

REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS OF CARBON NANOTUBES FROM PROPANE
GAS AND THEIR STUDY IN CATALYTIC OXIDATION
PROCESSES OF HYDROCARBONS**

Speciality: 2316.01 – “Chemical kinetics and catalysis”

Field of science: Chemistry

Applicant: **Narmin Alasgar Mustafayeva**

Baku – 2026

The work was performed at PLE "Institute of Chemistry" of the Ministry of Science and Education of the Republic of Azerbaijan in the Laboratory of Oxidation Processes in the Presence of Nanocatalysts.

Scientific supervisor: Corresponding Member of ANAS,
Doctor of Chemical Sciences, Professor
Eldar Bahadir Zeynalov

Official opponents: Corresponding Member of ANAS,
Doctor of Chemical Sciences, Professor
Tofiq Abbasali Aliyev

Doctor of Chemical Sciences,
Associate Professor
Aygun Zabit Aliyeva

Doctor of Philosophy in Chemistry,
Associate Professor
Sima Mammad Zulfugarova

Dissertation council FD 1.15 of Supreme Attestation Commission
under the President of the Republic of Azerbaijan operating at PLE
"Institute of Chemistry" of the Ministry of Science and Education of
the Republic of Azerbaijan

Chairman of the
Dissertation council:

Corresponding Member of ANAS,
Doctor of Chemical Sciences, Professor
Mahammad Baba Babanlı

Scientific secretary of the
Dissertation council:

Doctor of Philosophy in Chemistry,
Associate Professor
Ulviyya Ahmad Mammadova

Chairman of the
scientific seminar:

Doctor of Chemical Sciences, Professor
Arif Cavanshir Efendi



GENERAL CHARACTERISTICS OF THE WORK

The actuality and usage rate of the topic. Currently, most of the catalytic systems used in the chemical industry are based on heterogeneous catalysts containing metals and metal oxides. Although these types of catalysts have high stability, they are characterized by problems such as the high temperatures and pressures required to carry out the reactions, the use of large amounts of expensive and rare metals, as well as environmental pollution¹. Although homogeneous catalysts exhibit higher activity and selectivity, the difficulty of separating them from the reaction medium and reusing them limits their industrial application. For this reason, in recent decades, research has developed intensively in the field of applying nanoscale catalysts, particularly carbon-based nanomaterials, in catalytic systems². Nanocatalysts combine the advantages of homogeneous and heterogeneous catalysis systems, providing both high activity and selectivity, as well as easy recovery and long-term stability³. The high surface-to-volume ratio, high density of active centers, and tunable electronic structure of nanostructured materials facilitate the more efficient and energy-saving conduction of reactions. Therefore, the use of nanoscale carbon-based materials in catalytic reactions is of great scientific interest. Thanks to their high electrical conductivity, thermal stability, and large specific surface area, carbon nanotubes (CNT) serve as an effective support for the uniform distribution of metal particles on the surface and the adsorption of reactants, as well

¹ Akhtar, M.S., Ali, S., Zaman, W. Recent advancements in catalysts for petroleum refining // *Catalysts*, – 2024, 14 (12), - p. 1-22.

² Zhao, Y. A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion / Y.Zhao, K.Lu, H.Xu [et al.] // *Renewable and Sustainable Energy Reviews*, - 2021. v. 139, - p. 1-27.

³ Baruwa, A., Gbadeyan, O. J., Permaul, K. Revolutionizing biotechnology: the impact of nanocatalysts and nanomaterials—a comprehensive review // *Discover Mater.*, – 2025, 5 (89), - p. 1-19.

as for use as a direct catalyst⁴. In particular, iron-containing carbon nanotube catalysts can exhibit high activity and stability in hydrocarbon oxidation reactions, thanks to the variable valence redox properties of iron and the nanostructured stability of CNTs. The active centers formed on the surface of Fe-containing CNTs catalysts facilitate the adsorption and activation of both oxygen and hydrocarbons, resulting in the efficient progress of the reaction under low temperature and pressure conditions. The economic relevance of this research is that carbon nanotubes can be synthesized from inexpensive and local raw materials, such as propane gas, which is widely produced in Azerbaijan and can be manufactured in large quantities. This ensures the production of nanomaterials by utilizing local resources, reducing dependence on imports, and developing environmentally safe catalytic technologies. Thus, the study of the catalytic activity of Fe-containing carbon nanotube catalysts in the oxidation reactions of hydrocarbons is aimed at solving scientific problems in modern catalysis (investigation of the activity - structure relationship, development of highly active catalysts, energy efficiency, and environmental sustainability) aimed at solving the scientific problems in modern catalysis, and also represents an important and strategic scientific direction for Azerbaijan, ensuring the development of new generation catalyst systems that are economically efficient and suitable for industrial application.

Object and subject of the study. The object of the study is multi-walled carbon nanotubes (MWCNT) synthesized from propane gas and their catalytic properties. The subject of the research is the synthesis of carbon nanotubes by the vapor phase chemical deposition (CVD) method and the investigation of their catalytic activity in the oxidation reactions of various classes of hydrocarbons.

Objectives and tasks of the research. The main objective of the research is the synthesis of carbon nanotubes from propane gas, the

⁴ Esteves, L.M., Oliveira, H.A., Passos, F.B. Carbon nanotubes as catalyst support in chemical vapor deposition reaction: A review // Journal of Industrial and Engineering Chemistry, – 2018, 65 (1), - p. 1–15.

study of the physicochemical properties of the obtained CNTs and their catalytic activity in the oxidation reactions of hydrocarbons, consisting of the investigation of the structure-activity relationship.

To achieve the research's objective, the following tasks are planned:

- Synthesis of CNTs from carbon feedstock (propane gas) by the vapor-phase chemical deposition method, and determination of the optimal synthesis conditions (temperature, gas flow rate, reaction time);

- A comprehensive study of the physicochemical properties of the synthesized and selected CNTs using modern research methods;

- Investigation of the catalytic activity and stability of prepared systems based on carbon nanotubes, both as a direct catalyst and as a support, in the oxidation reactions of hydrocarbons;

- Investigation of the kinetic laws of the cumene oxidation reaction on synthesized metal (Fe)-containing carbon nanotube-based catalysts;

- Establishing the relationship between the catalyst's structure and its catalytic activity, and proposing a plausible reaction mechanism.

These tasks ensure systematic and comprehensive research at all stages, from the synthesis process to catalytic studies, thereby establishing the scientific basis for the use of CNTs derived from propane gas as a new generation of catalyst.

Research methods. The crystal structure of the synthesized MWCNT catalyst samples was investigated by X-ray diffraction analysis (XRD), and their morphological characteristics were studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Additionally, the product composition of the oxidation reactions catalyzed by the samples was analyzed using gas chromatography-mass spectrometry (GC-MS).

The main theses presented are as follows:

- The synthesis of MWCNT catalyst samples from propane gas feedstock, which is feasible for large-scale production in our country;

- The investigation of the structure of the synthesized catalysts using modern physicochemical analysis methods;

- Investigation of the catalytic activity of catalyst samples containing different amounts of Fe nanoclusters in the oxidation reactions of various classes of hydrocarbons;
- Study of the kinetic characteristics of reactions catalyzed by metal-containing carbon nanotubes.

Scientific novelty of the research. In this research, a hybrid CNT - metal catalytic system based on carbon nanotubes was synthesized. During the synthesis process, the CNT grew directly on the metal surface, resulting in metal particles being stabilized within the CNT matrix to form an inseparable hybrid structure. It was determined that in this material, the metal and the CNTs do not act as independent phases, but rather as a single complex, catalytic center. This characteristic indicates that in catalytic processes, CNT acts not only as a carrier but also as a direct active component, and is presented as the first scientific explanation of CNTs catalytic mechanism. According to the proposed mechanism, the electron interaction and charge transfer between the CNT and the metal reduce the energy barrier in the reaction, increasing its activity and rate. Thus, the research has established the scientific basis for creating a new generation of CNT-metal hybrid catalysts that are durable, stable, and effective against metal leaching.

