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**ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
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FT-IR Spectroscopic Study of the Radiation-Chemical Decomposition of n-Hexane on Nano-ZrO_2

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The radiation-chemical decomposition of n-hexane in the nano-ZrO_2 + n-hexane system under the action of gamma radiation at room temperature is studied by the method of Fourier-IR spectroscopy. The molecular and dissociative form of adsorption of n-hexane in zirconium nanodioxide was revealed. The intermediate products of the radiation-heterogeneous decomposition of n-hexane were analyzed.

Keywords: FT-IR spectroscopy, radiation-chemical decomposition, n-hexane, nano-ZrO_2.

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Introduction

The study of the radiation-chemical decomposition of hydrocarbons in a heterogeneous nanooxide-hydrocarbon system is of particular interest in radiation-heterogeneous catalysis and atomic-hydrogen energy. The conducted studies have shown that the use of nanopowders accelerates the radiation-chemical decomposition of hydrocarbons and increases the radiation-chemical yield of molecular hydrogen [1-4]. To date, the course of radiation processes in a heterogeneous nanooxide + hydrocarbon system has been little studied [1, 5-6]. In the literature, there are actually no data on the study of the radiation-chemical decomposition of n-hexane on the surface of nanooxides.

Therefore, this work is devoted to studying the radiation-chemical decomposition of n-hexane in a nano-ZrO_2+n-C_6H_{14} heterosystem at room temperature under the action of gamma rays by Fourier-IR spectroscopy. The kinetics of formation of molecular hydrogen (H_2) in the nanozirconium dioxide + n-hexane heterosystem at 300 K was also studied.

I. Experimental technique

We used ZrO_2 nanopowders with particle sizes d = 20 - 30 nm [6]. Prior to adsorption, zirconium dioxide samples were subjected to thermal vacuum treatment at a temperature T = 673 K and a pressure of 10^{-1}Pa for 120 h to remove organic contaminants and dehydroxylate the surface.

Fourier-IR absorption spectra were obtained on a Varian 640 FTIR spectrometer in the frequency range ν = 4000 - 400 cm^{-1} at room temperature. For this purpose, tablets with a thickness of 50 - 100 μm were obtained from ZrO_2 nanopowders. The adsorbate was liquid-phase n-hexane, from which foreign gases were removed by repeated freezing in a trap with liquid nitrogen, followed by evacuation. The adsorption of n-hexane was carried out according to the procedure [6].

The samples were irradiated with γ rays on a ^{60}Co isotope source with a dose rate of dD_γ / dt = 1.03 Gy/s. Dosimetry of the source was carried out with chemical dosimeters. The recalculation of the absorbed radiation dose in the systems under study was carried out by comparing the electron densities. In this case, the absorbed dose was D_γ = 5 - 94 kGy. The formation of gaseous decomposition products, molecular hydrogen and hydrocarbons, was controlled by chromatography and IR spectroscopy. Analysis of H_2 gases was carried out on a gas analyzer Agilent-7890, and hydrocarbons - on a Tsvet-102 chromatograph. IR absorption spectra of gaseous hydrocarbons were obtained in a gas cell with an optical path length of ~1 m. The radiation-chemical yields of these products have been determined.

II. The discussion of the results

Fourier transform IR absorption spectra of nano-ZrO_2 (curve 1), after adsorption of n-hexane (nano-ZrO_2+n-C_6H_{14}) (curve 2) and γ-irradiation of this system (curves 3-5) at room temperature in the range frequencies $\nu = 3500 - 400\ cm^{-1}$ are presented in Fig. 1. Changes in the spectra were traced both in the region of stretching and bending vibrations of C-H. It can be seen from Fig. 1 (curve 1) that there are no absorption bands (AB) on the surface of heat-treated nano-ZrO_2 due to the presence of water and hydrocarbon contaminants [6].

