

adsorbed water on the catalyst surface (3, 5).

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Effect of Sorbed Oxygen and Carbon Monoxide on the ESR of Zinc Oxide

We wish to report exploratory electron spin resonance (ESR) measurements which show that the interaction of oxygen and carbon monoxide with a zinc oxide catalyst can be studied by varying the gas phase. The observed resonance changes are tentatively interpreted in terms of the formation of sorbed paramagnetic species and changes in the electronic properties of the solid. In addition, we believe that our experiments suggest the possibility of determining the distribution of certain solid-state defects between the bulk and the surface of the solid.

The ZnO (S.P. 500, New Jersey Zinc Company) sample was mounted in a conventional high vacuum system. For the pretreatment heating procedure the portion of the stationary vacuum system containing the sample was surrounded by a movable furnace. Without opening the vacuum system the furnace could be replaced by the ESR cavity. The ESR measurements and the exposure of ZnO to ambient atmospheres were all made at room temperature. The Varian V-4502 spectrometer was operated at 9380 Mc/sec with a dual cavity and a 12-inch magnet. The multipurpose sample cavity employed 100 kc field modulation; the reference cavity employed 400 cps field modulation and was equipped

with a standardized pitch sample for the calibration of instrumental sensitivity and gyromagnetic ratio (g) or with a $10^{-2} M$ $MnSO_4$ solution for the determination of the magnetic field dispersion. The absolute values of g were determined to within $\pm 0.1\%$. The ESR measurements shown in Fig. 1 were made using a power level of 44 mwatts, at which power saturation effects, present for the $g = 2.004$ line but not for the $g = 1.96$ line, were shown not to account for the differences produced by varying the gas phase from vacuum to oxygen. The relative ESR signal heights were determined from the peak-to-peak heights of the derivative curves and were normalized for instrumental gain; all other ESR instrumental parameters were held fixed. The signal height was assumed to be proportional to the number of spins, since the line width remained sufficiently constant.

Figure 1 shows the effect on one sample of ZnO of a sequence of ambient atmospheres on the relative signal heights of three resonance signals measured as a function of time after pretreatment. The complete sequence of ambient gas exposures following pretreatment was carried out on five samples. The direction of the signal height change, i.e., increase, decrease, or no

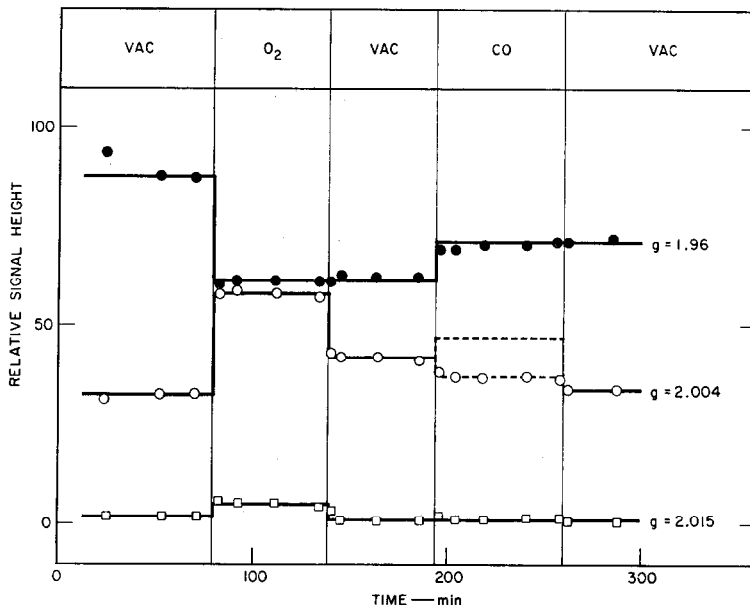


Fig. 1. Relative ESR signal heights of ZnO at room temperature in a sequence of ambient atmospheres as a function of time after pretreatment. Exposure at room temperature to the ambient atmospheres: Vac at 0.1μ , O_2 at 35μ , and CO at 1000μ Hg. Pretreatment: $550^\circ C$ in vacuum for 5 min. For a resonance at $g = 2.004$, dashed line indicates range of values observed in experiments upon exposure of the ZnO to CO. Microwave power, 44 mwatts.

change, on varying the gas phase was reproducible except for the $g = 2.004$ line going from vacuum to CO, for which the limits of the observed values are indicated by the dashed line. There was some variation in the relative heights of the three resonance signals from sample to sample which can be attributed to minor variations in pretreatment procedure.

Pretreatment of ZnO by heating to about $550^\circ C$ for 3–5 min in vacuum resulted in two strong resonances with g values of 1.96 and 2.004 and a very weak resonance with a g value of 2.015; the peak heights are shown in Fig. 1. We found that prolonged heating in vacuum causes the $g = 2.004$ line to become very weak. It should be noted that all three resonances were always relatively sharp; the line widths were below 6 gauss.

