

RESEARCH ARTICLE

Investigation of Conversion of N-Hexane to Gaseous and Liquid Products on the Surface of Modified Nano- Al_2O_3 Catalyst in Oxygen Medium Under the Influence of Gamma Rays

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Abstract

The temperature dependence of the product yield on the conversion of the hexane air mixture on the surface of the Al_2O_3 catalyst placed in the mini-flow reactor was studied. Transformation processes were studied comparatively on oxygen-modified and unmodified catalysts under the influence of surface radiation, and spectroscopic and gas-liquid chromatographic analyzes of the resulting products were performed.

Keywords: Gamma Radiation; Modified Catalyst Surface; Oxide Products

Introduction

The study of the kinetic interaction of the conversion of hexane to organic oxide products in the low temperature range in the atmosphere with the combined use of radiation technologies and nano-catalysts is of great importance in practice. The application of radiation to oxidation processes saves energy, time and achieves high yields [1, 2].

Energy saving requires the creation of new high-quality systems for the production of fuel from organic raw materials. Under the influence of ionizing radiation, it is possible to break various energetic chemical bonds on hydrocarbons of any molecular structure on the surface of nano-catalysts, to create new structural molecules by creating an unlimited number and variety of free radicals. Unlike classical methods, the application of radiation technologies can change the molecular structure of petroleum products and selectively change the quality of the product [1,3].

The study of the kinetic regularities of the conversion of hexane to organic oxide products in the low temperature range in the air environment with the combined use of radiation technologies and nano-catalysts is of great importance in practice [4-10].

After a long time, nanotechnology has picked up consideration as the oxidation form of vehicle catalyst framework for the upcoming era due to a few reasons. As shown, the transport segment could be a source of all discussed contaminations due to the utilization of fossil fills [11-13].

Investigation of oxidation processes on the surface of the nanoheterogeneous catalyst modified by the gamma radiation has demand for implementation. The emerged anion centers, influence of hole centers in radiolysis-catalytic transitions, and the working mechanism of these process are today's actual challenge [14].

Metal nanoparticles are widely used in heterogeneous catalysis due to their high reactivity. One of their main features is the large number of atoms on the surface due to the small size of the particles. These surface atoms are active atoms for catalysis [15-27].

In spite of the number of investigations dealing with decomposition of water in the presence of different catalysts under effect of ionizing rays, there are fewer studies devoted to this process in the presence of nanoparticles [28]. One option for reducing the air pollution caused by the transport sector is the change to alternative reserves like one of nano-catalysts, like more economically available of production. The research results show that the nano $\text{Al}_2\text{O}_3+\text{CuO}$ has a wide range in comparison with other catalysts using in the catalyst system. Interest in scientific-research works conducted in the field of radiation chemical conversion of water and hydrocarbons on the surface of nanocatalyst is increasing recently [29].

Polysaccharides are complex macromolecules long regarded as energetic storage resources or as components of plant and fungal cell walls. They have also been described as plant mucilages or microbial exopolysaccharides. The development of glycosciences has led to a partial and difficult deciphering of their other biological functions in living organisms. The objectives of glycobiology and glycochemistry are currently to correlate some structural features of polysaccharides with some biological responses in the producing organisms or in another one. In this context, the literature focusing on bioactive polysaccharides has increased exponentially during the last two decades, being sometimes very optimistic for some new applications of bioactive polysaccharides, notably in the medical field. Therefore, this review aims to examine bioactive polysaccharide, taking a critical look of the different biological activities reported by authors and the reality of the market. It focuses also on the chemical, biochemical, enzymatic, and physical modifications of these biopolymers to optimize their potential as bioactive agents [30-33].

Catalytic conversion of hexane in air on the surface of nano- Al_2O_3 catalyst, obtaining oxide products in liquid and gas phases was set as the main goal.

Experimental

Preparation of the samples: Initially, 10 g of Al_2O_3 catalyst is drawn at room temperature and filled into 30 ml ampoules. The finished samples are irradiated by processing in an air flow medium for $\tau = 50$ hours in a Co-60 isotope unit with a capacity of $P = 0.5$ kGy / h.

In the laboratory, the mini-flow device shown in Figure 1 is assembled and initially tested.

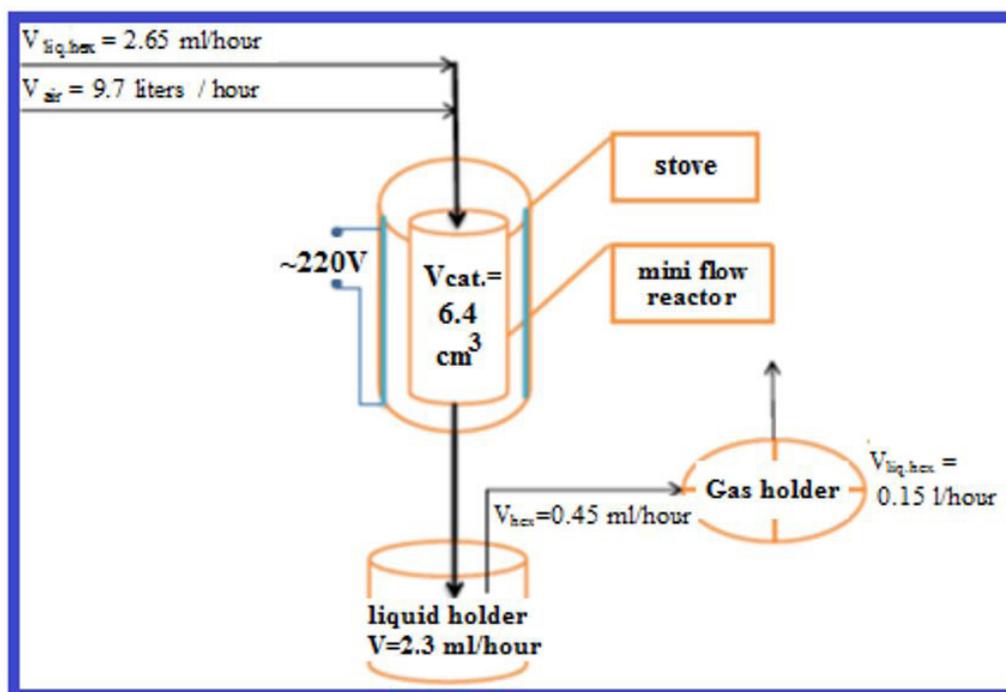


Figure 1: Working diagram of a mini flow reactor

The Hexane air mixture was taken in a ratio of 1:20. Air is injected into the system in the amount of $V_{\text{liq,hex}} = 2.65$ ml/hour and hexane and $V_{\text{air}} = 9.7$ liters / hour. The internal temperature of the reactor is regulated by thermostats in the range $\Delta T = 380 \div 420^\circ\text{C}$. Liquid products leaving the system are cooled and stored in liquid traps and gas products in gas traps.

