

Modelling of catalytic reactors with catalyst deactivation

IV. Parameter estimation of the rate equations of heterogeneous catalyst deactivation

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The paper deals with description of deactivation kinetics of heterogeneous catalysts caused by irreversible chemisorption of catalyst poison. Three model deactivation mechanisms are considered: the homogeneous mechanism with one type and two types of active sites and the shell progressive mechanism. A method of models parameters estimation from the rotating basket reactor measurements is proposed. The method is illustrated by hydrogenation of benzene on a nickel catalyst with thiophene as poison.

В работе описывается кинетика дезактивации гетерогенных катализаторов, вызываемой необратимой хемосорбцией каталитического яда. Рассматриваются три модельных механизма дезактивации: гомогенный механизм с активными центрами одного или двух типов и прогрессивный оболочечный механизм. Предлагается метод оценки параметров моделей на основе измерений вращающегося корзиночного реактора. Метод иллюстрируется на примере гидрогенизации бензола на никелевом катализаторе с тиофеном в качестве яда.

The paper of *Wheeler* [1] deals with deactivation of catalyst which is caused by chemisorption of catalyst poison. Two limit cases have been shown, uniform mechanism of poisoning and shell progressive mechanism. Practical systems are between these two limit cases. In the uniform mechanism of deactivation free access of catalyst poison into the whole catalyst pellet is assumed. The poison deposits uniformly and progressively throughout the pellet, the resistance to diffusion of poison is negligible. This can be expected for small catalyst pellets with large pore diameter and for low rates of poison chemisorption. In the shell progressive mechanism high affinity of the poison to the catalytic surface is assumed. The poison deposits preferentially in the pore mouth near the exterior surface of catalyst pellet. This leads to a deactivated shell surrounding the active pellet core. The border of the active core and shell is moving towards the pellet centre with time. The deactivated shell can slow down the diffusion of the reactants into the pellet interior. The shell progressive mechanism can be expected

ted for large pellets with narrow pores and large poison molecules. It is evident that the real deactivation processes are situated between these two limit cases (Fig. 1). A detailed review of the deactivation mechanism has been published by Butt [2].

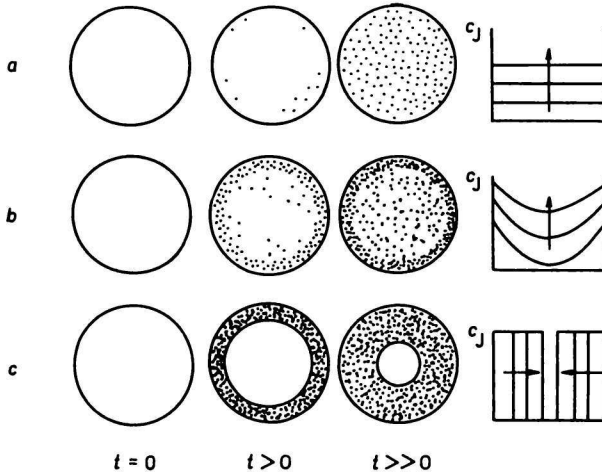


Fig. 1. Homogeneous and shell progressive mechanism of deactivation.
 a) Homogeneous mechanism; b) real mechanism; c) shell progressive mechanism.

Catalyst deactivation rate equation derivation

Catalyst activity

The catalyst activity at time t is defined as the ratio of the reaction rate at a given time t and reaction rate on the fresh catalyst at the same concentrations and temperature, *i.e.*

$$\Phi(T, c_A, c_B, \dots, t) = \frac{\xi_w^t(T, c_A, c_B, \dots, t)}{\xi_w^0(T, c_A, c_B, \dots, 0)} \quad (1)$$

This definition is suitable not only for deactivation by poisoning, but also for fouling and aging. In the most simple case, when deactivation causes only decrease of the rate constant, the activity can be expressed by the relation

$$\Phi = \frac{k_w}{k_w^0} \quad (2)$$

where k_w is the reaction rate constant on deactivated and k_w^0 on fresh catalyst at the same temperature. In the case of catalyst poison the activity is most affected by the catalyst poison concentration on the pellet surface.

The rate of the chemical reaction on partially deactivated catalyst

The rate of the chemical reaction on the catalyst, which is partially deactivated by the catalyst poison adsorbing on the surface, is in general a function of temperature, concentrations of all components, and the amount of poison adsorbed

$$\xi_w = \xi_w(T, c_A, c_B, \dots, a_j) \quad (3)$$

In most cases the right-hand side of eqn (3) can be expressed as a product of two terms: the catalyst activity and the reaction rate on the fresh catalyst [3]

$$\xi_w = \xi_w^0(T, c_A, c_B, \dots) \Phi(a_j) \quad (4)$$

In such case we say that the rate equation is in the separable form. The activity depends only on the amount of poison adsorbed. The rate of the poison sorption is

$$\frac{da_j}{dt} = f(T, c_A, c_B, \dots, a_j) \quad (5)$$

Uniform mechanism of deactivation with one type of active sites

Let us assume that in the system only one catalytic reaction together with independent deactivation caused by irreversible chemisorption of catalyst poison takes place by the scheme



Let us assume that the active sites for the main reaction are equal to the active sites for chemisorption of the poison and just one molecule of poison is adsorbed on one active site. Further assumption is that the adsorption rate of the poison is equal for all active sites regardless of whether they are free or whether reactants or products are adsorbed on them.

