IV RUSSIAN CONFERENCE WITH THE PARTICIPATION OF CIS COUNTRIES ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY

New Models of Catalyst Deactivation by Coke: II. Coking of Supported Platinum Catalysts

N. M. Ostrovskii

Boreskov Institute of Catalysis (Omsk Branch), Siberian Division, Russian Academy of Sciences, Omsk, Russia
Received September 18, 2000

Abstract—Metal and support deactivation upon the coking of supported metal catalysts occurs via different mechanisms. Several models of coking are presented. The most complete complex model is developed for supported platinum catalysts. It implies multilayer coke formation on support, the rapid formation of polymeric coke capable of self-regeneration by hydrogen directly in the course of reaction on platinum, and the slow conversion of this coke into graphite-like coke, which is removed only by oxidative regeneration. The models are experimentally supported for cyclohexane dehydrogenation.

INTRODUCTION

Deactivation of supported catalysts by coke has a number of specific features that influence its kinetics and the dependence of the catalyst activity on the coke concentration [1]. This is most clearly seen for the low-percentage supported metal catalysts used in reforming (Pt, Pt–Re, Pt–Sn on Al_2O_3), selective hydrogenation (Pd, Pd–Cu, and Pd–Au on Al_2O_3 and carbon), isomerization (Pt/Al_2O_3 + zeolite), etc.

The most important peculiarity of coking is that the main reaction predominantly occurs on metal, whereas coke is deposited on both metal and support. Moreover, only the overall coke concentration, which mostly consists of coke localized on support, can be measured.

Specific features of coking of supported metal catalysts are analyzed in many papers. Franck and Martino [2] reviewed numerous data on reforming catalysts. When studying the poisoning of metal catalysts, Trimm [3] gave particular attention to the coke formation mechanisms. Sarkany *et al.* [4] considered the types of coke formed on platinum and support and the difference in their formation and speculated the migration of coke precursors to support. Cabrol and Oberlin [5] examined the structure of coke scales and found them to have the same structure independent of their localization.

Bursian and Kogan [6] analyzed in detail coke redistribution between platinum and support under the action of modifiers (Sn, In, etc.) and discussed the nature of the coke-preventing effect during the modification of platinum catalysts of reforming, isomerization, and dehydrogenation.

Biswas *et al.* [7] considered the dynamics of the accumulation of two types of coke on platinum: reversible (which is rapidly formed during catalyst running-in) and irreversible. They also studied in detail the role of hydrogen in the self-regeneration of a reforming catalyst and proposed a mechanism and model of coke formation on platinum. Buyanov *et al.* [8–10] suggested a new mechanism of compensated decomposition during coke formation on platinum-group metals. In the framework of this mechanism, coke formation involves a number of intermediate half demolished hydrocarbon forms up to carbon, which can be either inserted into the near-surface layer of metal or converted into graphite. The slight dissolution of carbon in platinum was also observed in [11, 12]. It occurs at high temperatures with carbon diffusing to the surface upon cooling [11]. In the case of nickel and iron, carbon diffuses inside the metal crystallites, whereas, on platinum, carbon [13] and its precursors [14] diffuse over the surface.

The activation energy of surface diffusion is 25–35 kcal/mol [13], which is comparable to the conventional activation energies for many processes of hydrocarbon conversion. The specific feature of carbon units on platinum is that they are incorporated into active sites of certain reactions [14, 15]. In other words, carbon participates in active site formation under the action of the reaction mixture.

The findings of these and many other works provide a rather comprehensive description of the nature of the deactivation of supported catalysts and the mechanisms of coke deposition and redistribution.

However, to elucidate the deactivation kinetics, it seems insufficient just to describe the nature of phenomena and the mechanisms. Also necessary are the mathematical equations that allow the qualitative and quantitative analysis. The available models describe how the activity of a supported catalyst changes with time [16, 17] and do not describe its dependence on the coke concentration.

In this work, necessary models of different detail are presented that relate the activity of supported metal (Pt) to the overall coke concentration on a catalyst.
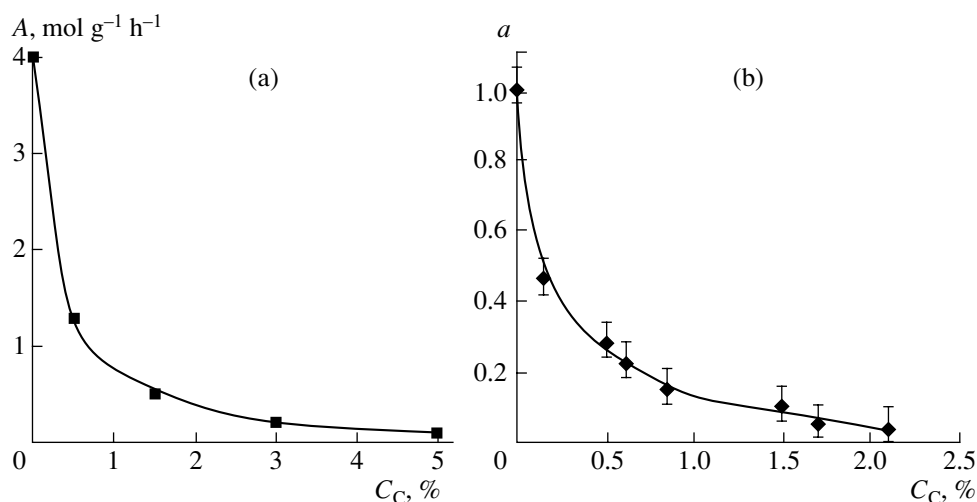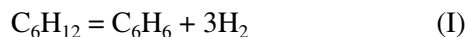
Fig. 1. The catalyst (Pt/Al$_2$O$_3$) activity (A, a) as a function of the coke concentration: (a) from [2] and (b) from [20].