Theoretical and practical significance of the research. In recent years, research in the field of nanomaterials and heterogeneous catalysis has been aimed at increasing energy efficiency and creating environmentally friendly technologies. This work involves the synthesis of carbon nanotubes from a low-cost raw material such as propane gas and the study of their catalytic properties. The study determined the effect of synthesis parameters on the structure and catalytic activity of CNTs, establishing a theoretical basis for their controlled synthesis. At the same time, the structure-activity relationship was investigated by determining the effect of the purity, structure, and metal content of the CNTs on catalytic activity and reaction rate. These results make a significant contribution to the development of heterogeneous catalysis science and the development of new-generation efficient catalyst systems.

From a practical standpoint, the use of propane gas as a starting raw material makes the synthesis of carbon nanobutlers more economical and technologically viable. The application of cheap and accessible resources reduces production costs, facilitating the large-scale industrial production and use of CNTs. The obtained CNT-based catalysts exhibit high activity and stability in important chemical processes such as the oxidation of various classes of hydrocarbons under mild reaction conditions, the synthesis of oxygenated compounds, and so on. These properties can increase the energy efficiency of industrial processes while also reducing environmental impact. At the same time, CNT-based catalysts are considered promising materials for reducing atmospheric pollution by oxidizing harmful hydrocarbons present in industrial and transportation emissions. Such technologies make a significant contribution to enhancing environmental sustainability in the energy sector and in waste treatment. Thus, the research conducted both clarifies the formation and catalytic laws of CNTs at a theoretical level and, at a practical level, lays the scientific foundation for the development of inexpensive, environmentally friendly, and efficient technologies. The results obtained contribute to the development of promising catalytic processes in the field of nanomaterials and heterogeneous catalysis.

Approval and application of the dissertation. The main results of the dissertation were presented and widely discussed at the following international and national-level scientific conferences: Abstracts of scientific conference “Nagiyev Readings” dedicated to the 110th anniversary of academician M.Nagiyev, (Baku, 2018); International scientific and practical conference "Innovative prospects for the development of oil refining and petrochemistry", dedicated to the 110th anniversary of academician V.S. Aliyev, (Baku, 2018); International Scientific Conference “Actual Problems of Modern Chemistry, (Baku, 2019); Akademik Y.H.Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutunun 90 illik yubileyinə həsr olunmuş “Müasir kimyanın aktual problemləri” Beynəlxalq Elmi Konfransı, (Bakı, 2019); X International Scientific-Technical Conference

“Advance in Petroleum and Gas Industry and Petrochemistry”, (Lviv, 2020).

Name of the organization where the dissertation was carried out. The dissertation was completed at the Research Center for High Technologies of the Ministry of Science and Education of the Republic of Azerbaijan and at the “Oxidation Processes with Nanocatalysts” laboratory of the “Institute of Chemistry” Public Legal Entity.

The total volume of the dissertation in characters, with the separate volumes of its structural sections indicated. The dissertation consists of an introduction (11986 characters), 4 chapters (chapter I – 57993 characters, chapter II – 42336 characters, chapter III – 19194 characters, chapter IV – 78504 characters), conclusions (2329 characters), and a list of 188 references used. The total volume of the work, including 40 figures, 14 tables, and 4 schemes, comprised 162 computer-printed pages and 212358 characters.

Publication of the research work. As part of the dissertation, 14 scientific works on the topic were published, including 9 scientific articles and 5 conference abstracts. Of the published articles, three were authored solo, and seven were printed in scientific journals included in international abstracting databases and indexing systems. All of the conference abstracts were published in the proceedings of international scientific conferences.

MAIN CONTENT OF THE THESIS

In the **first chapter** of the dissertation, the structure, physical and chemical properties of carbon nanotubes, their various synthesis methods, and the carbon sources used were investigated in detail. The current state of research on the application of carbon nanotubes in the field of heterogeneous catalysis was also analyzed [1, 4].

In the **second chapter**, a synthetic methodology for Fe@MWCNT(G-CVD-1) and Fe@MWCNT(G-CVD-5) was presented, using propane gas as the main carbon feedstock. To conduct comparative studies and perform pilot experiments in the initial stage of the work, samples Fe@MWCNT(CVD-179) and

Fe@MWCNT(CVD-184) were also synthesized using liquid cyclohexane as an alternative carbon source. To evaluate the potential of MWCNTs as a carrier in catalytic systems and to comparatively study their catalytic properties, the modification of nanoscale TiO₂ particles onto the surface of carbon nanotubes was also carried out [5, 10].

The research showed that a comparison of the two nanotechnology systems based on different carbon sources revealed that both possess favorable properties for application. However, the propane-based CVD process is superior due to its more stable operation, high productivity, and greater potential for industrial-scale application.

In this study, Fe@MWCNT(G-CVD-1) and Fe@MWCNT(G-CVD-5) were synthesized in a laboratory setup using the chemical vapor deposition (CVD) method at normal atmospheric pressure. The synthesis was carried out at 900°C using a ferrocene precursor, and the effect of the main process parameters on the morphological characteristics and yield of the obtained MWCNTs was studied. It has been determined that doubling the amount of ferrocene and the propane flow rate leads to an approximately twofold increase in yield and an increase in the amount of Fe nanoclusters in the catalyst [8, 13]. The structure and physicochemical properties of the synthesized carbon nanotube-based samples were investigated using modern analytical methods [4, 14]. According to the SEM results, the samples are characterized by a mainly homogeneously distributed boron-like structure and a smooth surface (figure 1).

The outer diameter of the nanotubes was ~10–40 nm, depending on the synthesis conditions, and they possess a linear morphology characterized by minimal curvature. The image shows the nanotubes entangled with each other in a dense network-like form.

TEM analyses showed that the nanotubes have a multilayer, long, tubular structure formed from concentric graphene layers (figure 2). The Fe nanoparticles, appearing as black dots on their ends and surfaces, represent the active centers of the catalyst. Aggregation of the Fe nanoparticles was observed in some areas.

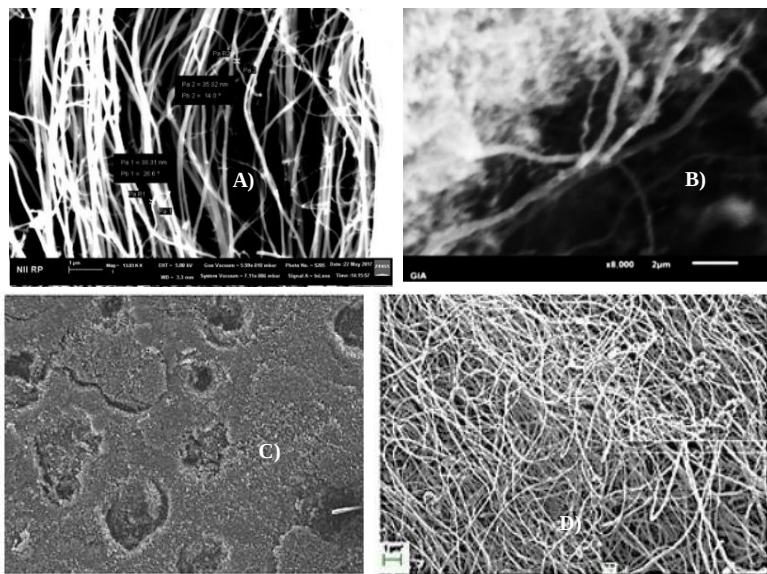


Figure 1. SEM analysis images of the Fe@MWCNT(CVD-179)(A), Fe@MWCNT(G-CVD-1)(B), and Fe@MWCNT(G-CVD-5)(C, D) samples [3, 13, 14].

