Problems in the Study of Catalyst Deactivation Kinetics

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Abstract—Problems arising in kinetic studies of catalyst deactivation and in catalyst stability tests are considered. The choice and substantiation of deactivation conditions, the primary analysis and interpretation of experimental data, and the construction of a kinetic model of deactivation are illustrated by examples. Accelerated deactivation for quick catalyst stability testing is discussed.

The most important properties of a catalyst are activity, selectivity, and stability. The first two determine the rate and "quality" of the reaction, and the third is necessary for these parameters to be stable throughout the service life of the catalyst

The deactivation of a catalyst should be viewed as an unsteady-state and nonequilibrium evolution caused by a quasi-steady-state reaction proceeding on this catalyst.

The deactivation rate is determined by the deactivation kinetics, the investigation of which has some specific features. In this paper, we discuss problems arising when choosing conditions for deactivation experiments, analysis of experimental data, setting up deactivation rate equations, and determining kinetic parameters of deactivation.

The same problems are faced in catalyst stability testing, which is among the basic challenges in industrial catalysis from both the methodological and practical standpoints. The difficulties involved in catalyst stability testing are commensurate with the significance of the problem. The main difficulty is that it is impossible to make stability tests on the real time scale. The only way of comparing and screening catalysts according to their stability is by testing them under special, severe conditions causing rapid deactivation. Some of the questions that arise when choosing appropriate testing conditions are also discussed in this paper.
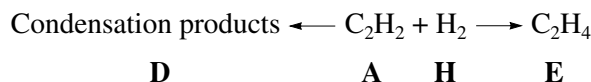
DEACTIVATION MECHANISM AND KINETICS

If there is a tentative hypothesis as to the reaction and deactivation mechanisms, it will be much easier to construct a kinetic model of deactivation. If the mechanisms are linear with respect to the intermediates, the deactivation kinetics can be described by the rather general equation [1, 2]

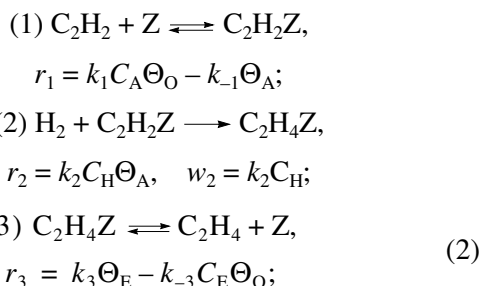$$-\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{r^0}{w_j} w_D \frac{a - a_S}{1 - a_S}, \qquad (1)$$

where $a = r/r^0$ is the relative activity of the catalyst, r and r^0 are the current and initial reaction rates, w_j is the weight of the rate-limiting step of the reaction, w_D is the weight of the deactivation step, a_S is the steady-state activity (which is observed when the deactivation rate r_D is equal to the self-regeneration rate r_R).

Equation (1) is obtained under the assumption that the reaction occurring on a catalyst undergoing deactivation is quasi-steady-state. This assumption implies that the deactivation and self-regeneration rates are much lower than the reaction rate. This condition is quite natural, since only catalysts satisfying it are commercially usable.
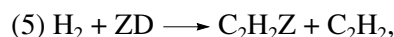
We will illustrate the derivation of a deactivation rate equation by the example of the selective removal of acetylene from the ethylene fraction of pyrolysis products:

$$\text{Condensation products} \longleftarrow C_2H_2 + H_2 \longrightarrow C_2H_4$$
$$\mathbf{D} \qquad\qquad \mathbf{A} \quad\ \mathbf{H} \qquad\quad \mathbf{E}$$

Here, catalyst deactivation is caused by the formation of the condensation products called green oil. Partial catalyst regeneration is due to hydrogen. A simplified mechanism of the process considered can be represented as

$$(1)\ C_2H_2 + Z \rightleftharpoons C_2H_2Z,$$
$$r_1 = k_1 C_A \Theta_O - k_{-1}\Theta_A;$$
$$(2)\ H_2 + C_2H_2Z \longrightarrow C_2H_4Z,$$
$$r_2 = k_2 C_H \Theta_A, \quad w_2 = k_2 C_H;$$
$$(3)\ C_2H_4Z \rightleftharpoons C_2H_4 + Z,$$
$$r_3 = k_3 \Theta_E - k_{-3} C_E \Theta_O; \qquad\qquad (2)$$
$$(4)\ C_2H_2 + C_2H_2Z \longrightarrow ZD,$$
$$r_D = k_D C_A \Theta_A, \quad w_D = k_D C_A \text{ (deactivation)};$$
$$(5)\ H_2 + ZD \longrightarrow C_2H_2Z + C_2H_2,$$
$$r_R = k_R C_H \Theta_D, \quad w_R = k_R C_H \text{ (self-regeneration)}.$$

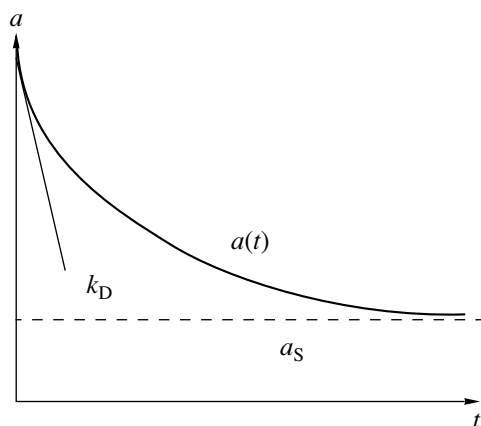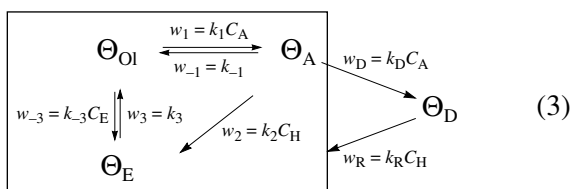**Fig. 1.** Graphical illustration for Eq. (10).

For clarity, this mechanism can be represented as the following graph:

$$\Theta_{Ol} \underset{w_{-1} = k_{-1}}{\overset{w_1 = k_1 C_A}{\rightleftarrows}} \Theta_A \xrightarrow{w_D = k_D C_A} \\ w_{-3} = k_{-3} C_E \updownarrow w_3 = k_3 \qquad w_2 = k_2 C_H \searrow \quad \Theta_D \\ \Theta_E \qquad\qquad w_R = k_R C_H \qquad (3)$$

If step 2 is rate-limiting and steps 1 and 3 are in equilibrium, then

$$r^0 = \frac{k_2 b_A C_A C_H}{1 + b_A C_A + b_E C_E}, \qquad (4)$$

where $b_A = k_1/k_{-1}$ and $b_E = k_{-3}/k_3$ are the adsorption coefficients of acetylene and ethylene, respectively.

