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ABSTRACT

of the dissertation for the degree of
Doctor of Philosophy

MODELING OF THE GAS-PHASE OXIDATIVE DEHYDROGENATION PROCESS OF METHYLCYCLOPENTENE AND 4-VINYLCYCLOHEXENE IN THE PRESENCE OF HETEROGENE OXIDE CATALYSTS

Speciality: 3303.01 – Chemical technology and engineering

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The work was performed at the “Optimization and mathematical modeling of the chemical processes” laboratory of the Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

The relevance of the topic and the degree of development. Recent years, interest in modeling non-stationary chemical processes has been growing rapidly. Currently, the method of mathematical modeling with computers has become a powerful tool in calculating chemical-technological processes, analyzing, optimizing them, and solving prediction problems, as well as increasing the effectiveness of scientific research. Most of them relate to the modeling of physicochemical systems, especially the modeling of chemical kinetics. At the moment, a number of software tools have been developed for modeling chemical-technological processes. Majority of these funds were provided by US and Canadian companies.

Computer modeling of modern chemical-technological systems (CTS) has fully proven its relevance and prospects. It is possible to increase the qualitative effectiveness of CTS management by means of modeling, on the other hand, it becomes possible to economically optimize their operating modes by considering and calculating various options for the productivity of facilities.

The scientific and technological revolution has created the need to use automated control systems and computing technology in all areas of human activity. Currently, one of the most efficient and perfect application areas of information technology is automated Information Management systems built on the basis of given basic concepts.

In modern times, the application of computer programming tools and methods is an integral part of scientific research.[1]

The efficiency of the production of the main product of chemical processes is measured by its yield per unit of time and selectivity (the share of converted raw materials in obtaining the main product). Firstly, it is necessary to improve these indicators in order to achieve good economic results. For this purpose, optimal conditions for the required course of the process are selected by using a statistical

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[1] Самарский, А.А. Математическое моделирование: Идеи. Методы. /А.А Самарский, А.П. Михайлов //-Примеры. 2-е изд., испр. -М.: Физматлит,-2002,-320 с.

mathematical model, and the conditions for the formation of the main and by-products of the process, kinetics, thermodynamics, hydrodynamics, heat and mass exchange are studied.

Considering the above mentioned points, for the optimization and mathematical modeling of the oxidative dehydrogenation process of C_6-C_8 unsaturated alicyclic hydrocarbons in the gas phase, kinetic analysis of the process in a heterogeneous oxide catalyst environment should be addressed as an important issue and the evaluation of kinetic coefficients should be carried out directly.

In solving optimization problems, a reactor selection that is appropriate for the modeled process is achieved by correctly describing the qualitative and quantitative characteristics of the object being modeled by using a mathematical model. However, it should not be overlooked that the general principle that any model can only be modeled within a given set of constraints and within the required identification accuracy is not overlooked.

The kinetic model of the oxidative dehydrogenation process of methylcyclopentene and 4-vinylcyclohexene in the gas phase can play a decisive role in selecting the optimal designs of most equipment included in the technological complex.[2]

One of the urgent problems is the development of appropriate software packages for conducting processes under various conditions, modeling and optimally designing the intended reactors.

In this regard, it is due to the fact that the reaction products are valuable substances in modeling the processes of oxidative dehydrogenation of C_6-C_8 unsaturated alicyclic hydrocarbons, for example, methylcyclopentene isomers to methylcyclopentadiene and 4-vinylcyclohexene to ethylbenzene and styrene, and their application in various fields of industry.

Taking into account the above mentioned points, the construction of new mathematical models of the oxidative dehydrogenation processes of methylcyclopentene isomers to methylcyclopentadiene, 4-vinylcyclohexene (divinyl[4-2] dimerization product) to styrene,

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[2] Alimardanov, H.M. Oxidative dehydrogenation of 4-vinylcyclohexene in the presence of modified forms of Ga, Pt-pentasils / H.M.Alimardanov, A.A. Alieva, S.A. Abasov // Neftekhimiya, -2010, Vol.50, №2, -p.136-140.

and the development of methods and algorithms for solving optimization problems of these catalytic processes are among the urgent issues.

The object and subject of the research. The object of the dissertation work was the optimization and mathematical modeling of the process of dehydrogenation of initial methylcyclopentene isomers to methylcyclopentadiene and 4-vinylcyclohexene to ethylbenzene, and styrene.

The aim and objectives of the research. The issues raised during the research are as follows:

- selection of the optimal reactor type for the mentioned processes, determination of regime parameters to obtain a given conversion rate in different types of reactors on the bases its kinetic model;
- comparative analysis of the optimality factor in implementing both processes in an ideal mixing and ideal compression-type reactor;
- investigation of differential equations for an ideal compression-type reactor to model the kinetic process of oxidative dehydrogenation of individual isomers of methylcyclopentene to methylcyclopentadiene;
- formulation of the model in the form of a system of algebraic equations in cases where the quasi-stationarity condition of the processes occurring in ideal mixing-type reactors is satisfied;
- Modeling and optimization of the reactor type based on a kinetic model of the oxidative dehydrogenation reaction of 4-vinylcyclohexene to ethylbenzene and styrene.

Research methods. In the dissertation work, relevant research is carried out based on the following theoretical provisions and methods:

- standard solution algorithms for linear and nonlinear differential equations;
- using linear and nonlinear programming methods to solve a number of special types of mathematical models;
- parametric programming;
- Lagrange equations;
- mathematical modeling on the bases of the statistical methods;
- the maximization principle for solving optimal management problems, etc.

The main provisions put forward for defense:

- Development of a kinetic model for the one-step production of methylcyclopentene isomers on the bases of the cyclohexanol and their oxidative dehydrogenation to methylcyclopentadiene in the presence of the Fe-Nd-O/HNa-MOR catalytic system;

- Development of a kinetic model for the oxidative dehydrogenation of 4-vinylcyclohexene to ethylbenzene and styrene in the presence of Fe-Nd-O/HNa-ZSM-5 and Pt-Ga-Gd-O/HNa-ZSM-5 catalytic systems;

- Constructing the approximate matrix of the regression model by using the BoxBenkinD software module, determining the difference between the experimental and obtained results by checking the calculation of the coefficient of the three-factor model and the model adequacy;

- Statistical analysis of data by using S-plus 2000 professional software to determine the coefficients in the equation, calculation of regression coefficients and selected pairwise correlation coefficients;

- Solving optimization problems by using Matlab software, which has modern linear programming algorithms;

- Determining the process conditions as the goal of theoretical optimization to achieve maximum yield of the target product per unit mass or volume of catalyst, determining the process regime parameters that ensure maximum yield of the main product, and selecting the reactor type;

Mathematical modeling and optimization of processes.

Scientific novelty of the research.

The kinetic regularities of the oxidative dehydrogenation reaction of individual isomers of methylcyclopentene over aluminum-copper-molybdenum and Fe-Nd-O/HNa-Mor catalysts were studied and a kinetic model has been developed. It has been found that 1-methylcyclopentene is mainly converted towards partial dehydrogenation and destructive oxidation, while 3-methylcyclopentene is additionally converted towards dehydrodemethylation;

- the kinetics of the oxidative dehydrogenation reaction of 4-vinylcyclohexene to ethylbenzene and styrene over a Pt, GaYMS (high modulus zeolite) catalyst modified with some f-element oxides were studied. A kinetic model was developed based on the proposed mechanism and its adequacy was determined by experimental results;

- the main parameters of kinetic models of processes (kinetic constants, exponential decays, activation energies) were identified and the hydrodynamic parameters of the models were evaluated by using mathematical calculation methods;
- the optimally selected reactor-type was determined based on calculations corresponding to the specified conversion rate of hydrocarbons in various types of reactors. According to these calculations, it is appropriate to carry out the above processes in an ideal compression-type reactor.Their theoretical optimization allows determining the optimal mode;
- optimal reactor designs were selected based on the targeted productivity of the processes;
- The developed mathematical models of the processes can be used for optimal control of both the oxidative dehydrogenation of methylcyclopentene to methylcyclopentadiene and 4-vinylcyclohexene to ethylbenzene and styrene.