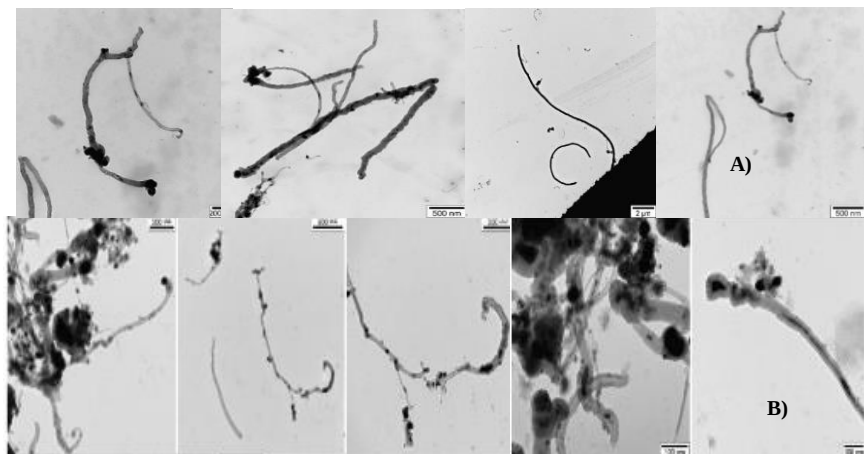


Figure 2. TEM analysis images of the Fe@MWCNT(G-CVD-1) (A) and Fe@MWCNT(G-CVD-5) (B) samples [13, 14].

The XRD results confirmed the presence of a crystalline graphite phase in the sample, and also showed the presence of Fe and Fe_3C phases (figure 3).

The results of the EDX spectra confirmed that the samples are mainly composed of carbon and iron elements (figure 4).

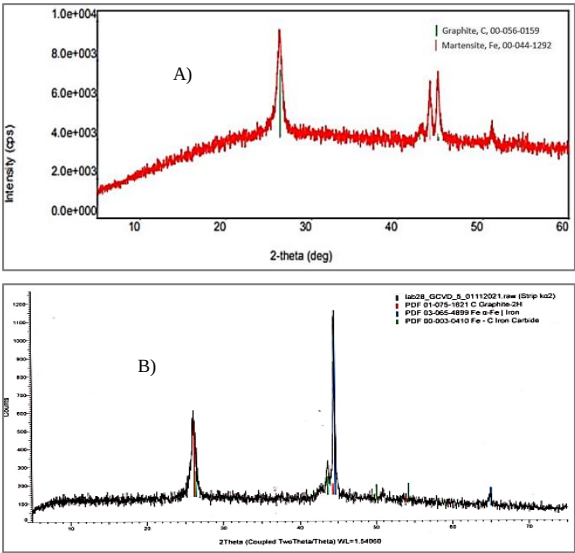


Figure 3. X-ray diffraction patterns of the Fe@MWCNT(G-CVD-1) (A) and Fe@MWCNT(G-CVD-5) (B) samples [11, 12].

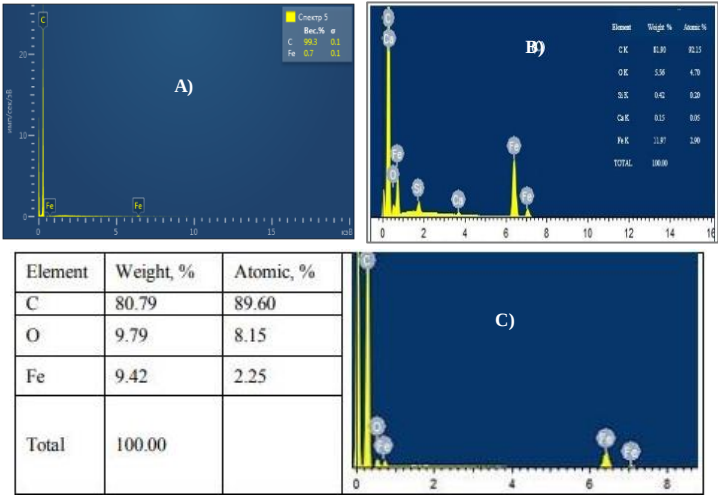


Figure 4. EDX analysis images of the Fe@MWCNT(CVD-179) (A), Fe@MWCNT(G-CVD-1) (B), and Fe@MWCNT(G-CVD-5) (C) samples [3, 13, 14].

Overall, the results of SEM, TEM, XRD, and EDX analyses confirmed that the synthesized Fe-containing samples possess a well-crystallized, multi-walled carbon nanotube structure.

The mass determination method was used to more accurately determine the amount of iron in the MWCNT catalyst samples (table 1).

Table 1.
Mass fraction of iron (Fe) in MWCNT catalyst samples.

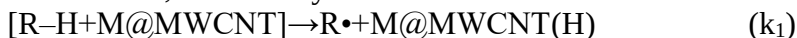
Catalyst samples	Fe mass content (%)
Fe@MWCNT(CVD-184)	3.7
Fe@MWCNT(CVD-179)	3.1
Fe@MWCNT(G-CVD-1)	9.8
Fe@MWCNT(G-CVD-5)	22.8

The **third chapter** presents the methodology for experiments conducted to study the catalytic activities of the synthesized MWCNT catalysts in the oxidation reactions of various hydrocarbons. The main factors affecting the reaction rate, including temperature, catalyst amount, and the composition of the oxidizing medium, were determined. Additionally, the operating principles of the gasometric and bubble-type laboratory setups used in the oxidation processes were described.

In the **fourth chapter**, the kinetic laws of the aerobic oxidation of various classes of liquid hydrocarbons were investigated in the presence of metal-carbon nanotube hybrid catalysts. The effect of temperature and catalyst amount on the reaction rate was studied, a possible mechanism for the process was proposed, and the obtained results were discussed.

The aerobic oxidation of cumene over the Fe@MWCNT catalyst occurs via an ion-radical mechanism. The process was carried out in an organic solvent in the presence of air oxygen. Based on the experimental results obtained, the oxidation of cumene in the presence of Fe@MWCNT proceeds via the following plausible mechanism [8, 11].

Chain initiation step (W_0): According to the proposed mechanism, the catalytic activity is formed due to the electronic interaction that arises between the Fe nanoparticles and the surface of the MWCNT. The aromatic ring of the cumene enters into a π - π interaction with the surface of the CNT, while the Fe centers cause the weakening of the triple C-H bond of the isopropyl group. At this stage, the cleavage of hydrogen from the triple bond, the weakest bond, is facilitated, and a cumyl radical is formed.



Here, RH is the cumene molecule, and $R\cdot$ is the cumeyl radical. It has been determined that the $R\cdot$ radicals generated from the adsorption and activation of the cumene molecule on the active surface of the Fe@MWCNT catalyst act as the primary active species for the development of subsequent chain oxidation stages. Additionally, the interaction of hydrocarbon molecules with molecular oxygen in the reaction medium leads to the formation of both carbon-centered $R\cdot$ radicals and hydroperoxyl $HO_2\cdot$ radicals. These resulting active radical species cause the chain mechanism to continue and the oxidation process to proceed.

The propagation stage: The carbon-centered radical generated in the initiation stage is kinetically unstable and immediately reacts with oxygen adsorbed from the air. At this stage, oxygen reacts with the radicals, leading to the formation of peroxy radicals and continuing the chain propagation. Based on the experimental conditions, it is assumed that in the proposed mechanism, oxygen participates in a partially activated state, adsorbed on the catalyst surface:



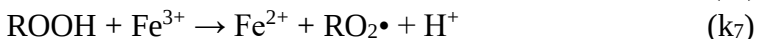
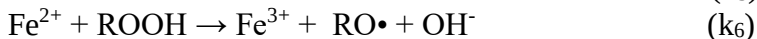
The resulting peroxy radical then causes the formation of cumene hydroperoxide and a new carbon-centered radical by abstracting a hydrogen atom from another cumene molecule.



These stages are fundamental to chain growth and explain the formation of cumene hydroperoxide.

Catalytic conversion of hydroperoxide and degenerative branching: In the next stage of the chain oxidation process, the

catalytic decomposition of the formed hydroperoxides occurs with the participation of Fe@MWCNT. The cumene hydroperoxide generated during the development stage of the chain oxidation process undergoes successive redox conversions on the Fe@MWCNT surface. In this stage, the catalytic system ensures the uninterrupted continuation of the radical chain by performing the degenerative branching function via the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. The MWCNT matrix acts as a conductive channel, accelerating the electron transfer in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox conversion. The catalyst accelerates the decomposition rate of hydroperoxides at this stage, leading to a sharp reduction in the induction period.



