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THE IMPACT OF MASS AND SIZE EFFECTS ON THE WATER RADIOLYSIS PROCESS IN Si+H_2O SYSTEM

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Abstract: It was studied the impact of mass and size effects on radiation-chemical yield of molecular hydrogen which is formed from the water radiolysis process under the influence of γ-quanta (^{60}Co, P=22 rad/sec) within the size (d=50, 100, 300÷500 nm) and mass (m=0.01, 0.02, 0.06, 0.12 g) of silicon in Si+H_2O system. It was defined that, radiation-chemical yield of hydrogen decreases with the increase of silicon size and it is directly proportional to silicon mass in low values of the ratio of silicon to water mass, but there is saturation state in the values higher than 1/200.

Key words: nanoparticle, radiolysis, radiation-chemical yield, compton scattering.

1. Introduction

The radiolysis process of liquids, especially water in nano- and micro-heterogeneous [1] systems remains as one of the actual problems of the day. Different researchers [2-10] have used various objects in water radiolysis process. The main products which are formed in solids-water system under the influence of ionizing rays (γ-quantum, neutrons, protons, high-energy ions, etc.) are molecular hydrogen, oxygen and hydrogen peroxide. Nanosize [11] materials are used more frequently compared with the products obtained from different sized objects under the influence of gamma-quanta. The obtained results indicate that, the speed of oxidation-reduction process becomes several times higher in the system of nano-particles+H_2O compared with pure water.

According to different reseachers and our results, radiation-chemical yield of molecular hydrogen depends on the type of solids, the band gap width, its size, overall system temperature [12], the mass of solids and properties of substances dissolved in water.

In the presented work, it was studied the influence of silicon mass on radiation-chemical yield of molecular hydrogen which was formed in radiolysis process under the influence of γ-quanta (*^{60}Co, P=22 rad/sec*) in various sized *(d=50, 100, 300÷500 nm)* silicon system hanging through vibration within the radiation in 5ml water.

2. Experimental part

Different sized (d=50, 100 və 300÷500 nm, «Skyspring Nanomaterials, Inc.», made in USA) silicon with high purity (99,9%) was used for studing the impact of size and mass effects on radiation-chemical yield of molecular hydrogen which is formed in radiolysis process under the influence of γ-quanta in Si+H_2O system. Required mass (m = 0.01; 0.02; 0.06 and 0.12 g) has been purified in special mode and added to thermal processed (T = 773K) ampule (V = 19 ml) after perfunctory processing of silicon (τ=72 hour) in open air in T=473K. Silicon is covered in an ampule by cooling and adding 5ml bidistillated water [12] after thermal processeing in a vacuum within 4 hours. The ampule was irradiated in special condition (with the condition of hanging nano-Si particle during irradiation in water by the help of vibrator). Absorption dose rate has been determined by Ferrosulfat and methane [13] methods.

The amount of hydrogen (accuracy 8%) has been determined by chromatography (Colour -102). The column with 1 m length and 3 mm internal diameter was used in chromatography. It was used activated charcoal with d=0.25÷0.6 mm size and high purity (99,9%) argon as gas carrier in the geyser.

3. Obtained results and discussions

It was studied the influence of size and mass of nano-Si on the amount of molecular hydrogen formed from radiolic decomposition of water under the impact of γ-quanta in $Si + H_2O$ system. In figure 1-3, it was given the dependence of amount of molecular hydrogen which is formed within radiolyc transformation of water on dose in silicon system with different size (d=50, 100 və 300÷500 nm) and mass (m=0,01(1); 0,02(2); 0,06(3) and 0,12 g(4)), which is subjected to suspension through vibrator during irradiation in 5ml water in room temperature (T=300K). As it is seen in three pictures, after a certain time stationary oblast starts.

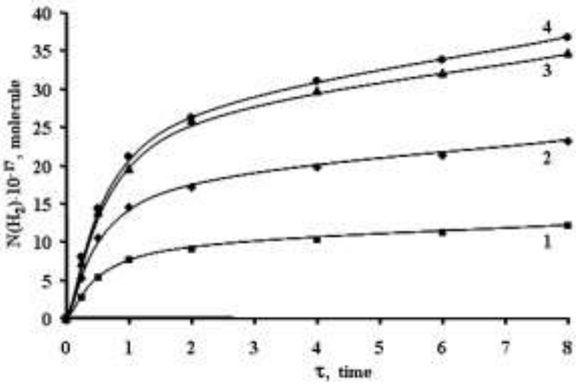

Fig. 1. The dependence of amount of molecular hydrogen formed during radiation-catalytic (P=22 rad/sec, T=300K) transformation of water on its mass in silicon (d=50 nm) system subjected to suspension through vibrator during irradiation in 5ml water -1(0,01 g); 2(0,02 g); 3(0,06 g); 4(0,12 g)