The adsorption rate can be expressed by a Langmuir-type rate equation

$$\frac{da_j}{dt} = k_{D\infty} c_j ([L] - [L_j]) \exp(-E_D/RT) \quad (6)$$

where $[L]$ is the total active site concentration and $[L_j]$ of which is occupied by the poison. Due to the assumption mentioned above, that just one molecule is adsorbed on one active site, one can write

$$\begin{aligned} [L] &= a_j^* \\ [L_j] &= a_j \end{aligned} \quad (7)$$

Then eqn (6) is as follows

$$\frac{da_j}{dt} = k_{D\infty}c_j(a_j^* - a_j)\exp(-E_D/RT) \quad (8)$$

If the dependence of catalyst activity on the adsorbed amount of the poison is linear

$$\Phi = \frac{[L] - [L_j]}{[L]} = \frac{a_j^* - a_j}{a_j^*} \quad (9)$$

the deactivation rate becomes

$$\frac{d\Phi}{dt} = -k_{D\infty}c_j\Phi\exp(-E_D/RT) \quad (10)$$

For simplicity let us consider the catalytic reaction the mechanism of which one can describe by the scheme



Under the assumption that the rate-controlling step is the second one, the following Langmuir—Hinshelwood rate equation can be developed

$$\xi_{sw}^0 = \frac{k_{w+}[L]K_A P_A}{1 + K_A P_A + K_B P_B} = \frac{k_w^0 K_A P_A}{1 + K_A P_A + K_B P_B} \quad (11)$$

where k_{w+} is the constant of the reaction rate (C) and $k_w^0 = k_{w+}[L]$ is the constant of the reaction on the fresh catalyst. If in the course of the reaction the catalyst poison occupies a part of active sites participating in the catalytic reaction for $[L] - [L_j]$ from eqn (9) we obtain

$$[L] - [L_j] = \Phi[L] \quad (12)$$

Then the catalytic reaction rate becomes

$$\xi_{sw}^e = \frac{k_{w+}\Phi[L]K_A P_A}{1 + K_A P_A + K_B P_B} = \Phi \frac{k_w^0 K_A P_A}{1 + K_A P_A + K_B P_B} = \Phi \xi_{sw}^0 \quad (13)$$

which is the product of activity and reaction rate on fresh catalyst (separable rate equation).

Uniform mechanism of deactivation with two types of active sites

In the previous chapter it has been assumed that the catalyst poison is adsorbed only on the active sites for the catalytic reaction. This assumption is not always satisfied. This is why two types of active sites are considered as the further alternative:

- active sites for the main reaction and for catalyst poison adsorption,
- active sites only for poison adsorption, *i.e.* inactive in the main reaction.

The total concentration of active sites for poison adsorption is given by the sum

$$[L] = [L_1] + [L_2] \quad (14)$$

Assuming that just only one molecule of poison is adsorbed on one active site we obtain

$$a_j = a_{j1} + a_{j2} \quad (15)$$

and the total adsorption rate is

$$\frac{da_j}{dt} = \frac{da_{j1}}{dt} + \frac{da_{j2}}{dt} \quad (16)$$

where

$$\frac{da_{j1}}{dt} = k_{D1\infty} c_j (a_{j1}^* - a_{j1}) \exp(-E_{D1}/RT) \quad (17)$$

and

$$\frac{da_{j2}}{dt} = k_{D2\infty} c_j (a_{j2}^* - a_{j2}) \exp(-E_{D2}/RT) \quad (18)$$

The catalyst activity is defined, in agreement with eqn (9) as the ratio of the free active site concentration and the concentration of all active sites for the main reaction, *i.e.*

$$\Phi_1 = \frac{a_{j1}^* - a_{j1}}{a_{j1}^*} \quad (19)$$

Analogously we can introduce

$$\Phi_2 = \frac{a_{J2}^* - a_{J2}}{a_{J2}^*} \quad (20)$$

Further we shall assume equality of activation energy of adsorption on both types of active sites, $E_{D1} = E_{D2} = E_D$. Then the ratio of eqns (17) and (18) is

$$\frac{da_{J2}}{da_{J1}} = \frac{k_{D2\infty}}{k_{D1\infty}} \frac{a_{J2}^* - a_{J2}}{a_{J1}^* - a_{J1}} \quad (21)$$

