A_t = A_0/(1 + k_A t^n), \qquad (5)$$

where A_0 and A_t are the activities of the fresh catalyst and that used for t hours, respectively; n is the exponent ($n = 0.5$ for laboratory conditions at 650–840°C); and k_A is the formal rate constant for deactivation.

Strictly speaking, one can describe catalyst deactivation by coke without the relations between the catalyst activity and its concentration. The model can be represented exclusively in the activity terms (a):

$$-\mathrm{d}a/\mathrm{d}t = f(C, T)a^n. \qquad (6)$$

where $a = r/r_0$ is the ratio of the current (r) and initial (r_0) reaction rates.

Upon integration, the activity is expressed in terms of the time and conditions of the catalyst operation $a = F(x, T, t)$. These models, usually referred to as the Levenshpil models, are also true for deactivation by coke and widely used for many processes.

Moreover, models (6) are more convenient for describing the experiments and optimizing the processes than models (2)–(4) because they contain only easily measurable parameters (a, t) and lack the coke concentration (C_C), which can be measured on a working catalyst in only a few processes.

Nevertheless, the coke concentration (or, the poison concentration during catalyst poisoning) is a more informative characteristic of the catalyst state than the time of its operation or the amount of the converted raw material. Therefore, the relations $a = \Phi(C_C)$ are necessary for the analysis of the reasons and the nature of deactivation (i.e., to elucidate the mechanism of coke action).

Linear Dependence

It is obvious from general considerations that one should know or assume the coke deposit structure to determine the function $a = \Phi(C_C)$. Indeed, if Θ_P is the fraction of the deactivated surface, the coke concentration can be calculated from the equation:

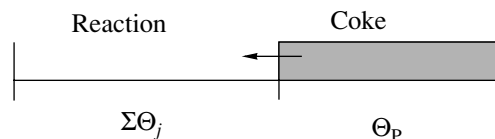$$C_C = \Theta_P \delta S_{sp} h \rho_C, \qquad (7)$$

where δS_{sp} is the fraction of the specific surface of a catalyst capable of coking (m²/g), and ρ_C and h are the density (g/m³) and thickness (m) of coke deposits, respectively.

If the h and ρ_C values remain unchanged during deactivation, an increase in the coke concentration is exclusively due to an increase in the Θ_P parameter. Although this mechanism is not very probable, it is still the only one that results in the linear dependence between the a and Θ_P parameters. It is easy to verify that $\delta S_{sp} h \rho_C = C_M$ is the maximal coke concentration on

the catalyst. Then, we obtain $\Theta_P = C_C/C_M$ and, taking into account that $a = 1 - \Theta_P$ [17],
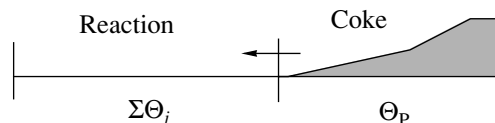
$$a = 1 - C_C/C_M, \quad \text{or} \quad a = 1 - \gamma C_C, \qquad (8)$$

where $\gamma = 1/C_M$. This linear relation accepted in [13] indicates that the thickness of the coke deposits remains unchanged during catalyst operation and that only the surface area covered with coke increases. Formally, this can be represented as follows:

This is implicit assumption when the linear relation $a = 1 - \gamma C_C$ is used.

In fact, coke deposits thicken and grow in all coke formation mechanisms. Therefore, the distribution of their thickness with time or the Θ_P value (which is the same) is always observed:

There are two prerequisites for linear relation (8) in this case. The first one is the monolayer or monomolecular nature of coke formation. The second is the avalanche-like coking that implies the slow formation of the first layer followed by the nearly instantaneous formation of the next layers. This leads to relation (8). The monolayer coke formation indicates that, upon blocking an active site by a coke precursor, further coke formation, if any, is very slow. Coke deposit growth in this case occurs exclusively along the horizontal direction. Then

$$a = 1 - C_C/C_m, \qquad (9)$$

where C_m is the capacity of the monolayer coke coverage, g/g.

Let us estimate the C_m values. The composition of coke deposits was analyzed in detail in [1]. For monolayer coke formation, the hydrogen/carbon ratio in coke is ~1. Then, the surface coke concentration is $(C_C)_s = (2–4) \times 10^{-4}$ g/m². Of course, coke only covers the working part of the surface and never all of the catalyst surface. This is usually 1–10% of the overall specific surface area. Then, $C_m = 0.07–0.12\%$ for catalysts with $S_{sp} = 15–30$ m²/g and $C_m = 0.5–1.5\%$ for those with $S_{sp} = 100–300$ m²/g. In many processes with a short period between regenerations (cracking or dehydrogenation), less than 0.2–1% of coke is accumulated [1, p. 128], which is comparable to the C_m estimate. This explains why the linear a-vs.-C_C relation is often used to describe these processes.

