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PARAMAGNETIC CENTERS BY X-RAY-IRRADIATION OF
ALUMINIUM HYDROXIDE*
EPR SPECTROSCOPY, RADIATION CHEMICAL YIELD AND KINETICS
OF THERMAL DECAY OF PARAMAGNETIC CENTERS

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EPR spectra of paramagnetic centers originating from X-ray-irradiation of aluminium hydroxide at room temperature have been measured. The EPR spectrum represents a superposition of EPR spectra of ionic centers O^- , holes of type $Al/O^- \setminus Al$ and trapped electrons. Radiation chemical yield of paramagnetic centers observed at room temperature (293 K) is $G(\Sigma \text{spins}) = (4.4 \pm 0.6)$ spins per 100 eV absorbed energy. The decay of paramagnetic centers in irradiated $Al(OH)_3$ was observed at 293 K. The rate constant of the paramagnetic centers decay in irradiated $Al(OH)_3$ is $k_2 = (0.0980 \pm 0.0019)$ $kg \cdot mol^{-1} \cdot min^{-1}$ and their half-life is 9.43 ± 0.18 days.

INTRODUCTION

The study of paramagnetic centers in irradiated aluminium oxide was given relatively great attention¹⁻²⁶. The authors of work¹⁴ registered O^- at 77 K with $\Delta H =$

*Dedicated to the memory of the late Genrikh Markovits Kolyari.

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= 4.3-5.0 mT and $g = 2.0155$ as well as $\text{Al}^{\text{O}^-}\text{Al}$ with 11 lines of hyperfine splitting (HFS) from two Al^{3+} nuclei with $a = 1.0$ mT, $g = 2.0036$ and Al^{2+} with six lines of HFS ($a_{\parallel} = 4.85$ mT, $a_{\perp} = 4.60$ mT, $g_{\parallel} = 1.985$, $g_{\perp} = 2.020$). F-center represents a singlet with $\Delta H = 1.0$ mT and $g = 2.0045$ (in the presence of adsorbed O_2 only). Dolidze et al.⁷ investigated the kinetics of formation of surface defects in irradiated Al_2O_3 and observed emission of electrons at ~ 373 K. Blaginina et al.²⁴ also observed the presence of Al^{3+}O^- centers in irradiated glass containing Al_2O_3 with $g = 2.0110$ and $\Delta H = 4.4$ mT. The non-symmetrical singlet observed by Davranov et al.²⁶ in the EPR spectrum of γ -irradiated Al_2O_3 with $\Delta H = 4.3$ mT was ascribed to ionic centers O^- ; while their radiation chemical yield was $G(\text{O}^-) \approx 10$ particles per 100 eV.

For the time being much less attention has been paid to the study of paramagnetic centers in irradiated aluminium hydroxyde. Glagolev et al.²⁸ investigated the radiation induced decomposition of aluminium hydroxide irradiated in air at 293-298 K. The hydroxide decomposition was followed gravimetrically up to 873 K. $\text{Al}(\text{OH})_3$ decayed even at 293-298 K and the radiation chemical yield of water by $\text{Al}(\text{OH})_3$ dehydration was 1. A broad singlet was registered in EPR spectra at 77 K, which probably contained several unresolved lines and a doublet with a splitting of 50.2 ± 0.5 mT, caused by stabilized H atoms with concentration of 2×10^{17} H atoms per one gram of $\text{Al}(\text{OH})_3$. H stabilized radicals at 143 K were no more observed and no EPR signal was observed at temperatures over 207 K. Shiyani et al.²⁹ investigated the possibility of the oxide-hydroxide ratio determination in Al_2O_3 - $\text{Al}(\text{OH})_3$ catalysts. Both components yield

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a broad EPR singlet signal with $g_1 = 2.009 \pm 0.005$ and $g_2 = 2.017 \pm 0.005$ and $H_1 = 2.3 \pm 0.05$ mT and $H_2 = 4.0 \pm 0.05$ mT for Al_2O_3 and $Al(OH)_3$, respectively.

The aim of our work was to determine the character of paramagnetic centers and the radiation chemical yield of paramagnetic center formation in X-ray-irradiated aluminium hydroxide at room temperature as well as the decay kinetics of these paramagnetic centers also at room temperature.

