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PRODUCTION OF MOLECULAR HYDROGEN IN NANO-SiO_2/H_2O SYSTEM WITH PARTICLE SIZE d = 20÷60 nm UNDER THE INFLUENCE OF GAMMA-QUANTA

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Abstract: The amount, rate of formation, and radiation-chemical yields of molecular hydrogen obtained from the process of radiolysis under the influence of gamma quanta (^{60}Co, P=9,276 rad/s, T=300K) in the nano-SiO_2/H_2O system with a mass of particle of m=0.2 g and size of a particle of d=20÷60 nm by changing of water mass (m=0.01÷0,8 g) were studied. It was found that the rate of formation and radiation-chemical yield of molecular hydrogen determined by increasing the mass of water: -1) decrease by 10 times for water, 2) increase by 8 times for nano-silicon dioxide, 3) for the common system, increase at the values of water mass of 0,01 g$\leq m_{H_2O}<$0,2 g, has the maximum at m_{H_2O}=0,2g and decrease at 0,2 g$< m_{H_2O}\leq$0,8 g.

Keywords: nanoparticles, radiolysis, radiation-chemical yield, Compton scattering

Recently, due to the rapid development of industry, the for the energy demand has increased sharply, and the use of nuclear energy [1] is increasing day by day, as traditional methods are both economically and environmentally unfavorable. Transforming nuclear energy into a more affordable form of energy remains one of today's needs. Unique physical, physicochemical and chemical properties of nano-sized materials have been discovered. Therefore, these materials are widely used in all fields of science and technology. One of these applications is the method of obtaining molecular hydrogen from the conversion of water used for the transition from nuclear energy to hydrogen energy with the help of nanoscale catalysts [2–15]. These methods are preferred in three forms of heterogeneous radiolysis of water. In the first case, water molecules are adsorbed on the nano-particle surface in the form of several monolayers, and the process mainly occurs at surface levels [3,10,11], in the second case in the system of nano-sized catalysts [2,5–9] suspended in liquid water at room temperature the process is going on both at the catalyst-water boundary and with electrons emitted from the catalyst surface and released into the water and, in the third case, radiation-thermocatatic processes in these systems [13-15] under the influence of temperature occur as a sum of two independent thermocatalytic and radiation-catalytic processes.

In the presented work, the amount, rate of formation, and radiation-chemical yields of molecular hydrogen obtained from the process of radiolysis under the influence of gamma quanta (^{60}Co, P=9,276 rad/s, T=300K) in the nano-SiO_2/H_2O system with a mass of particle of m=0.2 g and size of a particle of d=20÷60 nm by changing of water mass (m=0.01÷0,8 g) were studied.

1. Experimental part

After heat treatment in the open air at a temperature of T = 773K (t = 72 hours), the required mass of the SiO_2 (m = 0.2 g) is determined and then transferred to a heat-treated and cleaned ampoule (V=5 ml) under special conditions (T=773K). After 4 hours of thermal treatment (T=673K) of the nano-SiO_2 at vacuum conditions (P=10^{-3} mm. Hg) in the ampoule it was cooled, then the required amount of air-purified bidistilled water [16] was added and the ampoule was sealed. The ampoule was irradiated by ^{60}Co source with a dose rate of P = 9,276 rad/s at room temperature. The absorbed dose rate was determined using ferrosulfate and methane methods and in a specific research object, it was calculated using electron density comparison methods [16, 17].

It was revealed that in the nano-SiO_2/H_2O system, the final molecular products obtained from the radiation-heterogeneous transformation of water are H_2, O_2, and H_2O_2. Since some part of O_2 is captured on the surface and H_2O_2 remains in solution, there are great difficulties in determining their quantities. Therefore, more accurate information on the kinetic regularity of products obtained from the processes of radiation-heterogeneous transformation of water was based on the amount of molecular hydrogen. The amount of molecular hydrogen obtained from the radiation-heterogeneous conversion of water in the nano-SiO_2/H_2O system was analyzed on the "Agilent-7890" chromatograph. In parallel, a modernized "Chvet-102" chromatograph (accuracy 8-10%) was used to confirm the results. A column with a length of 1 m and an inner diameter of 3 mm was used in the chromatograph "Chvet-102". Activated carbon with a particle size of d=0.25÷0.6 mm inside the column and argon gas with a purity of 99.99% on both chromatographs as the gas carrier was used.