This relation can also be substantiated more strictly. Equations (7) and (8) are true only when the rate of

coke accumulation is directly proportional to that of an increase in the deactivated surface fraction (Θ_P), that is, when $dC_C = C_m d\Theta_P$ or $dC_C = -C_m da$. In other words, the linear dependence requires that

$$dC_C/d\Theta_P = \text{const} = C_m. \qquad (10)$$

This equation is true until coke formation is limited by the blocking of a free surface ($1 - \Theta_P$).

Exponential Dependence

Despite the simplicity and validity of the linear relation, the experimental functions $a = \Phi(C_C)$ often differ from the linear one. This may be due to the following facts: multilayer deposition via the consecutive scheme, dendrite growth via the carbide cycle mechanism, the polyfunctional nature of catalysts, etc. Each of these leads to certain types of the function $a = \Phi(C_C)$, which will be derived below.

In all these cases, exponential relation (3) is often used because it satisfactorily approximates different nonlinear (power, hyperbolic, etc.) relations up to certain coke concentrations. Moreover, this relation is quite simple, illustrative and contains only one formal parameter (γ).

At the same time, the exponential relation has physical prerequisites and may be derived on the basis of the deactivation mechanism upon certain assumptions. Formally, the equation $a = \exp(-\gamma C_C)$ is true if

$$da/dC_C = -\gamma a. \qquad (11)$$

This, in turn, imposes some limitations on the form of differential equations for the catalyst activity and coke concentration. These two equations are closely related because both of them follow from the deactivation stages. Therefore, condition (11) is only fulfilled at

$$da/dt = -k_P a, \quad dC_C/dt = k_C, \quad \gamma = k_P/k_C, \quad (12)$$

where k_P and k_C are the rate constants for deactivation and coke formation of different dimensions, respectively.

In other words, the exponential relation $a = \exp(-\gamma C_C)$ corresponds to the case when the rate of coke formation remains unchanged and independent of the catalyst activity. This is possible when coke is deposited on both active and deactivated sites at the same rate.

The equality of the rate constants for coke formation on the active and coked surfaces (which was assumed to verify Eq. (3)) seems unlikely. Therefore, the exponential relation should be considered as formal, and its wide application can be attributed to both the formal convenience and acceptable approximation of the true, more complex relations.

Thus, the use of Eq. (3) is quite reasonable for both the description of the experimental data and process optimization within the given C_C range. However, this relation cannot be used to identify the deactivation

mechanisms and, especially, to analyze the limiting cases of coke formation.

Probability Model

Beeckman and Froment [18] developed a probability model of catalyst coking that implies coke deposition on the active and coked surfaces. In this case, the catalyst activity is the product of two probabilities:

$$a = \varphi_A = PS. \qquad (13)$$

where S is the probability that the active site is not covered with coke; P is the probability that the active site is not locked due to pore congestion.

Pore congestion is assumed to occur when the coke deposits attain the pore size. The coke concentration is expressed as follows:

$$dC_C/dt = C_t \alpha M_C P S r_s^0 + P(1 - S)r_p, \qquad (14)$$

where C_t is the overall number of the active sites; α is the coke deposit density, moles of coke/moles of active sites; M_C is the molecular weight of the coke deposits, g/mol; r_s^0 is the initial rate of blocking the active sites (so that $S = \exp(-r_s^0 t)$); and r_p is the rate of coke growth (polymerization), g g^{-1} h^{-1}.

Unfortunately, Beeckman and Froment [18] failed to obtain any expression relating the catalyst activity to the coke concentration because of the model complexity. Time variations in the activity may be calculated from the following equations:

$$\varphi_A = \exp(-r_s^0 t) \quad \text{for} \quad t < t_{bl}, \qquad (15a)$$

$$\varphi_A = \exp(-r_s^0 t)(1 - e^{-Q})/Q,$$
$$Q = \sigma L[1 - \exp(-r_s^0(t - t_{bl}))] \quad \text{for} \quad t > t_{bl}, \qquad (15b)$$
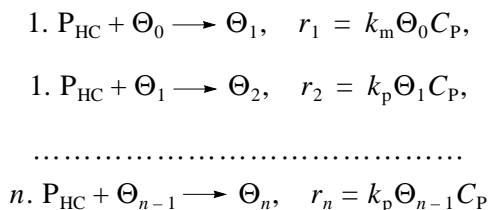
where t_{bl} is the time in which the coke macromolecule attains the pore size and blocks it and σL is the probability of active site localization in a pore of length L.

The calculations in terms of this model give the relations $a = \Phi(C_C)$ similar to the experimental one at $\sigma L \leq 1$. At $\sigma L > 1$, the shape of the nonlinear curves is determined by the porous structure of the catalyst grain [18]. The model is used to describe deactivation during 1-butene dehydrogenation on an Al–Cr catalyst [19]. Only ~15% of the active surface is blocked because of pore coverage with coke. This occurs in the first seconds of the process when ~0.01% of coke is accumulated. Marin et al. [19] showed that there is no need to apply this rather complex model to ordinary catalysts. However, it seems useful for zeolite catalysts.

