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Chemical Engineering Journal 120 (2006) 73–82

Chemical Engineering Journal

www.elsevier.com/locate/cej

General equation for linear mechanisms of catalyst deactivation

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Abstract

A rigorous approach to designing deactivation kinetic models is proposed, based on detail mechanisms of catalytic reaction and deactivation. It is demonstrated that deactivation equations can be derived using the Bodenstain principle of quasi-steady state approximation. A general equation applicable to any linear mechanism is suggested. Several examples are given regarding various reaction mechanisms and deactivation.

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Keywords: Catalyst deactivation; Linear mechanisms; General equation

1. Introduction

Widely used deactivation models are either partly or completely empirical. They are classified as one of two types:

1. The Levenspiel models [1] expressed in terms of relative activity a:

$$a = \frac{r}{r^0}, \qquad \frac{da}{dt} = -\psi(C, T)a^d \tag{1}$$

where r, r^0 are the current and initial reaction rates.

2. The Froment models [2] which are given in terms of coke concentration C_c:

$$\Phi(C_c) = \frac{r}{r^0}, \qquad \frac{dC_c}{dt} = -\phi(C, T, C_c) \tag{2}$$

Functions $\Phi(C_c)$ are traditionally represented in several standard forms:

$$1 - \gamma C_c, \quad (1 - \gamma C_c)^{-1}, \quad \exp(-\gamma C_c) \tag{3}$$

However, it is possible to derive the rigorous models in terms of both parameters a and C_c. In particular Corella and Asua [3] have found that in Eq. (1) $d=(m+h-1)/m$, where m and h are the numbers of active sites involved in the limiting stages of the main and deactivation reactions. Marin et al. [4] have developed a rigorous model of deactivation by coke in terms of active sites coverage and pore blockage.

In this paper, the rigorous deactivation kinetic model is represented in a general form applicable to any linear mechanism. First of all, the proposed model has a definitive structure of function $f(C,T)$ in Eq. (1). A special function of relative activity $\varphi(a)=(a-a_S)/(1-a_S)$ has been derived for the case of reversible deactivation.

1.1. *Quasi-steady state condition for deactivation*

The principle of quasi-steady state was formulated by Bodenstain and Semenov that is widely used in chemical kinetics. Frank-Kamenetsky formulates the mathematical condition of quasi-steady state approximation [5]. This idea is also the base of Temkin–Horiuti theory of stationary catalytic reactions [6]. The problems of catalytic reaction under steady state and quasi-steady state conditions are analyzed in detail in monographs of Kiperman [7] and Yablonskii et al. [8].

In accordance with [8] "…during the reaction, the intermediates concentrations are functions of observable substances, and are slaved to their values as though stationary ones", it follows that the concentration of intermediate (coverage, Θ_j) changes faster than concentration of reagents (C_i). Nevertheless, it does not mean that $d\Theta_j/dt \gg dC_i/dt$. On the contrary, the quasi-steady state condition is often formulated as $d\Theta_j/dt \approx 0$. Such a duality

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doi:10.1016/j.cej.2006.03.026

comes from the fact that the right part of equation for Θ_j is always the difference of formation and consumption rates of Θ_j:

$$\frac{d\Theta_j}{dt} = \sum (r_i)_{\text{form.}} - \sum (r_i)_{\text{cons.}} \qquad (4)$$

Under quasi-steady state condition, this difference tends to zero (in accordance with the nature of catalysis). The analogous values for reagents are equal to their formation rates.

A sufficiently complete analysis of physical backgrounds of quasi-steady state in catalytic reactions has been carried out by Yablonskii et al. [8], with the rigorous mathematical formulation of minor parameter problem in the system of differential equations.

As applied to deactivation, an important simplification of the Bodenstain method was proposed by Semenov [9]. He supposed that at quasi-steady state the conditions of Frank-Kamenetsky will not be fulfilled for all intermediates (coverage). Then for Bodenstain products the condition $d\Theta_j/dt \approx 0$ is fulfilled, and for others the differential equations should be written along with equations for reagents.

Obviously, this type of quasi-steady state corresponds entirely to the reaction accompanied by catalyst deactivation phenomena. Here the only intermediates (coverages) Θ_j, that take part in catalytic cycle, are Bodenstain products, but others Θ_{Di} represent active sites are switch-controlled due to poisoning, coking or another type of deactivation.

Then quasi-steady state conditions for catalytic reaction accompanied by catalyst deactivation can be presented as follows:

$$\frac{d\Theta_j}{dt} \approx \frac{d\Theta_j^0}{dt} = 0, \quad j = 1, ..., N;$$

$$\frac{d\Theta_{Di}}{dt} \neq 0, \quad i = 1, ..., M; \qquad \sum \Theta_j = 1 - \sum \Theta_{Di} \qquad (5)$$

The first equality in (5) means that quasi-steady state approximation is valid for the reaction on both fresh catalyst ($d\Theta_j^0/dt = 0$), and catalyst being deactivated ($d\Theta_j/dt \approx 0$). This is of fundamental importance for the reaction on deactivating catalyst, because gives the possibility to use the theory of stationary reactions for derivation of reaction rate equations.

Besides, it is necessary to note that deactivation and self-regeneration rates (r_D, r_R), are usually much lower than the reaction rate (r), and in turn, the rate of catalyst aging (r_A) is lower than rate of deactivation:

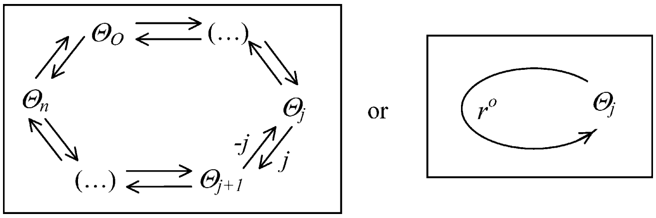
$$r \gg r_D \approx r_R \gg r_A \qquad (6)$$

This feature alone serves as a physical basis of quasi-steady state of the reaction on the catalyst being subjected to deactivation. Due to this reason, there is the possibility to realize commercial catalytic processes, in spite of catalyst deactivation.

2. Reaction rate at catalyst deactivation

Only linear mechanisms will be considered in this paper, in which the rates of reaction steps are linear with respect to the surface intermediates (coverages).

The one-route linear mechanism presented by the follow catalytic cycle will be considered here:



(M1)

In steady state (fresh catalyst) the reaction rate (r^0) is equal to the rate of any step of the mechanism (r_j^0):

$$r^0 = r_j^0 = w_j\Theta_j^0 - w_{-j}\Theta_{j+1}^0 \qquad (7)$$

where w_j, w_{-j} are the weights of the chosen step in forward and reverse directions.

