Oxidation of n-octane was carried out in a stationary reactor using immobilized manganese nanoparticles in various mass percentages (5 and 10 wt.%) on poly(4-vinylpyridine). It was found that manganese-containing catalysts immobilized in polymer are more active in the oxidation of n-octane than similar homogeneous catalysts. A kinetic model and an equation for calculating the oxidation of n-octane in the presence of a manganese-polymer catalyst were chosen for the calculation. Taking into account the kinetic model, the velocity constant of the specified process is calculated. A high conversion in the oxidation reaction of n-octane with molecular oxygen was obtained.

Keywords: n-octane, manganese-polymer catalyst, oxidation, kinetics.

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Introduction

Compounds such as aromatics and olefins are used as basic raw materials in industrial processes, but these compounds are very valuable themselves. Therefore, it is desirable to replace them with cheaper alternative raw materials. Due to the high content of alkanes and their relative cheapness, it is suitable for this purpose [1]. On the other hand, the oxidation products of n-alkanes have found application in the chemical industry. Therefore, it is interesting to convert paraffins into targeted chemicals using various heterogeneous catalysts. Mn, Co, V, Mo, Fe, Pd, etc. Metal-immobilized or hybrid catalysts are considered effective catalysts for the oxidation of hydrocarbons [2–9]. Nanocatalysts are also considered as an alternative to known catalysts and show good activity because nanoparticles have a high surface/volume ratio, which increases their activity and selectivity [10]. In the process of immobilization, the surface of metal nanoparticles is modified by functional groups, which increases the focus on nanoparticle catalysts [11–13]. Poly (vinylpyridine) (PVP) is used to make such complex catalysts (systems). The chemical bond of the pyridyl group to metals and its ability to form hydrogen bonds with polar particles increases. In such systems, the polymer matrix is involved in the immobilization of nanoparticles [10–11]. The easy removal of polymer-based catalysts from reaction mixtures, their reusability and compatibility with a wide range of solvents, their physical stability and resistance to reaction conditions expand their potential for future use as P4VP-based reagents [14]. Oxidation reactions of alkanes are carried out, for example, in the presence of molecular oxygen, such oxidation is less toxic than other oxygen donors [2].

In our previous work [15–18], a polymer metal catalyst based on the above was synthesized. Its use in the oxidation reactions of n-hexane and n-heptane has shown positive results. Fe-silicocite-1 was used in the study [19] to oxidize Na-Fe-ZSM-5 to n-octane C8 oxygenates. These catalysts were tested for n-octane oxidation in MeCN using H₂O₂ as an oxidizer. It was found that with the increase in MeCN, the selectivity of terminal products has increased. The results also showed that the Na-Fe-ZSM-5 catalyst has better selectivity for terminal products than the Na-Fe-Silicate-1. Triazole complexes of ruthenium were immobilized on mesoporous silicon as catalysts for octane oxidation. Reactions were known to continue with the loading of 0.01 mol% metal as a
catalyst. During this period, the maximum yield was 13.8%. Immobilized catalysts have shown good activity. They can be recycled when used in the oxidation of n-octane. During recycling, the activity decreases slightly [20]. The results of catalytic oxidation of octane on cobalt-replaced cerium (Ce0.90Co0.10O2 − δ) catalysts are given in [20]. The synthesized catalyst crystallizes with a fluorite structure. The results show that the conversion and selectivity of products (alkenes, oxygenates, aromatics, carbon oxides and cracking products) from n-octane vary according to the molar ratio of n-octane to oxygen. Product selectivity was determined during isoconversion for C8 products, aromatics, oxygenates and octanes. The catalyst exhibits higher activity due to an increase in the molar ratio from n-octane to oxygen and the reaction temperature.

The purpose of the work is to study the process of oxidation of n-octane in the presence of manganese-polymer catalyst and the application of the appropriate kinetic model to the process.

**Methodical part**

**General notes and items**

All reagents were obtained from Sigma-Aldrich and no additional purification was performed.

**Synthesis of metal-polymer complex catalysts**

The quaternation of the polymer (poly (4-vinylpyridine)) and the synthesis of immobilized catalysts (poly-4-vinylpyridine MnP4VP) are described in [15-17] and are not repeated in this article.

As a result of experience, it has been determined that in mild conditions it is possible to obtain targeted products with high selectivity.

**N-octane oxidation process**

The general method of catalytic oxidation of N-octane is described using the MnP4VP / MBAA model catalyst. Oxidation reactions were carried out in a stationary reactor with a volume of 15 ml. The oxygenation reaction was carried out in the presence of molecular O2 by adding 5.0 ml of pure n-alkane and 0.8 cm3 of catalyst to the reactor. The liquid phase in the reactor was mixed with an MS-5 magnetic mixer. The reaction mixture was carried out at a temperature of 303-383K and for 48 hours. The products were analyzed by gas chromatography HP-5column, Agilent 7890B chromatograph at a pressure of 5.41 psi (pound force per square inch) with a flow of carrier gas (H2 and N2) of 1.2 ml/min.