Deactivation, which includes steps 4 and 5, is described by the equation

$$d\Theta_D/dt = k_D C_A \Theta_A - k_R C_H \Theta_D. \qquad (5)$$

In the quasi-steady-state approximation, $\Theta_j = \Theta_j^0 (1 - \Theta_D) = (r^0/w_j)(1 - \Theta_D)$ [1, 2] and, hence, $\Theta_A = (r^0/k_2 C_H) \times (1 - \Theta_D)$ and Eq. (5) appears as

$$\frac{d\Theta_D}{dt} = \frac{k_D C_A}{k_2 C_H} r^0 (1 - \Theta_D) - k_R C_H \Theta_D. \qquad (6)$$

For the same reason, $a = r/r^0 = 1 - \Theta_D$, and we obtain the following equation for activity:

$$-\frac{da}{dt} = \frac{k_D C_A}{k_2 C_H} r^0 a - k_R C_H (1 - a). \qquad (7)$$

When the deactivation and self-regeneration rates are equal, $r_D = r_R$ and $a = a_S$. Therefore, $k_D C_A \Theta_A = k_R C_H \Theta_D$ and $k_D C_A (r^0/k_2 C_H) a_S = k_R C_H (1 - a_S)$. From these relationships, by expressing $k_R C_H$ (which is difficult to derive from experimental data) in terms of a_S and

substituting the result into Eq. (7), we obtain an equation similar to Eq. (1):

$$-\frac{da}{dt} = \frac{r^0}{k_2 C_H} k_D C_A \frac{a - a_S}{1 - a_S}. \qquad (8)$$

Substituting Eq. (4) for the reaction rate r^0, we finally obtain

$$-\frac{da}{dt} = \frac{k_D b_A C_A^2}{1 + b_A C_A + b_E C_E} \frac{a - a_S}{1 - a_S}. \qquad (9)$$

Note that the deactivation rate equation is second-order with respect to acetylene, while the main reaction is first-order. Any simplification of the mechanism of the main reaction will modify both the equation for r^0 and the deactivation rate equation. For example, at low temperatures, at which acetylene is strongly adsorbed, $1 + b_E C_E \ll b_A C_A$. Accordingly, the reaction rate equation (4) is pseudo-zero-order with respect to acetylene and the deactivation rate equation (9) is first-order with respect to acetylene:

$$r^0 = k_2 C_H, \quad -\frac{da}{dt} = k_D C_A \frac{a - a_S}{1 - a_S}. \qquad (10)$$

The parameters of the deactivation rate equation are easy to estimate from experimental, time-dependent activity data (Fig. 1). The deactivation constant k_D is equal to the slope of the activity curve at $t = 0$, and the steady-state activity a_S is given by the asymptote to this curve.

IF THE MECHANISM IS UNKNOWN …

The reaction mechanism and particularly the deactivation mechanism are well studied only for a few of the industrially important processes. Even if both are known, there remains the problem of correctly constructing the deactivation curve (Fig. 1) or, in other words, correctly deriving activity (a) data from measurable quantities such as concentration (C_i) and conversion (X).

If the mechanism and, accordingly, exact kinetic data are unknown, then, at least, the questions arise as to the choice of experimental conditions and the appropriate way of data analysis. To answer these questions, it is necessary to understand, at least roughly, how the $a = f(X)$ relationship depends on the reactor in which the experiments are carried out, on the kinetics of the main reaction, and on the deactivation kinetics. These dependences are considered in [1, 4] and are presented in the table for the simplest reaction A $\longrightarrow$ B.

When analyzing experimental data, the relative activity $a = r/r^0$ is often represented as the conversion ratio $a = X/X^0$. As is demonstrated in the table, this representation is correct only for zero-order reactions and leads to misinterpretation of deactivation data in the other cases.

Effect of the type of reactor and of the kinetics of the reaction A $\longrightarrow$ B on catalyst deactivation

Reactor type	Deactivation rate equation		
	zero order ($r = ka$)	first order ($r = kC_A a$)	second order ($r = kC_A^2 a$)
Gradientless reactor	$X = k\tau a / C_A^0$	$X = k\tau(1 - X)a$	$X = k\tau C_A^0 (1 - X)^2 a$
	$a = \dfrac{X}{X^0}$	$a = \dfrac{1 - X^0}{X^0}\dfrac{X}{1 - X}$	$a = \dfrac{(1 - X^0)^2}{X^0}\dfrac{X}{(1 - X)^2}$
Integral reactor	$\dfrac{dx}{dz} = \dfrac{k\tau}{C_A^0}a$	$\dfrac{dx}{dz} = k\tau(1 - x)a$	$\dfrac{dx}{dz} = k\tau C_A^0(1 - x)^2 a$
	$\langle a \rangle = \dfrac{X}{X^0}$	$\langle a \rangle = \dfrac{\ln(1 - X)}{\ln(1 - X^0)}$	$\langle a \rangle = \dfrac{1 - X^0}{X^0}\dfrac{X}{1 - X}$

Note: k is the reaction rate constant, τ is contact time, C_A^0 is the inlet concentration of A, x is conversion in the bed, X is conversion at the exit of the bed, X^0 is the initial conversion (at $t = 0$), $\langle a \rangle$ is the mean integral activity of the catalyst bed, and z is the bed height.

We will illustrate this point by a simple example. Suppose that the time dependence of conversion plotted in Fig. 2a ($X^0 = 0.9$) is observed for the reaction A $\longrightarrow$ B in the gradientless reactor. Suppose also that the reaction rate is described by the first-order equation $r = kC_A a$. Under the wrong assumption that $a = X/X^0$, we will obtain curve 1, which is similar to the $X(t)$ curve in Fig. 2b.

In fact, the material balance equation for A in the gradientless reactor is $C_A - C_A^0 = -r\tau$ or, in view of the expression for r, $C_A - C_A^0 = -k\tau C_A a$. Since $C_A = C_A^0 (1 - X)$, $X = k\tau(1 - X)a$; hence, $a = X/k\tau(1 - X)$. For a fresh catalyst, $a = 1$ and $X = X^0$; hence,

$$k\tau = \frac{X^0}{1 - X^0} \quad \text{and} \quad a = \frac{1 - X^0}{X^0}\frac{X}{1 - X}. \quad (11)$$

It is clear from Fig. 2b that the correct and incorrect $a(t)$ curves are very different both quantitatively and qualitatively. Furthermore, the $X(t)$ curve and the true $a(t)$ curve have different shapes.