MODEL OF MULTILAYER COKE FORMATION

Let us now consider the model of multilayer coke formation suggested for the consecutive mechanism

and partially described in [14, 15]. The equations of this model were derived based on the following scheme:

$$1.\ P_{HC} + \Theta_0 \longrightarrow \Theta_1, \quad r_1 = k_m\Theta_0 C_P,$$

$$1.\ P_{HC} + \Theta_1 \longrightarrow \Theta_2, \quad r_2 = k_p\Theta_1 C_P,$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

$$n.\ P_{HC} + \Theta_{n-1} \longrightarrow \Theta_n, \quad r_n = k_p\Theta_{n-1}C_P$$

Here Θ_n is the surface fraction occupied by n coke layers; Θ_0 and Θ_P are the overall fractions of the free and coked surfaces, respectively; P_{HC} is hydrocarbon, the coke source; C_P is its concentration; and k_m and k_p are the rate constants for the formation of the first (monolayer) and next coke layers, respectively.

The fractions of the active and coked surfaces may be expressed as follows:

$$\Theta_0 = 1 - \Theta_P, \quad \Theta_P = \sum_{n=1}^{N}\Theta_n. \qquad (16)$$

The rate of the first stage is actually proportional to the fraction of the surface occupied by an intermediate (Θ_j) involved in deactivation rather than to the fraction of the overall free surface $\Theta_0 = \sum\Theta_j$. However, this simplification does not influence the result because $\Theta_j = \Theta_j^0(1 - \Theta_P)$ [17] and Θ_j^0 is obviously included into the k_m parameter.
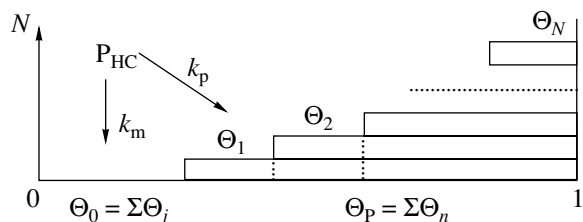
The overall rate of coke accumulation is the sum of the rate of monolayer formation and the sum of the rates of coke deposition on the next layers:

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_m C_P\Theta_0 + k_p C_P\sum_{n=2}^{N}\Theta_{n-1}, \qquad (17)$$

where ξ is the weight of coke formed from 1 mol of a hydrocarbon or its ability of coke formation (g/mol).

In view of Eq. (16), this equation takes the form:

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_m C_P(1 - \Theta_P) + k_p C_P(\Theta_P - \Theta_N). \qquad (18)$$

Scheme 1.

The activity depends on the formation of only the first layer, which blocks active sites. Then the Θ_P parameter may be expressed as follows:

$$\frac{C_m}{\xi}\frac{d\Theta_P}{dt} = k_m C_P(1 - \Theta_P). \qquad (19)$$

Here C_m is the monolayer capacity (g/g), that is, the maximal coke amount on the catalyst in the case of monolayer coke formation. Let us assume that the maximal capacity of every next layer takes the same value.

The relationship between the catalyst activity and the coke concentration may be obtained only upon the simultaneous solution of Eqs. (18) and (19). This is hampered by the second term in Eq. (18), which depends on both the Θ_P and Θ_N parameters (Θ_N is the fraction of the surface occupied by N coke layers). The main challenge in deriving the equation for deactivation in the case of multilayer coke formation is in eliminating the Θ_N parameter or expressing it in terms of other parameters. The simplest way to overcome this difficulty is to assume the absence of the last Nth layer and further coke formation over the whole surface of the coke deposits already formed. This assumption indicates infinite coke formation and seems to be poorly justified. However, it will be shown later that it is still quite reasonable at real coke concentrations.

Model of Infinite Coke Formation

If the coke deposits grow all over their surface, the rate of this growth is proportional to the Θ_P parameter within the framework of the mechanism represented in Scheme 1. Then, Eq. (17) takes the form

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_m C_P\Theta_0 + k_p C_P\Theta_P. \qquad (20)$$

In accordance with Eq. (18), this formally means that $\Theta_N = 0$. As before, in this case, $\Theta_0 = (1 - \Theta_P)$, and Eq. (19) for the Θ_P parameter remains the same. Now one can easily solve the system of Eqs. (19)–(20). Let us divide Eq. (20) by Eq. (19):

$$\frac{1}{C_m}\frac{dC_C}{d\Theta_P} = 1 + \frac{k_p}{k_m}\frac{\Theta_P}{(1 - \Theta_P)}.$$

If the mechanism of the main reaction is linear, then $a = 1 - \Theta_P$ and, hence,

$$-\frac{1}{C_m}\frac{dC_C}{da} = 1 + \varphi\frac{1-a}{a}, \text{ where } \varphi = k_p/k_m.$$

Upon integration, we obtain an equation that relates the a and C_C parameters [14, 15]:

$$C_C/C_m = (1 - \varphi)(1 - a) - \varphi\ln a. \qquad (21)$$

Figure 1 presents the plots corresponding to relation (21) at various φ values. The distinctive property of this equation is that it includes both the above linear and exponential relations as specific cases.

