



Obtained Molecular Hydrogen by Radiolysis of Water in Nano-SiO₂(d=20÷60 nm)/H₂O System Under the Influence of Gamma Rays

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Abstract: The amount molecular hydrogen obtained from radiolysis process, its formation rate and radiation-chemical yield are determined in the nano-SiO₂/H₂O system with a mass of m=0.2 g and d=20-60 nm particle size under the influence of gamma irradiation. In systems created by the adsorption of water on the surface of nano-SiO₂ under the influence of gamma rays, the radiation-chemical yield of molecular hydrogen obtained from the decomposition of water was less than 0.36 molecules/(100 eV). This means that the surface density of the energy transfer centers on the surface of nano-SiO₂ is very small. As the mass of water increases, the radiation of the nano-SiO₂ emitted from the surface of the nanoparticles in the liquid space between the particles increases, and the radiation of the resulting molecular hydrogen also increases. However, the radiation-chemical yield of molecular hydrogen obtained from the decomposition of water was less than 0.36 molecules/(100 eV) in systems created by the adsorption of water on the surface of nano-SiO₂ irradiated by gamma rays. This means that the surface density of the energy transfer centers on the surface of nano-SiO₂ is very small. When the intergranular space is filled with water, the electrons emitted from the surface of the solid to the liquid phase and the radiation-chemical yield of salvaged electrons in liquid phase increases.

Keywords: Nanoparticle, Radiolysis, Radiation-chemical Yield, Electron Emission

1. Introduction

Recently, an interest of nuclear energy [1] has been increasing day by day due to the rapid increase in energy demand due to the rapid development of industry and the ineffectiveness of traditional methods, both economically and environmentally. Converting nuclear energy into a more affordable form of energy remains one of actual problem in the science and industry. It's known that porous materials in nano dimensions have excellent physical, physico-chemical and chemical properties with high specific surface area (more than 50m²-g). Therefore, these types of materials are widely used in different fields of science and technology. One of these areas of application is the method of obtaining molecular hydrogen from the decomposition of water used for the transition from nuclear energy to hydrogen energy using nanoscale and high surface area catalysts [2-6, 16, 17]. Three of these methods are preferred. The first method is radiolysis process with adsorption of water on the surface of

nanoparticles which mainly occurs on the surface level [4, 11, 12] in the second method, the process is carried out both at the catalyst water boundary and with the solvated electrons emitted from the catalyst surface into the water in the system of nanoscale catalysts [2, 6-10, 17] suspended in water at room temperature; in the third method, the radiation-thermocatalytic processes of nanoparticles in contact with water vapor under the influence of temperature [14-16] occur as the sum of two independent thermocatalytic and radiation-catalytic processes.

On the other hand, since silicon and its various compounds are used as construction materials inside the reactor [18], these materials are exposed to temperature and ionizing radiation (neutrons, protons, gamma rays, electrons) in contact with water and water vapor used as decelerators, retarders and energy carriers, α -particles, high-energy ions, etc.). Therefore, it is important to predict any changes in the operating mode inside the reactor, both for the safety of the reactor and for the transition to hydrogen energy in

next-generation reactors.

Radiation-chemical yields of molecular products (H₂, O₂, H₂O₂, etc.) from radiation-heterogeneous decomposition of water by metals or metal oxides used in each of these research methods varies depending on their type, band-gap, particle size, saturation degree of adsorbed water on the particle surface, the temperature of the general system, the strength of the absorption dose, and the mass of metal or metal oxides suspended in the water.

In the presented work, the amount of molecular hydrogen obtained from radiolysis processes by changing the mass of water (m=0.01±0,8 g), its formation rate and radiation-chemical emissions were studied in the nano-SiO₂/H₂O systems with m=0,2 g weight and d=20÷60 nm particle size under the influence of gamma rays (⁶⁰Co, P=0,093 Gy/s, T=300K).

2. Method

High purity (99.9%) nano-SiO₂ particles (produced by “Skyspring Nanomaterials Inc.”, USA) with 20-60 nm particle size were used to study of the amount of molecular hydrogen obtained from the radiolysis processes of water in nanoparticles under the influence of gamma rays, the rate of formation and the factors affecting the radiation-chemical yields. Nano-SiO₂ was annealed at T=773K in air condition, then cooled. Required mass of the samples were determined and filled into high-purity ampoule. The sample was annealed (673 K) in the ampoule at vacuum (P=10-3torr) for 4 hours, then cooled and required amount of distilled water was filled at special condition [19].