ROUGH MODEL OF SEPARATE COKING

Let us consider as an example of how the activity of supported catalysts Pt/Al$_2$O$_3$ changes with the coke concentration in the course of cyclohexane dehydrogenation (I) (Fig. 1).

$$C_6H_{12} = C_6H_6 + 3H_2 \qquad \text{(I)}$$

The activity is completely suppressed at 0.07–0.2% of coke deposited only on platinum [18, 19]. Figure 1 shows that, because dehydrogenation occurs only on a metal and the activity is rather high at these concentrations, coke is either localized on the support or has such a structure that only its small part blocks the platinum surface.

Thermogravimetric studies [2, 19, 21] suggested that the most part of coke is deposited on support. Comprehensive investigations [5] showed that coke islands formed under reforming conditions are polyaromatic units with a size of ~2 nm, a ring number of at most 12, and a thickness of 2–3 monolayers independently of the coke concentration.

All these data strongly suggest that nonlinear curves in Fig. 1 cannot be described in terms of the models of multilayer coke formation [22]. The decisive factor in this case is coke distribution between metal and support. To be certain, it is desirable to verify, in the framework of the monolayer assumption, that coke deposition on support causes nonlinear relations similar to those presented in Fig. 1. Moreover, for the sake of simplicity, the coke concentration on metal may be neglected because of the low metal concentration in a catalyst (0.5%).

Then, the equation for the fraction of the deactivated platinum surface (Θ_P) should be similar to Eq. (19) in [22]:

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

Taking into account the above assumptions, Eq. (18), [22] as applied to the overall coke concentration on a catalyst (C_C), can be transformed into:

$$\frac{1}{\xi}\frac{dC_C}{dt} = k_s C_P(C_{max} - C_C)/C_{max}, \qquad (2)$$

where C_m is the capacity of the monolayer coke coverage of the active surface of supported metal; k_m is the rate constant for deactivation (and coke formation) on metal; k_s is the rate constant on support; C_{max} is the maximal coke concentration on a catalyst; C_P is the hydrocarbon (coke source) concentration; and ξ is the weight of the coke formed from 1 mol of hydrocarbon, g/mol.

Dividing the first equation by the second, we obtain

$$\frac{d\Theta_P}{dC_C} = \frac{k_m}{k_s}\frac{C_{max}}{C_m}\frac{1 - \Theta_P}{C_{max} - C_C},$$

$$\text{or } \frac{da}{dC_C} = -\varphi\frac{a}{C_{max} - C_C},$$

where $\varphi = \dfrac{k_m}{k_s}\dfrac{C_{max}}{C_m}$, and $a = r/r_0$ is the relative activity equal to the ratio of the current and initial reaction rates. For the linear mechanisms, $a = 1 - \Theta_P$ [23].

Upon integration, this equation takes the form:

$$\ln a = \varphi\ln\left(1 - \frac{C_C}{C_{max}}\right), \text{ or } a = \left(1 - \frac{C_C}{C_{max}}\right)^{\varphi}. \qquad (3)$$

This formula was first derived in [23] and subsequently used to describe the experimental data in [18, 24]. Model (1)–(2) may be referred to as metal deactivation during support coking. Its specific feature is that coke formation on metal is taken into account only when describing the catalyst activity (Eq. (1)) and neglected when considering the coke concentration (Eq. (2)). In other
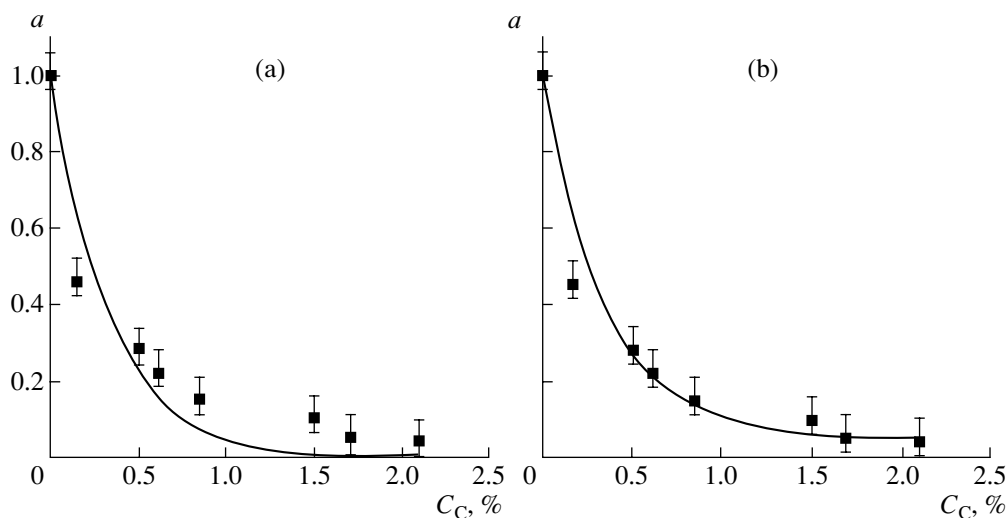
Fig. 2. The catalyst activity as a function of the coke concentration. A solid line corresponds to the description by Eq.: (a) (3) and (b) (7); points represent the experimental data from [20]. $C_{max} = 5\%$, $k_m/k_s = 13$.