As a result obtained concentration of H_2 was analyzed on the chromatograph "Gazachrome - 3101", and other hydrocarbon gases in the gas phase were analyzed on the device "Svet - 101". The sensitivity of the device to H_2 is $K = 8.6 \cdot 10^{13}$ molecules / ($\text{cm}^3 \cdot \text{mm}$). Quantity of hydrocarbons in liquid phase GC-450, Varian, USA, Column: 15mm x 0.25 mm ID x 0.25 μm CP-Sil 5CB (100% dimethylpolysiloxane), Carrier gas Nitrogen (constant pressure 15.0 psi), Injector: 300°C , 1177 Split / Splitless, Split ON at 0.75min, Split Ratio - 20, Autosampler: CP-8410 Option, injection volume - 1 μL liquid - in the gas analyzer, while functional changes in structural changes Infrared (IR), ultraviolet (UV) $\lambda = 200 \div 800\text{nm}$ -UV-Visible, Cary-50 Varian) spectrometers according to absorption spectra [9-11].

The amount of active centers formed on the surface of the catalyst and the amount of elements concentrated in them were studied using an electron microscope brand SEM (Scanning Electron Microscope, Zeiss, SIGMA / VP). The main purpose of the initial modification of the catalyst surface was to test the high activity of the selected catalyst in the conversion processes, the radiation resistance of the resulting centers and the longevity of reuse.

Results and Discussion

The conversion of hexane air mixture on the catalyst surface inside the mini reactor was studied. The process has been compared for two cases. In the first case, the surface is not modified, in the second case, the initially modified Al_2O_3 catalysts are used under the influence of radiation in the air at room temperature. Figure 2 shows the volume dependence of the volume of the hexane-air

mixture entering for both cases and the volume of products formed in the gas (Thermal processes (gas), Thermal processes (liquid)), Radiation-thermal processes (gas) and Radiation-thermal processes (liquid)) liquid phases leaving the reactor with the internal temperature of the reactor and the material balance.

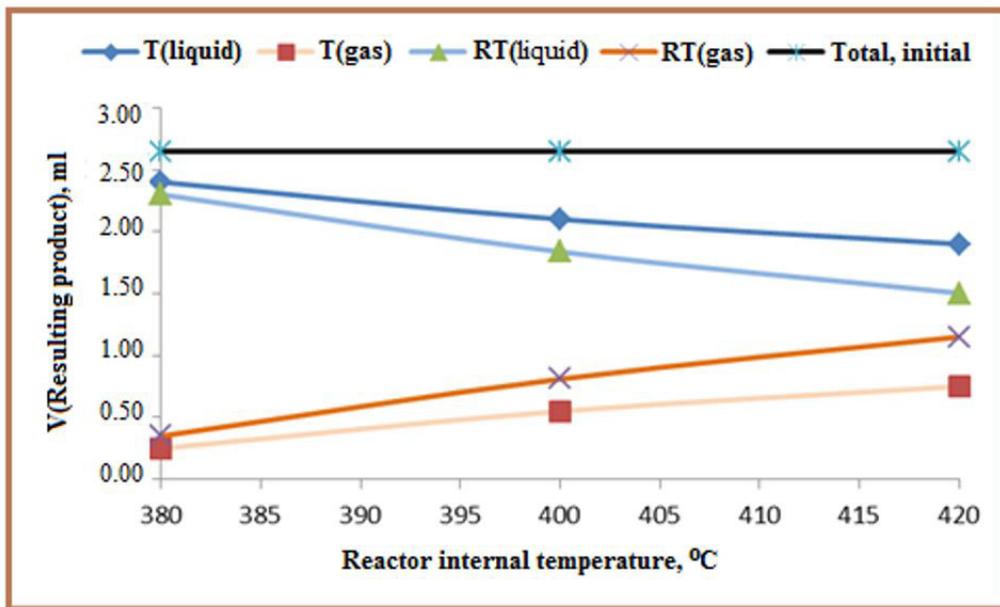


Figure 2: Balance of dependence of incoming and converted products on the internal temperature of the reactor

As can be seen from Figure 2, for both cases, the volume of excess liquid and gas products formed by the temperature varies linearly. If the amount of liquid product from the reactor, which is a non-modified catalyst, decreases by 9.5-12.5%, the amount of gas products will increase by 36-120%, while in modified catalysts the liquid phase will decrease by 18-20% and the gas phase will increase by 41-131%. Figures 3 and 4 show the temperature dependence of the CO and CO₂ gas concentrations of the hexane air mixture on the surface of the Al₂O₃ catalyst at the temperature of the mini-flow reactor.

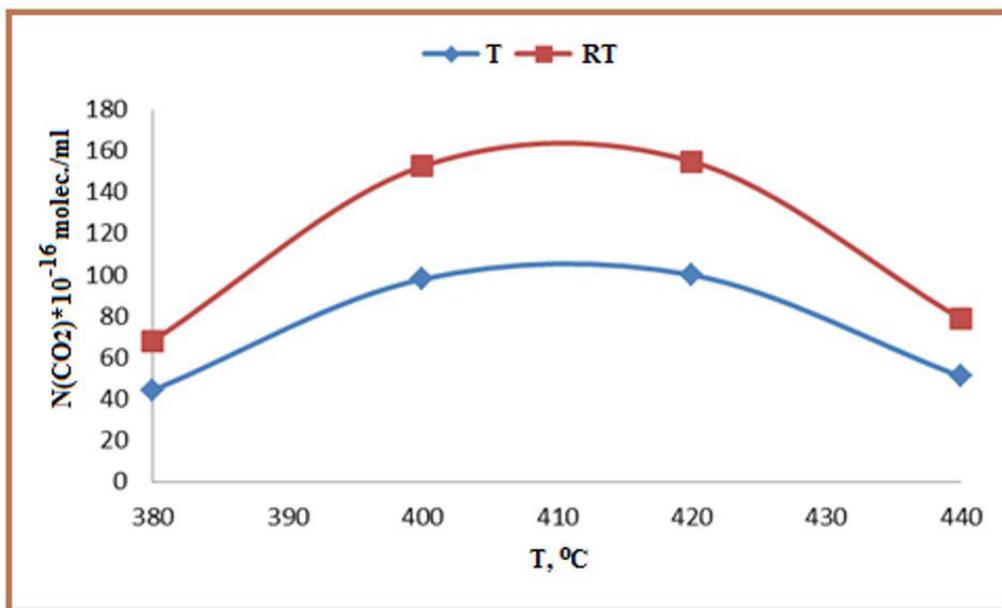


Figure 3: Dependence of reaction temperature of CO₂ gas formed from hexane air mixture on the surface of Al₂O₃ catalyst in mini flow reactor

