EFFECTIVENESS OF CATALYST EXTRUDATE OF TETRALOBED CROSS SECTION UNDER CONDITIONS OF INFLUENCE OF INTERNAL DIFFUSION

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

The results are summarized of mathematical modelling of the effect of internal diffusion on the rate of *m*-th order reaction taking place under non-isothermal conditions in the catalyst particle with tetralobed cross section. The effectiveness of the tetralobe-shaped extrudate is compared with that of cylindrical extrudate. The results obtained on the basis of mathematical modelling are confronted with the experimental data obtained on studying the dehydration reaction of cyclohexanol on cylindrical and tetralobed extrudates of γ-alumina under the conditions of influence of internal diffusion. The experimental data are in a qualitative agreement with the theoretical ones and confirm the higher effectiveness of shaped catalyst in comparison with the cylindrical extrudate catalyst.
Key words: Effectiveness factor; Internal diffusion; Polylobe-shaped pellets; Cyclohexanol dehydration.

Extruded catalysts with trilobed and tetralobed cross section are at present employed above all in hydrotreating of crude oil products and in some other processes of petroleum and petrochemical industry. Such shaped catalysts, owing to their high value of external surface to their volume, are noted for a considerably lower degree of effect of transport phenomena in comparison with the particles of cylindrical or spherical shape. Further priorities of profiled catalysts consist in lower pressure drop of packed catalyst bed at the given catalyst particle size. Application of such catalysts in three-phase sprayed reactors leads simultaneously to the increase of retention of liquid reaction mixture in reaction zone[1]. A certain disadvantage of employing the shaped catalysts is lower packing density compared with, *e.g.*, the bed formed by cylindrical particles.

The effect of internal diffusion on the rate of simple reaction taking place in an infinitely long isothermal catalyst particle of tetralobed cross section was described in paper[2]. In the work cited, a model was solved for a simple irreversible monomolecular reaction of reaction order equal 0 or 1, taking place in stationary state in the catalyst particle with tetralobed cross section. Simultaneously, the effect of external diffusion

on the reaction course was neglected in that work. In the reassuming study[3], the numerical results were compared with the experimentally found effectiveness of the shaped cobalt–molybdenum catalysts for hydrodesulfurization of gas oil.

The solution of the corresponding differential equations for describing the mass transfer and chemical reactions in extruded catalyst with five-pointed star cross section was presented in our recent work[4].

The aim of the present study is to yield a quantitative concept of the favourable effect of shaping the extruded catalyst on its effectiveness for the case of reaction accompanied with thermal effects. The results obtained by numerical solution of corresponding diffusion equations are further confronted with the experimental data measured on dehydrating cyclohexanol on shaped alumina catalyst with tetralobed cross section.

THEORETICAL

Mathematical Model of Diffusion in Shaped Catalyst Particle

The concept of steady state and neglecting the effect of mass or heat transfer by external diffusion pertains to the basic simplifying assumptions accepted when solving the model. In this work, the model of catalyst extrudate was solved of both infinite and finite length, *i.e.*, the two-dimensional and/or three-dimensional one. The reaction rate was described by a rate equation of power type.

The material and enthalpy balances take, in case of two-dimensional model, the form of the following system of partial differential equations:

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} - c^{\mathrm{m}} \Phi^2 \exp\left[\varepsilon^0 (1 - 1/t)\right] = 0 \qquad (1a)$$

$$\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} - c^{\mathrm{m}} \beta \Phi^2 \exp\left[\varepsilon^0 (1 - 1/t)\right] = 0 \ . \qquad (1b)$$

The boundary conditions follow from the symmetry of catalyst cross section:

$$\frac{\partial c}{\partial x}(x = 0, y) = \frac{\partial c}{\partial y}(x, y = 0) = \frac{\partial c}{\partial x}(x = y) = \frac{\partial c}{\partial y}(x = y) = 0 \qquad (2a)$$

$$\frac{\partial t}{\partial x}(x = 0, y) = \frac{\partial t}{\partial y}(x, y = 0) = \frac{\partial t}{\partial x}(x = y) = \frac{\partial t}{\partial y}(x = y) = 0 \ . \qquad (2b)$$