The weight of step is defined as ratio ($w_j = r_j/\Theta_j$) of step rate and coverage that take part in this step. The corresponding rules are given in [8]. For example in step:

$$\text{A} + \text{ZB} = \text{AZ} + \text{B}, \qquad r = kC_A\Theta_{ZB}, \qquad w = kC_A$$

This allows the simple derivation of the reaction rate equations using a different technique [6,8,10]. A general equation was derived in [8] using graph theory:

$$r^0 = \frac{\prod_j w_j - \prod_j w_{-j}}{\sum_i B_{f_i} + \sum_i B_{r_i} + \sum_i \sum B_{m_i}} \qquad (8)$$

Its numerator is a difference of weight products of all forward and reverse steps, i.e. it corresponds to the mass action law. Its denominator equals to the sum of carcass weights, which are formed by forward, reverse and by mixed steps in the reaction mechanism.

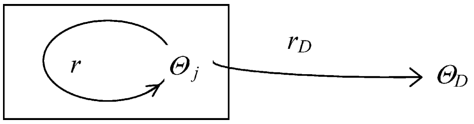
The equation of reaction rate under catalyst deactivation (r) is now derived. From the definition of relative activity (a) one can write:

$$r(t) = r^0 a(t) \qquad (9)$$

This relation is universal and does not depend on reaction and deactivation mechanisms. Thus, individual features of reaction reflect only in functions $r^0(C,T)$ and $a(C,T,t)$. This matter is at the heart of the problem of "separable" and "non-separable" deactivation kinetics that are widely discussed in literature, starting with Szepe and Levenspiel [11].

We claim that the necessary condition of "separable" kinetics is quasi-steady state condition. If it is not true then deactivation kinetics are not applicable, and then reagents and intermediates equally determine the process dynamics.

In order to substantiate the reaction rate equation, the following scheme is considered:



(M2)

Here r is the reaction rate, r_D the rate of deactivation; Θ_D is deactivated part of surface (or active centers).

Similarly to (7) one can write for the reaction rate:

$$r = r_j = w_j\Theta_j - w_{-j}\Theta_{j+1} \tag{10}$$

Under deactivation, due to quasi-steady state condition (5):

$$\sum \Theta_j = 1 - \Theta_D(t) \tag{11}$$

whereas at $t=0$: $\sum \Theta_j^0 = 1$, since $\Theta_D(0)=0$. Then, using results of [8–10], one can show that in a linear mechanism for any coverage the following relation is valid [12–14]:

$$\Theta_j(t) = \Theta_j^0[1 - \Theta_D(t)], \quad j = 1, ..., N \tag{12}$$

Substituting (12) in (10) we obtain that $r = (w_j\Theta_j^0 - w_{-j}\Theta_{j+1}^0)[1 - \Theta_D(t)]$.

Finally, taking into account (7) we have for the reaction rate on deactivating catalyst:

$$r(t) = r^0[1 - \Theta_D(t)] \tag{13}$$

From the comparison of this equation with (9) one can conclude that

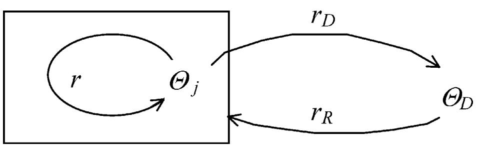
$$a(t) = 1 - \Theta_D(t) \tag{14}$$

So, for the reaction having linear mechanism, the reaction rate (under deactivation) can be represented in form of "separable" kinetics (Eqs. (9) or (13)).

It is necessary to note that these equations do not depend absolutely on the number of deactivation steps (Θ_D formation) and on their mechanisms. Deactivation steps can be reversible or irreversible, linear or nonlinear. Even when several deactivation phenomena are occurring (sintering, poisoning, coking) the reaction rate Eq. (13) remains the same. Concrete deactivation mechanism becomes apparent only in deactivation kinetics, i.e. via the function $a(C,T,t)$. So one can conclude that Eq. (13) is valid for linear reaction mechanisms and any deactivation mechanisms.

3. Rate of deactivation

Catalyst deactivation will be considered as a set of slow (in sense of (5) and (6)) steps of formation and consumption of deactivated centers (Z_D) are presented by coverage Θ_D. The following scheme may be used for visualization:



(M3)

where r_D, r_R are rates of catalyst deactivation and "self-regeneration".

The self-regeneration term is considered as a process of renewal of active centers by action of some reagent during the reaction, but not in regeneration period. This phenomenon is prevalent in many commercial processes. Hydrogen, water steam and oxygen are usually used for the purpose of self-regeneration, increasing the operating cycle by a factor of 10^2 to 10^3. They prevent or inhibit catalyst poisoning and coking in the processes of paraffins isomerization and naphtha reforming (H_2); olefins dehydrogenation and isomerization (H_2O); oxidative dehydrogenation (O_2).

Thus, deactivation is considered as partly reversible process. However, self-regeneration step (r_R) is not strictly the reverse step of deactivation (r_D). For example if Θ_j is the initial intermediate in deactivation step ($\Theta_j \to \Theta_D$), in self-regeneration step another intermediate can form ($\Theta_D \to \Theta_{j+1}$ or $\Theta_D \to \Theta_0$).

The deactivation equation for scheme (M3) is

$$\frac{d\Theta_D}{dt} = w_D\Theta_j - w_R\Theta_D \tag{15}$$

Certainly, this equation is not useful in practice and it should be rearranged. In order to carry out the rearrangement, two questions are of interest:

1. How to express the Θ_D through measured values—relative activity (a) and $f(C,T)$?
2. How to get rid of Θ_j in deactivation Eq. (15)?

The first question has a simple answer in the case of linear mechanisms—Eq. (14), $a = 1 - \Theta_D$. For the second question (7) and (12) are key relations. In according to (12) $\Theta_j = \Theta_j^0(1 - \Theta_D)$, and Θ_j^0 can be expressed through the rate and weight of j-th step $\Theta_j^0 = r_j^0/w_j$. In turn, due to (4) $r_j^0 = r^0$, then:

$$\Theta_j = \frac{r^0}{w_j}(1 - \Theta_D) \tag{16}$$

If j-th step of mechanism is reversible, then $\Theta_j = (r^0/w_j\varphi_j)(1 - \Theta_D)$. If all mechanism steps, except limiting one (j-th), are in equilibrium, then:

$$\varphi_j = \varphi = 1 - \frac{\prod_i^N C_i^{\nu_i}}{K_P}$$

where φ_j, φ are equilibrium parameters of step and of reaction. So, further analysis can be made for irreversible reactions ($\varphi_j = 1$).

