Modeling of Steady-State Internal Diffusion in a Porous Catalyst Particle taking into Account Reaction Reversibility

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Abstract: - The paper presents a mathematical model of steady-state internal diffusion in a catalyst grains in fixed-bed reactors. A key feature and scientific contribution of this work is the account of the reversible reaction stage based on the submitted concept of the reaction-diffusion number. By this, the characteristics of the transfer process in batch and flow-through apparatus are considered. The results of calculations carried out on the basis of the model have been also presented and a brief qualitative analysis has been given.

Key-Words: - Catalyst particle, internal diffusion, reaction reversibility, reaction-diffusion number, bath reactor, flow reactor.

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1 Introduction

Most catalytic reactions in industrial fixed-bed reactors occur on porous catalyst particles; this explains the research interest in the chemical processes and the heat and mass transfer phenomena taking place both on the surface and within these particles [1], [2], [3]. At the same time, due to the complexity of transfer processes in multiphase heterogeneous systems, the problem of mathematically describing them is far from being satisfactorily resolved [4], [5], [6]. One of the less-studied aspects of this problem is the influence of the reversibility of individual reaction stages on mass transfer kinetics [7], [8], [9].

According to the activated complex method, a unimolecular reaction is a first-order reaction and its rate constant, as in the case of bimolecular reactions, can be approximately calculated using the Arrhenius equation, with the pre-exponential factor determined according to the recommendations [10], [11].

The masses of the activated complex and the initial particle are the same in the case of unimolecular reactions [12], [13]. Therefore, the translational partition functions of the activated complex and the initial particle are equal and cancel each other. The rotational partition functions usually differ only slightly from each other, since the configurations of the activated complex and the initial particle are usually nearly identical. If the vibrational partition functions differ little from unity, then in this case, for unimolecular reactions in the usual temperature range, the rate constant is of the order of 10^{13} s^{-1}.

Applying the activated complex method [13] to the analysis of unimolecular reactions assumes that the Maxwell-Boltzmann distribution [14] is maintained within the system throughout the process. However, for gas-phase unimolecular reactions at low pressures, it is necessary to account for the deviation from the Maxwell-Boltzmann distribution caused by the conversion of active molecules into reaction products [15]. It turns out that the rate constant of a unimolecular reaction depends on the concentration of molecules in the gas mixture (both the molecules undergoing transformation and any other molecules present in the mixture)—that is, it depends on the gas pressure. The qualitative nature of this dependence is described by Lindemann's theory [16].

This theory proved unsuitable for quantitative description [12], [17]. Currently, the best agreement with experiment is provided by RRKM theory [11], which is based on the fundamental principles of Lindemann theory and transition-state theory.

However, unlike the latter, RRKM theory considers not only the activated complexes themselves but also all molecules possessing sufficient energy to transform into activated complexes without additional energy exchange [12].

These include all molecules with energy exceeding the activation energy, where this energy is concentrated in active degrees of freedom capable of energy exchange—including transfer to the

degree of freedom corresponding to the reaction coordinate [11]. In the simplest version of RRKM theory, only vibrational degrees of freedom are considered active.

Translational degrees of freedom are, in principle, inactive because, due to the law of conservation of momentum, the kinetic energy of translational motion cannot change in the intervals between collisions [18], [19]. Rotational degrees of freedom are strictly constrained by the law of conservation of angular momentum and are also considered inactive. If molecules possess degrees of freedom corresponding to internal rotation, the latter are considered active [20]. Furthermore, RRKM theory takes into account that the time required for a reacting particle to cross the potential barrier depends on the magnitude of the kinetic energy of translational motion along the reaction coordinate [21].

The brief review of sources known to the authors presented above leads to the conclusion that a sufficiently deep understanding has been achieved regarding the physicochemical principles and kinetics of the processes occurring within and on the surface of catalyst pellets.

However, the issue regarding the availability of mathematical models that suggest both reliable and sufficiently simple, as well as well-founded control parameters for engineering calculating and managing transport processes in catalytic reactors remains open. This problem is especially relevant concerning the need to account for reaction reversibility within the catalyst grains [21].

The primary objective and scientific contribution of the presented work lie in the development and qualitative analysis of a mathematical model describing a steady-state kinetic-diffusion process within a catalyst grain, accounting for the partial reversibility of the reaction. Furthermore, the study's novelty lies in examining the impact of reaction reversibility applying to two different reactor operating modes: batch reactors and flow reactors.

