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**Study of radiation-catalytic activity of n-$ZrO_2$ during the decomposition of hexane and hexane-water mixture**

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# STUDY OF RADIATION-CATALYTIC ACTIVITY OF n-$ZrO_2$ DURING THE DECOMPOSITION OF HEXANE AND HEXANE-WATER MIXTURE

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***Abstract:*** The kinetics of accumulation of molecular hydrogen and hydrocarbons during the radiolysis of hexane and a hexane-water mixture at various component ratios - hexane/water at T = 300K was studied. It has been established that n-$ZrO_2$ exhibits radiation-catalytic activity in the decomposition of hexane and hexane-water mixtures, as a result of which the accumulation rate of molecular hydrogen increases with increasing hexane content in the hexane-water mixture. The formation rates and radiation-chemical yields of hydrogen and hydrocarbons were determined.

***Keywords*:** n-hexane, nano-$ZrO_2$, γ-irradiation, molecular hydrogen, radiation-catalytic activity.

## 1. Introduction

Radiation-catalytic processes for producing molecular hydrogen from hexane and hexane-water mixture are of significant interest for discovering new ways of conversion and utilization of ionizing radiation for the production of molecular hydrogen, which is a universal energy carrier. The research results are crucial for understanding the mechanism of the processes in experimental conditions under the influence of ionizing radiation in the hexane, and hexane-water system, as well as in natural conditions in oil and gas fields under the influence of natural radionuclides. Recently, a certain part of the world's water basin has faced contamination with heavy hydrocarbons. Catalysts are used in radiolytic decomposition processes to increase the energy extraction rate from hexane and hexane-water systems and thereby improve the process efficiency. Therefore, the study of the principles of radiation-catalytic processes for hydrogen production in the hexane and hexane-water system with the participation of n-$ZrO_2$, is of significant interest in the realm of nuclear hydrogen energy and addressing environmental issues. n-$ZrO_2$ exhibits radiation-catalytic activity in the process of radiolytic decomposition of water. Radiolysis of a mixture of hydrocarbons with water is crucial for the discovery of new ways of conversion and the use of ionizing radiation in the production of a universal energy carrier - hydrogen. The outcomes of these studies are significant for understanding processes occurring in experimental conditions under the influence of ionizing radiation [1-4].

The results from a Fourier-IR spectroscopic study of the formation kinetics of molecular hydrogen during radiolysis in n-hexane and n-hexane-water model systems on the surface of n-$ZrO_2$ at room temperature under the influence of gamma radiation, Fourier-IR spectroscopic investigations of n-hexane and n-hexane-water systems are given in the work [5-7].

## 2. Methodology of the experiment

The kinetics of molecular hydrogen accumulation during the heterogeneous radiolysis of n-$ZrO_2$ + n-$C_6H_{14}$ and n-$ZrO_2$ + n-$C_6H_{14}$-$H_2O$ mixtures under static conditions in ampoules with a

volume of $V_{amp}$ = 15 $cm^3$ under the influence of gamma radiation has been studied. The system components were introduced into the ampoules in the form of steam using a vacuum adsorption unit. The ampoules were made by freezing the components at a temperature of liquid nitrogen T = 77K. In this case, experiment findings indicated that the hydrocarbon conversion did not occur upon the ampoule closure. The ampoules containing the samples were irradiated using a $^{60}Co$ γ-quantum isotope source. The absorption dose in the studied systems was calculated by comparing electron densities in the studied and dosimetric systems. The amount of each component was taken into account when calculating the radiation absorption dose rate in the hexane-water system.

The values of the absorption dose strength of radiation in water and hexane were determined based on their electron densities. Radiation dose rate values for individual components in dosimetric systems are given in the study [5].

Analysis of radiolysis products $H_2$, CO, and $O_2$ was conducted on an Agilent-7890 chromatograph. Distilled water, 99.0% purity UN11208 brand, Made in EC n-hexane was used. The purity of n-hexane was checked by chromatographic method.

Fourier-IR spectra of n-$ZrO_2$ + n-$C_6H_{14}$ and n-$ZrO_2$ + n-$C_6H_{14}$-$H_2O$ systems were taken on the Varian 640 FT-IR spectrometer in the range of 4000-400 $cm^{-1}$.