Taking into account (16) we obtain for (15):

$$\frac{d\Theta_D}{dt} = \frac{r^0}{w_j}w_D(1 - \Theta_D) - w_R\Theta_D \tag{17}$$

It can then be easily written in terms of relative activity. Since from (14) $a = 1 - \Theta_D$, then $da = -d\Theta_D$ and, therefore:

$$\frac{da}{dt} = -\frac{r^0}{w_j}w_D a + w_R(1 - a) \tag{18}$$

This equation is valid as a model of reversible deactivation kinetics for any one-route reaction occurring via linear mechanism. The concrete mechanism determine forms of reaction rate (r^0) and weight of steps (w_D, w_R, w_j) that are functions of temperature and concentrations.

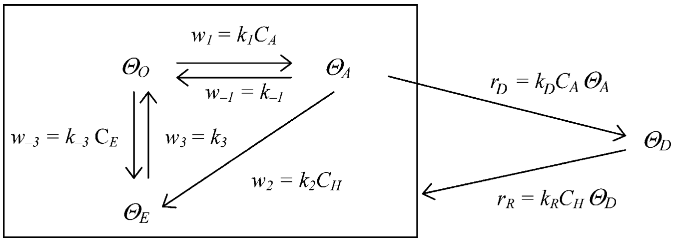
Example 1 *(Selective hydrogenation of alkynes).* The following demonstrates how the deactivation equation can be derived for selective hydrogenation of acetylene in ethene pyrolysis fraction:

$$\overset{\text{(D)}}{\text{condensation products}} \leftarrow \overset{\text{(A)}}{C_2H_2} + \overset{\text{(H)}}{H_2} \rightarrow \overset{\text{(E)}}{C_2H_4}$$

Deactivation occurs as a result of condensation product formation, so-called “green oil”. Partial self-regeneration is provided by hydrogen. The simplified mechanism is

(1) $C_2H_2 + Z \leftrightarrow C_2H_2Z, r_1 = k_1C_A\Theta_0 - k_{-1}\Theta_A$
(2) $H_2 + C_2H_2Z \rightarrow C_2H_4Z, r_2 = k_2C_H\Theta_A, w_2 = k_2C_H$
(3) $C_2H_4Z \leftrightarrow C_2H_4 + Z, r_3 = k_3\Theta_E - k_{-3}C_E\Theta_0$
(4) $C_2H_2 + C_2H_2Z \rightarrow ZD, r_D = k_DC_A\Theta_A, w_D = k_DC_A$ (deactivation)
(5) $H_2 + ZD \rightarrow C_2H_2Z + C_2H_2, r_R = k_RC_H\Theta_D, w_R = k_RC_H$ (self-regeneration)

For visualization, the mechanism is represented in graphical form:



(M4)

When the second step is limiting and first and third ones are in equilibrium:

$$r^0 = \frac{k_2b_AC_AC_H}{1 + b_AC_A + b_EC_E} = \frac{k_2b_AC_AC_H}{D}, \quad D = 1 + b_AC_A + b_EC_E \tag{19}$$

The deactivation equation (4-th and 5-th steps) have a form:

$$\frac{d\Theta_D}{dt} = k_DC_A\Theta_A - k_RC_H\Theta_D.$$

In according with (16) $\Theta_A = (r^0/k_2C_H)\,(1 - \Theta_D)$, therefore:

$$\frac{d\Theta_D}{dt} = \frac{k_DC_A}{k_2C_H}r^0(1 - \Theta_D) - k_RC_H\Theta_D$$

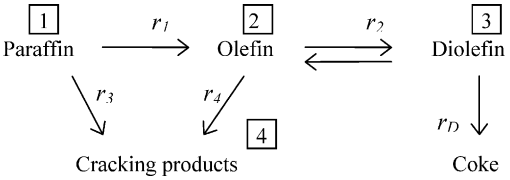
Since $a = 1 - \Theta_D$, and substituting r^0 from (19), we obtain:

$$-\frac{da}{dt} = \frac{k_Db_AC_A^2}{D}a - k_RC_H(1 - a) \tag{20}$$

Note that deactivation rate has second order kinetics with respect to acetylene, whereas the reaction rate is first order. Any simplification in the mechanism of the main reaction simplifies in turn the deactivation equation. For example, at low temperature the acetylene adsorption strength is higher, so $1 + b_EC_E \ll b_AC_A$ and therefore $D \approx b_AC_A$. Then reaction rate Eq. (19) becomes zero order with respect to C_A, and the deactivation Eq. (20) becomes first order:

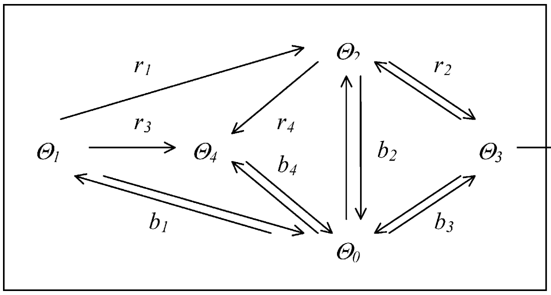
$$r^0 = k_2C_H, \qquad -\frac{da}{dt} = k_DC_Aa - k_RC_H(1 - a) \tag{21}$$

Example 2 *(Paraffins dehydrogenation).* The process of paraffins dehydrogenation (butane and isopentane) is intended for production of synthetic rubber monomers–butadiene and isoprene. The reactions are usually carried out on chromia–alumina catalysts in fluidized bed reactors. Catalyst deactivation is caused by coking. The main reactions are dehydrogenation, cracking and coking:



(M5)

The simplified mechanism can be presented in form of graph (M6), where Θ_i is coverage corresponds to reagent, r_j the reaction rate, Θ_0 the fraction of vacant sites on the surface, Θ_D the fraction of surface coverage by coke, b_i is the adsorption equilibrium coefficient.



(M6)

Self-regeneration is practically absent in these processes, which are carried out in the reactor-regenerator system with catalyst circulation. The residence-time consists of 6–12 min in reactor, and 12–20 min in regenerator.

It is supposed in [15], that all the reactions are proceed on the one type of active sites, and therefore the coking decreases all the reactions equally, without changing in selectivity.