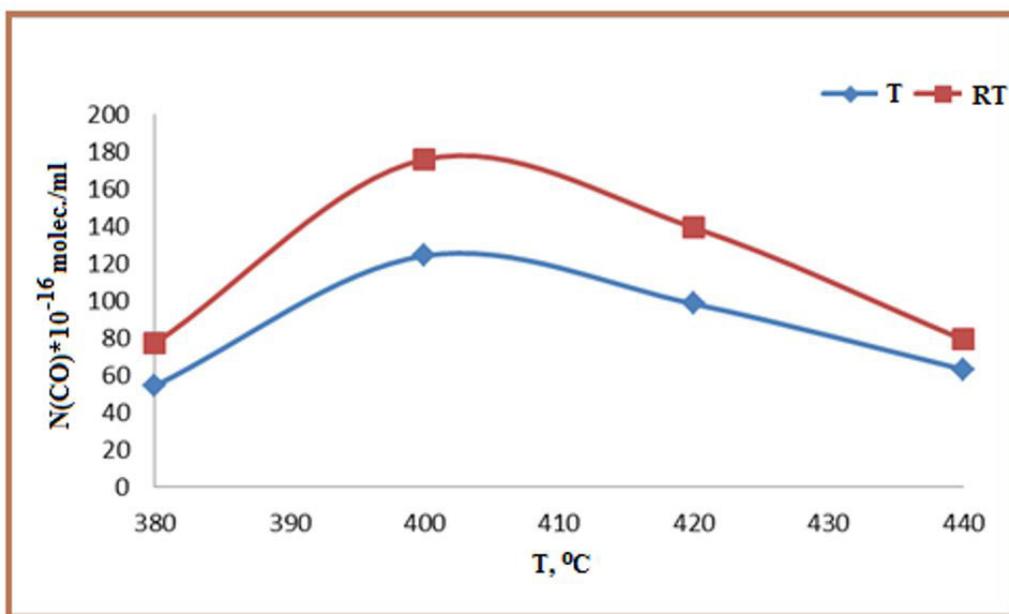


Figure 4: Dependence of the reaction temperature of CO gas formed from a mixture of hexane air on the surface of the catalyst Al₂O₃ in a mini-flow reactor

As can be seen from the figure, the amount of both gases is formed at a maximum of T = 400°C, thus increasing to CO-41 and CO₂ - 55%. Figure 5-9 shows the dependence of the hydrocarbon (Σ (C1-C5)) gases and their oxide compounds on the surface of the Al₂O₃ catalyst on the surface temperature of the mini-flow reactor.

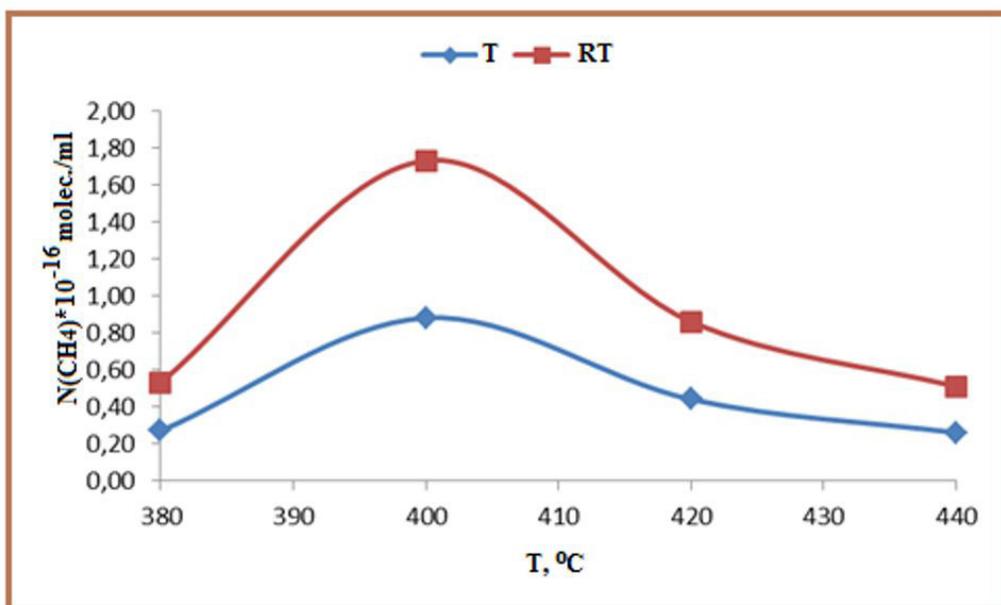


Figure 5: Dependence of the reaction temperature of CH₄ gas formed from a mixture of hexane air on the surface of the catalyst Al₂O₃ in a mini-flow reactor

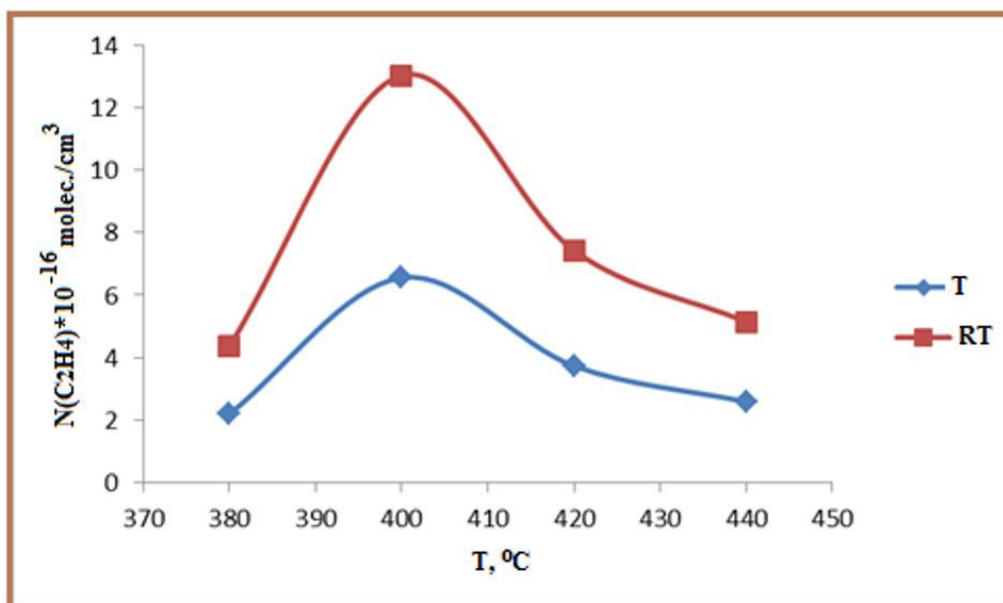


Figure 6: Dependence of reaction temperature of C_2H_4 gas formed from hexane air mixture on the surface of Al_2O_3 catalyst in mini flow reactor