Theoretical and practical significance of the research. As a result of theoretical optimization of the oxidative dehydrogenation processes of individual isomers of methylcyclopentene to methylcyclopentadiene, and of 4-vinylcyclohexene to ethylbenzene and styrene, their optimal technological regimes have been determined. Theoretical optimization of the processes on the baseds of kinetic equations was performed to ensure maximum catalyst productivity for the target products.

Parametric optimization based on the developed kinetic models was performed using appropriate software. The mentioned problems were solved by using the Nelder-Mead search method in the Matlab software system, and the structural dimensions of the reactor element were calculated.

The formula for determining the catalyst volume value on the basis of the maximum catalyst efficiency to achieve the appropriate rate of methylcyclopentadiene at the reactor outlet as a result of the oxidative conversion of 1-methylcyclopentene is

$$V_{\mathrm{cat}}^{1} = \frac{Q_1 \left[\frac{\mathrm{kg}}{\mathrm{h}}\right]}{q_1 \left[m^3 \frac{\mathrm{kg}}{\mathrm{h}}\right]} \approx 5.03\ m^3$$

Temperature and density gradients, mass and heat transfer that accompany industrial-scale processes are not taken into account in the kinetic model. Therefore, the yields of products obtained by theoretical optimization based only on kinetic models are conditionally considered to be maximal. At this stage, in order to obtain a more accurate description of the flow distribution, complete mathematical models of the processes were developed by adding heat balance equations and equations taking into account pressure changes to the kinetic equations.

Approbation and application. 10 articles and 9 report abstracts have been published on the topic of the dissertation. In total, 19 scientific works have been published.

The main results of the dissertation work were discussed at the following republican and international scientific conferences: IV Russian conference: Current problems of petroleum chemistry (with international participation) dedicated to the 100th anniversary of the birth of Prof. Z. A. Dorogochinsky (Zvenigorod, 2012); VIII Baku International Mamedaliyev Conference on Petroleum Chemistry (Baku, 2012); International form. (Saint Petersburg, 2013); Republican scientific conference dedicated to the 90th anniversary of academician T. Shakhtakhtinsky (Baku, 2015); Conference dedicated to the 93rd anniversary of the birth of the national leader H. Aliyev (Ganja, 2016); IX Baku International Mamedaliyev Conference on Petroleum Chemistry (Baku, 2016); International scientific conference "Actual problems of modern natural sciences" dedicated to the 94th anniversary of the birth of national leader H. Aliyev (Ganja, 2017); International scientific and technical conference dedicated to the 100th anniversary of academician B.G. Zeynalov (Baku, 2017); Scientific conference "Nagiyev Recitations" dedicated to the 110th anniversary of Academician M. Naghiyev (Baku, 2018); International conference dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the

Azerbaijan National Academy of Sciences (Baku, 2019); International Scientific Conference dedicated to the 100th anniversary of academician M. Mammadyarov, September 26-27, 2024; International Scientific Conference dedicated to the 110th anniversary of academician S.Mehdiyev, december 19-20, 2024.

The name of the organization where the dissertation work performed. The dissertation work was performed at the "Optimization and mathematical modeling of the chemical processes" laboratory of the Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan.

Personal participation of the author. The scientific research conducted on the topic of the dissertation, the conduct and analysis of experiments, the analysis of the dissertation, and the compilation of the dissertation were carried out directly by the applicant.

The total volume of the dissertation with a mark, indicating the volume of the structural sections of the dissertation separately: The dissertation consists of an introduction, 4 chapters, a conclusion, a list of 145 references, a list of abbreviations, and is printed on 146 pages, including 14 tables, 9 figures, 14 graphics and 5 schemes. The total volume of the dissertation, excluding tables, figures, list of abbreviations and list of references, consists of 161755 characters (introduction 13778 characters, chapter I 46110 characters, chapter II 60240 characters, chapter III 20960 characters, chapter IV 17345 characters and conclusions 3322 characters).

The introduction of the dissertation work justifies the relevance and degree of development of the posed problem, the object, subject, goal and objectives of the research, research methods, main provisions put forward for defense, scientific novelty of the work, theoretical and practical significance of the research, its approbation and application, the name of the organization where the dissertation work was performed, the personal participation of the author, and the total volume of the dissertation work with a mark are indicated.

The first chapter of the dissertation provides an analysis of existing research methods for the gas phase oxidative dehydrogenation process of methylcyclopentene and 4-vinylcyclohexene in the presence of heterogeneous oxide catalysts.

The second chapter is dedicated to the experimental study of the mechanism of oxidative dehydrogenation of individual isomers of methylcyclopentene and 4-vinylcyclohexene, and the construction of their kinetic model. The results of kinetic studies of the catalytic dehydrogenation of 1- and 3-methylcyclopentene to methylcyclopentadiene, and 4-vinylcyclohexene to ethylbenzene and styrene in the gas phase in the presence of air oxygen are presented, and the corresponding kinetic models are developed based on them.

The third chapter considers the issues of mathematical modeling of the oxidative dehydrogenation processes of individual isomers of methylcyclopentene and 4-vinylcyclohexene. Mathematical models of the processes were constructed taking into account the hydrodynamic structure of material and heat flows, and on the bases of the obtained model, density and heat flows were evaluated in the adiabatic regime with oxygen supply in sections.

The fourth chapter is dedicated to determining the types of reactors, their automatic control and regulation by using the "Matlab" program. The issue of theoretical optimization of both processes by sections and determination of the reactor type has been resolved.

At the end, the intended technological scheme and material balance are given. The results section summarizes the experimental and theoretical studies conducted on the indicated processes.

MAIN CONTENT OF THE WORK

The main method of obtaining methylcyclopentadiene is the dehydrogenation of methylcyclopentane, which is available in some resources in petroleum fractions or obtained from the hydroisomerization of benzene. Since dehydrogenation is carried out at temperatures of 590-620°C in the presence of aluminochrome catalysts, the production of methylcyclopentadiene is accompanied by coking and rapid deactivation of the catalyst.

One of the main goals of the presented dissertation is to develop kinetic and mathematical models of the oxidative dehydrogenation of methylcyclopentene isomers obtained from methylcyclopentane or cyclohexanol by a two-stage method of methylcyclopentadiene and to conduct research towards optimizing the process.

Construction of a kinetic model of the oxidative dehydrogenation reaction of methylcyclopentene isomers

Individual isomers of methylcyclopentene (1- and 3-MTPE) were obtained by passing cyclohexanol over H_3PO_4-treated γ-Al_2O_3 in a flow-type reactor at a volume rate of 0.5 s^{-1} at a temperature of 320-350ºC and connecting the resulting catalyst to a 15-plate rectification column at atmospheric pressure. The yield of isomers is 39-43%. The non-isomerized cyclohexene fraction (80-82ºC) is recycled back to the reactor.

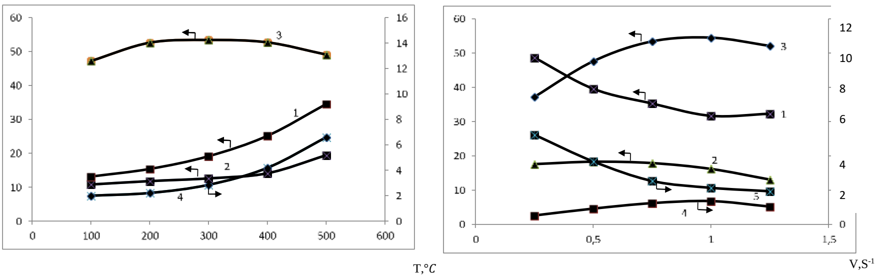
Both oxide and zeolite-based catalysts have been used in the experiments. An aluminum-copper-molybdenum system was used as the oxide, and zeolite-type systems on the bases of HNa-mordenite were used, containing iron-neodium (or gadolinium). Both catalysts were prepared by the impregnation method.

