RADIATION-TERMOCATALYTIC PROCESSES FOR HYDROGEN PRODUCTION FROM WATER

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The radiation-thermal-catalytic processes of water decomposition in the n-ZrO$_2$-n-Al$_2$O$_3$+H$_2$O system are investigated. The kinetics of molecular hydrogen accumulation was studied during radiolytic processes of water decomposition in the systems under study. The values of the accumulation rates and radiation-chemical yields of hydrogen during the radiolysis of water in the n-ZrO$_2$-n-Al$_2$O$_3$+H$_2$O system at various temperatures have been determined. Besides this, it was shown that the results obtained serve as a base for checking the scenarios of normal and emergency conditions of nuclear reactors refrigerated by water.

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INTRODUCTION

In nuclear power today, water-cooled nuclear reactors predominate. For the safety of the latter, of no small importance is the identification of patterns of accumulation of explosive products formed when radiation and temperature influence the heat transfer media and impurities contained in them in contact with the materials of nuclear reactors in normal and emergency modes of their operation. There are studies on thermal processes of interaction of water vapor with some materials of reactors. Information on the contribution of radiation-heterogeneous processes in the contact of water with reactor materials in the process of generating molecular hydrogen is missing. The development of the production of nanomaterials is determined by the key tasks of modern materials science and is closely related to technologies for producing various types of catalysts, adsorbents, etc. based on nanopowders. The transition to nanoscale materials leads on the one hand to a significant decrease in particle size, and on the other to a significant increase in the surface of the powder system. Thus, at the same time two factors – small size and high values of specific surface will play an important role when considering the processes involving nanoparticles. Recently, it has been established that a decrease in particle size to nanoscale leads to a significant change in physical properties [1–6]. Nanostructured materials have a well-developed surface and increased defects at the particle boundary, which is of great importance in radiation-heterogeneous processes with their participation, as well as in the development of highly sensitive detectors of ionizing radiation. To modify the physicochemical properties, materials are made based on mixtures of nanoscale oxides. As a result of the interaction between the components, changes occur in the concentrations of the surface acceptor centers, as well as the mechanical and physical properties of the components of the system. Information on the effect of temperature on the surface physicochemical and radiation-catalytic properties of the n-ZrO$_2$-n-Al$_2$O$_3$ binary system is limited. Therefore, in order to identify the effect of temperature on the radiation-catalytic properties, the kinetics of hydrogen production processes during heterogeneous radiolysis of

water in the n-ZrO$_2$-n-Al$_2$O$_3$+H$_2$O system at different temperatures has been investigated.

EXPERIMENTAL PART

ZrO$_2$ and Al$_2$O$_3$ nanopowders with a purity of 99.9% (manufactured by Sky Spring Nanomaterials, Inc., USA) with a particle size of $d = 20...30$ and $20...60$ nm were used. By the X-ray phase method, it was established that the ZrO$_2$ sample has a monoclinic centrally symmetric crystal structure. Before adsorption, samples of zirconium and aluminum dioxides were subjected to thermal vacuum treatment at $T = 673$ K and a pressure of 10^{-3} Pa for 8 h to remove organic contaminants and dehydroxylate surfaces.

For the study, bidistilled water was used, from which the extraneous gases were removed by repeated freezing in a trap with liquid nitrogen, followed by pumping. The adsorption of water vapor was studied by the method of [7]. Radiation decomposition of water in the n-ZrO$_2$-n-Al$_2$O$_3$+H$_2$O system was carried out at various temperatures $T = 373...673$K. Samples were irradiated at a ^{60}Co isotope source with a dose rate of $dD_\gamma/dt = 0.14$ Gy/s. The absorbed dose rate was determined by chemical ferrosulfate and cyclohexane dosimeters [8]. The absorbed dose of radiation in the systems under study was determined by comparing their electron densities with dosimetric systems [8].

The vials were opened in special cells. The products of radiolysis using a dispenser entered the chromatograph, where their composition and concentration of individual components were determined. The analysis was performed on an Agilent-7890 chromatograph. H$_2$ and O$_2$ were detected in the composition of radiolysis products. A certain part of the oxygen was captured by the oxides and dissolved in water, therefore, the oxygen yields in the composition of the radiolysis products are less than stoichiometrically possible.