## 3. Results and discussions

The kinetics of $H_2$ accumulation during heterogeneous radiolysis of a mixture of n-$C_6H_{14}$ and n-$C_6H_{14}$-$H_2O$ at T = 300K was studied. The accumulation of molecular $H_2$ based on kinetic curves is shown in Figure 1, and the formation rates of molecular hydrogen and radiation-chemical emissions were calculated. Radiation-chemical yield of products was calculated in two ways. To compare the obtained values with homogeneous systems and assess the radiation-catalytic activity of n-$ZrO_2$, radiation-chemical emissions G($H_2$) were calculated considering the energy absorbed by the entire system and each component. A comparison of the $G_{ads}$ ($H_2$) = 31.5 molecules/100 eV value of n-$C_6H_{14}$ during heterogeneous radiolysis with the G($H_2$) = 5.5 molecules/100eV value obtained during homogeneous radiolysis under identical conditions indicates that n-$ZrO_2$ n-$C_6H_{14}$ exhibits radiation-catalytic activity in the decomposition process.

The accumulation kinetics of $H_2$ during heterogeneous radiolysis of a mixture of n-$ZrO_2$-n-$C_6H_{14}$ and n-$C_6H_{14}$-$H_2O$ at T = 300K was studied. The formation of molecular $H_2$ based on kinetic curves is shown in Figure 1, and the formation rates of molecular hydrogen and radiation-chemical emissions were calculated.

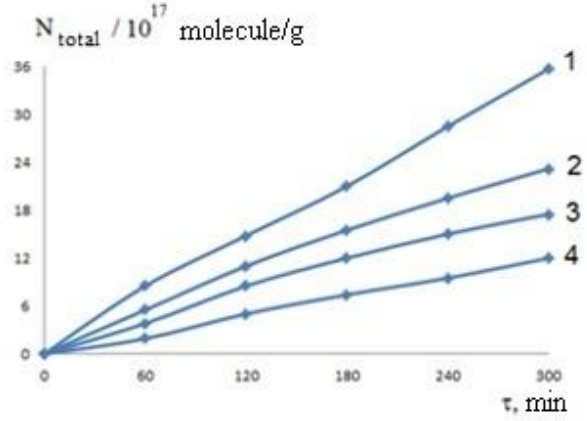


*Fig. 1. Kinetics of formation of molecular hydrogen during heterogeneous radiolysis in the system n-$C_6H_{14}$ and n-$C_6H_{14}$ + $H_2O$ on the surface of n-$ZrO_2$ at T = 300K, D=0.1 Gy/s: 1 - n-$ZrO_2$-n-$C_6H_{14}$ , 2 - 25%$H_2O$+75%$C_6H_{14}$ , 3 - 50%$H_2O$+50%$C_6H_{14}$ , 4 - 75%$H_2O$+255%$C_6H_{14}$*