words, the activity depends on metal coking, whereas the coke concentration depends on support coking.

It is clear that this model is rather rough, although it is the only one suggesting that the nonlinear dependence of the catalyst activity on the coke concentration in supported catalysts is largely due to the dual nature of catalysts rather than to the coke deposit structure.

Figure 2 compares the experimental data with the results of calculations by Eq. (3). The ratio $\varphi = k_m C_{max}/k_s C_m$ indicates how many times metal coking is quicker than that of the support. For the data in Fig. 2, $\varphi = 12$–14. Figure 2 also shows that Eq. (3) does not provide any quantitative interpretation of the experimental results because of the rough nature of the model. Moreover, this model neglects catalyst self-regeneration by hydrogen, which makes the deactivation of supported metal partially reversible.

The Effect of Self-Regeneration

Self-regeneration involves phenomena resulting in the regeneration of active sites in the course of the catalytic processes under the action of the reaction mixture rather than in a separate regeneration period.

Self-regeneration is typical of many commercial processes accompanied by catalyst deactivation. For example, to reduce catalyst coking, some processes are conducted in an excess of water vapors (olefin and ethylbenzene dehydrogenation) or hydrogen (reforming, hydrotreatment, hydrocracking, etc.). Substances of the reaction mixture (water vapor or hydrogen) react with the coke precursors, sulfur, and other contaminants to regenerate the catalytic properties of active sites and, thus, to prolong the time between catalyst regeneration 100–1000 times.

A general rate law for deactivation accompanied by self-regeneration was derived in [25] and can be used in the above case if the reaction occurs only over a supported component.

Taking into account the dimensions of parameters typical of deactivation by coke, the equation can be rewritten in terms of Θ_P as follows:

$$\frac{C_m}{\xi}\frac{d\Theta_P}{dt} = k_m C_P(1 - \Theta_P) - k_R C_R \Theta_P, \qquad (4)$$

where k_R is the rate constant for self-regeneration; C_R is the concentration of the component that ensures self-regeneration (in this case, hydrogen that favors the hydrogenation of coke precursors).

Transformations similar to those made in [25] give the equation of the activity (a):

$$\frac{C_m}{\xi}\frac{da}{dt} = -k_m C_P\frac{a - a_s}{1 - a_s}, \qquad (5)$$

where a_s is the steady-state activity, at which the rates of deactivation and self-regeneration are identical.

If the coke concentration on supported metal is still neglected, Eq. (2) remains unchanged. Dividing Eq. (5) by Eq. (2) gives

$$\frac{da}{dC_C} = -\frac{\varphi}{1 - a_s}\frac{a - a_s}{C_{max} - C_C}, \qquad (6)$$

where $\varphi = \dfrac{k_m}{k_s}\dfrac{C_{max}}{C_m}$.

Upon integration, we obtain the relation $a = \Phi(C_C)$ in the form:

$$a = a_s + (1 - a_s)\left(1 - \frac{C_C}{C_{max}}\right)^{\frac{\varphi}{(1-a_s)}}. \qquad (7)$$

Equation (7) fits the experimental data much better than Eq. (3), as follows from the comparison of Figs. 2a and 2b.

COMPLEX MODEL

Besides the obvious differences in the coking and deactivation of supported metal and support, a marked heterogeneity of coke formation on the metal itself is observed. This is typical of both supported crystallites [3, 7, 26] and single crystals [3, 12, 14]. Most researchers distinguish two different types of coke deposits on noble metals (largely, on platinum): (1) resin-like condensed substances (so-called polyenes [4] or polyarenes [27] with an H/C ratio of 1.5–2 and (2) dense, graphite-like coke [7, 8] with an H/C ratio of ~0.2.