Assuming all adsorption steps to be in equilibrium, the reaction rate equations on the fresh catalyst (r_j^0) are readily expressed as

$$r_1^0 = \frac{k_1b_1P_1}{D}, \qquad r_2^0 = \frac{k_2b_2P_2\varphi}{D}, \qquad r_3^0 = \frac{k_3b_1P_1}{D},$$
$$r_4^0 = \frac{k_4b_2P_2}{D}, \qquad D = 1 + b_1P_1 + b_2P_2 + b_3P_3 + b_4P_4,$$
$$\varphi = \frac{1 - P_3P_{H2}}{P_2K_P} \tag{22}$$

where P_i is the partial pressure and K_P is the equilibrium constant.

Because of uniform catalytic surface, the relations (12)–(14) are valid for all the reactions of mechanism (M6):

$$\Theta_i = \Theta_i^0(1-\Theta_D), \qquad r_j = r_j^0(1-\Theta_D), \qquad a = 1-\Theta_D.$$

Deactivation rate is proportional to the rate of coking that is determined by diolefin concentration (butadiene or isoprene) $r_D = k_D P_3 \Theta_3$, therefore:

$$-\frac{da}{dt} = \frac{d\Theta_D}{dt} = k_D P_3 \Theta_3 = k_D P_3 \Theta_3^0 (1-\Theta_D) = k_D P_3\, \Theta_3^0 a. \tag{23}$$

Due to the equilibrium of adsorption steps $\Theta_3^0 = b_3 P_3/D$. In commercial conditions at high temperature (500–580 °C), the adsorption does not inhibit the reaction, therefore $D \approx 1$. Besides, second reaction is close to thermodynamic equilibrium ($\varphi \to 0$ and $r_2^0 \approx 0$), therefore diolefin partial pressure (P_3) may be expressed through the olefin and hydrogen $P_3 = P_2 K_P / P_{H2}$.

Finally $P_2/P_{H2} \approx 1$, due to the shift of equilibrium to the left. Then $\Theta_3^0 \approx b_3 K_P$ and after substitutions the deactivation Eq. (23) becomes simple but unusual:

$$\frac{da}{dt} = -k_D b_3 K_P^2 a \tag{24}$$

Note that since parameters (k_D-deactivation constant, b_3-adsorption coefficient, K_P-equilibrium constant) are not dependant on concentration, then deactivation rate (24) should not depend on space velocity or contact time. This conclusion follows from only thermodynamic data and rather simple mechanism, however, it almost agrees with experimental data [16].

On the other hand, all mentioned parameters depend on temperature, therefore, the effective deactivation constant $k_D^* = k_D b_3 K_P^2$ is characterized by unusual high effective activation energy:

$$E^* = E_D - Q_3 + 2\Delta H_2 = 60\text{–}65\,\text{kcal/mol}$$

where E_D is the coking activation energy, Q_3 heat of diolefin adsorption, and ΔH_2 is heat of reaction of diolefin formation.

Unusual sensitivity of catalyst deactivation to the temperature follows from the above considerations. Even small increases of temperature can cause formation of “salamander” in a fluidized bed containing coke and catalyst [17]. This example shows evidently that deactivation kinetics becomes rather informative when the equation (especially *f*(*C*,*T*)-function) is derived, but not fitted only from the experiments.

4. Approximate equation for reversible deactivation

Eq. (18) can be considered as a final formula for linear mechanisms. However, it is rather difficult in practice to fit the self-regeneration parameters. Sometimes, the form of function (w_R) is unknown. The term w_R is eliminated from the equations by introducing the term of “residual” activity (a_S).

This “stationary activity” will be defined as the activity value that is achieved, when the rate of deactivation (r_D) and rate of self-regeneration (r_R) become equals to each other.

It is inevitable that $a_S \approx$ const must be established for reversible deactivation, since during catalyst poisoning the rate of deactivation is also decreased, but the rate of self-regeneration practically is not changed.

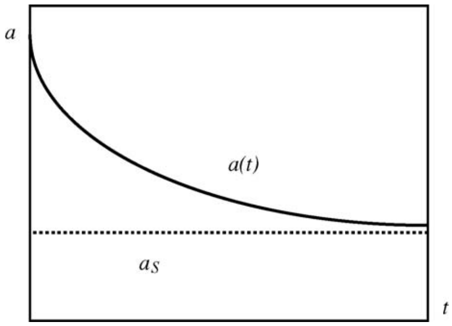


Fig. 1. The illustration of stationary (residual) activity a_S.

This is assumed to occur at the time $t = t_S$: $r_D(t_S) = r_R(t_S)$. Then one can write with some inaccuracy (ε) that corresponds to experimental error: $\Theta_D(t_S) = (\Theta_D)_S \pm \varepsilon$ and $a(t_S) = a_S \pm \varepsilon$.

For determining of a_S it is necessary to equate the right part of Eq. (18) with zero: $w_R(1-a_S) - r^0 a_S w_D / w_j = 0$, then:

$$a_S = \left[1 + \frac{r^0}{w_j}\frac{w_D}{w_R}\right]^{-1}, \quad \text{at}\, t \geq t_S \tag{25}$$

It is then possible to express the w_R through a_S and substitute in (18). After simple transformation, Eq. (18) takes the form:

$$\frac{da}{dt} \approx -\frac{r^0}{w_j} w_D \frac{a-a_S}{1-a_S}, \quad \text{at}\, t < t_S \tag{26}$$

From the mathematical point of view, such a substitution is not strictly correct, since the function w_R in Eq. (18) is expressed through the asymptotic solution of this equation. However, it becomes possible if $w_R \approx$ const, that is applied in most practical cases.

For example, in the process of acetylenes hydrogenation in pyrolysis fractions (mentioned above), the self-regeneration is provided by hydrogen. Because of hydrogen excess its concentration varied weakly, and therefore in (21) $w_R = k_R C_H \approx$ const. Then $k_R C_H$ can be expressed through a_S, and deactivation equation takes a form:

$$\frac{da}{dt} = -k_D C_A \frac{a-a_S}{1-a_S} \tag{27}$$

Eq. (26) may be thought of as an approximate equation of reversible deactivation. It was derived firstly in [12] and was proved in addition in [13,14].

Concurrently and independently, similar forms of equation were proposed in works [18–20]:

$$\frac{da}{dt} = -\psi(C,T)(a-a_S)^n \quad \text{or} \quad \frac{da}{dt} = -\psi(C,T)(a^n - a_S^n)$$

however, any analytical derivation of these equations and grounds of function ψ(*C*,*T*) were made.

The facility of approximate Eq. (26) is clearly seen even from Fig. 1. The value of a_S is easy to evaluate from the imaginary asymptote of deactivation curve, and k_D value—from its slope at $t = 0$.

