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STUDY OF MASS EFFECTS OF SILICON ON PROCESS OF THE WATER RADIOLYSIS IN THE NANO Si+H_2O SYSTEM UNDER THE INFLUENCE OF GAMMA – QUANTA

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The radiation-chemical yield of the molecular hydrogen received under the influence of gamma quanta (^{60}Co, P=22Rad/s, T=300K) to liquid water of constant volume (V=5 ml) in the process of a radiolysis of water at change of weight (m=0.01; 0.02; 0.06 and 0.12 g) and sizes of silicon particle (d=50, 100, 300÷500 nm) is defined. It has been revealed that at increase in mass of the silicon added to water the radiation-chemical yield of the molecular hydrogen received in the process of a water radiolysis grows in direct ratio (m<0.02 g) and depending on the size of particle after a certain mass value (m>0.02 g) the stationary area is observed. In the Si+H_2O system the maximum radiation-chemical yield of molecular hydrogen is equal to $G(H_2)$ =10.9; obtained 8.07 and 5.24 molecules/(100 eV), which is appreciably larger than that of pure water (G_0(H2) = 0.45 molecules/(100 eV) at the sizes of silicon particle d=50, 100, 300÷500 nm respectively. The mechanism explaining the received results is offered.

Keywords: *micro particle, radiolysis, radiation-chemical yield, Compton dispersion*

INTRODUCTION

Nanomaterials are widely applied in various fields of science and technology due to their unique physical and chemical properies. One of them is the research of final products and intermediates obtained by the radiolysis of liquids, especially water, with metal and metal oxides under the influence of ionizing rays (γ-quanta, electrons, protons, neutrons, α-partcles and high energetic ions, etc.). The dependence of the radiation-chemical yield of intermediate and final products obtained during research works on the particle size of metal or metal oxides (size effect), their type, the degree of water filling on the particle surface, their mass in the created suspension systems (mass effect), the temperature of the process and the type of ionizing beam has been studied. Monte-Karlo method calculated, on the basis of a model, the radiation-chemical yields of electron-hole (ion) pair formed in physical and physico-chemical stages of the process proceeding under the effect of ionizing waters on amorfous nano-SiO_2 system suspension in water. The holes formed in nano-SiO_2 as a result of migration can be partly localized in the volume by structural defects, and partly migrate up to surface. The electrons formed in nano-SiO_2 structure gradually lose their kinetic energy through elastic and non-elastic collision. As it mentioned above, a part of electrons can be localized by structural defects and another migrate to the surface. After the electrones migrated to the surface and emitted into water, first the thermal yield and then the radiation-chemical yield of the solvated electrons were calculated. The results showed that the radiation-chemical yield of the electrons emitted to water from nano-SiO_2 surface and solvated there varied depending on both the size of nano particles and the degree of porosity [8]. These results coincide with the results derived from experiments [1-6, 9-11].

In both cases a radiation-chemical yields of products of water transformation (hydrogen, oxygen, hydrogen peroxide, etc.) depend on: type of a solid body, width of the forbidden zone of a solid body; sizes of particles of a solid body; extents of filling of a surface of solid body particles by the adsorbed water; temperatures of the general system; the mass of a solid body; suspended in water.

In the presented work have been calculated the accumulation rate and radiation – a chemical yield of the molecular hydrogen received in the process of the radiation and heterogeneous transformation of water proceeding under the influence of γ-quanta (^{60}Co, P=22Rad/s, T=300K) to clear water (V=5 ml) and added to the same volume the silicon with various sizes of the particles which is evenly distributed by means of the vibrator.

MATERİAL AND METHODS

It has been taken silicon produced by the company "Skysping Nanomaterials. İnc", USA as an object of a research, with sizes of particle d=50 nanometer and purity of 99.9%. Originally silicon has been processed at T=473K, t=72 hours in the air environment, and after determination of the necessary weight is purified in special conditions and added to the ampoule (V=19 ml) which is thermally processed (T=773K). After heat treatment (T=673K) of silicon in an ampoule in vacuum conditions (P=10^{-3} mm Hg) within 4 hours, it has been cooled, and the necessary amount of the double distilled water purified from air in special conditions [7] has been adsorbed on his surface. Then ampoules have been soldered and irradiated in special conditions (by continuous hashing of system by the vibrator with the purpose to achieve suspension of silicon particles in water) on a source ^{60}Co at the power of dose P=22 Rad/s.

