

PACS: 78.67.Bf

**SIZE EFFECTS IN RADIATION-CATALYTIC PROCESSES OF WATER
DECOMPOSITION AND PERSPECTIVES OF USE OF
NANOCATALYSTS IN THIS FIELD**

A.A.Garibov

Institute of Radiation Problems of ANAS,

nukl@box.az

Abstract – It was obtained, that on the base of nanomaterials radiation-catalytic processes enable to transform ionizing radiation energy to chemical one with great efficiency. Radiation-heterogeneous systems with nanosize open a new actual direction in radiation processes and radiative study of materials.

Key words - radiation-catalytic processes, size effect, nanosize, hydrogen production, gamma quants, water decomposition

1. Introduction

On value of a capacity factor of use of radiation source energy, selectivity and efficiency of radiation-heterogeneous processes are one of the perspective directions of radiation processes. Interest to radiation-heterogeneous processes increased in connection with development of nuclear-energy system, nuclear energy transformation and atomic-hydrogen power engineering [1-5].

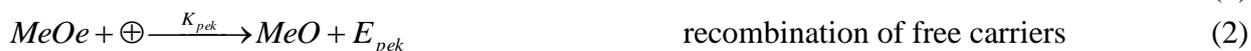
The physical stage of radiation-heterogeneous processes includes stages of absorption, transformation, and energy transfer of radiation sources. Effectiveness of radiation processes in heterogeneous systems generally depends on parameters of constituent stages [6].

In this work on examples of radiation-catalytic processes of hydrogen production from water the results of researches of influence of particles size of catalysts on effectiveness of transformation of ionizing radiation energy are presented.

2. Results and discussions

As research objects it has been taken oxide-coated compounds SiO₂, BeO, Al₂O₃ and aluminosilicates, beryllium-silicate. Physical stage of radiation-heterogeneous processes has been researched by model-calculated experiments. Calculation on commonly known model [2, 7] interaction processes of ionizing radiation with solid states, possessing radiation-catalytic activity, shows that in majority of researches the ionizing radiation energy will be transformed to energy of nonequilibrium charge carriers (electrons and holes), excited state and other defect conditions of oxides. It is established that, under the influence of ionizing radiation (γ-quantum) in all investigated oxide-coated systems there are competing processes of oscillation, localization and recombination of charge carriers.

Processes, occurring under influence of ionizing radiation in oxide-coated catalysts, can be schematically presented as following:





where, e, o, ex are free electrons, holes and excited states, L_D, L_A – electron donor and acceptor centers, L_p, L_n – localized state of holes and electrons, E_{rec} – recombination energy of free charge carriers, E_{rec in centr} – recombination energy in centers.

It is possible to determine the speed of oscillation of free charge carriers by the expression

$$\frac{dN_i}{d\tau} = G_0 \cdot \dot{D} \cdot 10^{-2} - W_{pek} - W_{лок} \quad (7)$$

Where, N_i – amount of free charge carriers, G_o – their initial yield, W_{rec}=K_{rec} [o] [e] – recombination speed in (e), W_{loc}=K_{loc} - localization speed in (7).

It has been studied individual and composite oxide-coated systems containing oxides of metals of II-IV group of periodic system. In them vacancy of cations and anions which are the centers of localization of nonequilibrium charge carriers generally in charged V_K²⁻ and V_A²⁺ (where 2=2+4). At capture of nonequilibrium charge carriers in (3) and (4), these centers pass to a condition V_K⁻⁽²⁻¹⁾ and V_A⁺⁽²⁻¹⁾ and apparently, signs of charges of these centers don't change. Therefore in these oxides the recombination of free particles in centers L_p and L_r in (5) and (6), due to insulation by electrostatic field of centers is complicated.

In steady-state regime and in the case of predominance of localization process under recombination W_{loc}>>W_{rec} within conditions 2(L_i)>> (N_i) the value of observed yields G(L_i) can be judged on yield of primary charge carriers.

It has been determined section and constants of localization and recombination speed of nonequilibrium carriers in oxide-coated catalysts, of which ratios at 77K K_{loc}/K_{rec}=2. The radius of electrostatistical interaction between localization centers and free charge carriers (R) at 77K approximately on an order exceeds Onzager's radius (r_c) R/ r_c≈ 10

It is established that regularities of influence of order degree in the example of SiO₂-A amorphous, SiO₂-II polycrystalline, SiO₂-M monocrystalline silicium dioxide and aluminum silicate and zeolite, thermal and biographical defects in the example of BeO in yield of nonequilibrium charge carriers.