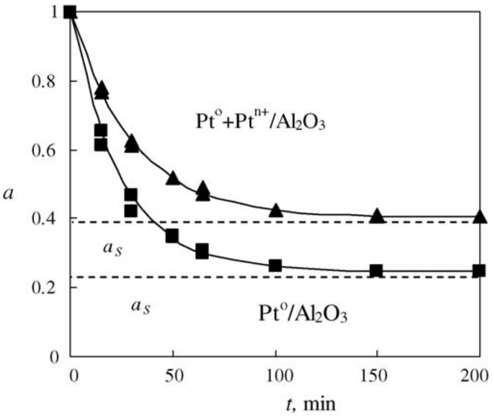


Fig. 2. Reforming catalyst deactivation during dehydrogenation of CH containing MCP [25]. Points: experiments; lines: according to Eq. (30).

Such a prior estimations are very useful for analysis of experimental data.

Example 3 *(Dehydrogenation of naphthenes)*. The reaction of naphthenes dehydrogenation into aromatics is considered, taking specifically the following examples: cyclohexane to benzene ($C_6H_{12} = C_6H_6 + 3H_2$) or methyl cyclohexane to toluene ($C_6H_{11}CH_3 = C_6H_5CH_3 + 3H_2$). These reactions are widely used for investigation of supported metal catalyst. Besides, they are main reactions in naphtha reforming process over Pt/γ-Al_2O_3 or Pt–Re/γ-Al_2O_3, Pt–Sn/γ-Al_2O_3.

The mechanism and kinetics of this reaction have been investigated in detail on several catalysts and under different conditions [21–24]. The simplified mechanism [21] and corresponding kinetic equation [21,23] are presented below:

1. $N + Z = AZ + 3H_2$
2. $AZ = A + Z$

$$r^0 = \frac{k_1 P_N}{1 + b_A P_A}\varphi, \quad \varphi = 1 - \frac{P_A P_H^3}{K_P P_N} \tag{28}$$

Here P_N, P_A, P_H are partial pressure of naphthenes, aromatics and hydrogen, k_1 the reaction rate constant of limiting step, b_A the adsorption coefficient, and K_P is the equilibrium constant.

Under typical reaction conditions ($T = 300$–$350\,°C$, H2/CH ratio $\lambda = 3$–5 mol/mol), catalyst deactivation is not observed. It becomes noticeable in the inert gas atmosphere [23], or in the presence of other hydrocarbons, for example methylcyclopentane (MCP). The last case corresponds to reforming of naphtha consisting of naphthenes and paraffins.

Deactivation of dehydrogenation active sites has a typical reversible character [24–26] due to the catalyst self-regeneration by hydrogen. Fig. 2 illustrates this fact and represents the influence of ionic platinum (Pt^{n+}) on stability of reforming catalyst [25]. The reaction feed was:

- Cyclohexane (CH): −65%
- Methylcyclopentane (MCP): −25%
- *n*-Hexane (*n*-C6): −7.5%
- Benzene (B): −2.5%

Reaction conditions: $T = 360\,°C$, $P = 1$ bar, $\lambda = 5$ mol/mol, gradientless reactor.

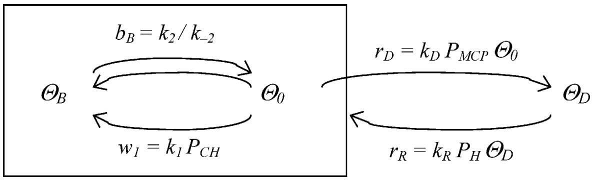
Such a condition provides only cyclohexane dehydrogenation, and MCP conversion does not exceed 1–3%. However, only MCP causes catalyst deactivation [27,28].

Under the experimental conditions, the kinetic equation (28) is reduced to a first order dependence:

$$r^0 = \frac{k_1 P_{CH}}{1 + b_B P_B}\varphi \approx k_1 P_{CH} \tag{29}$$

since at $T > 320\,°C$ the reaction is irreversible ($\varphi = 1$), and the influence of benzene adsorption is negligible ($b_B P_B \ll 1$).

The reaction and deactivation mechanism can be presented as follows:



(M7)

The deactivation equation (26) readily follows using this scheme. Since $w_j = w_1 = r^0$, then:

$$\frac{da}{dt} \approx -\frac{r^0}{w_1} w_D \frac{a - a_S}{1 - a_S} = -k_D P_{MCP} \frac{a - a_S}{1 - a_S} \tag{30}$$

It was mentioned before that MCP conversion is in the range 1–3%, therefore $k_D P_{MCP} \approx k_D^* \approx$ const. For experiments of Fig. 2 the following parameters of Eq. (30) were obtained:

Catalyst	k_D^* (min^{-1})	a_S
$Pt^0 + Pt^{n+}/\gamma$-Al_2O_3	0.02	0.40
Pt^0/γ-Al_2O_3	0.03	0.25

An important feature of the equation is, that parameters k_D^* and a_S do not change with time. Then one can write:

$$\frac{da}{dt} = -k_D^* \frac{a - a_S}{1 - a_S} = -k_E(a - a_S)$$

In this form the solution of the equation is convenient, but it is not quite correct for application because of effective constant $k_E = k_D^*/(1 - a_S)$ may not obey the Arrhenius dependency. In accordance with (25) a_S is affected by temperature dependencies of the rates of reaction, deactivation and self-regeneration. In the last example, as it follows from (30), $r^0 w_D / w_j = k_D P_{MCP}$, and $w_R = k_R P_H$. Therefore, the equation for $a_S = 1/(1 + k_D P_{MCP}/k_R P_H)$, and since $P_{MCP}/P_H = \gamma \approx$ const, then $a_S = 1/(1 + \gamma k_D/k_R)$. Parameters k_D and k_R are subjected to Arrhenius dependencies: $k_D = k_D^0 \exp(-E_D/RT)$, $k_R = k_R^0 \exp(-E_R/RT)$, therefore $a_S(T)$ will be determined by activation energies of deactivation and self-regeneration ($E_S = E_D - E_R$).

An example of $E_D = 30$ and $E_R = 10$ kcal/mol that illustrates a typical dependency $a_S(T)$ is presented in Fig. 3. It leads to decreasing of effective activation energy from 30 kcal/mol (for intrinsic constant k_D) to 15 kcal/mol (for effective constant k_E).