2 Problem Formulation

This section presents a mathematical model describing the process of steady-state internal diffusion within a porous catalyst particle, accounting for the reversibility of the decomposition reaction of the main component.

The model has been developed for the operating conditions of both batch reactors and flow-type apparatuses.

We consider the decomposition of a component X on the surface and within a porous catalyst grain, occurring according to the scheme of a partially reversible first-order reaction:

$$X \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y, \tag{1}$$

where k_1 and k_2 are the rate constants of the forward and reverse reactions, respectively.

In accordance with the above, the system of diffusion-kinetic equations in this case can be written in the form:

$$\frac{\partial c_1}{\partial t} = D_1\left(\frac{\partial^2 c_1}{\partial r^2} + \frac{2}{r}\frac{\partial c_1}{\partial r}\right) - k_1 c_1 + k_2 c_2, \tag{2}$$

$$\frac{\partial c_2}{\partial t} = D_2\left(\frac{\partial^2 c_2}{\partial r^2} + \frac{2}{r}\frac{\partial c_2}{\partial r}\right) + k_1 c_1 - k_2 c_2. \tag{3}$$

Here:

c_1, c_2 are the concentrations of components X and Y respectively,

D_1, D_2 are the corresponding internal diffusion coefficients,

r is the radial coordinate, t is the time.

General issues regarding the existence and uniqueness of solutions for such problems have been sufficiently well investigated [22], [23], [24].

The constructed further model is of an applied nature. The model submitted makes it possible to clearly identify the modified control parameter and ensure the convergence of the steady-state solution of system (2), (3) with accounting for the reaction reversibility, without introducing new mathematical difficulties.

3 Problem Solution

When formulating the problem of finding a steady-state solution to system (2), (3), the system can effectively be treated similar to a system of ordinary differential equations.

3.1 Steady-state Solution of System (2), (3) and Identification of Control Parameters

Thus, the steady-state solution to problem (2), (3) can be sought in the form:

$$c_i = K_i \frac{\exp(\alpha r)}{r}, \tag{4}$$

where α is the eigenvalue of the system of diffusion-kinetic equations (2) and (3), rewritten to search from a stationary solution.

The chosen solution form (4) is justified by the fact that—as subsequent derivations demonstrate—it avoids a singularity at the center of the grain, and it makes it possible to identify the main process control parameter.

Then, after transformations, the homogeneous system of linear equations with respect to constants K_1, K_2 reads

$$\begin{cases} K_1\left(\frac{\alpha^2}{r} - \frac{k_1}{rD_1}\right) + K_2 \frac{k_2}{rD_1} = 0 \\ K_1 \frac{k_1}{rD_2} + K_2\left(\frac{\alpha^2}{r} - \frac{k_2}{rD_2}\right) = 0 \end{cases}. \tag{5}$$

From the condition of existence of a non-trivial solution of system (5) we obtain the relation

$$\begin{vmatrix} \left(\frac{\alpha^2}{r} - \frac{k_1}{rD_1}\right) & \frac{k_2}{rD_1} \\ \frac{k_1}{rD_2} & \left(\frac{\alpha^2}{r} - \frac{k_2}{rD_2}\right) \end{vmatrix} = 0. \tag{6}$$

From (6) the following equation for the eigenvalues follows:

$$\frac{\alpha^4}{r^2} - \frac{\alpha^2}{r^2}\left(\frac{k_1}{D_1} + \frac{k_2}{D_2}\right) = 0. \tag{7}$$

The positive eigenvalue of the system (7) reads

$$\alpha = \sqrt{\frac{k_1}{D_1} + \frac{k_2}{D_2}}. \tag{8}$$

Figure 1 depicts the behavior of relationship (8).

The plots in Figure 1 are illustrative in nature, demonstrating the parameters relationship. Therefore, it is not intended for use as a nomogram for engineering calculations. The actual ranges of the control parameters in practical calculations must be determined based on the specific physical characteristics of the process in question.

