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CHEMICAL KINETICS AND CATALYSIS

Kinetics of the Radiation-Catalytic and Catalytic Decomposition of Water on a Surface of Nano-Zirconium

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Abstract—The kinetics of molecular hydrogen uptake is studied in the radiation-catalytic and catalytic decomposition of water on the surface of nano-Zr. The effect γ-radiation has on the nano-Zr + H_2O system at different temperatures is studied. Values of the uptake rates and the radiation–chemical yield of molecular hydrogen in radiation-catalytic processes are determined. Contributions from catalytic and radiation-catalytic processes to the uptake of molecular hydrogen upon contact between nano-Zr and water are determined.

Keywords: nano-zirconium, γ-radiation, molecular hydrogen, radiolysis

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INTRODUCTION

It is known that nanosized powders of zirconium and Zr dioxide are used in different devices. One such device is fuel cells, which serve to convert thermal energy to electrical energy. Thermal cells operate at rather high temperatures, and nanosized powders, particularly those of zirconium and Zr dioxide, are used to ensure their high quality. When nano-Zr is used as a component of construction material, we must consider the existence of phase transitions at high temperatures [1–6].

Zirconium is a rare metal that is widely used in atomic power engineering, radioelectronics, and other branches of technology, due to its exceptional properties. Because of the development of atomic engineering, zirconium is of interest as a possible material for building nuclear reactors. This means organizing the industrial production of flexible zirconium and alloys based on it. The value of zirconium as a construction material for nuclear science and energy is due to it having a small cross section of heat neutron capture (0.2 barn), high anticorrosion resistance, and good mechanical properties [7–12].

EXPERIMENTAL

Water radiolysis was performed under static conditions with special quartz ampules. The amount of nano-Zr in the ampules was around 4×10^{-2} g. Bidistilled water was used in our investigations. The water was introduced into the ampules in two ways. In the first, water from the vapor state (H_2O_v) was adsorbed on a surface of nano-Zr at $T = 77$ K. The amount of water introduced into the ampules corresponded to the density of water vapor at $\rho = 5$ mg/cm^3. In the investigated range of temperatures, equilibrium was reached between the amount of water in both the vapor and adsorbed states. In the second, water from a calibrated volume was introduced into the ampules until a sample of nano-Zr was fully coated with liquid water having mass $m_1 = 0.2$ g. The ampules with the samples were then cooled to 77 K and sealed.

Radiation- and radiation-thermal processes were conducted on isotope source ^{60}Co. The power of the absorbed dose of γ-radiation was determined with chemical (ferrosulfate, cyclohexane, and methane) dosimeters [13]. The products of radiation-heterogeneous processes were analyses on an Agilent-7890 gas chromatograph. It was found using the X-ray phase approach that our samples had two crystal modifications: α-Zr with a magnesium-type hexagonal lattice ($a = 3.231$ Å; $c = 5.148$ Å; $z = 2$; space group $P6_3/mmc$), and β-Zr with a cubic body-centered lattice ($a = 3.61$ Å, $z = 2$, space group Im3m). It was shown that water is adsorbed in nano-zirconium according to a molecular and dissociative mechanism. Intermediate products of radiation-heterogeneous water decomposition were registered: ion-radicals of molecular oxygen, hydrogen peroxide, zirconium hydride and hydroxyl groups. Comparative analysis of the changes in the absorption bands of molecular

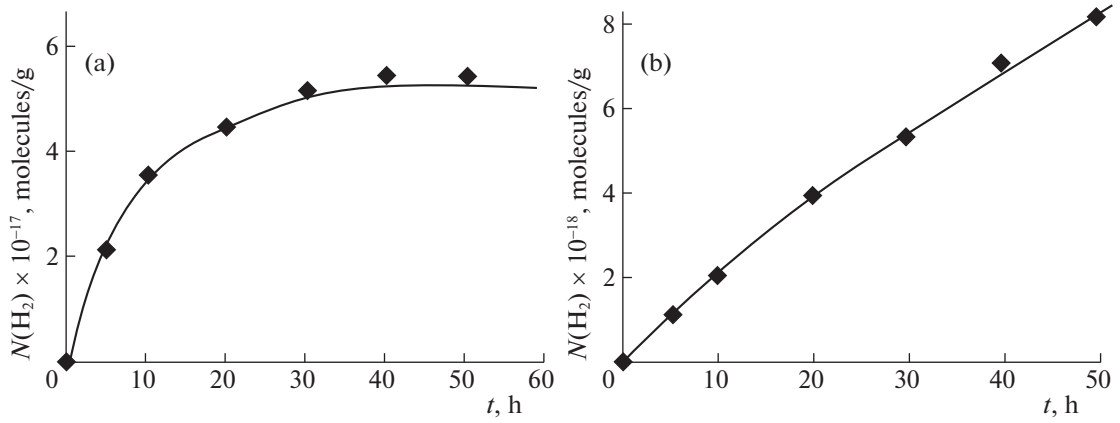

Fig. 1. Kinetic curve of molecular hydrogen formation during radiation-heterogeneous water decomposition in (a) nano-Zr + H_2O_v and (b) nano-Zr + H_2O_l at $T = 300$ K, $D = 0.15$ Gy/s.

water and surface hydroxyl groups showed they depended on the temperature, and the promotional role of radiation in the radiation-thermal processes of water decomposition was reevealed.