The values of concentration and temperature at the external surface of catalyst particle can be described by the boundary conditions of the Dirichlet type:

$$c_S = 1, t_S = 1 \ . \qquad (2c), (2d)$$

The Thiele modulus, Φ, was defined by the relation:

$$\Phi^2 = R_p^2 \frac{r^0 \rho}{D_{eff} C_S} \ . \qquad (3)$$

The choice of characteristic dimension, R_p, contained in the definition of Thiele modulus stems from the geometry of the catalyst particle cross section. In case of the tetralobe-shaped extrudate, R_p has the meaning of diameter of one lobe (Fig. 1), and in case of cylindrical extrudate, R_p is equal the cylinder radius. Another possibility is to define the characteristic dimension as the ratio of particle volume to its external surface, see, *e.g.*, paper[4]. Further parameters of the model are dimensionless activation energy ε^0 described by the equation:

$$\varepsilon^0 = \frac{E_{act}}{\boldsymbol{R} T_S} \qquad (4)$$

and reaction heat parameter β expressed by the relation:

$$\beta = \frac{(-\Delta H_r) D_{eff} C_S}{\lambda T_S} \ . \qquad (5)$$

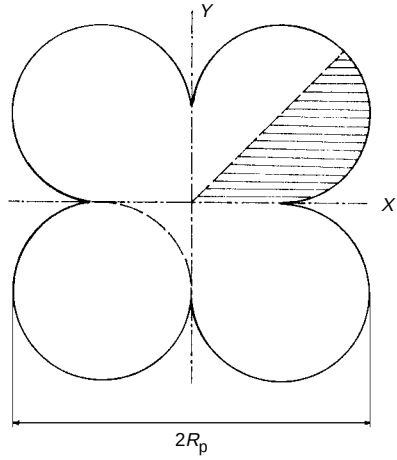

FIG. 1
Tetralobed cross section of extrudate. Characteristic dimension R_p indicated, balanced region of cross section marked by hatching

The system of partial differential equations (*1a*), (*1b*) with the corresponding boundary conditions (*2a*)–(*2d*) was solved by the finite difference method, analogously to the preceding works[2–4]. The equidistant rectangular network was applied. The extrudate external edge was replaced by a stepwise function in agreement with the used calculation scheme. With regard to the symmetry of the particle cross section, it was not necessary to solve the above-mentioned system of balance equations along the entire extrudate cross section. The balanced region is illustrated by hatching in Fig. 1. For the solution itself of system of algebraic equations obtained by replacing the derivatives in the balance equations by difference formulae, the Gauss–Seidel iteration algorithm[5] was used. With regard to the non-linearity of the system of difference equations (reaction order m different from 0 and 1, non-isothermal case), the Gauss–Seidel algorithm was combined with the Newton–Raphson method of the solution of systems of non-linear algebraic equations[6]. The effectiveness factor obtained on the basis of mathematical modelling was described by the following relation:

$$E = \frac{r}{r^0} = \frac{\int_0^V \exp\left[\varepsilon^0(1 - 1/t)\right] c^m \, \mathrm{d}V}{V} \quad . \tag{6}$$

To evaluate the experiment, the definition of Thiele modulus (*3*) was modified. Under the conditions of experiment described below, a significant manifestation of the Knudsen diffusion mechanism takes place. This conclusion can be stated on the basis of estimate of the Knudsen criterion of internal diffusion defined as a ratio of mean free path of molecules to mean diameter of cylindrical pore[7]. The estimate of the Knudsen criterion for the given reaction system and experimental conditions takes the value of about 3.5. The temperature dependence of the Knudsen diffusion coefficient of cyclohexanol, D_{col}, for the diffusion through a cylindrical pore is described by the following relation:

$$D_{\mathrm{col}} = \frac{2}{3} r_{\mathrm{pore}} \left(\frac{8\boldsymbol{R}T}{\pi M_{\mathrm{col}}} \right)^{1/2} \quad . \tag{7}$$

The effective diffusion coefficient of cyclohexanol diffusion through a porous catalyst is a function of catalyst porosity, ε, and its tortuosity, τ:

$$D_{\mathrm{eff}} = D_{\mathrm{col}} \frac{\varepsilon}{\tau} \quad . \tag{8}$$

After inserting relations (*7*) and (*8*) into the definition of Thiele modulus (*3*) and on replacing the cyclohexanol concentration at the catalyst external surface, C_{S}, by cyclo-

hexanol partial pressure on the basis of equation of state of ideal gas, the Thiele modulus Φ is given by the following relation:

$$\Phi^2 = \frac{3}{2}\left(\frac{\pi \boldsymbol{R} M_{\mathrm{col}}}{8}\right)^{1/2} R_{\mathrm{p}}^2 \frac{r^0 \tau \rho}{\varepsilon r_{\mathrm{pore}} p_{\mathrm{S,col}}} \sqrt{T} = 0.858\, R_{\mathrm{p}}^2 \frac{r^0 \tau \rho}{\varepsilon r_{\mathrm{pore}} p_{\mathrm{S,col}}} \sqrt{T} \quad . \tag{9}$$

