JOURNAL OF CATALYSIS 5, 314–324 (1966)

ESR Investigation of Gas–Solid Interactions

The Oxygen–Zinc Oxide System*

K. M. SANCIER

From the Solid State Catalysis Laboratory, Stanford Research Institute, Menlo Park, California

Received July 1, 1965; revised August 30, 1965

ESR measurements were combined with determinations of the amount of oxygen adsorbed or desorbed on ZnO in order to investigate the relationship between the solid state electronic properties of a semiconductor catalyst and the amounts and the nature of the adsorbed oxygen species.

The ESR spectral study indicates paramagnetic species associated with solid state donors ($g = 1.96$) and those associated with various adsorbed oxygen species ($g \sim 2$). The quantitative studies led to a tentative identification of the oxygen surface species and assignment of g value: O_2 ($g = 2.04$), O^- ($g = 2.010$), and O_2^- (no observable resonance). The electron transfer occurring between the solid and the various adsorbed species was studied in detail in an adsorption–desorption cycle.

Pretreatments such as heating the ZnO in vacuum or in oxygen were found to affect the ESR of the ZnO, the amount of oxygen adsorbed, and the character of the adsorbed species. With the ESR results as criteria of adsorption and charge transfer, appreciable oxygen adsorption occurs only when donor states are present in ZnO.

INTRODUCTION

This research is directed toward a fundamental problem of heterogeneous catalysis: the influence of the catalyst's solid state properties on the nature of the surface-adsorbed species. The goal of the investigation is to determine the identity of oxygen species adsorbed on ZnO and the effect of catalyst pretreatment on the various adsorbed species. It is of particular interest to investigate how the nature and amount of the various adsorbed species depend upon the electron transfer process between the bulk of the semiconductor and its surface. Toward this goal the results of the electron spin resonance (ESR) technique are combined with a simultaneous measurement of the amount of gas adsorbed or desorbed.

The ESR technique has been used to study gases adsorbed on solids (*1–8*), and to identify the catalytically active centers in solids (*9–11*). In our laboratory we have recently shown that ESR can be used to study electron transfer between the solid and the adsorbed species (*12*).

There are several reasons for selecting the ZnO-oxygen system for the current investigation. Our preliminary work (*12*) indicates that ESR would provide valuable information regarding the properties of reactants adsorbed on ZnO, and some recent studies have also dealt with certain aspects of the ESR of this system (*13–16*) and of ZnO itself (*17, 18*). Also the extensive physicochemical research on the ZnO-oxygen system is expected to provide a suitable background.

EXPERIMENTAL

Powdered ZnO (S.P. 500, New Jersey Zinc Co.) was situated in a vacuum apparatus so that ESR measurements could be made while the sample temperature and the ambient gas were independently varied. The apparatus consists essentially of a quartz tube (0.3-cm ID), metal valves (bellows), a

---

* This research was supported by several industrial companies and by Stanford Research Institute.

Pirani gauge, and a trap that could be cooled in liquid nitrogen. This apparatus could be disconnected from the gas-vacuum system at an O-ring joint and could be moved as a unit in order to replace the ZnO (about 0.15 g of ZnO as a 3-cm-long column). Known quantities of oxygen were admitted or removed from the ZnO chamber by using the calibrated volumes of the ZnO and Pirani chambers (about 15 cm^3 each) and the measured pressure (to as low as 1×10^{-5} Torr). The adsorption–desorption measurements were corrected to include the influence of a small air leak of 10^{-6} Torr cm^3 sec^{-1}. The temperature of the ZnO could be adjusted over the range of 100° to 570°K by a temperature controller (Varian) mounted in the ESR cavity. Temperatures up to about 800°K were achieved with a microfurnace, the use of which required removal only of the ESR cavity. Oxygen gas (Matheson) was of standard purity.

The ESR measurements were made with a Varian V-4502 X-band spectrometer with a dual cavity (TE_{104} mode, $Q = 9000$) and a 12-inch magnet, and measurements were made with a low-power bridge. The sample cavity employed 100-kc/sec field modulation. The other cavity employed 200-cps field modulation, and was equipped either with a sample of 0.1% pitch in KCl (Varian) or with a solution of 10^{-3} M $MnSO_4$ for calibrating instrumental sensitivities and evaluating g values. The measurements were all made at the same field modulation amplitude of about 5 gauss for the 100-kc channel; the microwave power was held constant at about 10 mW, except in power saturation studies; and the signals were normalized to an arbitrary instrumental gain. The ESR cavity–waveguide assembly was held in place by a brass jig which permitted vertical movement or removal of the cavity assembly.