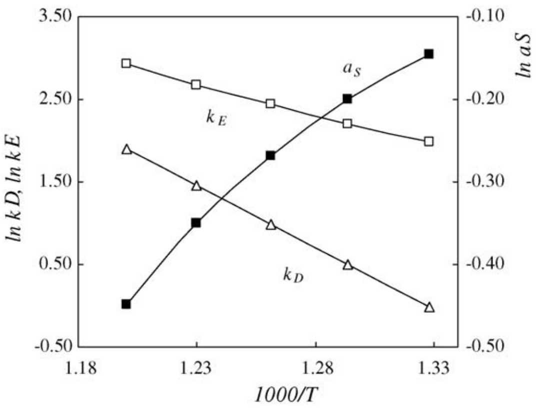
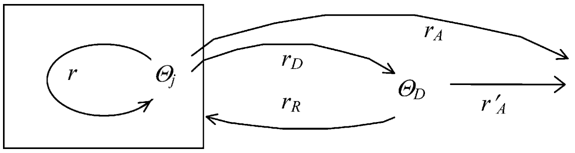


Fig. 3. The illustration of temperature dependency of a_S and k_E [43]. $E_D = 30$ kcal/mol; $E_E = 15$ kcal/mol; $E_S = 20$ kcal/mol.

5. Deactivation and aging

The process of catalyst aging is considered as slower than deactivation, so the irreversible decrease of catalyst activity takes place during the operation. The difference of aging and deactivation becomes apparent in cyclic processes. Inside each cycle, the catalyst is deactivated in the product period, and is renewed in regeneration period, whereas aging appears as falling of activity from cycle to cycle. The analysis of similar processes has been made by Fedotov and coworkers [29].

In processes having an extended operation of 0.5–1 year (reforming, hydrotreating) the deactivation and aging occur during one cycle. However, the initial fast falling of activity (deactivation) consists of only a small part of the catalyst life, and can be considered as quasi-steady state with respect to aging. Such an assumption allows simplification of the analysis of deactivation [12,13]. The process follows the scheme shown below:



(M8)

where Θ_D, Θ_A are the deactivated and aged surfaces, r the reaction rate, r_D, r_R the rates of deactivation and self-regeneration, r_A, r'_A are rates of aging.

Then according to scheme (M8) the system of deactivation equations is

$$\frac{d\Theta_D}{dt} = w_D\Theta_j - (w_R + w'_A)\Theta_D,$$
$$\frac{d\Theta_A}{dt} = w_A\Theta_j + w'_A\Theta_D. \qquad (31)$$

Here, according to quasi-steady state and similarly to (16):

$$\Theta_j = \frac{r^0}{w_j}(1 - \Theta_D - \Theta_A), \qquad a = 1 - \Theta_D - \Theta_A \qquad (32)$$

Therefore:

$$\frac{d\Theta_D}{dt} = \frac{r^0}{w_j} w_D(1 - \Theta_D - \Theta_A) - (w_R + w'_A)\Theta_D \qquad (33a)$$

$$\frac{d\Theta_A}{dt} = \frac{r^0}{w_j} w_A(1 - \Theta_D - \Theta_A) + w'_A\Theta_D \qquad (33b)$$

In this case $t = t_S$ also exists, at which deactivation and self-regeneration rates become equal $r_D = r_R$ and $d\Theta_D/dt = 0$. However, here $\Theta_D(t_S)$ is the maximum of function $\Theta_D(t)$. As for active surface dynamics, at $t > t_S$ the transit of temporary inactive sites (Θ_D) into absolutely inactive (Θ_A) takes place. Therefore, at first Θ_D is increased ($d\Theta_D/dt > 0$ at $t < t_S$), and then decreased ($d\Theta_D/dt < 0$ at $t > t_S$).

Taking into account that $a = 1 - \Theta_D - \Theta_A$, the equation for relative activity one can obtain from the system (33a) and (33b). It reduces to second order differential equation. For example at $w_A = 0$:

$$\frac{d^2 a}{dt^2} + \left(\frac{r^0}{w_j} w_D + w_R + w'_A\right)\frac{da}{dt} + \frac{r^0}{w_j} w_D w'_A a = 0$$

It is inconvenient to analyze and especially to apply this equation. Fortunately, the system (33a) and (33b) can be splitted in two independent equations in the case of condition (6):

$$r_A \ll r_D \approx r_R \ll r$$

It means that the reaction is quasi-steady state with respect to deactivation and deactivation is quasi-steady state with respect to aging. So, one equation will describe the fast period of deactivation, and another—slow period of aging. The time $t = t_S$, at which $r_D \approx r_R$, is the border of these periods.

5.1. *Equation for deactivation period*

At $t < t_S$, due to quasi-steady state, one can write taking into account (32):

$$\frac{d\Theta_A}{dt} \ll \frac{d\Theta_D}{dt} \quad \text{and} \quad da \approx -d\Theta_D \qquad (34)$$

Then at interval $[0, t_S]$ $d\Theta_A/dt \approx 0$ and $a \approx 1 - \Theta_D$. Summing (33a) and (33b) we obtain for a:

$$\frac{da}{dt} \approx -\frac{r^0}{w_j}(w_D + w_A)a + w_R(1 - a) \qquad (35)$$

After transformation, using term of stationary activity a_S, we obtain the equation like (26):

$$\frac{da}{dt} \approx -\frac{r^0}{w_j}(w_D + w_A)\frac{a - a_S}{1 - a_S}, \quad \text{at}\, t = 0, \quad a = 1 \qquad (36)$$

The difference arises from the fact that total rate of deactivation includes weights of deactivation (w_D) and aging (w_A) steps, and also in expression of “residual” activity a_S:

$$a_S = \frac{w_R}{(r^0/w_j)(w_D + w_A) + w_R} \qquad (37)$$

It is difficult in practice to determine the time $t = t_S$, after which Eq. (36) is no longer applicable. At extended times of

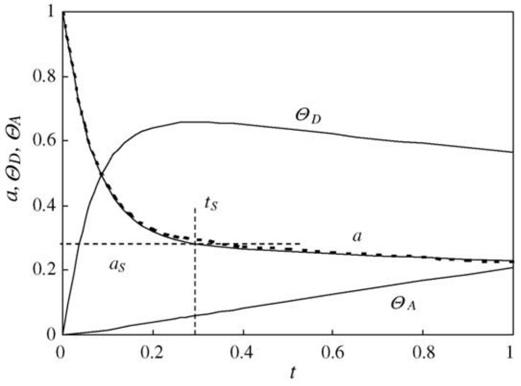


Fig. 4. Falling of activity under deactivation and aging. Solid lines: exact model (32), (33a) and (33b); dashed lines: approximate model (36) and (38); $t_S \approx 0.3$, $a_S = 0.284$.

operation the experimental data indicated that $a_S \neq \text{const}$ and slightly decreased. If such a decrease consists of more than 5–10% then the deactivation model should be completed by use of an aging equation.