During single measurements, the characteristic dimension of particles, R_{p}, the reaction rate in the kinetic region, r^0, and the temperature, T, were measured. As far as the resistance to heat transfer by external diffusion is eliminated, the temperature T occurring in relation (*9*) is, under the assumption of isothermal catalyst particle, identical with the temperature measured by a thermocouple located in the catalytic bed (see below). The partial pressure of cyclohexanol at the catalyst particle external surface, $p_{\mathrm{S,col}}$, was determined as the arithmetic mean of cyclohexanol partial pressure in feed and behind the catalytical bed. The values of catalyst porosity, ε, mean pore radius, r_{pore}, and apparent catalyst density, ρ, were known from porosimetric measurements. Considering that the value of catalyst tortuosity, τ, occurring in relation (*9*) was not known, the definition of Thiele modulus was modified:

$$\Phi_{\mathrm{mod}}^2 = 0.858\, R_{\mathrm{p}}^2 \frac{r^0 \rho}{\varepsilon r_{\mathrm{pore}} p_{\mathrm{S,col}}} \sqrt{T} \quad . \tag{10}$$

The relation between the modified Thiele modulus, Φ_{mod}, and the Thiele modulus, Φ, is given by the following equation:

$$\Phi_{\mathrm{mod}}^2 = \frac{\Phi^2}{\tau} \quad . \tag{11}$$

The tetralobe-shaped and cylindrical catalyst extrudates used in the experiment were obtained by extruding γ-alumina of the same type, and both the types of extrudates were noted for similar porous characteristics. Therefore, the same value of tortuosity was assumed for both the catalyst forms used.

On evaluating the experiment, the effectiveness of the catalyst extrudate was described by the value of the effectiveness factor defined as the ratio of actual reaction rate to the reaction rate measured in the kinetic region:

$$E = \frac{r}{r^0} \quad . \tag{12}$$

EXPERIMENTAL

Chemicals and Catalysts

Cyclohexanol (99%, Aldrich), γ-alumina (Pural SB, CONDEA, Germany, cylindrical extrudate, characteristic dimension R_p = 0.8 mm, mean length l = 6.5 mm), γ-alumina (Pural SB, CONDEA, Germany, tetralobe-shaped extrudate, characteristic dimension R_p = 0.7 mm, mean length l = 6.5 mm). Both the catalysts were shaped in Chemopetrol a.s., Litvinov, Czech Republic. Both the catalysts used were noted for similar physical properties whose values were measured at the Department of Inorganic Technology, Prague Institute of Chemical Technology. Their specific surfaces were 184 and 247 $m^2\ g_{cat}^{-1}$, porosities ε = 0.55 and 0.60, apparent densities ρ = 1.18 and 1.11 $g_{cat}\ cm^{-3}$, and mean pore radii 5.1 and 4.4 nm, respectively.

Experimental Set-up and Reaction Conditions

For the experimental study of the catalyst effectiveness under the conditions of influence of internal diffusion, the dehydration reaction of cyclohexanol was chosen catalysed by γ-alumina in the shape of cylindrical or tetralobed extrudates. The confrontation of the theoretical and experimetal data was made easy by the fact that a monomolecular reaction was concerned with the reaction order m = 1 (see ref.[8]) taking place with high selectivity. A certain complication was the reversibility of the model reaction and its mild thermal effect (the reaction enthalpy at 270 °C determined from heats of formation of components[9] is approximately $\Delta H \approx 60$ kJ mol^{-1}).

The reaction was performed[10] in the gas phase in a tube reactor of inside diameter 30 mm equipped with electrical heating mantle, the measuring thermocouple was located in the centre of the catalytic bed of length 10 cm formed by the catalyst diluted by glass spheres of diameter 2 mm. Liquid cyclohexanol was fed into the upper part of reactor with a proportional piston pump, and nitrogen was carried to the reactor inlet in molar cyclohexanol : nitrogen ratio 2 : 1. In the reactor upper part with inert packing, the evaporation of liquid cyclohexanol took place, and the reaction mixture was tempered to the reaction temperature. The reaction mixture flow rate was chosen for the formation of temperature profile not to take place along the catalyst bed owing to the reactor insufficient length. The measurements were carried out at atmospheric pressure. The change of extent of influence of internal diffusion was ensured by varying the reaction temperature in the interval of 250–280 °C. A cooler and separator of the liquid and gas phase were included behind the reactor. The taken samples of liquid product were analysed by a gas-chromatographic method (CHROM 4 chromatograph–Laboratorni pristroje, Prague, 5% SE-30 Chromaton N-super, isothermal regime 140 °C, FID).

