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OPTIMAL DESIGN OF THE OXIDATIVE DEHYDROGENATION OF METHYLCYCLOHEXANE INTO METHYLCYCLOHEXADIENE ON A MODIFIED ZEOLITE CATALYST

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Abstract: *Selection and theoretical optimization of the reactor type was carried out on the basis of a kinetic model of the process of selective oxidative dehydrogenation of methylcyclohexane into methylcyclohexadiene on a modified active metal-zeolite catalyst. It was determined that it was more expedient to carry out the process in an ideal tubular (packed-bed) type reactor. As a result of theoretical optimization of the process, optimal technological regimes were determined and the optimal design dimensions of the reactor element for a given capacity calculated. A complete mathematical model of the process was developed with regard to the effect of heat and pressure drop.*

Keywords*: methylcyclohexane, methylcyclohexadiene, oxidative dehydrogenation, clinoptilolite, reactor choice, theoretical optimization, mathematical model.*
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Introduction

Methylcyclohexadiene is widely used in the production of synthetic jet fuels. At present, the process of dehydrogenation of methylcyclohexane has not been studied properly. The development of dehydrogenation catalysts with high stability, catalytic activity and product selectivity at low temperatures and high pressures is a key issue in the industrialization of the dehydrogenation process of methylcyclohexane [1] . In this respect, the synthesis of the valuable product - methylcyclohexadiene-1,3 by oxidative dehydrogenation of methylcyclohexane is of great theoretical and practical importance [2]. Given certain shortcomings of industrial methods for obtaining this compound, the laboratory of the ANAS Institute of Catalysis and Inorganic Chemistry developed an effective zeolite catalyst for the oxidative dehydrogenation of methylcyclohexane into methylcyclohexadiene. It established that natural clinoptilolite containing 0.5% Co2+ and 0.25% Cr3+ exhibits relatively high activity in this reaction [3,4]. With the participation of this catalyst, the kinetic regularities of the process were studied and, on their basis, a theoretically substantiated kinetic model developed [4].

In the real devices, a chemical reaction is accompanied by physical processes and proceeds in the presence of hydrodynamics, heat and mass transfer. Thus, the chemical kinetics of the reaction does not fully reflect the real process. Therefore, macrokinetic factors must be taken into account by developing a mathematical model for the implementation of this process on an industrial scale.

The main purpose of this article is to address the issue of optimal design of the process under consideration. This, in turn, implies the selection of the reactor type based on the kinetic model, theoretical optimization, calculation of the optimal design dimensions of the reactor element in accordance with the given capacity and the creation of a complete mathematical model of the process.

Choice of the optimal type of reactor

The choice of the optimal reactor type for the process under consideration was made by comparing the volumes required to obtain a given conversion rate in different reactors based on its kinetic model. There are two basic types of ideal reactors, stirred tanks and tubular or packed-bed reactors [5]. The process was studied in these two types of reactors. The kinetic model of the oxidative dehydrogenation process of methylcyclohexane into methylcyclohexadiene on modified zeolites can be written as follows for an ideal tubular (packed-bed) type reactor:

$$\frac{dA_1}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_{11}P_{C_7H_{14}}\left\{\frac{-\sqrt{\frac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}+\sqrt{\left(\sqrt{\frac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}\right)^2+4\left(\frac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}}{2\left(\frac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}\right\}^2$$

$$\frac{dA_2}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_3P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\frac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\frac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)+\sqrt{\left(\sqrt{\frac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\frac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)^2+4\frac{k_3P_{C_7H_{14}}}{k_4}}}{2\frac{k_3P_{C_7H_{14}}}{k_4}}\right\}^2$$

$$\frac{dA_3}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_8P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\frac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)+\sqrt{\left(\sqrt{\frac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)^2+4\frac{k_8P_{C_7H_{14}}}{k_9}}}{2\frac{k_8P_{C_7H_{14}}}{k_9}}\right\}^2$$

$$\frac{dA_4}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = \frac{k_{13}K_1P_1K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}+$$

$$+\frac{k_{14}K_3P_3K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}+\frac{k_{15}K_4P_4K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}$$

