PRODUCTION OF MOLECULAR HYDROGEN FORMED BY THE THERMAL AND RADIATION-THERMAL TRANSFORMATION OF WATER IN THE NANO-Si+H_2O SYSTEM

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It were studied the regularities of the dependence of the yield of molecular hydrogen obtained during the thermal and radiation-thermal transformation of water under the action of gamma quanta (^{60}Co, P = 18.17 rad/s) on the nano-Si+H_2O system with particle sizes d_{Si} = 50 nm on the temperature (T = 300, 373, 473, 573, 623, and 673 K) of the total system and on the water vapor density (ρ = 0.25, 0.5, 1, 3, and 8 mg/cm^3) at a constant temperature of T = 673K. In this system, in a reaction medium with a water vapor density ρ=8 mg/cm^3 in the temperature range $300 \leq T \leq 473$ K, molecular hydrogen is obtained only by radiation-thermal, and in the temperature range $573 \leq T \leq 673$ K – by thermal and radiation-thermal methods. In the temperature range $300 \leq T \leq 473$ K, the activation energy of the radiation-thermal process is 1.07 kJ/mol, and in the temperature range $573 \leq T \leq 673$ K, the activation energy of the thermal and radiation-thermal processes is 68.6 and 53.83 kJ/mol, respectively. At a temperature of T = 673 K, the yield and the rate of formation of molecular hydrogen obtained in the thermal and radiation-thermal transformation of water vapor in the reaction medium increase in direct proportion to the its density at ρ < 3 mg/cm^3, and at ρ ≥ 3 mg/cm^3 a sharp decrease in the angle slope is observed.

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INTRODUCTION

Metals and metal compounds are materials widely used in science and various fields of technology (nuclear and thermonuclear reactors, in space and aerospace research, microcircuits). These materials, operating under various conditions (in contact with air, water, steam, etc.), are exposed to heat and ionizing rays (neutrons, protons, γ-quanta, electrons, ions, etc.). Therefore, the main problem facing scientific and technical workers is the early prediction of the processes occurring inside, on the surface of these materials and their environment. On the other hand, the study of products formed under these phenomena is of great value, as for science, and for energy and ecology.

To this end, researchers recently began to study the process of radiation-heterogeneous transformation of liquids, gases, especially the radiation-heterogeneous transformation of water [1–10]. The researchers conducted these processes under two conditions. It was studied firstly, the suspension of these materials in water, and secondly, the dependence of the amount, rate of formation, and radiation-chemical yield of molecular hydrogen obtained during the radiation-heterogeneous transformation of water adsorbed on the surface of these materials from:

- the kind of solid
- the width of the forbidden band of a solid,
- the particle size of a solid,
- the degree of water filling the surface of a solid,
- common system temperature,
- the density of water in the reaction medium
- the mass of a solid suspended in water.

From the results obtained it was clarified that the radiation-chemical yield of molecular hydrogen obtained by radiation-heterogeneous transformation of water under the influence of γ-quanta on metals and metal oxides significantly increases in comparison with pure water [1–11].

In the present work, it was studied the dependence of the yield and rate of formation of molecular hydrogen obtained in the process of radiation-heterogeneous transformation of water under the action of gamma quanta (^{60}Co, P = 18.17 rad/sec) on the surface of nano-silicon (nano-Si) with dimensions of particles d=50 nm, on the system temperature (T = 300, 373, 473, 573, 623 and 673 K) and on the density of water vapor (ρ = 0.25, 0.5, 1, 3 and 8 mg/cm^3) in the reaction medium.

EXPERIMENTAL PART

Nano-silicon of the "Skysping Nanomaterials. İnc", USA Company with purity of 99.9% was taken as the object of the study. Initially, at T = 473K, nano-Si in air was thermally treated for 72 hours and then cooled. Then we took the weight weighed in the balance and added to the quartz ampoule (V = 19 ml), purified under special conditions and thermally treated (T = 773 K), which was then thermally treated a few hours later at T = 473 K. After heat treatment of nano-Si (T = 673K) under vacuum conditions (P = 10^{-3} mm Hg) in an ampoule for 4 hours, it was cooled, and then the required amount of doubly-distilled water, purified from air was adsorbed on its surface [9, 10, 12].