For insignificant coke formation on the coked surface at $k_p \longrightarrow 0$, we have $\varphi \longrightarrow 0$. Then, from Eq. (21), we obtain the linear relation $C_C/C_m = 1 - a$ or $a = 1 - C_C/C_m$ similar to relation (2).

The exponential relation (3) is obtained when the rate constants of the monolayer and multilayer coke formation are identical, as also follows from Eqs. (11) and (12), that is, at $\varphi = 1$. Then, taking into account Eq. (21), we have $C_C/C_m = -\ln a$ or $a = \exp(-C_C/C_m)$.

Let us consider how Eq. (21) is used to describe available (Fig. 2) and experimental data on heptane reforming (Fig. 3). Figure 2 presents the experimental data from [20] for 1-butene dehydrogenation into divinyl on the Cr_2O_3–Al_2O_3 catalyst and the results of their interpretation. The mechanism of consecutive addition on oxide catalysts at moderate temperatures [21] ensures the application of the model of multilayer coke formation to this process. Moreover, Fig. 2 shows that the coke concentration is much higher than the monolayer capacity $C_m = 1$–1.5%. The C_m value can approximately be estimated by depicting a straight line from the point $a = 1$ through the points with the minimal coke concentration to the C_C axis. The error in description the data by Eq. (21) is 3%, whereas, for the exponential (Eq. (3)) and hyperbolic (Eq. (4)) relations, it is 10 and 16%, respectively.

Figure 3 illustrates the interpretation of the experimental results on heptane reforming. In the case of bifunctional catalysts of reforming, coke is deposited on the acid sites of a support via the consecutive mechanism [23]. The number of these sites may be determined from both the intensity of the IR spectra of adsorbed CO on Al^{3+} ions and the related activity in paraffin (e.g., heptane) isomerization [22]. In the course of heptane reforming on Pt/Al_2O_3, heptane isomerization occurs in parallel with aromatization into toluene, cyclization into N_5 naphthenes, and hydrocracking. The isomerization activity in Fig. 3 was calculated as the relative rate of isomer (iso-C_7) formation during n-heptane reforming [22].

The specific feature of the process is the induction period of catalyst operation, during which hydrocracking predominates and coke is accumulated in noticeable amounts (C_C^0). At the end of the induction period, the aromatization rate attains its maximal value and the process is assumed to begin ($a = 1$). In this case, Eq. (21) takes the form:

$$(C_C - C_C^0)/C_m = (1 - \varphi)(1 - a) - \varphi \ln a. \qquad (22)$$

The error in the experiment interpretation according to Eq. (22) is 6%, whereas, in the case of the exponential relation, it is 16%.

Thus, assuming infinite coke formation, one can also derive an equation that satisfactorily describes the experimental results and that has undoubted advantages against the conventional exponential equation. This can be due to the fact that the coke concentrations in the real
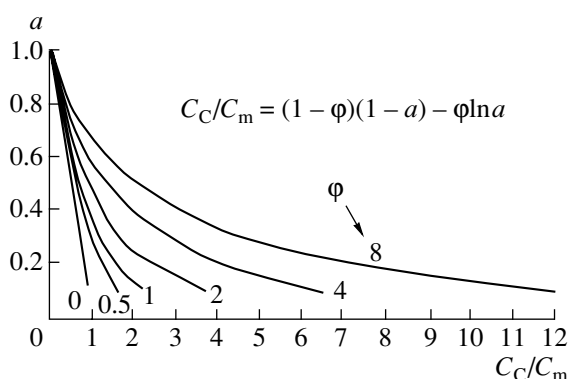
Fig. 1. The catalyst activity as a function of the coke concentration in the framework of the model of infinite multilayer coke formation.
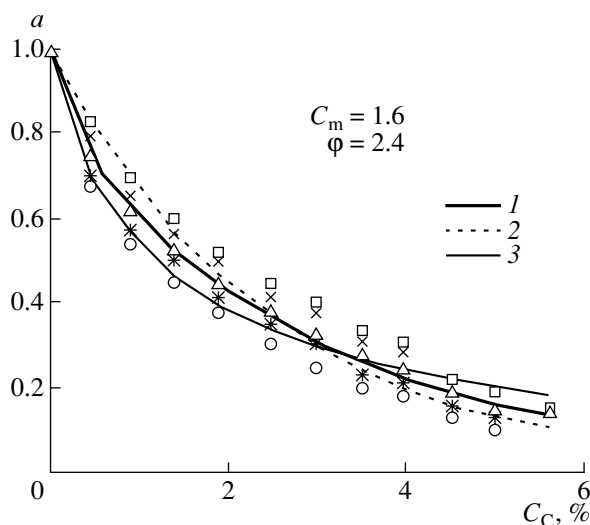