The results of the studies show that the qualitative composition of the catalysts obtained as a result of the conversion of individual MCPE isomers is similar, but the rates of accumulation of the reaction products differ from each other. Thus, 1-MCPE is mainly converted towards partial dehydrogenation and destructive oxidation with the accumulation of MCPD, C_2-C_5 hydrocarbons, and CO_2. 3-MCPE also undergoes oxidative dehydromethylation to cyclopentadiene along the above-mentioned pathways under the same conditions~~.1~~ Dehydromethylation of 1-MCPE is observed only during the migration of the double bond from the α to the β state. As a result, the accumulation of cyclopentadiene on the catalyst, which partially acts as a hydrogen acceptor, is more characteristic of 3-MCPE, which is probably due to the formation of a stable π-allyl radical on the catalyst surface during hydrogen uptake due to the detachment of a hydrogen atom from the triplet carbon atom.

Thus, 1-MCPE undergoes partial and destructive oxidation in this process, mainly to methylcyclopentadiene, C_2-C_5 hydrocarbons, and CO_2. 3-MCPE undergoes oxidative dehydrodemethylation to cyclopentadiene in addition to the above pathways under the same conditions.

Figures 1 and 2 show the effect of reaction temperature and feed rate. Since dehydrogenation is accompanied by double bond migration, the selectivity of the process for MCPD was calculated taking into account the sum of the isomers undergoing conversion.

In the temperature range of 573-633K, MCPE dehydrogenation mainly competes with the destructive oxidation of hydrocarbons. At higher temperatures (653-723K), the selectivity of the reaction for MCPD increases slightly, but an intensification of other side reactions is observed.

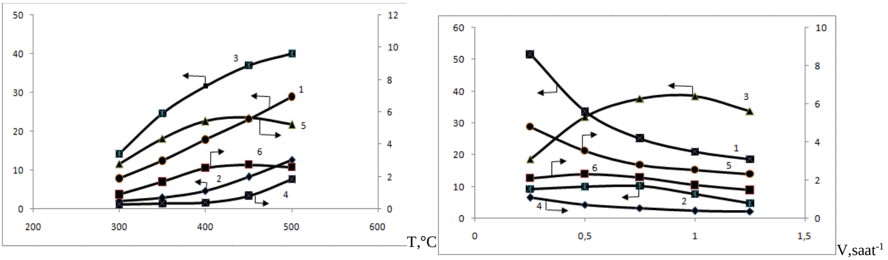


a) b)

Figure 1. Effect of temperature (a) and volume expansion rate (b) on the degree of oxidative dehydrogenation of 1-methylcyclopentene (1-$C_5H_7CH_3$: O_2=3.3:1, 1-$C_5H_7CH_3$:H_2O=1:5).

1. Conversion rate of methylcyclopentene in Figures 1 and 2; 2. Yield

of methylcyclopentadiene; 3. Selectivity; 4. Yield of benzene; 5. Yield of carbon dioxide



a) b)

Figure 2. Effect of temperature (a) and volume flow rate (b) on the degree of oxidative dehydrogenation of 3-methylcyclopentene (3-$C_5H_7CH_3$: O_2=3.3:1, 3-$C_5H_7CH_3$:H_2O=1:5)

The transformations can be written in the form of the following free equations on the basis of the experimental material:

$C_5H_7CH_3+0.5\ O_2 \xrightarrow{K_1} C_5H_5CH_3+H_2O$ I

$C_5H_7CH_3+O_2 \xrightarrow{K_2} C_6H_6+2H_2O$ II

$2C_5H_7CH_3 \xrightarrow{K_3} C_5H_5CH_3+C_5H_9CH_3$ III

$C_5H_7CH_3+2O_2 \xrightarrow{K_4} C_5H_6+CO_2+2H_2O$ IV

$C_5H_5CH_3+2.5\ O_2 \xrightarrow{K_5} C_4H_6+2CO_2+H_2O$ V

$C_6H_{10}+O_2 \xrightarrow{K_6} C_3H_6+C_2H_4+CO_2$ VI

$C_6H_6+4{,}5O_2 \xrightarrow{K_8} C_2H_4+4CO_2+H_2O$ VII

here $C_5H_7CH_3$ and $C_5H_5CH_3$ are the sum of the isomers MCPE and MCPD, C_6H_{10}-cyclohexene, C_6H_6-benzene, C_5H_6-cyclopentadiene, respectively.

$\sum_{n=1}^{13} x_{sc}X_n=0$ s=1,2,.....8 , here, s is the stage number; 13 is the number of reaction components; x_{sc} is the stoichiometric coefficient.

In case of marking the components like this

A_1-$C_5H_7CH_3$; A_2-$C_5H_5CH_3$; A_3-C_6H_{10}; A_4-C_6H_6;
A_5-$C_5H_7CH_3$; A_6-C_5H_6; A_7-C_4H_6; A_8 - C_3H_6; A_9 - C_2H_4; A_{10}-O_2;
A_{11}-CO_2; A_{12}-H_2O; A_{13}-$C_5H_9CH_3$

The reaction scheme can be written as:

$A_2+A_{12}-A_1-0.5A_{10}=0$

A_3-A_1=0
A_4+2A_{12}-A_3-A_{10}=0
A_{13}+A_2-2A_1=0
A_6+A_{11}+2A_{12}-A_1-2A_{10}=0
A_7+2A_{11}+A_{12}-A_2-2.5A_{10}=0
A_8+3A_{11}+A_{12}-A_2-3.5A_{10}=0
A_9+4A_{11}+A_{12}-A_2-5A_{10}=0

The numerical value of the velocity along the routes I-VIII(r_i) is related to the observed values of the accumulation rates of the individual components (ω_i) by the following equations:

$$\omega_{C_5H_7CH_3} = \omega_{1-C_5H_7CH_3} + \quad \omega_{3-C_5H_7CH_3} \qquad (1)$$

$$\omega_{C_5H_7CH_3} = -r_1 - r_2 - 2r_4 - r_5 \qquad (2)$$

$$\omega_{C_6H_{10}} = r_2 - r_7 \qquad (3)$$

$$\omega_{C_5H_5CH_3} = r_1 + r_4 - 3r_6 \qquad (4)$$

$$\omega_{C_5H_9CH_3} = r_4 \qquad (5)$$

$$\omega_{C_6H_6} = r_3 \quad -r_8 \qquad (6)$$

$$\omega_{C_2-H_4} = 3r_6 \qquad (7)$$

$$\omega_{CO_2} = r_5 + 2r_6 + r_7 + r_5 \qquad (8)$$

Taking into account the data of the chromatographic analysis of the composition of the contact gas, the rates of destructive oxidation of MCPD and benzene along the VI-VIII-r_6, r_7 and r_8 routes were assumed to be practically equal.

The determination of kinetic constants was carried out by minimizing the sum of squares of the difference between the calculated and experimentally determined values of the velocities using a random search method.