For an ideal mixing type reactor, the kinetic model of the process can be written as follows:

$$\frac{A_1}{\left(\dfrac{G_k}{n^0_{C_7H_{14}}}\right)}=k_{11}P_{C_7H_{14}}\left\{\frac{-\sqrt{\dfrac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}+\sqrt{\left(\sqrt{\dfrac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}\right)^2+4\left(\dfrac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}}{2\left(\dfrac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}\right\}^2$$

$$\frac{dA_2}{d\left(\dfrac{G_k}{n^0_{C_7H_{14}}}\right)}=k_3P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\dfrac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\dfrac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)+\sqrt{\left(\sqrt{\dfrac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\dfrac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)^2+4\dfrac{k_3P_{C_7H_{14}}}{k_4}}}{2\dfrac{k_3P_{C_7H_{14}}}{k_4}}\right\}^2$$

$$\frac{dA_3}{d\left(\dfrac{G_k}{n^0_{C_7H_{14}}}\right)}=k_8P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)+\sqrt{\left(\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\dfrac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)^2+4\dfrac{k_8P_{C_7H_{14}}}{k_9}}}{2\dfrac{k_8P_{C_7H_{14}}}{k_9}}\right\}^2$$

$$\frac{dA_4}{d\left(\dfrac{G_k}{n^0_{C_7H_{14}}}\right)}=\frac{k_{13}K_1P_1K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}+$$

$$+\frac{k_{14}K_3P_3K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}+\frac{k_{15}K_4P_4K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2}$$

$P_1=P_{C_7H_{14}}$, $P_2=P_{O_2}$, $P_3=P_{C_7H_{12}}$, $P_4=P_{C_7H_{10}}$, $P_5=P_{C_7H_8}$, $P_6=H_2O$; A_1, A_2, A_3 and A_4 according to indices C_7H_{12}, C_7H_{10}, C_7H_8 və CO_2 emissions.

Partial pressures of the components are calculated using the following formula:

$$P_i=\frac{n_i}{\sum n_i}P$$

P_i – *i*- partial pressures of the component, atm; P – total system pressure (1 atm).

The material balance for both types of reactors is as follows:

$$n_{C_7H_{14}}=n^0_{C_7H_{14}}-(A_1n^0_{C_7H_{14}}-A_2n^0_{C_7H_{14}}-A_3n^0_{C_7H_{14}}-A_4n^0_{C_7H_{14}})/100$$

$$n_{H_2O}=(A_1n^0_{C_7H_{14}}+A_2n^0_{C_7H_{14}}+A_3n^0_{C_7H_{14}}+5A_4n^0_{C_6H_{12}})/100$$

$$n_{O_2} = n^0_{O_2} - (\frac{1}{2}A_1 n^0_{C_7H_{14}} - \frac{1}{2}A_2 n^0_{C_7H_{14}} - 10.5A_4 n^0_{C_7H_{14}})/100$$

$$n_{C_7H_{12}} = A_1 n^0_{C_7H_{14}}/100$$

$$n_{C_7H_{10}} = A_2 n^0_{C_7H_{14}}/100$$

$$n_{C_7H_8} = A_3 n^0_{C_7H_{14}}/100$$

$$n_{CO_2} = 7A_4 n^0_{C_7H_{14}}/100$$

The process was studied for both types of reactors on the basis of given kinetic models in various technological modes: T = 320–400°C, space velocity V = 1000–3000 h–1, oxygen partial pressure atm, and partial pressure of methylcyclohexane using a personal computer.

Fig.1 shows the results of studies in the range of molar ratios of methylcyclohexane and oxygen = (0.00902 ÷ 0.02706) mol/h ÷ (0.01129 ÷ 0.03386) mol/h at 380 °C.

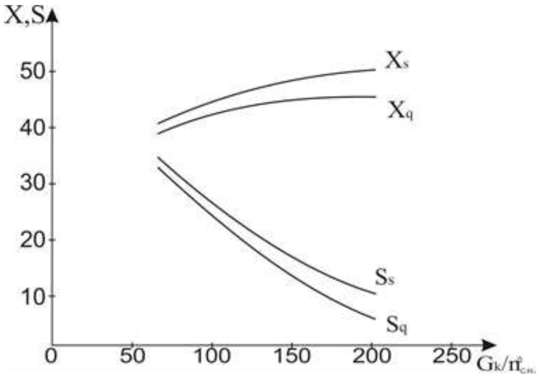

Fig. 1. Dependence of the conversion (X_s, X_q) rate and selectivity (S_s, S_q) of the process on the contact time in flow reactors of ideal mixing and tubular (packed-bed) reactor.

