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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OXIDATION OF n-C_6-C_8 ALKANES WITH THE PARTICIPATION OF NANOSCALE MANGANESE CATALYSTS IMMOBILIZED ON POLYMERS

Speciality: 2316.01 – "Chemical kinetics and catalysis"

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF THE WORK

The actuality and usage rate of the topic. The selective catalytic oxidation of saturated hydrocarbons is one of the important and rapidly developing fields of modern chemistry and catalysis. These processes form the scientific basis for the production of alcohols, aldehydes, and ketones, which are of great importance for the petrochemical industry, organic synthesis, the production of polymer materials, and other areas of chemistry. The direct oxidation of hydrocarbons allows for a reduction in the number of technological stages, an increase in the economic efficiency of processes, and the creation of more environmentally safe technologies[1].

However, the high chemical stability of n-alkanes significantly complicates their selective oxidation. The high strength of the C-H bonds in the molecule and the absence of functional groups are among the main factors that limit the reaction from being carried out under mild conditions. On the other hand, the initial oxidation products are more reactive than the starting n-alkanes and are therefore easily subjected to further conversions, which leads to a decrease in the selective yield of the target products. Therefore, the development of new catalytic systems capable of activating both the hydrocarbon molecule and molecular oxygen is considered one of the pressing problems in modern catalysis[2].

In recent years, interest in catalytic systems based on the immobilization of transition metal complexes on polymer carriers has increased significantly[3,4]. Such systems combine the high activity of

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[1] Xiaohui G., Yuting B., Hao Z., Xingyi W. Catalytic oxidation of n-decane, n-hexane, and propane over Pt/CeO_2 catalysts // ACS Omega, 2023, v.8, -p. 6791−6800

[2] Farook, A. Oxidation of n-heptane over functionalised chromium/silver bimetallic heterogeneous catalyst / A. Farook, C.Thiam-Seng, A. Ramasanthiran // Journal of Physical Science. – 2013. V.24, №1, – p.51–59

[3] Chen, S., Metal coordination center mediated microenvironment regulation of cobalt sites on poly(ionic liquid)s enhance selective oxidation of cyclohexane conversion / Chen, S., He, B., Li, Y. [et al.] // Chemical Engineering Journal, -2024. V.488, 150865

[4] Джардималиева, Г.И. Полимер-иммобилизованные кластеры и

homogeneous catalysts with the technological advantages of heterogeneous catalysts. The embedding of active centers in a polymer matrix increases their stability, facilitates the separation of the catalyst from the reaction medium, and expands its opportunities for reuse. However, the relationship between the structure of the polymer matrix and catalytic activity, the nature of the active centers, and their mechanism of action is still not well understood.

In this regard, the synthesis of manganese-containing polymer catalysts, the study of their physicochemical properties, and the application of the laws governing the selective catalytic oxidation of n-hexane, n-heptane, and n-octane with atmospheric oxygen using these catalysts are of significant scientific interest. Determining the effect of temperature, catalyst composition, metal amount, and substrate nature on the process's rate, selectivity, and catalyst stability allows for a deeper understanding of the catalytic oxidation mechanism and the development of new, highly efficient catalytic systems.

Thus, the development of manganese-based polymer catalysts for the selective catalytic oxidation of n-hexane, n-heptane, and n-octane with oxygen in air under mild conditions, the study of their catalytic properties, the nature of their active centers, and the kinetic laws of the process is of significant scientific and practical importance, both for fundamental chemistry and for applied catalysis.

Object and subject of the research. Manganese-based metal-polymer catalytic systems on a poly-4-vinylpyridine support for the oxidation of n-alkanes (n-C_6-C_8) under mild conditions were the object of the study, while the subject of the study was the synthesis of these systems and the investigation of their catalytic properties in the aforementioned reactions.

Aim and objectives of the study. The creation of immobilized metal-polymer catalysts based on poly-4-vinylpyridine and manganese compounds, the investigation of their catalytic properties in the liquid-phase oxidation reactions of n-alkanes (n-C_6-C_8) with atmospheric oxygen, and the study of the kinetic laws and selection of the selective

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наночастицы металлов в катализе / Г.И.Джардималиева, А.К.Жармагамбетова, С.Е.Кудайбергенов // Кинетика И Катализ, – 2020. – Т. 61, № 2. – С. 195–224

catalytic oxidation mechanism.

To achieve the research objective, the following tasks were set:

- Synthesis of metal-polymer catalysts immobilized on a poly-4-vinylpyridine and manganese complex base;
- Investigation of the physicochemical properties of the obtained catalysts using modern analytical methods;
- Study of the catalytic activity of the developed catalysts in the selective oxidation reactions of n-hexane, n-heptane, and n-octane with oxygen in air;
- Determining the effect of temperature, manganese content, reaction time, and other factors on the catalytic oxidation process;
- Investigating the kinetics of the process, determining reaction orders and activation energy;
- Investigation of the stability of the catalysts and their potential for reuse;
- Proposal of a coordination-controlled radical mechanism for the selective catalytic oxidation of n-alkanes (n-C_6–C_8) involving immobilized metal-polymer catalysts, based on experimental results.

To achieve the research objective, the following tasks were set:

- Synthesis of metal-polymer catalysts immobilized on the basis of poly-4-vinylpyridine and manganese compounds;
- Investigation of the physicochemical properties of the obtained catalysts using modern analytical methods;
- Investigation of the catalytic activity of the developed catalysts in the selective oxidation reactions of n-hexane, n-heptane, and n-octane with oxygen in air;
- Determining the effect of temperature, manganese amount, reaction time, and other factors on the catalytic oxidation process;
- Studying the kinetic laws of the process, determining the reaction orders and activation energy;
- Investigation of the stability of catalysts and their potential for reuse;
- Proposal of a coordination-controlled radical mechanism for the selective catalytic oxidation of n-alkanes (n-C_6–C_8) involving immobilized metal-polymer catalysts, based on experimental results.

Research methods. The following physicochemical methods

were used to investigate the morphological and catalytic properties of the catalysts prepared at various stages of the work:

Infrared Spectroscopy IR (Thermo Scientific “Nicolet IS 10), X-ray Phase RFA (”Bruker", “D2-Phaser”), Scanning Electron Microscopy SEM (JSM-6610LV, JEOL), Electron Paramagnetic Resonance EPR (Bruker's ELEXSYS-E580), Thermogravimetric Analysis TGA (TA Instruments SDT-Q600). In addition, the analysis of the feedstock and reaction products in the oxidation processes carried out using the catalysts under investigation was determined by an Agilent 7890B gas chromatograph with a FID detector.