These deposits differ in both structure and the deactivation action. Polymeric coke is readily removed by hydrogen and is, therefore, referred to as reversible [7], whereas graphite-like coke is called irreversible. The latter is not virtually hydrogenated by hydrogen, but undergoes slow gasification (which is 1000 times slower than the hydrogenation of reversible coke) [7]. The presence of reversible coke provides favorable conditions for the partial self-regeneration of platinum catalysts by hydrogen, thus ensuring their prolonged operation in reforming, isomerization, and dehydrogenation [21, 27, 28]. The major part of coke is formed on platinum in the first 1–2 h of reforming and then remains virtually unchanged [21, 29]. Nevertheless, the overall coke concentration on the catalyst is 10–20% in the end of its operation [7, 21]. This can be due to coke deposition on support.

Biswas *et al.* [7] studied the conditions and the rate of formation of both coke types on platinum and proposed a mechanism and a model to explain the experimental results:

$$\frac{dC_{rev}}{dt} = k_{rev}e^{-nC_{rev}} - (k_{irr} + k_h)C_{rev}, \qquad (8)$$

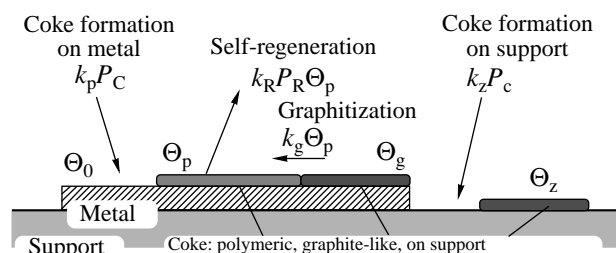$$\frac{dC_{irr}}{dt} = k_{irr}C_{rev} - k_g C_{irr}, \qquad (9)$$

where C_{rev} and C_{irr} are the concentrations of reversible and irreversible coke, respectively; k_{rev} and k_{irr} are the rate constants for their formation, respectively; k_h and k_g are the rate constants for reversible coke hydrogenation and irreversible coke gasification, respectively; and n is a formal model parameter.

The drawbacks of this model are neglecting coke deposited on support, the empirical first term in Eq. (8),

and the lack of the dependence between the coke concentration and the catalyst activity.

Mechanisms similar to that described in [7] were proposed in [8–10] (the mechanism of compensated decomposition) and [3] (the migration mechanism). Unfortunately, neither the mathematical models of the mechanisms, nor the chemical equations of the main steps are presented in those papers. The simultaneous consideration of these mechanisms can serve as a basis for the rather complete model of the deactivation of supported metal catalysts by coke. The first variant of such a model based on the mechanism of compensated decomposition was published in [24].

Here, I consider a more complete model and present its qualitative analysis. The mechanism of coke formation corresponding to this scheme can be represented as follows:

Here, Θ_0 is the fraction of the free metal surface; Θ_P is the fraction of the metal surface occupied by polymeric (or reversible) coke; Θ_g is the fraction of the metal surface occupied by graphite-like (or irreversible) coke; Θ_z is the fraction of the coked surface of support; P_C and P_R are the partial pressures of reactants that cause coke formation and self-regeneration, respectively; and k_p, k_g, and k_z are the rate constants for the formation of the relevant coke types.

The overall coke concentration on a catalyst (C_C) is equal to the sum of the concentrations of polymeric (C_p) and graphite-like (C_g) coke on metal, and coke localized on support (C_z):

$$C_C = C_p + C_g + C_z.$$

On the basis of Scheme 1, the rates of the formation of these coke types can be expressed as follows:

for polymeric coke (10)

$$dC_p/dt = \xi_p[k_p P_C(1 - \Theta_p - \Theta_g) - k_R P_R \Theta_p - k_g \Theta_p],$$

for graphite-like coke

$$dC_g/dt = \xi_g k_g \Theta_p, \qquad (11)$$

for coke on support

$$dC_z/dt = \xi_z k_z P_C(1 - \Theta_z), \qquad (12)$$

where ξ_p, ξ_g, and ξ_z are the weights of coke formed from 1 mol of the reactant (g/mol) proportional to the densities of the relevant coke types.

The overall rate of coke formation is

$$dC_C/dt = \xi_p[k_p P_C(1 - \Theta_p - \Theta_g) - k_R P_R \Theta_p]$$
$$- (\xi_p - \xi_g)k_g\Theta_p + \xi_z k_z P_C(1 - \Theta_z). \tag{13}$$

Equation (13) suggests that graphite-like coke changes the overall coke concentration only if $\xi_p \neq \xi_g$ because it is produced from the already formed, more porous polymeric coke. In most cases, this term can be neglected.