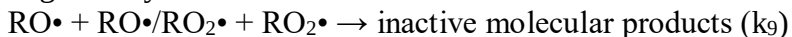
These interconversions maintain the intensity of the chain reaction by ensuring the continuous regeneration of radical particles. The synergistic structure of the Fe@MWCNT catalyst - that is, the interaction between the transition metal centers and the electron-conductive framework of the carbon nanotubes - facilitates the rapid and effective decomposition of hydroperoxides. As a result, both the formation of cumene hydroperoxide and its parallel decomposition occurred in the system, and the catalytic oxidation process was carried out at a higher rate compared to analogous reactions conducted under non-catalytic conditions. According to the proposed mechanism, a dynamic equilibrium is formed between these two processes, and the cumene hydroperoxide stabilizes at a certain low steady-state concentration, accumulating as an intermediate product.

The experimental results are explained by the internal β -cleavage of the alkoxy radical, generated from the conversion of a hydroperoxide with Fe^{2+} , leading to the formation of acetophenone with approximately 47.1% selectivity. This process is particularly intense at high temperatures (80°C):



Chain termination stage: In this stage, the active radicals formed in the reaction medium enter into mutual recombination reactions,

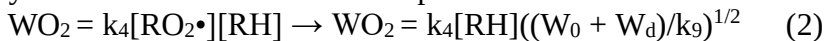
converting into inactive molecular products, and as a result, the chain process gradually dies out.



According to the proposed mechanism, the rate of oxygen consumption depends on the balance between the generation of radicals in the system and their recombination. Assuming a steady state, the generation rate of radicals is equal to the consumption rate during their termination stage. In this case, the concentration of the peroxy radical is determined by the square root of expression (1).

$$[\text{RO}_2\bullet] = ((W_0 + W_d)/k_9)^{1/2} \quad (1)$$

Taking into account the rate equation (2) for the interaction of the peroxy radical with cumene in the expression obtained:



Consequently, according to the classical radical-chain mechanism, the rate of the oxidation process can be expressed by the following (3) equation:

$$\text{WO}_2 = (W_0 + W_d)^{1/2} k_4 k_9^{-1/2} [\text{RH}] \quad (3)$$

Here, W_0 is the rate of formation of primary radicals resulting from the activation of cumene on the catalyst surface, W_d – the rate of generation of secondary radicals from the catalytic decomposition of hydroperoxide, k_4 and k_9 – rate constants, $[\text{RH}]$ – the concentration of cumene [8, 14]. As can be seen from Equation (3), the activity of the catalyst can be attributed to the acceleration of radical formation and, consequently, the increase in the oxygen consumption rate. On the other hand, a large value of k_9 leads to an acceleration of the radical recombination process. In this case, the probability of chain continuation decreases, and the oxygen consumption rate drops. This reflects the classic kinetic patterns characteristic of radical chain mechanisms.

The high electrical conductivity and advanced π -electron system of carbon nanotubes indicate that they act not only as carriers but also as active components involved in electron transfer. For this reason, it is insufficient to explain the catalytic effect of the Fe@MWCNT system solely by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ valence transitions. The electronic interactions occurring between the surface of the Fe nanoparticles and the carbon nanotubes can facilitate the activation of oxygen and

hydrocarbon molecules by influencing the electronic state of the active centers. At the same time, the inner channels and surface structure of the nanotubes prevent the aggregation of the metal particles, ensuring their high dispersion. Thus, the formation of catalytic activity in the Fe@MWCNT system can be attributed to the combined effects of electron exchange between the metal and carbon phases, interfacial charge transfer, and nanoconfinement.

The reaction is believed to proceed under predominantly kinetic-controlled conditions. This is evidenced by the shortening of the induction period, the rapid decomposition of the hydroperoxide, and the immediate increase in reaction rate upon the addition of the catalyst. The reaction was carried out under stirring conditions, and the reaction medium was intensively agitated throughout the process. Stirring improved the mass and heat transfer between the catalyst particles and the reaction medium, and also ensured a more uniform distribution of oxygen in the liquid phase. Therefore, it was assumed that the effect of external diffusion on the process was minimal and that the reaction proceeded mainly in the kinetic region.

The objective of the test experiments conducted as part of the research was to determine the performance of catalysts containing 3.1% (Fe@MWCNT(CVD-179)) and 3.7% (Fe@MWCNT(CVD-184)) iron nanoclusters were investigated for their initial catalytic activity in oxidation reactions. For the reaction, cumene and ethylbenzene were initially selected as representative alkylaromatic hydrocarbons containing triple and double C-C bonds with a bond energy of $\sim 300 \text{ kJ} \times \text{mol}^{-1}$, respectively, as the oxidized species. The results obtained show that at a constant temperature, increasing the amount of the CVD-179 catalyst leads to an increase in the reaction rate (figure 5). At 60°C, the reaction rate without a catalyst was low, which indicates that the process proceeds with a certain degree of thermal activation. The addition of the CVD-179 catalyst increased the reaction rate and influenced its kinetics (figure 5 A). This activity of the catalyst was also observed during the oxidation of ethylbenzene (figure 5 B) [2, 3].

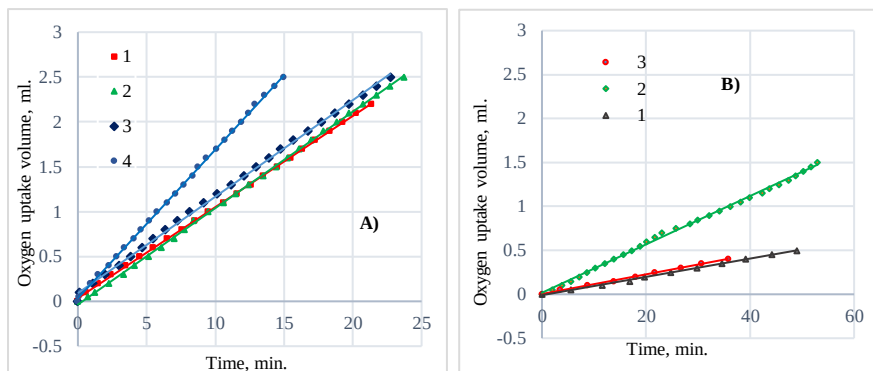


Figure 5. Oxidation of cumene (A: 0 mg (1), 5 mg (2), 10 mg (3), 20 mg (4)) and ethylbenzene (B: 0 mg (1), 10 mg (2), 20 mg (3)) of the Fe@MWCNT(CVD-179) catalyst (initiator - AIBN, $T = 60^{\circ}\text{C}$, $P_{O_2(\text{hava})} = 20 \text{ kPa}$).

The oxidation of cumene was also carried out with the CVD-184 sample. CVD-184 is the unpurified precursor of CVD-179. When the same amount of catalyst was used, CVD-179 showed higher activity (figure 6).

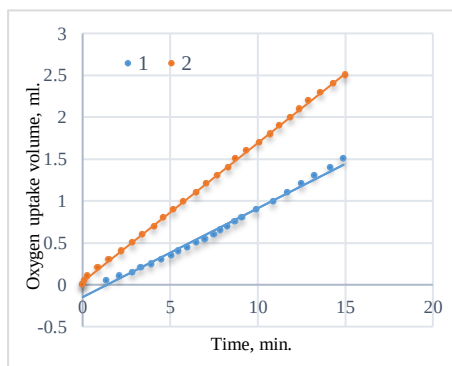


Figure 6. Kinetic dependencies of oxygen uptake during the aerobic oxidation of cumene in the presence of the Fe@MWCNT(CVD-179) (1) and Fe@MWCNT(CVD-184) (2) catalysts ($T = 60^{\circ}\text{C}$, initiator – AIBN, $P_{O_2(\text{hava})} = 20 \text{ kPa}$, MWCNT: 20 mg).