Table 1

Samples of oxide-coated systems	Yields G(L _i) on 100 e/s energy absorption	
	Hole center	Electron center
SiO ₂ -A	0,50	0,11
SiO ₂ -II	0,055	0,041
SiO ₂ -M	-	0,006
Amorph power Al·S	5,0	-
Zeolite HJ	1,16	-
zeolite Na J	1,33	-
BeO	4,0	0,08

Table 2. Kinetic parameters of localization processes of charge carriers in BeO

Energy of free carriers, E_i	$R=Ze^2/\epsilon E_i$ nm	σ -capture cross-section, sm^2	K_{capture} sm^3/s
$3/2 \kappa T$ ($T=77\text{K}$, $E_i=0,0099\text{eV}$)	$5,6 \cdot 10^2$	$2 \cdot 10^{-10}$	$1,2 \cdot 10^{-3}$
$3/2 \kappa T$ ($T=3007\text{K}$, $E_i=0,0099\text{eV}$)	$1,3 \cdot 10^2$	$5,6 \cdot 10^{-11}$	$6,1 \cdot 10^{-4}$
0,1 eV	51,8	$2,2 \cdot 10^{-11}$	$4,1 \cdot 10^{-4}$
$E_{ze}(E_g=10\text{eV}, E_{ze}=7,7 \text{ eV})$	0,67	$1,4 \cdot 10^{-14}$	$2,4 \cdot 10^{-6}$

In experiment with application of electron paramagnetic resonance the localized state of charge carriers is observed; yields depend on various parameters of irradiation conditions, such as temperature, radiation power, structural feature, electrophysical and dimension of single particles of oxide-coated systems. It is determined threshold E_{ch} energy of oscillation of nonequilibrium charge carriers under influence of γ radiation in oxide-coated systems. In the case of semiconductor oxides, $E_{ch}=(3\div 4)$ and in case of dielectric oxides, $E_{ch}=2.0$ Units.

Under optimal conditions for localization, it is defined the value of yield of localized states, satisfying specified threshold energy of oscillation

$$G_{(\text{loc.H.H.3.})} \approx 5-6 \text{ particles/ } 100\text{eV}$$

There is defective state on the surface of oxide-coated systems in the form of anion vacancy (Li)= $10^{12}-10^{13} \text{sm}^{-2}$ and consequently they are usually charged positively and create superficial electrostatic field ($E=10^7-10^8 \text{ V/}$). Under the influence of these fields from fixed depth of oxide-coated systems, there is a migration of charge carriers on the surface.

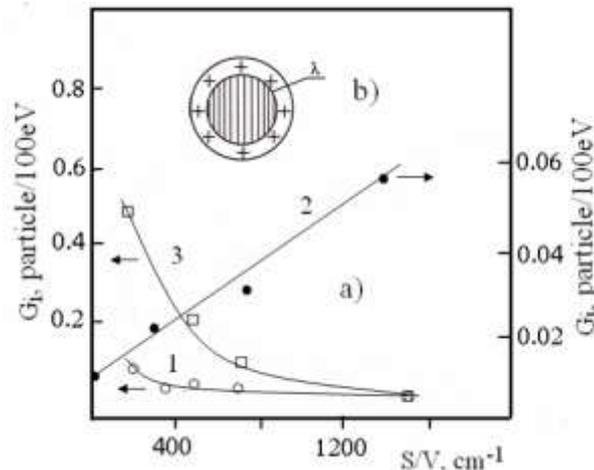


Fig. 1. Dependence of yield of electron (1), (2) and hole (3) centers under influence of gamma quanta at 77K on $\text{SiO}_2 - \text{M}$ (2) and $\text{SiO}_2 - \text{A}$ (1; 3) from ratio S/V and the scheme of distribution of localization centers in single particles of SiO_2 (b)