Computer calculations have found numerical values for the rate constants for the conversion of individual isomers to MCPE, which are given below:

For 1-MCPE

$$k_1 = 5.61 \cdot 10^4 exp(-72896.1/RT) l \cdot \mathrm{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$
$$k_2 = 1.034 \cdot 10^4 exp(-73471.6/RT) l \cdot \mathrm{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1}$$
$$k_3 = 5.51 \cdot 10^4 exp(-61722.7/RT) l \cdot \mathrm{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-2}$$
$$k_4 = 0.0021 \cdot 10^2 exp(-26765.6/RT) l \cdot \mathrm{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-2}$$
$$k_5 = 0.28 \cdot 10^2 exp(-30668.6/RT) l \cdot \mathrm{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$

$$k_6 = k_7 = k_8 = 1.72 \cdot 10^6 exp(-119027.2/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$

For 3-MCPE

$$k_1 = 1.32 \cdot 10^3 exp(-55211.7/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$

$$k_2 = 2.11 \cdot 10^4 exp(-83254.7/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1}$$

$$k_3 = 1.45 \cdot 10^3 exp(-39977.5/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-2}$$

$$k_4 = 0.028 \cdot 10^2 exp(-37598.2/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-2}$$

$$k_5 = 0.034 \cdot 10^2 exp(-42257.3/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$

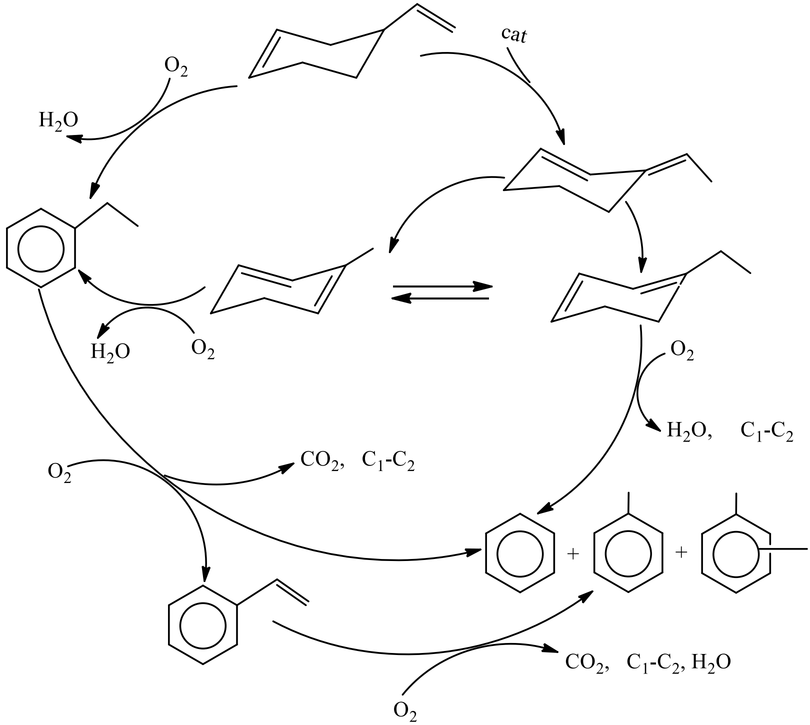
$$k_6 = k_7 = k_8 = 5.36 \cdot 10^5 exp(-96714.2/RT) l \cdot \text{h}^{-1} \cdot l_{cat}^{-1} \cdot kPa^{-1.5}$$

Kinetic model and mechanism of the process of oxidative dehydrogenation of 4-vinylcyclohexene1 to ethylbenzene and styrene on modified high-modulus zeolite

Oxidative dehydrogenation of 4-vinylcyclohexene (4-VCH) was carried out in a laboratory setup with a gradient-free reactor on HNa-YMS samples modified with zirconyl (ZrO^{2+}) and iron oxides (Fe^{3+}) and with Pt, Gu and Gd oxides. Higher results were obtained on Fe-Zr-O/HNa YMS.

The main kinetic parameters were obtained by varying the temperature range of 370-485°C at partial pressures of 4-VCH of 12.6-15.5 and oxygen of 1.55-5.1 kPa. N_2 and H_2O vapor were used as diluents. In addition to ethylbenzene and styrene, the reaction products included benzene, toluene-linked diene hydrocarbons – isomers of 3-ethylidene cyclohexene and ethylcyclohexadiene, as well as isomers of xylene, trimethylbenzene and ethylcyclohexene. Preliminary studies conducted in a flow reactor showed that the maximum yield of ethylbenzene and styrene is achieved in the temperature range of 470-485°C and at a molar ratio of 4-VCH: O_2: N_2 = 1: 0.1-0.2:4. Changing the size of the catalyst grains and the piston pulse frequency in the gradient-free reactor did not affect the rate of formation and accumulation of reaction products under these conditions, indicating the absence of internal and external diffusion barriers. The main kinetic parameters were obtained by varying the initial partial pressures of 4-VCH and O_2 at different temperatures and hydrocarbon volume feed rates.

The conversion of 4-VCH increases, but the selectivity towards the dehydrogenation products decreases With increasing temperature in the indicated range. In this range, selectivity depends mainly on the partial pressure of the initial hydrocarbon and oxygen. From the graph of the dependence of selectivity on the conversion of 4-VCH for the sum of ethylbenzene and styrene, it can be seen that when these dependence curves are extrapolated to the ordinate axis characterizing selectivity, as the conversion value approaches zero, the selectivity value differs from 100%. In other words, the oxidative dehydrogenation of 4-VCH occurs via a parallel-sequential mechanism. Taking into account the experimental results, its transformation can be given by the following scheme.



Under conditions where the conversion of 4-VCH is 60.0-61.5% (at a temperature of 470-485°C), the total amount of benzene, toluene, xylene and trimethylbenzene isomers, which are products of disproportionation and dehydrodealkylation, in the catalyst does not exceed 6.5-7.8%. The insignificant amount of these products allows us to ignore them in the kinetic description of the process. The following stepwise gross-stoichiometric route scheme has been proposed on the bases of the above discussions:

$I.\quad C_6H_9CH = CH_2(I) \xrightarrow{k_1} C_6H_8 = CH - CH_3(II\text{a}) \rightarrow \quad C_6H_7 - CH_3 - CH_3$ (II b,c)

$II.\quad II\ (a,b,c) + 0{,}5\ O_2 \xrightarrow{k_2} C_6H_5 - C_2H_5(III) + H_2O$

$III.\quad C_6H_5 - C_2H_5 + 0.5O_2 \xrightarrow{k_3} C_6H_5CH = CH_2(IV) + H_2O$

$IV.\quad C_6H_9CH = CH_2 + 0.5O_2 \xrightarrow{k_4} C_6H_5 - C_2H_5 + H_2O$

$V.\quad C_6H_9CH = CH_2 + O_2 \xrightarrow{k_5} C_6H_5CH = CH_2 + 2H_2O$

$VI.\quad II\ (a,b,v) + O_2 \xrightarrow{k_6}$ Products of **d**estructive oxidation $(V,VI) + 2H_2O$

Equation I corresponds to the isomerization of 4-vinylcyclohexene (4-VCH), i.e. the formation of the isomers ethylidenecyclohexene (C_6H_8=CH-CH_3) and ethylcyclohexadiene ($C_6H_7C_2H_5$). Equations II-V describe oxidative dehydrogenation, while equation VI refers to the destructive oxidation of hydrocarbons. The catalytic decomposition of 4-VCH and its isomerization products was not taken into account when choosing this scheme. Since it was previously determined that their conversion rate at temperatures above 485°C does not exceed 3-5% on a catalyst mixed with quartz glass.

The reaction rate for each individual route can be expressed by the following equations:

$$\left.\begin{aligned}
r_1 &= k_1 P_{4\text{-}VCH} \\
r_2 &= k_2 P_{3\text{-}ECHD} \cdot P_{O_2}^{0.5} \\
r_3 &= k_3 P_{EB} \cdot P_{O_2}^{0.5} \\
r_4 &= k_4 P_{4\text{-}VCH} \cdot P_{O_2}^{0.5} \\
r_5 &= k_5 P_{4\text{-}VCH} \cdot P_{O_2} \\
r_6 &= k_6 P_{3\text{-}ECHD} \cdot P_{O_2}
\end{aligned}\right\} \qquad (9)$$

The rates of conversion and accumulation of individual components of the processes (along routes I-VI) are determined by the following expressions:

$$\left.\begin{aligned} &\omega_{4\text{-}VCH} = -r_1 - r_4 - r_5 \\ &\omega_{3\text{-}ECHD} = r_1 - r_2 - r_6 \\ &\omega_{EB} = r_2 - r_3 + r_4 \\ &\omega_{ST} = r_3 + r_5 \end{aligned}\right\} \qquad (10)$$

The left side shows the rate of accumulation (or consumption) of the components of the reaction in this system. As it is obvious, the reaction rate for heterogeneous catalytic systems is calculated based on the change in the amount of substance over time and the unit mass of the catalyst. Since the rate of product formation as a result of our experimental studies is presented in the form of a change in pressure, we can write the following equations after appropriate transformations:

$$\omega_i = \frac{dn_i}{dG_{cat}} = \frac{dP_i}{d\left(\frac{G_{cat}}{V_{vol.flow}}\right)} \cdot \frac{1}{RT} \qquad (11)$$

here: n_i – i is a molar flow rate of the component (mol/h); P_i – partial pressure of the i component (kPa); $V_{vol.flow}$ – volume flow rate (m^3/h); T – temperature (K); R – total gas constant (C/(mol·K)); τ– contact time ((kg·h)/m^3).