Here, the question arises as to what the deactivation kinetics are as such. Indeed, neither the reaction rate equation ($r = kC_A a$) nor the $a = f(X)$ relationship provides information concerning the deactivation equation $da/dt = -r_D$ or, more specifically, the expression for r_D. The deactivation equation should either be derived
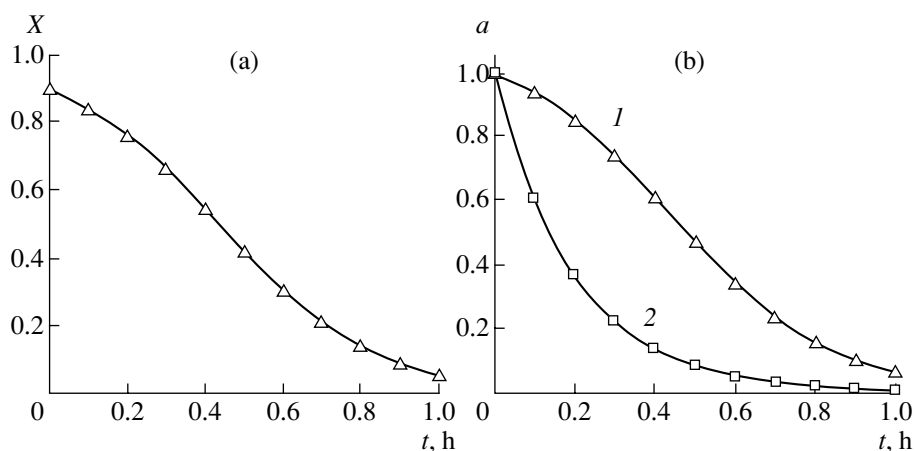

Fig. 2. Variation of (a) conversion and (b) relative catalytic activity caused by the deactivation of the catalyst in the reaction A $\longrightarrow$ B in a gradientless reactor: (1) $a = X/X_0$ and (2) $a = [(1 - X^0)/X^0][(X/(1 - X)]$.
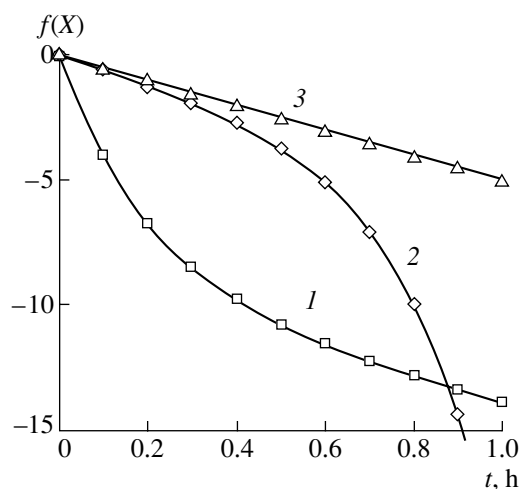
Fig. 3. Fitting the data presented in Fig. 2a to Eqs. (*1*) (15), (*2*) (16), and (*3*) (17).

from the hypothetical deactivation mechanism or be fitted to the observed a data. As applied to Fig. 2, the simple equation of independent deactivation, $da/dt = -k_D a$ or $a = \exp(-k_D t)$, provides an excellent description for the process. This is not surprising, since the "experimental" curve shown in Fig. 2a is fitted to this equation using formula (11). It is now clear that the delay period indicated by the $X(t)$ curve arises from the hydrodynamic features of the gradientless reactor rather than from deactivation kinetics.

Now we will demonstrate the way of fitting an equation to experimental data. Consider the following three cases:

deactivation by the initial substance,

$$da/dt = -k_D C_A a = -k_D C_A^0 (1 - X)a; \qquad (12)$$

deactivation by the reaction product,

$$da/dt = -k_D C_B a = -k_D C_A^0 Xa; \qquad (13)$$

and independent deactivation,

$$da/dt = -k_D a = -k_D C_A^0 a. \qquad (14)$$

Note that the term $C_A^0 = \text{const}$ in Eq. (14) is introduced only for the rate constant k_D to have the same dimensionality in all of the three equations.

By substituting the expression for a (Eq. (11)) into Eqs. (12)–(14) and solving the resulting equations, we obtain the following:

for deactivation by the initial substance,

$$\ln\left(\frac{X}{1-X}\right) + \frac{X}{1-X} = A_1 - k_D C_A^0 t; \qquad (15)$$

for deactivation by the reaction product,

$$\ln\left(\frac{X}{1-X}\right) - \frac{1-X}{X} = A_2 - k_D C_A^0 t; \qquad (16)$$

for independent deactivation,

$$\ln\left(\frac{X}{1-X}\right) = A_3 - k_D C_A^0 t. \qquad (17)$$

In each of Eqs. (15)–(17), the left-hand side is a linear function of time. Let us fit the experimental data used in the construction of the curve in Fig. 2a to Eqs. (15)–(17). It is demonstrated in Fig. 3 that only fitting to Eq. (17) gives a straight line. Therefore, the process obeys the rate law of independent deactivation and is described by Eq. (14).

The following point is of significance in analysis of deactivation data. The relationship between the catalytic activity and conversion (or product yield), $a = f(X)$, depends only on the kinetics of the main reaction and is independent of the deactivation kinetics. At the same time, the deactivation kinetics determine the $a(t)$ and $X(t)$ functions.

INTEGRAL REACTOR

Deactivation experiments are more often carried out in a plug-flow integral reactor than in a gradientless reactor. In the former case, the processing of experimental data is greatly complicated by the fact that the reactant concentrations and the activity of the catalyst vary along the reactor length, while measurements are taken only at the reactor outlet.

For this reason, the outlet conversion can be related only to the mean integral activity of the entire catalyst bed, $\langle a \rangle$ (table). Nevertheless, in many cases, this does not prevent the correct determination of deactivation parameters.

Let us return to the reaction A $\longrightarrow$ B, whose rate obeys the first-order equation $r = kC_A a$. The corresponding equations for the profiles of the concentration C_A and of the conversion $x = 1 - C_A/C_A^0$ along the bed height z appear as

$$\frac{dC_A}{dz} = -k\tau C_A a \quad \text{and} \quad \frac{dx}{dz} = k\tau(1-x)a. \qquad (18)$$

Integrating the second of Eqs. (18) with respect to z yields

$$\int_0^x \frac{dx}{1-x} = k\tau \int_0^1 a(z)dz.$$

At the bed exit ($z = 1$),

$$\ln(1 - X) = -k\tau\langle a \rangle,$$

$$\langle a \rangle = \int_0^1 a(z)dz, \quad \text{or} \quad 1 - X = e^{-k\tau\langle a \rangle}. \qquad (19)$$

For any other bed cross section ($z = z^*$),

$$\ln(1 - x^*) = -k\tau a^*, \quad a^* = \int_0^{z^*} a(z)\mathrm{d}z, \tag{20}$$

$$\text{or} \quad 1 - x^* = \mathrm{e}^{-k\tau a^*}.$$

For a fresh catalyst, $\langle a \rangle = 1$ and $X = X^0$; accordingly, $k\tau = -\ln(1 - X^0)$ and the function $\langle a \rangle = f(X)$ takes the form

$$\langle a \rangle = \frac{\ln(1 - X)}{\ln(1 - X^0)}. \tag{21}$$

Clearly, if the main reaction obeys another kinetic law, Eq. (19) will take another form (table). Let us continue the analysis of the first-order reaction. As in the case of the gradientless reactor, it is necessary to make some assumption as to the deactivation kinetics. Let the catalyst be deactivated by the initial substance (see Eq. (12)). Integrating Eq. (12) with respect to z yields

$$\int_0^1 \frac{\mathrm{d}a}{\mathrm{d}t} = -k_\mathrm{D} C_\mathrm{A}^0 \int_0^1 (1 - x)a\,\mathrm{d}z.$$

The integral in the left-hand side of this equation gives the time derivative of the mean integral activity. Substituting the expression for $(1 - x^*)$ from Eq. (20) into the right-hand side yields

$$\frac{\mathrm{d}\langle a \rangle}{\mathrm{d}t} = -k_\mathrm{D} C_\mathrm{A}^0 \int_0^1 \mathrm{e}^{-k\tau a^*} a\,\mathrm{d}z, \tag{22}$$

$$\text{or} \quad \frac{\mathrm{d}\langle a \rangle}{\mathrm{d}t} = -\frac{k_\mathrm{D} C_\mathrm{A}^0}{k\tau}(1 - \mathrm{e}^{-k\tau\langle a \rangle}).$$

Finally, substituting the expression for $\langle a \rangle$ from Eq. (21) into Eq. (22), we arrive at

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -k_\mathrm{D} C_\mathrm{A}^0 (1 - X)X. \tag{23}$$

Thus, we have obtained a deactivation equation in terms of outlet conversion, which is a measurable quantity.