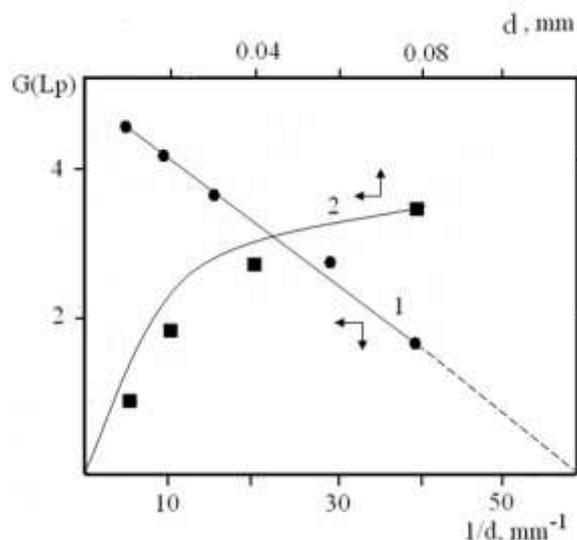


Fig.2 The influence of particle size of beryllium silicate (1) with [Be]/Si=1 and aluminum silicate (2) on the yield of localized state of nonequilibrium charge carriers.

For the purpose of identification of surface effect on migration processes of nonequilibrium charge carriers in the examples of SiO₂-A, SiO₂-P, SiO₂-M, beryllium silicate, aluminum silicate, it is studied the surface effect on yield of localized state κ.н.з..

In case of SiO₂ monocrystal in the volume, in which there is not a localization center, localization generally occurs at surface level. Other oxide-coated systems contain localization centers in volume and nature of dependence on dispersion of particles is approximately identical. For pure oxide-coated systems at surface layer to λ depth, there are migrations under the influence of surface field and there is recombination death of nonequilibrium carriers.

In case of especially pure silica gel value λ is defined

$$\lambda = R \left(1 - \sqrt[3]{1 - \frac{G(\ominus \Pi)}{G(\Pi \Pi)}} \right) \quad (8)$$

where R radius of separate microparticles of oxide, G(⊖Π) and G(ΠΠ)- yields of electron and hole centers.

Value of λ for exemplars of SiO₂ change 100-150 nm. And in case of Al-Si and Be-Si it is observed dependence of yield of both particles on size.

Let's imagine that, there is an ideal system, where surface field is absent. In this case yield κ.н.з. G₀, and in the presence of G_i field, for G_i we will get the following expression

$$G_i = G_0 \left(1 - \frac{\lambda}{R} \right)^3 \quad (9)$$

As it is seen that, at λ=R, G_i=0, etc the localization of nonequilibrium carriers doesn't occur, at λ>>R G_i= G₀; Thus, with size decrease of particles the influence of surface field increases and localization yield of particles decreases. At defined value λ=R generally all particles, formed under the influence of ionizing radiation, are migrated on the surface levels. λ of value for Al-Si and Be-Si depends on the relation of Be, Al/Si and change between 100-1000 nm.

The next stage at radiation-heterogeneous processes is transfer of ionizing radiation on substances exposed to a radiolysis. Nonequilibrium charge carriers in oxide-coated systems can move on diffusive shift

$$x = \sqrt{B\tau} \quad (10)$$

where x –diffusive shift, D – diffusion coefficient, τ - diffusion time.

By using literary data on $\tau_{\max} = 10^{-8} \div 10^{-10} \text{ c} |9|$ and mobility $\mu = 40 \text{ cm}^2 |B \cdot c| 10|$ it is defined approximate value in SiO_2 , which changes between 300-1000 nm.

In classical radiation-catalytic processes the size of catalyst particles of some orders exceeds diffusive length of shift of nonequilibrium charge carriers. Therefore diffusive shift can not provide efficient transfer of energy. Another possible way of particle transfer on surface levels is drift shift under the influence of surface fields.

$$d = \mu \cdot \varepsilon \cdot \tau \quad (11)$$

where μ - drift mobility of charges, τ - life time, ε - intense of surface field

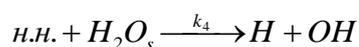
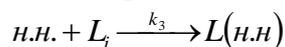
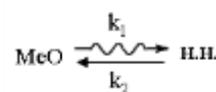
On the basis of well-known values of parameters, it is determined the value of drift shift of nonequilibrium charges in oxide-coated systems, which changes between 1000 ÷ 30000 nm.