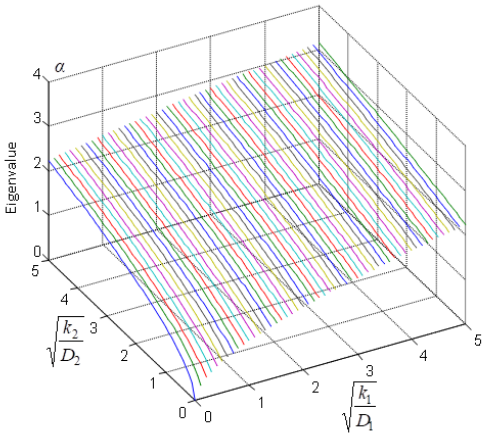


Fig. 1: Dependence of the eigenvalue of system (5) on the diffusion-kinetic parameters of the forward and reverse reactions
Source: created by the authors

The solution to the problem must necessarily satisfy the requirement of convergence at the center of the catalytic grain [25]. In order to satisfy this condition, the desired solution should be rewritten in the form [23]:

$$c_i = K_{i1} \frac{\exp(\alpha r)}{r} + K_{i2} \frac{\exp(-\alpha r)}{r}. \tag{9}$$

By this, the following condition must be met:

$$K_{i1} K_{i2} < 0. \tag{10}$$

As a result, after rearrangements, the solution can be reduced to the form

$$c_i = \tilde{K}_i \frac{\mathrm{sh}\left(r\sqrt{\frac{k_1}{D_1} + \frac{k_2}{D_2}}\right)}{r}. \tag{11}$$

Here the coefficient $\tilde{K}_i$ is determined from the boundary condition on the surface of the catalyst grain:

$$c_i(R) = c_{iS}. \tag{12}$$

As a result, the general formula takes the form:

$$c_i = c_{iS} \frac{R}{\mathrm{sh}\left(R\sqrt{\frac{k_1}{D_1} + \frac{k_2}{D_2}}\right)} \frac{\mathrm{sh}\left(r\sqrt{\frac{k_1}{D_1} + \frac{k_2}{D_2}}\right)}{r}. \tag{13}$$

The form of solution (13) allows to justify the introduction of the following dimensionless control parameter.

$$\phi = R\sqrt{\frac{k_1}{D_1}+\frac{k_2}{D_2}}. \quad (14)$$

Then equation (13) can be rewritten in the following form

$$c_i = c_{is}\frac{\mathrm{sh}(\bar{r}\phi)}{\bar{r}\,\mathrm{sh}(\phi)}, \quad (15)$$

where $\bar{r} = r/R$.

The resulting solution does not lead to a singularity at the point $\bar{r}=0$. Really, $\lim\limits_{x\to 0}\frac{\mathrm{sh}(x)}{x}=1$.

The next subsection addresses the issue of the asymptotic values of reactant concentrations c_{is} at the grain surfaces, which must appear in the expression (15) for the steady-state solution of the problem.

3.2 Asymptotics of the Steady-State Regime. Numerical Experiment

In order to determine the equilibrium concentration on the surface of a catalyst grain, it is necessary to solve the kinetic equations for the decomposition reaction.

In this case, the assumption is used that in the near-surface region the process is limited by the kinetic stage [26]. Moreover, the process proceeds differently in a batch reactor and in a flow reactor.

For a batch reactor, we obtain the following system of kinetic equations and initial conditions applying to the surface concentrations c_{is}:

$$\frac{dc_{1s}}{dt} = -k_1 c_{1s} + k_2 c_{2s}, \quad (16)$$

$$\frac{dc_{2s}}{dt} = k_1 c_{1s} - k_2 c_{2s}. \quad (17)$$

$$c_{1s}(0) = c_{10}, \quad c_{2s}(0) = 0. \quad (18)$$

The characteristic equation of the system has the well-known form:

$$\begin{vmatrix} -k_1-\lambda & k_2 \\ k_1 & -k_2-\lambda \end{vmatrix} = 0. \quad (19)$$

As a result we get:

$$c_{1s} = \frac{c_{10}}{k_1+k_2}\left[k_2 + k_1\exp\left(-(k_1+k_2)t\right)\right], \quad (20)$$

$$c_{2s} = \frac{k_1 c_{10}}{k_1+k_2}\left[1-\exp\left(-(k_1+k_2)t\right)\right]. \quad (21)$$

