The effect of γ-ray-radiation on surface physicochemical processes on Al_2O_3

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The effect of γ-ray-radiation on surface physicochemical processes on Al_2O_3

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The γ-adsorption effect was studied on γ-Al_2O_3 samples subjected to thermal vacuum treatment. As our experiments showed, the dependence of radiation adsorption centers on the preliminary annealing temperature has a non-monotonic nature. The maximum adsorption activity is observed at a temperature of 1073 K, and the minimum is in the temperature range of 700 - 900 K. The dose dependence of the amount of absorbed gas is also characterized by a maximum in the range of ~ 0.01 Mg. With γ-radiation of Al_2O_3, an EPR signal appears, possessing electron and hole transport regimes, with two maxima: 1 - in the dose range of ~ 0.01 MGy and 2 - in the dose range of 0.15 MGy.

Key words: adsorption, irradiation, adsorption centers, paramagnetic centers, defects, aluminum oxide

Introduction

Currently, it is an indisputable fact that the impact of nuclear radiation can cause fundamental changes in the physical and chemical properties of materials. This largely applies to the surface properties of oxide materials [1-4]. Since in many respects the change in the adsorption properties of a solid is a consequence of the appearance of radiation defects, then by studying the interaction of the adsorbate and the adsorbent, one can try to establish the nature of these defects. Thus, the study of the effect of radiation on solids with a developed surface and the study of adsorption processes on irradiated materials is a new area of study of electronic and structural factors that make it possible to understand the role of free and localized carriers of electric charges in the elementary catalysis and chemical adsorption acts, and to clarify the ability of adsorbed molecules to serve as traps for electrons and holes and to compete with other traps - structural defects or impurity atoms located on the surface of solids [5-7].

As the object of the study, we chose aluminum oxide aerogel (γ-Al_2O_3). The use of aluminum oxide (especially γ-Al_2O_3) as an important ceramic material has attracted much attention due to its wide application in industrial fields such as electronics, optics and mechanical engineering. γ-Al_2O_3 is also widely used as a catalyst due to its unique structural properties and comparative low-cost of the material [8].

Results of experiments and discussion of the research results.

In our studies, we used γ - Al_2O_3 with a specific surface area of S_{sp} = 150 m^2/g. The samples were used in powder form.

Samples for radiation treatment were prepared as follows: ampoules with Al_2O_3 samples pre-annealed in air or oxygen for 6-8 hours to remove traces of organic contaminants were pumped out in a vacuum at a given temperature for 6-8 hours. The ampoules were prepared in such a way that EPR measurements could be carried out simultaneously with adsorption studies.

After training, the ampoules were sealed under pumping and irradiated on a γ-installation at room temperature.

The radiation dose varied from 0.003 to 0.2 MGy at a dose rate of 0.0077 MGy/h.

The ampoules with the samples after irradiation were connected to the vacuum system and after the gas under study was let into the volume separated from the sample by a thin partition, they were again sealed off from the vacuum system. After this, the partition was broken with a striker and the gas and solid were brought into contact. The resulting change in pressure was recorded using vacuum meters.

The sample in our experiments was 1 g, and the initial pressure varied within 20-9 Pa.

