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IMPACT OF n-ZrO₂ ON THE RADIOLYSIS OF HEXANE

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Abstract: The kinetics of the accumulation of molecular hydrogen during the radiolysis of hexane and hexane-mixture is studied at different concentration of the components in the presence of nanoparticles ZrO₂ at T=300÷673 K. It is found that n-ZrO₂ displays radiation catalytic activity in the decomposition of hexane and hexane–water mixture, as a result of which the rate of accumulation of molecular hydrogen increases. It is established that the radiation chemical yield of molecular hydrogen G(H₂) grows sharply along with the temperature.

Key words: radiolysis, hexane, hexane-water, radiation chemical yield, molecular hydrogen, zirconium dioxide

1. Introduction

Radiation catalytic processes for obtaining molecular hydrogen from hexane and a hexane-water mixture are of great interest in identifying new ways of converting and using ionizing radiation to obtain a universal energy carrier of molecular hydrogen [1–6]. The results from such research can be useful in clarifying the mechanisms of the process under experimental conditions and the influence of ionizing radiation in hexane and hexane-water mixture; and in the natural conditions of oil and gas fields, under the effects of radiation from natural radionuclides. A large part of the world's water basin has been polluted by heavy hydrocarbons in recent years. Catalysts of radiolytic decomposition processes have been used to increase the productivity of the process and the rate of hydrogen formation from hexane and a hexane–water mixture. In the field of atomic hydrogen power engineering and solving environmental problems, it is of great interest to identify patterns in the radiation catalytic processes of the accumulation of hydrogen from hexane and hexane-water mixture in the presence of n-ZrO₂ [6].

This work is aimed to study the kinetics of obtaining molecular hydrogen during the radiation catalytic decomposition of hexane and hexane-water mixture at different ratios of the components at T = 300 K. The radiolysis of n-hexane was therefore been studied in some detail in [8, 10–14]. The radiolysis of mixtures of hydrocarbons and water is thus of interest in identifying new ways of converting and using ionizing radiation to obtain a universal energy carrier [12]. The results from these studies can be useful in clarifying mechanisms of the process under experimental conditions and the action of ionizing radiation in a hydrocarbon–water mixture. This work presents results from studying the kinetics of molecular hydrogen accumulation during the radiolysis of a model system of n-hexane and mixtures of n-hexane and water on a surface of n-ZrO₂ at various temperatures under the influence of gamma radiation.

2. Experimental

The kinetics of the accumulation of molecular hydrogen in the heterogeneous radiolysis of hexane was studied using n-C₆H₁₄–H₂O, n-ZrO₂ + n-C₆H₁₄ and mixtures n-ZrO₂ + n-C₆H₁₄–H₂O in sealed ampoules under static conditions and the influence of γ-radiation (volume

$V_{amp}=20\text{ cm}^3$; $m_{cat}=5\times 10^{-2}\text{g}$). The ampoules were filled with the components of the system in the vapor state using a vacuum adsorption unit. The ampoules were sealed by freezing the components with liquid nitrogen at $T=77\text{K}$. It was confirmed experimentally that no hydrocarbon transformations occurred when the ampoules with samples were sealed. The ampoule with the samples was irradiated using a ^{60}Co γ -ray source. The dosimetry was done by ferrous sulfate methods [4]. The absorbed dose in the test systems was calculated by comparing the electron densities in the test and dosimetric systems [4]. The content of each component was considered when calculating the absorbed dose for the hexane–water system.

The dose absorbed in water and hexane was determined based on their electron densities and dosimetric systems. The magnitudes of the doses of radiation in individual components were given in [2] in terms of the magnitude of an absorbed dose of radiation in dosimetric systems.

The ampoules were opened in a special cell, from which the products of radiolysis were transferred to the chromatograph. The contents of H_2 , CO , and O_2 were analyzed on an Agilent-7890 chromatograph, using distilled water and *n*-hexane with 99.0% purity. The purity of *n*-hexane was confirmed via chromatography.

3. Results and discussion

This study aimed to find efficient approaches to the production of the universal energy carrier from aqueous systems containing hydrocarbon impurities. Therefore, we studied the kinetics of buildup of molecular hydrogen in the γ -radiolysis of the water–*n*-hexane system.

We prepared water–*n*-hexane mixtures with different *n*-hexane concentrations and performed their radiolysis at $T=300\text{ K}$. The kinetics of buildup of molecular hydrogen in the radiolysis of water-*n*-hexane mixture was studied at various component ratios. Figure 1 demonstrates kinetic curves for the buildup of molecular hydrogen.