RESULTS AND DISCUSSION

The kinetics of molecular hydrogen accumulation was studied during radiation-heterogeneous radiolysis of water adsorbed on the surface of n-ZrO$_2$-n-Al$_2$O$_3$ systems at $T = 373...673$ K (Fig. 1).
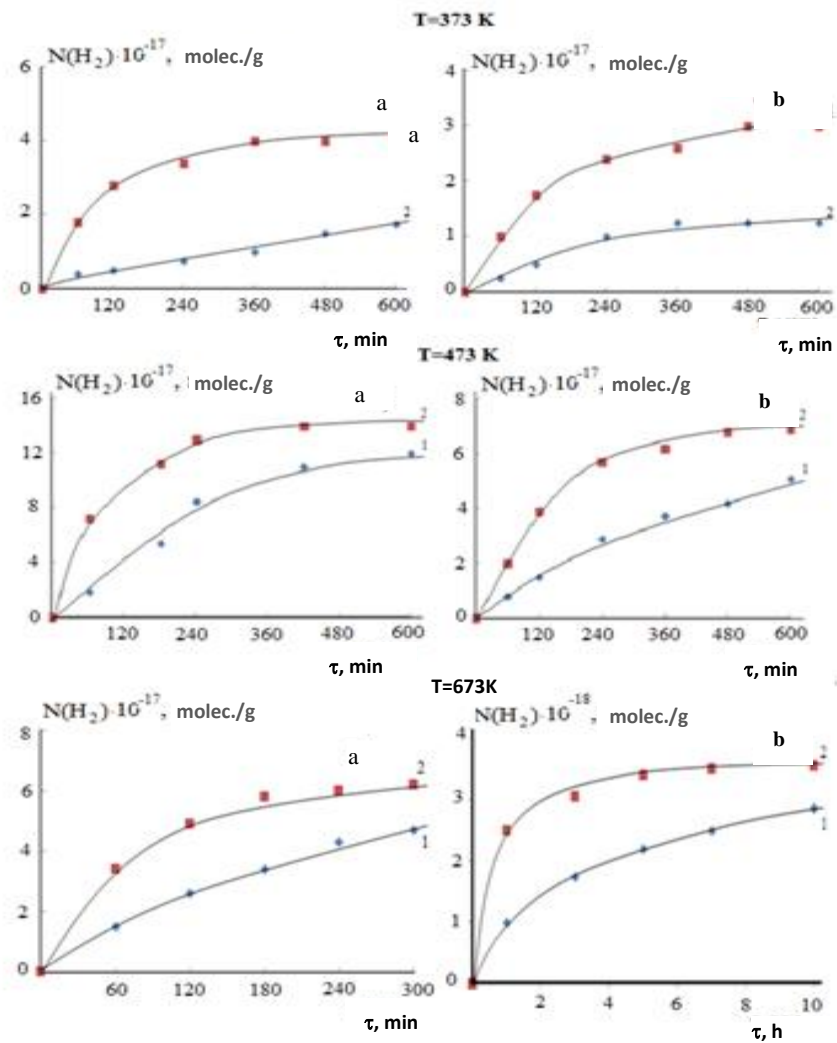
T=373 K

T=473 K

T=673K

Fig. 1. Kinetic curves of the accumulation of molecular hydrogen in radiation-thermal (a) and thermal (b)
decomposition of water in the n-ZrO₂-n-Al₂O₃ +H₂O system
at various temperatures – 373; 473, and 673 K respectively

The kinetics of molecular hydrogen accumulation was studied during radiation-heterogeneous radiolysis of water molecules adsorbed on the surface of the n-ZrO$_2$-n-Al$_2$O$_3$ binary system at various component ratios at T = 673 K (Fig. 2).
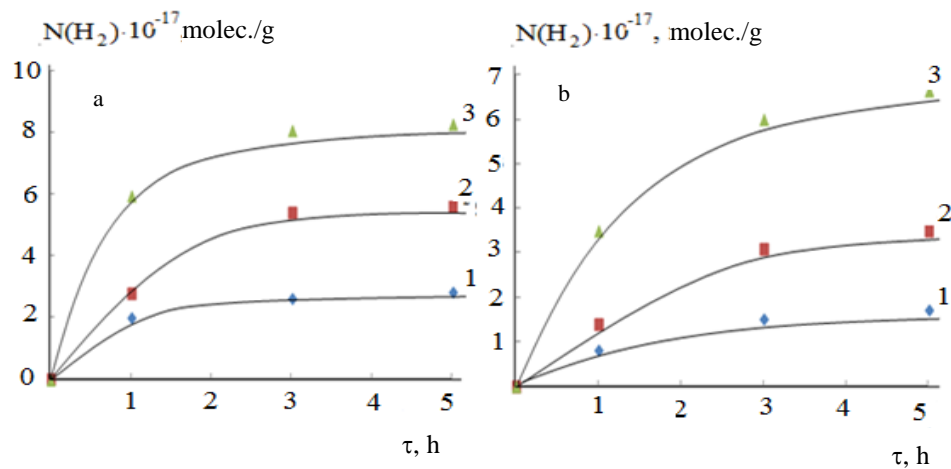

