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MODELLING OF HYDROCARBONS CATALYTIC CONVERSION PROCESS

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Abstract. A new experimental-computational method for designing the catalytic converters for gases purification contaminated with hydrocarbons based on researched mechanism of heterogeneous catalytic process which stages are described by mathematical models is developed.

Keywords: catalysis, mass transfer, conversion, activation energy, modeling.

1. Introduction

Heterogeneous catalytic process proceeds through several stages such as diffusion of initial substances from the gas flow to the external surface of the catalyst, diffusion of the initial substances in pores of catalyst particles, adsorption of initial substances on the catalyst surface, chemical reaction, desorption of reaction products from the catalyst surface, diffusion of products from the internal surface of catalyst particles to the surface of pores, diffusion of reaction products from the catalyst surface into the flow [1, 2].

Any of these stages is able to control the process, so the kinetic regularities of heterogeneous catalytic process can be controlled both by the laws of chemical kinetics and the mass transfer.

The aim of the study is the creation of calculation method for designing the catalytic converters for gases purification contaminated with hydrocarbons based on researched mechanism of the heterogeneous catalytic process which is described by appropriate mathematical models.

The objects of the study were the catalytic converters on metal carriers of different qualitative and quantitative composition and spatial geometry.

The catalytic converter of this type has no structural porosity therefore depending on conditions the limiting stage of the reaction processes on the surface are the rate of chemical reaction or diffusion of the initial reactants to the catalyst surface.

2. Experimental

2.1. Basic Theory

Initial gas mixture which undergoes the catalytic conversion contains oxygen in a large excess compared with the concentration of organic compounds. Assuming that the adsorption of reactants on the surface of the catalytic converter corresponds the Langmuir isotherm [1-6] and the surface of the catalytic converter is homogeneous, then the received experimental data may be considered as the reaction of the first order by hydrocarbons. Then the temperature dependence of the rate constant is described by the Arrhenius equation, and the degree of conversion of hydrocarbons in the kinetic region can be represented by Eq. (1) [4, 5, 7]:

$$X_k = 1 - \exp\left(-t \cdot \frac{273}{T} \cdot k_0 \cdot \exp\left(-\frac{E}{RT}\right)\right) \quad (1)$$

where k_0 – Arrhenius factor, s^{-1} ; E – activation energy of chemical reaction, J mol; R – universal gas constant, J/K·mol; t – contact time, s; T – temperature in the reaction zone, K.

Logarithm of Eq. (1) can be represented in the following form:

$$\ln\left(\frac{\ln(1-X)}{-t \frac{273}{T}}\right) = \ln k_0 - \frac{E}{RT} \quad (2)$$

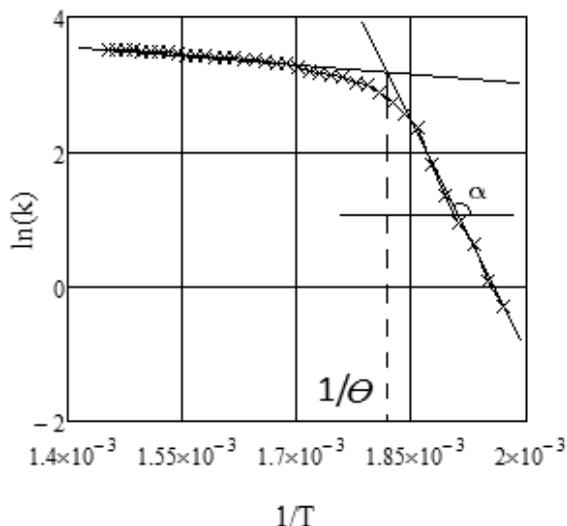


Fig. 1. The dependence of the rate constant logarithm of the hydrocarbon conversion process on the reverse temperature

The left-hand side of this expression is the logarithm of the process rate constant. Substitution of the experimental data in Eq. (2) allows to obtain the dependences (Fig. 1) from which the temperature of process transition to the external diffusion region θ , as well as the activation energy E ($E = -Rtg(\alpha)$) and the Arrhenius factor k_0 are found. The obtained values of activation energy E and Arrhenius factor k_0 allow with the help of Eq. (1) to obtain calculated dependence of the hydrocarbon conversion degree on the temperature (Fig. 2).

