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KINETICS OF RADIATION AND CATALYTIC DECOMPOSITION OF WATER IN THE PRESENCE OF NANO-ZIRCONIUM DIOXIDE

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The kinetics of molecular hydrogen accumulation at a gamma radiolysis of water on n-ZrO_2 surface is investigated. Influence of gamma radiations on n-ZrO_2+water systems is studied at various temperatures T = 300…673 K. Values of rates of molecular hydrogen accumulation at radiation, radiation-thermal and thermal processes are defined. Deposits of thermal and radiation-thermal processes at accumulation of molecular hydrogen in contact of n-ZrO_2 with water are revealed.

INTRODUCTION

Now the special attention to production of new technologies on production of dioxide of zirconium is paid. Dioxide of zirconium is used in metallurgy for receiving zirconium which is applied in nuclear reactors as constructional material. It possesses good strength, heat-insulating and dielectric properties in a wide interval of temperatures that in the turn allows to consider it as perspective material for production of the constructional materials [1, 2, 5, 8-15]. Use of dioxide of zirconium for fuel elements is caused by high ionic conductivity which is caused by transfer of anion oxygen vacancy. Nano dimensional systems in many respects differ from usual single-crystal systems therefore studying of their properties with water under influence of γ-radiations represents great practical and scientific interest [6-7].

In this work for the purpose of identification of zirconium dioxide influence on water radiolysis, the kinetics of accumulation of molecular hydrogen at radiolytic decomposition of water in n-ZrO_2+H_2O system at various temperatures T = 300…673 K is investigated.

EXPERIMENTAL PART

Researches were conducted in static conditions in special quartz ampoules with volume V = 1 cm^3. As object of research It were used zirconium dioxide nanopowder samples purity of 99.9%, d=20…30 nm, producing in "SkySpring Nanomaterials, İnc.", USA. Samples of dioxide of zirconium subjected to heat treatment at 573…673 K in the oxygen environment during 48 ch. Then heat treatment was carried out alternately 1h in oxygen and 1h in vacuum (P ~ 10^{-2} Pa) during 12 h at 573…67 3K. At the chosen processing modes in products of a radiolysis and a thermoradiolysis of water which can be formed in the presence of organic impurity, CO and CO_2 are absent.

The amount of dioxide of zirconium in ampoules was made approximately by m = $3 \cdot 10^{-2}$ q. For researches it was taken a double distilled water.

Water into ampoules was entered by two methods. In the first case in volume adsorptive device, water from a steam state adsorbed (H_2O_S) on a zirconium dioxide surface at 77 K. The amount of the entered water in ampoules corresponds to density of vapors of water in ampoules ρ = 5 mg/cm^3. At the studied intervals of temperatures, there is a balance between an amount of water at the steam and adsorbed state.

In the second case water from calibration volume was entered into ampoules to a full covering of a sample of zirconium dioxide by liquid water with mass m = 0.2 g. Then ampoules with samples, cooling to 77 K, soldered. Accuracy of introduction of water to ampoules was made by 2%. Ampoules with samples by means of a cycle of cooling, pumping out and defrosting were deairated till a full cleaning of water from soluble oxygen and other organic compounds. Temperature when carrying out experiments was maintained with ±1 ^oC accuracy.

Radiation and radiation-thermal processes carried out on an isotope source of γ-quanta ^{60}Co. Power of the absorbed dose of gamma radiation is determined by – ferrosulphate, cyclohexane and methane dosimeters [3, 4, 16]. The absorbed radiation dose in the studied systems is determined by the relation of their electronic density and dosimetric systems.

Ampoules opened in special cell, from where products of a radiolysis came to a chromatograph column. The analysis of products of radiation and heterogeneous processes was carried out on the gas-chromatograph "Tsvet-102" and gas analyzer "Gazokhrom-3101".

RESULTS AND THEIR DISCUSSION

The kinetics of accumulation of molecular hydrogen at a heterogeneous radiolysis of water in the presence of zirconium dioxide is studied. In Fig. 1,a,b. kinetic curves of hydrogen accumulation at a heterogeneous radiolysis of water in the presence of zirconium dioxide are given in two states.

On the basis of initial linear parts of kinetic curves, values of rates and a radiation-chemical yield of hydrogen in the studied systems are defined.