To describe deactivation, one should add the equation for the free surface (Θ_0) to the set of equations (10)–(12). If the overall reaction (or at least its rate-limiting step) occurs on metal, then $\sum \Theta_i = \Theta_0 = 1 - (\Theta_p + \Theta_g)$, and two equations (for the Θ_p and Θ_g parameters) are necessary to obtain a closed set of equations. These equations are similar to Eqs. (10) and (11):

$$\frac{C_m}{\xi_p}\frac{d\Theta_p}{dt} = k_p P_C(1 - \Theta_p - \Theta_g)$$
$$- k_R P_R \Theta_p - k_g \Theta_p, \tag{14}$$

$$\frac{C_m}{\xi_p}\frac{d\Theta_g}{dt} = k_g \Theta_p. \tag{15}$$

Taking into account that $d\Theta_0 = -d\Theta_p - d\Theta_g$, the equation for the free metal surface can be obtained by summation of Eqs. (14) and (15):

$$\frac{C_m}{\xi_p}\frac{d\Theta_0}{dt} = -k_p P_C(1 - \Theta_p - \Theta_g)$$
$$+ k_R P_R \Theta_p + (1 - \xi_g/\xi_p)k_g \Theta_p. \tag{16}$$

Obviously, Eq. (16) in this form is inconvenient for use and should be rearranged in terms of the relative activity (a).

For the linear mechanism of the main reaction, we have $a = \Theta_0 = 1 - \Theta_p - \Theta_g$. On the other hand, it is unimportant for the reaction whether or not Θ_p is converted into Θ_g because the active sites have already been blocked by polymeric coke (Θ_p). Moreover, $\xi_g/\xi_p \longrightarrow 1$ and, according to the data of [7, 14], $\xi_g/\xi_p \approx CH_{0.2}/CH_{1.5} \approx 0.9$. Therefore, the relevant term in Eq. (16) is small, and its effect at the first step of deactivation is negligible.

In the first rapid step at $t < t_s$, reversible coke is formed at a rate that quickly attains the value of the rate of self-regeneration by hydrogen [7, 26] at $t = t_s$. In the second slow step ($t > t_s$), a part of reversible coke is graphitized into the irreversible one.

The activity changes in a similar way. First, rapid deactivation occurs at a rate $k_p P_C(1 - \Theta_p)$ up to the attainment of the steady-state a_s value at $t = t_s$ when $k_p P_C(1 - \Theta_{ps}) = k_R P_R \Theta_{ps}$. Then, the activity slowly decreases at a rate $k_g \Theta_p$. This is in excellent agreement with the model of reversible deactivation accompanied by aging [25, 30]. The first, the second, and the third terms in Eq. (16) correspond to deactivation, self-regeneration, and aging, respectively.

Assuming that deactivation is pseudo-steady-state with respect to aging [25, 30], we have for the first step (at $t < t_s$) that $\Theta_g \approx 0$, $a \approx 1 - \Theta_p$, and $da \approx -d\Theta_p$. Then, from Eq. (16), we can derive an equation similar to Eq. (5):

$$\frac{C_m}{\xi_p}\frac{da}{dt} = -k_p P_C \frac{a - a_s}{1 - a_s} \text{ for } t < t_s, \tag{17}$$

where $a_s = k_R P_R/(k_p P_C + k_R P_R)$ at $t = t_s$.

In the second step (at $t > t_s$), coke graphitization, that is, the transformation of Θ_p into Θ_g, causes a shift of the equilibrium between the formation of polymeric coke and self-regeneration. Therefore, to maintain the equilibrium, the transformation of polymeric coke is compensated by its equivalent formation so that $d\Theta_g = -d\Theta_p$. Taking into account that, in this case, $a_s = 1 - \Theta_{ps}$, we have $a = a_s - \Theta_g$ and $da = -d\Theta_g$. Then, in view of Eq. (15), we arrive at:

$$\frac{C_m}{\xi_g}\frac{da}{dt} = -k_g a \text{ for } t \geq t_s. \tag{18}$$

The initial condition for this equation is $a = a_s$ at $t = t_s$.

Relation between the Activity and the Coke Concentration

This relation can easily be obtained by dividing Eq. (13) by Eq. (17) or (18).

When $t < t_s$, slow coke formation on support can be neglected. Then, substituting $a \approx 1 - \Theta_p$ and $\Theta_g \approx 0$ into Eq. (13) and dividing Eq. (13) by Eq. (17), we obtain $dC_C/da = -C_m$ and, consequently,

$$a = 1 - C_C/C_m \text{ for } t < t_s. \tag{19}$$

When $t > t_s$, deactivation and self-regeneration are at equilibrium and, therefore, the first two terms in Eq. (13) compensate each other. For the above reasons, the third term can be neglected. Upon substituting $\Theta_z = C_C/C_{max}$ in the fourth term (which is possible because of the predominating localization of coke on support), we arrive at

$$dC_C/dt \approx \xi_z k_z P_C(1 - C_C/C_{max}). \tag{20}$$

Dividing Eq. (20) by Eq. (18) and integrating the resulting equation with due regard to the fact that $a = a_s : C_C = C_s$, we have

$$a = a_s\left(\frac{C_{max} - C_C}{C_{max} - C_s}\right)^{\varphi_1 \frac{C_{max}}{C_m}}, \quad \varphi_1 = \frac{\xi_g k_g}{\xi_z k_z P_C}. \tag{21}$$

At low coke concentrations $C_C \ll C_{max}$, the right-hand side of Eq. (20) becomes constant, thus resulting in an exponential relation:

$$a = a_s \exp\left(\varphi_1 \frac{C_s - C_C}{C_m}\right) \text{ for } t > t_s. \qquad (22)$$

Equations (19), (21), and (22) are true for different steps of deactivation and coincide at $t = t_s$. In the step of reversible deactivation, temporal changes in the activity $a(t)$ are described by the exponential relation corresponding to Eq. (17), whereas the $a(C_C)$ function is linear. In the second slow step, both relations $a(t)$ and $a(C_C)$ are nonlinear and exhibit either the power or the exponential character.