Equation (1) describes the dependence of the hydrocarbon conversion degree on the temperature adequately but only at temperatures which are below θ . The temperature of process transition to the region of the external diffusion depends on such factors as contact time of gas with the catalyst, the hydrocarbon concentration, content of catalytically active elements on the surface of the carrier and the specific surface area of the catalyst carrier [2, 8].

In order to develop a model of the catalytic conversion process which occurs in the external diffusion region the differential equation of mass transfer and the equation of mass transfer in the criterial form were used [2]:

$$-\frac{dn}{Fdt} = b(C_g - C_s) \quad (3)$$

where n – amount of substance of hydrocarbons, mol; F – surface area of catalyst, m^2 ; b – mass transfer coefficient, m/s ; C_g – the concentration of hydrocarbons in the gas flow; C_s – concentration of hydrocarbons on the catalyst surface.

$$b = ARe^m Pr^n \frac{D}{L} \quad (4)$$

where Re – Reynolds number; Pr – Prandtl number; D – coefficient of molecular diffusion, m^2/s ; L – characteristic linear dimension, m .

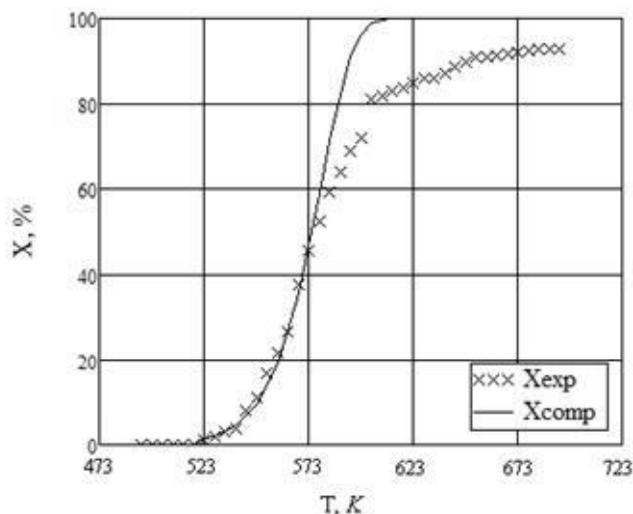


Fig. 2. Calculated X_{comp} and experimental X_{exp} dependences of the hydrocarbons conversion degree on the temperature

Determination of the experimental values of the mass transfer coefficient was carried out with the help of Eq. (5), which is the solution of Eq. (3). Solution of Eq. (3) is possible under the condition that the concentration of hydrocarbons on the surface of the catalytic converter is zero. This approximation is reasonable because in the course of the catalytic conversion process in the area of external diffusion the fast reaction proceeds on the catalyst surface; its rate exceeds the reagents supply rate from the gas flow to the catalyst surface.

$$b = \frac{V}{Ft} \ln\left(\frac{C_0}{C}\right) \quad (5)$$

where C_0 – the concentration of hydrocarbons in the gas flow at the reactor inlet; C – current concentration of hydrocarbons; V – reactor volume, m^3 .

The degree of conversion of hydrocarbons in external diffusion area is defined as follows:

$$X_D = 1 - \exp\left(-t_0 \frac{273}{T} b \frac{F}{V}\right) \quad (6)$$

where X_D – conversion degree in the area of external diffusion; t_0 – contact time of the gas mixture with a catalyst bed at inlet gas flow temperature, s .

2.2. Methods and Materials

The working volume of the reactor was filled with metal packing in the form of not closely twisted nichrome foil strips, into the surface of which catalytically active compounds were impregnated.

The total volume of packing was 10 cm^3 with a total phase contact surface of 130 cm^2 .

Temperature in the reactor was raised from 293 to 723 K with an average rate of $0.25^\circ/s$, the gas flow rate at the inlet of the reactor ranged from $5.5 \cdot 10^{-5}$ to $2.2 \cdot 10^{-4} \text{ m}^3/s$.

The average benzene content at the reactor inlet was 8 g/m^3 .

The composition of the gas mixture at the reactor outlet was analyzed by the OKSI 5M-5 chromatograph and Infrakar gas analyzer.

The experiments were performed under atmospheric pressure and conditions which were close to isothermal [9].

To determine the type of functional dependency of the mass transfer coefficient of the catalytic conversion process parameters a series of experimental studies was carried out in which contact time of the gas mixture with the catalyst bed, the concentration of hydrocarbons, which are served in the reaction zone, the content of catalytically

active elements on the surface of the carrier and the specific surface area of the catalyst carrier were varied.