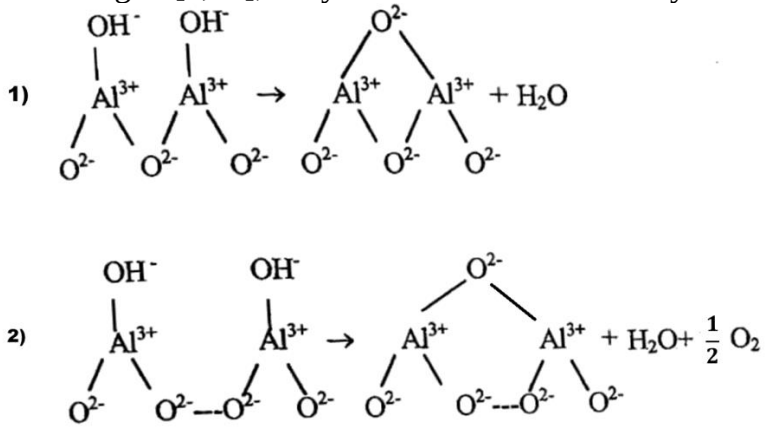
In this work we especially focused on the interaction of the aluminum oxide surface with oxygen. The g-adsorption effect was studied on γ-Al_2O_3 samples subjected to traditional thermal vacuum treatment. The main attention was paid to the study of the dependence of radiation-induced adsorption centers on the preliminary treatment temperature, the relationship between paramagnetic and adsorption centers, the mechanisms of gas absorption on the oxide, the surface structures formed by adsorbed molecules, and the nature of defects on the surface (and in the volume) of aluminum oxide. It is known that the - Al_2O_3 structure is a structural spinel. The oxide surface contains a hydrated layer, the state of which has a strong effect on its catalytic and adsorption capacity. Heating of aluminum oxide at 450-500 K leads to a loss of up to 50% of water [11]. An increase in the annealing temperature above 500 K can be accompanied by a gradual distortion of the g-form lattice of aluminum oxide. At temperatures above 800 K, the formation of new -θ -, α - Al_2O_3 phases is possible. Moreover, the restructuring of the oxide begins from the surface.

Unlike SiO_2, the processes of Al_2O_3 dehydration and rehydration on are almost reversible. The high concentration of OH groups on the surface leads to interaction between them and the establishment of a hydrogen bond. On the highly dehydrated surface of γ - there are aluminum atoms

with a coordination number of 3, which are strong electron-acceptor centers. Water adsorption forms AlOH groups with a coordination number of up to 4. Further adsorption of water by the coordination mechanism increases the coordination number to 5 and 6.

The coordination unsaturation of the surface aluminum atom depends on the number of OH groups bound to it (or on the temperature of preliminary calcination, which is the same thing), as indicated by the dependence of the adsorption activity of the surface on the concentration of hydroxyl groups on it.

According to [**9,15**], dehydration occurs in two ways:



The second scheme is implemented during the destruction of isolated hydroxides at high temperatures, and the process is accompanied by an increase in the n-conductivity of γ-Al_2O_3. As our experiments have shown, the dependence of radiation adsorption centers on the preliminary annealing temperature has a non-motoric character **(Fig.1.).**

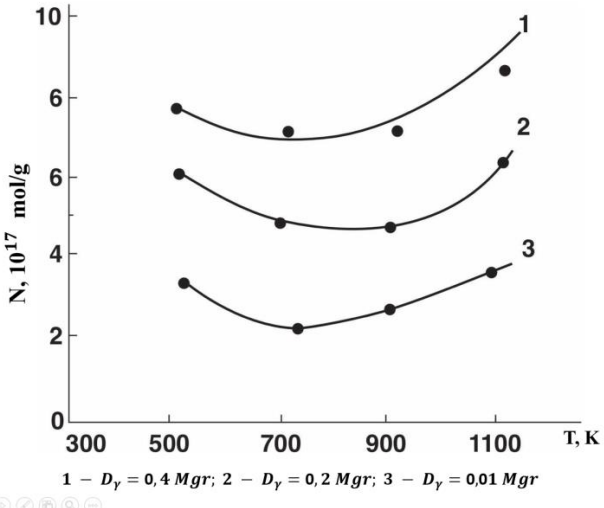


Fig.1.Temperature dependence of O_2 γ - adsorption on Al_2O_3

The maximum adsorption activity is observed at a temperature of 1073 K), and the minimum in the temperature range of 700 - 900 K.

Such a temperature dependence is possibly a consequence of phase changes occurring on Al_2O_3. The dose dependence of the amount of absorbed gas is also characterized by a maximum in the region of ~0.01 Mg (Fig.2).