Let us check the applicability of Eqs. (19) and (22) (Figs. 1 and 2) to cyclohexane dehydrogenation. Figure 3 presents the relevant results and shows that this model provides a better interpretation of experimental data than models (3) (Fig. 2a) and (7) (Fig. 2b).

Temporal Changes in Coke Concentration

The description of the dynamics of coke accumulation is not obligatory for the kinetic model of deactivation. For this purpose, the equations for the catalyst activity (e.g., Eqs. (17) and (18)) are sufficient. Nevertheless, the description of the curves of coke accumulation provides further support for the mechanism and model developed on their basis. To this end, it seems desirable to measure the concentrations of individual coke types. The results of such an experiment, conducted by Biswas *et al.* [7] are given in Fig. 4a as curves illustrating the temporal variations in the overall coke concentration and the fraction of reversible coke. Both curves corresponding to the reversible fraction bound the confidence interval, in which this value was determined. Figure 4b presents another example of such experimental results and their interpretation within the framework of models (8) and (9) [7].

To interpret the experimental data of [7] in terms of the above model, let us make necessary rearrangements of the equations that describe both the dynamics of reversible coke accumulation (Eq. (10)) and its overall concentration (Eq. (13)). In view of Eq. (17), the first two terms in these equations can be substituted by the following expression:

$$k_p P_C(1 - \Theta_p - \Theta_g) - k_R P_R \Theta_p = (a - a_s)/(1 - a_s). \quad (23)$$

Taking into account the above assumptions, Eqs. (10) and (13) can be rearranged to

$$dC_p/dt = \xi_p k_p P_C(a - a_s)/(1 - a_s) - \xi_g k_g \Theta_p, \quad (24)$$

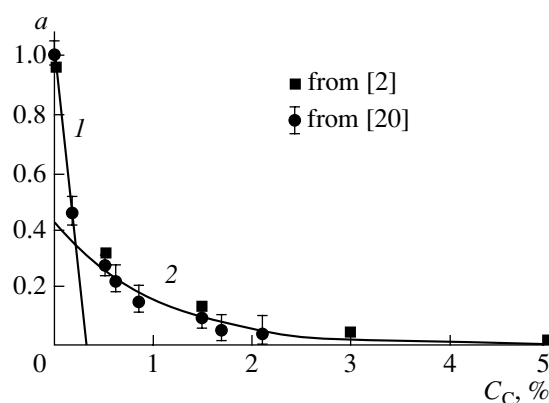$$dC_C/dt = \xi_p k_p P_C(a - a_s)/(1 - a_s) + \xi_z k_z P_C(1 - \Theta_z). \quad (25)$$

Fig. 3. The catalyst activity (a) as a function of the coke concentration (C_C). Solid lines correspond to the description by: (*1*) the set of Eqs. (19) ($C_m = 0.3$) and (2) Eq. (22) ($C_s = 0.2$, $\varphi_1 = 0.3$); points represent the experimental data from [2] and [20].

Then, we obtain from Eq. (19) that $a_s = 1 - C_s/C_m$ and, solving Eq. (17),

$$(a - a_s)/(1 - a_s) = e^{-\beta t}, \qquad (26)$$

where $\beta = \xi_p k_p P_C/C_s$.

Moreover, it is clear that $\Theta_p = C_p/C_m$ in Eq. (24) and, by analogy with Eq. (20), $(1 - \Theta_z) = (1 - C_C/C_{max})$ in Eq. (25). Then, Eqs. (24) and (25) may be rewritten in the form:

$$dC_p/dt = \xi_p k_p P_C e^{-\beta t} - \xi_g k_g C_p/C_m, \qquad (27)$$

$$dC_C/dt = \xi_p k_p P_C e^{-\beta t} - \xi_z k_z P_C(1 - C_C/C_{max}). \quad (28)$$

Now these equations are mutually independent and may be solved separately. The solution to Eq. (27) is

$$C_p = \frac{C_s}{1 - \alpha/\beta}(e^{-\alpha t} - e^{-\beta t}), \qquad (29)$$

where $\alpha = \xi_p k_g/C_m$.

The solution to Eq. (28) is more complex:

$$C_C = \frac{C_m}{1 - \gamma/\beta}(e^{-\gamma t} - e^{-\beta t}) + \gamma C_{max}(1 - e^{-\gamma t}), \quad (30)$$

where $\gamma = \xi_z k_z P_C/C_{max}$.