The experimental error in the cyclohexanol conversion determination amounted to about 10 rel.%.

RESULTS AND DISCUSSION

Results of Numerical Solution of Mathematical Models

It is evident from the comparison of results obtained by solving the two- and/or three-dimensional model of tetralobe-shaped extrudate that the transport phenomena in the direction of axial axis of extrudate have not a significant effect on the value of effectiveness factor[10], see also Fig. 2. Besides, the length of extruded catalysts, l, exceeds mostly four to ten times the value of characteristic dimension, R_p. When solving further

variants of the model, therefore, the simplifying assumption of a particle of infinite length was accepted ($R_p/l \to 0$).

The effect of reaction order m on the dependence of effectiveness factor on the value of Thiele modulus is illustrated in Fig. 3. The results are concerned obtained by solving the 2-D model for the reaction taking place in the isothermal catalyst particle with tetralobed cross section. The sensitivity of reaction rate to the decrease of concentration in the catalyst particle volume owing to the internal diffusion diminishes with decreasing reaction order. Therefore, the value of effectiveness factor at the given value of Thiele modulus increases with decreasing value of reaction order (see Fig. 3).

The dependences of effectiveness factor on the value of Thiele modulus depicted in Fig. 4 were obtained by solving the 2-D non-isothermal models. The case of exothermic reaction ($\beta > 0$) taking place in cylindrical and tetralobed extrudate is given here. The decrease of reaction rate brought about by the decrease of reactant concentration in the particle volume owing to the internal diffusion is, in the region of mean values of Thiele modulus, $\Phi \in (0.2; 10)$, compensated by the temperature growth owing to the insufficient carrying away of reaction heat from the internal space of catalyst particle. Therefore, the value of effectiveness factor may, in the interval said corresponding to the transient region between the kinetic and diffusion regime, acquire the values higher than unity. At a sufficiently high value of the reaction heat parameter, β, even the

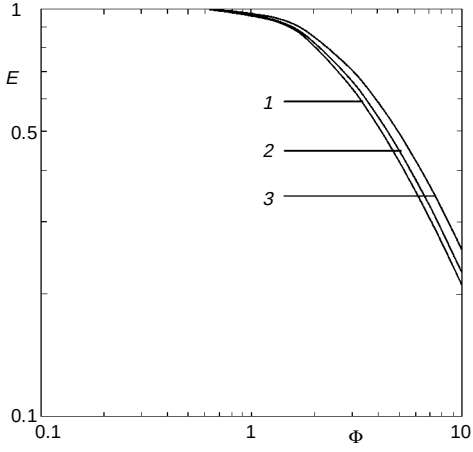

FIG. 2
Effect of catalyst extrudate geometry on its effectiveness – comparison of results of solving 2-D and 3-D isothermal model of extrudate[10] with tetralobed cross section, $m = 1$: *1* $R_p/l \to 0$ (2-D model), *2* $R_p/l = 0.5$, *3* $R_p/l = 1.0$

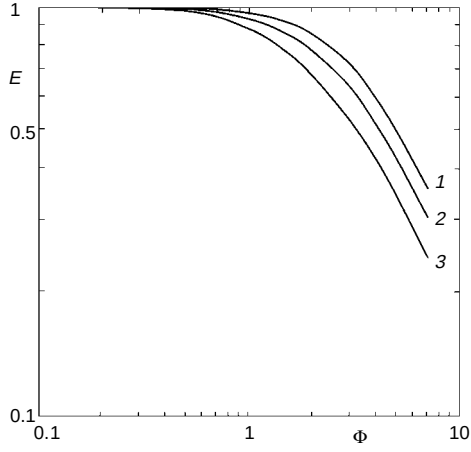

FIG. 3
Effect of reaction order on dependence of effectiveness factor on value of Thiele modulus. Isothermal 2-D model for reaction taking place in catalyst particle with tetralobed cross section: *1* $m = 0.5$, *2* $m = 1$, *3* $m = 2$

existence of multiple stationary states in a certain interval of values of Thiele modulus may occur in dependence on the reaction conditions (see Fig. 4). The interval of the values of Thiele modulus corresponding to the region of multiple stationary states is in case of the tetralobe-shaped extrudate narrower and is shifted to the higher values of Thiele modulus. The maximum of curve of effectiveness factor of the tetralobe-shaped extrudate also has lower value in comparison with the maximum of curve corresponding to the catalyst cylindrical extrudate. This fact corresponds to higher value of the ratio of particle external surface to its volume in case of the tetralobe-shaped extrudate in comparison with the cylindrical extrudate of the catalyst. However, it is necessary to realize that the value of dimensionless reaction heat parameter, $\beta = 0.5$, is a value considerably high. For most industrial catalytic processes, the parameter β acquires values lower than 0.1 (see ref.[11]).