Apparently from kinetic curves of accumulation of molecular hydrogen after certain time the stationary area is observed in both systems. Therefore in them it is possible to divide two sites:

I – area is characterized by rather high rate of accumulation of hydrogen in initial linear sites,

II – rather slow stage of accumulation of molecular hydrogen.

Values of rates of molecular hydrogen accumulation and radiation-chemical yields are determined by initial linear areas of kinetic curves (Table 1).

Table 1

Values of rates and radiation-chemical yields of molecular hydrogen at a radiation and heterogeneous radiolysis of water in two states at T=300 K

Irradiated systems and temperatures of process	$W(H_2)$, $mol.\cdot q^{-1}\cdot s^{-1}$	$G(H_2)$, mol./100 eV
$ZrO_2+H_2O_S$,T=300 K	$4.44\cdot10^{13}$	2.14
$ZrO_2+H_2O_l$,T=300 K	$2.78\cdot10^{14}$	13.5

For the purpose of identification of ZrO_2 influence on radiolysis of water the kinetics of accumulation of molecular hydrogen at radiolytic decomposition of water and ZrO_2+H_2O system is investigated at T=300 K. On Fig. 1,a the kinetic curve of accumulation of molecular hydrogen at a water radiolysis in the presence of ZrO_2 is given. On the basis of a kinetic curve the rate of process $W(H_2)$ and value of a radiation-chemical yield of molecular hydrogen $G(H_2)$ per 100ev of the energy absorbed by water is determined which are equal to 0.45 and 2.14 mol./100 eV for clear water and ZrO_2+H_2O system respectively.

The observed gain of $G(H_2)$ values at a water radiolysis in the presence of ZrO_2, in comparison with an yield at radiolysis of pure water can be explained by a contribution of secondary electronic radiations from ZrO_2 at influence of γ-quanta, δ-electrons and formation of the active centers of decomposition of water on a surface of ZrO_2.

Apparently at a heterogeneous radiolysis of water in a case of a full covering of zirconium dioxide layer ($ZrO_2+H_2O_l$), the observed values of a radiation-chemical yield of hydrogen approximately in ~ 6,3 times are more, than in a case at a heterogeneous radiolysis of water in the adsorbed state on a zirconium dioxide surface. It testifies that in case of finding of zirconium dioxide in volume of water there is an effective transfer of energy from a firm phase to water molecules.

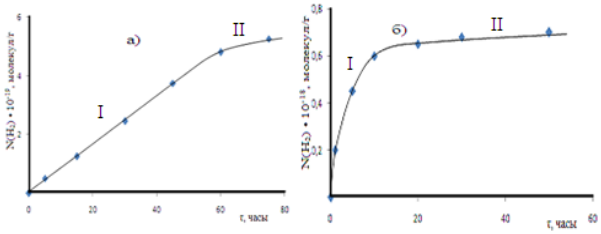

Fig. 1. Kinetics of formation of molecular hydrogen at the radiation and heterogeneous decomposition of water in n-$ZrO_2+H_2O_S$ systems, (a) (T=300 K, $\rho(H_2O)$=5 mg/cm^3, D = 0,33 Gy/s) and $ZrO_2+H_2O_l$, (b) (T = 300 K, $m(H_2O)$=0,02 q, D = 0,33 Gy/s)

Existence in kinetic curves of the second slow stage of a radiolysis testifies that, there is a diffusive complicated stage of a heterogeneous radiolysis of water in the presence of zirconium dioxide at 300 K. Influence of temperature on formation rates of molecular hydrogen at a heterogeneous radiolysis of water are studied on the example of $ZrO_2+H_2O_S$ systems as temperature increase in $ZrO_2+H_2O_l$ system in the closed ampoules experimentally isn't possible.