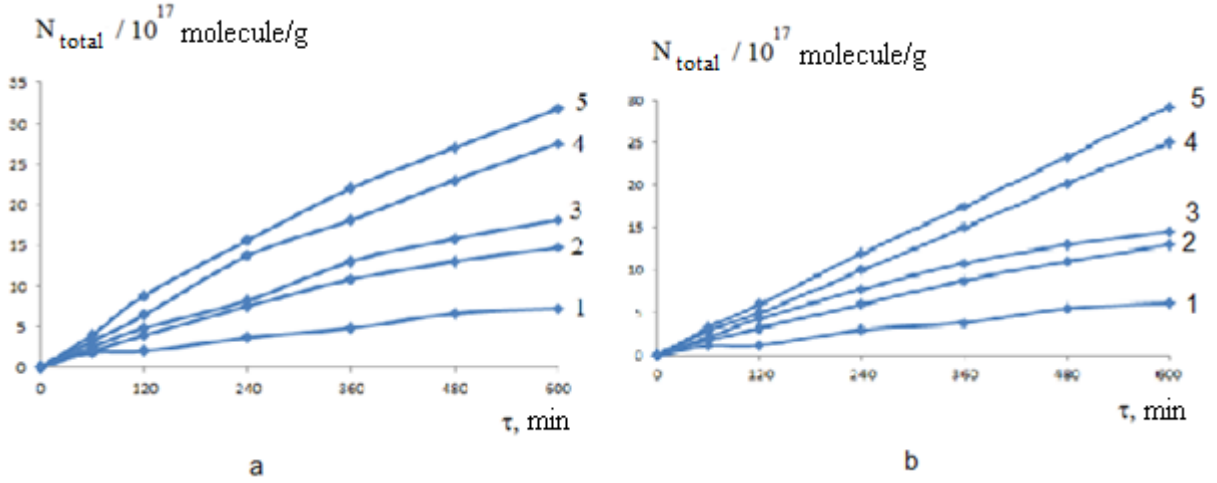


*Fig. 2. Kinetics of formation of hydrocarbons during heterogeneous radiolysis of n-$C_6H_{14}$ (a) and n-$C_6H_{14}$ + $H_2O$ (b) systems on the surface of n-$ZrO_2$ at T = 300K, D = 0.1 Gy/s: 1- methane, 2- ethane, 3 - propane, 4-butane, 5-pentane*

Radiation-chemical yields of products were calculated in two ways. To compare the obtained values with homogeneous systems and assess the radiation-catalytic activity of n-$ZrO_2$, radiation-chemical yields G($H_2$) were calculated, considering the energy absorbed by the entire system and each component (see Tables 1 and 2). Figure 2 illustrates the kinetics of the formation of $C_1$-$C_5$ hydrocarbons during radiolysis of the n-$ZrO_2$-n-$C_6H_{14}$ (a) and n-$ZrO_2$-n-$C_6H_{14}$ + $H_2O$ (b) systems [3].

**Table 1**

Values of the accumulation rate and radiation-chemical yields of molecular hydrogen depending on the hexane concentration

| *Systems* | *5%$C_6H_{14}$-95%$H_2O$* | *11,5%$C_6H_{14}$-88,5%$H_2O$* | *50%$C_6H_{14}$-50%$H_2O$* | *75%$C_6H_{14}$-25%$H_2O$* | *95%$C_6H_{14}$-5%$H_2O$* |
|---|---|---|---|---|---|
| G($H_2$), molecule/100eV | 1.1 | 2.0 | 2.9 | 4.5 | 5.1 |
| W·$10^{13}$, molecule/s | 0.72 | 1.39 | 2.0 | 3.11 | 4.83 |

**Table 2**

Values of accumulation rates and radiation-chemical yields of hydrocarbons

| *Hydrocarbon* | *methane* | *ethane* | *propane* | *butane* | *pentane* |
|---|---|---|---|---|---|
| W·$10^{13}$, molecule/s | 0.58 | 0.70 | 0.75 | 0.56 | 0.18 |
| G($H_2$), molecule/100eV | 0.15 | 0.18 | 0.2 | 0.15 | 0.09 |

Fourier-IR spectroscopic studies of n-$C_6H_{14}$ and n-$C_6H_{14}$ + $H_2O$ systems were also

conducted. The results of spectroscopic studies suggest that the ratios of the intensities of absorption bands characterizing the $CH_2$, and $CH_3$ groups vary depending on the dose rate. Valence and deformation oscillations of $CH_2$ and $CH_3$ occur in 2800-2970 $cm^{-1}$ and 1300-1500 $cm^{-1}$, respectively. The absorption bands belong to the long-chain type $(CH_2)$ n (n~4) and $CH_2$ lattice oscillations (spectral region $\nu$ = 650 - 850 $cm^{-1}$) [8].