Fig. 2. The catalyst activity as a function of the coke concentration during butene-1 dehydrogenation on Cr_2O_3–Al_2O_3. The points correspond to the experimental data [20], and the lines represent the results of calculations by Eqs. (1) (21), (2) (3), and (3) (4).

processes are far from their limiting (maximal) values. When the activity is lower than 30–50% of its initial value ($a = 0.3$–0.5), the catalyst is regenerated and it cannot accumulate noticeable coke amounts, which preclude the application of this model.

Let us finally consider the cases of Eq. (21) for the nonlinear mechanisms of the main reaction and/or deactivation during binary interactions.

If only the deactivation mechanism is nonlinear, equations for the Θ_P parameter and coke concentration take the form (similar to Eqs. (19) and (20)) [24]:

$$\frac{C_m}{\xi}\frac{d\Theta_P}{dt} = \nu_p k_{m1} C_P (1 - \Theta_P)^2, \qquad (23a)$$

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_{m1} C_P (1 - \Theta_P)^2 + k_p C_P \Theta_P, \qquad (23b)$$
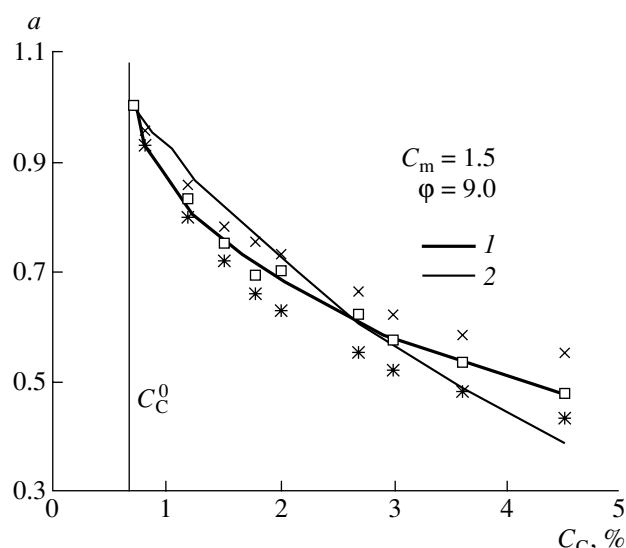
Fig. 3. The catalyst activity as a function of the coke concentration during heptane isomerization on Pt/Al_2O_3. The points correspond to the experimental data [22], and the lines represent the results of calculations by Eqs. (1) (22) and (2) (3). $C_C^0 = 0.7\%$.

where ν_p is a stoichiometric coefficient; and k_{m1} and k_p are the rate constants for the formation of the first and next coke layers, respectively.

Taking into account that $a = 1 - \Theta_P$ and $da = -d\Theta_P$, we arrive at

$$-\frac{1}{C_m}\frac{dC_C}{da} = \frac{1}{\nu_p} + \varphi_1\frac{1-a}{a^2}, \quad \varphi_1 = k_p/k_{m1}.$$

For binary interactions $\nu_p = 2$, and, upon integration, we obtain

$$C_C/C_m = (1/2 + \varphi_1/a)(1-a) + \varphi_1\ln a. \quad (24)$$

If the rate-limiting stage of the main reaction mechanism is nonlinear and taking into account the data of [24], we have $a = (1 - \Theta_P)^2$ and $da = -2(1 - \Theta_P)d\Theta_P$. Then,

$$1 - \Theta_P = \sqrt{a},$$
$$\Theta_P = 1 - \sqrt{a}, \text{ and } d\Theta_P = -da/2\sqrt{a}. \quad (25)$$

In the case of the linear deactivation mechanism, Eqs. (18) and (19) are true, and after substituting Eqs. (25) into them, we arrive at

$$C_C/C_m = (1 - \varphi)(1 - \sqrt{a}) - (\varphi/2)\ln a. \quad (26)$$

For the nonlinear deactivation mechanism, Eqs. (23) are true, and substituting Eq. (25) into them, we have

$$C_C/C_m = (1/2 + \varphi_1/\sqrt{a})(1 - \sqrt{a}) + (\varphi_1/2)\ln a. \quad (27)$$

For convenience, all four of these types of equations that relate the activity to the coke concentration in the

case of infinite multilayer coke formation are summarized in the table. The table also gives the limiting cases of these equations for monolayer ($\varphi \longrightarrow 0$) and uniform ($\varphi \longrightarrow 1$) coke formation. The plots corresponding to these equations are presented in Fig. 4 at several φ values.