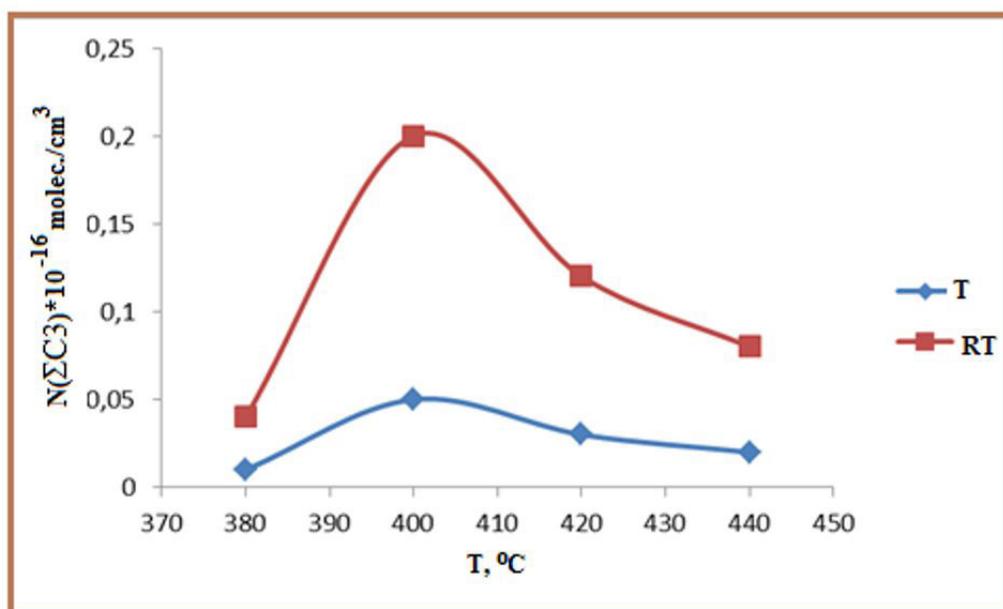


Figure 7: Dependence of the reaction temperature of ΣC_3 gas compounds formed from a mixture of hexane air on the surface of the catalyst Al_2O_3 in a mini-flow reactor

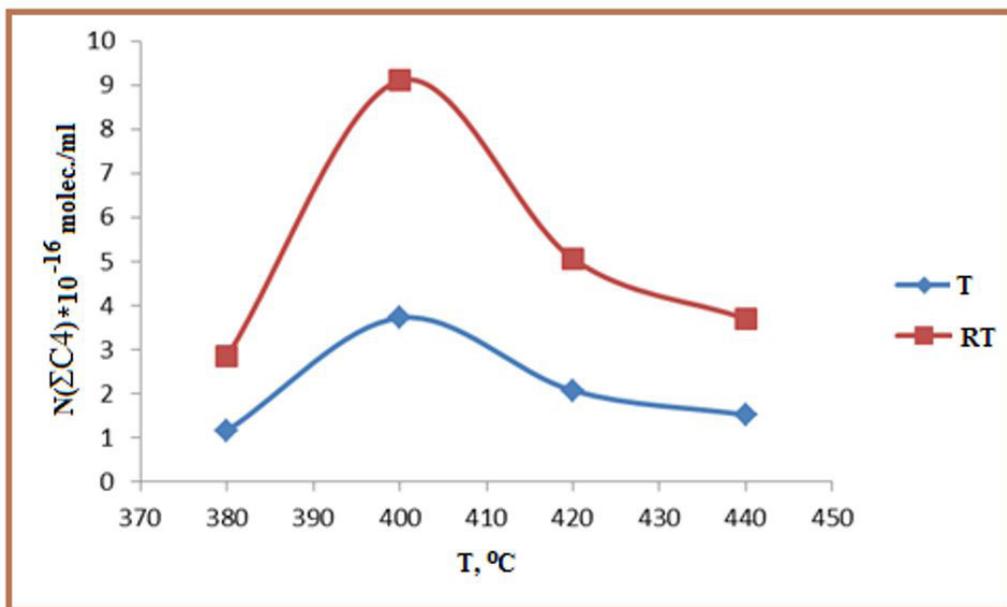


Figure 8: Dependence of the reaction temperature of ΣC4 gas compounds formed from a mixture of hexane air on the surface of the catalyst Al₂O₃ in a mini-flow reactor

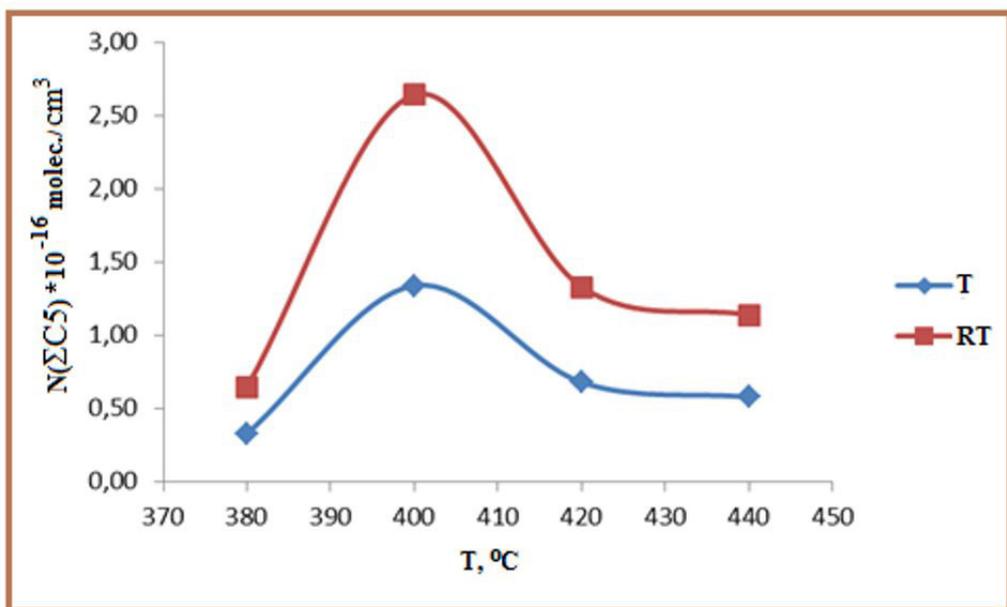


Figure 9: Dependence of reaction temperature of ΣC5 gas compounds formed from hexane air mixture on the surface of Al₂O₃ catalyst in mini flow reactor