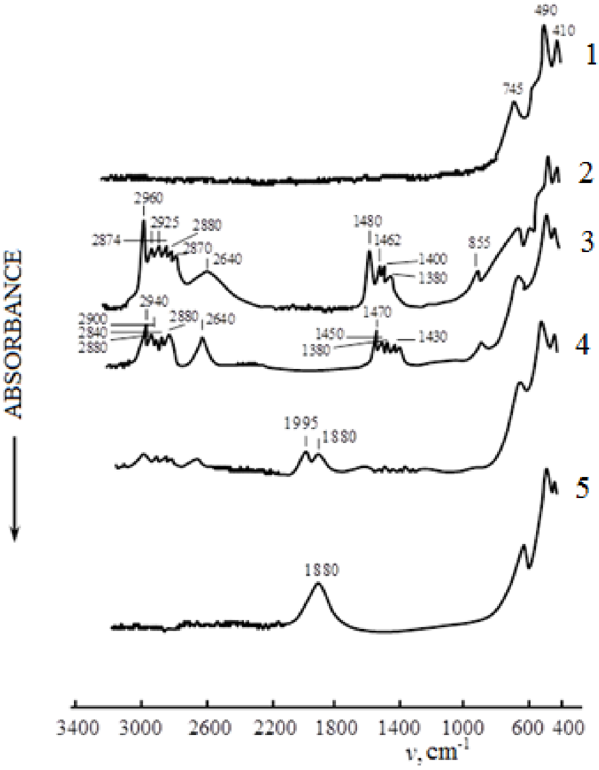

Fig. 1. Fourier transform IR absorption spectra of nano-ZrO_2 (1), nano-ZrO_2 + n-hexane heterosystems: initial (2), after γ-decomposition at D_γ = (3), 65(4) and 94 kGy (5).

In the IR spectra in the region of lattice vibrations of nano-ZrO_2 ($\nu = 800 - 400\ cm^{-1}$), AB appear with maxima at 745 and a doublet at 490 and 410 cm^{-1} (Fig. 1, curve 1). Bands at 745 and 490 cm^{-1} refer to asymmetric Zr-O_2-Zr and symmetric Zr-O stretching vibrations. The location and ratio of the intensities of these AB indicate that the zirconium dioxide nanopowders have a monoclinic modification [6]. When studying the processes of adsorption and radiation-chemical decomposition of n-hexane, the preservation of the position of the absorption bands of nano-ZrO_2 lattice vibrations and the constancy of their intensities is one of the main conditions for the identity of experiments.

In a non-irradiated heterosystem, after the adsorption of n-hexane on the surface of zirconium dioxide in the region of stretching vibrations C-H ($\nu = 3200 - 2700\ cm^{-1}$) (Fig. 1. absorption bands appear, indicating the occurrence of three forms of adsorption: physical adsorption (narrow bands at ν_{max} = 2960, 2925 and 2874 cm^{-1}), molecular form of adsorption (intense broad band at 2640 cm^{-1}) and insignificant dissociative chemisorption (weak absorption rates at 2860 and 2840 cm^{-1}) (Fig. 1, curve 2). adsorption is also confirmed by the formation of a number of AB in the region of deformation vibrations C-H ($\nu = 1500 - 1300\ cm^{-1}$) with maxima at ν_{max} = 1480, 1462, 1400 and 1380 cm^{-1} (Fig. 1, curve 2).