EXPERIMENTAL

Materials and irradiation

Accurately weighed sample of $Al(OH)_3$ (provided by the Research Institute of Treatment and Application of Plastics, Nitra, produced by Duslo, Šaľa, Czechoslovakia), was dried for 10 h at 433 K (at 453-473 K it dehydrates^{30,31} with formation of aluminium metahydroxide $AlO(OH)_3$) and sealed afterwards in vacuum (≈ 1 Pa) in an EPR tube made of SK-4B glass (U.S.S.R.). The size of particles was 1.2 to 1.4 μm . Unirradiated $Al(OH)_3$ gives no EPR signal. Two independent samples (0.0459 and 0.0596 g) were prepared. X-ray tube BKHV-6 (U.S.S.R.) with a Mo-anode was used for irradiation at 35 kV, 80 mA. The samples were irradiated in a Dewar flask at 293 K ($Al(OH)_3$) and 77 K (CH_3OH).

EPR spectroscopy

EPR spectra were measured by means of an RE-1306 spectrometer (U.S.S.R.) with 100 kHz HF-modulation and 0.27 mT LF-modulation; the intensity of the magnetic

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field was measured by an electronic Tesla-meter (U.S.S.R.). Mn^{2+} ions in pulverized MgO and diphenylpicrylhydrazine (DPPH, $g = 2.0036$) were used for g -factor determination and carbon standards with 2.4×10^{16} and 1.25×10^{16} spins were used for calibration of the instrument sensitivity. A nomograph for dual integration³² was used for area integration of the EPR signal. The sensitivity of the instrument was determined to be $N_{st}/S'_{st} = (2.39 \pm 0.15) \times 10^{15}$ spins per standard area unit at 293 K and $N_{st}/S'_{st} = (5.23 \pm 0.44) \times 10^{14}$ spins per standard area unit at 77 K. The paramagnetic center concentration was determined by the method³³ measuring signal amplitude of corundum used as an external standard.

Dosimetry

Dosimetry was accomplished by measuring the quantity of radicals generated by X-ray irradiation of methanol whose radiation chemical yield is known³⁴: $G(\Sigma R^{\bullet}) = (7.0 \pm 0.7)$ radicals/100 eV at 77 K. A sample of degassed methanol (0.0574 g) was used in which radicals were generated with a rate of $(1.307 \pm 0.022) \times 10^{16}$ radicals. $g^{-1} \cdot min^{-1}$ ($r = 0.9996$). That means the dose rate for methanol was $D = (29.9 \pm 3.1)$ Gy. min^{-1} .

RESULTS AND DISCUSSION

EPR spectrum identification

EPR spectrum of X-ray irradiated aluminium hydroxide (Fig. 1a) represents a wide unsymmetrical singlet (dashed line) with $\Delta H \approx 5.2 \pm 0.3$ mT, which belongs probably to the O^- ionic centers stabilized in the crystal

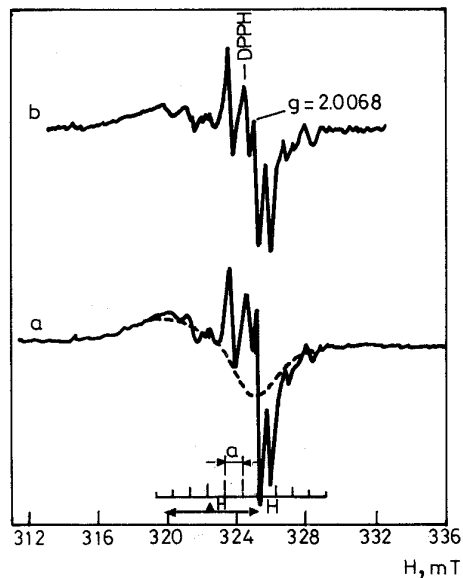
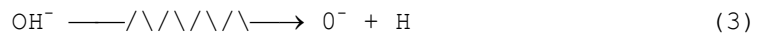
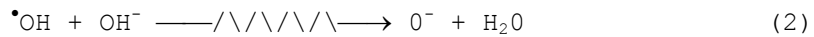
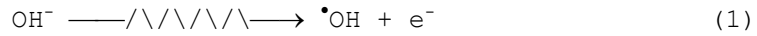