It is revealed that at $T \geq 473$ K a dioxide of zirconium possesses thermocatalytic activity in the process of water decomposition [10]:

$$H_2O_S \xrightarrow{ZrO2} H_2 + 1/2\ O_2\ . \qquad (1)$$

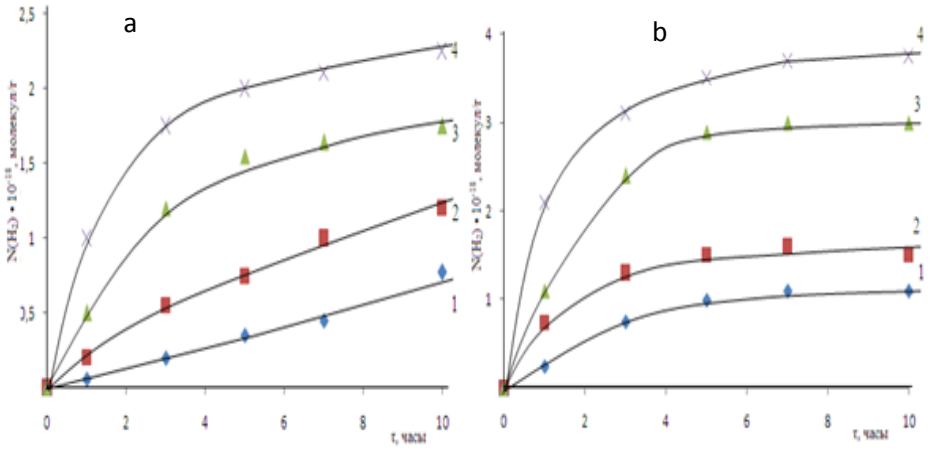

Fig. 2. Kinetics of accumulation of molecular hydrogen at thermal (a) and radiation-thermal (b) decomposition of water on a surface of n-ZrO_2 at the various temperatures:
1 – 373; 2 – 473; 3 – 573; 4 – 673 K (ρ_{H2O}=5 mq/cm^3, D=0,32…0,26 Gy/s)

Apparently, with increase in temperature the second slow stage of processes of accumulation of hydrogen which are observed at a radiation-heterogeneous radiolysis of water in the presence of zirconium dioxide at T=300 K isn't observed. In all kinetic curves after certain time the stationary area is observed. The radiation component of radiation-thermal processes in a first approximation defined as a difference:

$$W_R(H_2) = W_{RT}(H_2) - W_T(H_2), \qquad (2)$$

where $W_{RT}(H_2)$ – the rate of formation of molecular hydrogen at radiation-thermal process of decomposition of water; $W_T(H_2)$ – the rate of formation of molecular hydrogen at thermal process of decomposition of water; $W_R(H_2)$ – the rate of formation of molecular hydrogen at radiation processes.

Values of radiation-chemical yields are determined by value of rates of the radiation component of radiation-thermal processes of water decomposition. The received values of rates and radiation-chemical yields of molecular hydrogen are given in Table 2.

Table 2

Values of rates and radiation-chemical yields of molecular hydrogen at radiation-thermal, thermal and radiation processes of water decomposition in ZrO_2+H_2O_S system at various temperatures

T, K	$W_{RT}(H_2)$, mol.·q^{-1}·s^{-1}	$W_T(H_2)$, mol.·q^{-1}·s^{-1}	$W_R(H_2)$, mol.·q^{-1}·s^{-1}	$G(H_2)$, mol./100eV
300	–	–	$4.44\cdot10^{13}$	2.14
373	$9.17\cdot10^{13}$	$1.38\cdot10^{13}$	$7.8\cdot10^{13}$	4.8
473	$2.08\cdot10^{14}$	$5.56\cdot10^{13}$	$1.52\cdot10^{14}$	8.35
573	$3.33\cdot10^{14}$	$1.11\cdot10^{14}$	$2.22\cdot10^{14}$	13.6
673	$6.94\cdot10^{14}$	$2.78\cdot10^{14}$	$4.16\cdot10^{14}$	25.7

Comparisons of yield values of molecular hydrogen at radiation-heterogeneous processes in ZrO_2 + H_2O_S system in the range of temperatures T = 300…673 K, shows that, temperature stimulates process of a heterogeneous radiolysis and the hydrogen yield linearly grows with temperature from 2.14 to 25.7 mol./100 eV.

On the basis of temperature dependence of rates of processes in the Arrhenius coordinates are defined a value of their activation energy. Dependences of rates of radiation-thermal (1) and thermal (2) processes of molecular hydrogen accumulation at radiation-heterogeneous processes of water decomposition in the presence of zirconium dioxide are given in Fig. 3.

