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LETTERS TO THE EDITOR

Influence of the Nature of Alumina on the State of Oxygen on Its Surface

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Analysis of the state of the oxygen sublattice of the alumina surface layer is important for solution of such urgent problems as preparation of high-performance catalysts, solid electrolytes, and high-temperature superconductors. Manifestation of the structural features of various oxides in the functional composition and set of states of surface oxygen can be studied with such series of phases as boehmite, γ-alumina, and corundum, reflecting transition from hydroxide through defective spinel to hcp structure. In our study we used high-resolution IR spectrophotometry (IKS-25M). Samples of similar pore structure and dispersity (S_{sp} ~20 $m^2\ g^{-1}$; 100 mesh) were applied to a thin (~5 μm) cellulose film. The spectra were recorded relative to the initial film, with digital signal processing. Comparison of the spectra in the range of stretching vibrations of the hydroxy groups shows that for all the samples at least ten types of surface groups can be distinguished, giving rise to strong resolved absorption bands (3799, 3768*, 3757, 3751, 3748, 3745, 3740–3737, 3732, 3720*, and 3700* cm^{-1}).

The bands marked with an asterisk correspond to the centers of broad weakly structured absorption bands whose presence distinguishes γ-alumina from corundum and boehmite. The observed number of bands exceeds by a factor of two the number of nonequivalent isolated hydroxide ions according to the Peri model [1]. The fundamental band, common for all the samples, is that at 3748–3745 cm^{-1}, which in the case of γ-alumina is a doublet with approximately equal intensity of the components. In the spectra of the other samples, the long-wave component prevails. In the range 3600–3700 cm^{-1}, the spectra are similar, exhibiting a well-resolved vibration pattern of hydroxy groups and water molecules perturbed by hydrogen bonds. The bands in the spectrum of γ-alumina are by a factor of more than 2 stronger than in the spectra of the other samples.

The spectra reveal well-resolved absorption and emission activity of various states of molecular oxygen. To the triplet state ($^3\Sigma_g$) of molecular oxygen on the corundum surface corresponds a strong emission band at $\bar{\nu}_{max}$ 1557 cm^{-1}. To oxygen on the surface of γ-alumina and boehmite correspond weaker absorption bands at the same frequency. The ratio of the integral intensities of the bands in the series corundum–γ-alumina–boehmite is 3 : 2 : 1. The electronically excited state $^1\Delta_g$ on the corundum surface is responsible for a strong absorption band at 1457 cm^{-1} (0–1), observed also in the spectra of γ-alumina and boehmite. The ratio of the band intensities is the same as that determined for the triplet oxygen. For corundum, in the range of vibrational activity of the singlet state $^1\Sigma_g^+$ (1405–1300 cm^{-1}), there is a broad strong emission band with a maximum at 1365–1380 cm^{-1}. The spectra of γ-alumina and boehmite in this range contain a set of well-resolved absorption bands (1405, 1375, 1345 cm^{-1}) corresponding to vibrational transitions in the singlet molecule ($^1\Sigma_g^+$). These bands are by an order of magnitude less intense than the emission band observed with corundum.

The corundum surface is characterized by the highest concentration of singlet states whose polarizing effect determines the vibrational activity of triplet oxygen molecules. A striking feature of the spectra is the presence of strong absorption (corundum) and emission (boehmite, γ-alumina) bands at 2360 cm^{-1}, which can be assigned to vibrational transitions in polarized dimeric molecules; this assignment is supported by AM1 simulation [2]. The absorption bands of surface-polarized molecular nitrogen, which should lie below 2330 cm^{-1} [3] (at 2202 cm^{-1} according to [1]), were not detected. A characteristic feature of "active" alumina and boehmite is a strong absorption maximum at 668 cm^{-1} corresponding to individual peroxides.

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Thus, the surface of the aluminum oxides considered is characterized by stable existence of electronically and vibrationally excited molecular, dimeric, radical ion, and peroxide oxygen species, whose concentration is determined by the nature of the oxide.

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