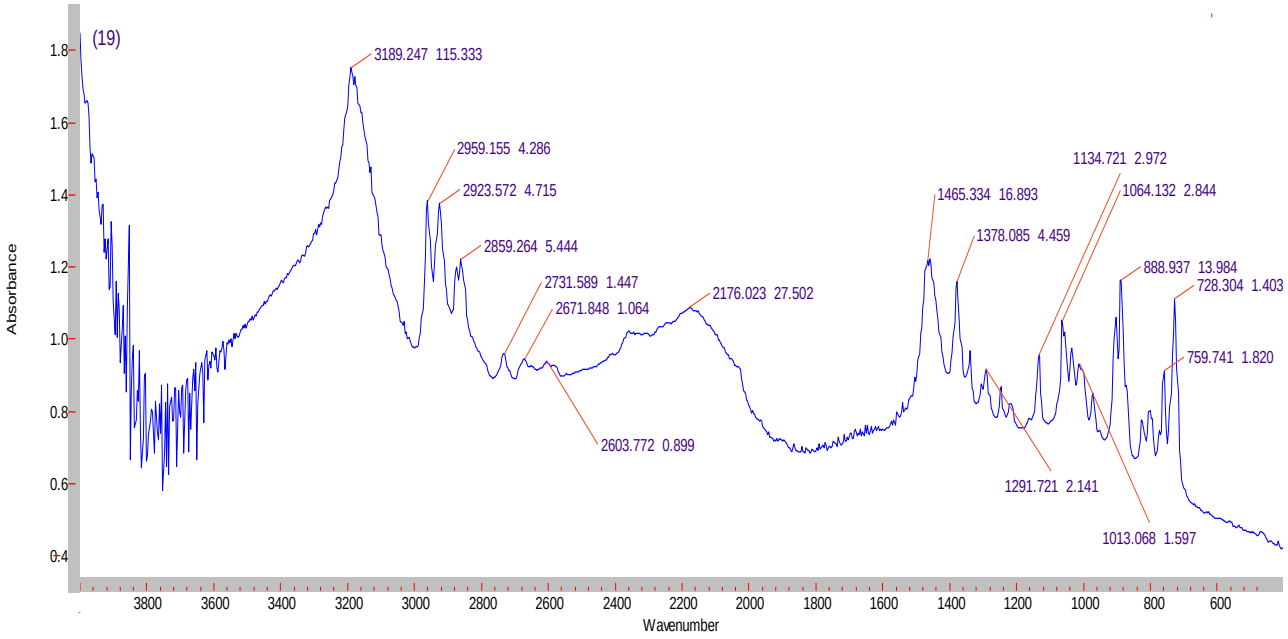


*Fig. 3. Fourier-IR spectrum of $C_6H_{14}$ + $H_2O$ (75:25) system (T=300K, $\tau$ =5 hours, D=0.1Gy/s)*

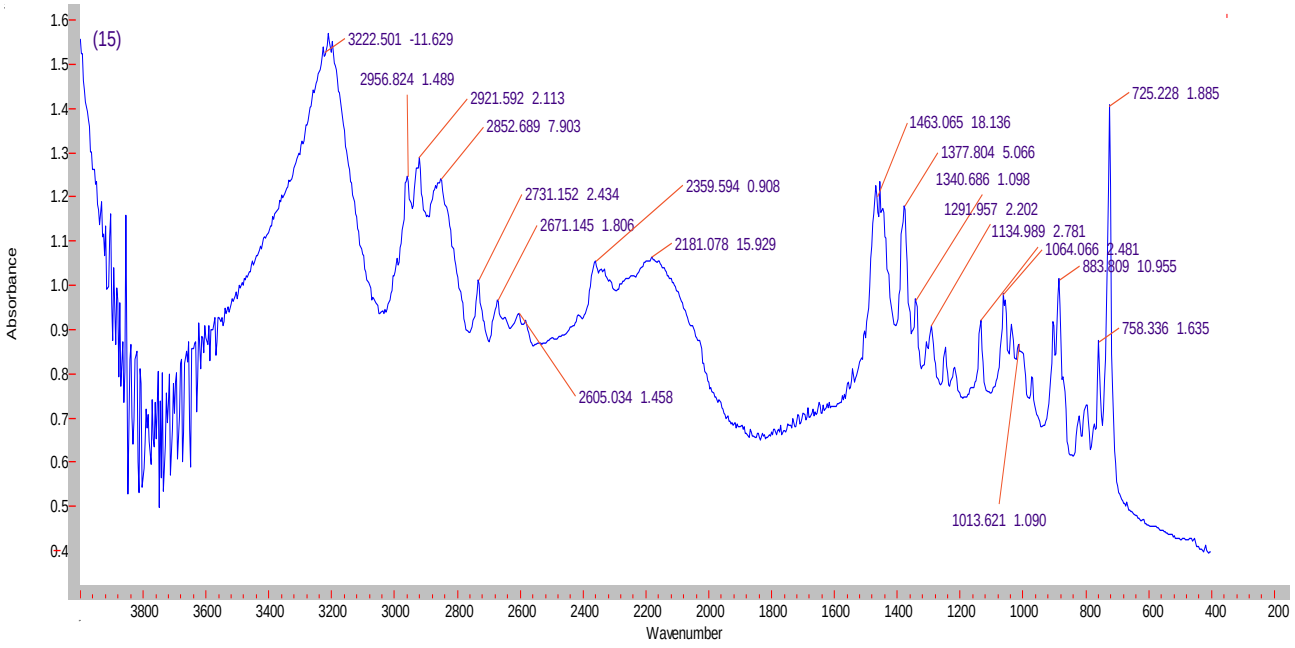


*Fig. 4. Fourier-IR spectrum of $C_6H_{14}$ + $H_2O$ (75:25) system (T =300K, $\tau$= 30 hours, D = 0.1 Gy/s)*