**The effect of the amount of catalysts**

The amount of Mn in the catalyst varies from 2% to 10%, and according to the results, the optimal concentration of manganese in the catalyst is ~ 5% wt. The best selectivity in the oxidation of N-octane was obtained when the amount of Mn in the complex was 5%. Thus, manganese concentration is an important factor in product selectivity and high yield.

**Kinetic studies**

The methodology of kinetic research was the same as in our previous work [15-17]. The kinetics of complex reactions of octane with oxygen oxidation was carried out by developed catalytic systems MnP4VP and MnP4VP / MBAA. It is important to select the optimal molar ratio for octane / oxygen. The experiments were carried out at atmospheric pressure in the temperature range of 303-383 K. The study of the kinetics of the octane oxidation reaction demonstrates stable catalytic activity and high selectivity compared to manganese-immobilized poly-4-vinylpyridine.

Changes in process parameters over time have been considered. To characterize the process, chemical reactions in stationary and non-stationary reactors were compared.

Since the course of the reaction at an arbitrarily selected point of the reactor is not characterized by stability, speed and time of reagents and product concentrations, the operating mode of the reactor is non-stationary. In other words, in this mode, the flow velocities at the outlet of the reactor depend on time. This change in performance is determined by two factors: the non-stationary mode and the change in the composition of the flow parameters at the inlet of the reactor.

As the catalyst changes its activity over time, there is a shift in the process parameters.
Oxidation reactions of octane (A) with oxygen (B) are non-stationary as all periodic processes. For example, reagents A and B are loaded into the reactor at the same time, and then the reaction mass is maintained over time. In this case, the concentration of A and B will change as the process continues due to the consumption and accumulation of reaction products over time.

Assume that reagent A is added to the reactor at the same time, and another oxidizing reagent B is added over time. In this case, A will be consumed over time and its concentration will decrease. The concentration of B will be constant, as its consumption in the reaction will be compensated in new parts by the supply of B. At the same time, the amount of reaction products will increase over time.

The positive or negative accumulation of matter or energy in the non-stationary reactor was evaluated. This type of periodic reactor is characterized by a positive accumulation of products and a negative accumulation (loss) of reagents. In the absence of heat exchange with the environment in the reactor in question, heat accumulation is observed due to an exothermic reaction. This causes the temperature in the system to rise by 3–5 K.

Stationary flow reactors are easier to model because their work is described by simpler equations. For example, in flow-mixing reactors, the reaction rate is characterized by algebraic equations. It is also easier to automate stationary processes.

The non-stationary process in the reactor complicates the description of the reactor and the control of its operation. Modeling was performed to estimate the non-stationary modes of processes occurring in the chemical reactors we considered.

Results and discussion

Application of catalyst

MnP4VP or MnP4VP/MBAA catalysts demonstrated long induction time (up to 72 hours) in the n-octane oxidation reaction under optimized reaction conditions (303–383°C, at atmospheric pressure).

Scheme shows the oxidation reaction of n-octane to the corresponding alcohols, aldehydes or ketones.

Table 1. Temperature $T = 313$ K, C$_8$H$_{18}$: O$_2$: manganese = 1: 3.38: 0.003 molar ratio in the presence of built-in and unbuilt metal-polymer catalysts of n-octane and the result of oxidation reaction at $t = 6$ s.

<table>
<thead>
<tr>
<th>№</th>
<th>The composition of the catalyst, wt. %</th>
<th>The conversion of n-octane, $\xi,$ %</th>
<th>The yield of the reaction products, $\omega,$ wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C$<em>8$H$</em>{18}$-1-ol</td>
<td>C$<em>8$H$</em>{18}$-2-ol</td>
</tr>
<tr>
<td>1</td>
<td>Mn (2%) P4VP *</td>
<td>9.1</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Mn (5%) P4VP *</td>
<td>11.3</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>Mn(2%)P4VP/MBAA**</td>
<td>20.2</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>Mn (5%)P4VP/MBAA**</td>
<td>46.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

$\xi,$ % – n-octane conversion, * – unbuilt metal-polymer catalyst; ** – built-in metal-polymer catalysts, P4VP = poly-4-vinylpyridine, MBAA = N, N’-methylene-bis-acrylamide.
OXIDATION OF n-OCTANE IN THE PRESENCE OF MANGANESE-POLYMER......

Samples were analyzed and calibrated by gas chromatography to determine the chemical compounds formed during the experiments and their quantity.