Consider the example of heptane aromatization, $\mathrm{C_7H_{16}} \longrightarrow \mathrm{C_6H_5CH_3} + 4\mathrm{H_2}$, which is among the key reactions in naphtha reforming. The rate of this reaction obeys the first-order equation $r = kC_\mathrm{hept}a$, where C_hept is the heptane concentration [1]. Since a number of other reactions occur in parallel, the rate constant k includes the selectivity of the reaction toward the desired product; however, this fact is not essential for deactivation analysis.

The deactivation of the catalyst is primarily caused by methylcyclopentane (MCP), which is an intermediate in this reaction: MCP decomposition leads to catalyst coking. The concentration of MCP (C_MCP) depends only slightly on heptane conversion because of the ther-

modynamic equilibrium established during the reaction [1]. Therefore, $C_\mathrm{MCP} = C_\mathrm{MCP}^0 \approx \mathrm{const}$. In view of these circumstances and the fact that $x = 1 - C_\mathrm{hept}/C_\mathrm{hept}^0$, the mathematical model of the process in the integral reactor takes the form

$$\frac{\mathrm{d}x}{\mathrm{d}z} = k\tau(1 - x)a, \tag{24a}$$

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = k_\mathrm{D} C_\mathrm{MCP}^0 \frac{a - a_\mathrm{S}}{1 - a_\mathrm{S}}. \tag{24b}$$

Since $C_\mathrm{MCP}^0 \approx \mathrm{const}$, we are dealing with independent deactivation, so Eq. (24b) is readily integrable with respect to bed height:

$$-\frac{\mathrm{d}\langle a \rangle}{\mathrm{d}t} = k_\mathrm{D} C_\mathrm{MCP}^0 \frac{\langle a \rangle - a_\mathrm{S}}{1 - a_\mathrm{S}}, \tag{25}$$

where, according to Eq. (21),

$$\langle a \rangle = \frac{\ln(1 - X)}{\ln(1 - X^0)}, \quad a_\mathrm{S} = \frac{\ln(1 - X_\mathrm{S})}{\ln(1 - X^0)}. \tag{26}$$

The solution of Eq. (25) is

$$\ln\frac{\langle a \rangle - a_\mathrm{S}}{1 - a_\mathrm{S}} = -\frac{k_\mathrm{D} C_\mathrm{MCP}^0}{1 - a_\mathrm{S}}t. \tag{27}$$

Fitting experimental data (Fig. 4a) to Eq. (27) allows k_D and a_S to be easily determined (Fig. 4b). In Fig. 4b, time t is replaced with the amount of feed converted, and $G = W_\mathrm{L}t$, where $W_\mathrm{L} = 50 \ \mathrm{h^{-1}}$ is the WHSV of the feed.

The above procedure is also valid for a catalyst deactivated by the initial substance or reaction product, but Eqs. (25) and (27) will be more complicated. If Eqs. (22) and (25) are analytically unsolvable, they should be solved by Runge–Kutta-like numerical methods.

STABILITY TESTING

Since the lifetime of many commercial catalysts is several months or even several years, it is impossible to carry out stability tests in real time. In this case, the only way of comparing and screening catalysts is by testing them under special, severe conditions causing rapid deactivation. Clearly, such a testing procedure should be well substantiated, comparatively simple, and capable of predicting the lifetime of catalysts under real operation conditions.

Although each process is obviously specific, there are general requirements for a testing procedure:

(1) The increase in the deactivation rate must be sufficiently large to make it possible to accomplish the stability tests within 1–2 weeks.

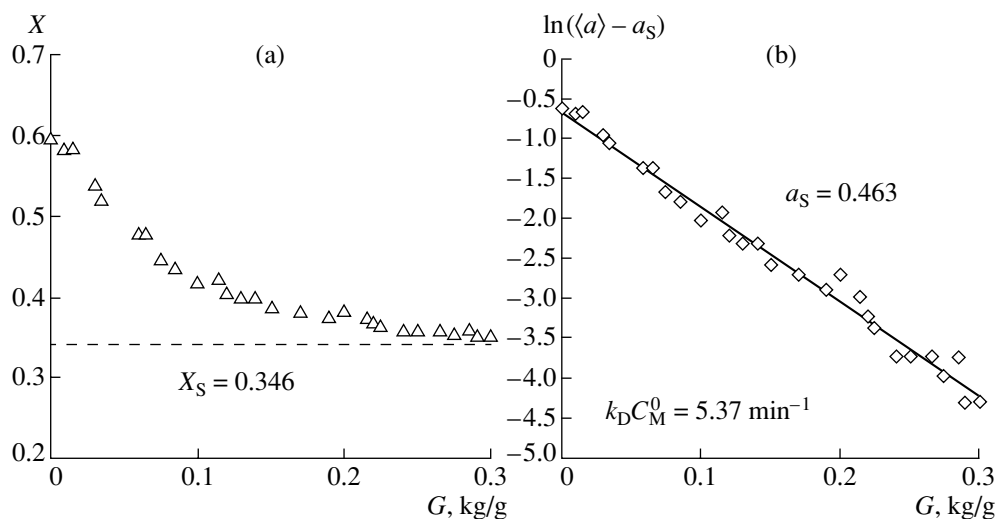(2) The state of the active sites of the catalyst must be the same as in the real process.

Fig. 4. Deactivation of the Pt/Al$_2$O$_3$ catalyst in heptane reforming in an integral reactor: (a) experimental data [1] and (b) the same data fitted to Eq. (27).
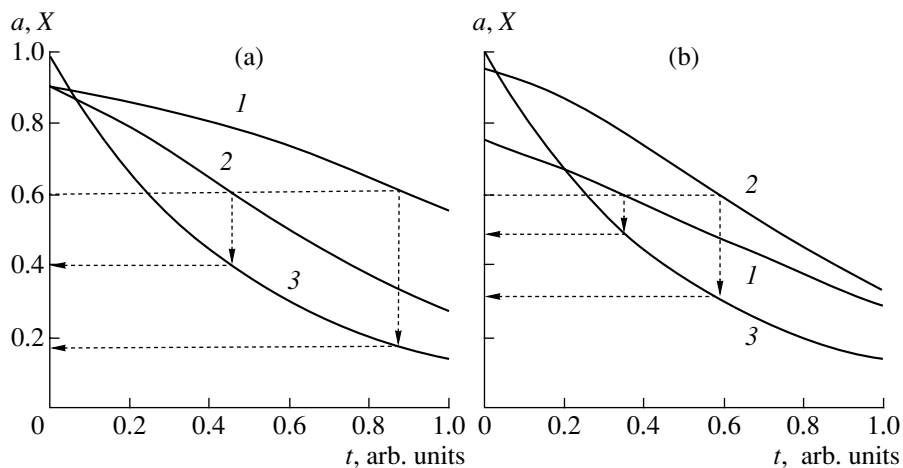

Fig. 5. Independent deactivation of the catalyst in the STR and PFR at a fixed (a) initial conversion and (b) contact time: (*1*) STR, (*2*) PFR, and (*3*) the relative activity of the catalyst.