This difference indicates that the catalytic activity is related not only to the amount of iron but also to the cleanliness of the sample's surface. The low activity of CVD-184 is attributed to the resinous

materials, polycyclic aromatic compounds, and other by-products remaining on the surface after synthesis. The coating of these substances on the active centers has led to a decrease in catalytic activity.

To evaluate the properties of MWCNTs as a carrier and to conduct a comparative study, the catalytic activity of the laboratory-prepared $\text{TiO}_2\text{@MWCNT}$ catalyst in the oxidation of cumene and the decomposition of cumene hydroperoxide reactions was investigated [6, 7]. Based on the experimental results, a temperature above 100°C , a reaction time of at least 2 hours, and a catalyst load of 1 wt.% were considered favorable for the aerobic oxidation of cumene. In these conditions, experiments conducted in a batch-type apparatus for 6 hours showed a maximum conversion of cumene of 76.38%, and the catalyst largely retained its activity over four consecutive cycles. However, a decrease in activity was observed in subsequent cycles. The obtained results indicate that the $\text{TiO}_2\text{@MWCNT}$ composite accelerates the decomposition of hydroperoxides generated during the aerobic oxidation of cumene at temperatures above 100°C . These results are consistent with the data obtained from the kinetic study of oxygen uptake during the cumene oxidation with initiator participation.

Based on the positive results from the experimental tests, the catalytic activity of $\text{Fe@MWCNT}(\text{G-CVD-1})$ and $\text{Fe@MWCNT}(\text{G-CVD-5})$ samples were investigated for their catalytic activity in the oxidation reactions of various hydrocarbons [6]. In the model oxidation reaction of cumene, an increase in temperature and catalyst amount for both catalysts was accompanied by an increase in catalytic activity. Figure 7 shows the effect of using different amounts of the G-CVD-1 catalyst at 60°C on the rate of the cumene oxidation reaction. In the absence of a catalyst, the reaction rate was very low ($7.2 \text{ mm}^3 \times \text{min}^{-1}$). However, when G-CVD-1 was added, the reaction rate increased significantly and varied proportionally with the increase in catalyst amount. These results indicate that the G-CVD-1 sample exhibits high catalytic activity in the oxidation of cumene.

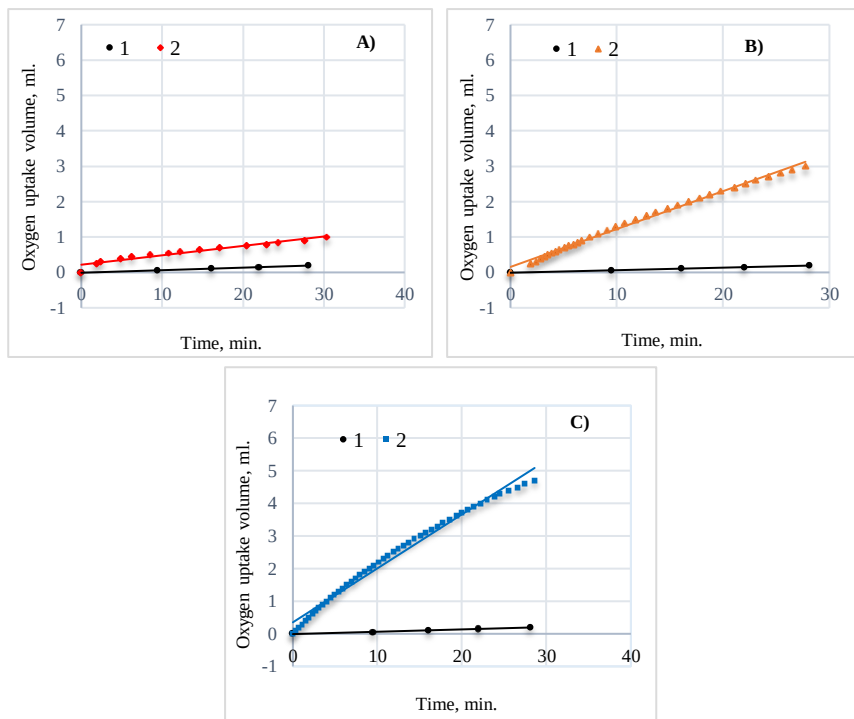


Figure 7. Kinetic dependencies of oxygen uptake during the aerobic oxidation of cumene in the presence of the Fe@MWCNT(CVD-1) catalyst ($T = 60^{\circ}\text{C}$, $P_{\text{O}_2(\text{hava})} = 20 \text{ kPa}$, (A): 0 mg (1), 5 mg (2(A)); 10 mg (2(B)); 20 mg (2(C))).

The oxidation of cumene over the Fe@MWCNT(G-CVD-1) catalyst was also investigated at 80°C . The results are shown in figure 8. Based on the results, the rate observed in the reaction carried out with 20 mg of the G-CVD-1 catalyst was the highest compared to all other experiments. This fact is fully consistent with the theory of surface adsorption and active centers, which explains the effect of heterogeneous catalysts on kinetics. Increasing the amount of catalyst facilitates the formation of more active centers in the reaction system, and as a result, the overall reaction rate increases. It has also been observed that the presence of the catalyst eliminates the induction period, and the reaction proceeds faster from the very beginning.

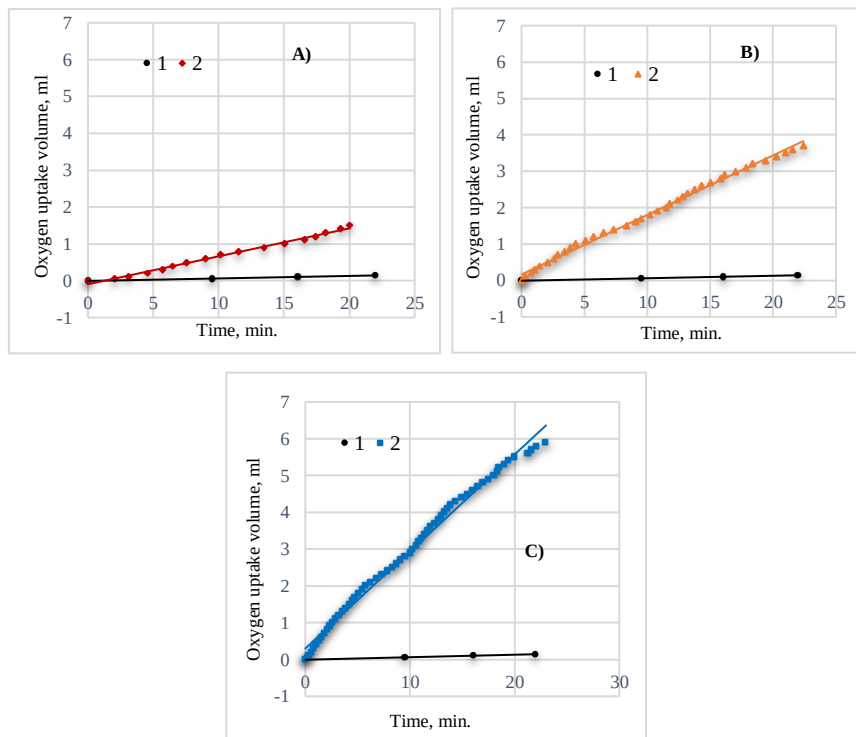


Figure 8. Kinetic dependencies of oxygen uptake during the oxidation of cumene in the presence of the Fe@MWCNT(CVD-1) catalyst ($T = 80^{\circ}\text{C}$, $P_{\text{O}_2(\text{hava})} = 20 \text{ kPa}$, 0 mg (1), 5 mg (2(A)), 10 mg (2(B)) 20 mg (2(C))).

Similar results were also obtained during the aerobic oxidation of cumene in the presence of the Fe@MWCNT(G-CVD-5) catalyst. The highest reaction rate was observed at 80°C when 20 mg of the catalyst was used (figure 9).

Table 2 presents the reaction rates calculated by the volumetric method for the aerobic oxidation of cumene over the Fe@MWCNT(CVD-1) and Fe@MWCNT(CVD-5) catalysts. The calculations were performed in Excel. Under all investigated conditions, the CVD-1 catalyst exhibited higher catalytic activity compared to CVD-5.