After ranging and integrating from 0 to a_{Ji}^* , $i = 1, 2$, we have

$$\ln \frac{a_{J2}^* - a_{J2}}{a_{J2}^*} = f \ln \frac{a_{J1}^* - a_{J1}}{a_{J1}^*} \quad (22)$$

or

$$\Phi_2 = \Phi_1^f \quad (23)$$

where

$$f = \frac{k_{D2\infty}}{k_{D1\infty}} \quad (24)$$

After introducing total catalyst activity

$$\Phi_c = \frac{a_J^* - a_J}{a_J^*} \quad (25)$$

from eqns (17) and (24) for its time derivate we have

$$\frac{d\Phi_c}{dt} = k_{D1\infty} c_J \{ \gamma \Phi_1 + f(1 - \gamma) \Phi_1^f \} \exp(-E_D/RT) \quad (26)$$

where

$$\gamma = a_{J1}^*/a_J^* \quad (27)$$

and

$$\Phi_c = \gamma \Phi_1 + (1 - \gamma) \Phi_1^f \quad (28)$$

The catalytic reaction rate can be again expressed as the product of catalyst activity with respect to the given reaction and the reaction rate on the fresh catalyst

$$\xi_w = \Phi_1 \xi_w^0 \quad (29)$$

Value of the parameter γ determines the ratio of the individual active sites on the surface. For $\gamma \approx 1$ the first type of the active sites are in excess (uniform mechanism with one type of active sites as limit case). If $f \approx 0$, i.e. $k_{D1} \gg k_{D2}$, the poison is adsorbed preferentially on the active sites 1.

Shell progressive mechanism of deactivation

As said in the introduction, in this mechanism we assume that the pellet consists of an unpoisoned core with unit activity surrounded by a poisoned shell with zero activity. This model corresponds to the shrinking core model in noncatalytic fluid—solid phase reactions [4].

In the course of deactivation the active core is getting smaller. To develop the rate of the core dwindle the following assumptions have been introduced:

- spherical catalyst pellets,
- linear dependence of catalyst activity *vs.* poison adsorbed amount,
- the rate-controlling steps are the poison diffusion through the deactivated shell and the chemisorption of the poison on the border of the shell and core.

The diffusion rate through the shell is

$$\xi = 4\pi r^2 D_j \frac{dc_j}{dr} \quad (30)$$

and the rate of chemisorption is

$$\xi = 4\pi r^{j2} k_s c_j^i \quad (31)$$

The total adsorbed amount in the pellet is given by

$$a = \frac{4}{3} \pi (R^3 - r^{j3}) \rho_s a_j^* \quad (32)$$

which leads to the poison adsorption rate

$$\frac{da}{dt} = \xi = -4\pi r^{j2} \rho_s a_j^* \quad (33)$$

From eqns (30) and (31) it follows

$$\frac{dc_j}{c_j} = \frac{r^{j2}}{r^2} \frac{k_s}{D_j} dr \quad (34)$$

After integration and rearranging

$$c_j^i = \frac{c_j^p}{1 + \frac{k_s r^j}{D_j R} (R - r^j)} \quad (35)$$

Substituting into the rate equation of chemisorption (31) and from the equality with (33) we obtain for the core dwindling

$$\frac{dr^j}{dt} = - \frac{k_s}{Q_s a_j^*} \frac{c_j^p}{1 + \frac{k_s r^j}{D_j R} (R - r^j)} \quad (36)$$

The mean pellet activity is given by the ratio of the active core volume to the whole pellet volume

$$\Phi = \left(\frac{r^j}{R} \right)^3 \quad (37)$$

and the deactivation rate is

$$\frac{d\Phi}{dt} = 3 \frac{r^{j2}}{R^3} \frac{dr^j}{dt} \quad (38)$$

Experimental

The method of estimation of the deactivation mechanism and corresponding rate equations parameters is illustrated on the example of hydrogenation of benzene on a Ni catalyst (Ni/alumina, 58 % Ni) in the presence of catalyst poison thiophene.

The kinetics measurements of reaction and deactivation have been carried out in an isothermal rotating basket reactor [5]. The volume of the gaseous phase in the reactor was approximately 100 cm³, the temperature in the reactor was regulated with accuracy 0.4 %. The composition of the reactor outflowing stream has been measured by the gas chromatograph. Benzene and thiophene concentrations have been determined by the direct calibration method.

To measure kinetics of reaction, pure benzene in the flow of hydrogen has been fed into the reactor (steady state measurement). To examine catalyst deactivation, the benzene contaminated by thiophene in the flow of hydrogen has been used. In such a way time dependence of the concentrations has been followed up to the total catalyst deactivation. The reaction kinetics has been measured at seven temperatures in the range from 50 to 150 °C, at each temperature benzene concentration *vs.* feed rate dependence has been investigated. The experimental conditions are listed in Table 1. To study deactivation kinetics five isothermal measurements have been performed, the experimental conditions are in Table 2.

