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FEATURES OF RADIATION-STIMULATED ADSORPTION OF WATER ON THE SURFACE OF BERYLLIUM AND ALUMINUM OXIDES

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Abstract: This paper presents the results of IR spectroscopic studies of radiation-stimulated adsorption of water in heterogeneous systems BeO/adsH_2O and γ-Al_2O_3/adsH_2O at room temperature. The spectrokinetic dependences of the relative optical densities of the bands of hydroxyl (OH) groups and water molecules on the dose of gamma irradiation have been studied. It is shown that the presence of wells in the region of low doses for intermediate particles and water molecules, the occurrence and difference of their depths, as well as the change in their half-widths indicate the difference in relaxation times associated with the difference in the nature of the interaction of these particles and water molecules with surface radiation defects.

Keywords: aluminum and beryllium oxides, radiation-stimulated adsorption, water, optical density, a dose of gamma radiation, IR-spectra

1. Introduction

Based on studies of the radiolysis of water with the participation of several dispersed metal oxides under the influence of gamma radiation, it was found that the use of powder oxides (SiO_2, TiO_2, ZrO_2, Al_2O_3, etc.) as a catalyst significantly increases the rate of accumulation of molecular hydrogen [1-2]. This sharply increases the radiation-chemical yield of H_2 in comparison with the yields of both homogeneous and heterogeneous decomposition of H_2O, in which micro-sized oxides are used as catalysts [3-4]. Among these oxides, the most promising are oxides of beryllium (BeO) and aluminum (γ-Al_2O_3) [5-6]. IR spectroscopy was used to study the hydroxyl cover and electron-acceptor properties of ZrO_2 [6,7]. In [4], the effect of gamma radiation on nano-SiO_2 and changes in the absorption bands of OH groups and water molecules at room temperature and an irradiation dose of 25-200 kGy. However, in the literature, there are virtually no spectroscopic data on the radiation adsorption of water in nano-BeO/ads.H_2O and nano-γ-Al_2O_3/ads.H_2O.

This work presents the results of an IR spectroscopic study of radiation-stimulated adsorption of water in heterogeneous systems BeO/adsH_2O and γ-Al_2O_3/adsH_2O at room temperature.

2. Methods of the experiment

We used BeO and γ-Al_2O_3 powders with a purity of 99.9% with particles of 4 and 6 μm. Before adsorption, the samples of beryllium and aluminum oxides were subjected to thermal vacuum treatment at T=973K and pressure 10^{-3}Pa for 8 hours for cleaning from organic contaminants and surface dehydroxylation.

Transmission spectra were recorded on a Specord 71 IR spectrometer in the range 4000-3000cm^{-1} at room temperature. For this, tablets with a thickness of 50-80 μm were pressed from BeO and γ-Al_2O_3 powders. The IR -spectra of the samples were measured in a quartz cuvette with CaF_2 windows, which makes it possible to obtain the spectra of adsorbed water decomposed by γ-radiation.

With the overlapping of bands related to different forms of adsorbed water, the total contour was decomposed into individual components according to the method [8].

Assuming that the Bouguer-Lambert-Beer law is fulfilled concerning the bands of adsorbed molecules, the concentrations of surface hydroxyl groups and water molecules in the samples under study were characterized by the relative optical density of these bands D/D_o, where D_o –is the optical density in the initial, D-in the irradiated sample.

When comparing the optical densities $D \sim \varepsilon cd$ and $D_o \sim \varepsilon_o c_o d$, it was assumed that the molar absorption coefficients of various forms of adsorbed particles before and after gamma irradiation are the same.

The adsorbate was bidistilled water, from which foreign gases were removed by repeated freezing in a trap with liquid nitrogen followed by pumping out. The adsorption of water vapor was studied by the method [1,7].

The samples were irradiated with a ^{60}Co isotope source with a dose rate $d\Phi_\gamma/dt$=1.03Gy/h. Dosimetry of the source was carried out with ferrosulfate and methane dosimeters [9].

3. The discussion of the results

IR spectra of BeO (a) and γ-Al_2O_3 (b) treated at 973 K, after adsorption of water (curves 1), BeO and γ-Al_2O_3 irradiated with a dose of 25 kGy with subsequent adsorption of water vapor (curves 2) are shown in Fig.1.

