

## CATALYTIC OXIDATION OF N-HEXANE ON IMMOBILIZED MANGANESE-CONTAINING POLYMER CATALYST

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### ABSTRACT

Novel catalysts, consisting of manganese-containing complex with immobilized quaternized non-crosslinked and cross-linked polymer poly-4-vinylpyridine (P4VP) which was used as a carrier, have been obtained. These catalysts were tested for liquid phase oxidation reaction of *n*-hexane. The studies were carried out in the temperature range 298 K - 408 K, molar ratios of hexane: oxygen = 1:3.38, and atmospheric pressure. As a result of the catalytic oxidation of *n*-hexane, the following products were obtained: hexan-1-ol, hexan-2-ol, hexan-3-ol, hexanal and hexanone. It was shown that non-crosslinked and crosslinked *N, N'*-methylene-bis-acrylamide (MBAA) manganese-containing (5 wt. %) the polymer catalyst MnP4VP exhibits high activity in the oxidation reaction of *n*-hexane. The reaction rate constant for the oxidation of *n*-hexane by oxygen to hexan-1-ol, hexan-2-ol, hexan-3-ol, proceeding with the participation of non-crosslinked and crosslinked MnP4VP catalysts at 303-383 K has been determined.

**Keywords:** *n*-hexane, immobilization, manganese-containing polymer, catalyst, hexan-1-ol, hexan-2-ol, hexan-3-ol.

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### INTRODUCTION

The catalytic oxidation is a key technology to convert raw materials into useful chemicals with a high degree of oxidation, such as alcohols, carbonyl compounds, epoxides, etc. [1, 2]. Oxygen is used as the main oxidizing agent in the chemical industry for oxidation processes due to economic and environmental reasons [3, 4]. The advance of such processes primarily depends on the use of metal-containing catalysts to increase both the reaction rate and selectivity of oxidation products [3 - 6].

The catalytic complexes of transition metals are used, for instance, for the selective oxidation of linear alkanes by means of molecular oxygen. Formation of highly active free and coordinated radicals leads to change in the structure of the catalytic complex and the properties of transition metal ions during the catalytic oxidation of hydrocarbons [4 - 6]. The number of oxidative reactions catalyzed by coordination compounds of transition metals has expanded significantly. In

manganese-containing compounds, Mn can exist in various oxidation states. Therefore, manganese compounds exhibit different reactivity in reactions, in particular with organic substances [4 - 6]. The manganese-containing catalysts are proven to be effective catalysts for the oxidation of alkanes, alcohols, aldehydes and amines [7 - 9].

Punniyamurthy et al. shown that the use of molecular oxygen as a source of an oxygen atom and the formation of several neutral by-products make catalytic oxidation an extremely desirable, economically viable, and environmentally acceptable reaction [7]. The progress achieved in oxidation of a carbon-carbon double bond to carbonyl compounds. It has been shown that achieved progress in the oxidation of C-H alkanes is impressive, and this grants access to rich raw materials for branches of chemical industries. The alkane's oxidation has been successfully carried out using environmentally friendly catalysts that can be recycled. This aspect is also important for the chemical industry in terms of environmental protection.

The review of Ishii et al. showed that innovation in the process of hydrocarbon oxidation under mild conditions was achieved using N-hydroxyphthalimide (NHPI) as a key compound [8]. Alkanes have been successfully oxidized by O<sub>2</sub> or air to oxygen-containing compounds such as alcohols, ketones and dicarboxylic acids. The process was carried out in the presence of an NHPI catalyst system and a transition metal such as Co or Mn. With the participation of the NHPI oxidation of alkylbenzenes by oxygen takes place at normal temperature and gas pressure. The xylenes and methylpyridines have also been converted to phthalic acids and pyridinecarboxylic acids, respectively, in high yields. Epoxidation of alkenes using hydroperoxides or H<sub>2</sub>O<sub>2</sub>, generated in situ from hydrocarbons or alcohols and O<sub>2</sub> in the presence of NHPI, has been demonstrated. The catalytic carboxylation of alkanes has been achieved by using CO and O<sub>2</sub> in the presence of the NHPI. The reactions of alkanes with NO<sub>2</sub> and SO<sub>2</sub> catalyzed by the NHPI provide production of nitroalkanes and sulfonic acids, respectively.