Thus, the values of surface concentrations c_{iS} corresponding to the steady-state regime in a batch reactor satisfy the following relationships:

$$c_{1S}(t\to\infty) = c_{10}\frac{k_2}{k_1+k_2}, \quad (22)$$

$$c_{2S}(t\to\infty) = c_{10}\frac{k_1}{k_1+k_2}. \quad (23)$$

Substituting the obtained asymptotics into the solution of the internal diffusion problem, we obtain:

$$\bar{c}_i = \frac{\bar{k}}{(1+\bar{k})}\frac{\mathrm{sh}(\bar{r}\phi)}{\bar{r}\,\mathrm{sh}(\phi)}. \quad (24)$$

Here $\bar{c}_i = c_i/c_{i0}$, $\bar{k} = k_2/k_1$, $\bar{r} = r/R$.

In the case of a flow reactor, the system of kinetic equations applying to the surface concentrations c_{iS} takes the form:

$$\frac{dc_{1s}}{dt} = -k_1 c_{1s} + k_2 c_{2s} + q(c_{10}-c_{1s}), \quad (25)$$

$$\frac{dc_{2s}}{dt} = k_1 c_{1s} - k_2 c_{2s} - q c_{2s}. \quad (26)$$

$$c_{1s}(0) = c_{10}, \; c_{2s}(0) = 0, \quad (27)$$

where q is the flow of reactants through the reactor.

Stationary solutions c_{iS} in the vicinity of the catalyst grain surface read

$$c_{1S} = \frac{1+k_2/q}{1+(k_1+k_2)/q}c_{10}, \quad (28)$$

$$c_{2S} = \frac{k_1/q}{1+(k_1+k_2)/q} c_{10}. \quad (29)$$

Similarly, we obtain the relationship for the steady-state concentration of the component X on the surface and in the depth of the catalyst grain:

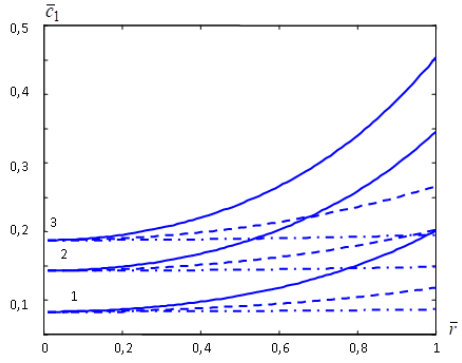
$$\bar{c}_i = \frac{1+\bar{k}_2}{(1+\bar{k}_1+\bar{k}_2)} \frac{\mathrm{sh}(\bar{r}\phi)}{\bar{r}\,\mathrm{sh}(\phi)}, \quad (30)$$

where $\bar{k}_1 = k_1/q$, $\bar{k}_2 = k_2/q$.

Below there are presented also some results of calculations carried out on the basis of the developed model for a batch reactor (Figure 2) and a flow reactor (Figure 3).

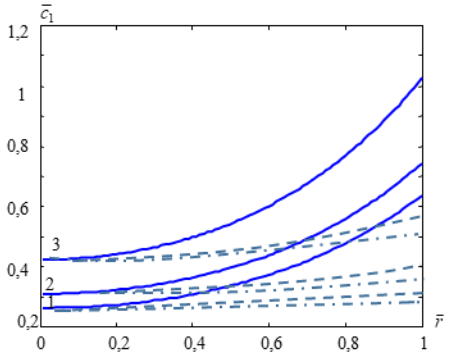
Numerical experiment demonstrates the obvious dependence of the reagent concentration inside the catalyst grain on the reaction-diffusion number. At low reaction-diffusion numbers $(\phi < 1)$, the change in reactant concentration within the particle from the centre to the surface is quite sharp. At high reaction-diffusion numbers, this change is not as significant. Moreover, this dependence is more pronounced in a flow reactor than in a batch reactor.

Like Figure 1, Figure 2 and Figure 3 are not presented by the authors as nomograms for practical calculations but rather to demonstrate the capabilities of the developed model. At the same time, the calculation procedure remains the same for practical applications; however, the proposed control parameter must be determined for specific physicochemical systems.