From the kinetic dependence curves of the gases collected in the system, it can be seen that the amount of gases formed by the conversion of n-hexane exposed to radiation on the catalyst surface increases depending on the dose of absorbed radiation.

Thus, the formation of hydrocarbon gases other than hydrogen and propane gases was less than that of pure hexane, which is an indicator of the formation of heavy hydrocarbons in the liquid phase. In addition to the redecomposition of large-molecular-weight hydrocarbons that have been exposed to radiation for a long time, the share of gaseous products in the radiation-chemical emission has little effect on the total emission.

Changes in the amount of oxide products of hydrocarbons in the liquid phase and the occurrence of isomerization and oxidation can be observed with the results obtained from the gas-liquid chromatograph. Under the influence of gamma rays at room temperature, the hexane-air ratio changes on the surface of nano- Al_2O_3 and the share of newly formed products changes. The initial radiation in the atmosphere creates additional anion centers on the surface of the nanocatalyst, which accelerates the conversion of hexane and increases the rate of conversion. Initially modified catalysts under the influence of surface radiation have a higher activity, and the rate of conversion on its surface is 14–20% higher than that of others.

As can be seen from Figures 5-9, a comparison of combustible gases in all temperature ranges shows that the process of gas formation in oxygen-modified catalysts under the influence of surface radiation has a higher yield and is many times higher than that of conventional catalysts (see Table 1). This can be explained by the surface activity of nanocatalysts in the system and the efficient transfer of absorbed energy to the system.

N	Gas product and its name of oxide compounds	Volume increase, $V(\text{RT})/V(\text{T})$, $\text{T}=380^\circ\text{C}$
1	CH ₄	1,96
2	CO ₂	1,54
3	CO	1,42
4	C ₂ H ₄	1,99
5	ΣC_3	4,00
6	ΣC_4	2,45
7	ΣC_5	1,97
8	ΣC_6	0,65
9	ΣC_7	2,26

Table 1: Growth rate of gas formation in oxygen-modified catalysts

Figure 10 shows the Arrhenius dependence of the liquid products formed on the surface of the modified and unmodified catalyst. Structural changes in the products of the liquid phase were studied by the results of infrared (IR), ultraviolet (UV) spectra and analyzes obtained from the liquid-gas chromatograph. As can be seen from the general results of the analysis, the liquid yield and its quantity in the modified catalysts under the influence of radiation in the surface air environment are more than 2 times higher than in the ordinary catalyst.

According to gas-gas chromatograph analysis, 22 liquid products are formed in superficially modified products, and 19 in conventional catalysts. The $\text{Ln}V / T$ dependence of the total volume output of products in the liquid phase under thermal and radiation-thermal effects is shown in Figure 10. As can be seen from the IR spectrum of products formed in the liquid phase, the functional group C=O formed at a wavelength of $\nu = 3038 \text{ nm}^{-1}$ is an indicator of the formation of ketone and aldehyde compounds. Changes in the amount of hydrocarbon gases in the liquid phase of the system, the formation of -O-H groups of isomerization and oxidation processes are the main indicators of incomplete oxidation processes.

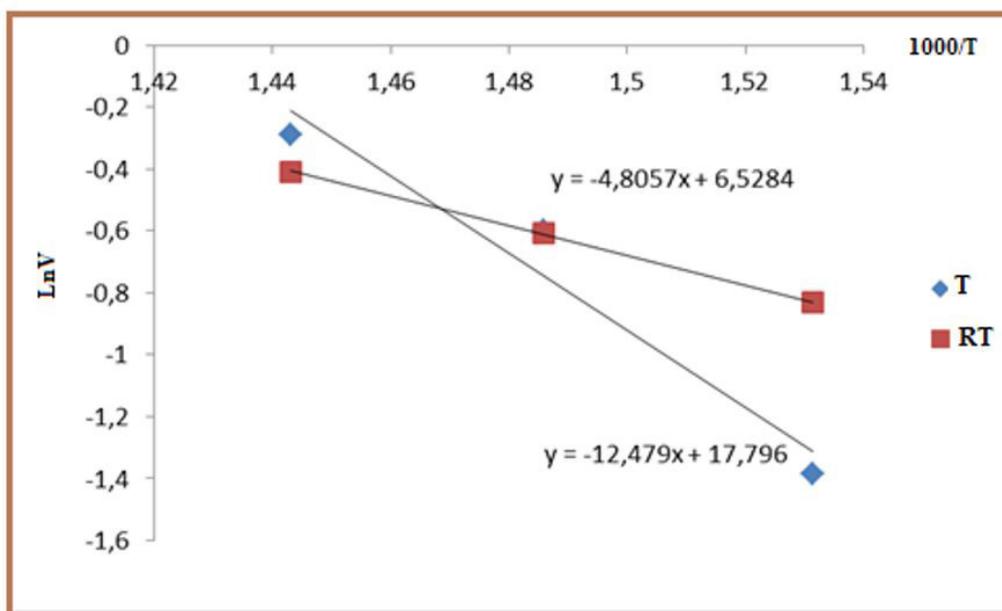


Figure 10: 1000/T Arrhenius dependence of LnV on liquid products formed on the surface of modified and unmodified catalysts

The obtained Arrhenius curves show that the volume output of oxidation products is higher due to the additional anion centers formed on the surface of the oxygen-modified Al_2O_3 catalyst under the influence of surface radiation, and they have a lower activation energy $\Delta E_{in} \leq 11.27 \text{ kCal./mol}$. $E_T = 17.796$ for thermal processes and $E_{RT} = 6.53 \text{ kCal./mol}$ for radiation-thermal processes. The change in the amount of oxide products of hydrocarbons in the liquid phase, the occurrence of the conversion/oxidation process was also observed with the results obtained from the gas-liquid chromatograph, and the difference in different temperature ranges is shown in Figure 10. Changes in the hexane-oxygen ratio on the surface of nano Al_2O_3 under the influence of gamma rays and a comparison of the amount of newly formed products show that the yield is higher in modified catalysts.