The main theses to be defended are as follows:

- The method for obtaining novel immobilized metal-polymer catalysts based on poly-4-vinylpyridine and manganese compounds;
- The kinetics of the selective catalytic oxidation of n-hexane, n-heptane, and n-octane with oxygen in air using the developed catalysts;
- Reaction orders with respect to the catalyst, air oxygen, and alkane, as well as the kinetic laws of the process, including activation energy;
- The nature of the coordination active centers and the influence of the polymer matrix on the properties of the catalytic system;
- The coordination-controlled radical mechanism of the selective catalytic oxidation of n-alkanes (n-C_6–C_8) over immobilized metal-polymer catalysts.

Scientific novelty of the research. A new metal-polymer catalyst based on manganese compounds immobilized on poly-4-vinylpyridine has been developed for the selective catalytic oxidation of n-alkanes (n-C_6–C_8) with molecular oxygen in air under mild conditions.

Based on kinetic, spectral, and catalytic studies, taking into account the properties of the developed metal-polymer system and the coordinated Mn(II) ⇄ Mn(III) ⇄ Mn(IV), the most plausible coordination-controlled radical mechanism for the catalytic oxidation of n-alkanes (n-C_6–C_8), involving Mn(IV) reversible transitions, has been proposed.

The nature of the catalytic active centers was rationalized as coordination nodes of isolated manganese immobilized in a poly(4-

vinylpyridine) polymer matrix. It has been shown that such a structure of the active centers ensures their independent operation, high selectivity of the process, and high stability of the catalyst during repeated use.

Theoretical and practical significance of the research. The theoretical significance of the research is based on the conclusions about the regularities of the selective catalytic oxidation of n-alkanes (n-C_6-C_8) with the participation of immobilized metal-polymer catalysts. The interrelationship between the structure of the coordination active centers, the kinetic parameters of the process, and the mechanism of catalytic oxidation has been established. Taking into account the main feature of immobilized metal-polymer catalytic systems, a coordination-controlled radical mechanism for the reaction has been proposed.

Effective immobilized metal-polymer catalysts have been synthesized based on poly-4-vinylpyridine and manganese complexes for the selective catalytic oxidation of n-alkanes (n-C_6–C_8) with atmospheric oxygen under mild conditions.

The obtained results can be used for the development of new catalytic systems for the processes of selective oxidation of hydrocarbons, as well as for the creation of resource-saving and more environmentally safe technologies for the production of oxygen-containing organic compounds.

Acknowledgment and application of the dissertation.

The main results of the dissertation were presented and discussed at the following republican and international conferences:

1. Scientific Research-2019, IV International Scientific Practical Conference (Czech Republic, Karlovy Vary-Russia, Moscow 2019);
2. XXI Mendeleev Congress on General and Applied Chemistry. Volume 1, Section 1 (Saint Petersburg 2019);
3. BHOS, 1st Republican Scientific Conference of Students "Perspectives in Chemistry and Chemical Engineering" Dedicated to the 96th Anniversary of National Leader H. Aliyev (Baku 2019);
4. BSU, 13th International Scientific Conference "Actual Problems of Chemistry" for doctoral students, master's students, and young researchers, dedicated to the 96th anniversary of the birth of

National Leader Heydar Aliyev (Baku, 2019);

5. BHOS, III International Scientific Conference of Students and Young Researchers "Sustainable Development in Chemistry and Chemical Engineering" dedicated to the 99th anniversary of the birth of National Leader H. Aliyev (Baku, 2022);

6. Scientific Collection «InterConf», (117): with the Proceedings of the 6th International Scientific and Practical Conference «Scientific Goals and Purposes in XXI Century» (Seattle, USA 2022);

7. BSU, 1st Scientific Conference of Baku and Regional Youth (Baku 2023);

8. BHOS, 5th International Scientific Conference of Students and Young Researchers "Towards Sustainable Chemistry and Chemical Engineering," dedicated to the 101st anniversary of National Leader H. Aliyev (Baku 2024);

9. ICIC, REPUBLICAN CONFERENCE dedicated to the 90th anniversary of the Institute of Catalysis and Inorganic Chemistry named after Academician M.Naghiyev, and the 100th anniversary of the birth of Academician Togrul Shahtakhtinsky (Baku 2025);

10. Grant project: Project "Creation of Memory-Effect Nanocatalysts for the Selective Oxidation of Normal Alkanes to Industrially Important Products," number EIF-ETL-2020-2 (36) -16 / 09/4-M-09, of the Science Development Fund under the President of the Republic of Azerbaijan (Baku 2020).

Name of the organization where the dissertation was carried out. The dissertation was carried out at the "Nanostructured metal-polymer catalysts" laboratory of the "Institute of Chemistry" Public Legal Entity of the Ministry of Science and Education of the Republic of Azerbaijan.

Structure and volume of the dissertation. The dissertation consists of an introduction (13.502), 4 chapters (Chapter I 63.995, Chapter II 30.158, Chapter III 26.392, Chapter IV 32.395 pages), conclusions (3.927), and a list of 263 references. Including 38 figures and 13 tables, the total volume of the work is 156 computer-printed pages with 170.888 symbols.

Degree of reliability of the research results.

The reliability of the obtained results is ensured by the use of

modern physicochemical analysis methods (FTIR, UV, EPR spectroscopy), the reproducibility of the experimental results, the application of generally accepted research methods for studying the kinetics of catalytic processes, as well as the conformity of the experimental results with the proposed reaction mechanism and the concepts accepted in modern scientific literature on the catalytic oxidation of hydrocarbons, is ensured.

This is also supported by publications in high-ranking scientometric databases (SCOPUS and Web of Science) and by theses presented at republican and international conferences. A total of 19 scientific works have been published on the dissertation topic. Of these, 10 are articles (9 of which are included in international abstracting and indexing systems), and 9 are conference abstracts. Six of the abstracts were published in the proceedings of international conferences, and three in the proceedings of republican scientific conferences.

The author's personal contribution includes defining the purpose and objective of the dissertation, synthesizing the catalysts, performing the majority of the theoretical and experimental research for the oxidation process, and preparing the scientific articles and presentations.

MAIN PART OF THE WORK

The introduction defines the relevance of the research topic, the purpose of the work, the problems to be solved, scientific innovations, the practical significance of the work, and the main theses to be defended.

In the first chapter, a review of the current state of research in the field of the oxidation reaction of n-alkanes was conducted, and methods for obtaining polymer-metal-based catalysts were also investigated [9, 10].