2. Results and discussions

In Figure 1, graphs of the dependence of the amount of molecular hydrogen obtained from the radiation-catalytic transformation of water in the nano-SiO_2/H_2O system (particle size of n-SiO_2 of d=20÷60 nm and mass of $m(SiO_2)$ = 0.2 g) on the duration (dose) of radiation of γ-quanta (^{60}Co, P=9,276 rad/s, T = 300K) by changing the mass of water (m = 0.01 (1), 0.02 (2), 0.04 (3), 0.08 (4), 0.2 (5), 0.4 (6), 0.8 (7) g)) are given.

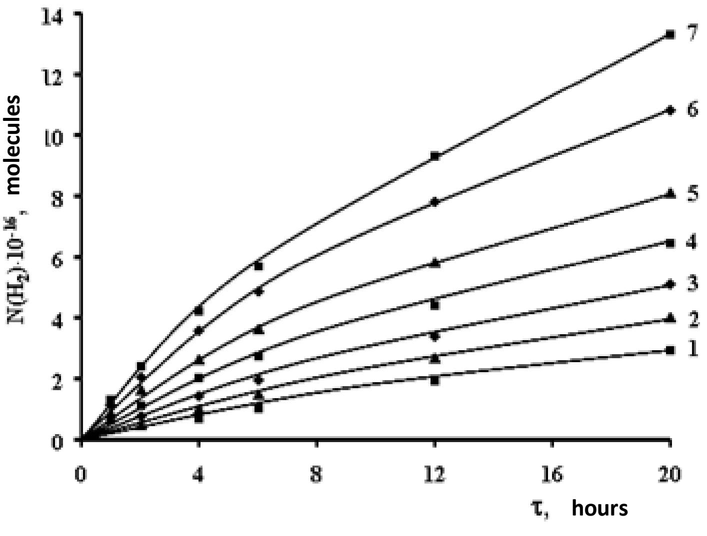

Fig.1. The dependence of the amount of molecular hydrogen obtained from the radiation-catalytic transformation of water in the nano-SiO_2/H_2O system on a duration (dose) of radiation under an influence of gamma-quanta (^{60}Co, P=9,276 rad/s, T=300K)

The rates of formation of molecular hydrogen from the linear parts of the kinetic curves (Fig. 1 (curve 1-7)) obtained from the studied systems (nano-SiO_2/H_2O) were determined for water, nano-silicon dioxide, and the general system. Formation rate are determined for:
clean water as

$$w_0(H_2) = \frac{N_0(H_2)}{m_{H_2O}t} \quad (1)$$

water added to nano-SiO_2 as:

$$w_{H_2O}(H_2) = \frac{N(H_2)}{m_{H_2O}t} \quad (2)$$

the total nano-SiO_2/H_2O system as:

$$w_{tot}(H_2) = \frac{N(H_2)}{m_{tot}t} = \frac{N(H_2)}{(m_{H_2O} + m_{SiO_2})t} = \frac{m_{H_2O}}{m_{H_2O} + m_{SiO_2}} \frac{N(H_2)}{m_{H_2O}t} = \frac{m_{H_2O}}{m_{H_2O} + m_{SiO_2}} w_{H_2O}(H_2) \quad (3)$$

and, finally, for the nano-SiO_2 as:

$$w_{SiO_2}(H_2) = \frac{\Delta N(H_2)}{m_{SiO_2}t} = \frac{N(H_2) - N_0(H_2)}{m_{SiO_2}t} \quad (4)$$

If we multiply the nominator and denominator of (4) by m_{H_2O}, make simple transformations, and take into account the expressions (1) and (2), we get the expression (5):

$$w_{SiO_2}(H_2) = \frac{m_{H_2O}}{m_{H_2O}} \frac{N(H_2) - N_0(H_2)}{m_{SiO_2}t} = \frac{m_{H_2O}}{m_{SiO_2}} \frac{N(H_2) - N_0(H_2)}{m_{H_2O}t} =$$
$$= \frac{m_{H_2O}}{m_{SiO_2}} \left(\frac{N(H_2)}{m_{H_2O}t} - \frac{N_0(H_2)}{m_{H_2O}t} \right) = \frac{m_{H_2O}}{m_{SiO_2}} \left[w_{H_2O}(H_2) - w_0(H_2) \right] \quad (5)$$

Here, $N_0(H_2)$ is the amount of molecular hydrogen obtained from the radiolysis of pure water and $N(H_2)$ is the amount of molecular hydrogen obtained from the radiolysis of water in the nano-SiO_2/ H_2O system, m_{H_2O}, m_{SiO_2} and $m_{üm} = m_{SiO_2} + m_{H_2O}$ - are masses of water, nano-SiO_2, and the total system respectively. The table shows the values obtained for the rate of formation of molecular hydrogen from the radiation-catalytic transformation of water in systems created by the addition of water with a mass of m = 0.01, 0.02, 0.04, 0.08, 0.2, 0.4, and 0.8 g on nano-SiO_2 under the influence of γ-quanta. Table 1 shows the values obtained for the rate of formation of molecular hydrogen from the radiation-catalytic transformation of water in systems created by the addition of water with a mass of m = 0.01, 0.02, 0.04, 0.08, 0.2, 0.4 and 0.8 g on nano-SiO_2 under the influence of γ-quanta:

Table 1

Rates of formation of molecular hydrogen obtained from the radiation-catalytic transformation of water in systems created by the addition of water of the mass m = 0.01, 0.02, 0.04, 0.08, 0.2, 0.4 and 0.8 g to nano-SiO_2 (m=0.2 g, d=20÷60nm) under the influence of γ-quanta (^{60}Co, P = 9,276 rad/s, T = 300K)

$w(H_2)$ 10^{-13}, molekules/g·s	m_{H_2O}, g						
	0,01	0,02	0,04	0,08	0,2	0,4	0,8
$w_{SiO_2}(H_2)$	0,23	0,35	0,53	0,83	1,22	1,55	1,80
$w_{H_2O}(H_2)$	4,55	3,5	2,65	2,1	1,33	0,775	0,45
$w_{tot}(H_2)$	0,22	0,32	0,44	0,59	0,665	0,52	0,36

Figure 2 shows the dependence of the radiation-chemical yield of molecular hydrogen on the mass of water calculated basis on of these rates ($w_{tot}(H_2)$, $w_{H_2O}(H_2)$, and $w_{SiO_2}(H_2)$) for the general system (curve 1), water (curve 2) and nano-SiO_2 (curve 3).

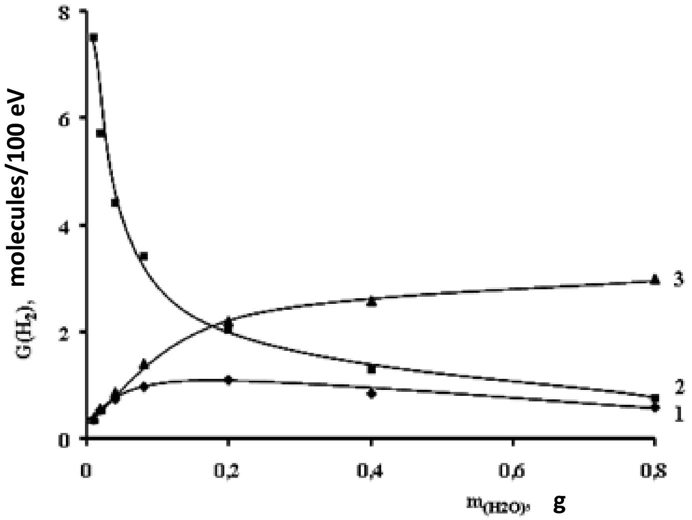

Fig.2. The dependence of the radiation-chemical yield of molecular hydrogen on the mass of water in the nano-SiO_2/H_2O system under an influence of gamma-quanta (^{60}Co, P=9,276 rad/s, T=300K).

The results obtained can be explained based on of known mechanisms of radiation chemistry. Thus, when γ-quanta with energy Eγ =1.25 MeV (^{60}Co) pass through SiO_2 and H_2O, Compton scattering occurs mainly in comparison with other processes (various scattering, photoeffect, electron-positron pair formation, photonuclear reaction, etc.). Depending on the angle of scattering in Compton scattering, the energies of Compton electrons vary in the range of 0 ÷ 1.02 MeV. Compton electrons, which have large kinetic energies, gradually lose their kinetic energies in both elastic and inelastic collisions in both phases and become thermal electrons. In an inelastic collision in the physical phase of the process, the next intermediate particles are created: 1) electron-hole pair $(SiO_2^+(h^+))$ and electron-excitation $\left(SiO_2^*\right)$ and electron (e^-) from direct single ionization of silicon dioxide molecules within nano-SiO_2:

$$SiO_2 \xrightarrow{\gamma} SiO_2^+(h^+), SiO_2^*, e^- \tag{6}$$

as well as electron-ion pair $\left(H_2O^+\right)$, electron excitation $\left(H_2O^*\right)$ and electron (e^-) from direct single ionization of water molecules in water:

$$H_2O \xrightarrow{\gamma} H_2O^+, H_2O^*, e^- \tag{7}$$

These particles ($h^+, H_2O^+, e^-, SiO_2^*, H_2O^*$) play an important role in the processes of obtaining molecular hydrogen in the radiation-heterogeneous conversion of water in the SiO_2/H_2O system.