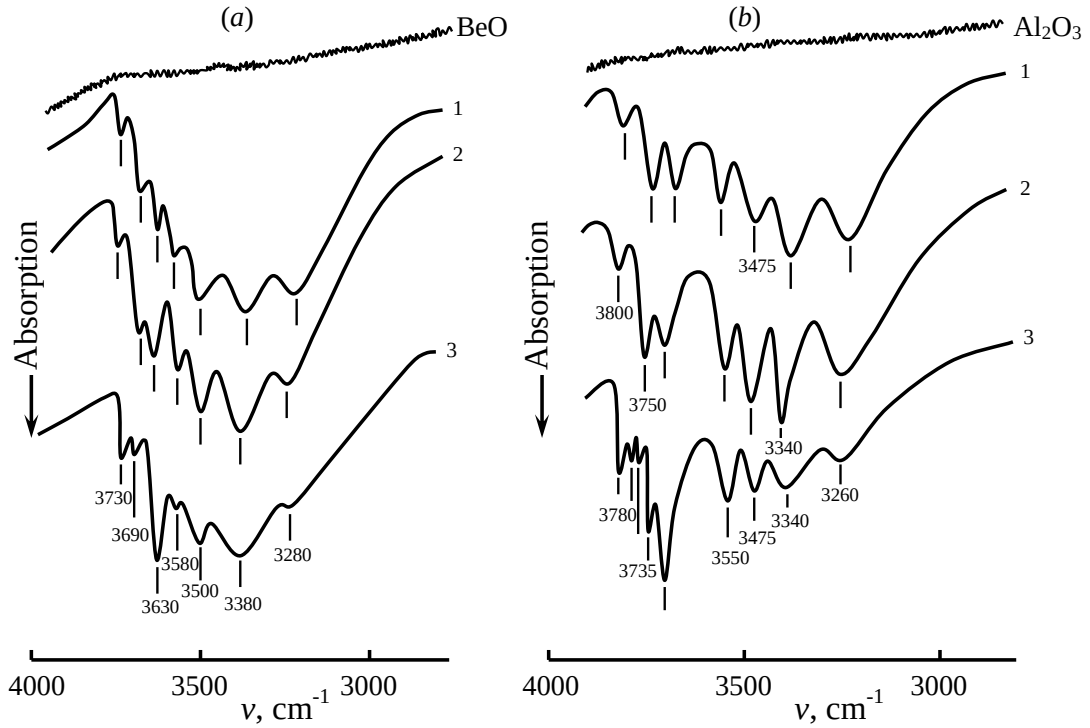

Fig. 1. IR spectra of BeO (a) and γ-Al_2O_3 (b) treated at 973 K after the adsorption of water vapor (1),BeO (a) and γ-Al_2O_3irradiated with a dose of 25 kGy with subsequent adsorption of water vapor (2), the BeO/adsH_2O and γ-Al_2O_3/adsH_2O systems irradiated with a dose of 25 kGy (3).

As seen from Fig. 1 (curves 1), the surfaces of BeO (a) and γ-Al_2O_3 (b), which have undergone vacuum heat treatment, are clean, since they do not contain absorption bands (AB) caused by the presence of water and hydrocarbon pollution. In an unirradiated heterosystem, after the adsorption of water in the region of stretching vibrations of hydroxyl (OH) groups, AB appears which indicates the occurrence of molecular and dissociative forms of adsorption. In the IR spectrum of BeO samples with adsorbed water, the absorption bands of free (isolated) hydroxyl groups are clearly found at 3735, 3630 cm^{-1} and hydrogen-bonded OH groups at 3580, 3500, 3420, 3380 cm^{-1}, as well as at 3690 and 3280 cm^{-1}, which refer to adsorbed water molecules.

As can be seen from Fig. 1b, in the AB region of free groups, in contrast to nano-BeO, nano-γ-Al_2O_3 is characterized by the presence of 5 absorption bands of OH groups with maxima at 3800, 3780, 3745, 3730 and 3700 cm^{-1}. Tables 1a and 1b show the frequencies of stretching vibrations (position of the AB) of surface free and hydrogen-bonded OH groups after water adsorption in BeO/adsH_2O and γ-Al_2O_3/adsH_2O heterosystems.

Table 1a

Position of absorption bands of surface OH-groups and H_2O molecules of beryllium oxide (BeO)

Absorption bands, cm^{-1}	Dehydration temperatures, K	Free OH-bands, cm^{-1}	Hydrogen-bonded groups, cm^{-1}		Molecules H_2O
			Proton acceptors	Proton donors	
OH-groups	473-973	3735, 3630	3720-3685	3580, 3500 3380	3690 3600-3000

Table 1b

Position of absorption bands of surface OH-groups and H_2O molecules of γ-aluminum oxide (γ-Al_2O_3)

Absorption bands, cm^{-1}	Dehydration temperatures, K	Free OH-bands, cm^{-1}	Hydrogen-bonded groups, cm^{-1}	Molecules H_2O
OH- groups	673-973	3880, 3180. 3745, 3730, 3700	3550, 3470, 3340	3680 3600-3560