The second chapter describes the preparation of manganese Mn and poly-4-vinylpyridine P4VP-based polymer-metal complex catalysts [3, 5-6], the stationary laboratory experimental setup used for the process, and the identification of the reagents and reaction products by various physicochemical methods; their properties and the

methodology for studying the elemental composition are provided.

The third chapter presents the results of experimental tests confirming the effective activation of the C-H σ-bond of the studied substrates (n-C_6-C_8) in the presence of the metal-polymer composite catalyst. In this study, it was determined that MnP4VP and MnP4VP/MBAA polymer-based heterogeneous catalysts can be successfully used for the selective oxidation of n-alkanes.

To study the activity of the polymer-immobilized catalytic systems, the reactions were carried out in the temperature range of 303-383 K, at an n-alkane: air molar ratio of 1:3.38, in a stationary-bed reactor as well as in a "MORI" type autoclave for six hours (hydraulic residence time t = 6 hours), and the optimal conditions that ensured the reaction proceeded in the kinetic region were selected [6-8, 11-14, 16, 17].

Table 1.

Results of the oxidation reaction of n-hexane at T = 313 K, in a molar ratio of n-C_6H_{14}: air = 1:3.38, and for a duration of t = 6 hours:

Experimental conditions: n-C_6H_{14}: air = 1:3.38, molar ratio, 0.3 g, catalyst, CH_3CN solvent, T = 313 K, P = 1 atm, t = 6 hours

№	Catalysts	Conversion of n-hexane, ξ,%	The yields of products, A, wt.%					S_{C6ol-1}, %	S_{C6ol-2}, %	S_{C6ol-3}, %
			C_6H_{13}-1-ol	C_6H_{13}-2-ol	C_6H_{13}-3-ol	Hexan al	Hexanone			
1.	Mn(2%) P4VP[x]	20.6	-	17.1	0.8	1.8	0.9	-	83	3.9
2.	Mn(5%) P4VP [x]	28.7	0.8	15.2	2.5	6.3	3.9	2.8	53	8.7
3.	Mn(10%) P4VP[x]	17.3	-	11.7	0.6	3.2	1.8	-	67.6	3.5
4.	Mn(2%) P4VP/MBAA [xx]	34.4	1.6	22.5	3.4	4.2	2.7	4.65	65.4	9.9
5.	Mn (5%) P4VP/MBAA [xx]	42.6	2.9	18.1	4.6	10.7	6.3	6.8	42.5	10.7
6.	Mn(10%) P4VP/MBAA [xx]	27.4	0.9	14.8	2.2	6.1	3.4	3.28	54	8.02

x-uncross linked; xx-crosslinked metal-polymer catalysts

As seen from Table 1, the formation of hexanol-1 was not observed in the presence of the uncrosslinked 2%MnP4VP and 10%MnP4VP catalysts (Table 1, experiments No. 1, 3), but when the polymer was crosslinked with N,N'-methylene bisacrylamide *MBAA*, hexanol-1 was obtained in yields of A ≈1.6% and A ≈0.9%, respectively (Exp. № 4, 6). The best activity for hexanol-2 was shown by the modified catalyst containing 2% metal, with a yield of 22.5%. The formation of the single alcohol was observed on both the crosslinked and uncrosslinked catalysts containing 5% Mn, with yields of 0.8 and 2.9%, respectively, and the highest selectivity was observed on the 5% Mn/MBAA-based catalyst, $S_{C6ol\text{-}1} \approx 6.8\%$ (exp. № 2 and 5). As can be seen from the data in the table, the highest selectivity was observed for hexanol-2 on the catalyst containing 2% MnP4VP, $S_{C6ol\text{-}2} \approx 83\%$. A higher amount of the carbonyl compounds - hexanone and hexanal was obtained on the catalyst containing 5 wt.p. % Mn, exp. № 2, 5. This is explained by the fact that in the MnP4VP and MnP4VP/MBAA complexes containing 5 wt.% Mn, the manganese particles are more evenly distributed on the P4VP support.

The conversion and product yields for the partial oxidation of n-hexane to target products (alcohols, aldehydes, ketones) over the MnP4VP (a) and MnP4VP/MBAA (b) catalysts as a function of temperature are given in Figures 1a and b, respectively. The temperature dependencies of the conversion and product yields are presented in Figures 1a and b.

A review of the graphs shows that for both the uncrosslinked (a) and MBAA-crosslinked (b) catalysts, the yields of aldehyde and ketone increase with increasing temperature across all studied temperature intervals (303–383 K), at the same time, side products (acid mixture) are formed at 383 K, but the temperature dependence curve of alcohols' yield passes through a maximum; At temperatures above 330 K, the decrease in the yield of hexan-1,2,3-ols is due to their oxidation to other oxygenated organic compounds (aldehydes and ketones). If we look closely at how the product yields change with temperature in Figure 1b, we can see that at a low temperature (303 K), the yield for alcohols was maximum, $\sum_{Alcohols} = 24.8\%$, but

as the temperature increased, the yield of alcohols gradually decreased, and hexanol-1 was no longer observed at 353 K, hexanol-2 at 373 K, and hexanol-3 at 343 K.

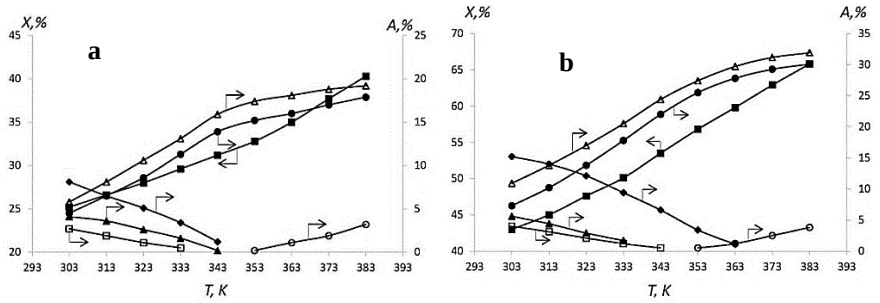


Figure 1. Oxidation of n-hexane over the MnP4VP (a) and MnP4VP/MBAA (b) catalysts: □-ol-1, ♦-ol-2, ▲-ol-3, Δ-aldehyde, ●-ketone, ○-mixed acid, ■-conversion, (C_6H_{14}:air=1:3.38 molar ratio, t=6 hours) [6].

To more clearly see the effect of temperature and time on the effectiveness of the oxidation reaction, Figure 2 comparatively presents the dependence of n-hexane conversion (ξ) on temperature (a) and time (b) for the prepared 2% and 5% MnP4VP/MBAA catalysts.