Power of the absorbed dose has been determined by ferrosulfate and methane ways. In the concrete studied object the power of the absorbed dose has been calculated with use of a method of comparison of electronic density [8, 10].

The products received by radiation and heterogeneous processes, such as H_2, O_2 and H_2O_2 have been determined by a chromatography method. Some part of O_2 keeps on a surface and H_2O_2 remains in solution and therefore errors are big when determining quantity of these products. Therefore, more exact information on kinetic regularity of process of radiation and heterogeneous transformation of water has been obtained on the basis of amount of molecular hydrogen.

Products of reactions are analyzed on the “Agilent-7890” chromatograph. For confirmation of results the upgraded “Colour-102” chromatograph (accuracy of 8-10%) has been in parallel used. In the “Colour-102” chromatograph the column of 1 m long with an internal diameter of 3 mm has been used. In a column an absorbent carbon with the diameter of particles d=0.25÷0.6mm has been used and the argon of high purity (99.9%) as the gas-carrier in each of two chromatographs has been used.

RESULTS AND DISCUSSION

In the figure 1 the dependence on time of the molecular hydrogen amount formed as a result of radiolytic transformations in system of pure water with the added silicon (Si+H_2O) suspensions (the size of silicon particles d=50 nanometer, weight (m=0.01 (curve 1); 0.02 (curve 2); 0.06 (curve 3) and 0.12 (curve 4)), V_{water}=5ml) under the influence of γ-quanta (^{60}Co, P=22Rad/s, T=300K) is given. In fig. 1 dependence under the same conditions are shown:

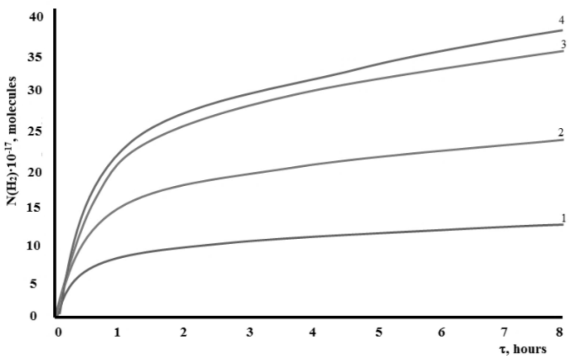

Fig. 1. The dependence on time of the molecular hydrogen amount, formed as a result of radiolytic (P=22Rad/s, T=300K) transformations in system of pure water (V=5 ml) with the added silicon (d=50 nanometer) of various weight (m=0.01g (curve1); 0.02g (curve2); 0.06g (curve3); 0.12g (curve4))

From linear parts of the kinetic curves (fig. 1), received on the basis of the studied systems, an accumulation rates - $w(H_2)$ and a radiation-chemical yield of molecular hydrogen $G(H_2)$ on every 100ev of the energy absorbed by the common system, have been determined and these data are shown in Table 1.

Table 1.

Dependence on the mass of silicon (m(Si)) of an accumulation rate ($w(H_2)$) and radiation-chemical yield ($G(H_2)$) of the molecular hydrogen received as a result of radiation and catalytic transformations (P=22Rad/s, T=300K) in the $Si+H_2O$ system (V_{water}=5 ml, the size of silicon particles d=50 nanometer)

d = 50 nanometer		
m(Si), g	**$w(H_2)\cdot 10^{-13}$, molecules/ (g·s)**	**$G(H_2)$, molecules/100eV**
0	0.61	0.436
0.01	5	3.64
0.02	9.67	7.03
0.06	13.4	9.05
0.12	15	10.9

As shown from the figure, a radiation-chemical yield of the molecular hydrogen received in the process of a water radiolysis grows in direct ratio to the mass of the silicon added to water (at $m_{Si}<0.02$ g), and after a certain mass value ($m_{Si}>0.02$ g) the stationary area depending on the sizes of particles is observed. In the Si+ H_2O system at the sizes of silicon particles d=50 the maximum radiation-chemical yield of molecular hydrogen was equal to 10.9 molecules/100eV respectively.

From the kinetic part of the curves obtained from Figure 2 (curves 1-3), the rate of molecular hydrogen formation - $w(H_2)$ and the energy output - $G(H_2)$ determined by nano-Si, which is a product of radiation-heterogeneous decomposition of water, were determined. The calculated results are given in table 2.