Table 1

Experimental conditions for reaction kinetics measurements

Temperature/K	320—420
Pressure/Pa	1.3×10^5
Inlet benzene concentration/mol m ⁻³	2.44
Mass of catalyst/g	0.662
Volumetric flow rate/10 ⁶ m ³ s ⁻¹	0.08—2.4
Catalyst diameter/mm	1.25—1.4

Table 2

Experimental conditions for catalyst deactivation kinetics measurements

Run	1	2	3	4	5
Temperature/K	413	389.7	356	346	327.7
Inlet benzene concentration/mol m ⁻³	1.73	1.83	2.00	2.06	2.18
Inlet thiophene concentration/mol m ⁻³	0.032	0.034	0.037	0.038	0.039
Volumetric flow rate/10 ⁶ m ³ s ⁻¹	0.598	0.674	0.586	0.607	0.568
Mass of catalyst/g	0.6615	0.6900	0.6250	0.6599	0.6877
Pressure/Pa · 10 ⁻⁵	1.31	1.30	1.31	1.30	1.30
$a\eta$ /mol kg ⁻¹	0.513	0.503	0.486	0.449	0.416

Rate equations parameter estimation

Estimation of reaction rate equation parameters of benzene hydrogenation

Under the assumption that the rate-controlling step is addition of molecular hydrogen to the adsorbed benzene, the rate equation of benzene hydrogenation is

$$\dot{\zeta}_w^0 = \frac{k_{w\infty} K_\infty P_B P_H \exp(- (E + Q)/RT)}{1 + K_\infty P_B \exp(- Q/RT)} \quad (39)$$

The benzene mass balance equation in a continuous stirred tank reactor at steady state conditions is

$$\dot{V}_0 c_{B0} + v_B W \dot{\zeta}_w^0 = \dot{V}_0 c_B \quad (40)$$

hence

$$\dot{\zeta}_w^0 = \frac{\dot{V}_0 (c_{B0} - c_B)}{(-v_B) W} \quad (41)$$

Reaction rate equation parameters have been estimated by the simplex method. As the objective function

$$F(k_{w\infty}, K_x, E, Q) = \sum_{i=1}^k \sum_{j=1}^n [\xi_{w,i,j}^{\text{exp}} - \xi_{w,i,j}^{\text{calc}}(k_{w\infty}, K_x, E, Q)]^2 \quad (42)$$

has been chosen, where k is the number of isothermal experiments, n the number of measurements at a given temperature, $\xi_{w,i,j}^{\text{exp}}$ is the reaction rate computed from eqn (41) and $\xi_{w,i,j}^{\text{calc}}(k_{w\infty}, K_x, E, Q)$ reaction rate computed from eqn (39).

Estimation of deactivation rate equations parameters

The model of an isothermal continuous stirred tank reactor in which catalyst deactivation caused by irreversible chemisorption of catalyst poison takes place is described by the system of equations:

— mass balance for the key component

$$\dot{V}_0 c_{B0} + v_B W \xi_w^{\text{po}} \Phi = \dot{V}_0 c_B + V_R \frac{dc_B}{dt} \quad (43)$$

— mass balance for the poison

$$\dot{V}_0 c_{J0} + W \frac{da_J}{dt} = \dot{V}_0 c_J + V_R \frac{dc_J}{dt} \quad (44)$$

— initial conditions

$$\begin{aligned} t = 0, \quad a_J = 0; \quad \dot{V}_0 c_{B0} + v_B W \xi_w^{\text{po}} &= \dot{V}_0 c_B \\ \dot{V}_0 c_{J0} + W \frac{da_J}{dt} &= \dot{V}_0 c_J \end{aligned} \quad (45)$$

If the rate of deactivation is considerably smaller than the rate of the catalytic reaction, the derivatives of concentrations with respect to time may be neglected, which means that a quasi-steady state is assumed. The mass balance equations become

$$\dot{V}_0 c_{B0} + v_B W \xi_w^{\text{po}} = \dot{V}_0 c_B \quad (46)$$

$$\dot{V}_0 c_{J0} + W \frac{da_J}{dt} = \dot{V}_0 c_J \quad (47)$$

In all mass balances we assumed constant volumetric flow rate through the reactor \dot{V}_0 .

From eqn (46) the reaction rate can be expressed

$$\xi_w^s = \Phi_{\xi_w^s}^s = \frac{\dot{V}_0(c_{B0} - c_B)}{(-v_B)W} \quad (48)$$

and the reaction rate on the fresh catalyst ξ_w^s can be computed from eqn (39). Their ratio at a given time is the catalyst activity

$$\Phi = \frac{\xi_w^s}{\xi_w^s} \quad (49)$$

The adsorbed amount of catalyst poison on the catalyst surface one can compute numerically from the relation

$$a_j = \frac{\dot{V}_0}{W} \int_0^t (c_{j0} - c_j) dt \quad (50)$$

Using these values of adsorbed amount and eqn (25) we get the catalyst activity Φ_c .

Uniform mechanism of deactivation with one type of active sites contains the rate constant $k_D = k_{D\infty} \exp(-E_D/RT)$. Its value for a given temperature has been estimated using the least-square criterion

$$F = \frac{1}{c_{B0}} \sum_{i=1}^n (c_{Bi, \text{exp}} - c_{Bi, \text{calc}})^2 + \frac{1}{c_{j0}} \sum_{i=1}^n (c_{ji, \text{exp}} - c_{ji, \text{calc}})^2 \quad (51)$$

the minimum of which has been found by the golden section method. The values $c_{B, \text{calc}}$ and $c_{j, \text{calc}}$ have been obtained by numerical solution of the mass balance eqns (46) and (47) for a given k_D . Values of $k_{D\infty}$ and E_D have been computed from the values of k_D by the least-square method using the linear form of the Arrhenius equation.