Then the ampoules were sealed and irradiated in a ^{60}Co source with a dose rate P = 18.17 rad/sec. The absorption dose rate was determined by ferrosulfate and methane methods. In a particular investigated object, the absorption dose rate was calculated using the method of comparing electron densities [12, 13].

Molecular products – H_2, O_2, and H_2O_2, obtained during the radiation-heterogeneous process, were determined by chromatographic method. Since part of

O_2, which is one of these products, is trapped on the surface, and H_2O_2 remains in solution, the errors are large in determining these products. Therefore, more precise information about the kinetic regularity of the process of radiation-heterogeneous water transformation was given on the basis of the amount of molecular hydrogen.

The reaction products were analyzed on an "Agilent-7890" chromatograph. To confirm the results, a modernized chromatograph Color-102 (accuracy 8…10%) was used in parallel. In the Tsvet-102 chromatograph, a 1 m long column with an inner diameter of 3 mm was used. Inside the column, activated charcoal was used with a particle size d = 0.25…0.6 mm and argon of high purity was used as a carrier in each of the two chromatographs.

RESULTS AND DISCUSSION

As the temperature in the nano-Si+H_2O system increases, the process of desorption of water, adsorbed on the surface of the particles, begins. Therefore, the dependence of the yield of molecular hydrogen, obtained both by thermal and radiation-thermal conversion of water in the reaction medium, on the density of water was considered.

In Fig. are shown the kinetic curves of molecular hydrogen obtained during radiation-thermal transformation of water under the influence of γ-quanta upon contact with nano-Si with dimensions $d = 50$ nm at a temperature $T = 673$ K and a water vapor density $\rho = 0.25$; 0.5; 1; 3, and 8 mg/cm^3, and in Fig. 2 under the same conditions, the kinetic curves of the dependence of the yield of molecular hydrogen obtained during the thermal transformation of water are given:

Based on the initial sections of the kinetic curves (τ = 0…30 min), the rates of formation of molecular hydrogen obtained under thermal ($W_T(H_2)$) and radiation-thermal ($W_{RT}(H_2)$) water conversions were determined. If the process of obtaining molecular hydrogen during radiation-thermal transformation of water contacting the surface of a nanoparticle is represented as the sum of two independent thermal and radiation-thermal processes, the radiation fraction should be calculated from expression (1):

$$W_R(H_2) = W_{RT}(H_2) - W_T(H_2)\,. \qquad (1)$$

The radiation-chemical yield of molecular hydrogen was calculated on the basis of the radiation fraction $W_R(H_2)$, and the results obtained are given in Tabl. 1.

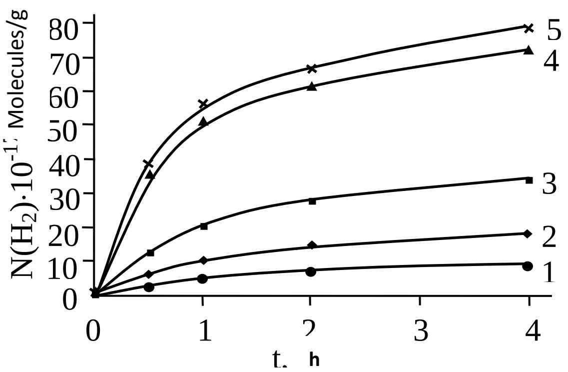

Fig. 1. Kinetics of obtaining molecular hydrogen at radiation-thermal transformation of water in contact with nano-Si particles d_{Si} =50 nm in size at temperature T = 673 K and water vapor density ρ= 0.25 (1); 0.5 (2); 1 (3); 3 (4), and 8 (5) mg/cm^3