As can be seen from Fig 1, the coefficient of utilization of the reaction volume at all degrees of conversion in the tubular (packed-bed) reactor is greater than in the mixing reactor. The increase in the degree of conversion from 35% to 50% is the ratio of the volumes of the studied reactors $V_{mix.}/V_{comp.}$ It rises from 1.23 to 1.45. Similar results are observed in other technological modes. Also, studies based on the kinetic model showed that the selectivity for the target product in the mixing reactor was less than in the tubular (packed-bed) reactor with increasing conversion.

Thus, studies based on kinetic models showed that the optimal reactor for the process of oxidative dehydrogenation of methylcyclohexane into methylcyclohexdiene was an ideal c tubular (packed-bed) type reactor.

Theoretical process optimization

A theoretical optimization of the process based on the kinetic equation was carried out to ensure the maximum productivity of the catalyst in terms of the target product - methylcyclohexadiene. As a result of theoretical optimization, the optimal technological regimes of the process were determined. Methylcyclohexadiene performance can be determined by the following formula:

$$q_{C_6H_7CH_3} = f\left(T, n^0_{C_6H_{11}CH_3}, \theta, \frac{G_{kat}}{n^0_{C_6H_7CH_3}}\right)$$

where $q_{C_6H_7CH_3}$ – performance of the catalyst for methylcyclohexadiene, gr/(h* gr$_{cat}$); T – reactor temperature, ^{0}C; $\frac{Gcat}{n^0_{C_6H_{11}CH_3}}$ – contact time, (gr$_{cat}$ *h)/mol; θ – molar ratio of methylcyclohexane into oxygen, non-uniform measurement; n_1^0 – initial cost of methylcyclohexane, mol/h.

Based on the developed kinetic model [4], the target function (optimization criteria) can be expressed as follows to determine the mode parameters that provide the maximum efficiency of the catalyst:

$$\max(q_{C_6H_7CH_3}) = f\left(T, n^0_{C_6H_{11}CH_3}, \theta, \frac{G_{kat}}{n^0_{C_6H_{11}CH_3}}\right)$$

According to the technological conditions, the following limitations were taken into account when determining the parameters:

$$320^0C \le T \le 400^0C$$

$$70 \le \frac{G_{kat}}{n^0_{C_6H_{11}CH_3}} \le 200$$

$$0.01 \le n^0_{C_6H_{11}CH_3} \le 0.05$$

$$0.5 \le \theta \le 2.0$$

The problem was solved on the basis of the kinetic model of the process and the material balance. In considering the existing limitations, the performance of the catalyst based on the kinetic model was calculated for each option using the following formula:

$$q = \frac{Xn^0_{C_6H_7CH_3} M_{C_6H_7CH_3}}{G_{cat}}$$

where $M_{C_6H_7CH_3}$ - molecular weight of methylcyclohexadiene.

The problem was solved on a personal computer using the "Matlab" software system [6] by using simplex search method of Nelder-Mead [7] and the following results were obtained: T=380^{0}C; $n^0_{C_6H_{11}CH_3} = 0.024$mol/h; θ=0.9; $\frac{G_{cat}}{n^0_{C_6H_{11}CH_3}} = 150$(gr$_{cat}$ h)/mol. As a result of these conditions, the productivity of the catalyst was $q_{C_6H_7CH_3}$=0.250 gr/(gr$_{cat}$ h), the degree of conversion of methylcyclohexane X=50%, the yield of methylcyclohexane was 15%.

Compilation of the complete mathematical model of the process

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Therefore, the yields of products obtained by theoretical optimization based only on kinetic models are conditionally maximized. At this stage, a complete mathematical model of the process was developed by adding heat equations and pressure drop equations to the kinetic equations to obtain a more accurate description of the flow distribution.

The best approximation process for an ideal tubular (packed-bed) reactor is to be carried out in a stationary bed catalyst reactor, and its mathematical model can be summarized as follows:

$$D_E\left(\frac{\partial^2 C_i}{\partial R^2}+\frac{1}{R}\frac{\partial C_i}{\partial R}\right)-q\frac{\partial g_i}{\partial l}+\sum_{j=1}^{m}\nu_{ij}r_j(\bar{c}_i,T)=0$$

$$\alpha_E\left(\frac{\partial^2 T}{\partial R^2}+\frac{1}{R}\frac{\partial T}{\partial R}\right)-qC_p\frac{\partial T}{\partial l}+\sum_{j=1}^{m}Q_j r_j(\bar{c}_i,T)=0$$

where D_E – effective diffusion coefficient; R – coordinate in the radial direction; g – mass density; - the stoichiometric coefficient of i-substance in νij – j reaction; q – mass velocity; r_j – j-speed of reaction; α_E – effective thermal conductivity of the layer; Q_j – thermal effect of j-reaction; T – reactor temperature; l – the length of the reactor; C_p – heat capacities of substances.