3. Results and Discussion

The experimental data are shown in Fig. 3.

The experimental data up to the conversion degrees X corresponding to 0.4 are best described by equation of irreversible transformation process of a simple first-order reaction (Eq. (1)).

Also it is experimentally shown that the conversion process in the external diffusion area and observed mass transfer coefficient value depend on the above mentioned factors (Fig. 4).

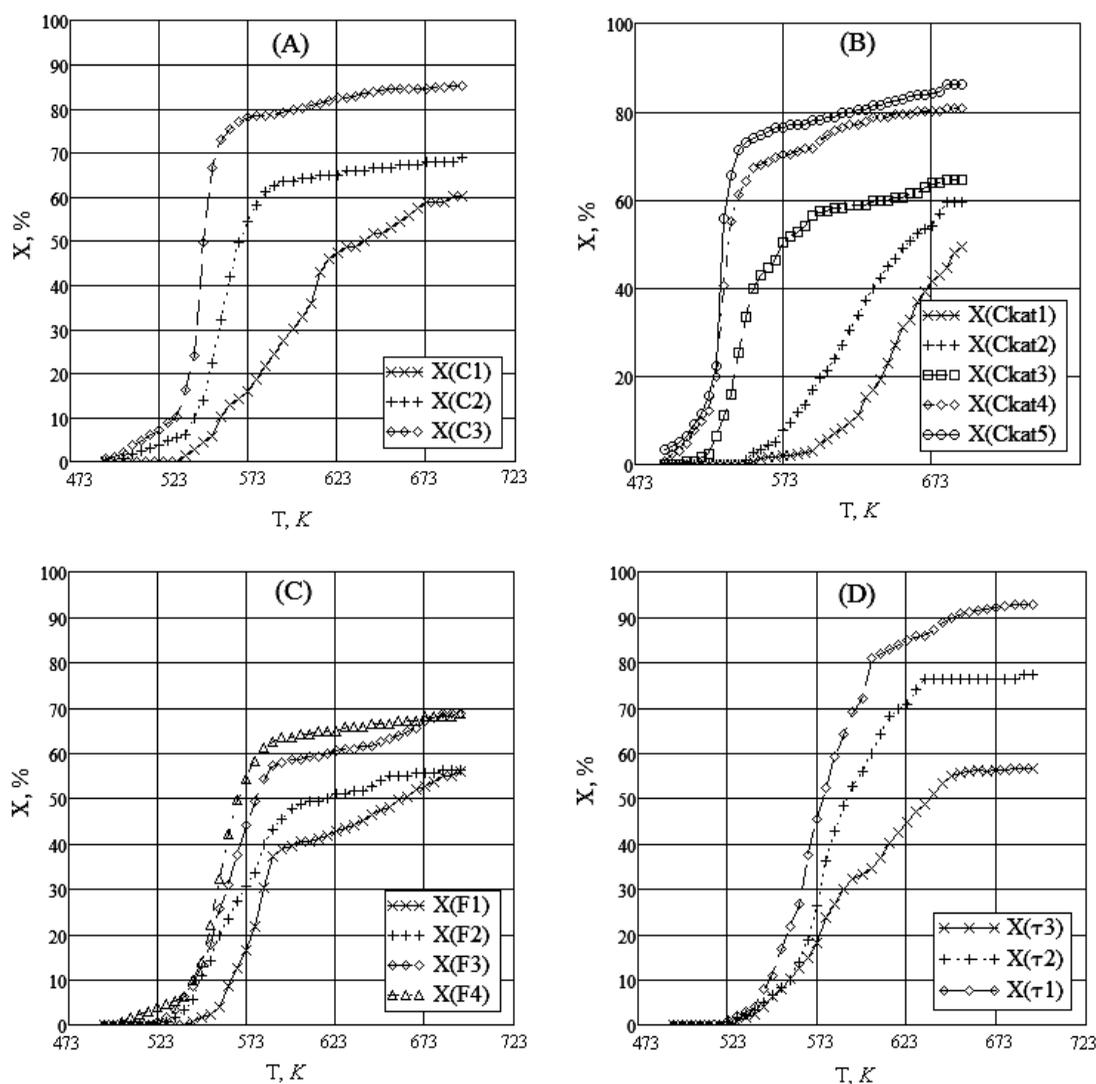


Fig. 3. Temperature dependences of hydrocarbon conversion degree on hydrocarbon concentration (a) in the gas flow ($C_1 = 4.1 \text{ g/m}^3$, $C_2 = 7.6 \text{ g/m}^3$, $C_3 = 10.7 \text{ g/m}^3$); concentration of catalyst components (b) on the support surface ($C_{kat1} = 0.009 \text{ mg/cm}^2$, $C_{kat2} = 0.018 \text{ mg/cm}^2$, $C_{kat3} = 0.069 \text{ mg/cm}^2$, $C_{kat4} = 0.459 \text{ mg/cm}^2$, $C_{kat5} = 0.917 \text{ mg/cm}^2$); the catalyst carrier surface area (c) ($F_1 = 3.04 \cdot 10^{-3} \text{ m}^2$, $F_2 = 5.99 \cdot 10^{-3} \text{ m}^2$, $F_3 = 9.04 \cdot 10^{-3} \text{ m}^2$, $F_4 = 12.49 \cdot 10^{-3} \text{ m}^2$) and the contact time (d) ($\tau_1 = 0.045 \text{ s}$, $\tau_2 = 0.112 \text{ s}$, $\tau_3 = 0.147 \text{ s}$)

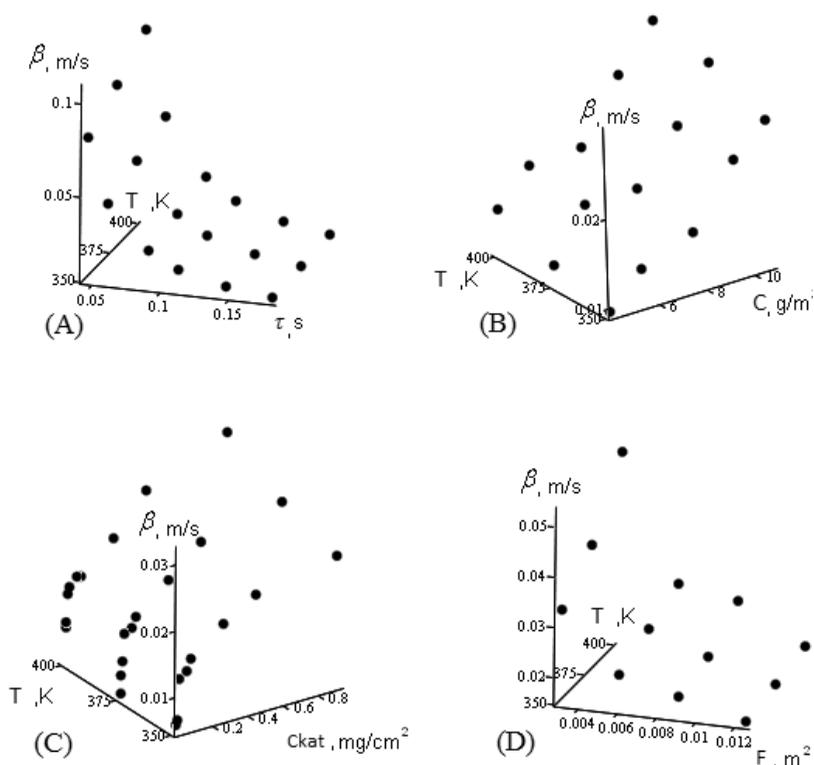


Fig. 4. Experimental temperature dependence of the mass transfer coefficient on the contact time (a); concentration of hydrocarbons (b); concentration of the catalyst-palladium (c) and the surface area of the carrier (d)