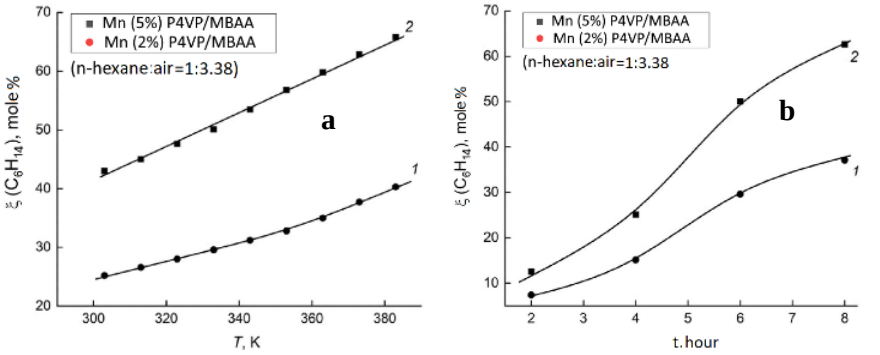


Figure 2. Dependence of n-hexane conversion (ξ) on temperature (a) and time (b) for the Mn (2 and 5%) P4VP/MBAA catalyst [6].

As shown in Figure 2a, the conversion of n-hexane increases with increasing temperature (T) and time (t) for different metal (Mn) percentages (2% and 5%), respectively. In the 2% Mn complex, ξ is ≈40 mol%, and in the 5% Mn complex, it is ≈70 mol%. The selectivity for the target product decreases after 6 hours. This may be related to the saturation of these active centers.

The catalytic properties of the crosslinked and uncrosslinked P4VP catalysts prepared with 2, 5, and 10% Mn-MBAA were studied in the oxidation reactions of n-heptane, and the results are presented in Table 2. The results of the chromatographic analysis of the obtained reaction products show that during oxidation, the products heptanol-1,2,3,4; heptanal, and heptanone were formed [4, 7, 8, 12, 13, 16].

Analysis of the data shows that the activity of the uncrosslinked catalyst (Mn P4VP (Mn -2-10 wt.%)) was low in studies conducted under the same reaction conditions. Thus, the target products, heptan-1-ol, heptanal, and heptanone, were not observed, and the yield of other products (heptan-2-ol, heptan-3-ol, heptan-4-ol) was lower compared to the MBAA-containing catalyst with the same percentage of metal. However, on the Mn (2%) P4VP and Mn (10%) P4VP catalysts, these values for the target products increased to ξ ≈10.3% and ξ ≈7.6%, respectively (Table 2, exp. 1 and 3), while on the catalyst containing MBAA, these values increased to ξ ≈23.2 and ξ ≈19.8% for the target products (exp. 2 and 4). As seen from the table, the best selectivity for heptanol-1 was observed in the crosslinked catalyst, but relatively high selectivity for heptanol-2 and heptanol-3 appeared in the uncrosslinked catalysts, with $S_{C7ol\text{-}2}$≈ 40.8% for 2%MnP4VP; for 10%MnP4VP, it was ≈35.5%; the highest selectivity for heptanol-3 was observed in the catalyst containing 10%MnP4VP, ~57.9%.

Table 2

Results of the oxidation reaction of n-heptane at T = 313 K, in a molar ratio of n-C_7H_{16}:air = 1:3.38, for t = 6 hours:

Experimental conditions:

n-C_7H_{16}:air = 1:3.38, m_{cat} = 0.3 g, solvent CH_3CN, T = 313 K, P = 1 atm, t = 6 hours

	Catalysts	Conversion of n-heptane, ξ, wt.%	The yields of products (A), wt.%							S_{C7O1-3}, %	S_{C7O1-2}, %	S_{C7O1-1}, %
			C_7H_{16}-1-ol	C_7H_{16}-2-ol	C_7H_{16}-3-ol	C_7H_{16}-4-ol	heptanal	heptanone				
								4,3	2			
1.	Mn (2%) P4VP*	10.3	-	4.2	5.8	0.3	-	-	-	56.3	40.8	-
2.	Mn(2%)P4VP /MBAA**	23.2	1.4	7.3	8.6	3.4	-	0.9	1.6	37.07	31.5	6.03
3.	Mn (10%) P4VP*	7.6	-	2.7	4.4	0.5	-	-	-	57.9	35.5	-
4.	Mn(10%)P4VP /MBAA**	19.8	1.2	5.9	7.5	2.2	1.6	0.5	0.9	37.9	29.8	6.06
5	Mn(5%)P4VP /MBAA**	36,1	2,6	6,5	7,6	5,8	5,5	3,7	4,4	21	18	7,2

Figure 3 comparatively presents the dependence of the conversion of n-heptane (ξ) on temperature (a) and time (b) over the 2% and 5% MnP4VP/MBAA catalysts at atmospheric pressure and in the temperature range of 300-380 K, over a 6-hour time interval.

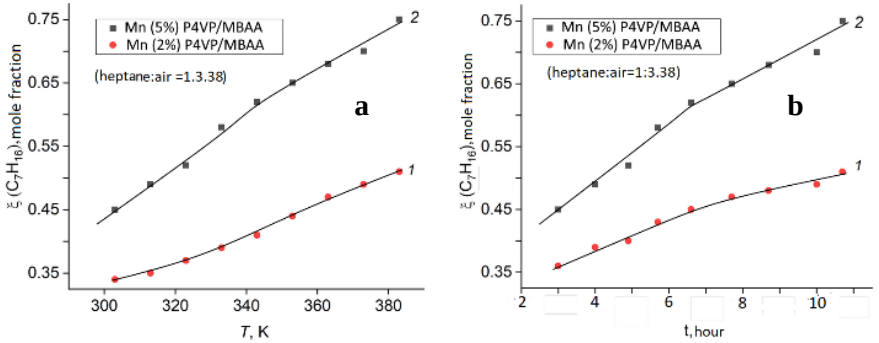


Figure 3. Dependence of the conversion of n-heptane (ξ) on temperature (a) and time (b) [16].

As seen from Figure 3a, the conversion of n-heptane increased with increasing temperature (T) for both metal (Mn) percentages, reaching a maximum at 380 K.

As shown in Figure 3b, increasing the reaction time from 120 to 360 minutes raises the conversion of n-heptane from 40% to 75%, which is mainly due to the conversion of the substrate into aldehyde and ketone, the amount of which doubles over this time interval.