Brief mechanism of processes occurring on the surface of the catalyst

SEM image The surface image of Al_2O_3 catalyst is shown in Figure 11 in white on the surface with a diameter of $\sim 6 \text{ nm}$. Large white spots appear in the form of a trio of intertwined fractals and a large number of fibers.

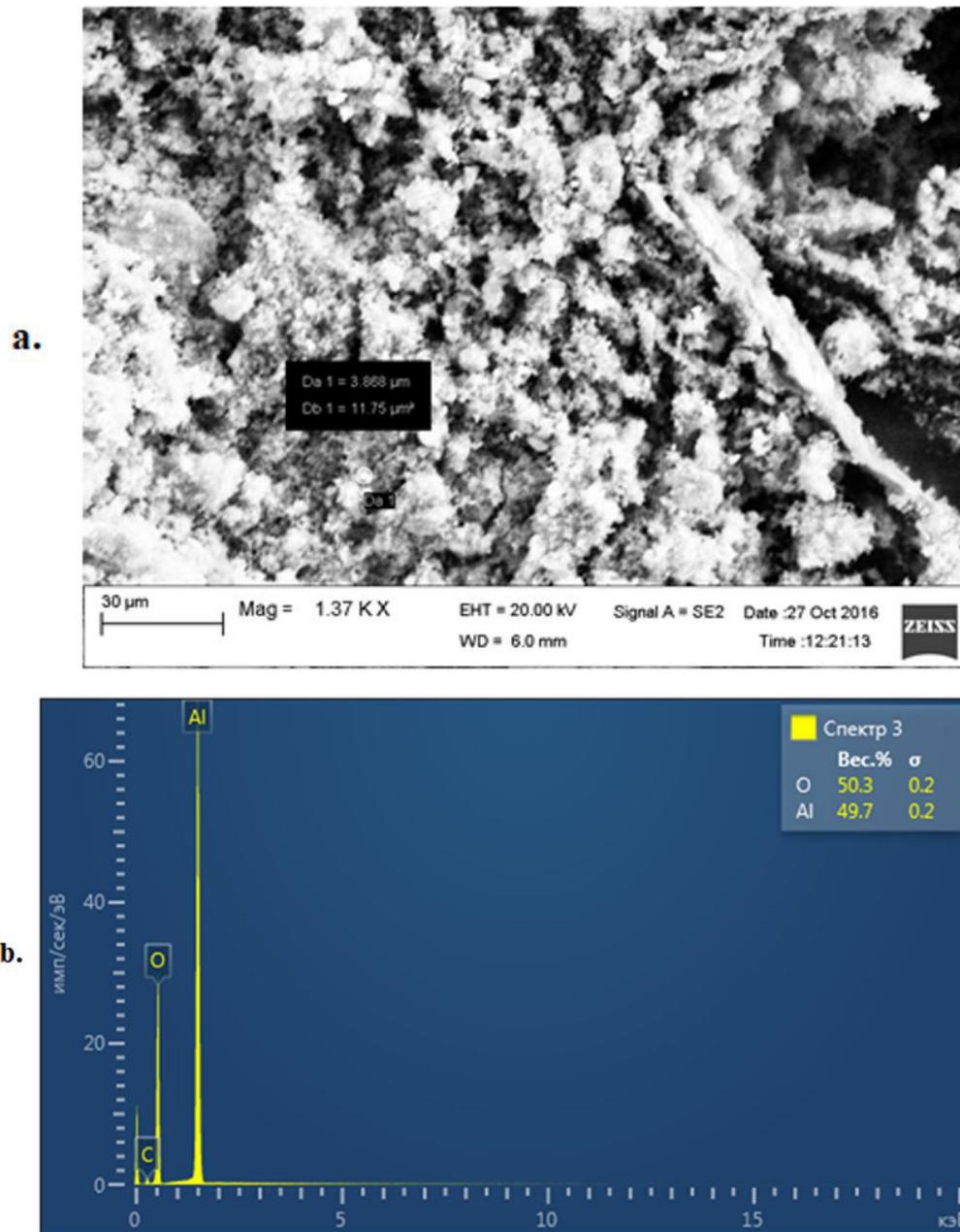


Figure 11: Surface images of the nano-catalyst under the influence of radiation in air (a) and spectra of element composition (b) ($T = 80^{\circ}\text{C}$, $D = 10\text{kGy}$) ($T = 80^{\circ}\text{C}$, $D = 8\text{kGy}$)

The catalyst samples were irradiated at different absorption doses, and as can be seen from the obtained images, the location, size and elemental composition of the active anion centers formed on the surface were studied depending on the absorption dose of gamma rays. It was found that the number of paramagnetic centers on the surface increases depending on the amount of absorbed dose.

Initially, the surface of the catalyst in the oxygen medium is modified under the influence of gamma rays. The dependence of the change in the amount of O atom on the surface of the catalyst on the surface of the catalyst at different absorption doses in an oxygen environment is given in Figure 12. $\Delta T = 24 \div 80^{\circ}\text{C}$, the dependence of the amount on the surface of nano- Al_2O_3 catalysts [O] -% - mass fraction on the absorbed dose shows that the proportion (mass) of atomic oxygen formed on the surface increases linearly in the range $D=0 \div 20\text{kGy}$ of the absorbed dose.

As a result, the process of formation of a layer of mono oxide on the surface begins [9-12]. At higher intervals, the process of stabilization or vice versa occurs regardless of radiation.