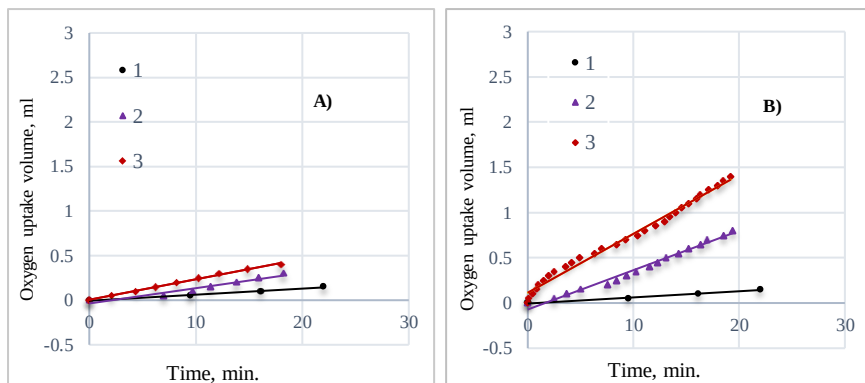


Figure 9. Kinetic dependencies of oxygen uptake during the oxidation of cumene in the presence of the Fe@MWCNTCVD-5 catalyst. $T_A = 60^\circ\text{C}$, $T_B = 80^\circ\text{C}$, $P_{O_2(\text{hava})} = 20 \text{ kPa}$, MWCNT: 0 mg (1), 10 mg (2), 20 mg (3).

Table 2.
Calculated overall reaction rates for the aerobic oxidation of cumene in the presence of Fe@MWCNT(CVD-1) and Fe@MWCNT(CVD-5) catalysts.

№	T, °C	$m_{\text{cat.}}$, mg	W , $\text{mm}^3 \cdot \text{min}^{-1}$	
			CVD-1	CVD-5
1	60	5	26.5	8
	80		45.3	19.8
2	60	10	107.1	34.6
	80		132.2	71.9
3	60	20	165.5	98.5
	80		190.9	158.1

The catalytic activity of the Fe@MWCNT(G-CVD-5) catalyst was also studied in the oxidation reactions of decalin and tetradecane, representatives of alicyclic and aliphatic hydrocarbons.

Based on the results, the Fe@MWCNT(G-CVD-5) catalyst exhibited higher catalytic activity in the oxidation of both hydrocarbons at a temperature of 140°C (figure 10).

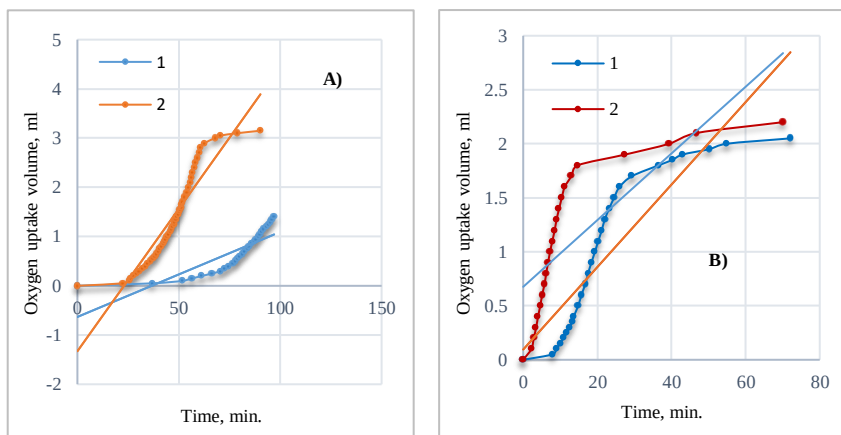


Figure 10. Kinetic dependencies of oxygen uptake during the oxidation of decalin (A) and tetradecane (B) in the presence of the Fe@MWCNT(G-CVD-5) catalyst. $T = 140^{\circ}\text{C}$, $P_{\text{O}_2(\text{hava})} = 20 \text{ kPa}$, 0 mg (1), 20 mg (2) [12].

The activity of the catalyst is directly related to the active metal nanoclusters in its structure. Figure 11 shows how the catalytic activity changes depending on the amount of metal nanoclusters for the 4 catalyst samples studied under steady-state conditions.

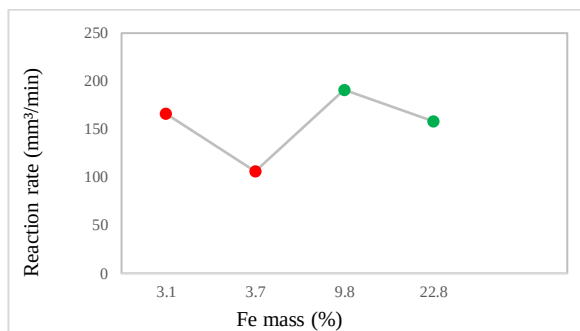


Figure 11. Effect of the amount of metal (Fe) on the rate of the chemical reaction under constant conditions (AIBN was used for samples containing 3.1% and 3.7% Fe).

According to the results, the activity of the CVD-179 sample, containing 3.1% metal, was lower than that of the G-CVD-1 sample, containing 9.8% metal. Increasing the metal mass fraction to 22.8% (G-CVD-5) did not lead to an increase in catalytic activity; instead, a

decrease was observed. Excessively increasing the metal load can lead to the aggregation of nanoparticles, the formation of large clusters, a decrease in the active surface area, and the partial blocking of pores. In this regard, the high activity of the G-CVD-1 sample was attributed not only to the total amount of metal but also to its high dispersion on the catalyst surface and the greater accessibility of the active centers.

Experimental results showed that the reaction rate increased with rising temperature for all catalysts. Based on the data in figure 12, a comparison of samples G-CVD-1 and G-CVD-5 indicates that higher catalytic activity was observed in the G-CVD-1 catalyst as the temperature increased.

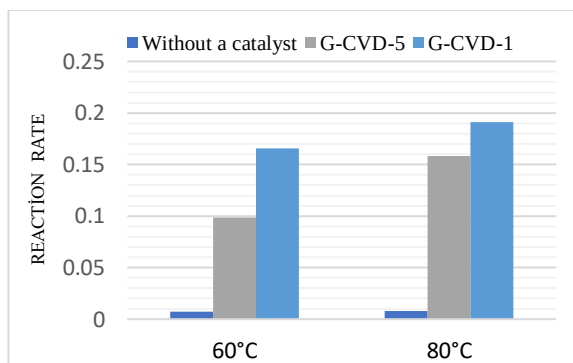


Figure 12. Comparison of the catalytic activities of the used Fe@MWCNT(G-CVD-1) and Fe@MWCNT(G-CVD-5) catalyst samples.

Based on the results of the studies, increasing the amount of the catalyst to 20 mg caused the overall reaction rate to reach a maximum (table 2). However, when the reaction rate per unit catalyst mass (specific reaction rate) is considered, the optimal amount was determined to be 10 mg (figure 13). Increasing the catalyst amount beyond 10 mg had a negligible effect on the overall reaction rate. This can be attributed to the underutilization of additional active centers. Therefore, from the perspective of process efficiency, an optimal catalyst amount of 10 mg was adopted.

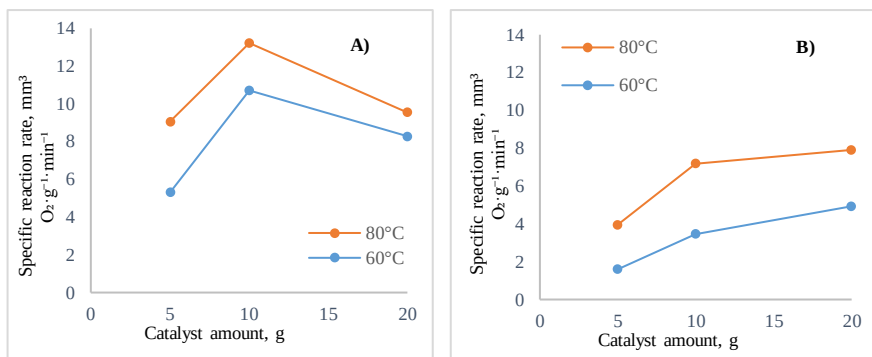


Figure 13. Variation of the reaction rate (specific reaction rate) per gram of catalyst as a function of catalyst amount at various temperatures. (A) - Fe@MWCNT(G-CVD-1) and (B) - Fe@MWCNT(G-CVD-5).