During the process, the temperature was maintained constant throughout the entire volume of the reactor. The conditions in the reactor were such that the amount of heat released or absorbed was minimal, and there was no temperature gradient.

According to Table 2, a comparison of the activity of the metal in the oxidation process for all three metal percentages in the synthesized metal-polymer catalysts shows that the catalyst containing 5%Mn w/% metal demonstrated the most effective results. Thus, at 313 K, the yield of the target products increased, and the conversion was higher compared to the other percentages. Specifically, with 2%MnP4VP/MBAA, $\xi \approx 23.2\%$, and with 10% MnP4VP/MBAA, $\xi \approx 19.8\%$, for 5% MnP4VP/MBAA, ξ was approximately 36.1%.

Table 3 shows the results of the oxidation reactions of n-octane in the presence of the crosslinked and uncrosslinked metal-polymer catalysts prepared with 2% and 10% Mn-containing MBAA [1, 11]. As can be seen, the 10%MnP4VP catalyst showed the best selectivity for octanal-3, with $S_{C8Ol\text{-}3} \approx 60.2\%$.

As with the other two substrates, the conversion of n-octane increased in the presence of the MBAA-containing catalyst, and the conversion to the target products was high, $\xi \approx 23.1$ and 22.4%. Thus, in the presence of the unmodified catalyst containing 2 and 10% Mn, the products octanol-1, octanal, and octanoic acid are not obtained, and the total conversion is only $\xi \approx 9.8$ and 7.8%, exp. 1, 3.

The temperature T and time t dependence of the conversion of oxofunctionalized n-octane in the presence of the studied catalyst was determined and is depicted in Figure 4.

Table 3

Results of the oxidation reaction of n-octane at T = 313 K, in an n-C_8H_{18}:air molar ratio of 1:3.38, and for a duration of t = 6 hours:

Experimental conditions: n-C_8H_{18}:air = 1:3.38, molar ratio, 0.3 g, CH_3CN as solvent, T = 313 K, P = 1 atm, t = 6 h

№	Catalysts	Conversion of n-octane, ξ, wt%	The yields of n-octane, A, wt%							S_{C8Ol-4}, %	S_{C8Ol-3}, %	S_{C8Ol-2}, %	S_{C8Ol-1}, %
			C_8H_{18}-1-ol	C_8H_{18}-2-ol	C_8H_{18}-3-ol	C_8H_{18}-4--ol	Octan al	octanone					
								4,3	2				
1.	Mn (2%) P4VP*	9.8	-	3.5	5.6	0.7	-	-	-	7.14	57.14	35.7	-
2.	Mn(2%)P4VP / MBAA**	23.1	1.2	6,1	6.5	7.4	-	0.5	1.4	32.03	28.13	26.4	5.2
3.	Mn (10%) P4VP*	7.8	-	2.6	4.7	0.5	-	-	-	6.41	60.2	33.3	-
4.	Mn(10%) P4VP/MBAA **	22.4	1.2	4.4	5.2	6.1	2.8	1.6	1.1	27.23	23.2	19.6	5.35

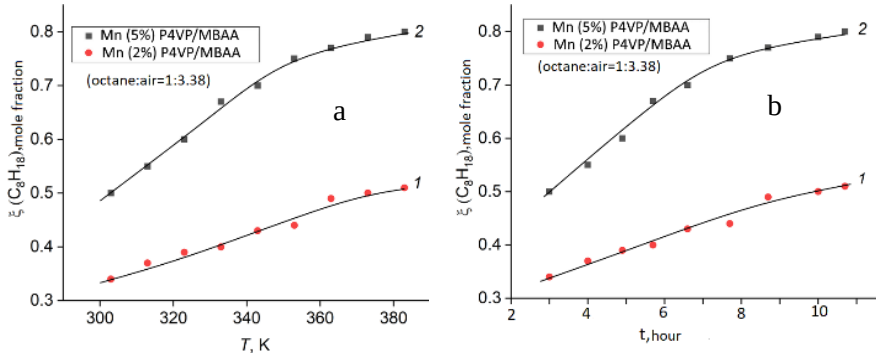


Figure 4. Dependence of the conversion of n-Octane (ξ) on temperature (a), time (b).

As seen in Figure 4a, the conversion of n-octane increases with both metal (Mn) concentrations (2% and 5%) as the temperature (T) increases, reaching a maximum at 380 K. The results presented in the time dependence plot of conversion (Figure 4 b) show that the conversion of n-octane increases from 30% to 50% as the process time is increased from 120 minutes to 360 minutes.

A closer examination of the results shows that at 313 K, an increase in yield and selectivity for the target products (alcohols, aldehydes, ketones) is observed, but as the temperature increases, the yield and selectivity for alcohols begin to decrease significantly. For example, at 313 K, the combined yield of alcohols (ol-2, ol-3, ol-4) in the 2%MnP4VP sample was 8.8% with selectivity, whereas at 353 K, it was 2.1%.

Thus, summarizing the results obtained on all three substrates, we see that the yield of the target products and the conversion of n-alkane to alcohols were higher at lower temperatures (313-333 K), but the yields of other products (aldehyde, ketone) increased as the temperature rose, with a maximum yield observed at 383 K. Also, at high temperatures (>353 K) for all three substrates, a mixture of small amounts of acids (acetic, propionic, etc.) is obtained, while the yield of the target product decreases.

Studies show that the catalyst's activity and selectivity depend on the amount of manganese in the polymer-based composite and the reaction conditions. Thus, among the three catalysts tested, the one containing 5% Mn (by weight) showed higher selectivity compared to the others [6, 8, 11, 16]. In octane, the amount of oxygenated compounds was much greater than in the other two substrates, and high selectivity for the product octanol-2 was observed because the energy required for the dissociation of the C-H bond is lower.

Comparative Study of the Catalytic Properties of a Ni-Based Metal-Polymer Complex

In the next stage of the study, the catalytic properties of nickel compounds immobilized on P4VP were investigated in the oxidation process of n-hexane [17].

The oxidation of n-hexane in the presence of the synthesized P4VP-nickel-containing catalyst was studied under the same conditions:

a temperature of 313-383 K, atmospheric pressure, and a nC_6:air molar ratio of 1:3.38 (Table 4).