RESULTS AND DISCUSION

We studied the uptake kinetics of molecular hydrogen during heterogeneous water radiolysis in systems of nano-Zr + H_2O_l and nano-Zr + $H_2O_п$. As a construction material, nano-Zr exibits radiation resistance and operability in nuclear reactors. The radiation–catalytic activity of nano-Zr can be determined in two ways, as was indicated above. Figure 1 shows the kinetic curves for the uptake of molecular hydrogen during heterogeneous water radiolysis in the presence of nano-Zr in two states. The rates and radiation-chemical yields of hydrogen were found from the initial linear portions of the kinetic curves for the investigated systems [14]. Two regions can be seen in the kinetic curve given in Fig. 1a: Region I is characterized by a relatively high rate of the hydrogen uptake on the initial linear portions. II has a relatively slow step of molecular hydrogen uptake.

In the kinetic curve shown in Fig. 1b, we can see a rise in the uptake rate of molecular hydrogen. This once again shows that when the catalyst bed is totally covered with water, not only the energy carriers obtained on the basis of zone transitions participate in the decomposition of water, but emitted electrons and δ-electrons with low energies as well. The hydrogen yield in nano-Zr + H_2O_l is therefore ultimately higher than in nano-Zr + H_2O_v. It is seen from Table 1 that during heterogeneous water radiolysis under conditions where a layer of nano-Zr (nano-Zr + H_2O_l) is completely covered, the observed radiation chemical yield of hydrogen is around 5.4 times higher than during the heterogeneous radiolysis of water in the adsorbed state on a surface of nano-zirconium. This shows that with nano-zirconium in the volume of water, there is an effective transfer of energy from the solid phase to the water molecules.

Table 1. Rates and radiation-chemical yields of molecular hydrogen during radiation-heterogeneous water radiolysis in two states at $T = 300$ K.

No.	Irradiated systems	$W(H_2)$, molecules g^{-1} s^{-1}	$G(H_2)$, molecules/100 eV
1.	Zr + H_2O_v	1.22×10^{13}	1.3
2.	Zr + H_2O_l	6.67×10^{13}	7.1

The presence on the kinetic curves of the second slow step of radiolysis shows there is a diffusion-hindered step of heterogeneous water radiolysis in the presence of nano-zirconium at $T = 300$ K. The effect temperature has on the rate of molecular hydrogen formation during the radiolysis of heterogeneous water was studied using the nano-Zr + H_2O_v system as an example, since the temperature of the nano-Zr + H_2O_l system in the sealed ampules cannot be raised during an experiment.

It was found that at $T \geq 373$ K, zirconium dioxide displays thermocatalytic activity in the decomposition of water [15]:

$$H_2O_v \rightarrow H_2 + (1/2)O_2. \quad (1)$$

We can obtain information on the radiation-catalytic and catalytic processes of hydrogen uptake experimentally during radiation heterogeneous processes of water decomposition. Thermoradiation and the thermal processes of water decomposition in the presence of nano-zirconium were conducted at identical conditions.

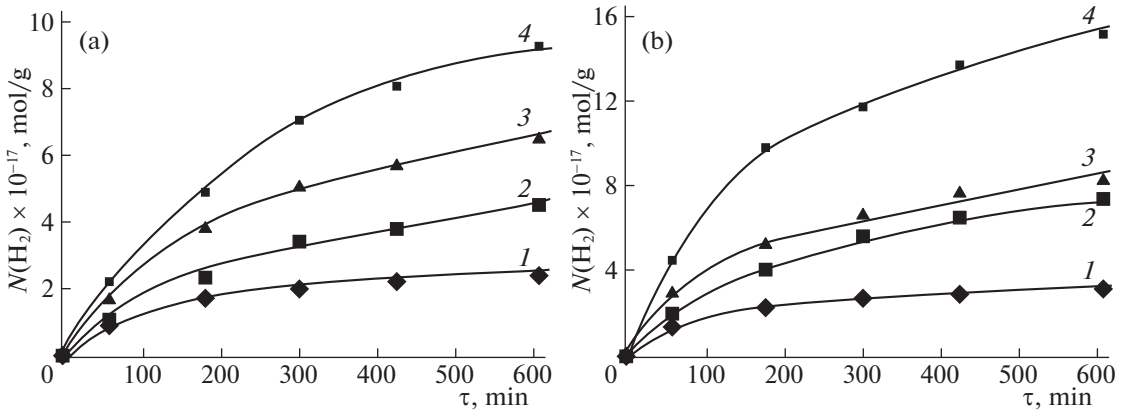

Fig. 2. Uptake kinetic of molecular hydrogen at (a) catalytic and (b) radiation-catalytic water decomposition on the surface of nano-Zr at different temperatures: *(1)* 373, *(2)* 473, *(3)* 573, *(4)* 673 K (ρ_{H_2O} = 5 mg/cm^3, D = 0.32–0.26 Gy/s).