To achieve the mass velocity of methylcyclohexane at the outlet of the reactor Q = 2000 kg/h, the value of the catalyst volume was determined based on the maximum productivity $\left(q=0.250\frac{gr}{gr_{cat}h}\right)$ of the catalyst using the following formula:

$$V_{cat}=\frac{Q}{q\cdot\rho_{cat}}\approx 9.5\ m^3$$

where ρ_{cat} – catalyst density, ρ_{cat}= 850 kg/m^3.

The height of the specified catalyst mass H = 4.4 m and it can be placed in a cylindrical reactor with a diameter of D = 1.7 m in the form of a seamless layer. The heat balance of the process is written as follows according to the material balance:

$$\sum Q_d=\sum Q_t$$

where Q_d – incoming heat, Q_t – heat that leaves. In practical calculations, it is necessary to take (Q_{it}) into account the heat losses:

$$\sum Q_d=\sum Q_t+\sum Q_{it}$$

The thermal effects of reactions play a very important role in chemical processes. The heat included here is as follows:

$$\sum Q_d = Q_1+Q_2+Q_3$$

Q_1 – temperatures of substances entering the apparatus, Q_2 – heat entering from the outside, Q_3 – thermal effects of physical or chemical transformations.

The heat balance equation includes the thermal effects of chemical reactions, as well as heat losses to the environment through the reactor walls. Accepting some simplifications, the above equation which takes into account temperature changes in general, can be expressed as follows:

$$\frac{dT}{dG_{cat}} = -\frac{\sum_{j=1}^{m} r_j \Delta H_{Rj}}{\sum_{i=1}^{n} n_i C_{pi}} - \frac{\alpha(T - T_x)}{\sum_{i=1}^{n} n_i C_{pi}}$$

where r_j – rates of formation of reaction products, mol/(kg$_{cat}$·h); ΔH_{Rj} – j- thermal effect of the reaction, kDj/mol; $C_{pi}\left(i = \overline{1,k}\right)$ – values of heat capacities of process components corresponding to the corresponding indices, Dj/(mol·K); α – thermal conductivity, Dj/(K·kg$_{cat}$·h); T_x – ambient temperature, K; T – temperature of the gas mixture, K; G_{cat} – amount of catalyst, kg; m – total number of reactions; n_i – mole velocity of the i-component, mol/h.

The below-cited are thermochemical equations for the oxidative dehydrogenation of methylcyclohexadiene for standard conditions [8]:

$$\begin{aligned}
&C_7H_{14} + 0.5O_2 \xrightarrow{k_{11}} C_7H_{12} + H_2O && \Delta H_0 = \text{-}12.851\ \text{kcal/mol}\\
&C_7H_{14} + 0.5O_2 \xrightarrow{k_{3}} C_7H_{10} + 2H_2O && \Delta H_0 = \text{-}70.533\ \text{kcal/mol}\\
&C_7H_{14} + 1.5O_2 \xrightarrow{k_{8}} C_7H_{8} + 3H_2O && \Delta H_0 = \text{-}124.421\ \text{kcal/mol}\\
&C_7H_{14} + 10.5O_2 \xrightarrow{k_{13}} 7CO_2 + 7H_2O && \Delta H_0 = \text{-}1030.994\ \text{kcal/mol}\\
&C_7H_{12} + 10O_2 \xrightarrow{k_{14}} 7CO_2 + 6H_2O && \Delta H_0 = \text{-}1013.123\ \text{kcal/mol}\\
&C_7H_{10} + 9.5O_2 \xrightarrow{k_{15}} 7CO_2 + 5H_2O && \Delta H_0 = \text{-}955.442\ \text{kcal/mol}
\end{aligned}$$

To solve the heat balance equation, it is necessary to determine the temperature dependence of the thermal effect of each reaction [8,9]:

1) for isobaric heat capacity of components:

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

2) for changes in the isobar heat capacity of the system:

$$\Delta C_{pj} = \Delta a_j + \Delta b_j T + \Delta c_j T^2 + \Delta d_j T^3 = \left(\sum_i \nu_i' a_i^{pro} - \sum_i \nu_i a_i^{init}\right) +$$
$$+ \left(\sum_i \nu_i' b_i^{pro} - \sum_i \nu_i b_i^{init}\right) T + \left(\sum_i \nu_i' c_i^{pro} - \sum_i \nu_i c_i^{init}\right) T^2 + \left(\sum_i \nu_i' d_i^{pro} - \sum_i \nu_i d_i^{init}\right) T^3$$