Irradiation of the nano-ZrO_2 + n-hexane heterosystem with γ-quanta at D_γ = 5 kGy at room temperature leads to the formation of additional AB in the spectra (Fig. 1, curves 3), which indicates the radiation-chemical decomposition of n-hexane on the nano-ZrO_2. The radiolysis of n-hexane in the nano-ZrO_2 + n-hexane heterosystem in the range of C-H (νCH) stretching vibrations is accompanied by the disappearance of the AB at 2960, 2925 and 2874 cm^{-1}, a decrease in the intensity of the absorbance band at 2640 cm^{-1} and at 2940, 2900, 2880, 2840 and 2800 cm^{-1} (Fig. 1, curve 3). The observed new narrow AB at 2940 -2800 cm^{-1} are associated with the formation of adsorbed hydrocarbons $C_1 - C_5$ 1430, 1420, 1400, 1380, 855 and 720 cm^{-1} (Fig. 1 curve 2). A weak absorbance band at 720 cm^{-1} refers to pendulum vibrations of the CH_2 group, unrelated to vibrations of the skeleton, and is characteristic of long paraffin chains of the –$(CH_2)n$- ($n \geq 4$) type [6].

With an increase in the dose of γ-irradiation D_γ to 65 kGy, the spectra are transformed: the intensities of some AB associated with adsorbed hydrocarbons decrease, which indicates their partial decomposition (Fig. 1, curve 4). A further increase in the value of D_γ up to 94 kGy leads to the complete decomposition of hydrocarbons (curve 5).

It should be noted that starting from the absorbed dose Dγ = 5 kGy, absorption bands with maxima at 1995 and 1880 cm^{-1} appear in the IR spectrum. The intensities of these bands redistribute with increasing absorbed dose. These AB refer to the stretching vibration of Zr- H and indicates the formation of surface hydrides of the Zr-H and Zr-H_2 types (Fig.1, curves 3-5), in the media of which the most stable form is Zr-H_2 [6].

As follows from the IR spectroscopic analysis, the radiolysis of n-hexane in the γ-irradiated heterosystem -n-hexane is accompanied by the formation of intermediate decomposition products - surface zirconium hydrides and zirconium alkyls.

In this case, the main end products of decomposition are gaseous hydrocarbons and molecular hydrogen, the formation of which was controlled by spectroscopic and chromatographic methods. IR absorption spectra of gaseous hydrocarbon products of n-hexane radiolysis in the region of out-of-plane C-H bending vibrations are shown in Fig. 2.

It can be seen that for small values of the absorbed dose of γ-irradiation (D_γ = 5 kGy) in the system in the spectrum of nano-ZrO_2 + n-hexane, AB appear with maxima at 800, 785, 770, 750 and 720 cm^{-1} (Fig. 2, curve

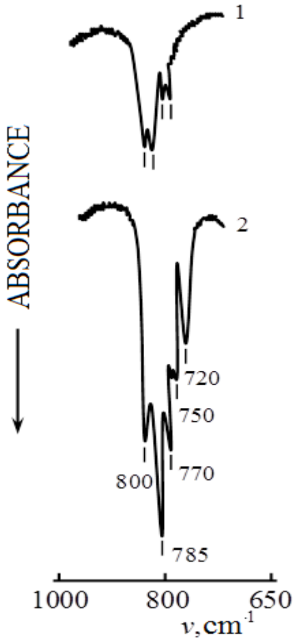

Fig. 2. IR absorption spectra of gaseous hydrocarbon products of n-hexane radiolysis in the nano-ZrO_2 + n-hexane system at D_γ=5 (1) and 94 kGy (2).

1), the location and half-width of which allow us to attribute them to hydrocarbons C_1- C_5 in the gas phase. With an increase in the absorbed dose to a value of 94 kGy, the intensities of the bands are redistributed and increase (Fig. 2, curve 2). Comparison of changes in the absorption spectra of intermediate and final hydrocarbon decomposition products of n-hexane in the γ-irradiated system ZrO_2 + n-hexane occurring depending on the absorbed dose of γ-irradiation shows that they are antiabatic in nature. The main changes occur in the absorbed dose range $5 \leq D_\gamma \leq 65$ kGy and are accompanied by the decay of intermediate and accumulation of final decomposition products. In this case, the complete radiolysis of n-hexane occurs at a value of Dγ = 65 kGy.