Thus, the system of equations (10) can be represented as follows:

$$\left.\begin{aligned} &\frac{dP_{4\text{-}VCH}}{d\left(\frac{G_{cat}}{V_{vol.flow}}\right)} = RT(-r_1 - r_4 - r_5) \\ &\frac{dP_{3\text{-}VCH}}{d\left(\frac{G_{cat}}{V_{vol.flow}}\right)} = RT(r_1 - r_2 - r_6) \\ &\frac{dP_{EB}}{d\left(\frac{G_{cat}}{V_{vol.flow}}\right)} = RT(r_2 - r_3 + r_4) \\ &\frac{dP_{ST}}{d\left(\frac{G_{cat}}{V_{vol.flow}}\right)} = RT \times (r_3 + r_5) \end{aligned}\right\} \qquad (12)$$

The calculation of the rate constants and exponential coefficients of the activation energies of the kinetic model was carried out by means of the Nelder-Mead search method by using the Matlab computer system. The optimization criterion was of the following form

$$F = min\sum_{i=1}^{m}\sum_{j=1}^{n}\left(\frac{\left|A_{ij}^{exp} - A_{ij}^{calc}\right|}{A_{ij}^{exp}}\right) \to min \qquad (13)$$

Here: A_{ij}^{exp}, A_{ij}^{calc} is the experimental yield value of the j component in the experiment; – the calculated yield value of the j component in the i experiment; m is the number of experiments; n is the number of components. The calculations have shown that the error rate of the experimental and calculated data does not exceed 5-6%. The values of the found constants are presented below:

$$k_1 = 1.45 \cdot \exp(-52794.1/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$

$$k_2 = 1.43 \cdot \exp(-68431.6/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1}$$

$$k_3 = 1.13 \cdot \exp(-56732.7/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-2}$$

$$k_4 = 3.02 \cdot 10^{-6} \exp(-55865/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$

$$k_5 = 4.27 \cdot 10^{-4} \exp(-43628.1/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$

$$k_6 = 3.24 \cdot 10^{-4} \exp(-21658.1/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$

here E is the activation energy in C/mol.

According to the results of the studies, the oxidative dehydrogenation of 4-VCH to ethylbenzene occurs when the catalyst surface is slightly saturated with oxygen. It is necessary to moderately saturated the catalyst surface with nucleophilic oxygen to obtain a high yield of styrene. This condition is achieved by modifying the catalyst with oxides of NTE ($La_2 O_3$, Gd_2O_3, Nd_2O_3, Tb_4O_7-1.5-2.0 mass %). In this case, the oxidative dehydrogenation of 4-VCH proceeds in the following stages.

1) Acid-base stage of the reaction:

$$C_6H_9 - CH = CH_2 \xrightarrow{+H^+} C_6H_9C^+H - CH_3 \xrightarrow[-H^+]{} C_6H_8 = CH - CH_3$$

$$C_6H_8 = CH - CH_3 \xrightarrow{+H^+} C_6^+H_8 - CH_2 - CH_3 \xrightarrow[-H^+]{} C_6H_7 - CH_2 - CH_3$$

$$C_6H_7 - CH_2 - CH_3 + Me^{n+}\,O^{2-} \rightarrow C_6^-\,H_6CH_2\,CH_3Me^{n+}\,OH^-$$

here $C_6H_8 = CH - CH_3$ is ethylidenecyclohexene, and $C_6H_7 - CH_2 - CH_3$ is ethylcyclohexa-1,3-diene.

2) oxidative reduction stage;

$$H_6C_6^-C_2H_5\,Me^{n+}\,\mathrm{O}H^- \rightarrow C_2H_5C_6H_6Me^{(n-1)+}OH^-$$

$$C_2H_5 - C_6H_6Me^{(n-1)+}OH^- \rightarrow C_2H_5C_6H_5Me^{(n-1)+}\square + H_2\mathrm{O}$$

3) Substrate dehydrogenation and desorption

$$C_2H_5C_6H_5Me^{(n-1)+}\square + 0{,}5\,O_2 \rightarrow C_2H_5C_6H_5Me^{n+}O^{2-}$$

$$C_6H_5 - C_2H_5Me^{n+}O^{2-} \rightarrow C_6H_5\,CHCH_3Me^{(n-1)}OH^-$$

$$C_6H_5CHCH_3Me^{(n-1)+}OH^- \rightarrow C_6H_5CH = CH_2 + Me^{(n-1)+}\square + H_2\mathrm{O}$$

Here, $C_6H_5 - C_2H_5$ is ethylbenzene, $C_6H_5 - CH = CH_2$ is styrene, Me^{n+}, $Me^{(n-1)+}$ are cations with different oxidation states, □ –is an anion vacancy on the catalyst surface.

The ethylbenzene:styrene ratio in the catalyst obtained in this system depends on the rate of desorption of ethylbenzene or phenylethenyl radical from the surface of the reduced catalyst.

Calculation of the structural dimensions of the reactor element for the oxidative dehydrogenation process of methylcyclopentene isomers

In order to achieve a mass flow rate of methylcyclohexadiene Q1=200 kg/h at the reactor outlet as a result of the oxidative conversion of 1-methylcyclopentadiene, we determined the catalyst volume value on the basis of the maximum catalyst productivity $\left(q_1 = 39.76\frac{\mathrm{kg}}{\mathrm{m^3_{cat}h}}\right)$ by using the following formula:

$$V^1_{cat} = \frac{Q_1\left[\frac{\mathrm{kg}}{\mathrm{h}}\right]}{q_1\left[\frac{\mathrm{kg}}{\mathrm{m^3{}_{cat}h}}\right]} \approx 5.03\ \mathrm{m}^3$$

The specified catalyst mass can be placed in a fixed-bed in a cylindrical reactor with a height of H=3.3 m and a diameter of D=1.4 m.

Similarly, to achieve a mass flow rate of methylcyclohexadiene Q_2=200 kg/h at the reactor outlet as a result of the oxidative conversion of 3-methylcyclopentadiene, we determined the catalyst volume value based on the maximum catalyst productivity $\left(q_2 = 28.57\frac{kg}{m^3_{cat}h}\right)$ by the following formula. Here, since the rate of oxidative conversion of 3-methylcyclopentadiene is relatively slow, a larger reactor element is required to achieve the same yield:

$$V^2_{cat} = \frac{Q_2\left[\frac{kg}{h}\right]}{q_2\left[\frac{kg}{m^3_{cat}h}\right]} \approx 7.00\ m^3$$

The specified catalyst mass can be placed in a fixed bed in a cylindrical reactor with a height of H=3.7 m and a diameter of D=1.54 m.