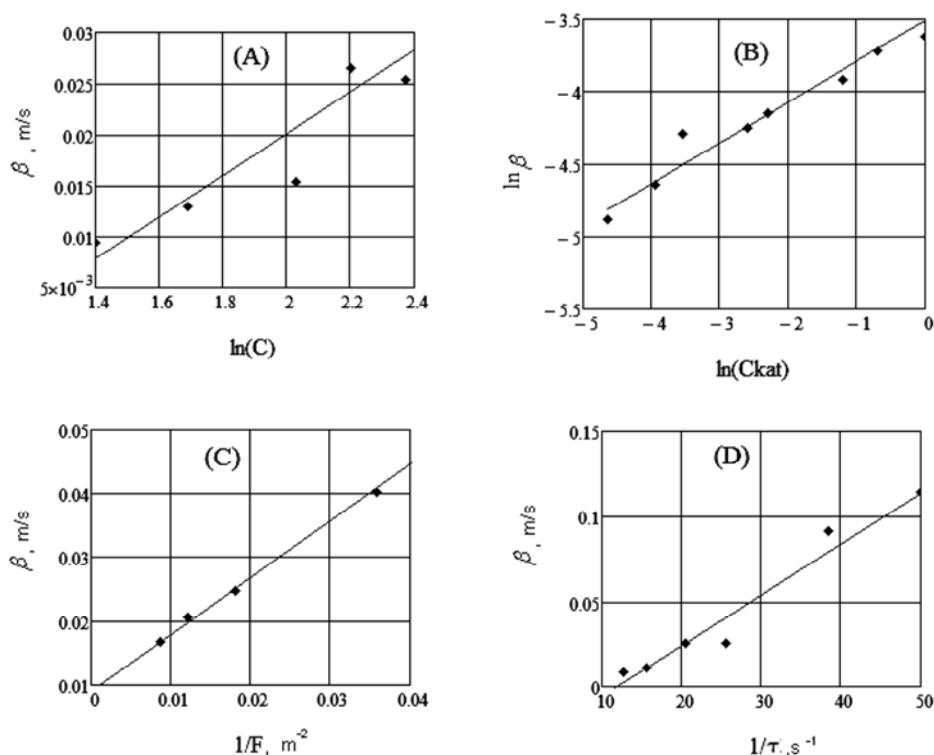


Fig. 5. Dependence of the mass transfer coefficient on the logarithm of the hydrocarbons concentration (a); on the concentration of catalytic components on the surface of the carrier in logarithmic coordinates (b); on the inverse surface of substrate (c) and on the inverse contact time (d)

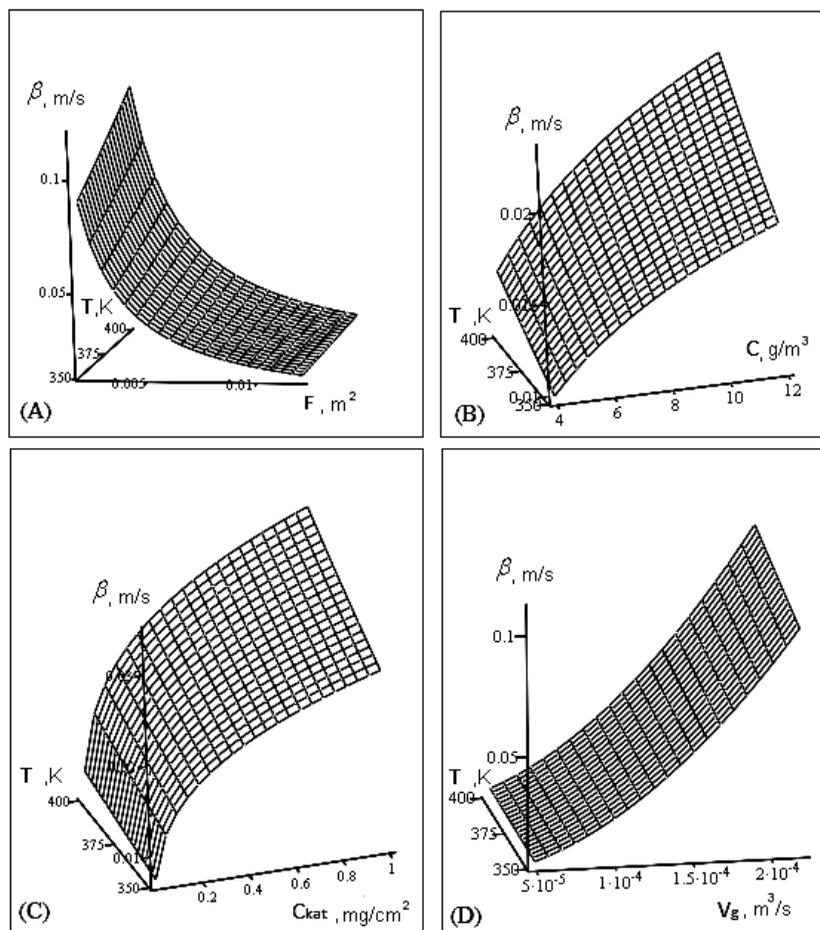


Fig. 6. Calculated temperature dependences of the mass transfer coefficient on the carrier surface (a); concentration of hydrocarbons (b); concentration of catalyst components on the carrier surface (c) and the gas flow velocity (d)

The experimental data were the basis for its description by means of Eqs. 4 and 5. From Eq. (5) it follows that the observed mass transfer coefficient value is proportional to the logarithm of the concentration of hydrocarbons in the gas flow entering the reactor which is confirmed by the linear dependence given in Fig. 5a.