The highest selectivity of the main products (alcohols, ketones, aldehydes, Table 1) was obtained at 313 K at 38% (total conversion 19.8%).

Metal-polymer catalysts synthesized on the basis of poly-4-vinylpyridine containing 5.0% Mn²⁺ ion of n-octane octanone-4,3, octanone-2, octanol-4, octanol-3, octanol-2, octanol-1 showed high activity in acquisition.

It was found that under the same conditions, low conversions were obtained with 10% Mn²⁺ catalyst (P4VP/Mn (10%)) (Table 1). However, high conversion rates of 24.8% and 45.1% were observed using P4VP/Mn (5%) and P4VP/Mn (5%)/MBAA complex catalysts.

**Kinetics of octane oxidation**

The effect of the obtained MnP4VP and MnP4VP/MBAA catalysts on the oxidation of octane to oxygen was studied in a flow reactor. The reaction was performed in an octane/oxygen = 1:3.38 molar ratio. In the experiments, the temperature was changed between 303–383 K at atmospheric pressure, respectively. The reactor is filled with octane (5 ml) and MnP4VP or MnP4VP/MBAA catalyst. The molar ratio of octane to catalyst was 0.038:(0.0012–0.006). An MS-5 magnetic mixer is placed in the reactor.

The selection of the kinetic model and the effect of the reaction parameters on the output were carried out as in the previous article [17]. A sequential reaction consisting of two monomolecular stages is considered: S → X → P. Here S is the initial substrate, X is the intermediate product, P is the final product, k₁ and k₂ are the reaction rate constants. Let us consider the kinetics of this reaction based on the law of mass action. In this case, we can write a system of three differential equations for the rate of reactions

\[
\frac{dc}{dt} = -k_1 c_S
\]

\[
\frac{dc}{dt} = -k_1 c_S - k_2 c_X
\]

\[
\frac{dc}{dt} = k_2 c_X
\]

where \(c_S\), \(c_X\), \(c_P\) are the concentrations of the substances S, X, P, respectively.

In (1) the integration of the system of equations allows to determine the time dependence of the concentrations \(c_S\), \(c_X\), \(c_P\). Approximation shows that the \(c_S\) concentration of the initial S substrate decreases monotonically over time. The concentration of the intermediate product X increases before \(c_X\) reaches a maximum and then decreases. The concentration P of the final product increases monotonically with time \(c_P\).

\[
\xi(C_{8}H_{18}) = \frac{[C_{8}H_{18}\text{init}]-[C_{8}H_{18}\text{final}]}{[C_{8}H_{18}\text{init}]} \cdot 100\%
\]

The kinetic constant was determined according to the conversion of the initially taken octane

\[
\xi(t) = \frac{A_0 - A(t)}{A_0} , \xi \in [0,1]
\]

where \(A_0\) is the initial concentration of the initial octane, \(A(t)\) is the molar concentration of the octane at any value of \(t\) (time). Assume that the initial concentrations of the starting materials are the same \(A_0 = B_0\). Then for any value of \(t\) is \(A(t) = B(t)\). Given this, the kinetic equation of the original substance can be written as follows:

\[
\frac{dA}{dt} = -kAB = kA^2, A = A(t), A(0) = A_0 = \text{const.}
\]

Equation (4) can be integrated and written as follows

\[
A(t) = \frac{A_0}{1+A_0kt}.
\]

From this equation (5) we can write the following equation for conversion

\[
\xi = \frac{A_0kt}{1+A_0kt}.
\]

The kinetic constant can be found from Equation (6)

\[
\xi = \frac{\xi_1}{1+\xi A_0kt}.
\]

Based on Equation (7) and the experimental results, the calculated values of the rate constant of oxidation of n-octane to alcohols in the presence of molecular oxygen are given in Table 2. The study of the kinetics of the catalytic oxidation reaction of n-octane shows that polymer-based, manganese-containing catalysts exhibit activity and selectivity.


Table 2. Calculated values of the rate constant of oxidation of n-octane to alcohols in the presence of molecular oxygen.