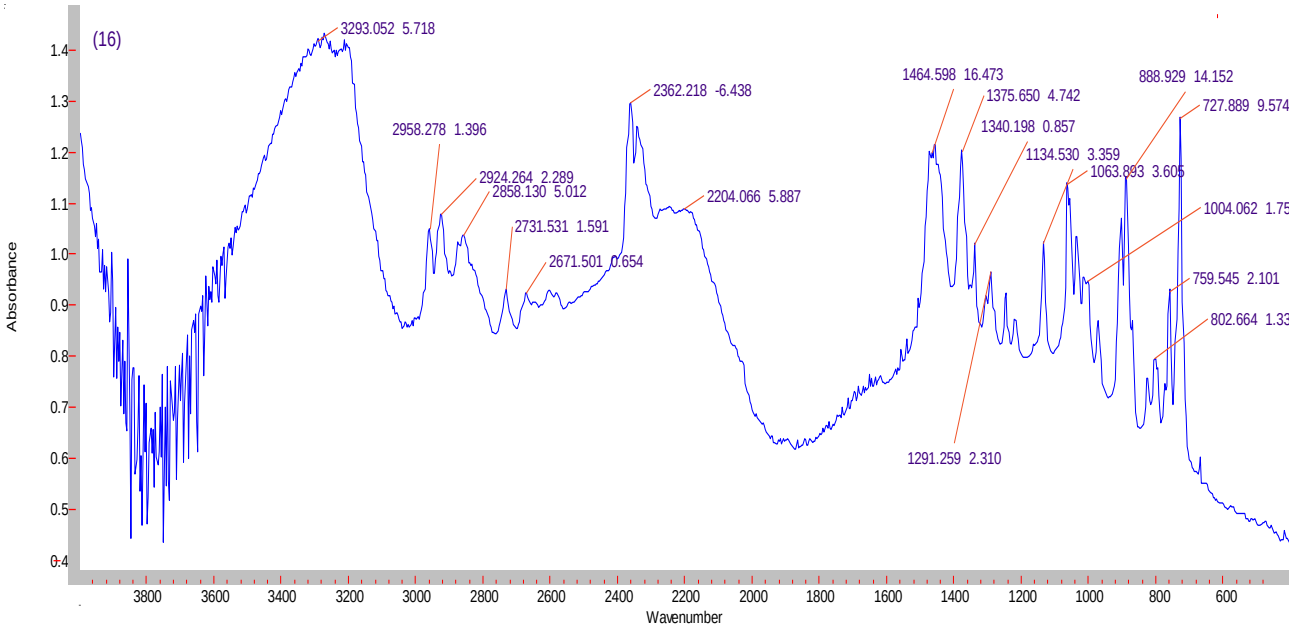


*Fig. 5. Fourier-IR spectrum of $C_6H_{14}$ + $H_2O$ (75:25) system (T=300K, $\tau$ = 50 hours, D = 0.1 Gy/s)*

During radiolysis of the n-hexane + water system (75: 25) after gamma radiation, five new bands are observed in the frequency range ν = 2600 - 2700 $cm^{-1}$, indicating the generation of heavier paraffin during radiation-chemical processes from the decomposition of n-hexane. The change and distribution of the peaks and intensities of absorption bands in the chain region of ($CH_2$) (ν = 650 - 850 $cm^{-1}$) indicates the formation of paraffin of type $C_1$ - $C_5$. The formation of $C_1$ - $C_5$ products is confirmed by the spectra of gases in the studied system. The decomposition of water in the studied system is followed by the formation of absorption bands of OH-groups in the spectra within the frequency range of ν = 3000 - 3600 $cm^{-1}$ (valence region), ν = 1700 - 1600 $cm^{-1}$ (deformation region). The olefin formation as a result of radiolysis of the n-hexane + water (75: 25) system was not observed in the IR spectra.