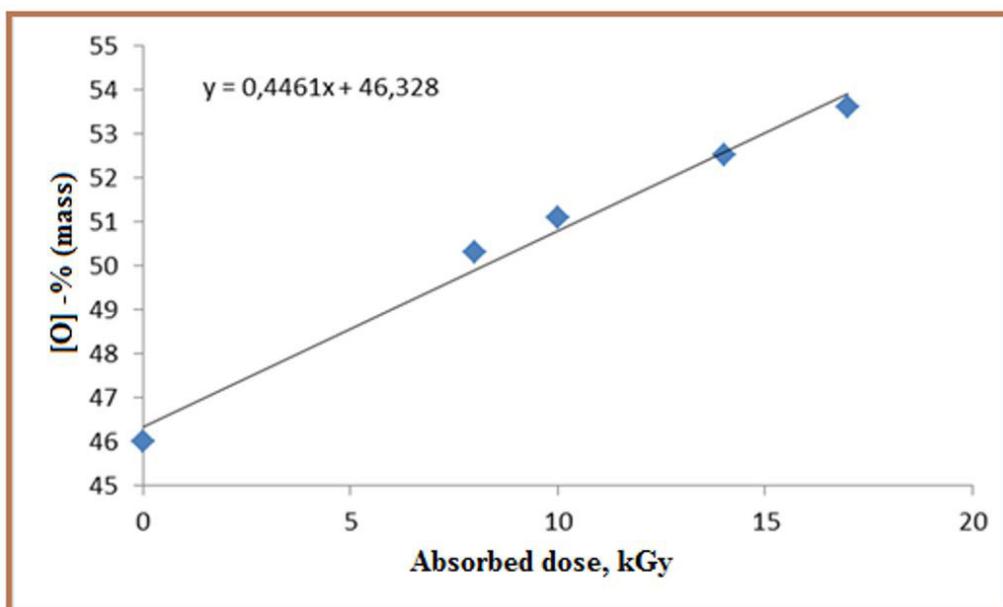
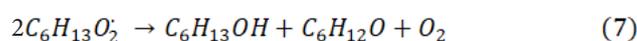
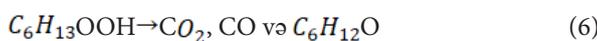
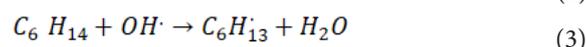
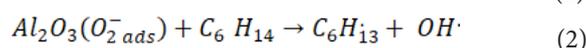
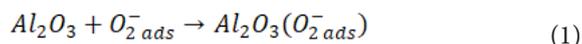


Figure 12: Dependence of the amount on the surface of nano- Al_2O_3 catalysts [O] -% - mass fraction on the absorbed dose ($T = 80^\circ C$)

Surface oxygen-modified catalysts create electron-hole centers on the surface and in volume depending on the dose absorbed when irradiated with gamma rays. As the size of the catalyst decreases, defects in volume, ie in the valence and conductivity zones, migrate more easily to the surface. As a result, additional energy (in the amount of valence band energy) is transferred to the surface, which ionizes the oxygen molecules adsorbed on the surface, increasing the concentration of anion centers (O^-) at the catalyst-gas mixture boundary (see Figure 12 and formula 1). As a result, the oxidation-reduction reactions that can occur on the surface of the catalyst are accelerated due to the additional anion centers formed at the boundary. In the next step, the O_2^- - anions formed on the surface are released by combining the electrons leaving the valence zone with the hole centers on the surface of the catalyst, which are finally desorbed from the catalyst surface as an electron-neutral molecule [10,12]. The general short mechanism of the initial oxidation stage of hexane on the catalyst surface can be shown in this way.



As can be seen, reactions (1,2) indicate the initial stage of oxidation reactions, reactions (3,4) to the formation of short-chain radicals, reactions (5, 6) to the formation of oxide products, and reaction (7) to the formation of oxide products. According to the short mechanism proposed above, it can be said that due to the proposed mechanism, the oxidation of hexane at room temperature, the conversion of hexa to oxide products in the gas and liquid phases occurs at low temperatures.

Thus, while the size of the catalysts decreases, the volume defects in nanosizes easily migrate to the surface, and additional defects appear on the catalyst surface, which accelerates the process of energy transfer and conversion to the system. Electrons formed on the surface migrate to the environment and accelerate additional transformations. Radiation plays a key role in the occurrence of surface defects, adsorption, and decomposition processes in catalytic reactions and, as a result, increases the yield of the final product. Excess electron density formed in radiation defects migrates from the surface to the adsorbents, thereby weakening the intramolecular chemical bonds of the adsorbent and accelerating the decomposition processes.

Innovation

- a. Modification of the catalyst surface with the application of radiation technologies.
- b. Study of the effect of radiation on the conversion of light hydrocarbon fraction.

Conclusion

In a mini-flow reactor, the temperature dependence of the yield of gaseous and liquid products from the oxidation of a mixture of hexane: air on the surface of an initially modified Al_2O_3 catalyst with oxygen under the influence of radiation was studied in the range of $\Delta T=380\div 420^\circ\text{C}$. It was found that as the temperature of the catalyst surface increases, the yield on liquid products increases by 14%, and the yield on gas products increases by 20%. Due to the additional anion centers (O-ads) formed on the surface of the oxygen-modified Al_2O_3 catalyst under the influence of radiation, the volume output of oxidation products is higher and has a lower activation energy ($\Delta E_{\text{in}} = 11.27 \text{ kCal / mol.}$).