In Fig. 4, the results are also plotted of solving the model for the case of reaction without thermal effects ($\beta = 0$), *i.e.*, for the case of isothermal catalyst particle. In harmony with the conclusions stated in paper[2], the tetralobe-shaped extrudate shows in the diffusion region higher effectiveness in comparison with the cylindrical extrudate.

In case of endothermic reaction ($\beta < 0$), too, the curves of effectiveness factor for both the compared catalyst particles decrease monotonously with increasing value of the Thiele modulus, the effectiveness factor in the transient and diffusion region being higher for the tetralobed catalyst (see Fig. 4).

Test of Stability of Catalytic Activity

The test of stability of catalytic activity was carried out with the crushed cylindrical extrudates of γ-alumina (mean particle diameter 0.36 mm) at the temperature of 280 °C. After reaching the steady state during about 1 hour, the measured cyclohexanol conver-

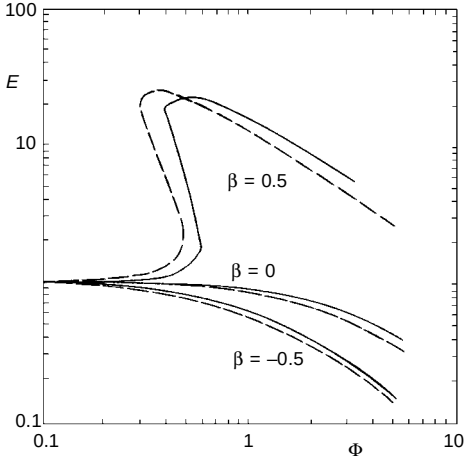

FIG. 4
Comparison of effectiveness of cylindrical and tetralobed catalyst extrudate under non-isothermal conditions, 2-D model, $m = 1$, $\varepsilon^0 = 20$: – – – – cylindrical extrudate, —— tetralobed extrudate

sion fluctuated within the range of accuracy of its experimental determination (see Fig. 5). Therefore, it is possible to assert that the experimental data obtained are not influenced, in the course of six hour's experiment, by a change of catalyst activity.

Elimination of Effect of External Transfer

Before the evaluation itself of the influence of internal diffusion on the reaction rate, it was necessary to limit the extent of effect of external mass and heat transfer. The increase of values of mass and heat transfer coefficients can be reached by increasing the feed flow rate and, thus, by increasing the turbulence of flow of reaction mixture.

To judge the effect of external transfer, the uncrushed cylindrical extrudates of γ-alumina were used at the highest experimental temperature 280 °C. Several different values of cyclohexanol feed were chosen in the experiment, and such an amount of catalyst was always put into the reactor that the value of kinetic coordinate should have the value $w/F = 20\ g_{cat}\ min\ mol^{-1}$. The measurements were carried out in the region of cyclohexanol conversion 2–8%, therefore in the range where the dependence of cyclohexanol conversion on the value of kinetic coordinate of the reactor, w/F, is linear. The measured dependence of cyclohexanol conversion on the cyclohexanol molar flow rate in feed is illustrated in Fig. 6. The cyclohexanol molar flow rate in feed, $F = 10.5\ mmol\ min^{-1}$ used for measuring the values of effectiveness factor is plotted here by the dashed line.

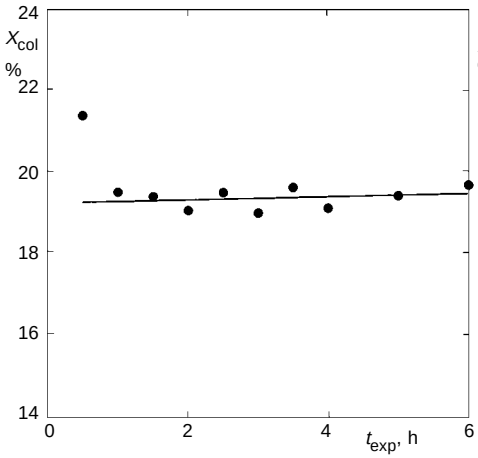

FIG. 5
Stability test of catalytic activity, crushed cylindrical extrudate, mean particle diameter d_p = 0.36 mm, $w/F = 5.86\ g_{cat}\ min\ mol^{-1}$, T = 280 °C