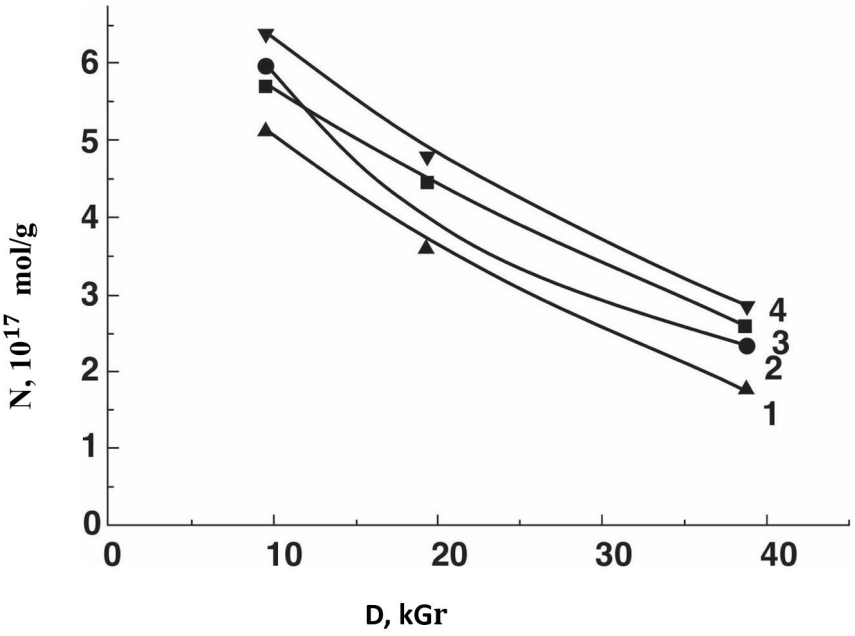


Fig.2. Dose dependence of O_2 γ -adsorption on Al_2O_3

A further increase in the dose is accompanied by radiation annealing of the adsorption centers.

As is known, at room temperature, non-irradiated aluminum oxide samples do not have EPR signals if the preliminary annealing temperature is less than 700 K.

Under g - irradiation of Al_2O_3, an EPR signal appears with g = 2.022 + - 0.005 ΔH = 4.3 + 0.2 mT and g = 1.9937 + 0.0005, ΔH = 0.93 mT (93 ers), which coincides with the description in the literature [10]. The dose dependence of the PMC oxide concentration is characterized by two maxima: 1 - in the region of a dose of ~ 0.01 MGy and 2 - in the region of 0.15 MGy **(Fig. 3).**

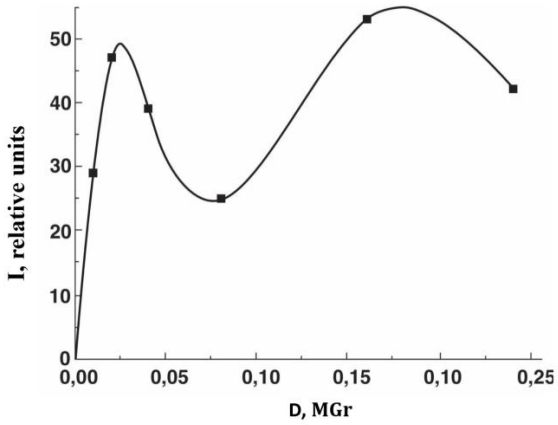


Fig.3. Dose dependence of PMC concentration on Al_2O_3 PMC irradiated with γ - rays

Thermal annealing of PMCs shows that above temperatures of 350 K, especially above 400 K, there is an intensive destruction of centers.

Experiments with adsorption of H_2 and O_2 show that along with hole centers of the O- type [1], electron centers (F+ - centers) are also present on the irradiated aluminum oxide [12]. **As can be seen from the figure (Fig.4.)**, the oxygen supply increases the signal intensity without changing its shape. Most likely, in this case, oxygen is adsorbed in the ion-radical form O_2 [**13**].