3) standard heat of j-reaction:

$$\Delta H_{298j} = \left(\sum_i \nu_i' \Delta H_{298}^{pro} - \sum_i \nu_i \Delta H_{298}^{init}\right)_j$$

4) j-reaction temperature change:

$$\Delta H_{Rj} = \int_{298}^{T} \Delta C_{pj} dT + \Delta H_{298j} = \Delta a_j (T - 298) + \frac{\Delta b_j}{2}\left(T^2 - 298^2\right) + \frac{\Delta c_j}{3}\left(T^3 - 298^3\right) +$$
$$+ \frac{\Delta d_j}{4}\left(T^4 - 298^4\right) + \Delta H_{298j}$$

and in view of the values of standard formation temperatures ΔH_{0i} and all reactions involved in the process by means of empirical coefficients of heat capacity, the temperature dependence of the ΔH_{Rj} thermal effects was determined in accordance with their stoichiometric scheme where: ν_i və $\nu_i^{'}$ – stoichiometric coefficients of the initial substances and the i-component of the reaction products; ΔH_{0i}^{init}, ΔH_{0i}^{pro} – standard formation temperatures of the initial substances and the i-component of the reaction products; ΔH_{Rj} – thermal effect of j-reaction; ΔH_{0j} – standard thermal effect of j-reaction. If we express the mass of the catalyst by its density, diameter and length of the reactor, the heat balance equation can be expressed as follows:

$$\frac{N_1^0}{\rho_k \cdot \frac{\pi D^2}{4}} \frac{dT}{dl} = -\frac{\sum_{j=1}^{m} r_j \Delta H_{Rj}}{\sum_{i=1}^{n} n_i C_{pi}} - \frac{\alpha(T - T_x)}{\sum_{i=1}^{n} n_i C_{pi}}$$

where A_i - i-output of the product,%; p_{cat} - density of the catalyst; l - length of the reactor; D-diameter of the reactor; r_j- j-speed of reaction.

The passage of reagents through flow-type reactors is accompanied by pressure losses. The process is carried out at atmospheric pressure. Although the pressure drop is not so great here, the pressure drop must be taken into account in order to obtain a more accurate and precise distribution of the productivity of the reaction products along the length of the reactor.

The calculation equation proposed by Ergun is used [5,10] to calculate the pressure drop for heterogeneous catalytic processes which well describes the experimental estimates of various authors on the resistance in the catalyst layer and can be used to calculate the pressure loss along the reactor length of the studied process:

$$\frac{dP}{dl} = -\left(\frac{150}{Re} + 1.75\right) \cdot \frac{\rho_{gas} u_0^2 (1-\varepsilon)}{d_p g \varepsilon^3},$$

where Re – is the Reynolds criterion, $\frac{d_p \rho_{gas} u_0}{\mu(1-\varepsilon)}$; D – diameter of the reactor, m; ρ_{gas} – gas density, kg/m^3; g – gravity, m/s^2; u_0 – linear speed, m/s; d_p – equivalent diameter of particles, m ; ε – porosity; μ – viscosity of gas, kg/m ·s); *l* – the length of the reactor, m.

Kinetic equations of the process of oxidative dehydrogenation of methylcyclohexane to methylcyclohexadiene, equations taking into account the heat balance and pressure drop form a complete mathematical model of the process:

$$
\begin{cases}
\dfrac{n_1^0}{\rho_{cat}\cdot\dfrac{\pi D^2}{4}}\dfrac{dA_1}{dl}=r^1_{C_7H_{12}}-r^2_{CO_2}\\
\dfrac{n_1^0}{\rho_{cat}\cdot\dfrac{\pi D^2}{4}}\dfrac{dA_2}{dl}=r^1_{C_7H_{10}}-r^3_{CO_2}\\
\dfrac{n_1^0}{\rho_{cat}\cdot\dfrac{\pi D^2}{4}}\dfrac{dA_3}{dl}=r^1_{C_7H_8}\\
\dfrac{n_1^0}{\rho_{cat}\cdot\dfrac{\pi D^2}{4}}\dfrac{dA_4}{dl}=r^1_{CO_2}+r^2_{CO_2}+r^3_{CO_2}\\
\dfrac{dP}{dl}=-\left(\dfrac{150}{Re}+1.75\right)\cdot\dfrac{\rho_{gas}u_0^2(1-\varepsilon)}{d_p g\varepsilon^3}\\
\dfrac{N_1^0}{\rho\cdot\dfrac{\pi D^2}{4}}\dfrac{dT}{dl}=-\dfrac{\sum\limits_{j=1}^{m}r_j\Delta H_{Rj}}{\sum\limits_{i=1}^{n}n_iC_{pi}}-\dfrac{\alpha(T-T_x)}{\sum\limits_{i=1}^{n}n_iC_{pi}}
\end{cases}
$$