Uniform mechanism of deactivation with two types of active sites (eqns (26) and (28)) contains three constants: $k_{D1} = k_{D1\infty} \exp(-E_{D1}/RT)$, γ , and f . The values of the constants γ and f have been estimated by minimizing the value of the objective function

$$G(\gamma, f) = \sum_{i=1}^k \sum_{j=1}^n (\Phi_{c, i, j, \text{exp}} - \Phi_{c, i, j, \text{calc}})^2 \quad (52)$$

by the simplex method. By $\Phi_{c, \text{exp}}$ and $\Phi_{c, \text{calc}}$ we denote the catalyst activity computed from experimental values of a_j and eqn (25) and the total activity computed from eqn (28), respectively. For the Φ_1 the experimental value given by the ratio (49) has been substituted. The value of k_{D1} for given γ and f has been estimated by minimizing the objective function (51) value by the golden section method.

The shell progressive mechanism has two parameters k_S and D_J , the values of which have been estimated by the simplex method. As the objective function the criterion (51) has been chosen.

The temperature dependences of parameters k_{D1} , k_S , and D_J have been obtained using Arrhenius equation (linear regression).

Results and discussion

The values of the reaction rate equation parameters for benzene hydrogenation and deactivation rate equations parameters are in Table 3. The comparison of experimental and theoretical outlet benzene and thiophene concentration time dependences is displayed in Figs. 2 and 3. The comparison of activities calculated from experimental values by eqns (25) and (49) with individual models is represented in Fig. 4. By the presented figures best agreement has been obtained by the uniform mechanism of deactivation with two types of active sites. Very good coincidence has been achieved in particular for outlet benzene concentration, better than for thiophene concentration. Of interest is Fig. 4,

Table 3

Values of the reaction rate equation and deactivation equations parameters

Reaction rate equation parameters for benzene hydrogenation
$k_{w\infty} = 0.588 \times 10^{-2} \text{ mol s}^{-1} \text{ kg}^{-1} \text{ Pa}^{-1}$
$K_\infty = 0.287 \times 10^{-5} \text{ Pa}^{-1}$
$E = 35.36 \text{ kJ mol}^{-1}$
$Q = -24.22 \text{ kJ mol}^{-1}$
Homogeneous mechanism of deactivation with one type of active sites
$k_{D\infty} = 6.183 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$E_D = 12.41 \text{ kJ mol}^{-1}$
Homogeneous mechanism of deactivation with two types of active sites
$k_{D1} = 2.367 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$E_{D1} = 9.18 \text{ kJ mol}^{-1}$
$\gamma = 0.2228$
$f = 0.537$
Shell progressive mechanism of deactivation
$k_{S\infty} = 29.08 \text{ m s}^{-1}$
$E_S = 17.91 \text{ kJ mol}^{-1}$
$D_{J\infty} = 0.856 \text{ m}^2 \text{ s}^{-1}$
$E_J = 22.7 \text{ kJ mol}^{-1}$

which illustrates the difference between activity computed from the ratio of reaction rate at a given time and the reaction rate on fresh catalyst (eqn (25)) and activity computed from the adsorbed amount. This fact is taken into account only in the uniform mechanism of deactivation with two types of active sites.