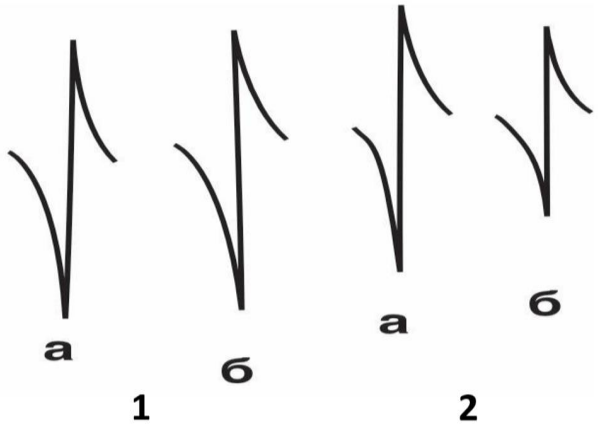


Fig.4. EPR spectra of irradiated Al2O3 containing adsorbed gases

а- original sample, б- gas injection (1-O_2 ; 2 - H_2)

With the adsorption of H_2, the EPR signal intensity decreases. In this case, it can be assumed that hydrogen atoms are adsorbed on the surface hole centers O- with the restoration of the hydroxyl cover.

Hole centers (O^-) can be formed during the gamma radiolysis of hydroxyl groups, resulting in the release of water molecules [9].

Acceptor centers (Al^{3+}) are formed during gamma irradiation of aluminum oxide due to the decomposition of hydroxyl groups, leading to the release of hydrogen atoms.

In the second case, a signal from hydrogen atoms should be observed. However, at room temperature, they quickly react with each other, forming molecular hydrogen. The signal from hydrogen atoms can only be replaced at nitrogen temperature. Thus, joint experiments with manometric and EPR spectroscopic methods have shown, on the one hand, that paramagnetic centers have an electron-hole character and they can serve as adsorption centers, on the other hand, that paramagnetic defects are formed both on the surface (change in signal intensity during gas adsorption) and in the volume (paramagnetic centers do not disappear during gas adsorption).

The following fact can be noted: The dose dependence and concentration of PMC and the number of adsorbed gas molecules differ from each other by the non-coincidence of maxima and different annealing temperature range. This once again indicates the presence of non-paramagnetic adsorption centers.

When irradiated, fast electrons are formed (created during the absorption of g-quanta by atoms), the energy of which depends on the energy of the primary g-quantum. If in the g-quantum energy range of 10-100 keV, photoelectrons are mainly formed, then at energies of 1 MeV and more, mainly Compton electrons are formed, and their energy will be of the order of the energy of the primary γ-quantum.

The energy of Compton electrons and photoelectrons, which appear during the absorption of g-quanta by the Co^{60} atom, is sufficient to form displaced atoms due to elastic collisions. In addition to elastic collisions, secondary electrons (Compton and photoelectrons) experience inelastic collisions with electrons of target atoms, causing ionization and excitation of the latter.

Thus, when solids are irradiated with γ-radiation, a wide range of different defects are formed in them, as a result of which significant changes occur in their physicochemical properties.

One of the manifestations of this is the phenomenon of radiation adsorption, in particular, γ-adsorption, discovered in the 1950's.

Although the general laws of this phenomenon are now well known, the detailed mechanism of adsorption (the connection of paramagnetic centers with adsorption centers, the role of hydroxyl groups in adsorption) has not yet been developed. Our studies, conducted using various methods, made it possible to clarify the mechanisms of radiation adsorption of oxygen, hydrogen on SiO_2, Al_2O_3, BeO, and other oxides [13, 14].

As was shown in our studies, preliminary treatment of the sample plays a large role in the phenomenon of radiation adsorption.

As already noted, the oxide surface is covered with hydroxyl groups and during calcination and radiation treatment they can be destroyed, while active centers are created on the surface that can become adsorption centers. On the other hand, with the destruction of surface hydroxyl groups, some of the adsorption centers that can form a hydrogen bond with adsorbate molecules are lost.

In addition, radiation treatment can destroy organic matter in the adsorbent volume and cause the diffusion of organic fragments to the surface, which, when they enter into a bond with an adsorbed gas molecule, can form new organic compounds, and thus, disguise the process of radiation adsorption. As noted above, when presenting the experimental results, the preliminary processing temperature varied from 473 K to 1073 K, i.e. the surface of the oxide samples, which had active adsorption centers before irradiation, and in g-adsorption processes also radiation centers, had a different number of potential centers before radiation treatment.