The spectrokinetic regularities of the accumulation of free hydroxyl (OH) groups and water molecules on the surface of γ-irradiated BeO and γ-Al_2O_3 have been studied. Results of changes in the relative optical densities (D/D_o) of free OH groups and water molecules depending on the dose of γ-irradiation are shown in Fig. 2a and 2b. As can be seen from the figures, with an increase in the irradiation dose (Φ_γ), the relative optical densities of the bands (D/D_o) of free (Fig. 2a, curves 1-4) OH-groups decrease to minimum values at Φ_γ=2.5 (for γ-Al_2O_3, curves 1,2) and 8-12 kGy (for BeO, curves 3,4).

At $\Phi_\gamma \geq 2.5$ and $\Phi_\gamma \geq$8-12 kGy, the value (D/D_o) of these groups monotonically increases to $\Phi_\gamma \leq 12.5$ and 25-30 kGy and with a further increase in $\Phi_\gamma \geq 12.5$ kGy and $\Phi_\gamma \geq$25-30 kGy goes to saturation. It was found that for hydrogen-bonded surface OH groups and adsorbed water

molecules, the change in optical density is satisfactory, and for free OH groups it is roughly described by the expression:

$$D/D_o \sim (1- \Phi_\gamma/ \Phi_{\gamma min})^{3/2} \sim \exp(-3\ \Phi_\gamma/2\ \Phi_{\gamma min})$$

The detected difference in the observed values of $\Phi_{\gamma min}$ for various hydroxyl OH groups and adsorbed water molecules is most likely associated with the difference in the mechanism of interaction of intermediate particles with structural defects in the layer of granules of dispersed oxides of beryllium and aluminum.

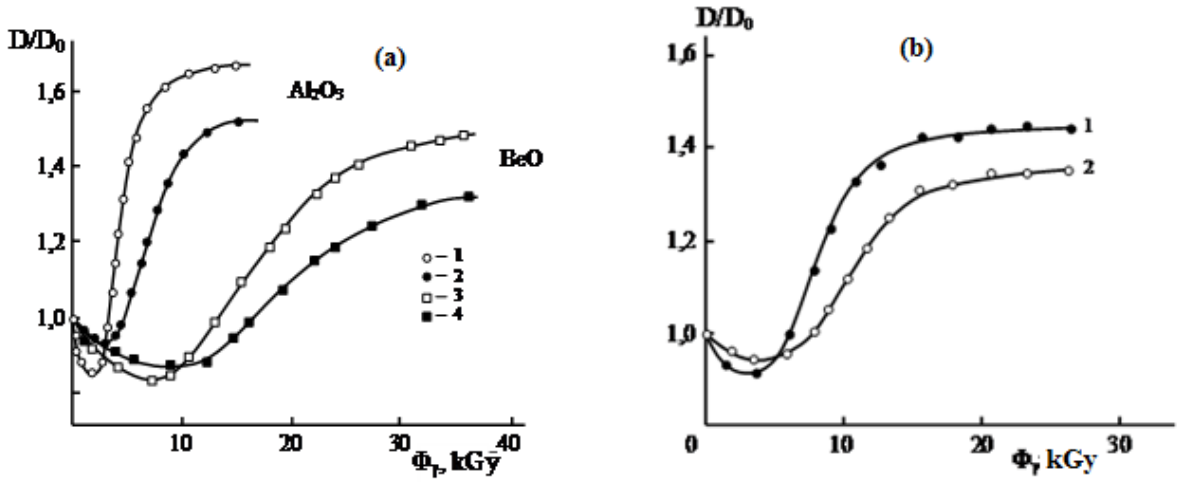

Fig. 2. (a). Dependence of the relative optical densities of the bands of free ν=3690 (1), 3730 (2), 3630 (3), and 3720 cm^{-1} (4) OH groups on the absorbed dose in γ-irradiated Al_2O_3 (1,2) and BeO (3, 4) followed by adsorption of water vapor.
(b). Dependence of the relative optical densities of the bands of water molecules on the absorbed dose in γ-irradiated Al_2O_3 (1) and BeO (2) with subsequent adsorption of water vapor.