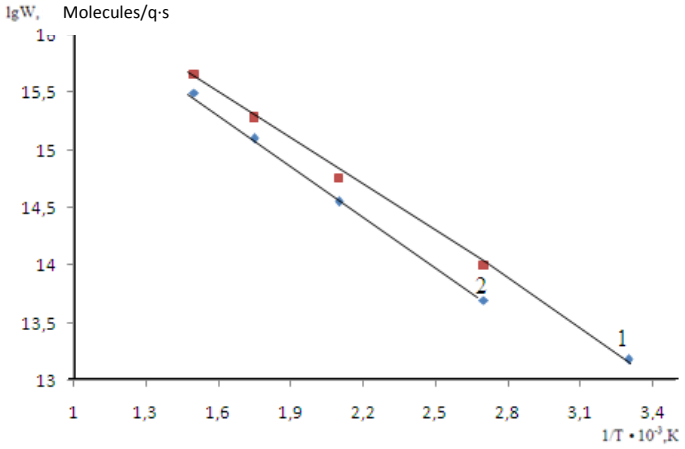

Fig. 3. Dependence of lgW on the reverse temperature at radiation – thermal (1) and thermal (2) decomposition of water in the presence of the nano-ZrO_2

Energy of activation of radiation-thermal and thermal processes of accumulation of molecular hydrogen are equal Ea=25.2 and 38.5 kJ/mol respectively. Apparently, energy of activation of thermal process of water decomposition in the presence of ZrO_2 is more, than radiation-thermal processes. At radiation-thermal processes of water decomposition the radiation generated active centers of a surface and secondary electronic radiations participate which possess bigger energy, than thermally active centers. Therefore, energy of activation of process of molecular hydrogen accumulation grows on a number of radiation-thermal and thermal processes.

Thus, on the basis of the received results it is possible to make the following conclusions. The kinetics of accumulation of molecular hydrogen at a gamma radiolysis of pure water and ZrO_2+H_2O system is investigated. It is established that the radiation-chemical yield for ZrO_2+H_2O system is more ($G(H_2)$=2.14 mol./100 eV), than at radiolysis of a pure water ($G(H_2)$=0.45 mol./100 eV). Besides, the kinetics of accumulation of molecular hydrogen at radiation, radiation-thermal and thermal processes in contact of ZrO_2 with water is studied. Formation of the surface-active centers and secondary electrons from ZrO_2, causes increase in rates of saturation of molecular

hydrogen at thermal and radiation-thermal processes in ZrO_2+H_2O system. Thus it is established that since $T \geq 473$ K there is also an accumulation of the thermal superficial active centers of water decomposition in ZrO_2 at thermal-radiation and thermal processes.

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КИНЕТИКА РАДИАЦИОННОГО И ТЕРМОКАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ВОДЫ В ПРИСУТСТВИИ НАНО-ДИОКСИДА ЦИРКОНИЯ

А.А. Гарибов, Т.Н. Агаев, Г.Т. Иманова, К.Т. Эюбов

Исследована кинетика накопления молекулярного водорода при γ-радиолизе воды на поверхности n-ZrO_2. Изучено влияние γ-излучений на систему n-ZrO_2+вода при различных температурах (T = 300…673 К). Определены значения скоростей накопления молекулярного водорода при радиационных, радиационно-термических и термических процессах. Выявлены вклады термических и радиационно-термических процессов при накоплении молекулярного водорода в контакте n-ZrO_2 с водой.

КІНЕТИКА РАДІАЦІЙНОГО І ТЕРМОКАТАЛІТИЧНОГО РОЗКЛАДАННЯ ВОДИ В ПРИСУТНОСТІ НАНОДИОКСИДА ЦИРКОНІЮ

А.А. Гарібов, Т.Н. Агаєв, Г.Т. Іманова, К.Т. Еюбов

Досліджена кінетика накопичення молекулярного водню при γ-радіолізі води на поверхні n-ZrO_2. Вивчено вплив γ-випромінювань на систему n-ZrO_2+вода при різних температурах (T = 300...673 К). Визначено значення швидкостей накопичення молекулярного водню при радіаційних, радіаційно-термічних та термічних процесах. Виявлено вклади термічних і радіаційно-термічних процесів при накопиченні молекулярного водню в контакті n-ZrO_2 з водою.