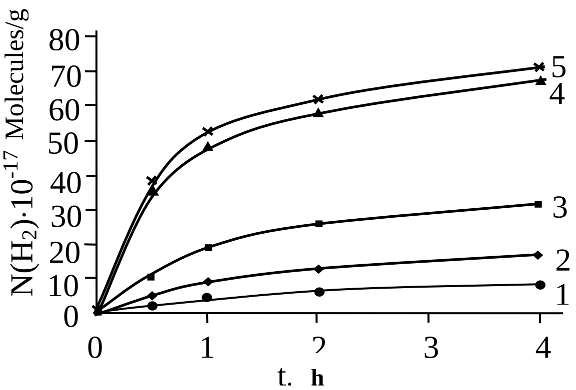

Fig. 2. Kinetics of molecular hydrogen production at the thermal transformation of water in contact with nano-Si particles d_{Si} =50 nm in size at a temperature of T = 673 K and a water vapor density of ρ = 0.25 (1); 0.5 (2); 1 (3); 3 (4.) and 8 (5) mg/cm^3

Table 1

The formation rate and the radiation-chemical yield $G(H_2)$ of molecular hydrogen obtained by the thermal ($W_T(H_2)$) and radiation-thermal ($W_{RT}(H_2)$) conversion of water vapor of various densities in contact with nano-Si at a temperature T = 673 K

The formation rates ($W(H_2)$) and the radiation-chemical yield ($G_R(H_2)$)	Water vapor density, mg/cm^3				
	0.25	0.5	1	3	8
$w_T(H_2)\cdot10^{-14}$, molecules/(g·s)	1.6	3.15	6.15	18.87	20.1
$w_{RT}(H_2)\cdot10^{-14}$, molecules/(g·s)	1.73	3.45	6.7	20.15	21.6
$w_R(H_2)\cdot10^{-14}$, molecules/(g·s)	0.13	0.33,88	0.55	1.28	1.5
$G_R(H_2)$, molecules/100 eV	1.15	2.65	4.85	11.3	13.2

In the reaction medium, the rate of formation and the radiation-chemical yield (Tabl. 2) of molecular hydrogen obtained in the thermal and radiation-thermal transformation of water in contact with nano-Si at a temperature of T = 673 K and a water vapor density of ρ_{H2O} = 0.25; 0.5; 1; 3, and 8 mg/cm^3 were observed as a function of the water density. At $\rho < 3$ mg/cm^3, the radiation-chemical yield of molecular hydrogen increases in direct proportion to the water density, and at $\rho \geq 3$ mg/cm^3 this proportionality is violated and a deceleration is observed. In this system, the dependence of the rate of formation of molecular hydrogen on the density of water can be represented by the Langmuir expression (2):

$$w_{T(RT)}(H_2) = \frac{k_{T(RT)} b \rho_{H_2O}}{1 + b\rho_{H_2O}} \quad , \qquad (2)$$

where $k_{T\ (RT)}$ is the rate of thermal and radiation-thermal processes, b is the equilibrium rate in adsorption processes, and the ρ_{H2O} is the density of water vapor. In the Langmuir equation, if we take into account that $b\rho_{H2O} << 1$ for small values of the water vapor density, the rate of formation of molecular hydrogen $w_{T(RT)}(H_2) = k_{T(RT)} b \rho_{H_2O}$ obtained by the thermal (radiation-thermal) transformation of water is directly proportional to the density of water vapor, and for values of $b\rho_{H2O} >> 1$ it assumes a constant value, equal to $w_{T(RT)}(H_2) = k_{T(RT)}$. The data obtained by us prove this.

In Fig. 3 kinetic curves of the influence of different temperatures on the yield of molecular hydrogen obtained by radiation-thermal conversion of water vapor of density ρ=8 mg/cm^3 in contact with nano-Si under the influence of γ-quanta are given.