The thermochemical equations for the oxidative dehydrogenation of methylcyclopentene to methylcyclopentadiene under standard conditions are given below:

$$\left.\begin{array}{lll}
\text{I.} & C_5H_7CH_3 + 0.5O_2 \xrightarrow{k_1} C_5H_5CH_3 + H_2O & \Delta H_0 = -57.08\ \text{kcal/mol} \\
\text{II.} & C_5H_7CH_3 \xrightarrow{k_2} C_6H_{10} & \Delta H_0 = -24.27\ \text{kcal/mol} \\
\text{III.} & C_6H_{10} + O_2 \xrightarrow{k_3} C_6H_6 + 2H_2O & \Delta H_0 = -67.11\ \text{kcal/mol} \\
\text{IV.} & 2C_5H_7CH_3 \xrightarrow{k_4} C_5H_9CH_3 + C_5H_5CH_3 & \Delta H_0 = -20.21\ \text{kcal/mol} \\
\text{V.} & C_5H_7CH_3 + 2O_2 \xrightarrow{k_5} C_5H_6 + CO_2 + 2H_2O & \Delta H_0 = -173.16\ \text{kcal/mol} \\
\text{VI.} & C_5H_5CH_3 + 2.5O_2 \xrightarrow{k_6} C_4H_6 + 2CO_2 + H_2O & \Delta H_0 = -215.48\ \text{kcal/mol} \\
\text{VII.} & C_5H_5CH_3 + 3.5O_2 \xrightarrow{k_7} C_3H_6 + 3CO_2 + H_2O & \Delta H_0 = -330.68\ \text{kcal/mol} \\
\text{VIII.} & C_5H_5CH_3 + 5O_2 \xrightarrow{k_8} C_2H_4 + 4CO_2 + 2H_2O & \Delta H_0 = -474.91\ \text{kcal/mol}
\end{array}\right\}$$

It is necessary to determine the temperature dependence of the heat effect $\Delta H_{R\,j}$ of each reaction to solve the heat balance equation:

1) for the isobaric heat capacity of the components:

$$C_{pi} = a_i + b_i T + c_i T^2 + d_i T^3$$

2) for the change in isobaric heat capacity of the system:

$$\Delta C_{pj} = \Delta a_j + \Delta b_j T + \Delta c_j T^2 + \Delta d_j T^3 = \left(\sum_i \nu_i' a_i^{\text{product}} - \sum_i \nu_i a_i^{\text{initial}} \right) +$$

$$+ \left(\sum_i \nu_i' b_i^{\text{product}} - \sum_i \nu_i b_i^{\text{initial}} \right) T + \left(\sum_i \nu_i' c_i^{\text{product}} - \sum_i \nu_i c_i^{\text{initial}} \right) T^2 + \left(\sum_i \nu_i' d_i^{\text{product}} - \sum_i \nu_i d_i^{\text{initial}} \right) T^3$$

3) *j*- standard heat of reaction:

$$\Delta H_{298j} = \left(\sum_i \nu_i' \Delta H_{298}^{\text{product}} - \sum_i \nu_i \Delta H_{298}^{\text{initial}} \right)_j$$

4) heat change of the *j*-reaction:

$$\Delta H_{Rj} = \int_{298}^{T} \Delta C_{pj} dT + \Delta H_{298j} = \Delta a_j (T - 298) + \frac{\Delta b_j}{2}\left(T^2 - 298^2\right) + \frac{\Delta c_j}{3}\left(T^3 - 298^3\right) +$$

$$+ \frac{\Delta d_j}{4}\left(T^4 - 298^4\right) + \Delta H_{298j}$$

and also, by using the values of standard heats ΔH_{0i} of formation and empirical coefficients of heat capacities, the temperature dependences of thermal effects ΔH_{Rj} were determined for all reactions involved in the process according to their stoichiometric schemes.

Here and – stoichiometric ratios of the initial substance ν_i and ν_i' and the i-component of the reaction products; $\Delta H_{0i}^{\text{initial}}$, $\Delta H_{0i}^{\text{product}}$ – standard heats of formation of the initial substances and the *i*-component of the reaction products; ΔH_{Rj} – heat effect of the *j*-reaction; ΔH_{0j} – standard heat effect of the *j*-reaction.

The kinetic equations for the oxidative dehydrogenation of methylcyclopentene to methylcyclopentadiene, along with equations that take into account heat balance and pressure drop, form a complete mathematical model of the process:

$$\left.\begin{aligned}
&\frac{dP_{C_5H_7CH_3}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V}\left(-r_1 - r_2 - 2r_4 - r_5\right)\\
&\frac{dP_{C_6H_{10}}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V}\left(r_2 - r_3\right)\\
&\frac{dP_{C_5H_5CH_3}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V}\left(r_1 + r_4 - 3r_6\right)\\
&\frac{dP_{C_5H_9CH_3}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V} r_4\\
&\frac{dP_{C_6H_6}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V} r_3\\
&\frac{dP_{C_5H_6}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V} r_5\\
&\frac{dP_{C_2-C_4}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V} 3r_6\\
&\frac{dP_{C_6H_6}}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \cdot \frac{RT}{V}\left(r_5 + 9r_6\right)\\
&\frac{dP}{dl} = -\left(\frac{150}{Re} + 1.75\right) \cdot \frac{\rho_{\text{газ}} u_0^2 (1-\varepsilon)}{d_p g \varepsilon^3}\\
&\frac{dT}{dl} = \rho_k \cdot \frac{\pi D^2}{4} \times \left\{ -\frac{\alpha(T - T_x)}{\sum_{i=1}^{n} n_i C_{pi}} - \frac{\sum_{j=1}^{m} r_j \Delta H_{Rj}}{\sum_{i=1}^{n} n_i C_{pi}} \right\}
\end{aligned}\right\}$$

It should be noted that this mathematical model is the same for the selective oxidative dehydrogenation processes of both individual isomers in terms of structural identity, but its parametric identity is different (in terms of kinetic constants and optimal structural dimensions).

Here: A_{ij}^{exp}, A_{ij}^{calc} is the experimental yield value of the j-component in the experiment; – the calculated yield value of the j-component in the i experiment; m is the number of experiments; n is the number of components. The calculations have shown that the error rate of the experimental and calculated data does not exceed 5-6%. The values of the found constants are presented below:

$$k_1 = 1.45 \cdot \exp\left(-52794.1/RT\right) \text{mol} \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot \text{кPa}^{-1.5}$$

$$k_2 = 1.43 \cdot \exp\left(-68431.6/RT\right) \text{mol} \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot \text{кPa}^{-1}$$

$$k_3 = 1.13 \cdot \exp\left(-56732.7/RT\right) \text{mol} \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot \text{кPa}^{-2}$$

$$k_4 = 3.02 \cdot 10^{-6} \exp(-55865/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$
$$k_5 = 4.27 \cdot 10^{-4} \exp(-43628.1/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$
$$k_6 = 3.24 \cdot 10^{-4} \exp(-21658.1/RT)\, mol \cdot h^{-1} \cdot gr_{cat}^{-1} \cdot кPa^{-1.5}$$

Optimal conditions for oxidative dehydrogenation of ethylbenzene and styrene in pentasil containing 4-vinylcyclohexanine and platinum gallium phosphorus

Selecting the optimal reactor type

The process of oxidative dehydrogenation of 4-vinylcyclohexene to ethylbenzene and styrene is carried out based on a defined kinetic model. The selection of the optimal reactor type for the process under consideration was carried out by comparing the reaction volumes required to achieve a given degree of conversion based on the kinetic model of the reactor.