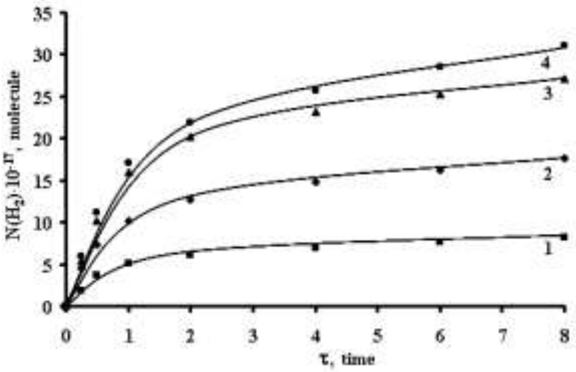

Fig. 2. The dependence of amount of molecular hydrogen formed during radiation-catalytic (P=22 rad/sec, T=300K) transformation of water on its mass in silicon (d=100 nm) system subjected to suspension through vibrator during irradiation in 5ml water -1(0,01 g); 2(0,02 g); 3(0,06 g); 4(0,12 g)

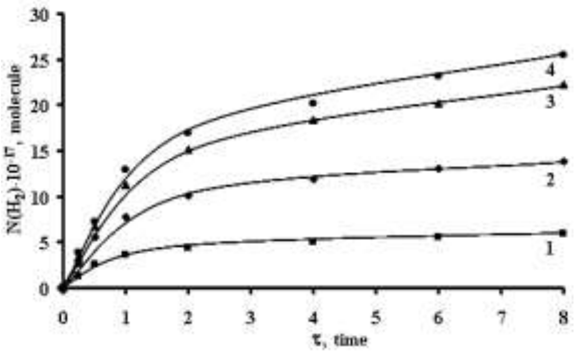

Fig. 3. The dependence of amount of molecular hydrogen formed during radiation-catalytic (P=22 rad/sec, T=300K) transformation of water on its mass in silicon (d=300÷500 nm) system subjected to suspension through vibrator during irradiation in 5ml water -1(0,01 g); 2(0,02 g); 3(0,06 g); 4(0,12 g)

It was defined the formation speeds (W(H_2)) and radiation-chemical yield $(G(H_2))$ of molecular hydrogen correspond to 100 eV adsorption energy by water from linear part of kinetic curvies (figure 1-3) which is obtained from studied systems. The formation speed of molecular hydrogen which is formed from radiation-catalytic decomposition (P = 22 rad / sec, T = 300K) of water occuring with the addition of silicon (d=*50, 100, 300÷500 nm)* in 5ml water and results obtained during the dependence of yield of molecular hydrogen on silicon mass (m=0,01; 0,02; 0,06; 0,12 g) were given in the table.

Table

The formation rate (W(H_2)) of hydrogen formed from radiation-catalytic conversion (P = 22 rad/sec, T = 300K) of water occuring with the addition of different sized silicon which is subjected to suspension by vibrator within irradiation in 5ml water and the dependence of radiation-chemical yield *(G(H_2))* on silicon mass *(m(Si))*

m(Si), g	d = 50 nm		d = 100 nm		d = 300÷500 nm	
	W(H_2)·10^{-13}, molecule /g·sec	G(H_2), molecule / 100 eV	W(H_2)·10^{-13}, molecule/ g·sec	G(H_2), molecule / 100eV	W(H_2)·10^{-13}, molecule/g·sec	G(H_2), molecule / 100eV
0	0,61	0,436	0,61	0,436	0,61	0,436
0.01	5	3,64	3,4	2,47	2,53	1,84
0.02	9,67	7,03	8,4	6,11	5,15	3,75
0.06	13,4	9,75	9,67	7,03	6,3	4,58
0.12	15	10,9	11,1	8,07	7,21	5,24

As γ-quanta influence on $Si + H_2O$ system, compton scattering takes places in both phase in the physical stage of process. The energy of compton electrons varies between 0 ÷ 1.02 MeV, by depending on the scattering angle. Compton electrons with high kinetic energy become thermal electrons by gradually loosing their energy in elastic and nonelastic collision in both phase. The electron-hole $(h^+ \cdot\cdot e^-)$ and a part of electron-ion $(H_2O^+ \cdot\cdot e^-)$ pair formed in nano-Si and water recombinate with its pair as a result of the influence of Coulomb interaction (Zaker effect), and some of them move away from each other. The main part of new generation δ-electrons is the electrons with 100 eV energy.