(3) The deactivation rate must be raised without changing the cause of deactivation.

Figuratively speaking, acceleration should not be accompanied by a "perestroyka"; that is, the number of active sites should decrease more rapidly in the test process than in the real process, but their states should be unaffected. This is the ideal situation at which one should aim in any particular case.

The state of active sites depends on the reactant concentrations (conversion), the concentration of the substance that causes deactivation, and temperature. The deactivation rate depends on the same parameters. Therefore, it is impossible to accelerate deactivation without changing at least one of these parameters. In turn, their effect depends directly on the type of reactor, the kinetics of the reaction, the ratio of the activation energy of the main reaction to that of deactivation, and, of course, the kind of deactivation.

Choosing a Reactor Type

We will consider two types of reactor, namely, the stirred tank (gradientless) reactor (STR) and the plug-flow (integral) reactor (PFR). Catalytic activity and conversion are differently related in these cases (table); therefore, for a given reaction, the same decline in activity in the course of the process will lead to different decreases in conversion (Fig. 5).

Consider a reaction A $\longrightarrow$ B proceeding at a rate $r = kC_A a$. Let us make tests in such a way that the conversion decreases from 90 to 60% as a consequence of the deactivation of the catalyst.
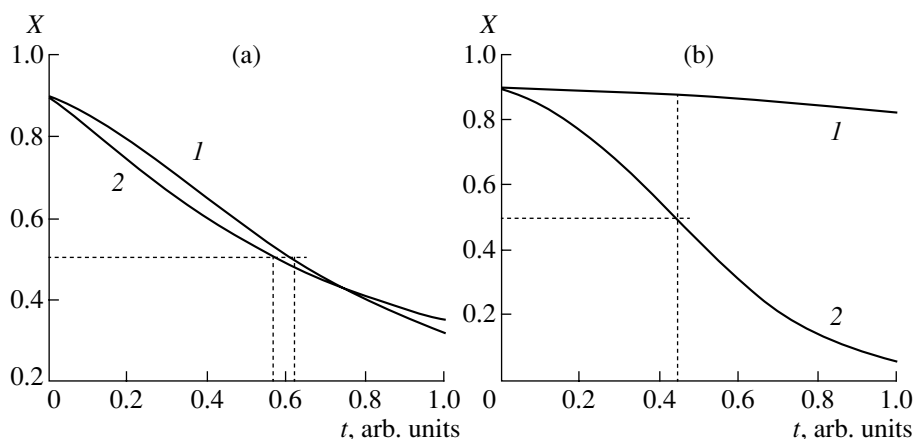
Fig. 6. Catalyst deactivation by the (a) reaction product and (b) initial substance in the (*1*) STR and (*2*) PFR.

If the deactivation is independent ($da/dt = -k_D C_A^0 a$), a test in the PFR will take a twice shorter time than the same test in the STR (Fig. 5a). The mean integral activity will fall to 40% in the PFR and to 20% in the STR. This difference is due to the large difference between the contact times in these reactors. If $k = 1$ s^{-1}, then, at $X^0 = 0.9$, $\tau = \dfrac{1}{k}\dfrac{X^0}{1-X^0} = 9.0$ s for the STR and $\tau = -\dfrac{1}{k}\ln(1-X^0) = 2.3$ s for the PFR.

If the tests were carried out at a fixed contact time (e.g., 3 s), the initial conversion would be 95% in the PFR and 75% in the STR (Fig. 5b). For the given final conversion of 60%, the reverse order of activities would be observed: the activity would fall to 30% in the PFR and to 50% in the STR.

If the catalyst is deactivated by the reaction product, the difference between the reactors is not large (Fig. 6a), since the product concentrations in the reactors ($C_B = C_A^0 X$) are nearly equal because of the high initial conversion (90%).

If the catalyst is deactivated by the initial substance, the difference between the reactors is the greatest (Fig. 6b). Since $C_A = C_A^0 (1 - X)$, C_A in the STR is low and is the same throughout the reactor volume. As a consequence, the catalyst is deactivated very slowly. In the PFR, the upstream half of the bed is in contact with a rather high concentration of A, which causes a considerable decrease in catalytic activity.

Acceleration of Deactivation
by Raising the Feed Flow Rate

The acceleration of deactivation by increasing the feed flow rate (shortening the contact time) is one of the

expedients most widely used in catalyst stability testing.

Consider the reaction $nA \longrightarrow B$, whose rate obeys the power law $r = k C_A^n a$. The relationships between the activity and conversion in the STR and PFR in this case are, respectively,

$$a = \frac{1}{k\tau C_{Ao}^{n-1}}\frac{X}{(1-X)^n},$$

$$\langle a \rangle = \frac{1}{k\tau C_{Ao}^{n-1}}\frac{1}{n-1}[(1-X)^{1-n} - 1], \quad n \neq 1. \tag{28}$$

As is clear from Eq. (28), the catalytic activity in these cases depends on the contact time τ in the same way: the shorter the contact time the higher the deactivation rate. However, it is necessary to remember that the conversions in the STR and PFR depend differently on the contact time. The relationships defined by Eq. (28) are plotted in Fig. 7.

The catalytic activity decreases in direct proportion to decreasing conversion only for the zero-order reaction, with equal slopes for the STR and PFR. As the reaction order increases, the activity versus conversion curve deviates progressively from linearity. If the initial conversions are equal, then, at any given current conversion, the reduction in activity is larger for the STR than for the PFR. If the initial conversions are different, the reverse situation may be observed (Fig. 5b). Therefore, by varying the contact time, it is possible to find such values of the initial conversion X^0 for the STR and PFR that the catalytic activities in these reactors decrease at approximately equal rates.