The kinetic regularity of the accumulation of molecular hydrogen during the radiolysis of n-hexane in the nano-ZrO_2 + n-hexane system has been studied. The dependence of the change in the concentration of H_2 (NH_2) on the absorbed dose of γ-irradiation (D_γ) is shown in Fig. 3.

Based on the kinetic curve, the rate of formation of molecular hydrogen and radiation-chemical output were calculated. The radiation-chemical yields $G(C_xH_y)$ of the products (hydrocarbons) formed as a result of the decomposition of n-hexane on the surface of nano-ZrO_2 under the influence of gamma rays (hydrocarbons) were calculated (Table 1).

In order to compare the obtained values with homogeneous systems and to determine the radiation-catalytic activity of nano-ZrO_2, radiation-chemical yields $G(H_2)$ were calculated taking into account the energy absorbed by each component. During heterogeneous radiolysis of hexane at T = 300 K, $G(H_2)$ = 8.1 molecules / 100 eV. It can be concluded that nano-ZrO_2 has radiation-catalytic activity in the processes of decomposition of n-C_6H_{14}.

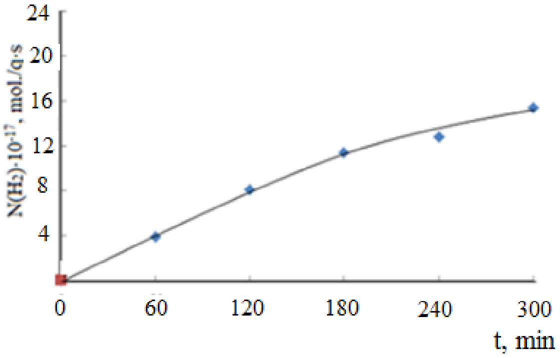

Fig. 3. Molecular hydrogen generation kinetics D_γ = 1.03 Gy/s in the process of radiation decomposition of n-C_6H_{14} on the surface of nano-ZrO_2.

Table 1

Radiation-chemical yields $G(C_xH_y)$ of products (hydrocarbons) of n-hexane decomposition on the surface of nano-ZrO_2 under the action of gamma radiation.

nano-ZrO_2+ n-C_6H_{14}, T=300K	
Hydrocarbons	$G(C_XH_Y)$,molec/100eV
Methane	4.9
Ethan	6.1
Propan	7.12
Buthan	2.3
Penthan	1.9

Conclusion

The radiation-chemical decomposition of n-hexane in the nano-ZrO_2 + n-hexane system under the action of gamma radiation at room temperature is studied by the methods of Fourier-IR spectroscopy and chromatography. According to the IR spectra. it is revealed that gamma irradiation of the nano-ZrO_2 + n-hexane heterosystem in the area of the absorbed dose of $5 \leq D_\gamma \leq 94$ kGy. it is accompanied by the formation of intermediate decomposition products - surface hydrides of zirconium and zirconium alkyls. It is established that complete radiation chemical decomposition of n-hexane occurs at the value of D_γ = 65 kGy. Kinetics of accumulation of molecular hydrogen was studied. The radiation-chemical yields of molecular hydrogen and hydrocarbons C_1-C_5 are determined. It was revealed that during radiolysis of n-hexane. hydrogen partially accumulates in the form of Zr hydride on the surface of zirconium dioxide.

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Фур'є трансформоване ІЧ дослідження радіаційно-хімічного розкладу n-гексану на нано-ZrO_2

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Методом ІЧ-Фур'є-спектроскопії досліджено радіаційно-хімічний розпад n-гексану в системі нано-ZrO_2 + n-гексан під дією гамма-випромінювання при кімнатній температурі. Виявлено молекулярно-дисоціативну форму адсорбції n-гексану в нанодіоксиді цирконію. Проаналізовано проміжні продукти радіаційно-гетерогенного розпаду n-гексану.

Ключові слова: ІЧ-Фур'є спектроскопія, радіаційно-хімічний розпад, н-гексан, нано-ZrO_2.