Fig. 1. EPR spectra of irradiated $\text{Al}(\text{OH})_3$ at 293 K: a - after 41 min irradiation; b - after 58 h standing at 293 K

lattice. Eleven lines of HFS can be observed in this wide singlet, which may be due to O^- electron interaction with magnetic moments of two Al^{3+} ions with a HFS constant of $a_{2\text{Al}^{3+}} = 1.03 \pm 0.03$ mT. This means that O^- type and $\text{Al}/\text{O}^- \backslash \text{Al}$ type holes were probably observed, as Shirikov et al.¹⁴ had observed in the case of γ -irradiated Al_2O_3 . In the center of EPR spectrum there is a narrow singlet with $\Delta H = 0.14 \pm 0.01$ mT obviously belonging to trapped electrons. The EPR spectrum in our case represents a superposition of several EPR spectrum types of paramagnetic centers of O^- , $\text{Al}/\text{O}^- \backslash \text{Al}$ and trapped electrons with a resulting $g = 2.0068$. The G-factor is higher than in case of a free electron, indicating that the observed spectrum contains O^- type holes and that its g-factor shift is caused by spin orbital bond

of oxygen¹⁴. In Figure 1b an EPR spectrum after 58 h of standing at 293 K is shown. The central narrow signal provided by trapped electrons decays obviously most rapidly.

It can be assumed that similarly to radiolysis of metal hydroxides of alkaline earths³⁵⁻³⁷ and also in the case of irradiation of Al(OH)₃ by ionizing radiation, the O⁻ ion-radicals arise in consequence of the following processes:



As can be seen from the EPR spectrum, a part of O⁻ centers is stabilized in the Al(OH)₃ crystal lattice and part of them interacts with Al³⁺ ions, creating O⁻ holes of the type Al/O⁻Al. Trapped electrons create an EPR signal which is observed in the center of the EPR spectrum. We did not observe H atoms at the room temperature.

Quantitative determination

Calculation of absorption mass coefficients $\left(\frac{\mu}{\rho}\right)$ of photons with various energies^{38,39} in Al(OH)₃ and methanol was used for X-ray absorption dose rate conversion in aluminium hydroxide:

$$\frac{\mu_a}{\rho} = \frac{\mu_{a1}}{\rho_1} \cdot \omega_1 + \frac{\mu_{a2}}{\rho_2} \cdot \omega_2 + \frac{\mu_{a3}}{\rho_3} \cdot \omega_3 \quad (4)$$

where μ_{a1}/ρ_1 , μ_{a2}/ρ_2 , and μ_{a3}/ρ_3 are mass absorption coefficients of each element and ω_1 , ω_2 , ω_3 are mass fractions of these elements. Using these calculated mass absorption coefficients $a_{Al(OH)_3}/\rho$ and a_{CH_3OH}/ρ and $K_{\mu/\rho}$ a relative ratio of X-ray absorption mass coefficients has been calculated:

$$K_{\mu/\rho} = \frac{a_{Al(OH)_3}/\rho}{a_{CH_3OH}/\rho} \quad (5)$$

where X-photon energies were: 10 keV = 4.84; 15 keV = 5.02; 20 keV = 3.58; 22.5 keV = 3.30; 30 keV = 2.94 and 35 keV = 2.03. As photons with energies less than 8-10 keV are absorbed in the EPR tube glass and the Mo-anode emits X-photons with maximum intensity at ≈ 22.5 keV, just this relative ratio of mass absorption coefficients was used for calculation of the $Al(OH)_3$ dose rate, i.e. a factor of 3.3. The dose rate of ionizing energy absorption in aluminium hydroxide

$\left(\begin{matrix} \bullet \\ D_{Al(OH)_3} \end{matrix} \right)$ was calculated according to the Eq. (6).

$$D_{Al(OH)_3} = K_{\mu/\rho} \cdot D_{CH_3OH} \quad (6)$$

The calculated average dose rate taken into account was $D_{Al(OH)_3} = (98.7 \pm 10.1) \text{ Gy} \cdot \text{min}^{-1}$. Since upon X-ray irradiation of $Al(OH)_3$ the paramagnetic centers arise with the rate of $2.711 \times 10^{16} \text{ spin} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ (Fig. 2), it was estimated that the initial radiation chemical yield is $G(\Sigma \text{spins}) = (4.4 \pm 0.6) \text{ spins per } 100 \text{ eV of energy absorbed}$.