The effect of the contact time on the deactivation is illustrated by the example of a methylacetylene hydrogenation catalyst (Fig. 8). Shortening the contact time from 5 to 3 s shortens the test duration by a factor of larger than 2. The test duration as a function of τ can be
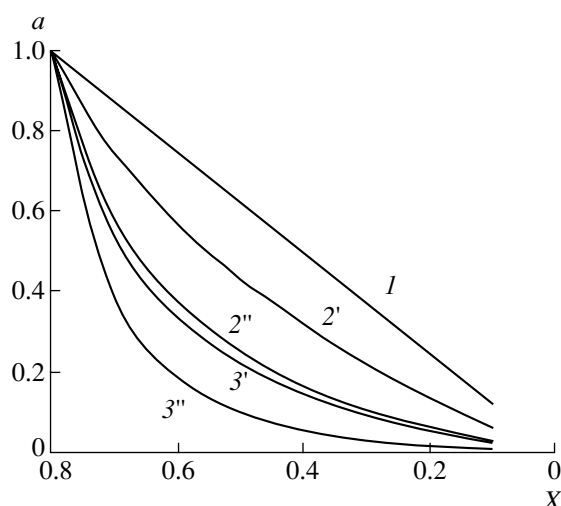
Fig. 7. Relationship between the catalytic activity and conversion for a reaction rate obeying the power law $r = kC_A^n a$: (*1*) $n = 0$ (STR and PFR), (*2'*) $n = 1$ (PFR), (*2''*) $n = 1$ (STR), (*3'*) $n = 2$ (PFR), and (*3''*) $n = 2$ (STR).

estimated using formula (29), which is obtained by solving Eqs. (22) and (23):

$$t = \frac{1}{k_D C_A^0}\left[\ln(e^{k\tau} - 1) - \ln\frac{X}{1-X}\right]. \quad (29)$$

Accelerating Effect of Temperature

Making stability tests at an elevated temperature is the most efficient way of accelerating the deactivation of a catalyst, since the reaction and deactivation rates are very sensitive to temperature. However, this way is the most "risky," because the composition of the adsorption layer and, accordingly, the state of the active sites depend strongly on temperature.

There are two ways of thermally controlling the deactivation process. In the first, the test is carried out at a fixed elevated temperature. The applicability of this technique to olefin dehydrogenation was discussed in earlier publications [1, 3]. In the other technique, the reaction temperature is gradually increased to compensate for the deactivation of the catalyst. This technique is widely used in the processes in which the catalyst is deactivated at a low rate (gasoline reforming, hydrotreating of petroleum fractions, isomerization, etc.).

Note that, in the second technique, a measurable quantity (conversion or product yield) rather than the catalytic activity is maintained constant. As a rule, the activity falls. The variation of a and X with time in this technique obeys the equations presented in the table, with the only difference being that the constants k and k_D are variable, depending on temperature T.
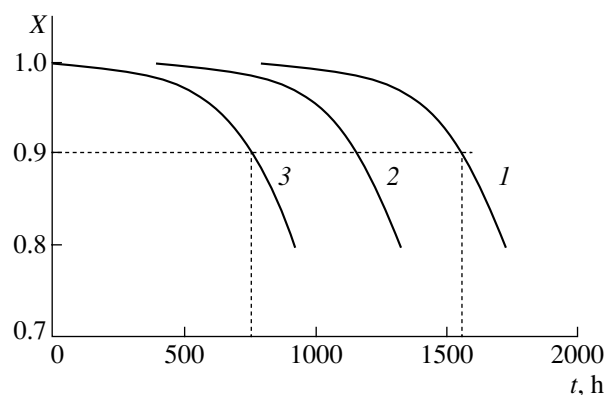

Fig. 8. Deactivation of a hydrogenation catalyst in the removal of methylacetylene from a polymerization stock. The contact time τ is (*1*) 5, (*2*) 4, and (*3*) 3 s.

Consider the simplest case, namely, a first-order reaction in a STR accompanied by an independent deactivation of the catalyst. For this reaction,

$$X = \frac{k(T)\tau a}{1 + k(T)\tau a} \quad \text{and} \quad a = \exp[-k_D(T)t], \quad (30)$$

where $k(T) = k_0\exp(-E/RT)$, $k_D(T) = k_{D,0}\exp(-E_D/T)$.

The behavior of the system and the possibility of carrying out accelerated stability tests depend on the relation between the activation energies of the reaction (E) and deactivation (E_D).

For $E_D < E$, the deactivation is less sensitive to temperature than the reaction. In this case, at a certain temperature rise rate (such that the conversion is constant), the catalytic activity will gradually decrease, obeying the linear law almost strictly (Fig. 9a).

However, there is a temperature limit above which a decrease in activity cannot be compensated for. Any further variation (either an increase or a decrease) in temperature will cause a reduction in conversion. Therefore, it is better to terminate the test at this point. The test can be continued only while maintaining the maximum possible conversion. In this case, the catalytic activity will remain constant and the temperature will decrease (Fig. 9).

For $E_D > E$, the deactivation process is more sensitive to temperature than the reaction. A sharper temperature rise is necessary to maintain $X = $ const (Fig. 9b). This will cause a more rapid decrease in the catalytic activity, so a temperature limit that cannot be exceeded will soon be reached. This case is likely to be the most convenient for catalyst stability testing.

Note that, in this method of studying the deactivation of catalysts, the formulas listed in the table cannot be directly used in the calculation of catalytic activity from conversion data. In these formulas, X^0 is not constant and is a function of temperature, as in Eq. (30) with $a = 1$.
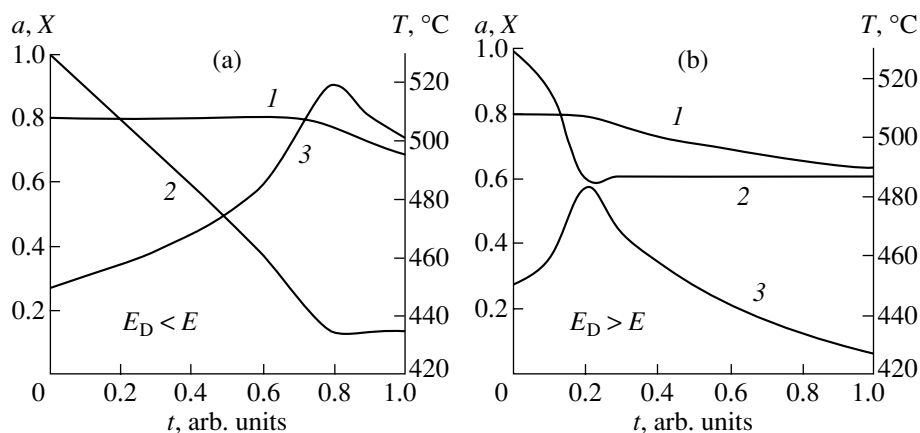
Fig. 9. Catalyst deactivation at a rising temperature at (a) $E_D < E$ and (b) $E_D > E$: (*1*) conversion (X), (*2*) relative activity (a), and (*3*) temperature (T).
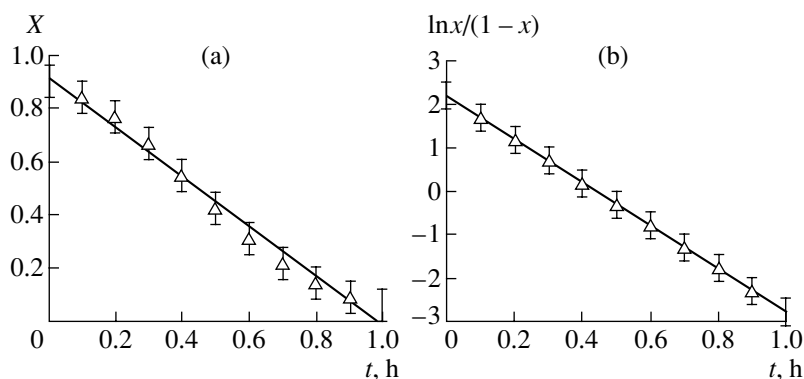

Fig. 10. (a) Misinterpretation and (b) correct interpretation of the experimental data presented in Fig. 2a.