After energy transfer on surface, their transmission on surface occurs by adsorbed molecules. Energy transfer on adsorbed molecules occurs in adsorbed centers, of which concentration depends on surface state of oxide-coated systems. Surface state of oxide-coated systems is a function of such parameters as surface nature, concentration of defective state, amount of adsorbed-active centers and adsorbed substances. The investigated oxide-coated systems can be divided into two groups by surface feature:

- a) Individual and complicated oxide-coated systems with «destructive» surface (SiO_2 , AlO_3 , BeO , Be-Si)
- b) Oxide-coated systems with surface structure – zeolites monosilicates

In both systems on surface there are electroacceptor centers of adsorbtion. Therefore electro single water molecule adsorbs in these centers. The reveal of possibility for controlling processes of adsorbed centers formation on surface of both systems by cation insertion and their change. The lower the acceptor level of cation is placed, and the higher donor level of molecule is placed, the stronger connection with surface there is. During adsorption of water molecule, on the surface it is formed complex $\text{Me} - \text{OH}_2$, which changes surface state and the surface possess electro single feature due to these complexes. The process of energy transfer is characterized by energy.

As it is seen that, capture of holes by adsorbed water molecules becomes important in condition $\Delta E < 0$: For this condition the potential of ionize of water molecule and change of wide band-gap of oxides are reached due to influence of adsorbed processes. Process mechanisms of localization, recombination and transfer of nonequilibrium charge carriers (NCC) under influence of γ -quantum on oxide system - H_2O in general view can be presented as follows:



$$W_1 = G_{h,h} \cdot \dot{D} \cdot 10^{-2}$$

$$W_2 = k_2 [N]^2 \quad (12)$$

$$W_3 = k_3 [N][L_1] \quad (13)$$

$$W_4 = k_4 [N][\text{H}_2\text{O}_s] \quad (14)$$

where, L-localization centers of NCC, N- NCC concentration, H_2O_s – surface adsorb state of water, k_i – speed constant.

From the point of competing process for radiation-chemical yield of hydrogen, we will achieve

$$G(H) = k_4 [H_2O_s] G_{h.h.} / (k_2 [N] + k_3 [L] + k_4 [H_2O_s]) \quad (15)$$

In order to define the length of energy transfer at 77K, it is studied the influence of dispersion of oxide catalysts on yield of semimagnetic products of radiolysis in the system of catalyst - H_2O . In this case each particle of catalyst can be imagined as a sphere, where nonequilibrium carriers are distributed in the whole volume equally. In the presence of adsorbed phase the defined part of nonequilibrium carriers from the depth will migrate on the surface and enters into interaction with them.

$$\lambda = R_0 \left(1 - \sqrt[3]{\frac{G_i}{G_0}} \right) \quad (16)$$

where, λ – energy transfer length; R_0 – size of separate fractions of the catalyst; G_i – yield of nonequilibrium charge carriers in the presence of adsorbed water molecules; G_0 – initial yield of n.c.c. in the absence of adsorbed water molecules

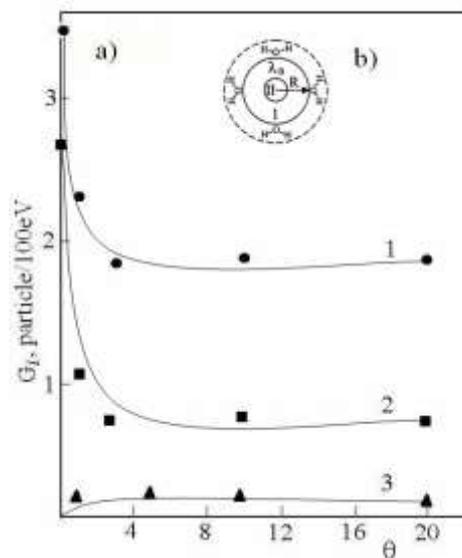


Fig.3 Dependence of radiation-chemical yields of hole centers for samples with particle size $R=40\text{mkm}$ (1), $R=20\text{mkm}$ (2) and H atoms (3) on the level of water fill up of surface of amorphous aluminum silicate ($Si/Al=5.5$, $S_{spf}=295\text{m}^2/\text{gr}$) at influence of γ -radiation $9,6\text{Gy/s}$ on the system $Al-Si + H_2O$ at 77K (a) and model of hole center distribution into individual particles of amorphous aluminum silicate at γ -radiation influence on the system $Al-Si + H_2O$ (b): I – range of effective energy transfer (λ_i); II – passive range