The ampoule was irradiated by ⁶⁰Co source with a dose rate of P=0,093 Gy/s. The power density of the absorption dose was determined using ferrosulfate and methane methods. The absorption dose at the studied object was calculated using methods for comparing electron densities [19, 20].

It was analyzed that the final molecular products of radiation-heterogeneous decomposition of nano-SiO₂/H₂O system are H₂, O₂ and H₂O₂. Since some of these products contain O₂ on the surface of the catalyst and H₂O₂ in solution, it is very difficult to determine their amount. Therefore, more accurate information on the kinetic regularity of products obtained from the radiation-heterogeneous decomposition processes of water was based on the amount of molecular hydrogen.

The amount of the obtained molecular hydrogen was analyzed on the “Agilent-7890” chromatograph. Simultaneously, a modernized chromatograph “ЦВЕТ-102” (accuracy, 8-10%) was used to confirm the results. “ЦВЕТ-102” chromatograph used a column with 1 m length and 3 mm inner diameter. The column used activated carbon with a particle size of d=0.25÷0.6 mm and argon

gas with a purity of 99.99% on both chromatographs as a gas carrier.

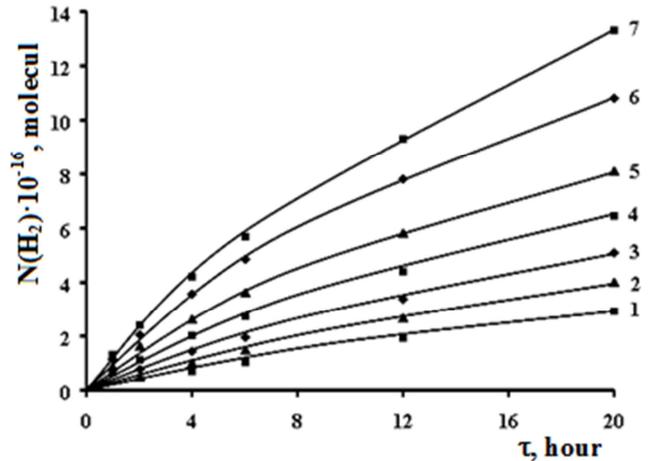


Figure 1. Irradiation time (dose) dependencies of the amount of molecular hydrogen obtained from radiation-heterogeneous decomposition of water (with varying mass, m=0.01(1), 0,02(2), 0,04(3), 0,08(4), 0,2(5), 0,4(6), 0,8g(7)) in the nano-SiO₂ system (with mass m=0.2 g and particle size d=20-60 nm) irradiated with gamma rays (⁶⁰Co, P=0,093 Gy/s, T=300K).

3. Result

In figure 1, the irradiation time (dose) dependencies of the amount of molecular hydrogen obtained from radiation-heterogeneous decomposition of water (with varying mass, m=0.01(1), 0,02(2), 0,04(3), 0,08(4), 0,2(5), 0,4(6), 0,8g(7)) in the nano-SiO₂ system (with mass m=0.2 g and particle size d=20-60 nm) irradiated with gamma rays (⁶⁰Co, P=0,093 Gy/s, T=300K).

The formation rate of molecular hydrogen were determined by water, nano-silicon dioxide, and overall system from linear parts of kinetic curves (figure 1, curve 1-7) of studied (nano-SiO₂/H₂O) systems. Formation rate of molecular hydrogen obtained by radiolysis of pure water was determined based on the expression (1):

$$w_0(H_2) = 0,01G_0(H_2)P = \frac{N_0(H_2)}{m_{H_2O}t} \quad (1)$$

Figure 1 shows the formation rate of molecular hydrogen from the kinetic part of the curves according to the water in the nano-SiO₂/H₂O system.

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

According to overall SiO₂/H₂O system:

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

According to nano-SiO₂, considering the $\Delta N(H_2) = N(H_2) - N_0(H_2)$ increase in molecular

hydrogen with the addition of nano-SiO₂ was determined using following expression:

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

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

where, G₀(H₂)=0,45 molecule/100 eV – radiation-chemical yield of molecular hydrogen obtained from radiolysis of pure water, N₀(H₂) and N(H₂) - the amount of molecular hydrogen obtained from radiolysis of pure water and nano-SiO₂/H₂O system, respectively. m_{H₂O}, m_{SiO₂} and m_{tot} = m_{SiO₂} + m_{H₂O} - mass of the water, nano-SiO₂ and total system, respectively. The formation rate of molecular hydrogen obtained from the radiation-catalytic decomposition of water in these systems is given for water (2), general system (3) and nano-SiO₂ (5) in the table 1.