The Cost of Formal Relationships

Above, we have discussed a number of interrelated aspects that should be taken into account in catalyst deactivation studies and stability tests. Let us see what are the possible consequences of the incorrect representation (primary analysis) of experimental data and of a wrong choice of fitting kinetic relationships.

Return to Fig. 2a, which shows a calculated $X(t)$ curve describing the independent deactivation of a catalyst in the STR ($da/dt = -k_D a$) for a first-order reaction ($r = kC_A a$). We will consider two limiting cases, specifically, data analysis without taking into account the reactor type and correct data interpretation.

Using the familiar relationship $a = X/X^0$ (which is invalid here, because the reaction is first-order) and allowing for a natural spread of experimental data, it is possible to fit the conversion data to a straight line (Fig. 10a). The slope of this line gives a deactivation rate constant of $k_D = 0.9$ h^{-1}.

For correct data interpretation, it is necessary to obtain Eq. (17) using formula (11) and to plot experimental data in terms of this equation (Fig. 10b). The

deactivation rate constant will then be $k_D = 5.0$ h^{-1}, which exceeds the first, incorrect estimate by a factor of larger than 5. An erroneous prediction of catalyst stability would lead to obvious consequences.

Consider the particular example of the deactivation of the platinum catalyst in the dehydrogenation of naphthenes (cyclohexane and methylcyclohexane). Relevant experimental data have been reported in many publications [1, 3, 5]. The $a(t)$ dependence observed in this case (Fig. 11) is characteristic of reversible deactivation accompanied by the self-regeneration of the catalyst under the action of excess hydrogen.

In this particular case, catalyst deactivation is due to coking caused by MCP added to the reaction mixture [1]. Above 310°C, the reaction obeys first-order kinetics. MCP in this reaction is converted to a small extent; therefore, $C_{MCP} \approx$ const and this value can be included into the deactivation rate constant. Thus, this reaction provides a typical example of independent deactivation.

In the formal description of experimental data in terms of Eq. (31a), the exponent n must be above unity (Fig. 11a). In the case considered, $n = 4$. Pal *et al.* [5]
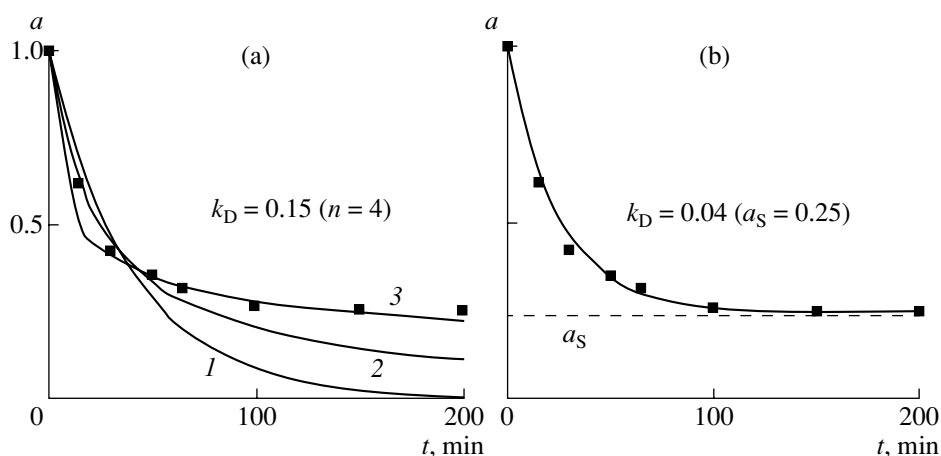
Fig. 11. Deactivation of the Pt/Al$_2$O$_3$ catalyst in cyclohexane dehydrogenation [1]: (a) formal description in terms of the power-law equation (31a) with $n = $ (*1*) 1, (*2*) 2, and (*3*) 4; (b) description taking into account catalyst self-regeneration.

assumed $n = 2$ for methylcyclohexane dehydrogenation. Attempts to interpret this relationship lead to the conclusion that four coke precursors at a time interact on the surface being deactivated. The probability of this mechanism is nearly zero. Furthermore, since the rate of self-regeneration (the hydrogenation of coke precursors) depends on temperature, n must also be temperature-dependent. This inference is in conflict with the very essence of the equation

$$\frac{da}{dt} = -k_D C_{MCP} a^n. \tag{31a}$$

In fact, according to the approach described in the first section, the deactivation rate is described by the equation

$$\frac{da}{dt} = -k_D C_{MCP} \frac{a - a_S}{1 - a_S}. \tag{31b}$$

This equation leads to the plot shown in Fig. 11b. Here, the temperature dependence of self-regeneration is accounted for by the quantity $a_S = 1/(1 + k_D C_{MCP}/k_R C_H)$, which depends on temperature, since k_D, k_R, and the hydrogen concentration C_H are functions of temperature.
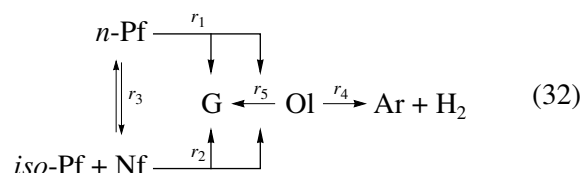
This example clearly demonstrates that the formal description not only leads to incorrect estimates of kinetic parameters (k_D) but also "incites" the researcher to a misinterpretation of the observed kinetic law. This may give rise to errors in process control.

INTERRELATION BETWEEN REACTION AND CATALYST DEACTIVATION KINETICS

It was noted in the first section that the deactivation rate equations are often related to the kinetics of the main reaction. Let us consider another aspect of this relationship. Reaction kinetics are generally studied under conditions that minimize the effect of deactivation. However, measurements taken under conditions of considerable catalyst deactivation can provide more information, since this regime is dynamic.

By way of example, we will consider the Zeoforming process, which is the production of high-octane gasoline from a low-octane straight distillate using a zeolite catalyst [6, 7]. Based on available experimental data for a variety of raw materials and catalysts, we constructed a kinetic model for the conversion of lumped components of gasoline [8]:

$$
\begin{array}{c}
n\text{-Pf} \xrightarrow{r_1} \\
\Big\updownarrow r_3 \qquad G \xleftarrow{r_5} Ol \xrightarrow{r_4} Ar + H_2 \\
iso\text{-Pf} + Nf \xrightarrow{r_2}
\end{array}
\tag{32}
$$

$$r_1 = k_1 Y_{n\text{-Pf}}, \quad r_2 = k_2 Y_{iso\text{-Pf}+Nf},$$

$$r_3 = k_3 Y_{n\text{-Pf}}(1 - Y_{iso\text{-Pf}+Nf}/K_{eq}Y_{n\text{-Pf}}) \tag{33}$$

$$r_4 = k_4 Y_{Ol}^2, \quad r_5 = k_5 Y_{Ol} Y_H,$$

where Ar, Ol, G, n-Pf, and iso-Pf + Nf are aromatic products, olefins, gases, n-paraffins, and iso-paraffins plus naphthenes, respectively; r_j is the rate of the jth reaction; Y_i is the mole fraction of the ith component; Y_H is the mole fraction of hydrogen; k_j is the rate constant of the jth reaction; and K_{eq} is the equilibrium constant.