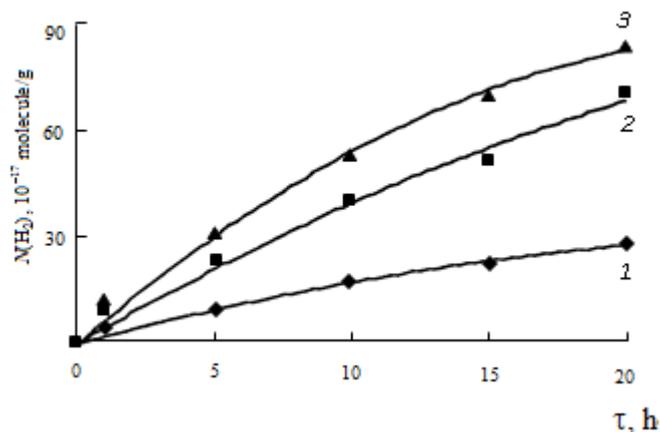


Fig. 1. Kinetics of buildup of molecular hydrogen in the radiolysis of water-*n*-hexane mixture at $T=300\text{ K}$, $\dot{D}=0.12\text{ Gy/s}$, and a hexane concentration of (1) 11.5, (2) 21.8, and (3) 50 wt %

Based on the kinetic curves, we determined the rates of formation and the radiation-chemical yields of molecular hydrogen. The radiolysis of pure water and *n*-hexane was performed under identical conditions. The results were fully consistent with published data on the radiolysis of water and *n*-hexane. The radiation-chemical yields of molecular hydrogen in the

radiolysis of pure water and n-hexane are equal to 0.45 and 5.30 molecule/100 eV, respectively [1, 10]. It was shown in [7] that n-ZrO₂ displays radiation catalytic activity in the radiolysis of water.

The kinetics of the accumulation of H₂ during heterogeneous radiolysis of n-C₆H₁₄ and mixtures n-C₆H₁₄-H₂O was studied at T=300 K. The rates and radiation chemical yields of molecular hydrogen were determined using the kinetic curves of the accumulation of H₂ shown in Figure 2. The radiation chemical yield of products was calculated in two ways. To compare our data and those for homogeneous systems, and to determine the radiation catalytic activity of n-ZrO₂, we calculated the radiation chemical yields G(H₂), allowing for the energy absorbed by each component and the entire system.

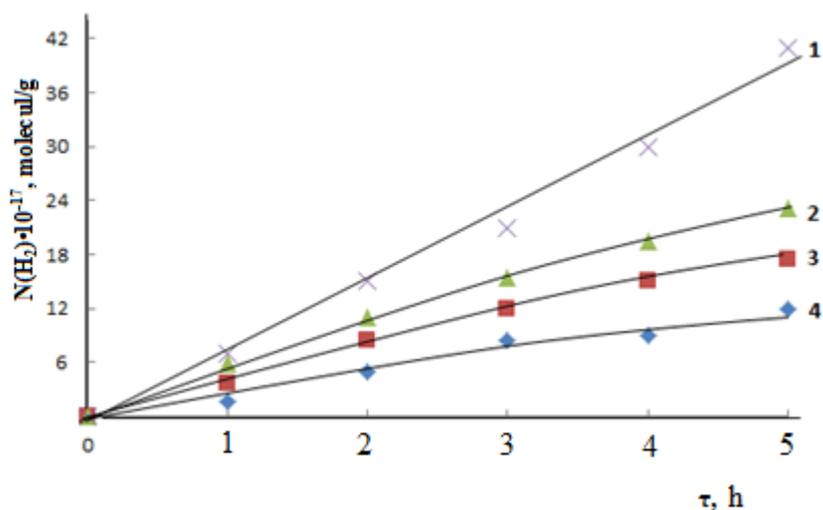


Fig. 2. Kinetics of molecular hydrogen accumulation in the heterogeneous radiolysis of mixtures n-C₆H₁₄ and n-C₆H₁₄-H₂O at T = 300 K, D = 0.11 Gy/s: (1) n-ZrO₂ + n-C₆H₁₄, (2) 11.5% H₂O + 88.5% C₆H₁₄, (3) 50% H₂O + 50% C₆H₁₄ and (4) 88.5% H₂O + 11.5% C₆H₁₄

A comparison of G(H₂) = 31.5 molecules/100 eV for the heterogeneous radiolysis of n-C₆H₁₄ and G(H₂) = 5.5 molecules/100 eV for the homogeneous radiolysis of n-C₆H₁₄ under identical conditions show that n-ZrO₂ displays radiation catalytic activity during the decomposition n-C₆H₁₄.

The energy efficiency of converting the energy of ionizing radiation into that of molecular hydrogen is characterized by G_{total}(H₂), so values of this quantity are used below. Figure 3 shows dependence G_{total}(H₂) on the weight content of n-C₆H₁₄ in a n-C₆H₁₄-H₂O mix at T = 300–673 K.

