The Adsorbed State of Oxygen on Zinc Oxide as Revealed by the Electron Spin Resonance Method

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The asymmetrical doublet ESR signal around $g=2.0$ obtained when a small amount of oxygen is introduced on zinc oxide has been ascribed to the adsorbed peroxy radical or to the molecular oxygen ion by several workers.[1] None of them has, however, dealt with the dynamical characteristic of this signal. It is known from the simple temperature rising method that adsorbed oxygen on zinc oxide at room temperature is transformed into at least two types, near 200 and 370°C, when subjected to gradual heating up to 500°C.[2] Such changes in the adsorbed type has now been investigated by the ESR method. It has been found that the doublet signal is transformed into a singlet one above 170°C and that it decays at much higher temperatures.

The sample tube for the ESR measurement was connected, by means of several flexible joints, to a high vacuum apparatus. The Pirani gauge was affixed close to the tube so that the pressure of the oxygen inside could be measured during the ESR measurement. A sample of zinc oxide placed in the tube was outgassed at 500°C for one hour, and then oxygen (10^{-1} mmHg) was introduced onto the adsorbent kept at room temperature. After having been shortly pumped off, the sample was heated at a rate of about 10°C per min.; changes in the doublet signal due to heating were followed in situ, while the pressure inside

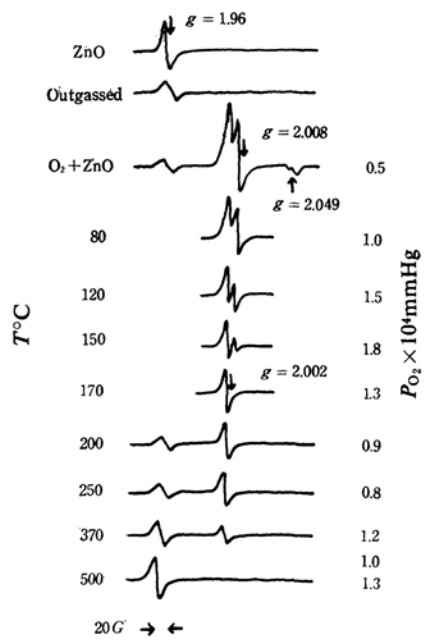

Fig. 1. ESR Spectra for O_2 on ZnO. The spectra were observed at the temperature shown by the respective figure on the left, except for those of the upper three and the last three, which were determined at room temperature. The pressure of oxygen inside the tube, as shown by the figure on the right, ranges from 0.5×10^{-4} to 2×10^{-4} mmHg.

1) E. V. Baranov, V. E. Kholmagorov and A. N. Terenin, *Dokl. Acad. Nauk SSSR*, **146**, 125 (1962); Y. Fujita and T. Kwan, *Shokubai (Catalyst)*, **5**, 206 (1963); R. J. Kokes, *Proceedings of The Third International Congress on Catalysis*, North-Holland Pub. Co., Amsterdam (1965), p. 484.

2) M. Sedaka, N. Dokoshi, Y. Fujita and T. Kwan, presented at the 18th Annual Meeting of the Chemical Seciety of Japan, April, 1965. Cf. T. Kwan, "Hikari-kagaku to sono Oyo" Kagaku-Dojin, Kyoto (1965), p. 109.

the tube was being measured simultaneously. The ESR measuement was made with a JEOL-type P-10 spectrometer at the X band. The signals obtained, along with the heat treatment, are shown in Fig. 1.

Here we shall confine ourselves only to the change in the doublet signal at $g=2.008$, 2.002. The transition of the doublet to a singlet at $g=2.002$ is apparent. It took place near 170°C when the second type of adsorption* set in, as judged from the pressure change. This singlet was stable for a time beyond 250°C, but it appeared to decay near 370°C. The decay seemed to be associated with the appearance of the third type of adsorption.**

A singlet signal of the same g-value and of the same shape as that mentioned above was found to appear even when N_2O was introduced onto the outgassed zinc oxide sample at room temperature. Thus, it seems very likely that the transition of the doublet to the singlet is due to the dissociation of the molecular oxygen ion into atomic species as O^-.

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* By the first type will be meant the oxygen adsorbed at room temperature.

** The third type is most probably O^{2-}, which is non-paramagnetic. Thus, the appearance of this type may mean the recovery of the original zinc oxide; this suggestion agrees with the resemblance of the ESR spectra between the initial and the final state.