The presence of the catalyst had a significant effect on the conversion degree of the cumol and the distribution of oxidation products. In an experiment conducted in a bubble-type apparatus with the G-CVD-1 catalyst, the composition of the products was determined by GC–MS (table 3).

Table 3.
Conversion degree and selective distribution of reaction products of cumene with the Fe@MWCNT(G-CVD-1) catalyst.

Catalyst	Conversion, %	Product distribution, %						
		AsP	PP	CHP	AMS	BA	Phenol	Other
G-CVD-1	91.5	47.1	34.3	7.3	4.2	3.5	1.9	1.7

Catalyst – 20 mg; cumene – 25 ml; T = 80 °C; reaction time 6 hours; AsP – acetophenone, PP – 2-phenyl-2-propanol, CHP – cumene hydroperoxide, AMS - α -methyl styrene, BA – benzaldehyde.

Based on the results presented in table 3, the achievement of a 91.5% conversion rate during the oxidation of cumene with the Fe@MWCNT(G-CVD-1) catalyst demonstrates the catalyst's high activity. The predominance of acetophenone (47.1%) and 2-phenyl-2-propanol (34.3%) in the product distribution indicates that the reaction

proceeds primarily via selective oxidation of the triple carbon on the isopropyl group. The detection of cumene hydroperoxide in a relatively low amount (7.3%) confirms that it is converted into the final products after being formed as an intermediate product.

Considering the catalytic activity of the Fe@MWCNT(G-CVD-1) and Fe@MWCNT(G-CVD-5) catalysts at various temperatures and amounts in our study, the activation energy was calculated using the Arrhenius equation. Since the reaction activation energy was calculated from the oxygen uptake rates by the volumetric method, it was considered the effective activation energy. Since the reaction conditions are the same in all experiments, the concentration-dependent term in the rate expression remains constant, and therefore, using reaction rates instead of rate constants does not affect the calculation of the activation energy. The calculated activation energy values for the G-CVD-1 and G-CVD-5 catalysts are given in table 4.

Table 4.
Kinetic parameters of the oxidation reaction in the presence of the Kumolun Fe@MWCNT(G-CVD-1) and Fe@MWCNT(G-CVD-5) catalysts.

Catalysts	m_{cat} , mg	W_2/W_1 , $mm^3 \times min^{-1}$	Activation energy, $kkal \times mol^{-1}$	
G-CVD-1	5	1.709	E_1	6.26
	10	1.234	E_2	2.46
	20	1.154	E_3	1.67
G-CVD-5	5	2.475	E_1	10.6
	10	2.078	E_2	8.56
	20	1.605	E_3	5.52

The activation energy values presented in table 4 once again demonstrate that the G-CVD-1 catalyst has a higher efficiency. The obtained results are considered acceptable for heterogeneous catalytic systems.

After use, the Fe@MWCNT(G-CVD-1) catalyst was separated from the system by simple filtration and was subsequently reused several times without a noticeable change in its activity. Table 5 shows that only a negligible change in conversion was recorded over 7 consecutive reaction cycles in the presence of the catalyst. The absence of a significant decrease in the reaction rate during repeated

tests indicated that the iron nanoclusters were not leached from the carbon framework and demonstrated the high chemical/structural stability of the catalytic centers.

Table 5.
Studies on the reusability of the Fe@MWCNT(G-CVD-1) catalyst.

Reaction cycle	I	II	III	IV	V	VI	VII
Reaction rate ($\text{mm}^3 \times \text{min}^{-1}$)	190.9	190.1	189.5	189.5	188.7	188.5	187.9
Cumol conversion (%)	91.5	90.9	90.4	89.2	88.7	88.5	88.1

The catalytic performance of the Fe@MWCNT(G-CVD-1) and homogeneous $\text{Co}(\text{CH}_3\text{COO})_2$ catalysts in the aerobic oxidation of cumene was compared under the same experimental conditions. As can be seen from the time-dependent oxygen uptake kinetic curves in figure 14, the process proceeds at a higher and more sustained rate with the participation of Fe@MWCNT(G-CVD-1). Thus, the reaction rate was $190.9 \text{ mm}^3 \cdot \text{min}^{-1}$ for G-CVD-1 and $14.6 \text{ mm}^3 \cdot \text{min}^{-1}$ for $\text{Co}(\text{CH}_3\text{COO})_2$.

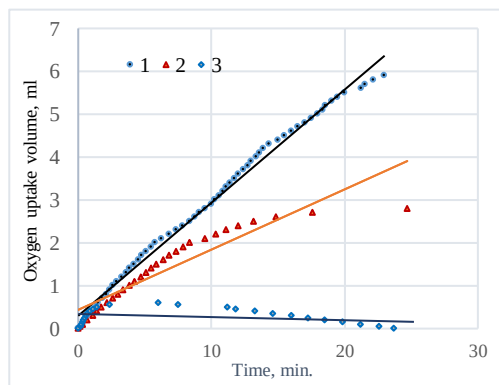


Figure 14. Fe@MWCNT(G-CVD-1)(1), Comparison of oxygen uptake rates in the aerobic oxidation of cumene over the TiO_2 @MWCNT(2) and $\text{Co}(\text{CH}_3\text{COO})_2$ (3) catalysts (cumene = 10 ml, catalyst = 20 mg, $T = 80^\circ\text{C}$).

These results indicate that the heterogeneous Fe@MWCNT catalyst has higher catalytic activity compared to cobalt(II) acetate under the chosen conditions. The oxygen uptake involving $\text{Co}(\text{CH}_3\text{COO})_2$ primarily occurs in the first 3 - 5 minutes of the reaction and decreases sharply in the subsequent stage, indicating the low sustainability of the process.

The catalytic activity of the Fe@MWCNT(G-CVD-1) catalyst was also compared with the TiO_2 @MWCNT system synthesized by us. Although oxygen uptake was observed with both catalysts under the same reaction conditions, the process was faster for the G-CVD-1 sample (figure 14). This result indicates that under the chosen conditions, the Fe-containing active centers are more efficient than the TiO_2 -based system in activating oxygen and cumene. Based on previous results, TiO_2 @MWCNT exhibited high activity at a higher temperature, mainly under conditions above 120°C , with a maximum cumene conversion of 76.38%. The catalyst maintained its activity for four consecutive cycles, with a decrease observed in subsequent cycles. In contrast, Fe@MWCNT(G-CVD-1) exhibited high activity at a lower temperature and retained its catalytic properties for seven consecutive cycles. Thus, the G-CVD-1 catalyst demonstrated superior activity to the TiO_2 @MWCNT system, both by operating under more favorable temperature conditions and by exhibiting higher stability during reuse.

Overall, the results obtained show that in the Fe@MWCNT(G-CVD-1) catalytic system, carbon nanotubes do not just act as a support, but together with the metal nanoparticles, they form a unified active catalytic system and exhibit high catalytic activity in the aerobic oxidation reactions of various classes of hydrocarbons. This characteristic allows the Fe@MWCNT(G-CVD-1) catalyst to be evaluated as a promising catalyst for the aerobic oxidation processes of complex hydrocarbon mixtures.

RESULTS

1. Fe@MWCNT catalyst samples were synthesized by a vapor-phase chemical deposition method. The composition, structure, and physicochemical properties of the catalyst samples were investigated using modern analytical methods. Analyses revealed that during synthesis, Fe nanoclusters were formed from the thermal decomposition of ferrocene and were distributed, immobilized, and located both within the internal channels and on the surface of the carbon nanotube matrix [7, 11, 13, 14].