<table>
<thead>
<tr>
<th>T, K</th>
<th>Q, mol/h</th>
<th>t, min</th>
<th>(A_0, \text{mol/m}^3)</th>
<th>(\xi, %) (C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;)</th>
<th>(k \times 10^3), m&lt;sup&gt;3&lt;/sup&gt;/mol·min&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.0308</td>
<td>360</td>
<td>30</td>
<td>0.50</td>
<td>9.26</td>
</tr>
<tr>
<td>313</td>
<td>0.0297</td>
<td>370</td>
<td>27</td>
<td>0.55</td>
<td>1.22</td>
</tr>
<tr>
<td>323</td>
<td>0.0287</td>
<td>379</td>
<td>25</td>
<td>0.60</td>
<td>1.60</td>
</tr>
<tr>
<td>333</td>
<td>0.0275</td>
<td>387</td>
<td>19</td>
<td>0.67</td>
<td>2.81</td>
</tr>
<tr>
<td>343</td>
<td>0.0264</td>
<td>396</td>
<td>17</td>
<td>0.70</td>
<td>3.52</td>
</tr>
<tr>
<td>353</td>
<td>0.0255</td>
<td>407</td>
<td>15</td>
<td>0.75</td>
<td>4.88</td>
</tr>
<tr>
<td>363</td>
<td>0.0244</td>
<td>417</td>
<td>13</td>
<td>0.77</td>
<td>6.13</td>
</tr>
<tr>
<td>373</td>
<td>0.0232</td>
<td>430</td>
<td>12</td>
<td>0.79</td>
<td>7.29</td>
</tr>
<tr>
<td>383</td>
<td>0.0221</td>
<td>437</td>
<td>11</td>
<td>0.80</td>
<td>8.36</td>
</tr>
</tbody>
</table>

Conclusion

Built and unbuilt (MnP4VP/MBAA and MnP4VP) complex catalysts were synthesized and used to oxidize octane with oxygen. These complex catalysts have been tested for selective oxidation of n-octane in a stationary reactor. Optimal conditions (303–383 K, atm pressure, within 7 hours) were obtained for good selectivity for the main n-octane products. Experiments show that these oxidation reactions proceed more rapidly through the action of manganese ions in the catalyst. The studied catalysts were used for a reaction time of 72 hours. A kinetic model was selected for the oxidation of n-octane in the presence of a manganese-polymer catalyst. Taking into account the kinetic model, it is possible to estimate the effect of the composition of the manganese-containing polymer catalyst, the ratio of the initial components, temperature, contact time of the components on the reaction rate constant and conversion. The calculated value of the rate constant of the oxidation reaction of n-octane satisfactorily describes the experimental data. Optimal results were obtained with high conversion of n-octane in a mixture with oxygen (for example, conversion at 383 K \(\xi = 0.75\)). Based on the calculated values of the rate constant of the oxidation reaction, it is clear that the complex reaction is gradual.

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Conflict of interest

The authors declare that they have no conflict of interest.

References


MANQAN-POLİMƏR KATALİZATORU İŞTİRAKINDA n-OKTANIN ÖKSİLDİƏLMƏSİ VƏ UYĞUN KINETİK MODELİNİN SEÇİLMƏSİ

A.F.İsazada, Ü.A.Mammədova, M.M.Əsadov, N.A.Zeynalov, D.B.Tağiyev
Müxtəlif kiçik faizində (5 və 10 wt%) poli(4-vinilpiridindən) şəxsiyyətindən n-oktanın oksidlaşması aparıldı. Müəyyən etdikdə ki, polimər oksidlaşmış manqan tərkibli katalizatorlar, analoji homogen tərkibli katalizatorlarla müqayisədə n-oktanın oksidlaşmasına də daha çox aktivlik göstərirdilər. Manqan-polimer katalizatoru işıqta kadınca n-oktannın oksidlaşması üçün kinetik model və hesablamada sənət tələblərinin seçilmədi. Kinetik modeli nəzərə alarə, tərkibində nəyanı olan polimer katalizatorunun işıqta kadına n-oktannın oksidlaşması reaksiyasının sürət sabiti hesablanırdı. Molekulyar oksigen işıqta kadına n-oktannın oksidlaşması zamanı yüksək konversiya alədi edildi.

Açar sözər: n-oktan, manqan-polimer katalizator, oksidlaşmış, kinetika.

OKISLENIE n-OKTANA V PRISUSTVIII MARGANEÇ-POLİMERNOGO KATALIZATORA I VYBORY SOOTVETSTVUJUJSHIYI KINETICHESKOJI MODELII

A.F.İsazada, Ü.A.Мамедова, М.М.Асадов, Н.А.Зейналов, Д.Б.Тагиев
Окисление n-октана проводили в стационарном реакторе, с использованием иммобилизованных наночастиц марганца в различных массовых процентах (5 и 10 мас.% на поли(4-винилпирдине). Установлено, что иммобилизованные в полимер марганецсодержащие катализаторы более активны в окислении n-октана, чем аналогичные гомогенные катализаторы. Для расчета выбрана кинетическая модель и уравнение расчета процесса окисления n-октана в присутствии марганец-полимерного катализатора. С учетом кинетической модели рассчитан константа скорости указанного процесса. Получена высокая конверсия в реакции окисления n-октана молекулярным кислородом.

Ключевые слова: n-октан, марганец-полимерный катализатор, окисление, кинетика.