Table 4

Oxidation of n-hexane with nickel catalysts immobilized on Poly(4-vinylpyridine):

Experimental conditions: C_6H_{14}:air = 1:3.38, mkat = 0.3 g, solvent CH3CN, T = 313 K, P = 1 atm, t = 6 hours

№	Catalysts, wt. % Ni	Conversion of ξ, % n-C_6H_{14}	Yields of the products A, wt.%					Selectivity		
			C_6H_{14}-1-ol	C_6H_{14}-2-ol	C_6H_{14}-3-ol	hexanal	hexanon	S_{c6ol}-1	S_{c6ol}-2	S_{c6ol}-3
1	Ni2%-P4VP /MBAA	37.3	-	24.6	0.7	9.9	2.1	-	66	1,9
2	Ni5%-P4VP /MBAA	47	0.9	8.8	1.2	19.6	16.5	1,9	18,7	2,55
3	Ni10%-P4VP /MBAA	30.3	-	5.7	-	14.4	10.2	-	18,8	-

As seen from the table, the study of the reaction rate during the oxidation of n-hexane depends on various factors. The reaction rate is influenced by the concentration of the reactants, the composition and concentration of the catalyst, and the temperature at which the reaction is carried out. The experimental results showed that the 5%Ni-containing complex exhibited selectivity for all three alcohols, with the percentage of C_6H_{14}-2-ol being greater than the others, at Sc6ol-2 ≈ 18.7%. However, in the presence of the 2%Ni catalyst, the oxidation and selectivity to C_6H_{14}-2-ol were higher, with Sc6ol-2 ≈ 66%.

The experimental results show that the studied Ni-based catalyst exhibited a lower yield of alcohols and a higher yield of aldehyde and ketone in the oxidation of n-hexane compared to the Mn-containing catalyst.

Overall, the results indicate that catalysts prepared based on

transition metal complexes immobilized on the P4VP macrocyclic ligand exhibit high efficiency in the oxidation of n-alkanes under mild conditions, in C-H bond activation, and in the formation of the target products.

Investigation of the possible reaction mechanism.

From the processes studied above, it is clear that the coordination ability of the N heteroatom in the polymer ring plays a crucial role in activating the C-H bond, which is in a low-polarity and nearly inert state, and in directing the reaction for the P4VP and the Mn-based transition metal catalyst.

Based on a combination of kinetic studies, spectral data (FTIR, UV, EPR), analysis of reaction products, and investigation of catalyst stability, a coordination-controlled radical mechanism for the selective catalytic oxidation of n-alkanes involving immobilized metal-polymer catalysts has been proposed.

I.Formation of the coordination-active center

$P4VP+Mn^{2+} \rightarrow P4VP\text{-}Mn^{2+}$

II. Activation of oxygen

$P4VP\text{-}Mn^{II}+O_2 \rightleftarrows [P4VP\text{–}Mn^{III}\text{-}O_2^{*-}]$

III. Formation of a reactive oxygen species

The possible involvement of the Mn(IV)–O^* species in the oxygen activation process is considered an intermediate step, but the specific structure of this form has not been experimentally determined.

IV. Oxidation of the alkane

$P4VP\text{-}Mn^{IV}\text{-}O^{*}+RH \rightarrow P4VP\text{–}Mn^{III}\text{–}OH+R^{\bullet}$

V. Formation of the peroxyl radical

$R^{\bullet}+O_2 \rightarrow ROO^{\bullet}$

VI. Hydroperoxide formation

$ROO^{\bullet}+RH \rightarrow ROOH+R^{\cdot}$

VII. Product formation

$ROOH \rightarrow ROH \rightarrow RCHO/RCOR \rightarrow RCOOH$

VIII. Regeneration

$Mn(II) \rightleftarrows Mn(III) \rightleftarrows Mn(IV)^*$

This mechanism is not simply a repetition of the schemes available in the literature. It is distinguished by the following features:

1. The mechanism is initiated not by the reaction of Mn with

oxygen, but by the formation of an immobilized P4VP–Mn coordination center.

2. The role of the polymer matrix is not limited to a carrier function; it is retained throughout the entire catalytic cycle and participates in the activity of the active center.

3. The mechanism combines coordination activation and radical intermediate stages. In this case, radicals are considered to be short-lived intermediates that form in the vicinity of the active center.

4. The individual steps of the mechanism have been confirmed based on our experimental results (the presence of Mn(III)—EPR, ROOH groups—IR spectroscopy, kinetic studies, and analysis of reaction products).

In Chapter Four, the results of the investigation of the oxidation reactions of n-C_6-C_8 alkanes to target products (alcohols, aldehydes, ketones) in the presence of the synthesized metal-polymer catalyst are presented within the framework of formal kinetics laws [6, 8, 11, 13, 15-18].

The experimental and theoretical study of the catalytic oxidation reaction of alkanes has allowed us to describe the kinetic laws of these reactions. First, based on the proposed chemical transformation schemes, the final chemical equations for the specific reaction steps of the experimentally determined intermediate complex interactions for these oxidation reactions were selected.

Based on the proposed chemical conversion schemes [6, 8, 11, 16], kinetic models for specific reactions involving n-alkanes (n-hexane, n-heptane, n-octane) were constructed using the mathematical treatment of experimental data.

At this stage of the study of oxidation reactions, it is difficult to establish a kinetic model for the overall reaction of n-alkanes with MnP4VP and MnP4VP/MBAA catalysts. This is because there is no mathematical apparatus to construct and solve the system of differential equations that would correspond to the mathematical description of this overall reaction. In this work, the complex oxidation reaction mechanism was divided into individual stages, which were studied independently. This allowed the problem of mathematical analysis to be broken down into separate, simpler components. This, in turn, reduces the number of

equations in the mathematical description of the reaction. In the case under consideration, the inverse problem of chemical kinetics can be adequately solved. The kinetic quantities calculated in this way can be used to build a kinetic model of a generalized mechanism for the catalytic oxidation of n-alkanes.

Based on laboratory research data, we estimate the rate constants and activation energies for the individual intermediate stages of the reactions. This allows for the investigation of kinetic models for specific oxidation reactions.

Thus, based on the stages considered for the establishment of kinetic models for the complex catalytic oxidation reaction involving MnP4VP and MnP4VP/MBAA, the following conclusions can be drawn:

1. The development of a kinetic model for a complex catalytic oxidation reaction requires a large volume of experimental data, kinetic measurements, and computational data.

2. The development of kinetic models for such reactions requires enhancing algorithms for solving systems of nonlinear differential equations. To determine the kinetic parameters, it is necessary to solve specific direct and/or inverse kinetic problems.

3. The solution of forward or inverse kinetic problems for determining kinetic parameters requires the selection of effective computational models.

4. The selection of effective methods for the numerical solution of direct chemical kinetics problems is complicated by the difficulty of the mathematical description of catalytic oxidation reactions.