The review of Khusnutdinov et al. summarizes data on the use of manganese compounds as catalysts for the oxidation of alkanes, alcohols, aldehydes and amines [9]. It was shown that Mn and manganese compounds (both salts and complexes) exhibit catalytic activity with respect to various organic compounds. It was indicated that novel catalysts for the large-scale synthesis of important compounds will be developed based on manganese compounds, including those covering organic and inorganic matrices.

In view of the foregoing, the study of the catalytic oxidation of normal hexane (n-C<sub>6</sub>H<sub>14</sub>) is of practical interest. C<sub>6</sub>H<sub>14</sub> is the valuable reagent that can be used in production of substances important for industry. So, hexane can be used in production of substances which are important for industry and it is also a good organic solvent. In addition, hexane is used as extracting solvent for vegetable oils. Derivatives of the C<sub>6</sub>H<sub>14</sub> are used as additives to improve fuel characteristics. Focusing on kinetics of reaction of hydrocarbons' oxidation, manganese-containing polymer catalysts also deserve attention. The literature data on the catalytic oxidation of alkanes with the participation of similar catalysts are scattered and contradictory [10].

The ways of formation of polymer-immobilized nano-size particles of the metals directly in the polymer medium have been considered in work [11 - 15]. It was

shown that compositions thus obtained are characterized not only by the most uniform distribution of these particles in the volume, but also by the strong chemical interaction between the components.

In view of the foregoing, the search for new effective catalysts for the liquid phase oxidation of n-hexane by oxygen was the task of this work.

## EXPERIMENTAL

In order to select the optimal conditions for the oxidation of hexane, a manganese-containing polymer catalyst was prepared and used. The "c.f.a." brand n-hexane was taken as an initial component. Samples of the catalysts were prepared immediately before measurements. To achieve high swelling of the polymer in a solution of H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH = 1:1, the polymer was quaternized [16, 17]. In the experiments used quaternized non cross-linked and cross-linked polymer poly-4-vinylpyridine (P4VP).

The polymer was quaternized with benzyl chloride. Solutions of the polymer with a concentration of 1 g / 100 ml were heated to 333 K and at this temperature benzyl chloride in amounts of 10 % - 60 % by weight of dissolved polymer was added to the solution. After 6 hours of stirring, P4VP samples quaternized to various degrees were obtained. The quaternized polymer was precipitated with 0.1 N NH<sub>4</sub>OH solution, washed with diethyl ether from excess benzyl chloride and dried in vacuum 10<sup>-2</sup> Pa at 313 K to constant weight. To obtain immobilized metal- polymer complexes (MPC), a MnCl<sub>2</sub>×4H<sub>2</sub>O solution was added into ethanol solutions of quaternized P4VP samples. Chemical precipitation of manganese was carried out from aqueous solutions according to the known method [18].

To restore Mn (II), the redox agent NaBH<sub>4</sub> was added to the obtained solutions, taking into account the amount of manganese in the composition of the taken salt. Then, 0.1 N NH<sub>4</sub>OH was added to the solution until complete MPC precipitation. The precipitated MnP4VP complexes were washed with water to remove excess Mn (II) cations and dried in a vacuum of 10<sup>-2</sup> Pa at a temperature of 313 K. The completeness of manganese reduction was monitored visually. Therefore, the use of a potentiometric method for controlling the reduction of metal was not necessary [19].

The immobilization of the polymer [11 - 15] P4VP

with manganese was carried out in two ways: 1) adding a solution of manganese salt to a cross-linking agent in an ethanolic solution of P4VP; 2) adding a solution of the Mn salt after the crosslinking agent MBAA in the ethanolic solution of P4VP.