Table 1. Formation rates of molecular hydrogen obtained from radiation-catalytic decomposition of water (with varying mass, m=0.01, 0.02, 0.04, 0.08, 0.2, 0.4, 0.8 g) in the nano-SiO₂ system (with mass m=0.2 g and particle size d=20-60 nm) irradiated with gamma rays (⁶⁰Co, P=0,093 Gy/s, T=300K).

w(H ₂)10 ⁻¹³ , molecule/g·se	mH ₂ O, g						
	0,01	0,02	0,04	0,08	0,2	0,4	0,8
w _{SiO₂} (H ₂)	0,23	0,35	0,53	0,83	1,22	1,55	1,80
w _{H₂O} (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 determined on the basis of these rates (w_{tot}(H₂), w_{H₂O}(H₂), w_{SiO₂}(H₂)) for the general system (curve 1), water (curve 2) and nano-SiO₂ (curve 3).

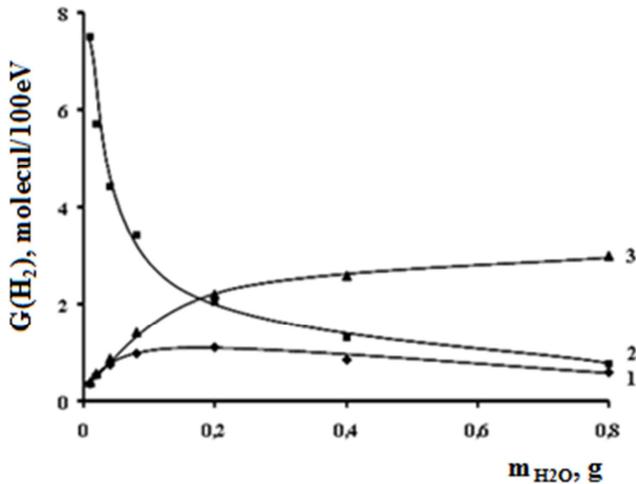


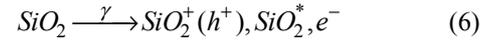
Figure 2. The dependence of the radiation-chemical yield of molecular hydrogen obtained by radiation-catalytic decomposition of water on the mass of water in the γ -irradiated (⁶⁰Co, P=0,093 Gy/s, T=300K) nano-SiO₂/H₂O system.

Obtained results can be explained based on the known mechanisms of radiation chemistry. Thus, mainly Compton

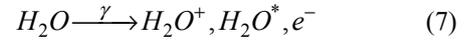
If we multiply the numerator and denominator of expression (4) by m_{H₂O}, with a simple transformations considering the expressions (1) and (2):

scattering occurs in comparison with other processes (photoeffect, electron-positron pair formation, photonuclear reaction, etc.) in the SiO₂, H₂O, SiO₂/H₂O systems under the influence of E_γ=1,25 MeV (⁶⁰Co) energy of gamma rays. The energy of Compton electrons are varies in the range of 0-1.02 eV depending on the scattering angle. Depending on their kinetic energy, the Compton electrons passes from the nanoparticle several times into the liquid phase or vice versa, gradually losing their kinetic energies in both elastic and inelastic collisions and becoming thermal electrons in nano-SiO₂/H₂O systems. In an inelastic collision in the physical phase (10⁻¹⁵-10⁻¹² s) of the process:

- 1) electron (e⁻) -hole (SiO₂⁺(h⁺)) pair and electron-excitation (SiO₂^{*}) from direct single ionization of molecules within nano-SiO₂:



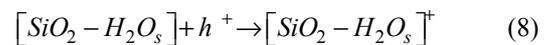
- 2) electron-ion (H₂O⁺) pair and electron-excitation (H₂O^{*}) from direct single ionization of molecules in water:



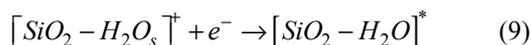
active intermediate, unbalanced energy carriers (6, 7) are formed.

If the energy required to form an electron-hole pair inside SiO₂ under the influence of ionizing radiation (gamma rays, electrons) is 19,1 eV [21], then the radiation-chemical yield of the electron-hole pair is G(h⁺ -e⁻)=5,2 pairs/(100 eV), the radiation-chemical yield of the electron-excitation (exciton) states is equal to G(exc)=2,5 exc/(100 eV). These active intermediates (h⁺, H₂O⁺, e⁻, SiO₂^{*}, H₂O^{*}) play an important role in the process of obtaining molecular hydrogen from the radiation-heterogeneous decomposition of water in the SiO₂/H₂O system.