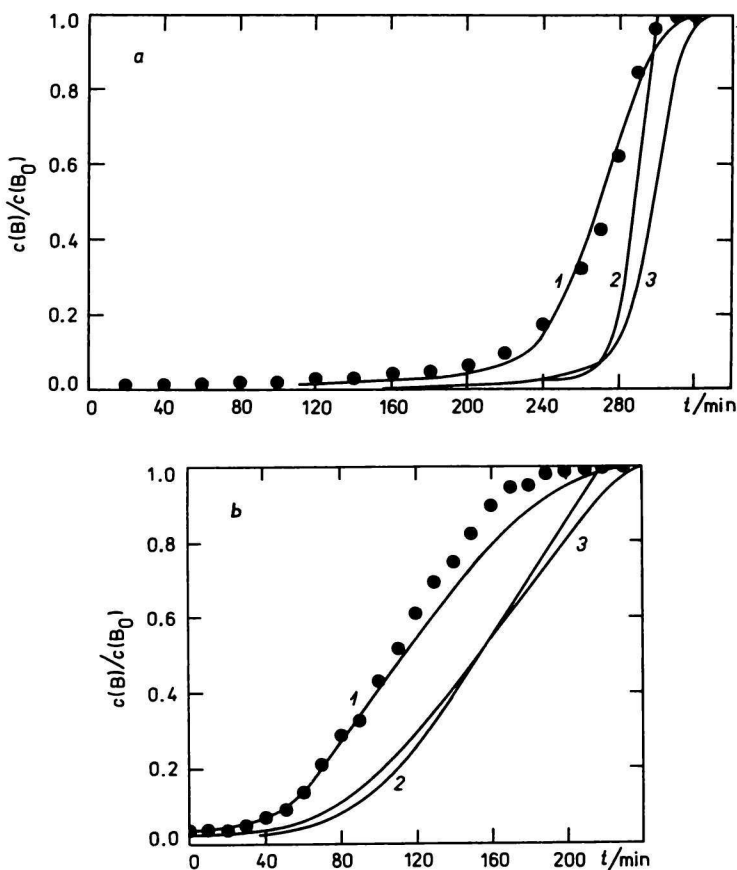


Fig. 2. Exit benzene concentration vs. time.

1. Homogeneous model of deactivation with two types of active sites; 2. shell progressive mechanism; 3. homogeneous mechanism of deactivation with one type of active sites.

● Experiment; a) $T = 413$ K; b) $T = 346$ K.

From the estimated values γ and f it follows that the adsorption rate of poison on the second type of active sites is approximately the half of the adsorption rate on the first type of active sites, the concentration of which is five times lower than the others ones. In Fig. 5 the experimental and theoretical time dependence of these two activities is displayed. The description by the shell progressive model

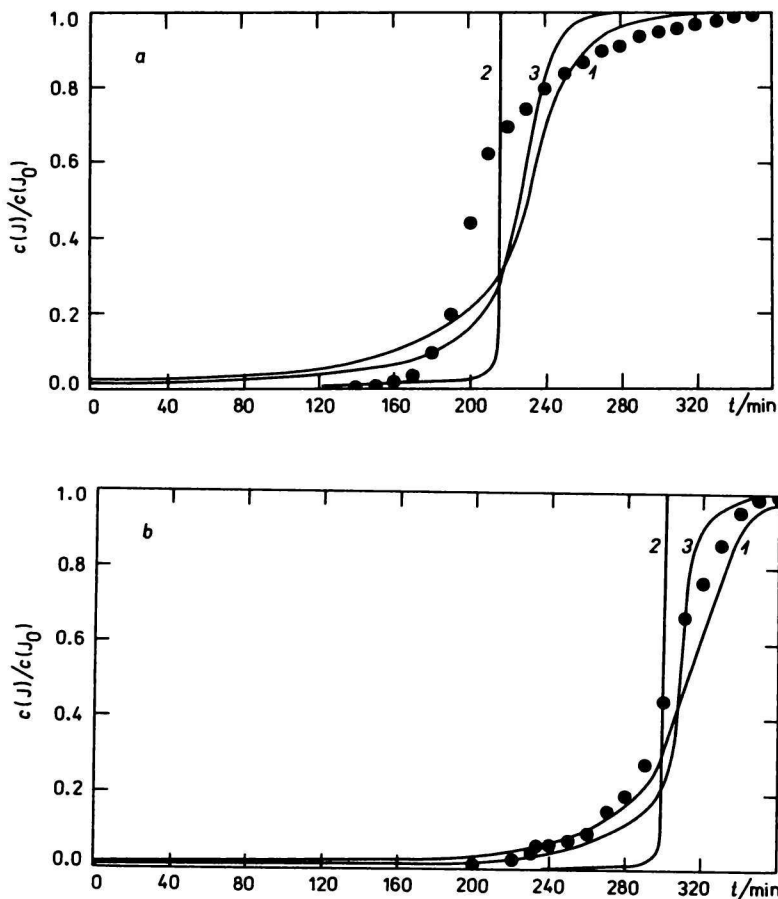


Fig. 3. Exit thiophene concentration vs. time.
Designation as in Fig. 2.

is not as good as by the uniform ones. The outlet thiophene concentration differs from experimental one. This model provides good coincidence in the case of large catalyst pellets [6]. The theoretical movement of the border of active core and shell with time for individual temperatures is exhibited in Fig. 6. The temperature dependences of deactivation rate constants and catalyst poison diffusion coefficient are presented in Figs. 7—10. Arrhenius equation provides good fit of values obtained from isothermal measurements. The last Fig. 11 illustrates the temperature dependence of equilibrium adsorbed amount computed from experimental values by eqn (50).