To obtain a crosslinked MnP4VP/MBAA catalyst, quaternized P4VP samples were crushed and dissolved in ethanol, 8 % - 10 % solutions were prepared, and crosslinking agent MBAA was added to the solutions. Grinding and mixing were carried out for 1 - 3 min in a ball mill with a ball diameter of 0.8 cm. The particle size of the crushed mixture was in the range of 0.05 mm - 0.1 mm. Tablets were pressed with a diameter of 8 mm and a thickness of 0.2 mm - 0.4 mm from a mixture of MnP4VP and MBAA. These tablets were heated for 2 - 3 hours in evacuated to  $10^{-2}$  Pa quartz ampoules at 393 K - 403 K.

To determine the properties of the prepared catalysts, the following methods were used: X-ray phase analysis (XRD; D2-Phaser Bruker diffractometer), IR spectroscopic analysis (FTIR spectroscopy Nicoletisio VSA), scanning electron microscopy (SEM and EDS on Sigma VP. Carl Zeiss Jena).

The properties of the obtained catalyst samples MnP4VP and MnP4VP/MBAA were studied in the oxidation reaction of n-hexane by oxygen in a laboratory stationary reactor in a variable temperature regime (the reaction temperature was varied in different experiments). The reaction reactor contained a housing with a bottom, in which a mixing device was placed, a charge catalyst in the form of fine particles and hexane. The reactor also has fittings for introducing oxygen and outputting reaction products.

The reaction was carried out at molar ratios of oxygen/hexane = 3.38. The temperature in different experiments varied within the range of  $T = 298$  K - 383 K. Hexane in an amount of 5 mL and the catalyst MnP4VP or MnP4VP/MBAA in an amount of  $0.8 \text{ cm}^3$  were loaded into the reactor. The molar ratio of hexane to manganese contained in the polymer was 0.038:(0.0012-0.006). The reactor was placed on a magnetic stirrer brand "MS-5" with heating. The heating temperature was regulated by a contact thermometer. The identification of the obtained data was carried out on the Agilent 7890B gas chromatograph with column HP-5 with a gas carrier velocity ( $\text{H}_2$  and  $\text{N}_2$ ) of  $1.2 \text{ mL min}^{-1}$  and a pressure of 5.41 psi (pound-force per square inch).

The kinetics of the catalytic oxidation of hexane to the target products of alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol) was carried out in a flow reactor in the form of a tube of constant cross section with an unchanged volume, setting a constant flow of the initial reacting substances [20]. Prior to the start of the process, MnP4VP or MnP4VP/MBAA catalysts were loaded into the reactor in an amount of  $0.8 \text{ cm}^3$ . In different experiments, the temperature varied within the range  $T = 303$  K - 383 K. In this case, after a while, the stationary mode is established. Here, as in static conditions, the temperature can vary both in time and in volume. The temperature was kept constant throughout the reactor volume and throughout the experiment. The amounts of heat released or absorbed were small and there were no temperature gradients. The kinetics of oxidation of n-hexane by oxygen into alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol) was studied at a constant flow of reactants after establishment of stationarity in the reactor, taking into account the residence time of the mixture [20].

In the process of oxidation of n-hexane into various products, yield, selectivity and conversion were determined experimentally by a known technique [3].

## RESULTS AND DISCUSSION

IR spectroscopic method was used to determine the number of functional pyridine groups in the polymer that entered the quaternization reaction [21]. IR spectra were taken for vinylpyridine homopolymer, its quaternary salt homopolymer with benzyl chloride, as well as for homopolymer mixtures in which the ratio of these components was changed from 1:10 to 10:1. IR spectra of samples of vinylpyridine P4VP homopolymer had bands of valence oscillations at  $1598 \text{ cm}^{-1}$ , belonging to free pyridine groups (Fig. 1a). For the quaternized pyridine group, the vibrational band in the IR spectra corresponds to a wavelength of  $1637 \text{ cm}^{-1}$ , which is absent in the P4VP spectra (Fig. 1b). Using the IR spectral properties of the catalyst samples, the optical density and concentration of quaternized pyridine groups in the polymer were determined; the concentration of these groups is 70 % - 90 % of the amount of taken benzyl chloride.