5.2. *Equation for aging period*

At $t > t_S$ the parity of deactivation and self-regeneration rates comes true ($r_D \approx r_R$), therefore, further decrease of activity happens only due to the aging. Then $d\Theta_D \approx -d\Theta_A$ and, equating the right-hand side of (33a) and (33b) we obtain the correlation of a and Θ_D in the aging period:

$$a = \frac{w_R}{(r^0/w_j)(w_D + w_A)} \Theta_D$$

This expression is differentiated, $d\Theta_D/dt$ substituted from (33a) and w_R expressed through a_S from (37). Then we obtain a deactivation equation for aging period, i.e. at $t > t_S$:

$$\frac{da}{dt} \approx -\left(\frac{r^0}{w_j} w_A \frac{a_S}{1 - a_S} + w'_A\right) a, \quad \text{at } t = t_S, \quad a = a_S \tag{38}$$

Thus, Eqs. (36) and (38) approximate the system (33a) and (33b) and allow us to analyze separately deactivation and aging processes.

An example of such approximation is presented in Fig. 4. It was accepted in calculations that weights of steps are constants: $\alpha = 10.0$, $\beta = 4.0$, $\gamma_1 = 0.1$, $\gamma_2 = 0.3$, where

$$\alpha = \frac{r^0}{w_j} w_D, \qquad \beta = w_R, \qquad \gamma_1 = \frac{r^0}{w_j} w_A, \qquad \gamma_2 = w'_A$$

6. Equation structure and properties

The structure of equation of deactivation kinetics is rather important from both formal and physical points of view. It reflects a physical meaning of equation, its resolvability, parameters mutual effect, and the method of parameters estimation. Deactivation equation structure was examined in 50th by Maxted [30] and Wheeler [31]. The first attempt to justify the equation form has been made by Szepe and Levenspiel [11]. They postulate that deactivation rate may be presented as a product of functions:

$$-\frac{da}{dt} = f(C, T)\varphi(a) \tag{39}$$

where $f(C,T)$ is the function related to reaction condition and $\varphi(a)$ is the function of catalyst state (activity).

The power mode of functions was postulated:

$$f(C, T) = k_D C_i^n, \qquad \varphi(a) = a^d$$

where n and d values have to be evaluated from experiments.

Such an empirical form was widely used for the fitting of experimental data [19,23,32,33], as well as for optimization of the processes accompanied by catalyst deactivation [34–36].

A considerable contribution to the rigorous ground of power dependencies has been made by Corella and coworkers [3,37,38]. They proved a formula for deactivation rate order (d) with respect to activity:

$$-\frac{da}{dt} = f(C, T)a^d, \quad d = 1 + \frac{h - 1}{m} \tag{40}$$

where m, h are the number of active sites involved in the limiting steps of reaction and deactivation.

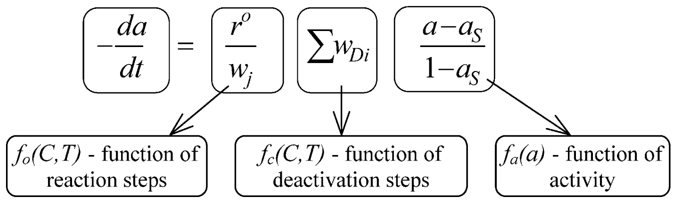
As for the function $f(C,T)$, it traditionally considers to be depending only on concentration of component causes deactivation. In several works [23,39–42] a different form of function $f(C,T)$ were derived for concrete mechanisms. However, general form of $f(C,T)$ was not determined. Such substantiation was published by Ostrovskii and coworkers in [12–14,43] and presented here.

As it follows from previous consideration and examples, the deactivation kinetic equation for linear mechanisms is always reduced to the form:

$$-\frac{da}{dt} = f_o(C, T)\ f_c(C, T) f_a(a) \tag{41}$$

where $f_o = r^0/w_j$ is a function depends only on the reaction kinetics, $f_c = w_{D_j}$ the function determined by deactivation kinetics, and $f_a = (a - a_S)/(1 - a_S)$ is a function depends only on the catalyst activity.

An example of such a form is Eqs. (26) or (36) that is valid for any reaction occurring via the mechanism in which all steps (including deactivation) are linear with respect to intermediates (Θ_j, Θ_D). For structure visualization, Eqs. (26) and (36) can be presented in the form:



(42)

It is clear from above consideration that in order to derive the deactivation equation in form of (42) the only quasi-steady state condition (5) is sufficient. Indeed, the formulas (12) $\Theta_j = \Theta_j^0(1 - \Theta_D)$ and (16) $\Theta_j^0 = r^0/w_j$ result from condition (5), are key relations provided “separable” character of Eqs. (26), (36) and (42).

This allows the following supposition to be formulated: if the reaction occurs via the linear mechanism and quasi-steady state approximation is valid, then deactivation kinetics is always reduced to the “separable” equations.

6.1. Concentration dependency

As it seen from Eq. (42) such a dependency is a product of functions $f_o(C,T)f_c(C,T)$. The question is—how substantial is this improvement comparing with Eq. (39)?

From the formal point of view, Eq. (42) will reduce to (39) after the opening f_o and f_c functions. However, Eq. (42) already contains the information about the structure of $f(C,T)$. It is important for deriving the deactivation equation, and for the analysis of physical meaning of parameters. Besides, the form of (42) shows itself, how to obtain these functions based on stepwise mechanism. Finally, the equation shows that deactivation rate depends on concentration of reagents not only taking part in deactivation $f_c(C,T)$, but also of reagents involving in the main reaction $f_o(C,T)$.

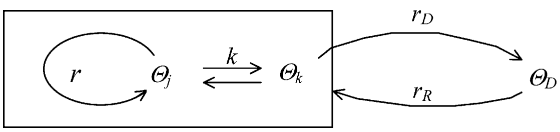
Examples 1–3 confirm the influence of the reaction kinetics on deactivation equations.

It is important that proposed equation contains the weight of reaction steps (w_j), but not the rates (r_j), i.e. the intermediates concentrations (Θ_j) already are excluded from the equation. This delivers us to derive the equation from the mechanism each time, and give the possibility to write the equation at once having only the net of steps.

Let consider now some characteristics of f_o and f_c functions. The function $f_c = \sum w_{Di}$ reflects the influence of deactivation steps on activity falling. It has a traditional form and is proportional to the concentration of catalyst poison (C_P). Usually $w_{Di} = k_{Di}(C_{Pi})^n$, and therefore $f_c(C,T)$ obey to Arrhenius temperature dependency.