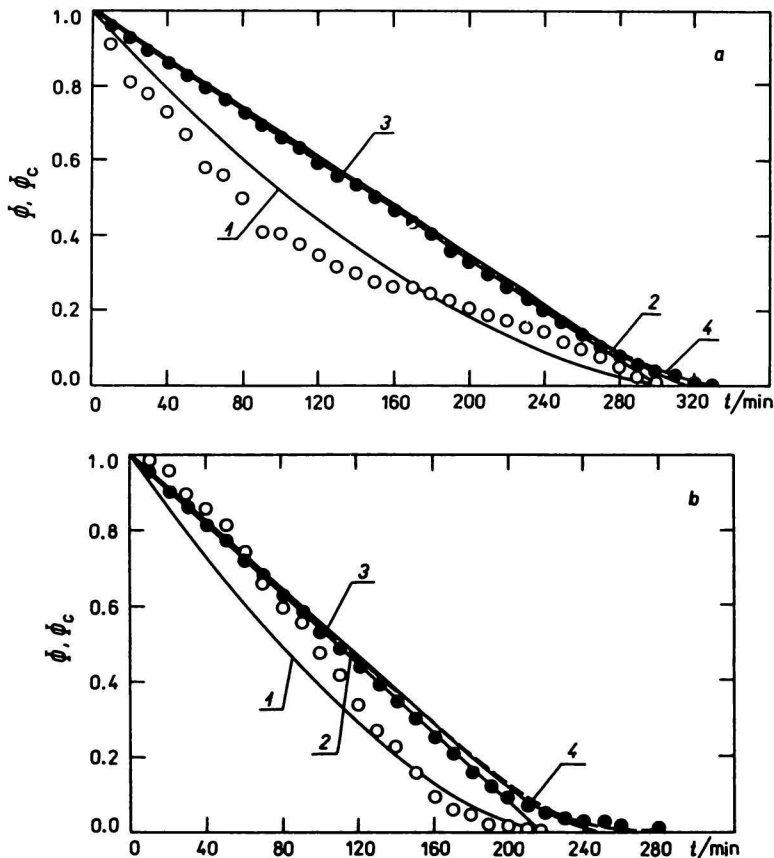


Fig. 4. Catalyst activity vs. time.

a) $T = 413 \text{ K}$; b) $T = 346 \text{ K}$.

Φ : \circ experiment; 1. homogeneous model of deactivation with two types of active sites; 2. shell progressive mechanism; 3. homogeneous mechanism of deactivation with one type of active sites. Φ_c : \bullet experiment; 4. homogeneous mechanism with two types of active sites.

Conclusion

In the paper a method of deactivation rate equations parameter estimation is presented. It is illustrated in the case of benzene hydrogenation on a nickel catalyst with thiophene as the poison. Three deactivation mechanisms (uniform with one and two types of active sites and shell progressive mechanism) of irreversible catalyst poison chemisorption are considered. The best agreement has been achieved by the uniform mechanism with two types of active sites.

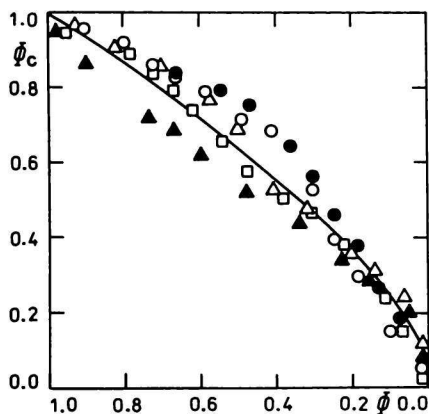


Fig. 5. Comparison of catalyst activity $\Phi = \xi_w / \xi_w^0$ and total catalyst activity Φ_c obtained from eqn (25).
 ○ 413 K; ● 389.7 K; △ 356 K; ▲ 346 K; □ 327.7 K.

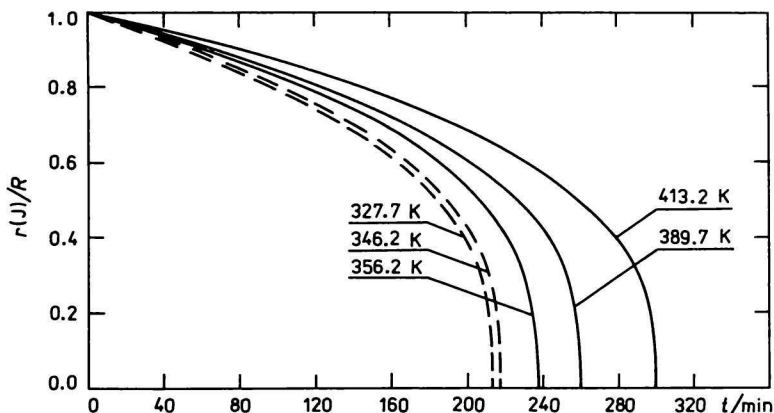


Fig. 6. Movement of the border of active core and shell vs. time for individual temperature shell progressive mechanism.

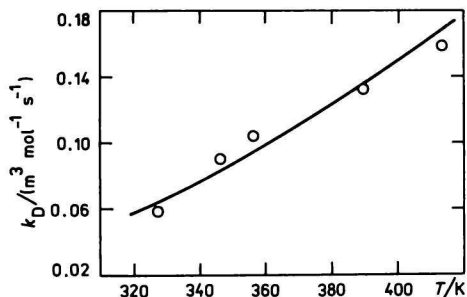


Fig. 7. Temperature dependence of deactivation rate constant.

Homogeneous mechanism with one type of active sites.

○ Values obtained from isothermal measurements; — description by Arrhenius equation.

