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The Stabilization of O_2^- on γ-Al_2O_3

The EPR spectra of the superoxide ion, O_2^-, on various surfaces have been extensively cataloged (*1*). They are characterized by $g_{\parallel} > g_{\perp}$ with the value of $g_{\parallel}$ varying with the oxidation state of the ion on which the superoxide ion is adsorbed. The principal values of the g tensors for the other oxygen radicals are sufficiently different from the values expected theoretically for the superoxide ion that the simple determination of the g values and the general shape of the powder spectrum are evidence enough to identify the superoxide ion provided, of course, a source of oxygen is present.

Despite the widespread occurrence of O_2^- on surfaces, harsh preparative conditions had been necessary to produce the O_2^- and to stabilize it on the γ-Al_2O_3 surface. In the two reported cases (*2*, *3*), γ-irradiation of the γ-Al_2O_3 in the presence of oxygen was necessary for the production and subsequent stabilization of the O_2^- surface signal characterized by $g_{\parallel} = 2.038$ and $g_{\perp} = 2.006$. They also report a hyperfine splitting of 3.6 G on the $g_{\perp}$ resonance. Quite recently Che *et al.* (*3*) reported a surface O_2^- spectrum on γ-Al_2O_3 characterized by the following parameters: $g_z = 2.039$, $g_y = 2.009$, $g_x = 2.004$, and $A_z = 5.4$, $A_y = 3.6$, and $A_x = 5.2$ G.

The work reported in this note involves the production and stabilization of the O_2^- ion on γ-Al_2O_3 during the decomposition of N_2O at elevated temperatures. The preparative conditions are much less severe than the γ-irradiation previously required.

The alumina in this investigation was RA-1 γ-Al_2O_3 obtained from Reynolds Metals Company with a reported surface area of 225 m^2/g BET and an iron impurity content of approximately 0.05%. Air Products medical-grade N_2O was used without further purification. A Varian E-3 spectrometer was used to collect data at room temperature and at liquid nitrogen temperature. A Varian E-9 and an Air Products Cryotip EPR shroud were used to collect data at 13°K using liquid helium. All reported g values are relative to DPPH ($g = 2.0036$).

The samples were prepared according to the following procedure. RA-1 γ-Al_2O_3 was vacuum treated (nominal 10^{-3} Torr vacuum) for 2 hr at 873°K. While at 873°K, N_2O was passed over the γ-Al_2O_3 for an additional 2 hr. With the gas flowing the sample was cooled to room temperature. In order to achieve the best possible resolution of the spectra it was found advanta-

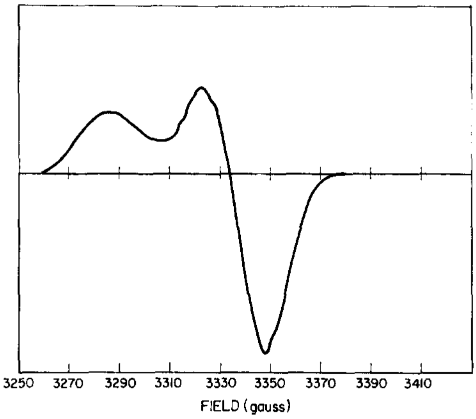

FIG. 1. EPR spectrum of superoxide ion on γ-Al_2O_3. Spectrum was recorded at 77°K. Sample has had excess oxygen removed by pumping at 195°K.