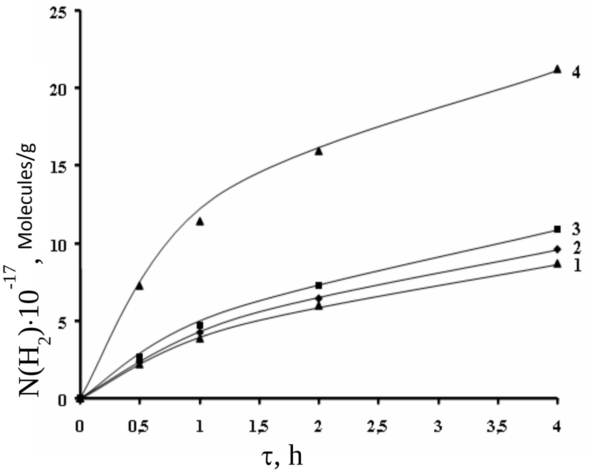

Fig. 3. Effect of temperature (T = 300 (1), 373 (2), 473 (3), 573K (4)) on the yield of molecular hydrogen obtained by radiation-thermal conversion of water vapor of density ρ=8 mg/cm^3 in a contact with nano-Si

At the second stage, the process was carried out under the same conditions only under the influence of temperature. And then from the linear parts of the kinetic curves of both thermal and radiation-thermal (Fig. 3) processes, the rates of formation of molecular hydrogen (1) were determined, and then the radiation-chemical yield. The results are shown in Tabl. 2.

Table 2

Effect of temperature on the formation rate and the radiation-chemical yield of molecular hydrogen obtained by thermal and radiation-thermal transformation of water under the influence of γ-quanta on nano-Si, contacting in the reaction medium with water vapor of density ρ=8 mg/cm^3

T, K	$w_T(H_2)$, molecules/(g·s)	$w_{RT}(H_2)$, molecules/(g·s)	$w_R(H_2)$, molecules/(g·s)	$G_R(H_2)$, molecules//(100 eV)
300	–	$1.23\cdot 10^{14}$	$1.23\cdot 10^{14}$	10.85
373	–	$1.32\cdot 10^{14}$	$1.32\cdot 10^{14}$	11.65
473	–	$1.45\cdot 10^{14}$	$1.45\cdot 10^{14}$	12.80
573	$2.40\cdot 10^{14}$	$3.88\cdot 10^{14}$	$1.48\cdot 10^{14}$	13.10
623	$7.22\cdot 10^{14}$	$8.71\cdot 10^{14}$	$1.49\cdot 10^{14}$	13.15
673	$2.01\cdot 10^{15}$	$2.16\cdot 10^{15}$	$1.50\cdot 10^{14}$	13.20

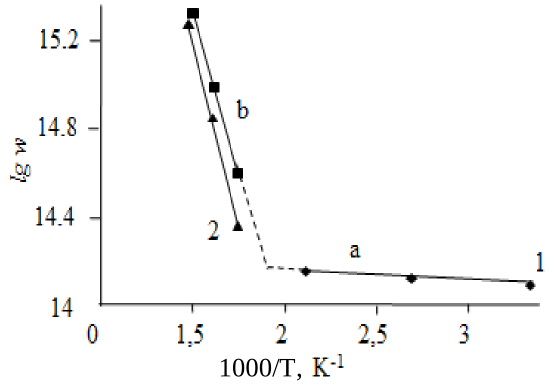

Fig. 4. Dependence of the rate of formation of molecular hydrogen obtained by thermal (2) and radiation-thermal (1) conversion of water vapor of density ρ=8 mg/cm^3 in contact with nano-Si, on the temperature

The activation energies of the processes in the Arrhenius coordinates (lgW(H_2), 1/T) were determined from the dependence of the rate of formation of molecular hydrogen upon thermal and radiation-thermal transformation of water vapor of density ρ=8 mg/cm^3 in the nano-Si + H_2O system. In the temperature range 300≤*T*≤473K in the nano-Si+H_2O system, the yield of molecular hydrogen produced from water vapor is observed only at the radiation-thermal process and the activation energy of this process is equal to 1.07 kJ/mol (Fig. 4(1a)). In the temperature range 573≤*T*≤673K molecular hydrogen forms both in radiation-thermal (Fig. 4(1b)) and thermal transformation of water (Fig. 4 (2)), and activation energies of the both processes are 53.83 and 68.6 kJ / mol, respectively.