Conclusion

As a result of radiation treatment, dehydroxation of the oxide surface occurs. If we consider that during adsorption, part of the oxygen is spent on the reaction of oxidation of organic matter, which can be adsorbed by forming a hydrogen bond on OH groups, then with an increase in the dose, the rate of such a reaction should decrease. Thus, with such an adsorption mechanism, if it were the only one, starting from a certain dose, either equilibrium or an increase in pressure in the system would be observed - this was not observed in the experiment. Consequently, H-centers located on the surface do not play a decisive role.

When irradiated with γ-rays, paramagnetic centers with electron and hole properties are formed on aluminum oxide. The maximum intensity of EPR signals is observed at a pretreatment temperature of 673 K. The decrease in the intensity of EPR signals with a further increase in temperature is explained by a decrease in the number of surface paramagnetic centers. Oxygen adsorption is accompanied by an increase in the intensity of EPR signals on aluminum oxide. Hydrogen adsorption causes a decrease in the number of paramagnetic centers.

Saturation of paramagnetic centers occurs at radiation doses significantly exceeding the saturation doses for adsorption centers.

References

1.Dey S. et al.. Radiation tolerance of nanocrystalline ceramics: insights from Yttria Stabilized Zirconia. Sci. Rep. 5, 7746 (2015
2. Petrik, N.G.; Alexandrov, A.B.; Orlando, T.M.; Vall, A.I. Radiation-induced processes at oxide surfaces and interfaces relevant to spent nuclear fuel storage.- Transactions of the American Nuclear Society; ; v. 81; p. 101-102
3.Was G. S. Fundamentals of Radiation Materials Science (Springer, New York, 2007).
4. Zinkle S. J. & Was G. S. Materials challenges in nuclear energy. Acta Mater . 61, 735–748 (2013)
5.Rollett D., Wang Y., Carpenter J. S., Beyerlein I. J. & Misra A. Design of radiation tolerant materials via interface engineering. Adv. Mater. 25, 6975–6979 (2013)
6. Hwang S.-H., Yatsu K., Lee D.-H., Park I.-J., Kwon H. Effects of Al2O3 surface passivation on the radiation hardness of IGTO thin films for thin-film transistor applications (2022) Applied Surface Science, 578 , art. no. 152096/.
7. Man Ding Damage Effect of ALD-Al2O3 Based Metal-Oxide-Semiconductor Structures under Gamma-Ray Irradiation.Micromachines (Basel) 2021 Jun; 12(6): 661.. doi: 10.3390/mi12060661
8. M. Trueba and S. P. Trassati, Eur. J. Inorg. Chem. 17, 3393 (2005).DOI: 10.7868/S0370274X15210122

9. Chukin G.D. Structure of aluminum oxide and hydrodesulfurization catalysts. Reaction mechanisms. Moscow: 2010. – 288 p
10. G. V. Mamin, S. B. Orlinsky, A. A. Rodionov, M. S. Tagirov. EPR study of ordered aerogel based on Al2O3. JETP Letters, Vol. 102, Issue 9, 2015.
11. N. Mukhambetov, A. A. Lamberov, B. V. Yavkin, M. R. Gafurov, G. V. Mamin, and S. B. Orlinskii, J. Phys. Chem. C 118, 14998
12. D.V. Ananchenko, S.V. Nikiforov, G.R. Ramazanova, R.I. Batalov, R.M. Bayazitov, G.A. Novikov. Luminescence of F-type defects and their thermal stability in sapphire irradiated with pulsed ion beams. Optics and Spectroscopy, 2020, Vol. 128, No. 2.
13.T. Tusseyev; A. Kuykabayeba; O. Doszhanov; A.Danlybaeva Impact of Gamma-Ray radiation on SiO_2 hydroxyl cover AIP Conf. Proc. 3020, 030009 (2024) https://doi.org/10.1063/5.0193755
14. Tusseyev T., Polyakov A.I., Bitenbayev M.S. Accumulation of radiation adsorption centers on the surface of irradiated oxides. Universities Bulletin. Physics. – 2011. v. 54, № 1/3. pp. 294-297
15. Rabin H, Klick P. // Phys. Rev. -1960, 117, 4, 1005-1012.