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LETTERS TO THE EDITOR

Composition of Molecular Oxygen Thermally Desorbed from the Surface of Aluminum Oxides

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To develop procedures for evaluating the "activity" of aluminum oxides and elucidating its origin, it is important to obtain new experimental data on the state and behavior of the oxygen sublattice, primarily to reveal the relationship between the structural forms of the oxide and surface properties in sorption–desorption processes involving oxygen. The suggested spectrum of oxygen states in these processes is diverse [1].

The goal of this study was to determine the relative content in gas samples of various oxygen species thermally desorbed from such samples of alumina as boehmite, γ-oxide, and α-oxide (corundum), corresponding to structural transition from the hydrated form to the close-packed condensed structure in the course of thermal dehydration. The samples were of analytically pure grade. The structures were identified with a CAD-4 X-ray diffractometer. Thermal desorption products were analyzed by gas chromatography [2] and also by high-resolution IR spectrophotometry [3]. Comparison of the temperature-programmed desorption spectra of molecular oxygen shows that the most active desorption of oxygen occurs at 50°C. The next peak is observed at 600°C, and the last peak, at 900°C. In the series considered, γ-oxide shows the highest desorption activity. This is quite consistent with the features of crystal structure of cubic aluminum oxide, resembling the spinel structure, namely, with the presence of ~10% vacant sites in the cationic sublattice. The oxygen content (μmol g^{-1} alumina) in the gas samples obtained at 600°C was 2.2 for corundum, 3.4 for γ-oxide, and 0.42 for boehmite. Chromatographic analysis of thermally desorbed samples showed the presence of oxygen in the ground triplet state and in two electronically excited singlet states.

A characteristic feature of the gas samples thermally desorbed from the surface of all the specimens at 400°C is the absence of the most stable electronically excited state $^1\Delta_g$. The molar ratio singlet ($^1\Sigma_g^+$) : triplet in these samples was 1.3 for corundum, 1.9 for γ-oxide, and 1.5 for boehmite. γ-Oxide is characterized by the maximal content of singlet oxygen species in samples desorbed in the entire examined temperature range (50–1000°C). At 900°C, the molar ratio $^3\Sigma_g : {}^1\Delta_g : {}^1\Sigma_g^+$ is 1 : 1.8 : 1 for γ-oxide, 1 : 0 : 1 for corundum, and 1 : 1.4 : 1.1 for boehmite. The $^1\Delta_g$ form is absent in samples obtained by desorption from corundum at temperatures above 400°C.

The increased relative content of triplet oxygen in samples desorbed from boehmite is apparently due to the presence of significant amounts of water as thermal dehydration product. Water shows high efficiency in collision deactivation of electronically excited molecules [4]. The step character of the process is confirmed by simultaneous presence in the samples of the most excited ($^3\Sigma_g^+$) and intermediate ($^1\Delta_g$) states. Corundum ensures direct radiative deactivation of the singlet molecules.

The IR study of gas samples reveals the presence of well-resolved absorption bands originating from the singlet states of oxygen: $^1\Delta_g$, 1458–1456 cm^{-1} (0–1); $^1\Sigma_g^+$, 1405 and 1379–1373 cm^{-1} (0–1, 1–2). A series of bands are observed at positions corresponding to the main vibrational transitions in the triplet oxygen molecule: 1556 (0–1), 1531 (1–2), 1510–1514 (2–3), and 1485 cm^{-1} (3–4) [5]. The activity of these molecules is due to polarization in the course of deactivation of singlet states. The intensity ratio of the IR bands is consistent with the results of the chromatographic analysis. The IR spectra also reveal the presence of small amounts of the radical ions O_2^- and O_2^+ and of the O_2^{2-} ions (1070–1145, 1870–1880, 800–900 cm^{-1}). Detection of electronically excited molecules in samples obtained at relatively low temperatures (20–200°C) suggests the existence of long-lived singlet oxygen states on the oxide surface.

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