Adsorption on the surface of a metal and metal oxide is possible with the participation of oxide atoms that play a non-constant role, and due to unsaturated coordination metal atoms. Strong adsorption of electron-donor water molecules on the surface of nano-Si is formed with the participation of Si^4 ions and this binding energy [14] is equal to 100…140 kJ/mol. Complexes formed between water molecules and Si^{4+} ions, which are catalytic acceptor centers on the surface of nano-Si, play a huge role in the production of molecular hydrogen during the thermal and radiation-thermal transformation of water.

In the physical stage of the process[2, 15–19], such types of energy carriers as electron-ion pairs (Si^+ - e, H_2O^+ - e^-), formed by the ionization of molecules, and electron-excited states (Si^*, H_2O^*) (excitons) are formed in Si, H_2O, Si+H_2O systems under the influence of ionizing rays (γ-quanta, electrons, etc.):

$$Si(H_2O) \rightarrow Si^*(H_2O^*),\ Si^+(H_2O^+),\ M^+,\ e. \quad (3)$$

A certain part of the electrons formed by (3) in accordance with the Onsager effect, recombining with their ion, can form an electron-excited state (exciton). The remaining part of the energy carriers, depending on the temperature and the intensity of the external surface, migrating to different distances, is localized in structural defects, while the other part, migrating to the surface, can localize at the centers of the surface. Some of the electrons migrating to the surface are emitted from the surface and pass into water adsorbed on the surface or water vapor. The energy carriers formed inside the nanoparticles transmit a part of their energy to the water molecules in contact with them (exciton and recombination energy transfer), causing their excitation and decomposition, resulting in the formation of the intermediate - H, OH, O, and molecular - H_2, O_2, H_2O_2 products.

The intermediate products [20] formed under the influence of temperature and γ-quanta and directly involved in the formation of molecular hydrogen as a result of the thermal and radiation-thermal transformation of water can be symbolically represented in the form below: Active intermediates, by adsorbing water molecules in a vaporous form, form intermediately active complexes:

Active intermediate products, transferring their excitation energy to water molecules, result in the formation of highly reactive intermediate products H and OH as a result of water transformation:

$$Me^*_{T(R)} - H_2O_s \rightarrow Me - OH + H\ . \quad (6)$$

As a result of the attachment of neighboring Me-OH sites, an oxygen bridge forms on the surface, which means the oxidation of the surface:

$$Me - OH + Me - OH \rightarrow Me - O - Me + H_2O\ , \quad (7)$$

Finally, as a result of thermal and radiation-thermal water splitting, molecular hydrogen is formed:

$$H + H \rightarrow H_2. \quad (8)$$

The following conclusions were obtained from the researches:

$$Me^*_{T(R)} + H_2O_q \rightarrow Me^*_{T(R)} - H_2O_s \quad (5)$$

- In the Si + H_2O system at a constant temperature T=673 K, and for water vapor density values ρ=0.25; 0.5; 1; 3, and 8 mg/cm^3, the rate of formation of molecular hydrogen obtained by thermal and radiation-thermal transformation of water grows directly in proportion to its density, and at the value of p ≥ 3 mg/cm^3 growth retardation is observed.
- In the nano-Si + H_2O system, in a reaction medium with a constant water vapor density of ρ=8 mg/cm^3, molecular hydrogen is obtained: 1) in the temperature range 300 K≤T≤473 K only as a result of radiation-thermal processes, and the activation energy of these processes is E_R = 1.07 kJ/mol and 2) in the temperature range 573K≤T≤673K as a result of thermal and radiation-thermal processes, and the activation energy of these processes is 68.6 and 53.83 kJ/mol, respectively.
- In the Si + H_2O system in the temperature range 300 ≤ T ≤ 673 K, the radiation-chemical yield of molecular hydrogen obtained by thermal and radiation-

thermal water conversion calculated for the radiation fraction is $G(H_2)$ = 10.85…13.2 molecules/100 eV.