At low coke concentrations $C_C < C_{max}$, the second term in the right side of Eq. (28) is constant, and we have

$$C_C = C_m(1 - e^{-\beta t}) + \gamma_1 t, \qquad (31)$$

where $\gamma_1 = \xi_z k_z P_C$

Figure 5 illustrates the description of the experimental results by Eqs. (29)–(31). For this purpose, the experimental data of [7] are rearranged into a more convenient form for processing. Taking into account that the catalyst sample in the experiments of [7] was 185 mg, the coke amount was converted into its concentration.
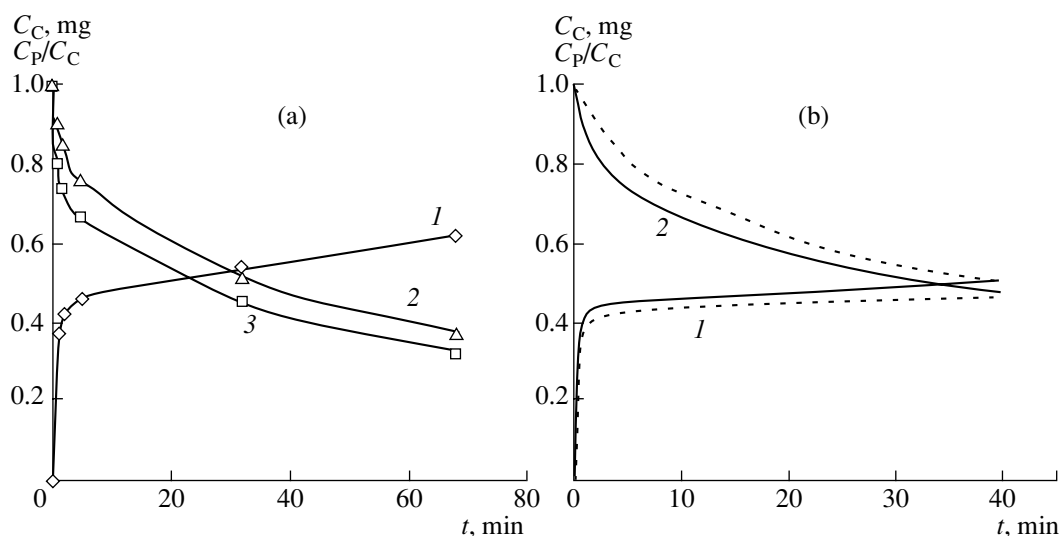
Fig. 4. Time variations in (*1*) the overall coke concentration C_C and (*2*, *3*) the fraction of reversible coke C_p/C_C. (a) Experimental data from [7]; curves *2* and *3* bound the confidence interval. (b) A solid line represents the experimental results, a dotted line represents the calculated data from [7].

Moreover, the fraction of reversible coke C_p/C_C inadequately reflects its concentration variations because it can decrease with an increase in the overall coke amount, whereas the C_p value remains virtually unchanged in this case.

Figure 5 presents the data in new coordinates and shows that the concentration of reversible coke C_p slowly decreases probably because of its transformation into graphite-like coke. This process is reflected by the second term in the right-hand side of Eq. (27).

Figure 5 shows that the proposed model provides a much better qualitative and quantitative description of experimental results than that developed by Biswas *et al.* [7] (Eqs. (8) and (9), Fig. 4). The model developed in this work reflects the difference in the rates of the formation of polymeric and graphite-like coke on metal and contains parameters that consider their structure. It also relates the concentrations of different coke types and its overall concentration to the catalyst activity in various reactions occurring on both metal and support. These properties of the model ensure its application to describe gasoline reforming on platinum catalysts [30–32].

REFERENCES

1. Buyanov, R.A., *Zakoksovanie katalizatorov* (Catalyst Coking), Novosibirsk: Nauka, 1983.
2. Frank, J.-P. and Martino, G.P., *Chemical Industries. Vol. 20: Deactivation and Poisoning of Catalyst*, Oudar, J. and Wise, H., Eds., New York: Marcel Dekker, 1985, p. 205.
3. Trimm, D.L., *Chemical Industries. Vol. 20: Deactivation and Poisoning of Catalyst*, Oudar, J. and Wise, H., Eds., New York: Marcel Dekker, 1985, p. 151.
4. Sarkany, A., Lieske, H., Szilagyi, T., and Toth, L., *Proc. 8th Int. Congr. on Catalysis*, Berlin, 1984, vol. 2, p. 613.
5. Cabrol, R.A. and Oberlin, A., *J. Catal.*, 1984, vol. 89, p. 256.
6. Bursian, N.R. and Kogan, S.B., *Problemy dezaktivatsii katalizatorov* (Problems of Catalyst Deactivation), Novosibirsk: Institute of Catalysis, 1989, p. 14.
7. Biswas, J., Gray, P.G., and Do, D.D., *Appl. Catal.*, 1987, vol. 32, p. 249.
8. Boronin, A.N., Bukhtiyarov, V.I., Kvon, R., *et al.*, *Izv. Sib. Otd. Akad. Nauk SSR, Ser. Khim.*, 1990, no. 2, p. 75, 79.
9. Chesnokov, V.V., Buyanov, R.A., Pakhomov, N.A., and Zaikovskii, V.I., *Kinet. Katal.*, 1991, vol. 32, p. 1494.
10. Boronin, A.I., Bukhtiyarov, V.I., Kvon, R., *et al.*, *Surf. Sci.*, 1991, vol. 258, p. 289.
11. Hamilton, J.C. and Blackely, J.M., *J. Vac. Sci. Technol.*, 1978, vol. 15, p. 559.
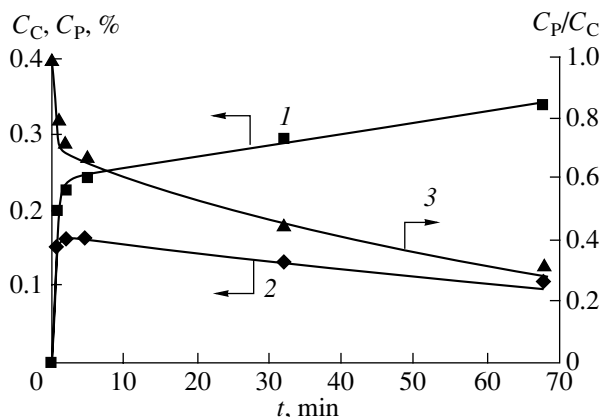12. Olander, D.R. and Balooch, M., *J. Catal.*, 1979, vol. 60, p. 41.