5. The inverse problem solution method significantly reduces the time for kinetic parameter estimation, which increases the reliability of the kinetic model of a complex multi-step oxidation reaction. The use of a set of parameters calculated in similar or previous studies reduces the uncertainty of the inverse problem solution. Thus, the above features have been taken into account in the study of the catalytic oxidation of n-alkanes using modeling methods. To this end, the functionality of similar systems under study and the available computational resources were analyzed. Criteria for selecting efficient numerical methods for solving inverse kinetic problems were established.

The kinetic parameters of the oxidation process of n-C_6-C_8 alkanes were determined based on the observed changes in the initial reaction rates, which depend on temperature and time.

Before the process, 0.3 g of catalyst was loaded into the reactor. The reaction was carried out at atmospheric pressure under n-alkane/air oxygen = 1:3.38 conditions. The kinetic model was selected based on experimental results as follows.

Based on the kinetic equations of the reactions [6, 8, 11, 16-18], the kinetic constant was determined by considering the conversion degrees of the starting materials

$$\xi\ (\tau) = \frac{A_0 - A(\tau)}{A_0}, \xi\ \epsilon\ [0,1] \qquad (1)$$

A_0 is the initial concentration of the substrate, and A(τ) is the molar concentration of the corresponding substrate at any value of τ (time). If the initial concentrations of the reactants are assumed to be the same, $A_0 = B_0$, then at all times t, A(τ) = B(τ).

From this, the kinetic constant is determined:

$$k = \frac{\xi}{1-\xi}\frac{1}{A_0 \cdot \tau} \qquad (2)$$

Experimental studies[5,6,7] indicate that the thermochemical oxidation of n-alkane in the presence of a Mn-containing catalyst can be considered a first-order reaction. In a closed system, the rate of such reactions is determined by temperature and the concentration of n-alkane, and the reaction rate for these processes is expressed as follows:

$$-\frac{d[n-\text{alcane}]}{d\tau} = k[n-\text{alcane}] \qquad (3)$$

where k is the absolute reaction rate constant at the corresponding temperature. By writing the Arrhenius equation in this form, Ea was calculated.

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$$\ln k = -\frac{E_a}{R} \cdot \left(\frac{1}{T}\right) + \ln A \quad (4)$$

Considering the parameters in equation (4) as constant and constructing the dependence of *ln k* on *1/T*, it was determined that the activation energy for the oxidation of n-hexane in the presence of the respective catalysts is *50 kJ/mol*.

Table 5

Overall rate constants for the oxidation of n-hexane to alcohols in atmospheric pressure in the presence of the MnP4VP catalyst (n-hexane:air = 1:3.38) reaction [6].

T, K	Q, mole/hour	t, min	A_0, mole/m^3	ξ	$k_e \times 10^5$, m^3/ mole·min
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 at the reactor inlet, τ - residence time of the mixture in the reactor

Table 6.

Overall (effective) rate constants for the oxidation of n-hexane to alcohols (hexan-1-ol, hexan-2-ol, hexan-3-ol) in the presence of air using the MnP4VP/MBAA catalyst [6].

T,K	Q, mole/hour	t, min	A_0, mole/m^3	ξ	$k_e \times 10^5$, m^3/ mole·min
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

In the chemical processes studied [6, 8, 11, 13, 15-18], it has been determined that the initial reaction rate increases with increasing temperature.

The effect of oxygen consumption ($Qv(O_2)$ = 50–300 mL min^{-1}) on the initial rate of intermediate formation during the catalytic oxidation of n-alkanes was studied, and it was determined that the initial reaction rate increases with increasing oxygen consumption. This is because the degree of coverage of the catalyst surface by oxygen molecules increases, and consequently, the number of elementary steps between oxygen and n-alkanes increases accordingly.

The oxidation rate of n-alkanes continuously decreases with the increase in the initial concentration of n-alkanes ($C(C_nH_{2n+2})$ = 1.28–3.84 mol L^{-1}). This indicates a stronger adsorption of n-alkanes on the catalyst surface compared to oxygen.

The study of the kinetic characteristics of the oxidation reaction of n-heptane was carried out within the framework of the assumption of the reaction as a sequential two monomolecular stages: $S \overset{k_1}{\rightarrow} X \overset{k_2}{\rightarrow} P$

Here, S is the initial substrate, P is the final product, and k_1 and k_2 are the reaction rate constants.

The time dependencies of the concentrations of the initial S substance and the products c_S, c_X, and c_P were determined.

The concentration of the S initial reactant, c_S, decreases monotonically with time. The concentration of the intermediate product, X, increases, reaches a maximum, and then decreases, while the concentration of the final product, P, increases monotonically with time.

For the transformation shown above, we can define c = c_S, x = c_X, p = c_P, with initial conditions: c = c_0, x = p = 0. Taking this into account, we can write the following relations for specific cases:

$$c = c_0 e^{-k_1 t}$$

$$x = \frac{k_1}{k_2 - k_1} c_0 (e^{-k_1 t} - e^{-k_2 t}) \qquad (5)$$

Analysis of equation (5) shows that the conversion rate of complex sequential reactions is determined by the slowest step. Equation (5) can be used as a mathematical model for the kinetics of n-heptane conversions.

The activation energy, Ea, for the oxidation reaction of n-heptane, The activation energy Ea was determined to be 47 kJ/mol for the reaction of n-heptane: air (initial reagent molarity ratio of 1:3.38) at 383 K, with $\xi = 0.75$ conversion in less than 7 hours [8, 13, 16].

Table 7

Overall rate constants for the atmospheric pressure oxidation of n-heptane with air oxygen to alcohols (n-heptane: air = 1:3.38) reaction in the presence of a manganese-containing polymer catalyst [8].

T, K	Q, mole/hour	t, min	A_0, mole/ m^3	$\xi, \%(C_7H_{16})$	$k\times 10^5$, m^3/mole·min
303	0.0341	360	38	0.45	0.60
313	0.0327	370	34	0.49	0.76
323	0.0315	379	32	0.52	0.89
333	0.0304	387	28	0.58	1.27
343	0.0289	396	26	0.62	1.58
353	0.0277	407	24	0.65	1.90
363	0.0262	417	22	0.68	2.32
373	0.0251	430	20	0.70	2.71
383	0.0243	437	18	0.75	3.81

Q is the volume of the initial mixture at the reactor inlet, and τ is the residence time of the mixture in the reactor.

The results of the study of the kinetic laws of the n-octane oxidation reaction are presented in Table 8.

Table 8

Overall rate constants for the oxidation of n-octane to alcohols with oxygen at atmospheric pressure (n-octane:air = 1:3.38) in the presence of a manganese-containing polymer catalyst [11].