Certain sample treatments altered the electrical conductivity of the ZnO and thereby altered the cavity Q and the ESR sensitivity. Corresponding changes were produced in the values of I_g, M_g, and I_p (for given settings of gain and modulation amplitude), where I_g is the peak-to-peak height of the recorded first-derivative curve, M_g is the first moment which is proportional to the number of unpaired spins, and the subscript g indicates the g value of the ESR line of the sample. I_p is the peak-to-peak height of the recorded first-derivative curve of the 0.1% pitch sample, and its value was used to correct for changes in cavity Q by calculating the normalized signal intensity $I_g^* = I_g/I_p$ and the normalized first moment of the derivative curve $M_g^* = M_g/I_p$. The values of M_g^* have also been normalized to 1 g of ZnO.

Absolute spin intensity calibrations were made using 1.1×10^{-3} g DPPH ground with 1 g of ZnO; 3.6×10^{-3} g of DPPH in 100 ml of benzene; and ZnO doped with 6.8×10^{17} indium atoms per cm^3 (resonance at $g = 1.96$). DPPH was used as supplied by Eastman Chemical Co., and the ZnO:In and its In concentration were supplied by the New Jersey Zinc Co. These preparations were introduced into the 0.3-cm ID quartz tube and the first moment of the resonances determined. All results were normalized as described above; with ZnO an arbitrary packing density was employed. For the three preparations it was determined that the spin intensity calibration factor $S = 1.2 \pm 0.6 \times 10^{15}$, and the product SM_g^* provides the number of spins/g ZnO for a given resonance.

RESULTS

ZnO Pretreatment

ESR examination shows that pretreatment of ZnO affects both the electronic properties of the solid and the nature and quantities of adsorbed oxygen species. Of principal interest are the ESR signals at a g value of 1.96 and at g values in the range of 2.0033 to 2.04. The 1.96 line is attributed to mobile electrons in either the conduction band and/or a shallow donor band (*14, 15, 17, 18*) and probably arises from defects such as interstitial zinc and/or oxygen ion vacancies (*14–18*). The 2.0033 to 2.04 lines appear to be associated with adsorbed species, some of which are oxygen; the probable identification of some of these lines has been discussed (*12, 13, 15, 16*). Two other signals were observed in ZnO (both in Mallinckrodt, reagent grade, and in New Jersey Zinc Co., S.P. 500): a weak, narrow line at $g = 2.0028$ (~5 gauss) and a broad line at $g = 2.10$ (~500 gauss); since these signals were unaffected by pretreatment or oxygen adsorption, they will not be considered further.

Pretreatments such as heating in vacuum or in oxygen result in characteristic changes in the ESR spectrum of ZnO. The temperature and the duration of pretreatment determine not only the magnitude of these changes but also the subsequent effect of oxygen adsorption. Some typical results are summarized in Table 1 (reference is made to this Table by the letters in brackets). Because of the difficulty of computing the contributions of overlapping lines (in the range 2.033 to 2.04) the results in this Table are useful mainly for understanding trends in behavior. Some typical ESR spectra are shown in Fig. 1.

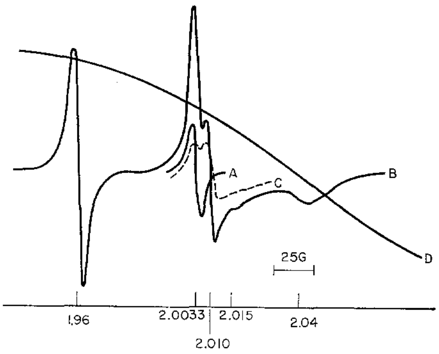

FIG. 1. ESR Spectra of ZnO at 290°K. (A) Vacuum-heated at 770°K for 5 min, and then (B) exposed to 0.05 Torr oxygen. (C) Fresh ZnO vacuum-heated at 770°K for 10 min and exposed at 290°K to 10^{-3} Torr oxygen, and then (D) exposed to 760 Torr oxygen (ordinate expanded by factor of 5).

In general, desorption of the ZnO by heating in vacuum increased the first moment of the 1.96 line and decreased that of the lines with g values in the range of 2.0033 to 2.04 [A to D]. Subsequent oxygen adsorption decreased the first moment of the 1.96 line which then approached a lower limit after sufficient adsorption. Pretreatment by heating in oxygen tends to destroy the 1.96 line, an observation reported in earlier work (*13*, *15*). The relatively long period of vacuum heating then required to restore the 1.96 line [E], compared with that required for untreated ZnO [B], indicates that donor defects destroyed by the thermal oxidation were slowly reformed.

A crude desorption measurement showed that the untreated ZnO was covered with about a monolayer of adsorbed gases, chiefly CO_2, H_2O, and O_2, approximately in the ratio 5:5:1. For this measurement the gases desorbed upon heating the ZnO to 700°K (after initial outgassing for several minutes at 290°K to remove weakly adsorbed gases) were qualitatively analyzed by the pressure rise in a system of known volume containing a trap whose temperature was maintained at 77°, 193°, or 290°K. The ESR results also show that species other than oxygen had been adsorbed on untreated ZnO [B to D]. For example the 2.003 line, which is assumed to be due to such species, appeared during vacuum heating but essentially disappeared after extensive desorption [B to D].