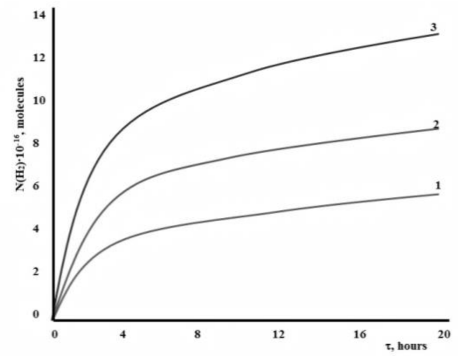

Fig. 2. Water adsorbed on the surface of silica with particle size d=50(3), 100(2), 300÷500 nm (1) under the influence of γ-quanta (^{60}Co, P=18.17 rad/sec, T=300K) θ=4) dependence of the amount of molecular hydrogen obtained from its decomposition on the irradiation time

Formation rates and energy yields of molecular hydrogen obtained from radiolytic splitting of water in d=50 nm particle size nano-Si/H_2O systems created under the influence of γ - quanta (60Co, P=18.17 rad/sec, T=300K) with the degree of water filling of the silicon particle surface (θ≤2) increases in direct proportion, and finally, at values of θ>2, the inclination angle decreases sharply. As it can be seen, the size effect in the radiolytic decomposition of water with its presence up to certain values of the particle sizes of silicon (d≤100 nm) manifests itself more clearly. If the energy yield of molecular hydrogen obtained from the radiolysis of adsorbed water at the surface levels in the particle sizes where the size effect is observed is - $G_{ads}(H_2)$, while in the homogeneous phase (pure water) $G_{hom}(H_2)$ = 0.45 molecules/100·eV, $G_{ads}(H_2$) Ghom(H_2) relationship shows that part of the energy absorbed by silicon is transferred to water adsorbed on the surface through energy carriers (electron-hole pair, excitons, various radiation defects, etc.).

Table 2.

γ - radiation-heterogeneous splitting of water in systems created with adsorbed water (θ=4) on the Si surface with particle size d=50, 100, 300÷500 nm under the influence of γ-quanta (^{60}Co, P=18.17 rad/sec, T=300K) the rate of formation of the received molecular hydrogen determined by Si - w(H_2) and energy output - G(H_2)

Molecular hydrogen formation rate - w(H_2) and energy yield - G(H_2)	*Si/H₂O*		
	50 nm	100 nm	300÷500 nm
$w(H_2)\cdot 10^{-13}$, molecule/(g·s)	3,1	1,96	1,3
$G(H_2)$, molecule/(100 eV)	2,7	1,7	1,15

In the Si/H_2O adsorbed system, the process of obtaining molecular hydrogen from the radiation-heterogeneous decomposition of water can be explained on the basis of the existing mechanisms of radiation-heterogeneous processes.

CONCLUSION

On the basis of the conducted researches it is possible to come to conclusions that:

In suspended systems created by nano-Si/H_2O with d=50, 100 and 300÷500 nm particle size under the influence of γ - quanta (60Co, P=22 rad/sec, T=300K), energy carriers (electron- due to hole pairs, excitons, different types of radiation defects, etc.), the amount of molecular hydrogen determined by the total system (water) obtained from the radiation-heterogeneous splitting of water, or water, the rate of formation and energy output of the mass of silicon added to water $m_{Si}\leq$ 0, At values of 02 g, it increases in direct proportion to it, and at values of m_{Si}>0.02 g, the angle of inclination decreases sharply depending on the particle size. According to those dimensions, the energy yields of molecular hydrogen are G(H_2) =10.9; obtained 8.07 and 5.24 molecules/(100 eV), which is appreciably larger than that of pure water ($G_0(H_2)$ = 0.45 molecules/(100 eV)).

G(H_2) = 10 for the maximum energy yields of molecular hydrogen obtained from water splitting and determined for water in suspension systems created by nano-Si/H_2O with d=50, 100 and 300÷500 nm particle size under the influence of γ - quanta, 9; Values of 8.07 and 5.24 molecules/100eV were obtained. In this system, it was determined that the energy output of molecular hydrogen increases in direct proportion to the mass of Si at values of $m_{Si}\leq$0.02g, and at values of mSi>0.02g, the angle of inclination decreases sharply depending on the particle size.

Due to the energy transmitted from a firm phase to a liquid phase under the influence of γ-quanta in the nano-Si+H_2O system, radiation-chemical yields of the molecular hydrogen received as a result of radiolytic transformation of water are equal to G(H_2) = 10.9 molecules/100eV for particles with sizes d=50 nanometer respectively that is notable more in comparison with clear water (G(H_2) = 0.45 molecules/100eV).