Experiments [14-17] and theoritical calculations [18-23] show that the radiation chemical yield of electron-ion pair formed in water under the influence of γ-quanta and electrons is 3,4 pair /100 eV in the physical and physical-chemical stages of process ($10^{-15}\div10^{-12}$ sec.), but the radiation chemical yield of electron-hole pair is 16,5 pair/100 eV in nano-Si. Absorbiton dose is 2.33 times higher in nano-Si than H_2O. Therefore, the concentration of new generation δ-electrons or thermal electrons differ several times in both phase. These electrons can easily convert from solid to liquid phase or vice versa. As the most of electrons converted from solid to liquid are 100eV, the concentration of electrons gets higher than other parts around the solid particle in d = 20 nm space. Thermal electrons can be catched in water by trap and be solvated. Reactions of molecular hydrogen (1-3) obtained from radiolytic decomposition occuring between solvated $\left(e^-_{aq}\right)$ electrons and water molecules and protonated water (H_3O^+) can be described as follows:

$$2e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^- \quad (1)$$

$$e^-_{aq} + H + H_2O \rightarrow H_2 + OH^- \quad (2)$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \quad (3)$$

Localized holes form H_2O^+ ion in contact with water in nanoparticle-water boundary and this ion recombinates with thermal electrons and forms electron – excited water molecule. Excited H_2O^* water molecule with low life expectancy form intermediate H and OH products (4) by dissociation:

$$h^+ + H_2O \rightarrow H_2O^+ \xrightarrow{e^-} H_2O^* \rightarrow H + OH \quad (4)$$

It becomes clear from the results of research work that:
- radiation-chemical yield of molecular hydrogen formed from the water radiolysis process occuring under the influence of γ- quanta in $Si + H_2O$ system decreases with the increase of silicon size. The yield with nanoparticles with the size of 50, 100 and 300÷500 nm got the value of 10.9; 8.07 and 5.24 molecule/100eV respectively,
- the radiation-chemical yield of molecular hydrogen is directly proportional to silicon mass in low values of the ratio of silicon mass to water mass in $Si + H_2O$ system, compared to pure water, but there is saturation state in the values higher than 1/200.

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ВЛИЯНИЕ МАССЫ И РАЗМЕРНЫЙ ЭФФЕКТОВ НА ПРОЦЕСС РАДИОЛИЗА ВОДЫ В СИСТЕМЕ $Si+H_2O$

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Резюме: Изучено влияние массы и размерных эффектов на радиационно-химический выход молекулярного водорода, образовавшегося в процессе радиолиза воды под действием γ-квантов (60Co, P=22 рад/сек) путем изменения размера (d=50, 100, 300÷500 нм) и массы (m=0.01, 0.02, 0.06, 0.12 гр) кремния в системе $Si+H_2O$. Было определено, что радиационно-химический выход водорода уменьшается с увеличением размера кремния и прямо пропорциональна кремниевой массе при низких значениях отношения массы кремния к массе воды, но наблюдается состояние насыщения в значениях выше, чем 1/200.

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

$Si+H_2O$ SİSTEMİNDƏ SUYUN RADİOLİZİ PROSESİNƏ KÜTLƏ VƏ ÖLÇÜ EFFEKTLƏRİNİN TƏSİRİ

Y.D. Cəfərov, S.M. Bəşirova, S.M. Əliyev

Xülasə: $Si+H_2O$ sistemində silisiumun ölçüsünü (d=50, 100, 300÷500 nm) və kütləsini (m=0.01, 0.02, 0.06, 0.12 q) dəyişməklə γ-kvantların (^{60}Co, P=22 rad/san) təsirilə suyun radiolizi prosesindən əmələ gələn molekulyar hidrogenin radiasiya-kimyəvi çıxımına kütlə və ölçü effektlərinin təsiri öyrənilmişdir. Müəyyən olunmuşdur ki, hidrogenin radiasiya-kimyəvi çıxımı silisiumun ölçüsü artdıqca azalır və silisiumun kütləsinin suyun kütləsinə nisbətinin kiçik qiymətlərində hidrogenin çıxımı silisiumun kütləsi ilə düz, nisbətin 1/200-dən böyük qiymətlərində isə doyma halı müşahidə olunur.

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