In general for the ESR lines with g values in the range of 2.0033 to 2.04 the intensities are increased by oxygen adsorption. In order for these ESR lines to be observed, it is necessary that the ZnO exhibit a 1.96 line prior to the adsorption. For example, the 2.0033 to 2.04 lines do not appear when untreated or oxidized ZnO is exposed to oxygen [A and F].

The changes of the ESR spectrum depend upon oxygen pressure as well as pretreatment of the ZnO. After longer periods of vacuum heating of the ZnO, oxygen adsorption resulted in lower intensities of the 2.0033 line relative to the 2.010 line [B to D]. After prolonged vacuum heating and for oxygen pressures less than 10^{-2} Torr, oxygen adsorption at 290°K was essentially irreversible, as judged from the fact that the 2.0033 and 2.010 lines could not be decreased by subsequent evacuation at 290°K. A similar observation was reported by Kokes (*15*). At higher pressures the 2.015 line became weakly evident (Fig. 1, curve B). At still higher oxygen pressures (>1 Torr) the lines in the range of $g = 2.003$ to 2.04 broadened, in a way similar to other observations (*12*, *15*).

The 2.04 line was observed for oxygen pressures equal to and greater than about

TABLE 1

Typical Effects of Pretreatment and of Oxygen on the ESR of ZnO

Treatment[a]	Normalized first moment			
	$M^*_{1.96}$	$M^*_{2.0033}$	$M^*_{2.010}$	$M^*_{2.04}$
[A] Untreated: Unchanged by 760 Torr O_2 3 days or by subsequent evacuation.	0.1	—	—	—
[B] Vac., 600°K, 10 min	4	0.5	—	—
(1) 0.05 Torr O_2	1	1.0	1.5	—
(2) 10^{-3} Torr O_2	1	0.8	0.8	—
[C] Vac., 770°K, 5 min[b]	5	0.3	—	—
(1) 0.05 Torr O_2[c]	1	2	1.5	1
(2) Vac., heat, 370°K	1	1	0.7	—
[D] Vac., 770°K, 10 min	6	—	—	—
(1) 10^{-3} Torr O_2[d]	1	0.1	1.4	—
(2) 0.05 Torr O_2	0.8	0.1	1.5	1
(3) 10^{-3} Torr O_2	0.8	0.1	1.4	—
(4) 760 Torr O_2, 18 hr[e]	0.8	—	[f]	700
(5) 160 Torr O_2, 3 min	0.8	—	[f]	500
(6) Vac., 570°K, 1 min	2	—	—	—
[E] 760 Torr O_2, 770°K, 10 min	0.3	—	—	—
(1) Vac., 3 min	0.3	—	—	100
(2) Vac., 770°K, 15 min	0.7	—	—	—
(3) Vac., 770°K, 90 min	2	—	—	—
(4) 10^{-3} Torr O_2	0.3	—	0.5	—
[F] 760 Torr O_2, 770°K, 2.5 hr	0.1	—	—	—
(1) 760 Torr O_2, 2 days	0.2	—	—	—
(2) Vac., 3 min	0.2	—	—	—

[a] In general, the sequence of treatments proceeds from [A] to [F]. All treatments at 290°K unless otherwise noted. All ESR measurements at 290°K. Estimated reproducibility about ± 15% in a given series, and about ± 25% from one series to another.

[b] Figure 1, curve A.

[c] Figure 1, curve B.

[d] Figure 1, curve C.

[e] Figure 1, curve D.

[f] 2.010 line pressure-broadened and overlapped by 2.04 line.

0.05 Torr at which pressure $M^*_{2.04} = 1$ [C and D]. At 760 Torr oxygen the 2.04 line was intense and broad (~500 gauss) and reached one-fourth of its maximum spin intensity in about 10 min but required many hours to reach the ultimate value. Evacuation to lower pressures of such an equilibrated ZnO at 290°K resulted in a decrease of linewidth (to 25 gauss at 10^{-3} Torr) and a large increase in peak heights of the resonance, and within a period of a few minutes there was essentially no loss in spin intensity [D 4–5]. Upon thus lowering the oxygen pressure, the ensuing large increase in the peak height was used as a sensitive criterion of this type of oxygen adsorption, for example, that oxygen adsorption of this type did not occur on untreated [A] or oxidized [F] ZnO. The adsorbed species giving rise to the 2.04 line are evidently weakly adsorbed since the line intensity rapidly decreased at temperatures greater than 350°K. The broad 2.04 line exhibited considerable unresolved structure when the ZnO, after equilibration at 160 Torr oxygen, was cooled to 100°K. At this pressure the ESR lines due to gaseous molecular O_2 are not detectable because of pressure-broadening effects.