For oxygen sorption-desorption both irreversible and reversible behavior of signals are shown in Fig. 1. The decrease of the $g = 1.96$ line on oxygen sorption is irreversible on evacuation, while the in-

creases of the signal heights of the $g = 2.004$ and 2.015 lines on oxygen sorption are largely reversible.

For carbon monoxide sorption on ZnO, which had undergone the sequence: pretreatment, O_2 exposure, and evacuation as shown in Fig. 1, the $g = 1.96$ signal height always increased irreversibly. The behavior of the $g = 2.004$ signal was variable on carbon monoxide sorption; sometimes it exhibited an increase, or sometimes a decrease as shown for the sample whose results are plotted in Fig. 1. However, on evacuation, subsequent to the carbon monoxide sorption, the signal height of $g = 2.004$ line always decreased. Carbon monoxide produced no detectable change in the extremely weak $g = 2.015$ signal.

At this stage of our investigation we believe that certain limited conclusions can be drawn and tentatively we propose an interpretation of the spectral changes.

The resonance signals at $g = 2.004$ and 2.015, resulting from short-time pretreatment procedure, have not been previously

reported. The line at $g = 1.96$ was obtained by Kokes (1) by prolonged heating. The origin of the $g = 1.96$ signal has been variously assigned to un-ionized donors and/or conduction electrons (1), to oxygen ion vacancies (2), and to mobile electrons either in conduction and/or in shallow donor bands (3). We have no evidence at present from which to deduce the origin of the lines at $g = 2.004$ or 2.015 ; however, these g values suggest assignments to essentially free electrons, e.g., conduction electrons or paramagnetic species.

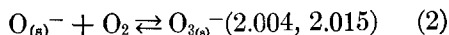
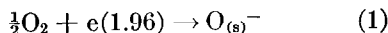
Our first conclusion concerning oxygen based on the peak height changes on sorption-desorption (irreversible for the $g = 1.96$ signal and reversible for the $g = 2.004$ and 2.015 signals) is that the changes can be attributed to well-known (4, 5) irreversibly and reversibly sorbed oxygen, respectively. It is unlikely that uncharged, sorbed molecular oxygen contributes significantly to our observed ESR spectra since the ESR spectrum (6) of oxygen sorbed on porous glass is very broad (~ 2000 gauss). Under the conditions of our experiments, gas phase molecular oxygen exhibited only one resonance, at about $g = 1.97$.

Kokes (1) found a decrease in the intensity of the $g = 1.96$ signal on oxygen sorption which he attributed to a decrease in number of solid-state electrons accompanying the formation of a sorbed oxygen ion, $O_{(s)}^-$. We found that increasing the O_2 pressure from 35 to 1000 μ resulted in only a very small additional decrease in the peak height of the $g = 1.96$ signal. The existence of a limited decrease for the $g = 1.96$ signal leads to the conclusion that it is possible to determine separately for the surface and for the bulk the concentrations of certain types of solid-state defects.

Our third conclusion is that the reversible increase of both the $g = 2.004$ and 2.015 signal heights on oxygen sorption could be caused by reversible, sorbed paramagnetic oxygen species. This conclusion is supported by the observation that line broadening of the $g = 2.004$ signal occurred at a high O_2 pressure. An increase of the O_2 pressure from 1 to 18 mm caused the

line to broaden about 50%; upon evacuation the original line width was restored. The existence of this reversible broadening is taken as evidence that the surface-sorbed species are subject to dipolar relaxation by the gas molecules. It is possible that the simultaneous changes in the signals at $g = 2.004$ and 2.015 are due to a single, reversibly sorbed paramagnetic species such as $O_{3(s)}^-$ or $O_{2(s)}^-$. This suggestion is substantiated* by the reported (7) anisotropic g values of 2.004 and 2.015 for ozonate salts and 2.002 and 2.175 for superoxide salts.

The interpretation of the oxygen results that we presently favor can be summarized by Eqs. (1) and (2). Our assignment of the g values is given in parentheses after the species.



The results with CO are included in this preliminary report to illustrate that experimentally significant ESR changes can be observed with gases other than oxygen. The signal height changes accompanying the CO exposure of the ZnO and subsequent evacuation are only tentatively interpreted as spin concentration changes, since at this time the detailed investigation of possible power saturation and line width effects is still in progress. It is premature to speculate on the extent to which resonance changes caused by CO shown in Fig. 1 are due to reaction with irreversibly sorbed oxygen.

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* After submitting the manuscript Professor Richard J. Kokes was kind enough to send us his unpublished ESR results which indicate that peroxy linkages can arise from O_2 sorption on ZnO.

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