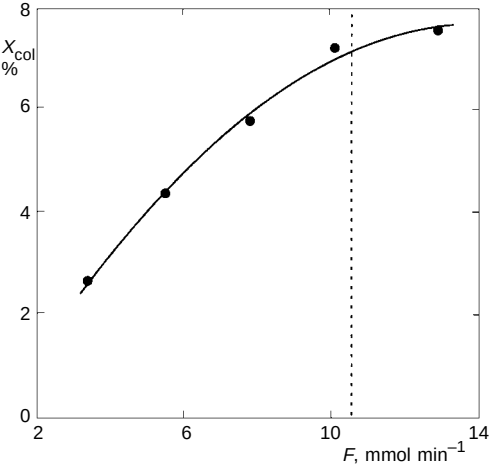

FIG. 6
Test of effect of external diffusion, uncrushed cylindrical extrudate, $w/F = 20\ g_{cat}\ min\ mol^{-1}$, T = 280 °C. Cyclohexanol molar flow rate in feed $F = 10.5\ mmol\ min^{-1}$ chosen for measurement of effectiveness factor indicated

At this cyclohexanol molar flow rate in feed, about 10% decrease takes place in cyclohexanol conversion, compared with the kinetic region, therefore, to a decrease comparable with the experimental error in determining the reaction rate. Use of higher feed flow rate would be connected with the formation of temperature profile along the catalytic bed owing to the insufficient reactor length, and the measurement under such conditions would be unreliable.

Effect of Catalyst Particle Size on Reaction Rate

To determine the values of effectiveness factor, it is necessary to mesure reaction rate in the diffusion region (with defined effect of internal diffusion) and in the kinetic region (on eliminating the effect of internal diffusion). The extent of effect of internal diffusion depends above all on the catalyst particle size. Therefore, it was necessary to find such a catalyst particle size ensuring the elimination of influence of internal diffusion.

The dependences were measured of cyclohexanol conversions on the reactor kinetic coordinate, *w/F*, for a crushed and sieved catalyst of various dimensions. The measurements took place at the temperature of 280 °C, *i.e.*, at the highest experimental temperature used. In single measurements, the cyclohexanol molar flow rate in feed was changed at a constant amount of catalyst put into the reactor. The results of such a measurement on using crushed alumina tetralobed extrudates are given in Fig. 7. Within the range of cyclohexanol conversions 0–20%, a considerable manifestation of equilibrium of the reaction studied does not occur, and the conversion curves are in this interval of conversions practically linear. To determine the reaction rate, it is therefore possible to utilize the method of initial reaction rates. For the measurements in the kinetic region, the catalyst particle size 0.36 mm was chosen. Approximately 10% dif-

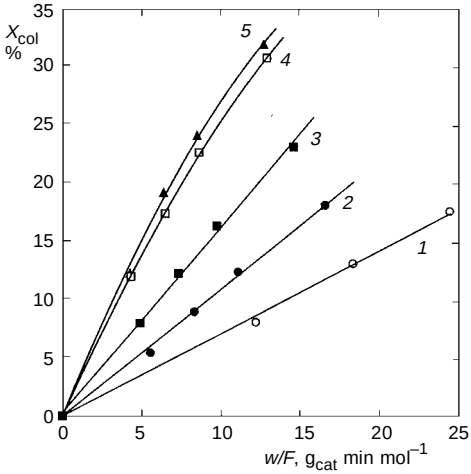

FIG. 7
Effect of catalyst particle size on reaction rate. Tetralobe-shaped extrudate, T = 280 °C: *1* uncrushed extrudate, *2* d_p = 1.03 mm, *3* d_p = 0.72 mm, *4* d_p = 0.52 mm, *5* d_p = 0.36 mm

ference between the reaction rate measured with the catalyst of this dimension and the reaction rate measured with the catalyst of the second smallest size (0.52 mm) – see Fig. 7, is comparable with the experimental error in determining the reaction rate.

Effectiveness Factor of Internal Diffusion

The experimentally found value of effectiveness factor was determined on the basis of relation (*12*). For the measurement in the diffusion region, an uncrushed catalyst in shape of cylinders and tetralobes was used. For the measurement in the kinetic region, these catalysts were used as crushed and sieved particles of size 0.36 mm. The cyclohexanol conversion was measured at various reaction temperatures, and the reaction rate was determined by the method of initial reaction rates, *i.e.*, as a ratio of the measured cyclohexanol conversion and the reactor kinetic coordinate. Always such an amount of catalyst was put into the reactor that the cyclohexanol conversion should not be higher than 10%. The measurements were carried out with the molar flow rate of fed cyclohexanol F = 10.5 mmol min^{-1}. The reaction rate was determined with an experimental error of about 10% as a mean value of two independent measurements.