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ПОЛУЧЕНИЕ МОЛЕКУЛЯРНОГО ВОДОРОДА, ОБРАЗОВАННОГО ТЕРМИЧЕСКИМ И РАДИАЦИОННО-ТЕРМИЧЕСКИМ ПРЕВРАЩЕНИЕМ ВОДЫ В СИСТЕМЕ НАНО-Si+H_2O

Я.Д. Джафаров, С.М. Баширова, К.Т. Эюбов, А. А. Гарибов

Исследованы закономерности зависимости выхода молекулярного водорода, полученного при термическом и радиационно-термическом превращении воды под воздействием гамма-квантов (^{60}Co, P = 18,17 рад/с) на систему нано-Si+H_2O с размерами частиц d_{Si} = 50 нм, от температуры (T = 300, 373, 473, 573, 623 и 673 K) общей системы, а также от плотности пара воды (ρ = 0,25; 0,5; 1; 3 и 8 мг/см^3) при постоянном значении температуры T = 673 K. В этой системе в реакционной среде с плотностью паров воды ρ = 8 мг/см^3 и в интервале температур $300 \le T \le 473$ K молекулярный водород получается только радиационно-термическим, а в интервале температур $573 \le T \le 673$ K – термическим и радиационно-термическим способами. При $300 \le T \le 473$ K энергия активации радиационно-термического процесса составляет 1,07 кДж/моль, а при $573 \le T \le 673$ K энергии активации термического и радиационно-термического процессов соответственно – 68,6 и 53,83 кДж/моль. При T = 673 K выход и скорость образования молекулярного водорода, полученного при термическом и радиационно-термическом превращении паров воды в реакционной среде, растут прямо пропорционально их плотности (ρ < 3 мг/см$^{3)}$, а при значениях ρ ≥ 3 мг/см^3 наблюдается резкое уменьшение скорости образования молекулярного водорода.

ОТРИМАННЯ МОЛЕКУЛЯРНОГО ВОДНЮ, УТВОРЕНОГО ТЕРМІЧНИМ І РАДІАЦІЙНО-ТЕРМІЧНІМ ПЕРЕТВОРЕННЯМ ВОДИ В СИСТЕМІ НАНО-$Si+H_2O$

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Досліджено закономірності залежності виходу молекулярного водню, отриманого при термічному і радіаційно-термічному перетворенні води під впливом гамма-квантів (^{60}Co, P = 18,17 рад/с) на систему нано-$Si+H_2O$ з розмірами частинок d_{Si} = 50 нм, від температури (T = 300, 373, 473, 573, 623 і 673 K) загальної системи, а також від щільності парів води (ρ = 0,25; 0,5; 1; 3 і 8 мг/см^3) при постійному значенні температури T = 673 K. У цій системі в реакційному середовищі з щільністю парів води ρ = 8 мг/см^3 і в інтервалі температур $300 \leq T \leq 473$ K молекулярний водень виходить тільки радіаційно-термічним, а в інтервалі $573 \leq T \leq 673$ K – термічним і радіаційно-термічним способами. При $300 \leq T \leq 473$ K енергія активації радіаційно-термічного процесу становить 1,07 кДж/моль, а при $573 \leq T \leq 673$ K енергії активації термічного і радіаційно-термічного процесів – 68,6 і 53,83 кДж/моль. При T = 673 K вихід і швидкість утворення молекулярного водню, отриманого при термічному і радіаційно-термічному перетворенні парів води в реакційному середовищі, ростуть прямо пропорційно їх щільності ($\rho < 3$ мг/см^3), а при значеннях $\rho \geq 3$ мг/см^3 спостерігається різке зменшення швидкості утворення молекулярного водню.