T, K	Q, mole/hour	t, min	A_0, mole/ m^3	$\xi, \%(C_8H_{18})$	$k\times 10^5$, m^3/mole·min
303	0.0308	360	30	0.50	9.26
313	0.0297	370	27	0.55	1.22
323	0.0287	379	25	0.60	1.60
333	0.0275	387	19	0.67	2.81
343	0.0264	396	17	0.70	3.52
353	0.0255	407	15	0.75	4.88
363	0.0244	417	13	0.77	6.13
373	0.0232	430	12	0.79	7.29
383	0.0221	437	11	0.80	8.36

Optimized conditions (303-383 K, atmospheric pressure, for 6 hours) were obtained for the increase in selectivity to the main products of n-Octane. The catalysts studied were used for a 6-hour reaction time.

Considering the kinetic model, it was possible to evaluate the effect of the composition of the manganese-containing polymer catalyst, the molar ratio of the initial components, temperature, and the interaction time of the components on the reaction rate constant and conversion.

RESULTS

1. New Mn-containing poly-4-vinylpyridine based catalysts were synthesized [3, 5-6, 14], and their catalytic properties were investigated in the oxidation of n-C_6–C_8 alkanes to the corresponding alcohols, aldehydes, and ketones with atmospheric oxygen in the liquid phase at 303–383 K. It was found that the catalysts exhibit high catalytic activity and selectivity and can be reused, largely retaining their catalytic properties for 5–6 consecutive cycles [6-8, 11, 14, 16].

2. The elemental and phase composition of the synthesized manganese polymer-based catalysts and the distribution of elements in the complex were investigated by SEM/EDS, AAS, and RFA methods, respectively, and EPR, Fourier IR spectra, and TGA/DTA thermograms were recorded. It has been shown that the synthesized samples are polymer-based compounds containing MnO_x nanoparticles [1-3, 5-6, 19].

3. The dependence of the oxidation reactions of n-alkanes (n-C_6-C_8) with oxygen in air on the amount of polymer-immobilized manganese (2, 5, 10%) was studied, and the optimal amount of manganese (5%) was determined: at 313 K, the conversion of n-C_6H_{14} was ≈ 42.6%, n-C_7H_{16} ≈ 36.1%, and n-C_8H_{18} ≈ 34.4%.

The formation of alcohols was determined to be the main product in the oxidation reactions of n-alkanes, catalyzed by a manganese-containing polymer catalyst. At 313 K, the highest selectivity to alcohols during the oxidation of n-alkanes over 5%MnP4VP/MBAA was $S_{C6Ol\text{-}2}$ ≈ 42.5% for n-hexane; for n-heptane, $S_{C7Ol\text{-}3}$ ≈ 21%, and for n-octane $S_{C8Ol\text{-}}$

$_4 \approx$ 22.6% alcohols were observed [6-8, 11, 16].

4. It has been shown that for n-alkanes (n-C_6-C_8) in the temperature range of 303-383 K and under atmospheric conditions, the yield of the reaction products (alcohols, aldehydes, ketones) can be controlled by varying the concentration of the initial components, temperature, and contact time of the components during oxidation with atmospheric oxygen. The yield of alcohols decreased while the yields of aldehydes and ketones increased with an increase in temperature from 313 K to 383 K. In the presence of 5%MnP4VP/MBAA, the yield of aldehydes and ketones at 383 K was $\sum A \approx 48.2\%$ for n-hexane, for n-heptane $\sum A \approx 13.6\%$, and for n-octane $\sum A \approx 14.3\%$ [6-8, 11, 16].

5. The kinetics of the oxidation of n-alkanes (n-C_6-C_8) to their corresponding alcohols, aldehydes, and ketones in the temperature range of 303-383 K was studied in the presence of the synthesized catalysts, and the values of the activation energy were given. It has been shown that for these reactions, the initial activation energy Ea for all three alkanes investigated was in the range of 40-50 kJ/mol (9.5-11.9 kcal/mol) within the first 10-15 minutes [6, 8, 11, 13, 15, 16, 18].

6. A kinetic model was selected, and rate constants were calculated for the oxidation reaction of n-alkanes (n-C_6-C_8) with oxygen in air to target products (alcohols, aldehyde, ketones) in the presence of the 5%Mn-P4VP-MBAA catalyst. It has been shown that for the catalytic oxidation reaction of n-heptane over 5%Mn-P4VP/MBAA at t = 6 hours, the calculated rate constant value ranges from 303–383 K, at atmospheric pressure, k = (0.60–3.81)• 10^{-5} m^3/(mol•min) range at atmospheric pressure, over the temperature interval of 303–383 K, for the catalytic oxidation reaction of n-heptane under 5%Mn-P4VP/MBAA and t = 6 h conditions. The reaction was found to obey a first-order kinetic model with respect to alkane, air oxygen, and catalyst [6, 8, 11, 15, 16, 18].

7. Based on kinetic, spectral, and catalytic studies, considering the properties of the created metallopolymer system and the coordinated Mn(II) ⇄ Mn(III) ⇄ Mn(IV) the most plausible coordination-controlled radical mechanism for the catalytic oxidation of n-alkanes (n-C_6–C_8), involving reversible transitions, has been proposed. The nature of the catalytically active centers is rationalized as coordination nodes of isolated manganese immobilized in a poly-4-vinylpyridine polymer

matrix. It has been shown that such a structure of the active centers ensures their independent operation, high selectivity of the process, and high stability of the catalyst during repeated use.

8. The activity and selectivity of the Mn-containing catalysts were compared with the activities observed in the oxidation of n-hexane for the Ni-containing polymer-metal catalysts synthesized by us. It was found that the 2, 5, and 10% Ni-P4VP/MBAA catalysts show lower selectivity to alcohols compared to the Mn-containing catalyst. For example, in the presence of 5%Ni-P4VP/MBAA, the alcohol yield was only $\sum_{Alcohols} \approx 10.9\%$ [17].

THE MAIN RESULTS OF THE DISSERTATION HAVE BEEN PUBLISHED IN THE FOLLOWING ARTICLES AND THESES:

1. Isazade, A.F. Synthesis of manganese nanoparticles in the poly-4-vinylpyridine environment and check the catalytic properties in the reaction of n-octane / A.F. Isazade, U.A. Mammadova, N.A. Zeynalov // Scientific Research-2019, IV International Scientific Practical Conference Czech Republic, Karlovy Vary-Russia, Moscow, -2019, -p.8-10.
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