Phase composition of the non-crosslinked P4VP homopolymer and the crosslinked MPC was determined by XRD. The P4VP that was used has an amorphous structure (Fig. 2a), and after MBAA crosslinking it, the degree of crystallinity increases and diffraction reflexes

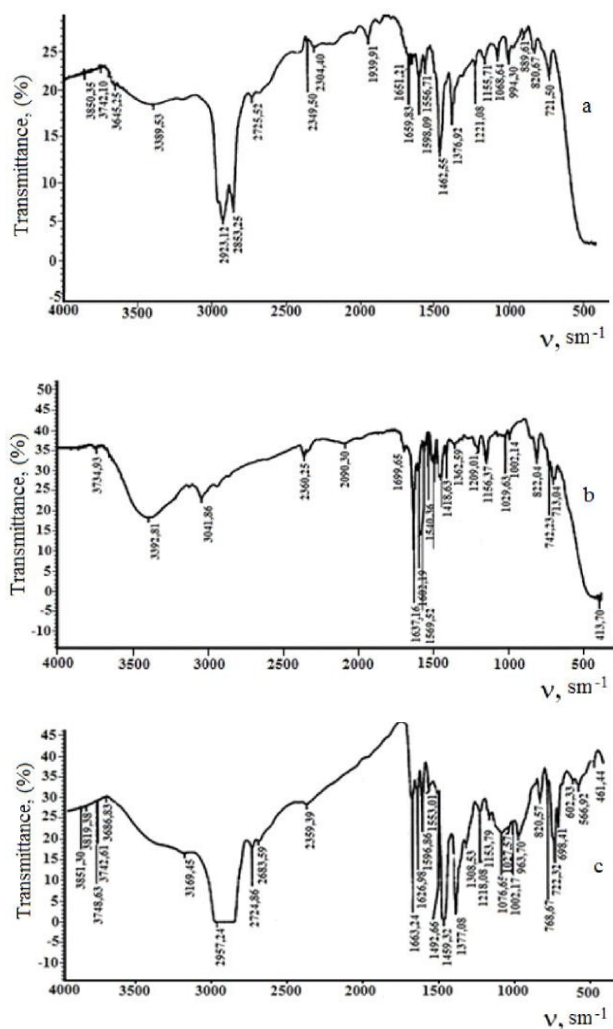


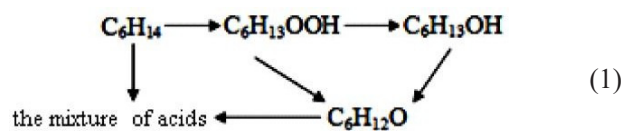
Fig. 1. IR spectra: a) poly-4-vinylpyridine (P4VP); b) quaternary salt of poly-4-vinylpyridine (P4VP); c) manganese-containing polymer complex of poly-4-vinylpyridine (MPC MnP4VP).

appear, characteristic of pure manganese (Fig. 2b). This, apparently, can be explained by the hardening of the polymer structure as a result of the immobilization of manganese and the formation of an intermacromolecular complex [13 - 17].

The use of the redox agent  $\text{NaBH}_4$  in the  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  solution of quaternized MPC samples leads to the reduction of Mn (II) in the presence of the P4VP polymer. Due to reduced manganese, pores are formed on the surface of the obtained MnP4VP complex, which have the shape of a ball with a diameter of 23.5  $\mu\text{m}$  - 236  $\mu\text{m}$  (Fig. 3a). Fig. 3 (b) shows a typical energy dispersive X-ray (EDR) spectrum of a sample of a manganese-containing polymer complex poly-4-vinylpyridine (MPC MnP4VP).