Fig. 2. Kinetic curves of molecular hydrogen production in radiation-thermal (a) and thermal (b) radiolysis
of water in the n-ZrO₂-n-Al₂O₃ +H₂O system at T = 673 K, D = 0.14 Gy/s.
1 – 83.3% n-ZrO₂+16.7% n-Al₂O₃; 2 – 50.0% n-ZrO₂+50.0% n-Al₂O₃; 3 – 16.7% n-ZrO₂+83.3% n-Al₂O₃

Based on the kinetic curves, the values of the accumulation rates and the radiation-chemical yields of molecular hydrogen were determined. The observed values of the parameters of hydrogen production are given in Table and in Fig. 2. Comparison of the yield values of molecular hydrogen in the presence of individual samples of n-ZrO$_2$ and n-AI$_2$O$_3$ shows that n-ZrO$_2$ has a relatively high radiation-catalytic activity. As can be seen from Table, during the transition from n-ZrO$_2$ to n-Al$_2$O$_3$, the values of the radiation-chemical yield of molecular hydrogen decrease linearly.

Based on the content of the components and the values of the radiation-chemical yields, it is possible to determine the hydrogen yields in the heterogeneous radiolysis of water with the participation of the n-ZrO$_2$-n-Al$_2$O$_3$ mixture by additive summation:

$$\Sigma G_i = x_1 G_1 + (1 - x_1)G_2, \qquad (1)$$

where x_i, G_i is the fraction of individual components in the mixture and the value of the radiation-chemical yield of hydrogen in the presence of these nanooxide samples. The value of the yield of hydrogen is

determined by the expression (1), which corresponds to the experimentally observed dependencies. The decrease in yield with the addition of n-Al$_2$O$_3$ to n-ZrO$_2$ suggests that there is an interaction between the components – n-ZrO$_2$ and n-Al$_2$O$_3$, as a result of which the radiation-catalytic activity of the n-ZrO$_2$-n-Al$_2$O$_3$ system decreases.

The observed difference in the values of $G(H_2)$ in radiation-heterogeneous radiolysis of water in the presence of n-ZrO$_2$ and n-Al$_2$O$_3$ is explained by the electrophysical model of heterogeneous radiolysis. According to this model, the main contribution of the solid phase during heterogeneous radiolysis of water is to convert the energy of ionizing radiation into the energy of non-equilibrium charge carriers and excited states, as well as transfer the absorbed energy through these carriers to surface-adsorbed water molecules [9, 10]. For oxide dielectrics, the threshold energy (E_{th}) of the formation of non-equilibrium charge carriers is equal to [9, 11]:

$$E_{th} = 2Eg, \qquad (2)$$

where Eg is the band gap of oxide dielectrics.

Values of $G(H_2)$ and accumulation rates of molecular hydrogen during thermal $W_T(H_2)$ and radiation-thermal $W_{RT}(H_2)$ decomposition of water on the surface of n-ZrO$_2$, n-Al$_2$O$_3$ oxides and n-ZrO$_2$-n-Al$_2$O$_3$ system at temperatures $T = 373\ldots673$ K