The holes formed inside the nanoparticles under the influence of ionizing radiation can migrate, some of them inside the particle, and some of them to the surface of the particle and can be localized on the surface. Holes localized in the nanoparticle-water boundary form $H_2O_s^+$ ions in contact with adsorbed water molecules. By recombining this ion with thermal electrons or tunnel electrons, an electron-excited water molecule is formed. An exciting water molecule with a short lifespan dissociates to form intermediate H and OH products (8):

$$H_2O_s^* \rightarrow H + OH \quad (8)$$

On the other hand, some of the electrons formed inside the nanoparticles are emitted inside the particle, some on the particle surface, and some over the particle surface into the water. Electrons emitted from a solid into a liquid phase can gradually lose their kinetic energy in an elastic and inelastic collision in water first transform into thermal electrons and then convert to solvated electrons in water. The process of obtaining molecular hydrogen (9-11) during radiolytic reactions between solvated electrons and water molecules and protonated water molecules can be described as follows:

$$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^- \quad (9)$$

$$e_{aq}^- + H + H_2O \rightarrow H_2 + OH^- \quad (10)$$

$$e_{aq}^- + H_3O^+ \rightarrow H + H_2O \quad (11)$$

The results of the study show that the rate of formation of molecular hydrogen and radiation-chemical yield, determined by increasing the mass of water:

- decrease by 10 times if determined for water,
- increase by 8 times if determined for nano-silicon dioxide
- increase at the values of water mass of 0,01 g$\leq m_{H_2O} <$0,2 g, has the maximum at m_{H_2O} =0,2 g and decrease at 0,2 g$< m_{H_2O} \leq$0,8 g for the common system.

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ПОЛУЧЕНИЕ МОЛЕКУЛЯРНОГО ВОДОРОДА В СИСТЕМЕ нано-SiO2/H2O С РАЗМЕРОМ ЧАСТИЦ d = 20 - 60 нм ПОД ВЛИЯНИЕМ ГАММА-КВАНТОВ

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Резюме: Исследованы количество, скорость образования и радиационно -химические выходы молекулярного водорода, полученного в процессе радиолиза системы нано-SiO_2/H_2O с массой частицы $mSiO_2$= 0,2 г и размером частицы $dSiO_2$= 20 ч 60 нм под действием y-квантов (^{60}Co, P = 9,276 рад/с, T=300K) при изменении массы воды ($т_{H_2O}$ = 0,01^0,8 г). Установлено, что скорость образования и радиационно-химический выход молекулярного водорода, определяемые увеличением массы воды: 1) уменьшаются в 10 раз для воды, 2) увеличиваются в 8 раз для нанодиоксида кремния, 3) для общей системы, увеличиваются при значениях массы воды 0,01 г m_{H_2O} <0,2 г, имеют максимум при = 0,2 г и уменьшаются при 0,2 г < $т_{H_2O}$ <0,8 г.

Ключевые слова: наночастицы, радиолиз, радиационно-химический выход, комптоновское рассеяние.

QAMMA-KVANTLARIN TƏSİRİLƏ d=20÷60 nm HİSSƏCİK ÖLÇÜLÜ nano-SiO_2/H_2O SİSTEMİNDƏ MOLEKULYAR HİDROGENİN ALINMASI

Y.D. Cəfərov, S.M. Bəşirova, K.T. Eyyubov, S.M. Əliyev

Xülasə: γ-kvantların (^{60}Co, P=9,276 rad/san, T=300K) təsirilə, m=0,2 q kütləli, d=20÷60 nm hissəcik ölçülü nano-SiO_2/H_2O yaradılan sistemlərdə, suyun kütləsini (m=0.01÷0,8 q) dəyişməklə gedən radioliz prosesindən alınan molekulyar hidrogenin miqdarı, əmələgəlmə sürəti və radiasiya-kimyəvi çıxımları tədqiq edilmişdir. Müəyyən edilmişdir ki, suyun kütləsinin artırılması ilə təyin edilən mokekulyar hidrogenin ələgəlmə sürəti və radiasiya-kimyəvi çıxımı: 1) suya görə təyin edilərsə, 10 dəfə azalma, 2) nano-silisium dioksidə görə təyin edilərsə, 8 dəfə artıma, 3) ümumi sistemə görə təyin edilərsə, suyun kütləsinin 0,01 q≤ m_{H_2O} <0,2 q qiymətlərində artma, m_{H_2O} =0,2 q qiymətində maksimum, 0,2 q< m_{H_2O} ≤0,8 q qiymətlərində isə azalma müşahidə olunur.

Açar sözlər: nanohissəcik,radioliz, radiasiya-kimyəvi çıxım, kompton səpilməsi