The EDR spectrum made it possible to quantify the concentration of manganese in the sample.

The catalytic oxidation reaction of n-hexane was studied in the above-mentioned conditions in the presence of quaternized Mn/P4VP and MnP4VP/MBAA polymeric catalysts Mn/P4VP. Taking into account the experimental data (Table 1) and in accordance with [23], the reaction of hexane oxidation to various products can be represented by the scheme (1):



It was found that samples of manganese-containing catalysts based on cross-linked and non-crosslinked P4VP exhibit a relatively high activity in the reaction of oxidation of hexane to various products in the temperature range 298 K - 408 K, molar ratios of oxygen/hexane = 3.38, and at atmospheric pressure (scheme (1)).

The characteristics (yield, selectivity, conversion) of hexane oxidation to various products depend on the concentration of manganese, temperature, and the molar ratio of oxygen/hexane reagents.

Table 1 shows that MnP4VP and MnP4VP/MBAA catalysts containing 2 wt. % manganese are selective

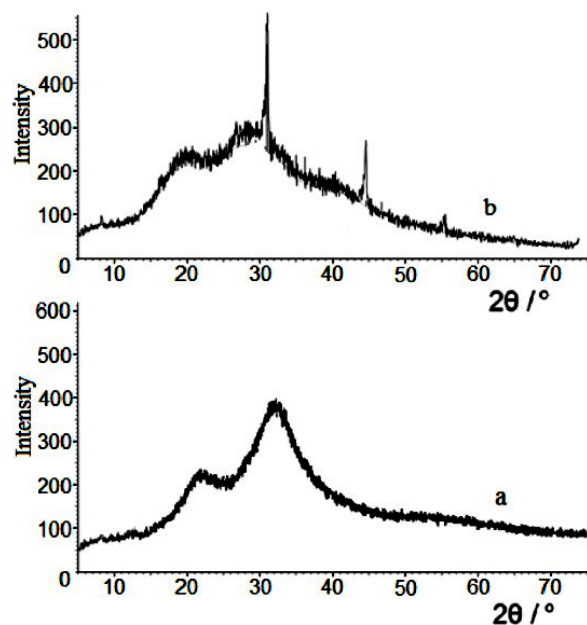


Fig. 2. Diffractograms: a) the original polymer poly-4-vinylpyridine (P4VP); b) manganese-containing polymer complex poly-4-vinylpyridine (MPC MnP4VP).

Table 1. The results of testing of non-crosslinked and cross-linked metal-polymer catalysts in the oxidation reaction of n-hexane at  $T = 333$  K, molar ratio of reagents  $C_6H_{14}:O_2$ :manganese = 1:3.38:0.003 and  $t = 6$  h.

№	The composition of the catalyst, wt. %	The conversion of hexane, $\xi$ , %	The yield of the reaction products, $\omega$ , wt. %				
			hexan-1-ol	hexan-2-ol	hexan-3-ol	hexanal	hexanone
1.	P4VP	-	-	-	-	-	-
2.	The quaternized P4VP	-	-	-	-	-	-
3.	Mn (2%) P4VP*	21.6	-	16.4	0.5	3.4	1.3
4.	Mn (5%) P4VP*	29.9	0.5	3.4	1.6	13.1	11.4
5.	Mn (10%) P4VP*	19.3	-	1.3	0.3	9.7	8
6.	Mn (2%) P4VP /MBAA <sup>xx</sup>	40.5	-	25.7	0.9	10.7	3.2
7.	Mn (5%) P4VP /MBAA <sup>**</sup>	50.1	1.2	9.4	1.7	20.5	17.3
8.	Mn (10%) P4VP/MBAA <sup>**</sup>	34.8	0.2	6.4	0.6	15.9	11.7

\*-non-crosslinked; \*\*-crosslinked metal-polymer catalysts, P4VP – poly-4-vinylpyridine, MBAA- *N,N'*-methylene-bis-acrylamide

for the formation of hexan-2-ol. When the content (MnP4VP/MBAA and MnP4VP) of Mn 2 wt. % the catalytic system is characterized by a more uniform distribution of manganese particles on the carrier sur-

face. This apparently can be linked to improvement of reaction efficiency and maximum yield of hexan-2-ol. To obtain other alcohols, carbonyl compounds, hexanone and hexanal (scheme (1)), the optimal concentration of manganese in the catalyst was  $\sim 5$  wt. %.