Model of the Finite Number of Layers

In accordance with Eq. (18), coke deposition at the coked surface terminates when $(\Theta_P - \Theta_N) \longrightarrow 0$, that is, when the last layer covers the whole surface of the coke deposits (Θ_P). Then, there should be the maximal number of layers N and the related maximal coke concentration C_{max}. Therefore, the model of finite coke formation should include one of these parameters (N or C_{max}).

Lee [25] was the first to develop such a model. Based on a scheme similar to Scheme 1, he introduced a new function $f = \Theta_n/\Theta_{n-1}$. For the layers starting from the second layer, the f parameter changes with time but is independent of the layer number. In terms of the f parameter, the expression for the overall coked surface area $\Theta_P = \sum \Theta_n$ is

$$\Theta_P = \Theta_1\left(1 + \sum_{n=1}^{N} f^n\right), \text{ or } \Theta_P = \Theta_1\frac{1-f^N}{1-f}. \quad (28)$$

Within the framework of the model [25], the activity ($a = 1 - \Theta_P$) is related to the coke concentration (C_C) as follows:

$$\frac{C_C}{C_m} = (1-a)\left(\frac{1}{1-f} - \frac{Nf^N}{1-f^N}\right),$$
$$\varphi\frac{1-a}{a} = \frac{f(1-f^N)}{1-f}. \quad (29)$$

The f and N values should be determined by the simultaneous numerical solution of Eqs. (29), which is rather inconvenient in practice.

For infinite coke formation (i.e., if $N \longrightarrow \infty$), the model [25] gives:

$$\frac{C_C}{C_m} = (1-a)\left(1 + \varphi\frac{1-a}{a}\right). \quad (30)$$

The limiting case of monolayer coke formation (at $\varphi = 0$) coincides with that described by Eq. (21), that is, $a = 1 - C_C/C_m$.

At $\varphi = 1$, the model [25] gives the hyperbolic relation $a = 1/(1 + C_C/C_m)$, whereas Eq. (21) gives the exponential relation $a = \exp(-C_C/C_m)$. The comparison of these relations used to describe our experimental results (Fig. 2) and their application in other works provide evidence for the exponential relation. This also indicates that Eq. (21) has a more significant physical meaning than Eq. (30). Moreover, as shown above, the
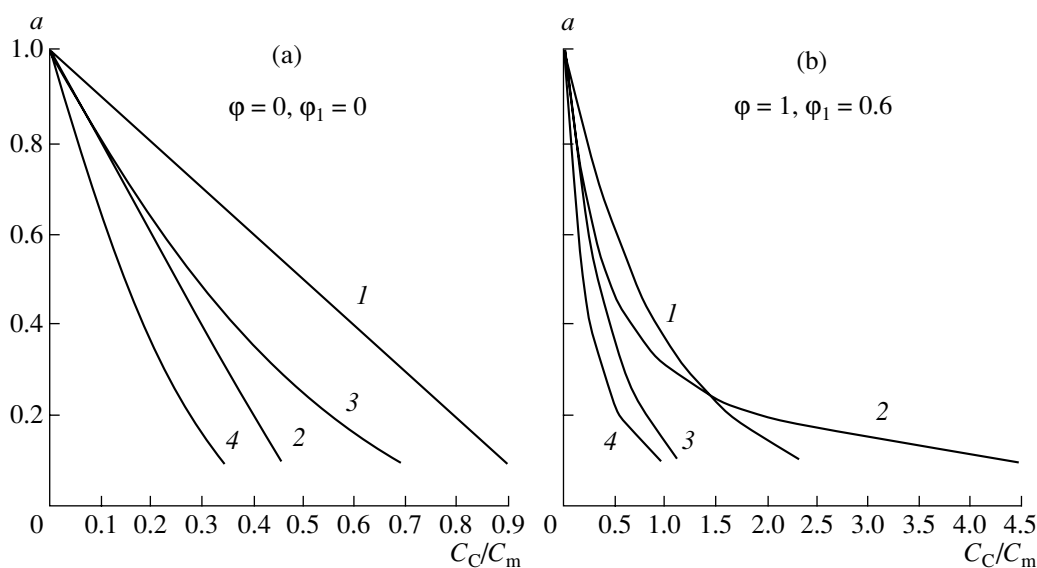
Fig. 4. The catalyst activity as a function of the coke concentration within the framework of the model of infinite multilayer coke formation (a) monolayer and (b) uniform deposition. Calculations by Eqs. (*1*) (21), (*2*) (24), (*3*) (26), and (*4*) (27).

exponential relation is directly derived from the deactivation equations.