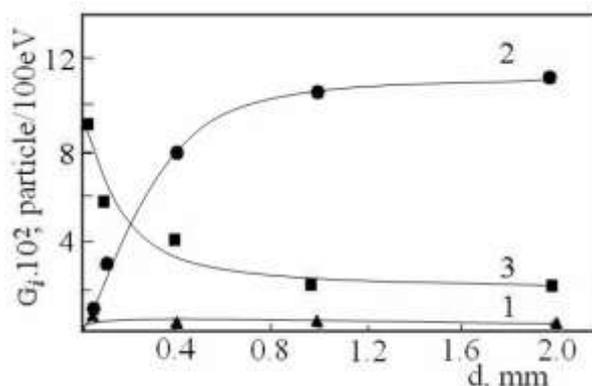


Fig.4 Influence of particle size on yield of electron (1), hole (2) centers and H atoms (3) under influence of γ -quantum= $7,1 \text{ Gy/s}$ at 77K on system $\text{SiO}_2 - \text{A} + \text{H}_2\text{O}$ ($\theta = 5$).

In Fig. 3 is presented yield dependency of hole centers on stages of water fill up in different atomic hydrogen. Value of λ for Al-Si and Be-Si changes $> = 300 \div 20000 \text{ nm}$.

In figure 4 the influence of fraction size on the yield of H atoms of nonequilibrium charge carriers is presented under influence of γ -quantum on system $\text{SiO}_2\text{-A} + \text{H}_2\text{O}$ at 77K . On the base of these results the value of λ is determined, which changes in interval $(20 \div 30) 10^3 \text{ nm}$.

In this way in radiation-catalytic processes energy transfer by absorbed catalyst to adsorbed molecule occurs in the fixed depth of single particles of catalysts. The efficiency is the samples of catalyst of particle size that corresponds to the length of free energy transfer λ (length in nano interval). In order to improve these conclusions, it has been carried out comparative kinetics of accumulation of molecular hydrogen in water radiolysis in the presence of different modifications Al_2O_3 and $\gamma \text{ Al}_2\text{O}_3$ c $R_0 = 5+50 \text{ nm}$ (Fig. 5).

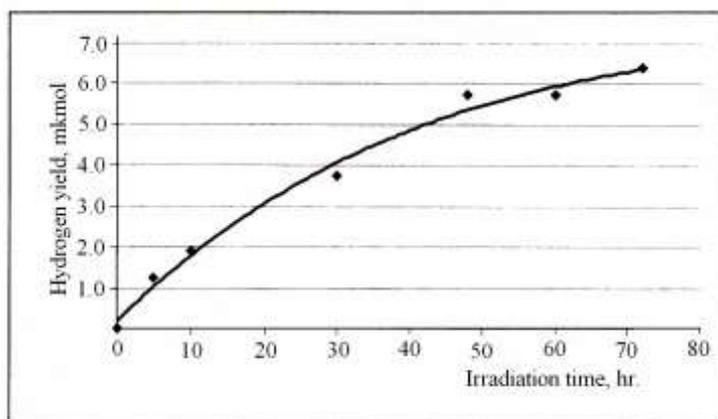


Fig.5 Kinetic dependence of molecular hydrogen, which have been formed in decomposition of dissolved nanoparticles Al_2O_3 size 20nm ($T=297\text{K}$, $P=1.26\text{kGy/h}$) in water

Table 3 Radiation-catalytic activity of different modifications Al₂O₃ and H₂O - Al₂O₃ in the process of hydrogen production from water.

Catalysts	C _{specific} . m ² /g	Θ (H ₂) ; molec 100 eV θ = 1	Λ nm
η Al ₂ O ₃	160	1,10	8
γ Al ₂ O ₃	210	0,52	3
δ Al ₂ O ₃	70	0,35	5
α Al ₂ O ₃	0,78	0,29	369

The length of energy transfer is determined by the expression

$$\lambda = \frac{G_i(H.H.) \cdot V_{y0.}}{G_0(H.H.) \cdot S_{y0.}} \quad (17)$$

In Fig.5 it is presented kinetic curve of H₂ accumulation in heterogeneous water decomposition in the presence of Al₂O₃ c R₀ = 20nm. Radiation-chemical yield of hydrogen on energy absorbed by catalyst, are equal to 12.7molecul/100eV, which is approximately more by order than simple catalysts.