The influence of the main reaction kinetics on deactivation rate is more complicated, that is reflected in function $f_o(C,T)$. Note that $f_o = r^0/w_j = \Theta_j^0$ represents the maximal surface coverage by substance involved in deactivation step. Since Θ_j^0 is expressed through the reaction rate (r^0) and weight of step (w_j), in which Θ_j is consumed, then deactivation rate *almost* ever depends on (r^0). The word “almost” is not used by chance. When j-th step coincides with the reaction limiting step ($j = l$), then $r^0 \approx w_l \equiv w_j$, therefore $r^0/w_j \approx 1$ and the reaction kinetics is excluded from deactivation equation. It take place in Example 3, where in Eq. (21) $r^0/w_2 \approx 1$ and it includes only $f_c = k_D C_A$.

A separate consideration should be done in the case when the dangling vertex of the reaction graph takes part in deactivation mechanism. It means that the intermediate is responsible for deactivation, is not involving in the catalytic cycle, but is in “equilibrium” with other intermediate.



(M9)

Here k-th step necessarily should be in equilibrium. If it is irreversible but slow, then it becomes deactivation step. If it is irreversible but fast, then catalyst deactivates immediately, and the quasi-steady state consideration makes no sense.

Taking into account this requirement, it is easy to show that

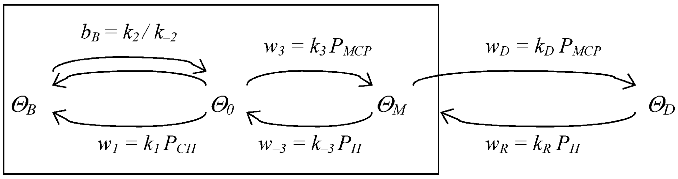
$$\Theta_k = \left(\frac{w_k}{w_{-k}}\right)\Theta_j = K_k\Theta_j$$

where K_k is the ratio of weights of k-th step.

Now Θ_j may be expressed through the reaction rate $\Theta_j^0 = r^0/w_j$, and deactivation equation may be wrote as early:

$$-\frac{da}{dt} \approx \frac{r^0}{w_j}K_k w_D \frac{a - a_S}{1 - a_S} \tag{43}$$

In order to illustrate this case, the reaction of cyclohexane (CH) dehydrogenation in the presence of MCP may be considered (see Example 3). There is the assumption that during MCP adsorption on the active Pt sites (Θ_0) deactivation occurs not at once (as accepted in scheme (M7)), but via the formation of surface intermediate of methylcyclopentene (Θ_M). It does not take part in the reaction, but blocks the active sites due to the reaction like Diels–Alder. Then the scheme (M7) transforms as follows:



(M10)

In this mechanism, Θ_M is a dangling vertex; therefore, the value of Θ_M cannot be expressed directly through the reaction rate. However, since formation Θ_M and its hydrogenation steps are in equilibrium, then $k_3 P_{MCP}\Theta_0^0 = k_{-3} P_H \Theta_M^0$, from which $\Theta_M^0 = \Theta_0^0 b_M P_{MCP}/P_H$, where $b_M = k_3/k_{-3}$ is the constant of step equilibrium.

Now Θ_0^0, that is involved in catalytic cycle, can be expressed through the reaction rate $\Theta_0^0 = r^0/w_1$, and it gives $\Theta_M^0 = (r^0/w_1)b_M P_{MCP}/P_H$. The rate of deactivation in (M10) equals to $r_D = k_D P_{MCP}\Theta_M = k_D\ P_{MCP}\Theta_M^0(1 - \Theta_D)$, therefore we obtain similarly to (30):

$$\frac{da}{dt} \approx -k_D b_M \frac{P_{MCP}^2}{P_H}\frac{a - a_S}{1 - a_S} \tag{44}$$

It follows from the comparison of (30) and (44) that the new step changes significantly the equation of deactivation. The deactivation order with respect to MCP is changed, and hydrogen concentration not only affects the value of a_S (see Example 3), but also involves in Eq. (44). The temperature dependency of deactivation rate also changes, since $(k_D)_{eff} = k_D b_M$ and consequently $(E_D)_{eff} = E_D - Q_M$, where Q_M is a heat of MCP chemisorption.

6.2. Temperature dependency

The influence of temperature on deactivation rate is rarely analyzed in the literature. It comes from the fact that experimental data are usually isothermal. Besides, in traditional models having form $f(C,T) = k_D C_i^n$, the temperature influence does not go beyond the Arrhenius dependency $k_D = k_D^0 \exp(-E_D/RT)$.

However, in practice the more complicated influence of temperature is observed, as Example 2 shows for the reaction of paraffins dehydrogenation. Eq. (42) represents the feasible temperature dependencies. It is seen from (42) that if the reaction kinetics (r^0) has Langmuir form (not power), then in traditional deactivation model $f(C,T) = (k_D)_{\text{eff}} C^n$, the deactivation constant $(k_D)_{\text{eff}}$ will not obey the Arrhenius dependency. Eq. (20) may serve as an example. Another reason for non-Arrhenius dependency comes from self-regeneration (Fig. 3) when the equation includes a_S that also depends on temperature.

6.3. Activity dependency

In the case of linear mechanisms, the rate of deactivation (da/dt) is proportional to the current value of (a). The activity order more than one may arise only in nonlinear mechanisms that have been proved by Corella and coworkers [3,37,38] (see Eq. (40)).

As it was demonstrated in this paper, in reversible deactivation, caused by self-regeneration, the rate of deactivation is proportional to $(a - a_S)$. At formal approach such a dependency (Figs. 1 and 2) may be described by power-mode function: $da/dt = -f(C,T)a^d$, where $d > 1$. For example in the case of Fig. 2 $d = 4$ that leads to wrong interpretation of deactivation features.

7. Conclusion

A general equation of catalyst deactivation kinetics has been derived, which is applicable for any reaction having linear stage mechanism. The equation has a form of so-called "separable" deactivation model. The rate of deactivation equals to the product of thee functions: $-da/dt = f_o(C,T) f_c(C,T) f_a(a)$. $f_o(C,T)$ depends only on the main reaction steps of mechanism; $f_c(C,T)$ is determined by deactivation steps; $f_a(a)$ is a function of relative activity.

When deactivation is partly reversible (due to self-regeneration by one of reagents), the function $f_a(a)$ includes "stationary" or residual activity a_S. This parameter was defined as the activity that is achieved when the rate of deactivation and rate of self-regeneration become equals to each other.

In the case of simultaneous deactivation and aging the a_S gives the possibility to split the complex model in two independent equations for deactivation and aging processes.

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