2. Based on a comparative analysis, it was determined that for the synthesis of carbon nanotubes, increasing the Fe loading from 3.7% to 22.8% with the propane based gas phase CVD method, compared to the cyclohexane-based aerosol CVD method, was characterized by an increased Fe loading from 3.7% to 22.8%, a higher yield of 0.55 - 1.6 g within 30 minutes, and the formation of fewer side carbon phases compared to the cyclohexane-based aerosol CVD method [3, 13, 14].

3. Among the Fe@MWCNT catalysts synthesized from propane gas, the highest catalytic activity was determined in the Fe@MWCNT(G-CVD-1) sample containing 9.8% Fe, achieving a 91.5% conversion in the liquid-phase oxidation of cumene. An increase in the Fe content was accompanied by a decrease in catalytic activity [14].

4. The research results showed that selecting an optimal reaction temperature of 80°C and a catalyst amount of 10 mg ensures the maximum catalytic activity of the Fe@MWCNT catalyst. The high activity observed in the G-CVD-1 sample was attributed to the synergistic interaction between the metal nanoparticles and carbon nanotubes enhancing the catalytic process [14].

5. A structure-activity relationship has been established for the Fe@MWCNT catalysts: the size of the metal nanoparticles, reduction in the amount of metal nanoparticles within the MWCNT and their homogeneous distribution on the MWCNT surface led to an increase in catalytic activity, which indicates that the metal nanoclusters immobilized within the MWCNT play a crucial role in the catalytic process [13].

6. In the cumene oxidation reaction, the Fe@MWCNT(G-CVD-1) catalyst exhibited higher catalytic activity compared to the $\text{Co}(\text{CH}_3\text{COO})_2$ and $\text{TiO}_2\text{@MWCNT}$ catalysts. Under the same reaction conditions, the maximum reaction rate was $190.9 \text{ mm}^3/\text{min}$ for G-CVD-1, while it was 14.6 and $150.5 \text{ mm}^3/\text{min}$ for the $\text{Co}(\text{CH}_3\text{COO})_2$ and $\text{TiO}_2\text{@MWCNT}$ catalysts, respectively [9, 10, 12].

7. Comparison of the Fe@MWCNT(G-CVD-1) catalyst with the metal - free MWCNT system showed that the carbon nanotubes act as an active carrier in this catalytic system, owing to their high electronic conductivity, along with the Fe nanoparticles, participate in forming the catalytic activity as a joint, hybrid catalytic system.

The main results of the dissertation were published in the following scientific publications:

1. Zeynalov, E.B., Huseynov, A. B., Magerramova, M. Y., Salmanova, N. I., Abdurehmanova, N. A. Impact of as-prepared carbon nanotubes on the chain oxidation reactions of hydrocarbons // International scientific and practical conference "Innovative prospects for the development of oil refining and petrochemistry", dedicated to the 110th anniversary of academician V.S. Aliyev – Baku: – 2018, – p. 133.

2. Zeynalov, E.B., Huseynov, A.B., Friedrich, J.F., Magerramova, M.Y., Abdurehmanova, N. A. Testing of carbon nanotubes as possible active constituents in a model oxidation environment // Abstracts of scientific conference “Nagiyev Readings” dedicated to the 110th anniversary of academician M.Nagiyev- Baku: - 2018, - p. 145.

3. Abdurahmanova, N.Ə., Zeynalov, E.B., Hüseynov, Ə.B., Əhmədova, L.İ., Nadiri, M.İ., Nağıyev, Y.M. Tsikloheksandan termokatalitik piroliz yolu ilə alınan çoxlaylı karbon nanoborularının alkil aromatik karbohidrogenlərin oksidləşmə proseslərinə təsiri //

Azərbaycan Texniki Universitetinin Elmi Əsərləri, – Bakı: – 2018, – № 3, – s. 78-85.

4. Zeynalov, E. B., Friedrich, J. F., Tagiyev, D. B., Huseynov, A. B., Magerramova, M. Y., N.A.Abdurahmanova. Review on nanostructures from catalytic pyrolysis of gas and liquid carbon sources // Materials Testing, – Germany: – 2018, – № 7–8, – p. 783–793.

5. Abdurəhmanova, N.Ə., Abdullayeva, S. Q., Hüseynov, Ə. B., Zeynalov, E. B. TiO_2 @CNTs metal saxlayan karbon nanoborularının sintezi və onların karbohidrogenlərin oksidləşmə proseslərində katalitik aktivliyinin tədqiqi // Beynəlxalq elmi konfrans “Müasir Kimyanın Aktual Problemləri”, – Bakı: – 2019, – s. 325.

6. Zeynalov, E. B., Akhmedova, L. İ., Abdurahmanova, N. A., Nagiyev, Y. M., Nadiri, M. İ. Catalytic effect of TiO_2 -modified carbon nanotubes on cumene hydroperoxide decomposition reaction // International Scientific Conference “Actual Problems of Modern Chemistry”, – Baku: – 2019, – p. 357.

7. Abdurahmanova, N.Ə. TiO_2 @ÇLKNB katalizatorunun iştirakı ilə kumilhidroperoksidin parçalanması // Gənc Tədqiqatçı Elmi-praktiki jurnal, – Bakı: – 2019, – № 2, – s. 78–83.

8. Zeynalov, E., Huseynov, A., Abdurəhmanova, N., Esedzadeh, G. Target synthesis of an oxidation nanocatalyst // X International Scientific-Technical Conference “Advance in Petroleum and Gas Industry and Petrochemistry”, – Lviv, Ukraine: – 2020, – p. 95–97.

9. Zeynalov, E. B., Huseynov, E. R., Salmanova, N. I., Abdurahmanova N.A. Nano-grade titanium dioxide on the nanocarbon carrier as catalyst in aerobic oxidation of alkyl aromatic hydrocarbons // Chemical Problems, – Baku: – 2020, – № 3, – p. 351–360.

10. Abdurahmanova, N.A. Study of catalytic activity of the modified multi-walled carbon nanotubes in the aerobic oxidation of cumene // Processes of Petrochemistry and Oil Refining (PPOR), – Baku: – 2020, – № 2, – p. 268–275.

11. Zeynalov, E., Huseynov, A., Huseynov, E., Salmanova, N., Nagiyev, Y., Abdurəhmanova, N. Impact of as-prepared and purified multi-walled carbon nanotubes on the liquid-phase aerobic oxidation

of hydrocarbons // Chemistry & Chemical Technology, – Ukraine: – 2021, – № 4, – p. 479–485.

12. Mustafayeva, N.A. Fe-containing carbon nanotubes as catalysts in the aerobic oxidation reactions of decalin and tetradecane // Azerbaijan Chemical Journal, – Baku: – 2022, – № 3, – p. 87–92.

13. Zeynalov, E., Friedrich, J., Huseynov, A., Mustafayeva, N., Qasimov, E. Oxidation kinetics of a commercial diesel fuel and its fraction in the presence of metal-containing multi-walled carbon nanotube admixtures // Chemistry & Chemical Technology, – Ukraine: – 2025, – № 2, – p. 385–394.

14. Mustafayeva, N.A., Zeynalov, E. B., Huseynov, A. B., Nagiyev, Y., Nadiri, M. İ., Magerremova, M. Study of catalytic activity of multi-walled carbon nanotubes synthesized from propane gas in the model oxidation reaction of cumene // Serbian Chemical Journal, – Serbia: – 2025, – № 10, – p. 1189–1201.



The defense will be held on 30 October 2026 at 11⁰⁰ at the meeting of the Dissertation council FD 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at PLE “Institute of Chemistry” of the Ministry of Science and Education of the Republic of Azerbaijan.

Address: AZ 1073, Baku, H. Javid avenue 113.

Dissertation is accessible at the PLE “Institute of Chemistry” of the Ministry of Science and Education of the Republic of Azerbaijan Library.

Electronic version of the abstract is available on the official website (www.kqki.az) of the PLE “Institute of Chemistry” of the Ministry of Science and Education of the Republic of Azerbaijan.

Abstract was sent to the required addresses on 29 September 2026.

Signed for print: 25.09.2026

Paper format: 60x84^{1/16}

Volume: 36 445

Number of hard copies: 20