Fig. 5. Time variations in (*1*) the overall coke concentration C_C, (*2*) reversible coke concentration C_p, and (*3*) the fraction of reversible coke C_p/C_C.

13. Martin, M. and Hydson, J.B., *J. Vac. Sci. Technol.*, 1978, vol. 15, p. 474.

14. Davis, S.M., Zaera, F., and Somorjai, G.A., *J. Catal.*, 1982, vol. 77, p. 439.

15. Sterba, M.J. and Haensel, V., *Ind. Eng. Chem. Prod. Res. Dev.*, 1976, vol. 15, p. 3.

16. Rabinovich, G.R. and Levinter, M.E., *Izv. Vyssh. Uchebn Zaved., Khim. Khim. Tekhnol.*, 1980, vol. 23, no. 2, p. 196.

17. Schipper, P.H., Graziani, K.R., Choi, B.C., and Ramage, M.P., *Int. Chem. Eng. Symp. ISCRE-8*, 1984, Ser. 87, p. 33.

18. Ostrovskii, N.M. and Demanov, Yu.K., *Khim. Tekhnol. Topl. Masel*, 1991, no. 2, p. 35.

19. Barbier, J., Marecot, P., Martin, N., *et al.*, *Catalyst Deactivation*, Delmon, B. and Froment, G.F., Eds., Amsterdam: Elsevier, 1980, p. 53.

20. Ostrovskii, N.M., Chalganov, E.M., Demanov, Yu.K., *et al.*, *React. Kinet. Catal. Lett.*, 1990, vol. 41, p. 277.

21. Parera, J.M., Figoli, N.S., Trassano, E.M., *et al.*, *Appl. Catal.*, 1983, vol. 5, p. 33.

22. Ostrovskii, N.M., *Kinet. Katal.*, 2001, vol. 42, no. 3, p. 354.

23. Ostrovskii, N.M., *Problemy dezaktivatsii katalizatorov* (Problems of Catalyst Deactivation), Novosibirsk: Inst. of Catal., 1989, p. 145.

24. Reutova, O.A. and Ostrovskii, N.M., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol*, 1993, vol. 36, no. 7, p. 64.

25. Ostrovskii, N.M. and Yablonskii, G.S., *React. Kinet. Catal. Lett.*, 1989, vol. 39, p. 287.

26. Biswas, J., Bickle, G.M., Gray, P.G., and Do, D.D., *Proc. 4th Int. Symp. on Catalyst Deactivation*, Delmon, B. and Froment, G.F., Eds., Antwerpen, 1987, p. 553.

27. Srivastava, R.D., Prasad, N.S., and Pal, A.K., *Chem. Eng. Sci.*, 1986, vol. 41, p. 719.

28. Pakhomov, N.A., Buyanov, R.A., and Chesnokov, V.V., *Tezisy dokladov 2-go Vsesoyuznogo soveshchaniya po problemam dezaktivatsii katalizatorov* (Proc. 2nd All-Russia Workshop on the Problems of Catalyst Deactivation) Ufa, 1989, pt. 2, p. 23.

29. Barbier, J., Corro, G., Zhang, Y., *et al.*, *Appl. Catal.*, 1985, vol. 13, p. 245.

30. Ostrovskii, N.M., *Doctoral (Eng.) Dissertation*, Novosibirsk: Institute of Catalysis, 1998.

31. Ostrovskii, N.M. and Belym, A.S., *Khim. Prom-st.*, 1999, no. 8, p. 522.

32. Duplyakin, V.K., Belyi, A.S., and Ostrovskii, N.M., *Proc. 2nd Int. Seminar "New Challenges in Catalysis"*, Putanov P., Ed., Novi Sad, 1999, p. 89.