Let us now consider another description of finite coke formation (based on Scheme 1) without the addi-

tional function *f*, which was partially reported in [14]. Let us try to represent the second term in Eq. (17) by the coke concentration. The effect of this term is observed only upon a dramatic (nearly linear) decrease

The catalyst activity as a function of the coke concentration on multilayer coke formation

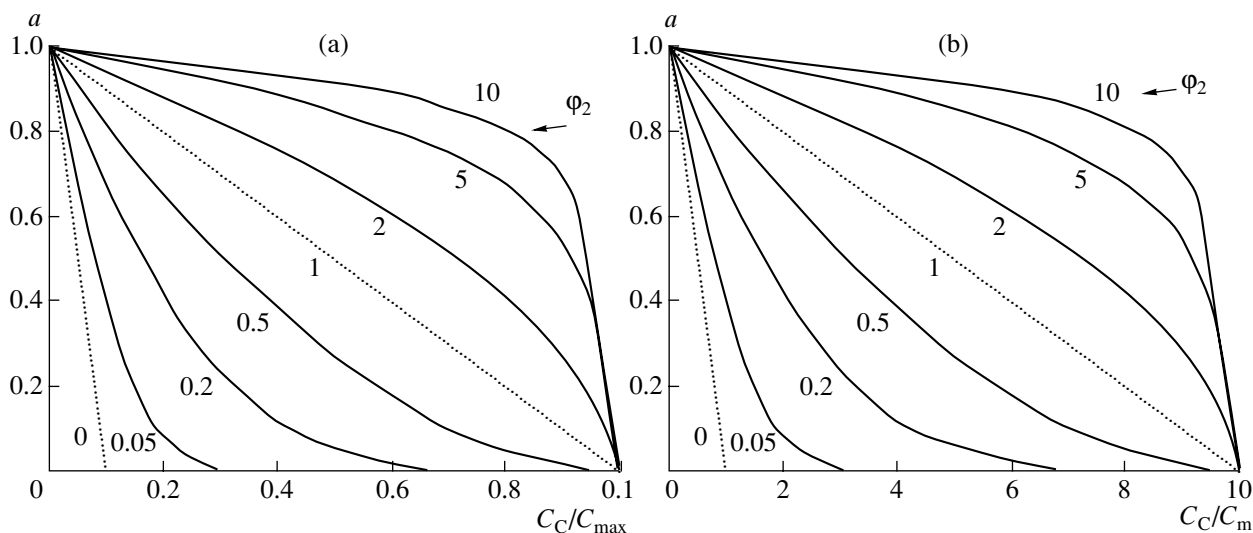| Mechanism of		Relation between the activity (*a*) and the coke concentration (C_C)	
main reaction	deactivation		
Linear $a = 1 - \Theta_P$ $d\Theta_P = -da$	Linear $\dfrac{d\Theta_P}{dt} \sim (1 - \Theta_P)$	$\dfrac{C_C}{C_m} = (1 - \varphi)(1 - a) - \varphi \ln a$ $\varphi = 0: \quad a = 1 - C_C/C_m$ $\varphi = 1: \quad a = \exp(-C_C/C_m)$	(21)
	Nonlinear $\dfrac{d\Theta_P}{dt} \sim (1 - \Theta_P)^2$	$\dfrac{C_C}{C_m} = \left(\dfrac{1}{2} + \dfrac{\varphi_1}{a}\right) + (1 - a) - \varphi_1 \ln a$ $\varphi_1 = 0: \quad a = 1 - 2C_C/C_m$ $\varphi_1 = 1: \quad \dfrac{C_C}{C_m} = (1 - a)\dfrac{2 + a}{2a} + \ln a$	(24)
Nonlinear $a = (1 - \Theta_P)^2$ $d\Theta_P = -\dfrac{da}{2\sqrt{a}}$	Linear $\dfrac{d\Theta_P}{dt} \sim (1 - \Theta_P)$	$\dfrac{C_C}{C_m} = (1 - \varphi)(1 - \sqrt{a}) - \dfrac{\varphi}{2} \ln a$ $\varphi = 0: \quad a = (1 - C_C/C_m)^2$ $\varphi = 1: \quad a = \exp(-2C_C/C_m)$	(26)
	Nonlinear $\dfrac{d\Theta_P}{dt} \sim (1 - \Theta_P)^2$	$\dfrac{C_C}{C_m} = \left(\dfrac{1}{2} + \dfrac{\varphi_1}{\sqrt{a}}\right)(1 - \sqrt{a}) - \dfrac{\varphi_1}{2} \ln a$ $\varphi_1 = 0: \quad a = (1 - 2C_C/C_m)^2$ $\varphi_1 = 1: \quad \dfrac{C_C}{C_m} = (1 - \sqrt{a})\dfrac{2 + \sqrt{a}}{2\sqrt{a}} + \dfrac{1}{2} \ln a$	(27)

Fig. 5. Activity as a function of the coke concentration calculated by (a) Eq. (35), $C_C/C_{max} = 0.1$ and (b) Eq. (37), $N = 10$.