1- $\bar{k} = 0{,}2$; 2- $\bar{k} = 0{,}4$; 3- $\bar{k} = 0{,}6$;
solid line- $\phi = 0{,}5$; dotted line--- $\phi = 1{,}5$;
dash-dot line-.- $\phi = 2{,}5$

Fig. 2: Dependence of dimensionless concentration on the current dimensionless radius of grain in a batch reactor.
Source: created by the authors



1- $\bar{k}_1 = 1, \bar{k}_2 = 0{,}1$; 2- $\bar{k}_1 = 1, \bar{k}_2 = 0{,}6$;
3- $\bar{k}_1 = 0{,}2, \bar{k}_2 = 0{,}1$;
solid line- $\phi = 0{,}5$; dotted line--- $\phi = 1{,}5$;
dash-dot line-.- $\phi = 2{,}5$

Fig. 3: Dependence of dimensionless concentration on the current dimensionless radius of the grain in a flow reactor
Source: created by the authors

The authors plan to further develop the model to account for the actual flow structure within the reactor and to analyze existing experimental data in order to adapt the model.

4 Conclusion

Modeling the internal diffusion process in a catalyst grain using the submitted concept of the reaction-diffusion number allowed us to describe the steady-state transfer process taking into account the reversible reaction stage. Dimensionless relationships were obtained for both a batch reactor and a flow-through apparatus. Due to their simplicity and compactness, the results of this study can be useful both in engineering calculations and in processes control methodologies.

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work, the author(s) utilized artificial intelligence (AI) technologies solely for the purpose of linguistic refinement and grammatical correction. Following the application of these tools, the author(s) comprehensively reviewed, verified, and edited the resulting text. The author(s) maintain full accountability and responsibility for the accuracy, integrity, and final content of the publication.

References:

[1] Baronas R., Ivanauskas F., Kulys J., Modeling Biosensors at Steady State and

Internal Diffusion Limitations. In *Mathematical Modeling of Biosensors: An Introduction for Chemists and Mathematicians*, 2009, pp. 9-20, Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-90-481-3243-0_2.

[2] Grebenkov D. S., Krapf D., Steady-state reaction rate of diffusion-controlled reactions in sheets. *The Journal of Chemical Physics*, Vol. 149, No.6, 2018, pp.1-12. https://doi.org/10.1063/1.5041074.

[3] Wu D., Yang M., Yu J., Dyballa M., Yang P., Li M., Hou G., Dai W., The role of adsorption and diffusion in improving the selectivity and reactivity of zeolite catalysts, *Chemical Society Reviews*, Vol. 54, No. 20, 2025, pp. 9192-9244. https://doi.org/10.1039/d5cs00220f.

[4] Yamada H., Tagawa T., Nagao S., Kato S., Investigation of gas diffusion phenomena in porous catalyst support pellets based on microstructure, *Catalysis Today*, Vol. 375, 2021, pp. 30-35. https://doi.org/ 10.1016/j.cattod.2020.04.056.

[5] Heikkinen N., Lehtonen J., Puurunen R.L., An atomic layer deposition diffusion–reaction model for porous media with different particle geometries, *Physical Chemistry Chemical Physics*, Vol. 26, No. 9, 2024, pp.7580-7591. https://doi.org/10.1039/d3cp05639b.

[6] He J. H., Iranian D., Point solution concept for analysis of reaction-diffusion in porous catalysts. *Journal of Computational Applied Mechanics*, Vol. 56, No. 4, 2025, pp. 711-719. https://doi.org/10.22059/jcamech.2025.390100.1535.

[7] Keil F. J., Diffusion and reaction in porous networks, *Catalysis Today*, Vol. 53, No. 2, 1999, pp. 245-258. https://doi.org/ 10.1016/S0920-5861(99)00119-4.

[8] Ghosh S., Pal D., Diffusion and Surface Reaction in Porous Cubical Catalyst: A Mathematical Approach, *Recent Innovations in Chemical Engineering (Formerly Recent Patents on Chemical Engineering)*, Vol. 15, No. 1, 2022, pp. 60-69. https://doi.org/10.2174/2405520415666211229122346.

[9] García J. R., Bidabehere C. M., Sedran U., Unsteady state diffusion-adsorption-reaction. Selectivity of consecutive reactions on porous catalyst particles, *International Journal of Chemical Reactor Engineering*, Vol.20, No. 1, 2022, pp.83-96. https://doi.org/10.1515/ijcre-2021-0003/html.

[10] Gargurevich I.A., Chemical Reaction Thermodynamics and Reaction Rate Theory, *Journal of Chemical Engineering & Process Technology*, Vol. 7, No. 02, 2016, pp. 1-11.https://doi.org/10.4172/2157-7048.1000287.