where $r^1_{CO_2}$, $r^2_{CO_2}$, $r^3_{CO_2}$ – rates of carbon dioxide formation from methylcyclohexane (C_7H_{14}), methylcyclohexene (C_7H_{12}) and methylcyclohexadiene (C_7H_{10}) ; $r^1_{C_7H_{12}}$, $r^1_{C_7H_{10}}$, $r^1_{C_7H_8}$ – formation rates of methylcyclohexane, methylcyclohexadiene and toluene.

Conclusion

Thus, based on the above results, we can conclude that the optimal reactor for the process of selective oxidative dehydrogenation of methylcyclohexane into methylcyclohexadiene is an ideal tubular (packed-bed) type reactor, and it is more expedient to carry out the process in a stationary catalytic reactor. The adequacy of the developed mathematical model was tested on an experimental device and its accuracy was proved. Studies on a mathematical model showed a relatively small pressure drop (from 1 atm to 0.9 atm). This does not affect the overall process and there is no need to increase the linear flow rate. There is also some increase in temperature along the length of the reactor (from 380°C to 385°C). Allowing for the small temperature difference, there is no need to use expensive isothermal reactors, and an adiabatic type reactor can be used for the process under study. The results obtained can be used in the development of the process of the oxidative dehydrogenation of methylcyclohexane into methylcyclohexadiene on a modified active metal seolite catalyst.

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MODİFİKASİYA OLUNMUŞ SEOLİT KATALİZATORU ÜZƏRİNDƏ METİLTSİKLOHEKSANIN METİLTSİKLOHEKSADİENƏ OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏSİ PROSESİNİN OPTİMAL LAYİHƏLƏŞDİRİLMƏSİNİN ELMİ ƏSASLARI

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Xülasə: *Modifikasiya olunmuş aktiv metalseolit katalizatoru üzərində metiltsikloheksanın metiltsikloheksadienə selektiv oksidləşdirici dehidrogenləşdirmə prosesin kinetik modeli əsasında reaktor tipinin seçimi və nəzəri optimallaşdırılması aparılmışdır. Müəyyən olunmuşdur ki, baxılan prosesi ideal tipli reaktorda aparılması daha məqsədəuyğundur. Prosesin nəzəri optimallaşdırılması nəticəsində optimal texnoloji rejimləri təyin olunmuşdur. Reaktor elementinin verilmiş məhsuldarlığa görə optimal konstruktiv ölçüləri hesablanmışdır. İstilik effektlərini və təzyiq düşgüsünü nəzərə alaraq prosesin tam riyazi modeli tərtib olunmuşdur.*

Açar sözlər: *metiltsikloheksan, metiltsikloheksadien, oksidləşdirici dehidrogenləşmə, klinoptilolit, reaktor seçimi, nəzəri optimallaşdırma, riyazi model.*

НАУЧНЫЕ ОСНОВЫ ОПТИМАЛЬНОГО ПРОЕКТИРОВАНИЯ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ МЕТИЦИКЛОГЕКСАНА В МЕТИЛЦИКЛОГЕКСАДИЕН НА МОДИФИЦИРОВАННОМ ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ

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Аннотация: *На основе кинетической модели процесса селективного окислительного дегидрирования метициклогексана в метилциклогексадиен на модифицированном цеолитном катализаторе осуществлен выбор оптимального типа реактора и теоретическая оптимизация данного процесса. Было выявлено, что реактор идеального вытеснения является наиболее целесообразным для ведения рассматриваемого процесса. В результате теоретической оптимизации были определены оптимальные технологические режимы. Исходя из заданной производительности, рассчитаны оптимальные конструктивные размеры реакторного элемента. С учетом тепловых эффектов и перепада давления составлена полная математическая модель процесса.*

Ключевые слова*: метилциклогексан, метилциклогексадиен, окислительное дегидрирование, клиноптилолит, выбор реактора, теоретическая оптимизация, математическая модель.*