in the activity even in the case of infinite coke formation (Figs. 1 and 4). In this case, the overall fraction of the coked surface changes slowly, but coke is still accumulated over it. The surface fraction occupied by $(n - 1)$ coke layers is taken to be proportional to the $(C_m - C_n)$ difference, where C_n is the coke concentration in the nth layer that covers the $(n - 1)$th layer:

$$\Theta_{n-1} \sim (C_m - C_n)/C_m. \tag{31}$$

Substituting this expression and $\Theta_0 = 1 - \Theta_P$ into (17), we arrive at

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_m C_P(1 - \Theta_P) + kC_P\left(\sum_{n=2}^{N} C_m - \sum_{n=2}^{N} C_n\right)/C_m. \tag{32}$$

Note that $k \neq k_p$ because of the approximate nature of Eq. (31).

The sums in Eq. (32) may be expressed as follows:

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

and their difference may be rearranged to:

$$(C_{max} - C_m) - (C_C - C_1) = (C_{max} - C_C) - (C_m - C_1).$$

Taking into account that $\Theta_0 = (C_m - C_1)/C_m$, as follows from Scheme 1, and that $\Theta_0 = 1 - \Theta_P$, as follows from Eq. (16), we have $C_m - C_1 = C_m\Theta_0 = C_m(1 - \Theta_P)$. Then the difference in the sums in Eq. (32) is $(C_{max} - C_C) - C_m(1 - \Theta_P)$. Upon the relevant substitutions, Eq. (32) takes the form:

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_m C_P(1 - \Theta_P)$$
$$+ kC_P[(C_{max} - C_C) - C_m(1 - \Theta_P)]/C_m,$$

or

$$\frac{1}{\xi}\frac{dC_C}{dt} = (k_m C_P - kC_P)(1 - \Theta_P)$$
$$+ kC_P(C_{max} - C_C)/C_m. \tag{33}$$

The Θ_P parameter is still expressed by Eq. (19) because deactivation is also caused by the formation of only the first layer of coke deposits. Dividing Eq. (33) by Eq. (19), we obtain:

$$\frac{1}{C_m}\frac{dC_C}{d\Theta_P} = \left(1 - \frac{k}{k_m}\right) + \frac{k}{k_m}\frac{(C_{max} - C_C)}{(1 - \Theta_P)C_m}.$$

In the activity terms $a = 1 - \Theta_P$, $d\Theta_P = -da$, this equation may be rearranged to:

$$-\frac{dC_C}{da} = (1 - \varphi_2)C_m + \varphi_2\frac{C_{max} - C_C}{a}, \tag{34}$$

where $\varphi_2 = k/k_m$.

Note that the parameters $\varphi = k_p/k_m$ in Eq. (21), $\varphi_1 = k_p/k_{m1}$ in Eq. (24), and $\varphi_2 = k/k_m$ in Eq. (34) have the same physical meaning, but different numerical values.

Equation (34) is a linear nonuniform equation, the solution to which is

$$\frac{C_C}{C_{max}} = 1 - \frac{C_m}{C_{max}}a - \left(1 - \frac{C_m}{C_{max}}\right)a^{\varphi_2}. \tag{35}$$

Equation (35) may be represented in another form to compare with Eqs. (21)–(27):

$$\frac{C_C}{C_m} = \frac{C_{max}}{C_m} - a - \left(\frac{C_{max}}{C_m} - 1\right)a^{\varphi_2}. \tag{36}$$

Taking into account that the C_{max}/C_m ratio is equal to the overall number of the coke layers N, Eq. (36) may also be rearranged to:

$$\frac{C_C}{C_m} = N - a - (N-1)a^{\varphi_2}. \qquad (37)$$

Figure 5 presents the plots corresponding to Eqs. (35) and (37) at various φ_2 values. The limiting cases of Eq. (35) are

(1) $\varphi_2 = 0$: $C_m = C_{max}$. As for the other equations considered above, we obtain the linear ratio $a = 1 - C_C/C_m$;

(2) $\varphi_2 = 1$. We obtain another linear relationship $a = 1 - C_C/C_{max}$.

Figure 5 illustrates these two limiting cases. The curves between the straight lines $\varphi_2 = 0$ and $\varphi_2 = 1$ are similar to those obtained within the framework of the model of infinite coke formation (Fig. 1).

The relations at $\varphi_2 > 1$ are of special interest. They correspond to the case of substantial coke deposition at an insignificant decrease in the activity. Nevertheless, the long period of insignificant deactivation is followed by its avalanche decrease or so-called critical deactivation. Such deactivation is often observed in practice [26, 27] and may be described in the framework of the model of infinite coke formation. Therefore, relations (35)–(37) are more likely in the processes with prolonged catalyst operation (because of its self-regeneration), especially after catalyst regeneration.

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