It is known that a typical model for an ideal compression reactor is presented in the form of ordinary differential equations. In turn, a typical mathematical model for an ideal mixing reactor is presented in the form of the following expression.

$$\left.\begin{aligned}
\frac{P_{4\text{-VTH}}}{\left(\frac{G_{cat}}{V_{vol.flow}}\right)} &= RT(-r_1 - r_4 - r_5) \\
\frac{P_{3\text{-ETHD}}}{\left(\frac{G_{cat}}{V_{vol.flow}}\right)} &= RT(r_1 - r_2 - r_6) \\
\frac{P_{EB}}{\left(\frac{G_{cat}}{V_{vol.flow}}\right)} &= RT(r_2 - r_3 + r_4) \\
\frac{P_{ST}}{\left(\frac{G_{cat}}{V_{vol.flow}}\right)} &= RT \times (r_3 + r_5)
\end{aligned}\right\} \qquad (14)$$

This process was investigated in ideal compression and ideal mixing reactors using a personal computer based on the established equations. As a result of the studies, it was found that the reaction volume utilization rate in the ideal compression reactor was higher than in the ideal mixing reactor, and as the conversion rate increased from 20% to 50%, the $V_{M.R.}/V_{C.R.}$ ratio of the investigated reactors increased from 1.23 to 1.45. The same results were obtained for other reaction conditions. Studies on the basis of the kinetic model showed that the selectivity (in terms of product) does not change significantly in the mixing reactor with an increase in the conversion rate.

Thus on the bases of the above mentioned results, it can be noted that 4-VCH is an ideal compression reactor for the oxidative dehydrogenation process of ethylbenzene and styrene. Such a hydrodynamic regime can be approached with reactors with a fixed catalyst bed.

Theoretical optimization of the process

Theoretical optimization of the process under consideration was carried out on the basis of the developed kinetic model. The purpose of theoretical optimization was to determine the maximum productivity conditions of the process, that is, to determine the conditions for the extraction of the maximum target product per unit mass. There are two target products in this process: ethylbenzene and styrene. The function of maximizing the extraction of these products (ethylbenzene + styrene) was taken as the optimization criterion. The main regime parameters were selected to characterize these conditions: the molar concentration of the starting 4-vinylcyclohexene, oxygen, the process temperature and the contact time. Thus, the optimization criterion is expressed in the form of the following functional dependence:

$$q = f\left\{P^0_{4\text{-VCH}}, P^0_{O_2}, T, \frac{G_{cat}}{V_{vol.flow}}\right\} \qquad (15)$$

here: Q is catalyst productivity on styrene and ethylbenzene, T – temperature (K), $P^0_{4-VCH}, P^0_{O_2}$ is VCH–4-vinylcyclohexene (kPa) and

$P^0_{O_2}$ the initial molar concentration of oxygen (kPa).

In order to determine the optimal control conditions, in order to determine the optimal regimes that ensure the maximum productivity of the catalyst for the target product, this criterion is expressed as follows:

$$\max(g_{ST}) = f\left\{P^0_{4\text{-VCH}}, P^0_{O_2}, T, \frac{G_{cat}}{V_{vol.flow}}\right\} \qquad (16)$$

The following restrictions are imposed on the operating parameters:

$$320\ {}^0C \leq T \leq 490\ {}^0C \quad \Delta T = 5^0 C$$

$$12 \leq P^0_{4\text{-VCH}} \leq 16 \quad \Delta P_{C_5H_7CH_3} = 0.5\ \text{кPa}$$

$$1 \leq P^0_{O_2} \leq 5 \quad \Delta P_{O_2} = 0.5\ \text{кPa}$$

$$35 \leq G_{cat}/V_{vol.flow} \leq 125 \quad \Delta\left(\frac{G_{cat}}{V_{vol.flow}}\right) = 5\,\frac{kg\,h}{m^3}$$

Parametric optimization based on the kinetic model of oxidative dehydrogenation of 4-vinylcyclohexen-1 to ethylbenzene and styrene is performed by using a PC and appropriate software. Parametric optimization allows to obtain all the yield indicators of the target products by sequentially selecting all the parameters of the process within the specified ranges and to select the best option based on the optimization criterion. In this case, the following formula is used to calculate the catalyst efficiency for each option:

$$q = \frac{X n^0_{4\text{-VCH}} M_{4\text{-VCH}}}{G_{cat}} \qquad (17)$$

here, M is the molar mass of 4-vinylcyclohexene-1, g/mol; X is the degree of conversion, %; G is the mass of the catalyst, g; n^0 is the initial volume flow rate of 4-vinylcyclohexene-1, mol/h. The catalyst productivity is as follows when the molar flow rate is expressed by the Mendeleev-Clapeyron equation by using the partial effect:

$$q = \frac{X\left(\frac{P^0_{4-\text{VCH}} V_{\text{vol.flow}}}{\text{RT}}\right) M_{4-\text{VCH}}}{G_{\text{cat}}} \qquad (18)$$

The optimization is solved by means of the Nelder-Mead search method by using the Matlab software system. In this case, the optimal process temperature was T = 470°C, the catalyst yield was q=0.0045 g/(g cat h 0.0045g/(g_{cat} h), the conversion rate of 4-vinylcyclohexene-1 was X=72%, the styrene yield was 22%, and the ethylbenzene yield was 38%.

"Calculation of the structural dimensions of the reactor element

Let us define the total production of the two target products for the conversion of 4-vinylcyclohexene-1 into ethylbenzene and styrene in the oxidative dehydrogenation process as Q=250 kg/h.

Therefore, according to the specified maximum catalyst production $\left(q = 17.85\frac{kg}{m_{cat}^{3}h}\right)$, the volume of required catalyst will be:"

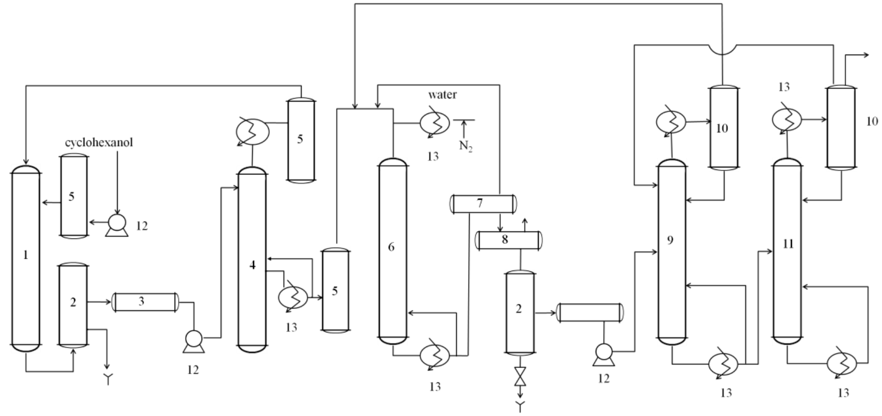
$$V_{cat} = \frac{Q\left[\frac{kg}{h}\right]}{q\left[\frac{kg}{m_{cat}^{3}h}\right]} \approx 14\ m^{3} \tag{19}$$

A given volume of catalyst can be placed in a fixed-bed in a cylindrical reactor element, with structural dimensions: diameter D=1.8 m, reactor height H=5.5 m.

Schematic diagram of the oxidative dehydrogenation process of methylcyclopentene to methylcyclopentadiene

The selection of the optimal reactor type based on the kinetic model and mathematical modeling of the oxidative dehydrogenation process of methylcyclopentene allows us to develop a principle technological scheme of this process (scheme 1).

In the principle technological scheme, cyclohexanol is fed to the dehydration reactor (1) through a heat exchanger (5). Since the process is carried out here at 350-380°C, isomerization of the cyclohexene formed simultaneously with dehydration also occurs. The isomerization degree in this reactor is 39-42%. After the reaction product is separated from water in the separator column (2), it is sent to the dryer (3). The dried hydrocarbon mixture is sent to the rectification column (4) via a pump.



Scheme 1. Principal technological scheme of the process of obtaining methylcyclopentadiene by oxidative dehydrogenation of methylcyclopentene.

The 64-72°C fraction separated during rectification consists of ~95-98% methylcyclopentene isomers and is directed to the dehydrogenation reactor by passing through a steam heater (5). The 80-82°C fraction separated from the rectification column (consists of 96-98% cyclohexene) is recirculated to column (1) for isomerization. It is sent to reactor (6) to carry out the dehydrogenation process. At the same time, the cyclohexanol fraction (residue) is recirculated back to the reactor (1). Thermocouple housings made of 1x18H9T stainless steel are used as the reactor, and pipes equipped with a metal mesh are used to hold the catalyst. The reactor is also supplied with heated air through air cleaning devices and a heater. The air supply rate is measured by a rheometer. Heat transfer is carried out through a cooler placed in the catalyst-bed.