[11] Klippenstein S.J., Spiers memorial lecture: theory of unimolecular reactions, *Faraday Discussions*, Vol. 238, 2022, pp.11-67. https://doi.org/10.1039/d2fd00125j.

[12] Forst W., *Theory of unimolecular reactions*, Elsevier, 2012. ISBN 0-12-262350 -9.

[13] Ferreira J.M.M., Sousa-Aguiar E.F., Aranda D.A.G., FCC catalyst accessibility—a review, *Catalysts*, Vol.13, No. 4, 2023, pp. 784-810. https://doi.org/10.3390/catal13040784

[14] Sosna B., *Spatially resolved probing of diffusion and reaction in porous catalyst pellets*, (Doctoral dissertation), Technische Universität Hamburg, 2020. https://doi.org/10.15480/882.3179.

[15] Yazovtseva O.S., Gubaydulli I.M., Peskov E.E., Sukharev L.A., Zagoruiko A.N., Computer simulation of coke sediments burning from the whole cylindrical catalyst grain, *Mathematics*, Vol. 11, No. 3, 2023, pp. 669-684. https://doi.org/10.3390/math11030669

[16] Leitner D.M., The microcanonical Lindemann mechanism for unimolecular reactions, *The Journal of Chemical Physics*, Vol. 163, No. 8, pp. 1-11. https://doi.org/10.1063/5.0280949

[17] Yang W., Cloete S., Morud J., Amini S., An effective reaction rate model for gas-solid reactions with high intra-particle diffusion resistance. *International Journal of Chemical Reactor Engineering*, Vol. 14, No. 1, 2016, pp. 331-342. https://doi.org/10.1515/ijcre-2015-0127/html.

[18] Chepak-Gizbrekht M.V., Knyazeva A.G., Grain-boundary diffusion modeling in a microstructural material, *Computational Materials Science*, Vol. 184, 2020, https://doi.org/10.1016/j.commatsci.2020.10989

[19] Xu S., Zheng K., Boruntea C.R., Cheng D.G., Chen F., Ye G., Zhou X., Coppens, M.O., Surface barriers to mass transfer in nanoporous materials for catalysis and separations, *Chemical Society Reviews*, Vol. 52, No. 12, 2023, pp. 1-15. https://doi.org/10.1039/d2cs00627h

[20] Di Giuliano A., Gallucci K., Foscolo P.U., Determination of kinetic and diffusion

parameters needed to predict the behavior of CaO-based CO2 sorbent and sorbent-catalyst materials, *Industrial & Engineering Chemistry Research*, Vol. 59, No. 15, 2020, pp. 6840-6854. https://doi.org/10.1021/acs.iecr.9b05383

[21] Uzyanbayev R.M., Yusupova R.R., Gizzatova E. R., Mathematical modeling of mass-heat transfer processes on the grain of a catalytic cracking catalyst, In *Journal of Physics: Conference Series*,Vol. 1745, No. 1, 2021, pp. 1-5, IOP Publishing. https://doi.org/ 10.1088/1742-6596/1745/1/012051.

[22] Evans L.C., *Partial differential equations*, Vol. 19, 2022, American mathematical society. ISBN 978-1-4704-6942-9.

[23] Edwards C.H., Penney D.E., Calvis D.T., *Differential Equations and Linear Algebra*, 2020, Pearson Higher Ed. ISBN13: 9780136054252.

[24] Kraut E.A., *Fundamentals of mathematical physics*, 2007, Courier Corporation ISBN-13: 978-0-486-45809-0.

[25] Bukur D. B., Mandić M., Todić B., Nikačević N., Pore diffusion effects on catalyst effectiveness and selectivity of cobalt based Fischer-Tropsch catalyst, *Catalysis Today*, Vol. 343, 2020, pp. https://doi.org/146-155. 10.1016/j.cattod.2018.10.069.

[26] Sosna B., Korup O., Horn R., Probing local diffusion and reaction in a porous catalyst pellet, *Journal of catalysis*, Vol. 381, 2020, pp. 285-294. https://doi.org/10.1016/j.jcat.2019.11.005.

Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- Meirim Amantay carried out the simulation and numerical study.
- Arnold Brener formulated the problem and proposed the research concept.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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