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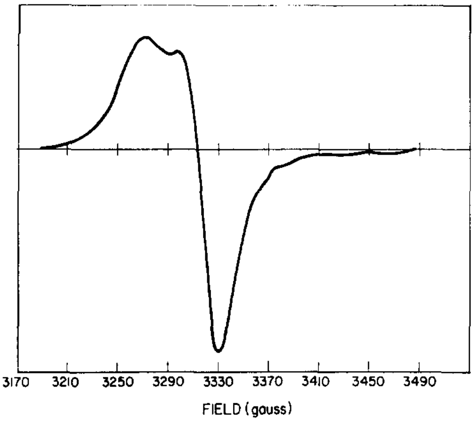

FIG. 2. EPR spectrum of superoxide ion on γ-Al_2O_3 at 77°K which shows the broadening effects of oxygen on the resolution of the spectrum.

geous to evacuate the sample further at 195°K to a nominal pressure of 10^{-3} Torr for 2 hr. The sample was then sealed in the EPR tube at this temperature and pressure. The spectrum of this sample recorded at 77°K is shown in Fig. 1. This latter treatment removes loosely bound adsorbed oxygen which, along with N_2, is a product of the homogeneous thermal decomposition of N_2O(*4*). If this oxygen is not removed by pumping at 195°K, significant broadening of the signal occurs as shown in Fig. 2.

The increase in the EPR linewidth of O_2^- upon increasing oxygen pressure over the sample has been observed by others (*5*, *6*). Interestingly, despite the presence of oxygen this broadened signal is resolved at 13°K and is identical to the spectrum shown in Fig. 1. Apparently, at the elevated temperatures the signal is collisionally broadened by gas-phase oxygen. This explanation is strengthened by the presence at 77°K of the characteristic gas-phase EPR spectrum (*7*) of oxygen, a complex multiline resonance pattern extending over several thousand gauss. The sample which has been evacuated at 195°K does not show this oxygen spectrum.

The presence of the superoxide ion, which has been stabilized on γ-Al_2O_3 after the above treatment is confirmed by its characteristic EPR spectra shown most clearly in Fig. 1. As mentioned above, the principal values of the g tensors for the other possible oxygen radicals, O^-, O_3^-, and O_2^+ (*1*, *8*), rule out their existence as do the g values for the common oxygen radicals of nitrogen (*8*).

The O_2^- spectrum is readily visible at room temperature if the sample is pumped at 195°K. On the other hand, the signal height is less than doubled and the width is unchanged on cooling the sample from 300 to 77°K. There is no resolvable hyperfine structure observed. The spectrum of the RA-1 γ-Al_2O_3 as received from the manufacturer and after the vacuum treatment at 873°K for 2 hr described above is devoid of the O_2^- resonances at 77°K in this particular region of the spectrum. Likewise, an RA-1 γ-Al_2O_3 sample which is prepared as the N_2O sample described above, but in the presence of O_2 rather than N_2O, is devoid of the O_2^- signal.

From Fig. 1, g values of $g_{\parallel} = 2.040$ and $g_{\perp} = 2.006$ can be assigned readily to this powder spectrum. These are in excellent agreement with those previously reported (*2*, *3*) for O_2^- on irradiated γ-Al_2O_3. The general correctness of these g values was substantiated, and the values refined by computer simulating the powder spectra displayed in Fig. 1 using the algorithm of Toy *et al.* (*9*). The best fit values resulting from a nonlinear least-squares fitting procedure were $g_z = 2.040$, $g_y = 2.008$, and $g_x = 2.004$ using a Gaussian linewidth of 19.5 G. It was not possible to fit the spectrum assuming axial symmetry despite the general appearance of the spectra. An improved fit results if a model spin Hamiltonian of the form,

$$\mathcal{H} = \mu_\beta \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H} + \vec{S} \cdot \overleftrightarrow{A} \cdot \vec{I}, \tag{1}$$

which includes the effect of an unpaired electron interacting with the Al nucleus ($I = \frac{5}{2}$), is used to simulate the spectra