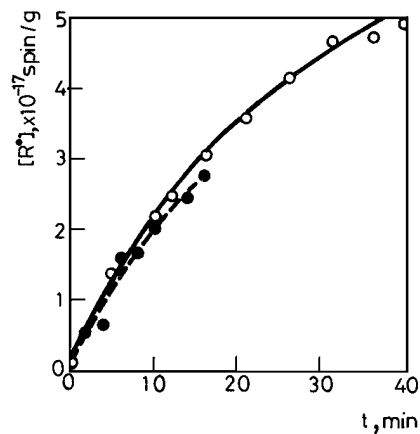


Fig. 2. Formation rate of paramagnetic centers in $\text{Al}(\text{OH})_3$ irradiated by X-rays: (o) - 0.0596 g; (●) - 0.0459 g

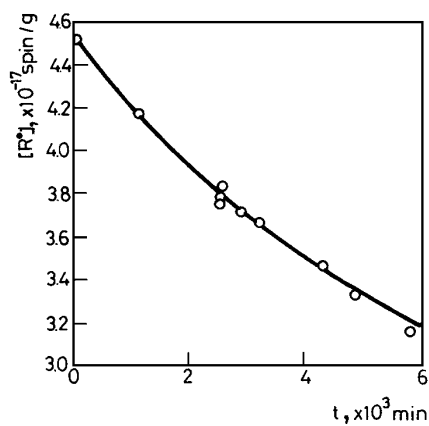


Fig. 3. Decay rate of paramagnetic centers in irradiated $\text{Al}(\text{OH})_3$ at 293 K

Decay of paramagnetic centers

Further the decrease of paramagnetic centers in irradiated $\text{Al}(\text{OH})_3$ was investigated by sample standing at 293 K (Fig. 3). It is obvious from Fig. 3 that the de-

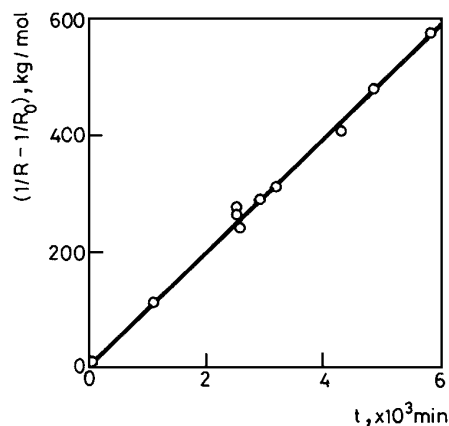


Fig. 4. Decay of paramagnetic centers in irradiated $\text{Al}(\text{OH})_3$ at 293 K (in second order reactions coordinates)

pendence is nonlinear so it was transformed to second order reaction coordinates $(1/R - 1/R_0)$ vs. t (the concentration of spins was first converted to the number of moles of spins per kg) in which the dependence is linear ($r = 0.998$) with a slope $\text{tg } a = 0.0980 \pm 0.0019$ (Fig. 4). This means that in the investigated time interval the decay of paramagnetic centers in irradiated $\text{Al}(\text{OH})_3$ can be described by the rate constant $k_2 = (0.0980 \pm 0.0019) \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ and their decay half-life is $(13580 \pm 263) \text{ min} = (9.43 \pm 0.18) \text{ days}$.

CONCLUSION

It can be concluded that by X-ray radiolysis of aluminium hydroxide at room temperature, paramagnetic centers originate, which represent ionic centers of O^- anion-radicals, $\text{Al}/\text{O}^- \backslash \text{Al}$ type holes and trapped elec-

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trons. These paramagnetic centers are sufficiently stable at room temperature (293 K) and in the time interval of 6000 min their decay can be described by a second order reaction.

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