References

1. Bragin OV, Liberman AL (1981) Transformations of Hydrocarbons on Metal-Containing Catalysts, M.; *Chemistr* 264 p.
2. Makarov IE, Ponomarev AV, Ershov BG (2007) Radiation-induced synthesis of branched liquid alkanes *High Energy Chemistry* 41: 55-60.
3. Ivanova AA, Gilmutdinov AT (2013) Isomerization of the pentane-hexane fraction. *High technologies in modern science and technology* 59-63.
4. Kuznetsova LI, Kazbanova AV (2012) Textural properties and crystal structure of the modified tungstate - zirconium dioxide anions - catalyst for the isomerization of light alkanes, *Petrochemistry* 52: 377-9.
5. Ivanova AA, Gilmutdinov AT (2013) Study of low and medium temperature isomerization of the pentane-hexane fraction, *Oil and Gas Business* 1: 341-8.
6. Bikmetova LI, Kazantsev KV (2013) Study of Pt/SO₄/ZrO₂ systems deposited on SiO₂ and Al₂O₃ in the n-hexane isomerization reaction, *Chemistry for Sustainable Development* 1: 47-53.
7. Akurpekova AK, Zakarina NA, Akulova GV (2016) Isomerization of the n-hexane fraction on Pt catalysts supported on montmorillonite pillared with zirconium. V Russian conference, Actual problems of petrochemistry.
8. N Azakarina, AK Akurpekova (2017) Isomerization of pentane-hexane fraction on the Pt-catalyst supported on Zr pillared Tagan Montmorillonite, *Bulletin of National Academy of Sciences of the republic of Kazakhstan* 1: 59-68.
9. Hokman Mahmudov, Telman Suleymanov, Zumrud Sabzaliyeva, Gunel Imanova, Haji Vahid Akhundzada, et al. (2021) Kinetic Interaction of Hexan Conversion and Oxidation on the Surface of an Al₂O₃ Nanocatalyzer at Room Temperature under the Effect of Gamma Radiation, *Journal of Chemistry* 9493765: 6.
10. HM Mahmudov, SH Hasanov, AH Ahmadova, TY Suleymanov, SA Huseyinova, I.A. et al. (2020) Kinetics of the carbon monoxide reaction on the surface of a radiation-modified nanocatalyst. *News of ANAS Physical-technical and mathematical sciences series, Physics and Astronomy* 5: 54-9.
11. Hasanov SH, Mustafayev II, Mahmudov HM (2018) Investigation of convertation of carbon monoxide to carbon dioxide on the surface of mixed nano-catalyst in initial trimmed of modification of radiation, *International Journal of Scientific & Engineering Research* 9: 1-5.
12. Galanov Sergey Ivanovich, Sidorova Olga Ivanovna, Gryaznova Elena Nikolaevna, Shiyan Lyudmila Nikolaevna (2014) Influence of manganese content in aluminum oxohydroxide - a precursor of MnOx - Al₂O₃ catalysts - on catalytic activity in the oxidation reaction of C₁-C₃ hydrocarbons, *Bulletin of the Tomsk Polytechnic University, Chemistry and chemical technologies* 325: 150-5.
13. SV Kudryashov, A Yu. Ryabov, GS Shchegoleva, EE Sirotkina (2007) Modeling of the oxidation reaction of cyclohexane, *Bulletin of the Tomsk Polytechnic University* 311: 115-20.
14. Zh Kh.Tashmukhambetova, LA Shokorova, VV Sokolov, IV Naymushina, IS Chanysheva (2012) New nanoscale catalysts for the oxidation of hydrocarbons with oxygen based on metal complexes, *Bulletin of KazNU. Chemical series* 4: 29-37.

15. GT Imanova, TN Agayev, SH Jabarov (2021) Investigation of structural and optical properties of zirconia dioxide nanoparticles by radiation and thermal methods, *Modern Physics Letters B* 2150050-14.
16. I Ali, GT Imanova, AA Garibov, TN Agayev, SH Jabarov, et al. (2021) Gamma rays mediated water splitting on nano-ZrO₂ surface: Kinetics of molecular hydrogen formation, *Radiation Physics and Chemistry* 109431.
17. GT Imanova, SH Hasanov (2020) Observation the initial radiation to the surface of mixed nano catalyst on oxidation processes, *International Journal of Scientific and Engineering Research* 869-73.
18. GT Imanova (2021) Gamma Rays Mediated Hydrogen Generation By Water Decomposition On Nano-ZrO₂ Surface, *Modern Approaches on Material Science* 508-14.
19. TN Agayev, Sh Z Musayeva, GT Imanova (2021) Studying the Kinetics of Formation of Molecular Hydrogen during the Radiolysis of Hexane and a Mixture of C₆H₁₄-H₂O on a Surface of n-ZrO₂, *Russian Journal of Physical Chemistry A*, (2021) 270-2.
20. GT Imanova (2020) Kinetics Of Radiation-Heterogeneous And Catalytic Processes Of Water In The Presence Of Zirconia Nanoparticles, *Advanced Physical Research* 94-101.
21. GT Imanova, TN Agaev, AA Garibov, SZ Melikova, SH Jabarov, et al. (2021) Radiation-thermocatalytic and thermocatalytic properties of n-ZrO₂-n-SiO₂ systems in the process of obtaining hydrogen from water at different temperatures, *Journal of Molecular Structure* 130651.
22. Gunel Talat Imanova, Mustafa Kaya (2021) Importance of the Radiations in Radiolysis Processes for Hydrogen Generation, *Book - Generis publishing* 50.
23. Imran Ali, Gunel T Imanova, XY Mbianda, Omar ML Alharbi (2022) Role of the radiations in water splitting for hydrogen generation, *Sustainable Energy Technologies and Assessments* 101926.
24. Gunel Imanova (2022) Molecular hydrogen production by radiolysis of water on the surface of nano-ZrO₂ under the influence of gamma rays, *Synthesis and Sintering* 2: 9-13.
25. Murat Akdemir, Duygu Elma Karakas, Gunel T Imanova, Hilal Demir Kivrak, Mustafa Kaya (2021) High Efficiency Biomass-Based Metal-Free Catalyst as a Promising Supercapacitor Electrode for Energy Storage, *SSRN Electronic Journal*, Elsevier publishing.
26. DE Karakaş, M Akdemir, GT Imanova et al. (2022) Biomass-based metal-free catalyst as a promising supercapacitor electrode for energy storage. *J Mater Sci: Mater Electron*.
27. Sami Barkaoui, Gunel Imanova (2022) Hydrothermal Synthesis of Co₃O₄ Urchin-Like and their Catalytic Properties in Co Oxidation, *Juniper Online Journal Material Science (JOJMS)* 7: 555704.
28. Raposo MPFJ, Morais RMSC, Morais AMMB (2013) Bioactivity and applications of sulphated polysaccharides from marine microalgae. *Mar. Drugs* 11: 233-51.
29. Li Z, He X, Liu F, Wang J, Feng J (2018) A review of polysaccharides from *Schisandra chinensis* and *Schisandra sphenanthera*: Properties, functions and applications. *Carbohydr. Polym* 184: 178-90.

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30. Yen HW, Hu IC, Chen CH, Ho SH, Lee DJ, et al. (2013) Microalgae-based biorefinery—From biofuels to natural products. *Biore-sour. Technol* 135: 166-74.
31. Pereira S, Zille A, Micheletti E, Moradas-Ferreira P, De Philippis R, et al. (2009) Complexity of cyanobacterial exopolysaccharides: Composition, structures, inducing factors and putative genes involved in their biosynthesis and assembly. *FEMS Microbiol. Rev* 33: 917-41.
32. Markou G, Nerantzis E (2012) Microalgae for high-value compounds and biofuels production: A review with focus on cultivation under stress conditions. *Biotechnol. Adv* 2013, 31, 1532–1542. Kraan, S. Algal polysaccharides, novel applications and outlook. In *Carbohydrates—Comprehensive Studies on GlycoBiology and Glycotechnology*; Chang, C.-F., Ed.; InTech: Rijeka, Croatia 489-532.
33. Arad SM, Levy-Ontman O (2010) Red microalgae cell-wall polysaccharides: Biotechnological aspects. *Curr. Opin. Biotechnol* 21: 358-64.