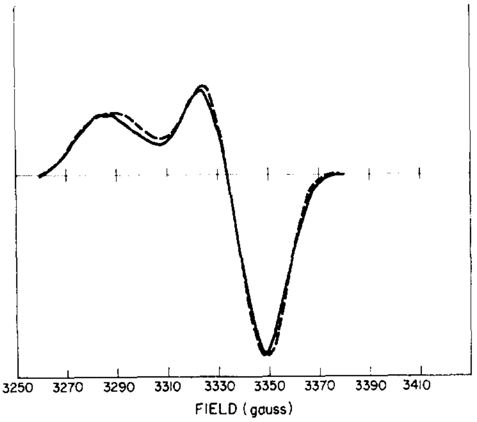

FIG. 3. Experimental spectrum of the superoxide ion along with simulated spectrum (solid curve) resulting from a nonlinear least-squares fit of the data to a Gaussian line shape and the following parameters: $g_z = 2.040$, $g_y = 2.008$, $g_x = 2.004$, and $A_z = 4.9$, $A_y = 3.8$, $A_x = 3.7$ G.

displayed in Fig. 1. If the g values are set equal to those determined above and the hyperfine splitting constants are then varied to achieve the best fit, the following parameters result: $A_z = 4.9$, $A_y = 3.8$, and $A_x = 3.7$ G with Gaussian linewidth of 13.6 G. The results of this fit are shown in Fig. 3. Not surprisingly, the inclusion of hyperfine splitting in the fitting procedure dramatically improves the fit, while at the same time generates values in close agreement with the case where the actual splitting has been resolved (*2*). However, since the hyperfine splitting has not been resolved in this case, a phenomenon with the same angular dependence as the hyperfine cannot be excluded. One possibility would be the presence of another closely related site with slightly different g values. Regardless of whether hyperfine coupling is included in the simulation, the fit indicated a decidedly Gaussian character to the lineshape of the sample which has been evacuated at 195°K to remove excess gas-phase oxygen. Because the superoxide at 77°K is apparently immobile and dipole–dipole broadened, it displays a Gaussian line shape. Likewise, since the superoxide ion in the sample which has not been pumped at 195°K, and, therefore contains excess oxygen, is collionsionally and dipole–dipole broadened at 77°K, the line shape is decidedly Lorentzian in character. At 13°K where the collisional broadening is no longer a consideration, the line shape is best described as Gaussian.

The appearance of the O_2^- ion from the thermal decomposition of N_2O is surprising. Studies of this decomposition on an irradiated ZnO surface (*10*) have revealed the stabilization of the O^- ion. It was proposed in this study that the N_2O acted as an electron sink, trapping the free electrons at the surface via a reaction of the type,

$$N_2O + e^- \rightarrow N_2 + O^-. \qquad (2)$$

The subsequent reaction of the O^- ion with another molecule of N_2O, according to the reaction,

$$N_2O + O^- \rightarrow N_2 + O_2^-, \qquad (3)$$

was not observed. Similar behavior was observed on pure Fe_2O_3 (*11*) activated *in vacuo* at 673°K. Tench and Lawson (*12*) observed the formation of O^- from the reaction of N_2O with electrons trapped on the surface of MgO. This O^- further reacted with O_2 to produce O_3^-. In the present study there has been no indication of the formation of the O^- ion or the O_3^- ion. Likewise, there has been no indication of electrons, trapped or free, on the surface prior to the admission of N_2O. Clearly, further work which might consider the possible involvement of the impurity iron as an electron donor is necessary before a mechanism can be postulated for the formation of the O_2^- ion from the reaction sequence described above. Nonetheless, the demonstrated ease of production and stabilization of the superoxide ion on γ-Al_2O_3 via N_2O decomposition promises to be exploited further in studies where this ion can function as a molecular probe of the γ-Al_2O_3 surface.

SUMMARY

The techniques for preparing and stabilizing the superoxide ion, O_2^-, from the thermal decomposition of N_2O over γ-Al_2O_3 are reported. The characteristic EPR spectrum of this surface-stabilized species is discussed along with the effects of adsorbed oxygen on the EPR line shape. The spectrum has been simulated with the following parameters: $g_z = 2.040$, $g_y = 2.008$, $g_x = 2.004$ and $A_z = 4.9$, $A_y = 3.8$, and $A_x = 3.7$ G. The mild conditions used in the preparation of this species are emphasized.

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