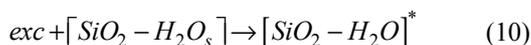
The holes formed inside the nanoparticle by ionizing radiation can be trapped by drift [22], part of which can be trapped by structural defects inside the particle, and another part can be transported to the particle surface and trapped by an adsorbed complex of water [SiO₂ - H₂O_s] on the surface and formed ion-complex as follow:



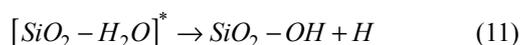
This ion-complex cause to electron-excitation of complex by recombination with heat or tunneling electrons:



On the other hand, the excitons formed by ionizing radiation can be absorbed inside the nanoparticle and transmit their energy to a water complex adsorbed on the surface at a distance. In this case, the electronic-excitation of the complex is observed:

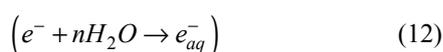


The energy of the short-lifetime electron-excitation complex ($SiO_2 - H_2O_s$)^{*} [23] is transferred to the adsorbed water molecule and causes its decomposition, resulting in the formation of intermediate products H, OH:

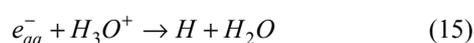
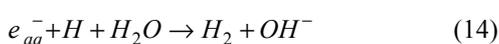
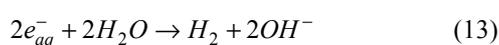


In order to obtain H and OH intermediate products from the decomposition of water molecule, it is necessary to break the bond between them ($E_{rab}=5.1$ eV). Therefore, the connection between the transmitted exciton energy (E_{exc}) and the communication energy must satisfy the $E_{exc} \geq E_{rab}$ condition.

On the other hand, the Compton electrons formed inside the nanoparticle under the influence of irradiation and each new generation of δ -electrons they create gradually lose their kinetic energies in elastic and inelastic collisions inside the particle, some are captured by structural defects inside the particle and some are transported to the particle surface. The electrons transported to the surface are localized on the surface which are kinetic energies smaller than surface potential, some some parts are reflected and returned to the particle, while large ones are emitted into the water beyond the particle surface. The electrons emitted from surface of the solid to liquid phase gradually lose their kinetic energy by elastic and inelastic collisions in water and firstly converted into heat electrons, and then can salvaged in the water [24]:



It has been proved both experimentally [25] and theoretically [26-30] in systems produce by suspension of nano-SiO₂ in water that the radiation-chemical yield of salvaged electrons (12) in the liquid phase is higher than in pure water, and this value varies depending on the size of the nanoparticles. The production of molecular hydrogen (13-16) by the radiolytic decomposition between salvaged electrons (e_{aq}^-) and water molecules, as well as protonated water molecules (H_3O^+) in the intergranular liquid phase can be described as follows:



Here it becomes clear that, one pair of electron-hole pairs or two excitons are used to obtain one molecule of hydrogen. Reactions (8-11,16) play a major role in the production of molecular hydrogen from the radiation-heterogeneous decomposition of water adsorbed on the surface of nano-SiO₂ under the influence of gamma rays. However, the radiation-chemical yield of molecular hydrogen obtained from the decomposition of water was less than 0.36 molecules/(100 eV) in systems created by the adsorption of water on the surface of nano-SiO₂ irradiated by gamma rays. This means that the surface density of the energy transfer centers on the surface of nano-SiO₂ is very small. When the intergranular space is filled with water, the electrons emitted from the surface of the solid to the liquid phase and the radiation-chemical yield of salvaged electrons in liquid phase increases. As a result, the radiation-chemical yield of molecular hydrogen obtained by reactions (13-16) also increases.

4. Conclusion

It can be concluded that radiation-chemical yield of molecular hydrogen obtained by radiolysis processes with varying mass of the water in the range of $m_{H_2O}=0.01-0,8$ g in nano-SiO₂/H₂O systems (mass - $m=0.2$ g, particle size - $d=20-60$ nm) irradiated with gamma rays (⁶⁰Co, P=0,093 Gy/s, T=300K) as follow:

1. if determined for water, a decrease in $G(H_2)=7.5-0.74$ molecules/100eV,
2. if determined for nano-silicon dioxide, the increase in $G(H_2)=0,38-2,98$ molecules/100eV,
3. if determined for overall system, a decrease in $G(H_2)=0,36-0,98$ molecules/100eV in the range of mass of the water $0.01 \leq m_{H_2O} \leq 0.2$ g, the maximum in $G(H_2)=1.1$ molecules/100eV when $m_{H_2O}=0.2$ g, and partial decrease are observed in $G(H_2)=0.85-0.6$ molecules/100eV in the range of $0,2 \text{ g} < m_{H_2O} \leq 0,8$ g.

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