Effect of quantity of catalytic elements which are contained on the surface of the carrier on the observed value of the mass transfer coefficient was explained with the use of ideas about the adsorption mechanism of the carrier surface coverage by the catalytic elements. This effect is described adequately by an equation which is equivalent to the adsorption isotherm [8, 10]:

$$b = aC_{kat}^{1/b} \quad (7)$$

where a and b - empirical constants which are specific to each pair of "hydrocarbon-catalyst".

Then the dependence of the experimental values of the mass transfer coefficient from the concentration of catalytically active compounds on the surface of the

carrier has the form of a straight line in logarithmic coordinates (Fig. 5b).

The observed dependence of the mass transfer coefficient on the carrier surface (Fig. 5c), as well as on the contact time (Fig. 5d) defined by Eq. (5) has a linear character.

Obtained mass transfer coefficient dependence on the parameters allows to obtain the general dependence 8:

$$b = AC_{kat}^{1/b} \ln(C_0) Re^m Pr^n \frac{D}{LF} \quad (8)$$

By substituting Eq. (8) in (6) the mass transfer coefficients were obtained for carried out experiments (Fig. 6).

The adequacy of Eqs. (1) and (6) with identified values of the parameters is confirmed by comparing of the calculated values of the hydrocarbon conversion degree in the kinetic region (X_k), external diffusion region (X_D) and experimentally found (X_{exp}), which reflects Fig. 7.

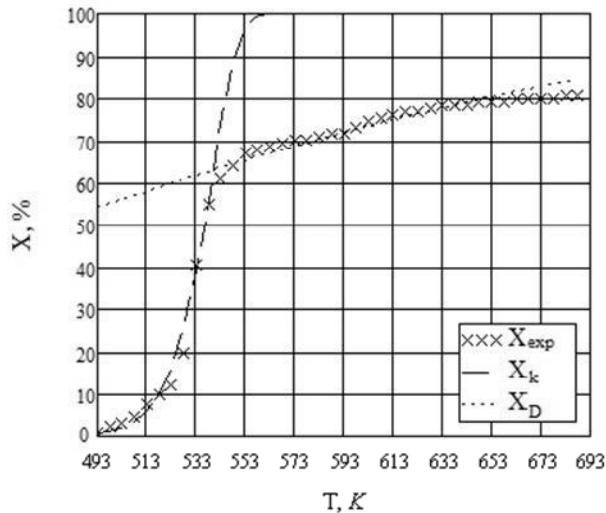


Fig. 7. Experimental and calculated dependences of the hydrocarbons conversion degree in the kinetic and external diffusion regions

4. Conclusions

The resulting mathematical model shows the main control factors related to the process of harmful gas emissions conversion which allow to control effectively the conversion process and predict its behavior. Content of catalytically active elements on the carrier surface, the specific surface area of the carrier, the concentration of harmful substances in the gas flow, the temperature of the gas flow and catalyst layer and the gas flow rate were assigned to the control factors. Controlled parameter is the mass transfer coefficient.

The proposed Eqs. (1) and (6) describe the hydrocarbons conversion degree dependence on various parameters and are the basis for calculation and designing

the catalytic converters for gases purification which are contaminated by hydrocarbons with a predetermined geometric parameters and the specific surface area of the carrier.

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МОДЕЛЮВАННЯ ПРОЦЕСІВ КАТАЛІТИЧНОЇ КОНВЕРСІЇ ВУГЛЕВОДНІВ

Анотація. Створено новий експериментально-розрахунковий метод розрахунку каталітичних перетворювачів для очищення забруднених вуглеводнями газів на основі розкритого уявлення про механізм перебігу гетерогенно-каталітичного процесу, стадії якого описані математичними моделями.

Ключові слова: каталіз, масообмін, конверсія, енергія активації, моделювання.