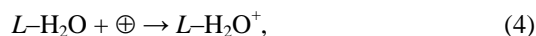| No	System	T, K	D, Gy/s	$W_T(H_2)$, molec./(g·s)	$W_{RT}(H_2)$, molec./(g·s)	$G(H_2)$, molec./100 eV
1	n-ZrO$_2$			$1.0 \cdot 10^{13}$	$5 \cdot 10^{13}$	4.5
2	n-Al$_2$O$_3$			$0.69 \cdot 10^{13}$	$2.78 \cdot 10^{13}$	2.75
3	n-ZrO$_2$+n-Al$_2$O$_3$ (3:1)	373	0.14	$0.84 \cdot 10^{13}$	$4.2 \cdot 10^{13}$	4.0
4	n-ZrO$_2$+n-Al$_2$O$_3$ (1:1)			$0.67 \cdot 10^{13}$	$3.34 \cdot 10^{13}$	3.1
5	n-ZrO$_2$+n-Al$_2$O$_3$ (1:3)			$0.51 \cdot 10^{13}$	$2.91 \cdot 10^{13}$	2.7
No	System	T, K	D, Gy/s	$W_T(H_2)$, molec./(g·s)	$W_{RT}(H_2)$, molec./(g·s)	$G(H_2)$, molec./100 eV
1	n-ZrO$_2$			$5.56 \cdot 10^{13}$	$2.08 \cdot 10^{14}$	8.35
2	n-Al$_2$O$_3$			$2.22 \cdot 10^{13}$	$5.83 \cdot 10^{13}$	4.15
3	n-ZrO$_2$+n-Al$_2$O$_3$ (3:1)	473	0.14	$5.02 \cdot 10^{13}$	$1.81 \cdot 10^{14}$	7.5
4	n-ZrO$_2$+n-Al$_2$O$_3$ (1:1)			$4.45 \cdot 10^{13}$	$1.0 \cdot 10^{14}$	6.7
5	n-ZrO$_2$+n-Al$_2$O$_3$ (1:3)			$2.57 \cdot 10^{13}$	$6.78 \cdot 10^{13}$	4.8
No	System	T, K	D, Gy/s	$W_T(H_2)$, molec./(g·s)	$W_{RT}(H_2)$, molec./(g·s)	$G(H_2)$, molec./100 eV
1	n-ZrO$_2$			$2.78 \cdot 10^{14}$	$6.94 \cdot 10^{14}$	25.7
2	n-Al$_2$O$_3$			$4.17 \cdot 10^{13}$	$9.44 \cdot 10^{13}$	8.6
3	n-ZrO$_2$+n-Al$_2$O$_3$ (3:1)	673	0.14	$2.59 \cdot 10^{14}$	$4.45 \cdot 10^{14}$	21.2
4	n-ZrO$_2$+n-Al$_2$O$_3$ (1:1)			$1.52 \cdot 10^{14}$	$2.61 \cdot 10^{14}$	12.9
5	n-ZrO$_2$+n-Al$_2$O$_3$ (1:3)			$1.17 \cdot 10^{14}$	$1.93 \cdot 10^{14}$	8.1

The values of the band gap for n-Al$_2$O$_3$ and n-ZrO$_2$ are 6.2 and 5.42 eV, and the threshold energy for the generation of nonequilibrium charge carriers (E_{th}) is 12.4 and 10.8 eV, respectively. The values of the radiation-chemical yield of nonequilibrium charge carriers are determined by the expression $G(n.c.c) = 100/E_{th}$ and equal to 8.06 pairs/100 eV and 9.22 pairs/100 eV, respectively. The energy of secondary electrons formed as a result of primary acts in the interaction of gamma quanta with oxides varies in a wide range of $E_{sec} \geq 10^3 \ldots 10^2$ eV, and the mean free

path of these electrons in oxide dielectrics varies in the range $L_{fp} \sim 10 \ldots 10^2$ nm. In addition, under the action of secondary electron radiation in oxide dielectrics, the next generation of nonequilibrium charge carriers and excited states is formed.
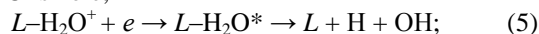
Water molecules on the surface of oxides are in the adsorbed state on the surface of the acceptor centers:

$$L_s + H_2O \rightarrow L\text{–}H_2O, \qquad (3)$$

where L_s is the surface-acceptor centers, L–H_2O is an adsorption complex interacting with non-equilibrium charge carriers and excited states:

$$L-H_2O + \oplus \rightarrow L-H_2O^+, \quad (4)$$

where $\oplus$ is hole;

$$L-H_2O^+ + e \rightarrow L-H_2O^* \rightarrow L + H + OH; \quad (5)$$
$$H + H \rightarrow H_2; \quad (6)$$
$$OH + OH \rightarrow H_2O_2. \quad (7)$$

The decomposition products of water are separated by surface fragments and, therefore, unlike recombinations of products are difficult. Taking into account reactions (3) – (6), the yields of nonequilibrium charge carriers and hydrogen should satisfy the relation:

$$G(H_2) = \frac{1}{2}G(n.c.c.). \quad (8)$$

As can be seen, in the case of heterogeneous radiolysis of water in the adsorbed state in the presence of nanooxides, only a certain part of non-equilibrium charge carriers participate in the process of water decomposition, and the rest emit into the contacting medium. The components formed as a result of the interaction of primary ionizing radiation with nanooxide dielectrics are surrounded by liquid water. In these systems, nanocomponents play a major role in the conversion of the energy of ionizing radiation into low-energy, secondary electron radiation into the liquid phase. Each particle of nanooxides plays the role of the center of radiation of secondary electrons and ions. In the space between the nanoparticles, a region of high concentration of electrons and ions is formed, which play the role of a microplasma cell, where the effective conversion of the energy of secondary electron radiation to the chemical energy of hydrogen occurs [12, 13].