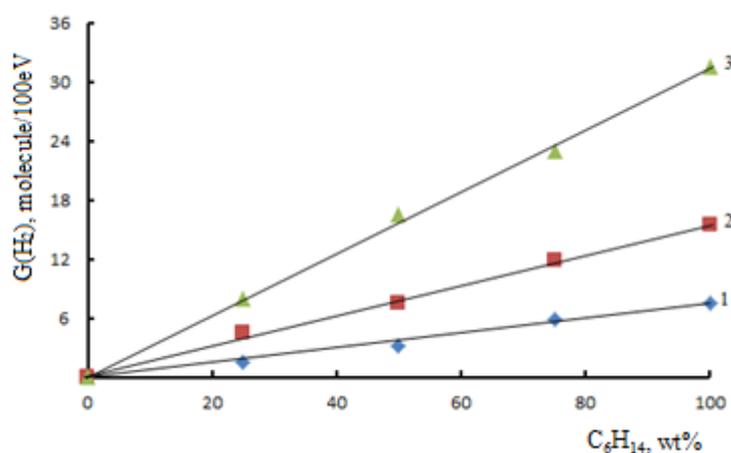


Fig. 3. Dependences of the radiation chemical yield of molecular hydrogen during the radiation catalytic decomposition of the $n\text{-C}_6\text{H}_{14}\text{-H}_2\text{O}$ system in the presence $n\text{-ZrO}_2$ on the content of hexane in the mixture at different temperatures, $D = 0.12 \text{ Gy/s}$; $T = 300(1), 473(2)$ and $673 \text{ K}(3)$

As can be seen, raising the temperature from 300 to 673 K had a different effect on the yield of molecular hydrogen during the heterogeneous radiolysis of different systems. The temperature effect grew along with the content of $n\text{-C}_6\text{H}_{14}$ in the mixture. Based on the temperature dependence of the radiation chemical yield of molecular hydrogen, the activation energies for the radiation catalytic decomposition of H_2O , $n\text{-C}_6\text{H}_{14} + \text{H}_2\text{O}$, and $n\text{-C}_6\text{H}_{14}$ were $E_1 = 43.9$, $E_2 = 4.52$ and $E_3 = 4.24 \text{ kJ/mol}$, respectively. This indicates secondary processes of the transformation of primary radiolysis products into molecular hydrogen take place in hydrocarbon-containing mixtures:



Processes (1)–(3) require specific activation energy (E_{act}), which for (2) is less than for (1) [15]. The yield of hydrogen therefore, grows along with the content of $n\text{-C}_6\text{H}_{14}$ and the temperature of the process in the mixture. The observed yield of molecular hydrogen during the radiation catalytic decomposition of $n\text{-C}_6\text{H}_{14}\text{-H}_2\text{O}$ at $T=673 \text{ K}$ and content $\text{Chexane} > 50 \text{ wt \%}$ was $G(\text{H}_2) > 21.6 \text{ molecules/100 eV}$ [9]. In the case of pure hexane, $G(\text{H}_2)=37.4 \text{ molecules/100 eV}$. The obtained indicate that under the given conditions, there is a chain mode of the transformation of the primary products of the decomposition of $n\text{-C}_6\text{H}_{14}$ and $n\text{-C}_6\text{H}_{14}\text{-H}_2\text{O}$ into molecular hydrogen.

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ВОЗДЕЙСТВИЕ n-ZrO₂ НА РАДИОЛИЗ ГЕКСАНА

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Резюме: Исследована кинетика накопления молекулярного водорода при радиоллизе гексана и смеси гексан–вода при различной концентрации компонентов в присутствии наночастиц ZrO_2 при $T=300\div 673K$. Установлено, что n-ZrO₂ проявляет радиационно-каталитической активностью в процессах разложения гексана и смеси гексан–вода, в результате чего скорость накопления молекулярного водорода увеличивается. Установлено, с увеличением температуры радиационно-химический выход молекулярного водорода $G(H_2)$ резко возрастает.

Ключевые слова: радиоллиз, гексан, смеси гексан-вода, радиационно-химический выход, молекулярный водород, нано-диоксид циркония

NANO-ZrO₂ –İN HEKSANIN RADIOLİZİNƏ TƏSİRİ

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Xülasə: nano-ZrO₂-in səthində heksan və heksan-su qarışığının radiolizi zamanı molekulyar hidrogenin əmələgəlmə kinetikası komponentlərin müxtəlif konsentrasiyasında $T=300\div 673K$ intervalında öyrənilmişdir. Aşkar olunmuşdur ki, nano-ZrO₂ radiasiya katalitik aktivliyə malik olması heksan və heksan-su qarışığının parçalanması nəticəsində molekulyar hidrogenin əmələgəlmə sürəti artırır.

Müəyyən olunmuşdur ki, temperaturun artması ilə molekulyar hidrogenin $G(H_2)$ radiasiya kimyəvi çıxımının kəskin artmasına səbəb olmuşdur.

Açar sözlər: radioliz, heksan, heksan-su qarışığı, radiasiya kimyəvi çıxım, molekulyar hidrogen, nano-sirkonium dioksid