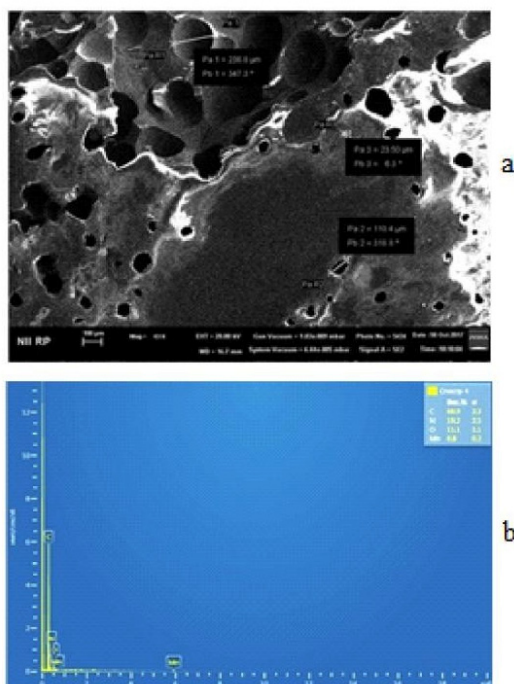


Fig. 3. SEM image (a) and energy dispersive X-ray spectrum (b) of the surface of the manganese-containing polymer complex poly-4-vinylpyridine (MPC MnP4VP).

Fig. 4 a, b show the temperature dependences of the yield of products ( $\omega$ , wt. %) of hexane oxidation by oxygen with the participation of non-crosslinked Mn-P4VP (fig. 4a) and crosslinked MnP4VP/MBAA (fig. 4b) catalysts. The maximum yield of products (hexanal and hexanone) is observed at a temperature of 383 K and a molar ratio of oxygen/hexane = 3.38. At a temperature of 353 K and above (383 K), a mixture of acetic and propionic acids is formed (2 % - 4 %). The yield of hexan-1-ol, hexan-2-ol, hexan-3-ol significantly decreases as a result of their conversion to products of deep oxidation (hexanal, hexanone and a mixture of acids).

Fig. 5 a, b show the dependence of the conversion on temperature and time with the participation of the non-crosslinked MnP4VP (1) and crosslinked MnP4VP/MBAA (2) catalysts. With increasing temperature and reaction time of the oxidation of hexane, the conversion increases. At relatively high temperatures, the oxidation of hexane is accompanied by the formation of a mixture of acids.

The indicated in scheme (1) the hexane oxidation reactions by oxygen proceed under the same conditions and the overall (effective) reaction rate constants ( $k_e$ ) are