The measured values of reaction rate in diffusion region and the corresponding values of effectiveness factor described by relation (*12*) are given in Table I. The values of modified Thiele modulus, Φ_{mod}, for single measurements, as obtained on the basis of relation (*10*), are also presented in Table I. The values of effectiveness factors lay within the range $E \in (0.1; 0.5)$, and in harmony with the theory, 40–70% higher values were found in case of mesurements with the tetralobed extruded catalyst compared with the values of effectiveness factor corresponding to the cylindrical extrudates.

On the basis of a regression analysis of the reaction rate values as a function of temperature, the activation energy was estimated of the reaction in kinetic and diffusion regions for both the forms of alumina used. The values of activation energy for the

TABLE I
Dependence of reaction rate on temperature

T, °C	r, mol g_{cat}^{-1} min^{-1}		r_{cor}, mol cm^{-3} min^{-1}		Φ_{mod}		E	
	tetralobe	cylinder	tetralobe	cylinder	tetralobe	cylinder	tetralobe	cylinder
250	0.0027	0.0013	0.0014	0.0012	2.317	2.146	0.530	0.376
260	0.0040	0.0019	0.0021	0.0017	3.319	3.184	0.396	0.264
270	0.0052	0.0028	0.0027	0.0019	4.342	4.721	0.302	0.172
280	0.0070	0.0040	0.0036	0.0026	5.839	6.588	0.225	0.132

cylindrical and tetralobed extrudates of γ-alumina are not identical. The estimate of activation energy in the kinetic region for tetralobed extrudate amounts to 144 kJ mol^{-1} (for cylindrical extrudate 177 kJ mol^{-1}), and in the diffusion region then 76 kJ mol^{-1} (for cylindrical extrudate 91 kJ mol^{-1}). The activation energy of the reaction strongly influenced by internal diffusion is, in harmony with the theory, a half in comparison with the activation energy of the reaction taking place in the kinetic region. The higher value of activation energy of cyclohexanol dehydration on using the cylindrical extrudate may be connected with a lower specific surface and lower porosity of this catalyst.

The packing density of catalytic bed formed by the tetralobe-shaped catalyst extrudates ($\zeta = 0.52$ g$_{cat}$ ml^{-1}) is lower than the packing density of bed formed by the cylindrical extrudates ($\zeta = 0.63$ g$_{cat}$ ml^{-1}). Therefore, the values of reaction rate in the diffusion region, r_{cor}, were also determined related not to the catalyst mass but to the volume of catalytic bed (see Table I). The values r_{cor} corrected in this way were determined on the basis of the following relations:

$$r_{cor,\,tet} = \xi_{tet} r_{tet} \qquad (13a)$$

$$r_{cor,\,cyl} = \xi_{cyl}\, r_{cyl}\, \frac{r^0_{tet}}{r^0_{cyl}} \ . \qquad (13b)$$

The ratio r^0_{tet}/r^0_{cyl} is the correction for unequal rate of reaction taking place in the cylindrical and tetralobed catalyst particle in the kinetic region. Even if it is possible to put, into the given volume of reactor, larger amount of catalyst in the shape of cylindrical extrudates than of catalyst of tetralobe-shaped extrudates, the reaction rate related to

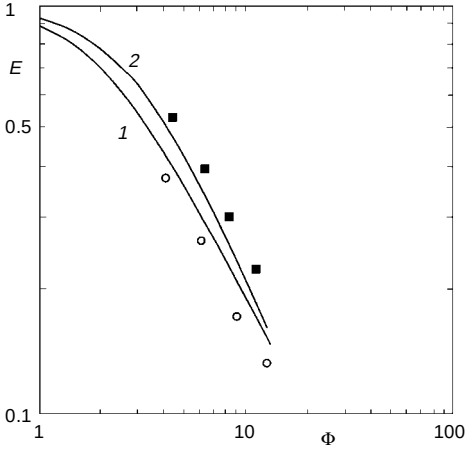

FIG. 8
Comparison of calculated and experimentally found dependences of effectiveness factor on value of Thiele modulus. 2-D isothermal models solved for reaction with reaction order $m = 1$ taking place in cylindrical (*1*) and tetralobe-shaped (*2*) catalyst extrudate. Experimental values determined for tortuosity of both catalyst forms used, $\tau = 3.5$: ❍ cylindrical extrudate, ■ tetralobed extrudate

the reactor volume is higher in case of the tetralobe-shaped extrudate. The reason is higher effectiveness of extrudate with tetralobed cross section.