The quality of the description of experimental data for two different feeds can be judged from Fig. 12.

An analysis of dynamic experimental data obtained for a catalyst undergoing deactivation (while raising the reaction temperature in steps) [9] enabled us to construct a new model taking into account the catalyst deactivation [10]. This analysis has demonstrated that the above kinetic model not only should be supple-
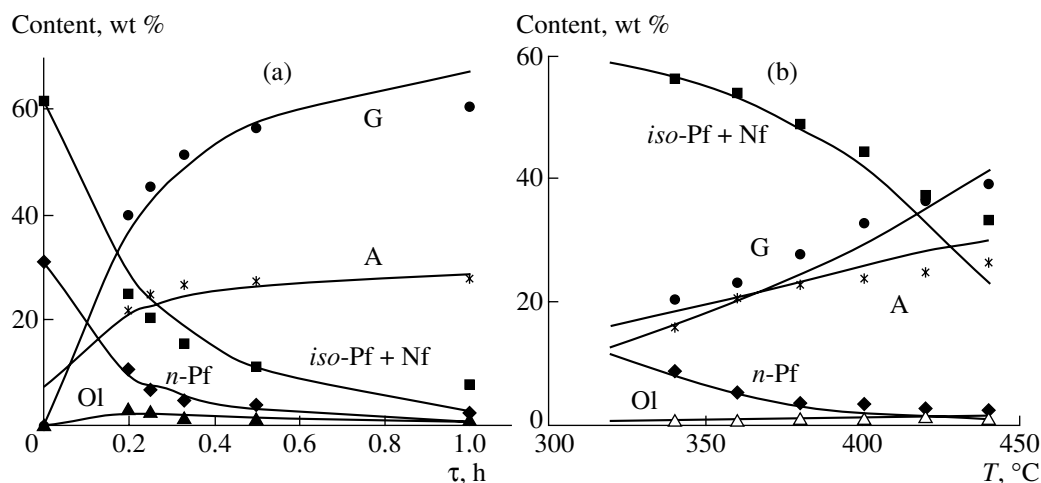
Fig. 12. (a) Composition of the product mixture resulting from the conversion of the light naphtha fraction as a function of the contact time. (b) Composition of the product mixture resulting from the conversion of a mixture of octane, isooctane, and cyclohexane as a function of the reaction temperature. The points are experimental data [7], and the lines are calculated using Eqs. (32) and (33) [8].
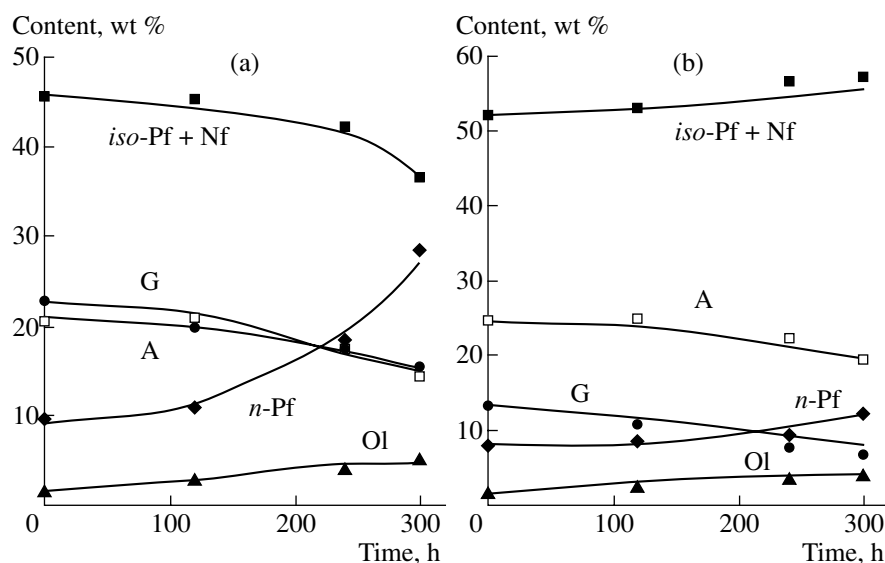

Fig. 13. Evolution of the product mixture in light naphtha conversion on the (a) original and (b) modified catalysts undergoing deactivation. The points are experimental data [9], and the lines are calculated using Eqs. (34) and (35) [10].

mented with deactivation equations but also needs to be modified [10]:

$$r_1 = k_1(1 - \Theta_{Ol})Y_{n\text{-}Pf}a_C, \quad r_2 = k_2(1 - \Theta_{Ol})Y_{iso\text{-}Pf + Nf}a_C,$$

$$r_3 = k_3(1 - \Theta_{Ol})Y_{n\text{-}Pf}[1 - Y_{iso\text{-}Pf + Nf}/(K_{eq}Y_{n\text{-}Pf})]a_C, \quad (34)$$

$$r_4 = k_4\Theta_{Ol}^2 a_P, \quad r_5 = k_5\Theta_{Ol}Y_H a_P,$$

$$\frac{da_C}{dt} = -k_C\Theta_{Ol}a_C, \quad \frac{da_P}{dt} = -k_{eq}\Theta_{Ol}^2 a_P^2. \quad (35)$$

Here, a_C and a_P are the relative activities of active sites covered with condensed and polymeric (low-condensed) coke, respectively, and $\Theta_{Ol} = b_{Ol}Y_{Ol}/(1 + b_{Ol}Y_{Ol})$

is the surface concentration of adsorbed olefins (the olefin coverage of the surface).

The principal feature of the modified model is that olefin adsorption inhibits the olefin conversion reactions (r_4 and r_5). Experimental deactivation data for the original catalyst and for the same catalyst with an enhanced stability and the description of these data in terms of the modified model are presented in Fig. 13. Note that the modifications made to the kinetic model allow other data to be better described. Furthermore, the modified model is less sensitive to the nature of the feed. The improved catalyst (Fig. 13b) is characterized

by a changing heat of olefin adsorption, Q_{Ol}: $b_{Ol}(T) = b_{Ol}^0 \exp(Q_{Ol}/RT)$.

In this paper, we have discussed only some of the problems arising in kinetic studies of catalyst deactivation and in catalyst stability tests. Among the other challenges in this area, note the description of catalyst deactivation by a number of simultaneous mechanisms (such as poisoning, coking, sintering, and phase transitions of the active component) and the prediction of the behavior of the catalyst in an industrial reactor from the results of laboratory-scale or pilot tests. All of these problems are reducible, to a considerable extent, to the problem of representing, processing, and interpreting experimental data. This is the reason why we have devoted this publication to demonstrating, by simple examples, possible approaches to this problem.

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