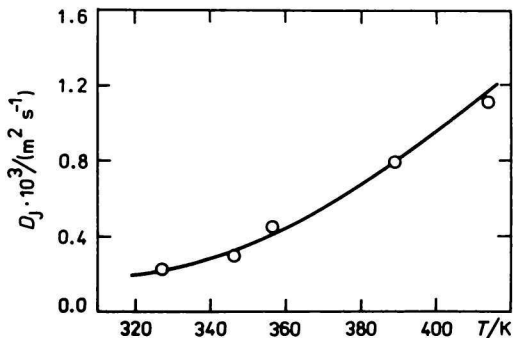


Fig. 8. Temperature dependence of diffusion coefficient of poison. Shell progressive mechanism. Designation as in Fig. 7.

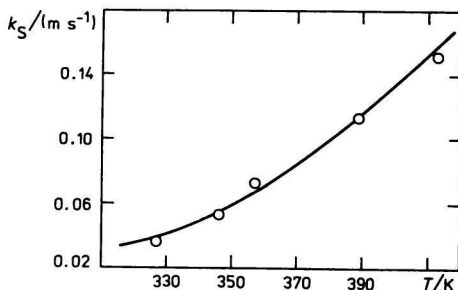


Fig. 9. Temperature dependence of surface reaction rate constant. Shell progressive mechanism. Designation as in Fig. 7.

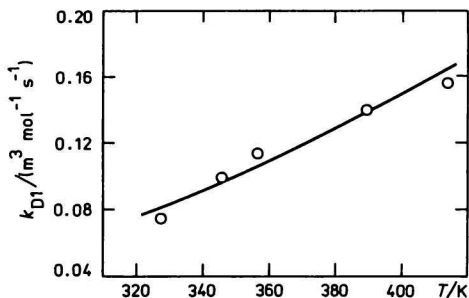


Fig. 10. Temperature dependence of deactivation rate constant. Homogeneous mechanism with two types of active sites. Designation as in Fig. 7.

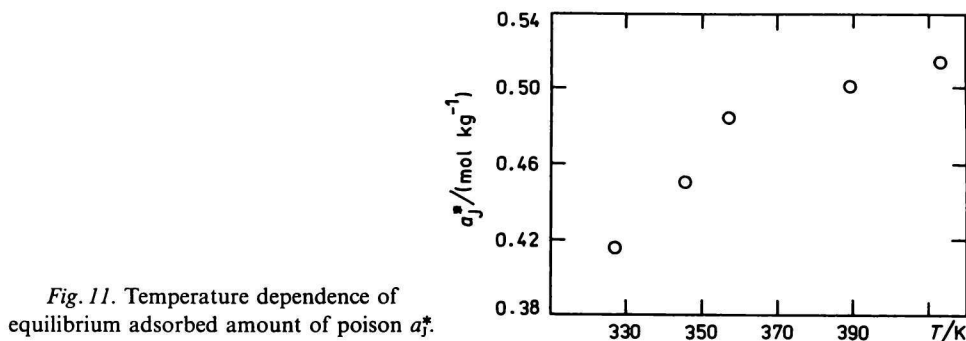


Fig. 11. Temperature dependence of equilibrium adsorbed amount of poison a_j^* .

Symbols

a	adsorbed amount of poison	mol
a_j	adsorbed amount of poison on the catalyst	$mol kg^{-1}$
a_j^*	equilibrium adsorbed amount of poison	$mol kg^{-1}$
c	concentration	$mol m^{-3}$
D	diffusion coefficient	$m^2 s^{-1}$
E	activation energy	$J mol^{-1}$
F	objective function, eqns (37), (51)	
f	parameter of deactivation rate equation, eqn (24)	
G	objective function, eqn (52)	
K_∞	adsorption constant for benzene at $T \rightarrow \infty$	Pa^{-1}
$k_{w\infty}$	frequency factor of catalytic reaction	$mol kg^{-1} s^{-1} Pa^{-1}$
k_D	deactivation rate constant	$m^3 mol^{-1} s^{-1}$
L	active site	
$[L]$	concentration of active sites	$mol m^{-3}$

P	partial pressure	Pa
Q	adsorption heat of benzene	J mol^{-1}
R	radius of a pellet	m
r	radius	m
T	temperature	K
t	time	s
V	volume of reactor	m^3
\dot{V}	volumetric flow rate	$\text{m}^3 \text{s}^{-1}$
W	mass of catalyst in the reactor	kg
γ	parameter of deactivation rate equation, eqn (27)	
ξ	reaction rate	mol s^{-1}
ξ_w	reaction rate	$\text{mol kg}^{-1} \text{s}^{-1}$
ξ_w^0	reaction rate on the fresh catalyst	$\text{mol kg}^{-1} \text{s}^{-1}$
ρ_s	catalyst density	kg m^{-3}
ν	stoichiometric coefficient	

Indices

Lower:

A	component
B	key component, benzene
C	total
D	deactivation
J	poison
R	reactor
S	surface reaction
w	mass of catalyst
0	inlet in reactor
1	the first type of active sites
2	the second type of active sites

Upper:

j	active core
p	surface
°	fresh catalyst

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