## *References*


1. T.N. Agayev, N.N. Gadzhieva, S.Z.Melikova, Fourier-Transform IR spectroscopic study of nano-$ZrO_2$+nano-$SiO_2$+nano-$H_2O$ system upon the action of gamma radiation, Journal of Applied Spectroscopy, 85(2), 365(2018); https://doi.org/10.1007/s10812-018-0658-9
2. I.I. Mustafayev, H.M. Hajiyev. Low-carbon radiation-thermal pyrolysis of lignites / Journal of Radiation Problems, 2022, v.9, n.2, p.5-13
3. Sh.Z. Musayeva, Impact of n-$ZrO_2$ on the radiolysis of hexane, Journal of Radiation Researches, 8(1), 42(2021)
4. T.N. Agayev, N.N. Gadzhieva, S.Z. Melikova, Sh.Z. Musayeva, A.G. Aliyev, FT-IR spectroscopic study of the radiation-chemical decomposition of n-hexane on nano-$ZrO_2$, Physics and Chemistry of Solid State, 24(3), 429(2023); DOI: 10.15330/pcss.24.3.429-432
5. P. Tilman, P. Glaes, B. Tilquin, Free radical component of the radiolysis of solid n-hexane, Radiat. Phys. Chem., 15, 465(1980); https://doi.org/10.1016/0146-5724(80)90168-5
6. Y. Tabata, Pulse radiolysis of irradiated systems (CRC Press, 1991).

7. H.M. Mahmudov, T.Y. Suleymanov, S.M. Aliyev et all. Kinetics and mechanism of formation of gaseous products obtained by radiation-catalytic conversion of n-hexane on the surface of nano-$ZrO_2$ // Journal of Radiation Researches, 2018, v.5, N2, p.122-128
8. Colin N.Banwell, Elaine M. McCash, Fundamentals of Molecular Spectroscopy (McGraw Hill Education, 4th Edition, 2017).

## ИССЛЕДОВАНИЕ РАДИАЦИОННО-КАТАЛИТИЧЕСКОЙ АКТИВНОСТИ n-$ZrO_2$ В ПРОЦЕССЕ РАЗЛОЖЕНИЯ ГЕКСАНА И СМЕСИ ГЕКСАН-ВОДА

**Т.Н. Агаев, С.З. Меликова**

***Резюме:*** Исследована кинетика накопления молекулярного водорода и углеводородов при радиолизе гексана и смеси гексан- вода при различном соотношении компонентов- гексан/вода при T=300K. Установлено, что n-$ZrO_2$ обладает радиационно-каталитической активностью в процессах разложения гексана и смеси гексан-вода, в результате чего скорость накопления молекулярного водорода увеличивается с увеличением содержании гексана в смеси гексан-вода. Определены значения скорости образования и радиационно-химические выходы водорода и углеводородов.

***Ключевые слова:*** н-гексан, нано-$ZrO_2$, γ-облучение, молекулярный водород, радиационно-каталитическая активность.

## HEKSAN VƏ HEKSAN-SU QARIŞIĞININ PARÇALANMASI ZAMANI n-$ZrO_2$-in RADİASİYA-KATALİTİK AKTİVLİYİNİN TƏDQİQİ

**T.N. Ağayev, S.Z. Məlikova**

***Xülasə:*** Heksanın və heksan-su qarışığının müxtəlif komponent nisbətlərində T = 300K-də radiolizi zamanı molekulyar hidrogen və karbohidrogenlərin əmələgəlmə kinetikası öyrənilmişdir. Müəyyən edilmişdir ki, n-$ZrO_2$ heksan və heksan-su qarışıqlarının parçalanmasında radiasiya-katalitik aktivliyə malikdir, bunun nəticəsində heksan-su qarışığında heksanın miqdarı artdıqca molekulyar hidrogenin əmələgəlmə sürəti artır. Hidrogen və karbohidrogenlərin əmələgəlmə sürətləri və radiasiya-kimyəvi çıxımları müəyyən edilmişdir.

***Açar sözlər:*** n-heksan, nano-$ZrO_2$, γ-şüalanma, molekulyar hidrogen, radiasiya-katalitik aktivlik.