In Fig. 6 it is presented dependence of Θ(H₂)= φ (R₀) for Al₂O₃ with nano size, as it is seen by increase of particle size of Al₂O₃ from 5 to 50 nm, radiation-chemical yield of hydrogen decreases from 17 to 12 molecul/100 eV.

3. Conclusion

Thus, in this way on the base of nanomaterials radiation-catalytic processes enable to transform ionizing radiation energy to chemical one with great efficiency. Radiation-heterogeneous systems with nanosize open a new actual direction in radiation processes and radiative study of materials.

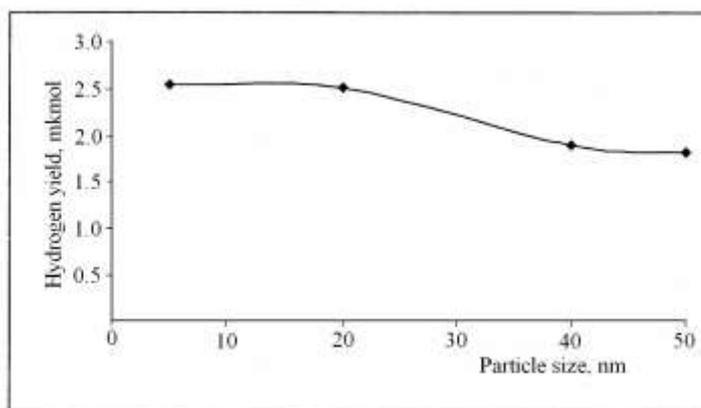


Fig.6 Yield dependence of molecular hydrogen in the system of dissolved nanoparticles Al₂O₃ of various sizes in water at radiolysis process (T=297K, P=1.26kGy/h)

References

1. Wong P.K., Allen A.O. Charge transfer to molecules on the surface of irradiated porous glass // J.Phys.Chem, 1970, № 74 (4), pp.744-748.
2. Wong P.K. Energy transfer mechanisms on some gamma irradiated synthetic solute surface // Radiat.Effects, 1973, в.19, pp.87-92.
3. Lay A.Lerne and Lav Tandon. H₂ production in radiolysis of water on UO₂ and other oxides // J.Phys.Chem. B 2003, 107, pp.13623-13628.
4. Garibov A.A., Gezalov Kh.B., Kasumov R.D., Agayev T.N. Radiation gamma induced heterogeneous reaction in BeO+H₂O using EPR. // J.Radiation Phys.Chemistry, 1987, в.30, 3, pp.197-199.
5. Гарибов А.А. Радиационно-каталитическое действие оксидных катализаторов в процессе разложения воды. В кн. Радиационно-каталитические процессы в дисперсная средах, Новосибирск, «Наука» 1992, с.120-161.
6. Гарибов А.А., Калинин А.А., Комиссаров Б.С., Красноштанов В.Ф. Математическое моделирование процесса получения водорода при радиационно-термокаталитическом разложении воды. Вопросы атомной науки и техники. Серия Ядерная техника и технология, 1989, б.2, с.28-31
7. Гарибов А.А., Джафаров Я.Д., Алиев А.К., Искендеров С.М., Красноштанов В.Ф. Расчет поглощенной дозы γ -излучения в оксидных диэлектриках, ж.Атомная энергия, 1987, т.63, в.4, с.269-270.
8. Гарибов А.А., Велибекова Г.З., Касумов Р.Д., Гезалов Х.Б., Агаев Т.Н. Закономерности переноса энергии при гетерогенном радиолиза воды в присутствии аморфного алюмосиликат. ж.Химия Высоких Энергии, 1990, т.24, №3, с.204-209.
9. Александров А.Б., Алукер Э.Д., Васильев И.А., Негаев А.Ф., Чернов С.А. В кн. Введение в радиационную физико-химию поверхности щелочно-галогенных кристаллов, Рига, Зинатие, 1989, с.244.
10. Силин А.Р., Трухин А.Н. В кн. Точечные дефекты и элементарные возбуждение в кристаллах и стеклообразном SiO₂ // Рига, Зинатие, 1985, с.206-214.