The oxidative dehydrogenation process of methylcyclopentene is carried out at atmospheric pressure on Fe-Nd-0/HNaM in a stationary state. The temperature in the upper layer of the catalyst is 400-420°C, and in the middle and lower layers - 450-470°C. The feed rate is 0.5-1.0 s^{-1}. The air flow rate is 0.1-0.15 l/min. The catalyst has a service life of 100 hours, in other words, it works without losing its activity during this period. The reaction product (6) is cooled from the reactor (6) through a heat exchanger-cooler to 25-40°C and enters the precipitator. Here, the organic layer is separated from the water layer and fed to the dimerization column (8). The light fraction (MCPE and benzene) is recirculated to the dehydrogenation reactor. The dimer of methylcyclopentadiene enters the receiver.

The material balance of the MCPE dehydrogenation process was compiled on the bases of the results obtained in the laboratory facility:

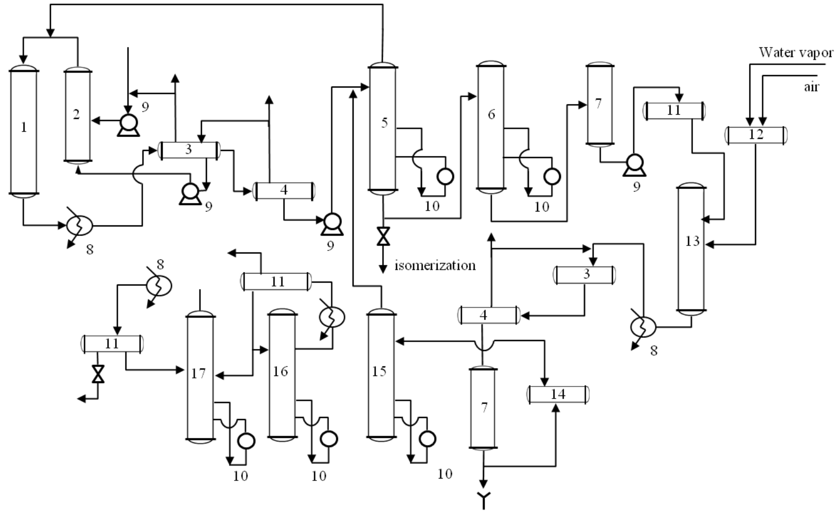
- the yield of liquid products is 94.0%, the amount of gas and water, as well as losses - 6%.
- the yield of MCPD in the form of dimers is 88.0% of the potential.
- the amount of MCPE extracted and recycled from the light fraction is 95.2% of the potential.

Principle technological scheme and material balance of the oxidative dehydrogenation process of 4-vinylcyclohexene to ethylbenzene and styrene

The oxidative dehydrogenation process of 4-vinylcyclohexene in the presence of a Fe-Nd-O/HNa-Mor catalyst consists of three main stages:

1. [4-2]cyclodimerization of divinyl in the presence of a copper-containing catalyst;
2. Obtaining a mixture of ethylbenzene and styrene by oxidative dehydrogenation of 4-vinylcyclohexene in a flow system;
3. Separation of ethylbenzene and styrene from the catalyst with a high degree of purity by rectification.

In the principle technological scheme given in Scheme 2, these stages are technologically sequentially combined into one process.



Scheme 2. Schematic diagram of the process for obtaining ethylbenzene and styrene by oxidative dehydrogenation of 4-vinylcyclohexene.

THE RESULTS

1. A kinetic model has been developed for the production of methylcyclopentene isomers from cyclohexanol and the production of methylcyclopentadiene from it by oxidative dehydrogenation.

The issue of statistical studies of the dependencies of indicators characterizing the functionalization of the process has been resolved on the bases of the experimental results. The volume of the experiment and the effectiveness of optimization depend on the number of levels [5,8,9,13].

2. The BoxBenkinD software module was used to build the regression model. The program provides for the construction of an approximate matrix, calculation of the coefficient of the three-factor model, and regression analysis to check the adequacy of the model (according to Fisher's criterion), as well as calculation of the difference between the experimental data and the obtained results [10,16].

3. Modern computer tools create broad opportunities for processing information and empirically selecting a regression equation, for example, by comparing the values of the residual variance ($S_{resid.}^2$) calculated for different models.

The dependence of the target product yield on the factor was assumed to be in the form of linear regression.

y=b(1)+b(2)·x1+b(3)·x2+b(4)·x3+b(5)·(x1·2-2/3)+b(6)·(x2·2-2/3)[19]

4. Matlab, a modern linear programming algorithm, was used to solve the optimization problem. The solution of the optimization problem showed that the highest yield of cyclohexanol is obtained when Y_{1opt}=40, X_1=15.49 KPa, X_2=1.55 KPa, and X_3=483^{0}C.

The numerical values of the rate constants of the kinetic model were determined by using a special software system. Thus, the following constants were defined for the conversion of 1-methylcyclopentene:

$$k_1 = 1.25 \cdot \exp(-72896.1/\mathrm{RT})\mathrm{mol} \cdot \mathrm{h}^{-1} \cdot \mathrm{gr}_{\mathrm{cat}}^{-1} \cdot \mathrm{кPa}^{-1.5}$$

For the conversion of 3-methylcyclopentene:

$$k_1 = 2.94 \cdot 10^{-2}\exp(-55211.5/\mathrm{RT})\mathrm{mol} \cdot \mathrm{h}^{-1} \cdot \mathrm{gr}_{\mathrm{cat}}^{-1} \cdot \mathrm{кPa}^{-1.5}$$

The process was studied for both types of reactors by using a personal computer on the bases of the given kinetic models in various technological regimes: T=623-723 K, volume velocity *v*=62.9-426.2 h^{-1}, initial partial pressure of hydrocarbon $P_{C_5H_7\mathrm{CH}_3}$ =12.7-15.5 kPa and initial partial pressure of oxygen P_{O_2} = 1.5-4.7 kPa [19].

5. The aim of theoretical optimization is to determine the process conditions to achieve the maximum yield of the target product per unit mass (or volume) of the catalyst, that is, to determine the process regime parameters that ensure the maximum yield of the main product. The following were used as the main regime parameters characterizing these conditions: the initial molar value of methylcyclopentene, the initial molar value of oxygen, the process temperature and the contact time. Then, the optimization criterion can be expressed by the following functional dependence: $q_{C_5H_5\mathrm{CH}_3} = f\left\{P^0_{C_5H_7\mathrm{CH}_3}, P^0_{O_2}, \mathrm{T}, \frac{G_{\mathrm{cat}}}{V}\right\}$,

Parametric optimization was performed by using appropriate software on the basis of a kinetic model developed for the oxidative dehydrogenation of methylcyclopentene to methylcyclopentadiene.

The catalyst volume value is determined on the basis of the maximum catalyst productivity by the following formula for achieving a mass flow rate of methylcyclopentadiene Q_1=200 kg/h at the reactor outlet as a result of the oxidative conversion of 1-methylcyclopentene:

$$\left(q_1 = 39.76 \frac{\mathrm{kg}}{m^3_{\mathrm{cat}}\mathrm{h}}\right) \text{[14,15,17].}$$

6. According to the mathematical modeling of the oxidative dehydrogenation processes of methylcyclopentene isomers to methylcyclopentadiene and 4-vinylcyclohexene to ethylbenzene and styrene, the optimal regime and technological parameters were evaluated, which allowed the design of the apparatus to be selected. A possible technological scheme of the processes was investigated and a material balance was given [1,2,3,4,6,7,11,12].

The main results of the dissertation work have been published in the following articles and theses:

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