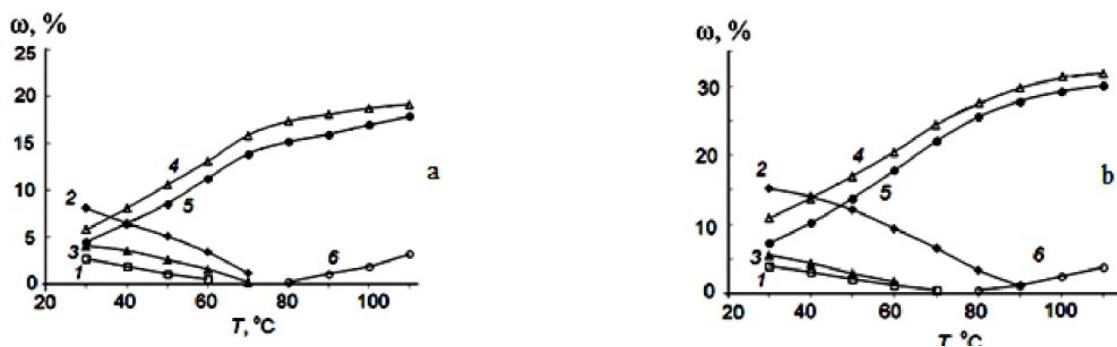
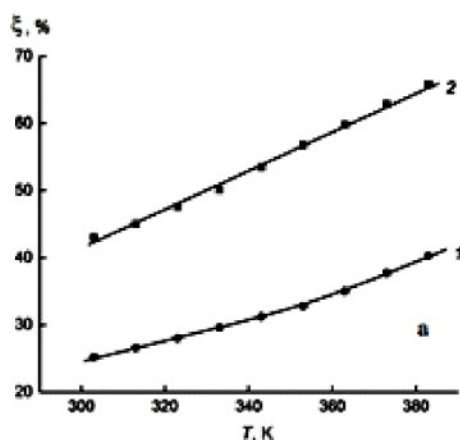


Fig. 4. The dependence of the yield of products ( $\omega$ , %) of the reaction of oxidation of hexane by oxygen on the temperature with the participation of catalysts of non-crosslinked manganese-containing poly-4-vinylpyridine (MnP4VP) (a) and crosslinked with the N,N'-methylene-bis-acrylamide manganese-containing poly-4-vinylpyridine (MnP4VP/MBAA) (b) (Mn content in the polymer (5 wt.%)) (time of the experiment  $t = 6$  h): 1 - hexan-1-ol; 2 - hexan-2-ol; 3 - hexan-3-ol; 4-hexanal; 5-hexanon, 6-the mixture of acetic and propionic acids.

calculated for them. A comparative analysis of the calculation of the reaction rate constant indicates a spread in the values of  $\rho$ . A direct dependence of the rate of the studied brutto-reaction (scheme (1)) of the oxidation of n-hexane by oxygen to the target products of alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol) on temperature is observed. Such reactions proceed through an intermediate complex [23 - 25], which then reacts with the second component.

The constant  $k$  of reactions was determined by the conversion of the initial substances  $\xi$  [3, 26] by the ratio:

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



$A_0$  is the initial concentration of the starting substance,  $(t)$  is the molar concentration of the corresponding substance at any given values of  $t$  (time) of the reaction. If the initial concentrations of the starting substances are the same  $A_0 = B_0$ , then for any values of  $t$  we have  $A(t) = B(t)$ . Then the kinetic equation of the starting material for the reaction can be written:

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

When the equation (2) is integrated, it was obtained:

$$(t) = B(t) = \frac{A_0}{1 + A_0kt} \quad (3)$$

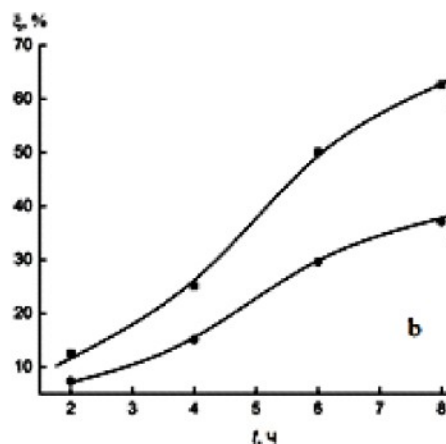


Fig. 5. The dependence of the conversion of ( $\xi$ ) n-hexane on temperature (a) and time (b) on catalysts in the reaction of hexane oxidation: non-crosslinked manganese-containing poly-4-vinylpyridine (MnP4VP) (1), crosslinked with the N, N'-methylene-bis-acrylamide manganese-containing poly-4-vinylpyridine (MnP4VP/MBAA) (2) (Mn content in the polymer (5 wt. %)).