Under the given experimental conditions, it is possible to expect only weak resistance to the heat transfer inside the catalyst particle. The values of effectiveness factor determined experimentally were therefore compared with the values obtained by solving the 2-D isothermal models for the first-order reaction. On the basis of the comparison of the experimentally determined and calculated values of effectiveness factor, the value of tortuosity of the catalysts used was estimated on using relation (*11*). It takes a realistic value $\tau \approx 3.5$. With regard to the simplifying assumptions accepted in solving the mathematical models, this estimate of tortuosity is to be considered orientational. Comparison of the experimental and calculated dependences of effectiveness factor on the Thiele modulus is illustrated in Fig. 8. The value of Thiele modulus, Φ, in case of experimental data was determined from the value of modified Thiele modulus, Φ_{mod}, in terms of relation (*11*) for tortuosity $\tau = 3.5$. The experimental data are in qualitative agreement with the theoretical ones. The values of effectiveness factor pertaining to the given value of Thiele modulus are higher in case of the tetralobe-shaped extrudate of the catalyst. Both the experimental and calculated points plotted in logarithmic coordinates form in the diffusion region, in harmony with the theory, straight lines with the slope approaching the value –1.

CONCLUSION

The results of this study document the possibility of intensification of a catalytic process by increasing the external surface of catalyst particle which leads to the increase of value of effectiveness factor.

Theoretical concept of increasing the value of effectiveness factor obtained by solving the mathematical model of shaped catalyst with tetralobed profile are in qualitative agreement with the experimental data measured for cyclohexanol dehydration on so shaped γ-alumina.

In a next work, attention will be paid to the experimental study of more complex reaction systems influenced by transport phenomena. The effect of catalyst shaping on reaction rate and selectivity will be studied in systems of side and consecutive reactions.

LIST OF SYMBOLS

C	reactant concentration, mol m^{-3}
C_S	reactant concentration at catalyst particle external surface, mol m^{-3}
$c = C/C_S$	reactant dimensionless concentration
D_{col}	Knudsen diffusion coefficient of cyclohexanol, Eq. (*7*), $m^2\ s^{-1}$
D_{eff}	effective diffusion coefficient of cyclohexanol diffusion, Eq. (*8*), $m^2\ s^{-1}$
d_p	mean diameter of crushed catalyst particles, m

E	effectiveness factor, Eqs (*6*), (*12*)
E_{act}	activation energy of reaction, J mol^{-1}
F	molar flow rate of cyclohexanol in feed, mol s^{-1}
ΔH_r	reaction ethalpy, J mol^{-1}
l	length of catalyst extrudate, m
M_{col}	molar mass of cyclohexanol, kg mol^{-1}
m	reaction order
$p_{S,col}$	partial pressure of cyclohexanol at external surface of catalyst particle, Pa
$\boldsymbol{R}$	gas constant, $\boldsymbol{R}$ = 8.314 J mol^{-1} K^{-1}
R_p	characteristic dimension of catalyst particle, m
r	reaction rate, mol kg_{cat}^{-1} s^{-1}
r^0	reaction rate in kinetic region, mol kg_{cat}^{-1} s^{-1}
r_{cor}	corrected reaction rate, Eqs (*13a*), (*13b*), mol m^{-3} s^{-1}
r_{pore}	mean pore radius, m
T	temperature, K
T_S	temperature at external surface of catalyst particle, K
$t = T/T_S$	dimensionless temperature
t_{exp}	time of experiment duration, s
V	catalyst particle volume, m^3
w	catalyst mass, kg_{cat}
X, Y	spatial coordinates, m
X_{col}	conversion of cyclohexanol, %
$x = X/R_p$, $y = Y/R_p$	dimensionless spatial coordinates
Φ	Thiele modulus, Eq. (*3*)
Φ_{mod}	modified Thiele modulus, Eqs (*10*), (*11*)
β	dimensionless parameter of reaction heat, Eq. (*5*)
ε	catalyst porosity
ε^0	dimensionless activation energy, Eq. (*4*)
λ	thermal conductivity of catalyst, W m^{-1} K^{-1}
ρ	apparent density of catalyst, kg_{cat} m^{-3}
τ	catalyst tortuosity
ξ	packing density of catalytic bed, kg_{cat} m^{-3}

Subscripts

cat	catalyst
col	cyclohexanol
cor	corrected
cyl	cylinder
S	external surface of extrudate
tet	tetralobe

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