With increase in concentration of particles of silicon in the Si+H_2O system, the energy transferred to water grows and it in turn is the reason of increase in a yield of molecular hydrogen. Radiation–chemical yield of the molecular hydrogen received in the process of a water radiolysis grows in direct ratio (m<0.02 g) and depending on the sizes of particles after a certain mass value (m>0.02 g) the stationary area is observed. In the same system has been defined the dependence between a yield of the molecular hydrogen formed at radiation and catalytic transformation of water under the influence of γ-quanta and the mass of silicon - G(H_2) = f (m_{Si})**.**

Regularities of dependence of a radiation-chemical yield of the molecular hydrogen formed at radiation and heterogeneous transformation of water in the $Si+H_2O$ system from the sizes of particles have been revealed.

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QAMMA – KVANTIN TƏSİRİ ALTIDA NANO $Si+H_2O$ SİSTEMİNDƏ SUYUN RADİOLİZİ PROSESİNƏ SİLİSİUMUN KÜTLƏSİNİN TƏSİRİNİN ÖYRƏNİLMƏSİ

S.M. Bəşirova

Qamma kvantlarının (60Co, P=22Rad/s, T=300K) təsiri altında alınan molekulyar hidrogenin suyun radiolizi prosesində sabit həcmli maye suya (V=5 ml) radiasiya-kimyəvi məhsulunun kütləsinin (m=0,01; 0,02; 0,06 və 0,12 q) və silisium hissəciyinin ölçülərinin (d=50, 100, 300÷500 nm) dəyişməsi müəyyən edilir. Müəyyən edilmişdir ki, suya əlavə edilən silisiumun kütləsi artdıqca suyun radiolizi prosesində alınan molekulyar hidrogenin radiasiya-kimyəvi çıxımı birbaşa nisbətdə (m<0,02 q) və ondan sonrakı qiymətlərində hissəciklərin ölçüsündən düz mütənasib asılı olaraq artır. müəyyən edilmiş kütlə dəyəri (m>0,02 q) qiymətlərində isə stasionar sahə müşahidə edilir. $Si+H_2O$ sistemində molekulyar hidrogenin maksimum radiasiya-kimyəvi çıxışı $G(H_2)$ =10,9-a bərabərdir; daha sonra 8,07 və 5,24 molekul/(100 eV) qiymətləri alınmışdır ki, bu da silisium hissəciklərinin d=50, 100, 300÷500 nm ölçülərində müvafiq olaraq təmiz sudan ($G0(H_2)$ = 0,45 molekul/(100 eV) nəzərə çarpacaq dərəcədə böyükdür. Alınan nəticələri izah edən mexanizm təklif olunur.

Açar sözlər: *mikrohissəcik, radioliz, radiasiya-kimyəvi çıxım, Kompton səpilmıəsi*

ИЗУЧЕНИЕ ВЛИЯНИЕ МАССЫ КРЕМНИЯ НА ПРОЦЕСС РАДИОЛИЗА ВОДЫ В НАНО СИСТЕМЕ $Si+H_2O$ ПОД ВОЗДЕЙСТВИЕМ ГАММА – КВАНТОВ

С.М. Баширова

Радиационно-химический выход молекулярного водорода, полученного под действием гамма-квантов (60Со, Р=22Рад/с, Т=300К) в жидкую воду постоянного объема (V=5 мл) в процессе радиолиза определяеться при изменение массы (m=0,01; 0,02; 0,06 и 0,12 г) и размеров частиц кремния (d=50, 100, 300÷500 нм). Выявлено, что при увеличении массы кремния добавляемого в воду радиационно-химический выход молекулярного водорода, полученного в процессе радиолиза воды, растет прямо пропорционально (m<0,02 г) и зависит от размера частиц, затем при определенном значении массы (m>0,02 г) наблюдается стационарная область. В системе $Si+H_2O$ максимальный радиационно-химический выход молекулярного водорода равен $G(H_2)$ =10,9; получили 8,07 и 5,24 молекул/(100 эВ), что заметно больше, чем у чистой воды ($G0(H_2)$ = 0,45 молекул/(100 эВ) при размерах частиц кремния d=50, 100, 300÷500 нм соответственно Предложен механизм, объясняющий полученные результаты.

Ключевые слова: *микрочастица, радиолиз, радиационно-химическая эмиссия, Комптоновское рассеяние*.