The presence of wells in the region of low doses simultaneously for intermediate particles and water molecules, the occurrence and difference of their depths, as well as the change in their half-widths indicate the difference in relaxation times associated with the difference in the nature of the interaction of these particles and water molecules, both with neutral and ionized surface radiation defects. When comparing the half-widths of wells in the region of low doses of free OH groups (Fig. 2a, curves 1-4) and water molecules (Fig. 2b, curves 1-2), it shows that the interaction of the former occurs with electrically neutral radiation defects. A decrease in the half-widths of wells for hydrogen-bonded OH-groups and H_2O molecules is a consequence of a decrease in the probability of interaction of these particles with neutral radiation defects. This indicates that, depending on the bond strength of OH groups and water molecules, interactions occur both by electrically neutral, empty, and ionized radiation defects. The role of the second type of ionized defects increases with an increase in the bond strength between OH groups and H_2O molecules. It was found that the adsorbed water molecules interact with both types of radiation defects due to the occurrence and enhancement of the dipole-orientation effect.

With an increase in the dose of $\Phi_\gamma \geq 12.5$ kGy and $\Phi_\gamma \geq 25$-30 kGy, in the stationary region, regardless of the type of OH groups and water molecules, the constancy of D/D_o is associated with a decrease in the filling density of radiation (electrically neutral and charged) acceptor defects and their transition to donor defect states. This transition, in turn, limits the

recapture of these intermediate particles with surface defects. This shows that, depending on the radiation dose, it is possible to vary and change the probability of transition from one surface energy level to another (from acceptor to donor and vice versa), which confirms the available facts [10].

4. Conclusion

The radiation-stimulated adsorption of water in heterogeneous systems $BeO/ads H_2O$ and γ-$Al_2O_3/ads H_2O$ at room temperature has been studied.It was found that, under the influence of gamma quanta, the centers of water adsorption on the surface of aluminum and beryllium oxides at room temperature arise by molecular and dissociative mechanisms. It is shown that in radiation-stimulated systems $BeO/ads H_2O$ and γ-$Al_2O_3/ads H_2O$ free hydroxyl groups interact with cations, hydrogen-bonded groups with ionized ones, and molecular water with both neutral and with ionized centers.It has been revealed that the occurrence of the effect of low doses in the spectrokinetic regularities of the accumulation of radiation-adsorbed water molecules and their intermediate active particles on the surface of oxides is associated with a change in the mechanism of interaction between their structural defects, having different electronic configurations.

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ОСОБЕННОСТИ РАДИАЦИОННО-СТИМУЛИРОВАННОЙ АДСОРБЦИИ ВОДЫ НА ПОВЕРХНОСТИ ОКСИДОВ БЕРИЛЛИЯ И АЛЮМИНИЯ

Н.Н. Гаджиева

***Резюме*:** В настоящей работе представлены результаты ИК–спектроскопических исследований радиационно-стимулированной адсорбции воды в гетерогенных системах BeO/адс.H_2O и γ-Al_2O_3/адс.H_2O при комнатной температуре. Изучены спектрокинетические зависимости относительных оптических плотностей полос гидроксильных (ОН) групп и молекул воды от дозы гамма облучения. Показано, что наличие ям в области малых доз для промежуточных частиц и молекул воды, проявление и отличие их глубин, а также изменение их полуширин свидетельствуют о различии времен релаксации, связанных с различием природы взаимодействия этих частиц и молекул воды с поверхностными радиационными дефектами.

***Ключевые слова*:** оксиды алюминия и бериллия, радиационно - стимулированная адсорбция, вода, оптическая плотность, доза гамма- облучения, ИК- спектры

BERİLLİUM VƏ ALÜMİNİUM OKSİDLƏRİNİN SƏTHİNDƏ SUYUN RADİASİYA-STİMULLAŞDIRILMIŞ ADSORBSİYASININ XÜSUSİYYƏTLƏRİ

N.N. Hacıyeva

***Xülasə*:** Təqdim edilmiş işdə BeO/ads.H_2O və γ-Al_2O_3/ads.H_2O heterogen sistemlərdə otaq temperaturunda suyun radiasiya-stimullaşdırılmış adsorbsiyasının İQ-spektroskopik tədqiqat nəticələri verilmişdir. Hidroksil (OH) qrupların və su molekulunun udulma zolaqlarının nisbi optik sıxlıqlarının qamma şüalanma dozasından spektro-kinetik asılılıqları öyrənilmişdir. Göstərilmişdir ki, kiçik doza oblastında aralıq hissəciklər və su molekulu üçün oyuqların təzahürü, onların dərinliyinin müxtəlıfliliyi, həmçinin onların yarımeninin dəyişməsi relaksasiya zamanının fərqlənməsinə dəlalət edir ki, bu da həmin hissəciklərin və su molekulunun səthi radiasiya defektlərilə qarşılıqlı təsir təbiətinin müxtəlifliyi ilə əlaqədardır.

Açar sözlər: alüminium və berıllium oksidlər, radiasiya-stimullaşdırılmış adsorbsiya, su, optik sıxlıq, qamma süalanma dozası, İQ-spektrlər