To identify patterns of the effect temperature has on radiation-heterogeneous processes in a nano-Zr–water system, we studied the uptake of molecular hydrogen at different temperatures. Kinetic curves of the radiation catalytic and catalytic processes of water decomposition at temperatures T = 373–673 K are shown in Fig. 2. Upon a rise in temperature, the second slow step in hydrogen uptake is missing from some curves.

In the first approximation, the radiation component of the radiation thermal processes is determined as

$$W_p(H_2) = W_{pT}(H_2) - W_T(H_2), \quad (2)$$

where $W_p(H_2)$ is the rate of the formation of molecular hydrogen in the radiation composition process; $W_{pT}(H_2)$ and $W_T(H_2)$ are the rates of the formation of molecular hydrogen in the radiation-thermal and thermal processes of water decomposition.

The values of radiation-chemical yields were found from the rates of formation of molecular hydrogen during the radiation-composition and radiation-thermal processes of water decomposition (Table 2).

A comparison of the yields of molecular hydrogen from the radiation-heterogeneous process in the nano-Zr + H_2O_v system in the range T = 300–673 K shows that temperature accelerates the heterogeneous radiolysis. The yield of hydrogen in this case grows linearly along with temperature, from 1.3 to 8.4 mol/100 eV.

Figure 3 shows the dependences of the rates of the (1) radiation-thermal and (2) thermal processes of molecular hydrogen uptake upon the radiation-heterogeneous decomposition of water in the presence of nano-zirconium. The energies of activation were found from the temperature dependence of the rates in Arrhenius coordinates.

The energies of activation of radiation-thermal and thermal processes of molecular hydrogen uptake are E_a = 22.3 and 33.8 kJ/mol, respectively. The energy of activation of thermal water decomposition in the presence of nano-Zr is higher than the one for the radiation-thermal process. Radiation-generated active surface centers and secondary electron radiation, which have higher energies than thermal-active centers, participate in the radiation-thermal decomposition of water. The energy of activation of molecular hydrogen uptake therefore rises in thermal processes, compared to radiation-thermal processes [14, 15].

Table 2. Rates and radiation-chemical yields of molecular hydrogen during the radiation-catalytic, catalytic, and radiation processes of water decomposition in the nano-Zr + H_2O_v system at different temperatures

T, K	$W_{pT}(H_2)$, mol, g^{-1} s^{-1}	$W_T(H_2)$, mol, g^{-1} s^{-1}	$W_p(H_2)$, mol, g^{-1} s^{-1}	$G(H_2)$, molecules/100 eV
300	—	—	1.22×10^{13}	1.3
373	4.1×10^{13}	2.6×10^{13}	1.5×10^{13}	2.1
473	5.56×10^{13}	2.77×10^{13}	2.79×10^{13}	3.7
573	8.88×10^{13}	5.00×10^{13}	3.88×10^{13}	5.17
673	1.33×10^{14}	0.70×10^{14}	0.63×10^{14}	8.4

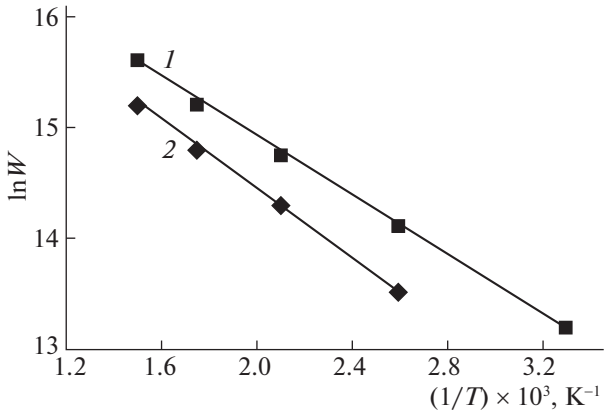

Fig. 3. Dependence of ln W on inverse temperature during (*1*) radiation-catalytic and (*2*) catalytic decomposition of water in the presence of nano-Zr + H_2O.

CONCLUSIONS

The kinetics of molecular hydrogen uptake was investigated during the γ-radiolysis of pure water and nano-Zr + H_2O systems. It was found that the radiation-chemical yield was higher for the nano-Zr + H_2O ($G(H_2)$ = 1.30 molecules/100 eV), than during the radiolysis of pure water ($G(H_2)$ = 0.45 molecules/100 eV). The kinetics of molecular hydrogen uptake was studied for the radiation, radiation-catalytic and catalytic processes of nano-Zr in contact with water. It was shown that the formation of surface-active centers and secondary electrons in the presence of nano-Zr was due to an increase in the rates of molecular hydrogen uptake during catalytic and radiation-catalytic processes in the nano-Zr + H_2O system. It was found that along with the uptake of surface-active centers of water decomposition, catalytic and radiation-catalytic processes proceed in nano-Zr when $T \geq 373$ K, [16–19].

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