Table 2. Overall (effective) rate constants of the oxidation reaction of n-hexane by oxygen to alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol), flowing with the participation of a quaternized non-crosslinked manganese-containing polymer catalyst (poly-4- vinylpyridine-MnP4VP).

T, K	Q, mol h <sup>-1</sup>	t, min	A <sub>0</sub> , mol m <sup>-3</sup>	ξ	k <sub>e</sub> × 10 <sup>5</sup> , m <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>
303	0.0560	340	35	0.25	2.80
313	0.0245	350	35	0.27	3.02
323	0.0243	355	34	0.28	3.22
333	0.0337	360	35	0.30	3.40
343	0.0228	370	34	0.31	3.57
353	0.0221	390	35	0.33	3.61
363	0.0212	400	34	0.35	3.96
373	0.0200	410	34	0.38	4.39
383	0.0180	415	34	0.40	4.72

Q – volumetric flow rate of the initial mixture at the inlet to the reactor; t – the residence time of the mixture in the reactor.

Table 3. Overall (effective) rate constants of the oxidation reaction of n-hexane by oxygen to alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol), flowing with the participation of a quaternized crosslinked with the N, N' - methylene-bis-acrylamide manganese-containing polymer catalyst (poly-4-vinylpyridine-MnP4VP).

T, K	Q, mol h <sup>-1</sup>	t, min	A <sub>0</sub> , mol m <sup>-3</sup>	ξ	k <sub>e</sub> × 10 <sup>5</sup> , m <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>
303	0.018	340	35	0.43	6.34
313	0.017	350	35	0.45	6.68
323	0.015	355	35	0.48	7.43
333	0.014	360	36	0.50	7.72
343	0.012	370	35	0.54	9.06
353	0.010	390	35	0.57	9.71
363	0.018	400	34	0.60	11.03
373	0.017	410	34	0.63	12.21
383	0.018	415	34	0.66	13.76

Starting from equation (3) we can describe:

$$\xi = \frac{A_0 kt}{1 + A_0 kt} \quad (4)$$

Hence, the reaction rate constant is determined by the relation:

$$k = \frac{\xi}{1 - \xi} \frac{1}{A_0 t} \quad (5)$$

The reactions of the oxidation of n-hexane by oxygen to the target products of alcohols (hexan-1-ol, hexan-

2-ol, hexan-3-ol) was carried out with the participation of quaternized, non-crosslinked and crosslinked manganese-containing catalysts MnP4VP at 303-383 K. Based on the experimental data, the overall (effective) rate constant was calculated using the formula (5).

The results are shown in Table 2 and 3. In tables t characterizes the residence time of the mixture (hexane + oxygen) after establishing stationarity in the reactor.

The time and temperature dependences of the properties of the proceeding reactions of hexane oxidation to produce various products (see scheme (1)) are similar to each other.

## CONCLUSIONS

Quaternized non-crosslinked and crosslinked manganese-containing polymeric (based on poly-4-vinylpyridine (P4VP) and N, N'-methylene-bis-acrylamide (MBAA)) catalytic systems for the oxidation of n-hexane to obtain hexan-1-ol, hexan-2-ol, hexan-3-ol, hexanal and hexanone have been synthesized. It has been established that manganese-containing complexes formed in the catalytic reaction are responsible for the oxidation of hexane by oxygen. It has been found that at 303 K the selectivity for C<sub>6</sub>H<sub>13</sub>OH (hexan-1-ol, hexan-2-ol, hexan-3-ol) is 24.8 %, and the conversion of hexane, depending on the composition of the catalytic system, is 43 %. The studied manganese-containing complexes can significantly increase the rate of the oxidation reaction of alkanes, which is important for organic synthesis. Overall (effective) rate constants of the oxidation reaction of n-hexane by oxygen to alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol) proceeding with the participation of quaternized non-crosslinked and crosslinked manganese-containing polymeric (poly-4-vinylpyridine-MnP4VP) catalysts at 303-383 K have been calculated.

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