Table shows the experimentally obtained values of the accumulation rates of molecular hydrogen for thermal $W_T(H_2)$ and radiation-thermal $W_{RT}(H_2)$ processes, as well as the values of $G(H_2)$ depending on the ratio of the components ZrO_2 and Al_2O_3 at different temperatures ($T = 373\ldots673$ K). As can be seen from the table, the highest $G(H_2)$ values in these systems are observed at a ratio of 75 wt.% n-ZrO_2–25 wt.% n-Al_2O_3 (3:1), which is due to the higher radiation activity of the surface centers of the Zr^{4+} type. A comparative analysis of the values of $W_T(H_2)$, $W_{RT}(H_2)$ shows that in the temperature range $T = 373\ldots673$ K under consideration, the accumulation rate of H_2 during radiation-thermal processes is significantly higher compared with thermal processes. This indicates the stimulating role of radiation in these processes. The dependences of the radiation-chemical yield of molecular hydrogen in the heterogeneous radiolysis of water on the ratio of the components are shown in Fig. 3.

As can be seen from the graph, at $T = 673$ K with an increase in the molar percentage of n-Al_2O_3 in the mixture, the hydrogen yield decreases from 25.7 to 8.6 molec./100 eV in the case of pure n-Al_2O_3.
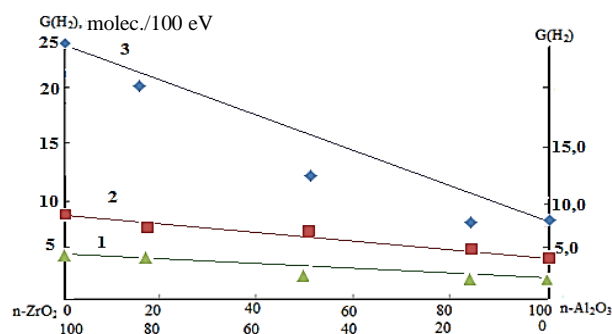

Fig. 3. Dependence of the radiation-chemical yield of molecular hydrogen in the heterogeneous radiolysis of water in the presence of the binary system n-ZrO_2-n-Al_2O_3 on the ratio of components at different temperatures: 373 (1); 473 (2), and 673 K (3)

CONCLUSION

The relatively high yield of molecular hydrogen in a mixture with a high content of n-ZrO_2 indicates that as a result of the action of gamma rays in the volume of n-ZrO_2, secondary electron radiations and energy sources are formed with relatively high yields, which effectively affects the process of water decomposition. Thus, with radiation-catalytic processes of water decomposition, due to the efficient transformation of energy transfer, the presence of strong acceptor centers of the surface and interparticles of nanoscale spaces for the realization of radiation processes involving secondary electron radiation from nanocatalysts, high yields of molecular hydrogen can be achieved.

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РАДИАЦИОННО-ТЕРМОКАТАЛИТИЧЕСКИЕ ПРОЦЕССЫ ПОЛУЧЕНИЯ ВОДОРОДА ИЗ ВОДЫ

Т.Н. Агаев, С.З. Меликова, Х.Ф. Гаджиева

Исследованы радиационно-термокаталитические процессы разложения воды в системе n-ZrO_2-n-Al_2O_3+H_2O. Изучена кинетика накопления молекулярного водорода при радиолитических процессах разложения воды в исследуемых системах. Определены значения скоростей накопления и радиационно-химических выходов водорода при радиолизе воды в системе n-ZrO_2-n-Al_2O_3+H_2O при различных температурах. Полученные результаты могут служить основой для пересмотра сценария нормальных и аварийных режимов работы водоохлаждаемых ядерных реакторов.

РАДІАЦІЙНО-ТЕРМОКАТАЛІТИЧНІ ПРОЦЕСИ ОТРИМАННЯ ВОДНЮ З ВОДИ

Т.Н. Агаєв, С.З. Меликова, Х.Ф. Гаджієва

Досліджено радіаційно-термокаталітичні процеси розкладання води в системі n-ZrO_2-n-Al_2O_3+H_2O. Вивчено кінетику накопичення молекулярного водню при радіолітичних процесах розкладання води в досліджуваних системах. Визначено значення швидкостей накопичення і радіаційно-хімічних виходів водню при радіолізі води в системі n-ZrO_2-n-Al_2O_3+H_2O при різних температурах. Отримані результати можуть бути основою для перегляду сценарію нормальних і аварійних режимів роботи водоохолоджуючих ядерних реакторів.