Microwave power saturation measurements were made on the various ESR signals. Over the range of about 0.1 to 50 mW, and at oxygen pressures of about 10^{-3} Torr, essentially no saturation effects were detectable at 290°K for the signals at g values of 1.96, 2.0033, and 2.010. The 2.04 line (760 Torr oxygen) showed slight but not certain saturation. The power saturation effect previously reported (*12*) for the 2.004 line applied to the reversibly adsorbed oxygen species is probably associated with CO_2 and/or H_2O surface species which had not been completely desorbed. The partially reversible intensity of the 2.0033 line due to oxygen adsorption–desorption [B and C] cannot, however, be entirely accounted for by power saturation effects.

Thus the several different ESR lines and their dependence on ZnO pretreatment and oxygen pressure indicate several types of adsorbed species, some of which are due to adsorbed oxygen. The subsequent results are primarily concerned with the oxygen species.

Adsorption–Desorption Studies

In this section quantitative results are presented in order to develop (in the Discussion) the relationship between nonequilibrium oxygen adsorption and electron transfer from the bulk to the surface of the ZnO, and also to identify the various forms of adsorbed oxygen. For this study the ZnO was pretreated by vacuum heating at 770°K for 30 min. While the first moment of the 1.96 line, $M^*_{1.96}$, was increased by moderate vacuum heating (Table 1 [B to D]), it was then decreased by further vacuum heating (770°K for 30 min). The resulting maximum was qualitatively retraced upon oxygen adsorption (Fig. 2A). Oxygen adsorption produced principally the 2.010 line, which is of primary interest in this investigation. Oxygen adsorption also produced a weak 2.003 line whose intensity after small amounts of oxygen adsorption remained independent of further oxygen adsorption.

The adsorption study was carried out at 290°K. Desorption, which immediately followed the adsorption study, was carried out by heating the ZnO (1–2 min) to the lowest temperature which provided the desired pressure, about 5×10^{-4} Torr, in the combined ZnO and Pirani chambers. The

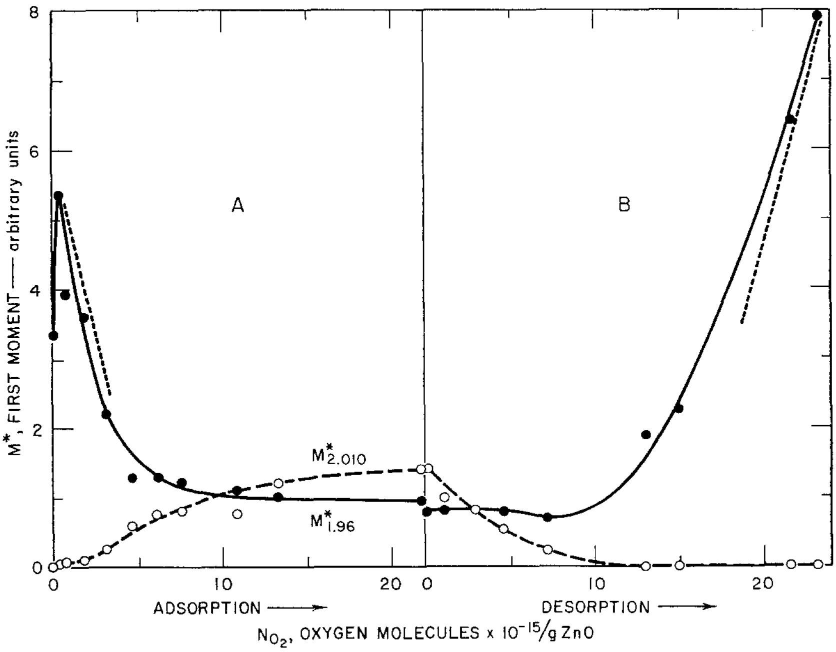

FIG. 2. Dependence of $M^*_{1.96}$ and $M^*_{2.010}$ upon amount of oxygen, N_{O_2}, (A) adsorbed and (B) desorbed. Prior to adsorption, ZnO was heated in vacuum at 770°K for 30 min. Desorption measurements immediately followed those of desorption. All ESR measurements were made at 290°K. Dotted lines indicate change of $M^*_{1.96}$ corresponding to one electron/O_2 molecule.

desorption temperature was increased from 290° to 670°K for the first five data points and then from 700° to 770°K for the next four points of Fig. 2B. A known amount of gas could then be pumped out of the isolated Pirani chamber. Upon cooling the ZnO to 290°K the residual oxygen in the ZnO chamber was reduced by ZnO adsorption to a pressure less than 10^{-4} Torr.

After each adsorption or desorption step the ESR spectrum was taken with the ZnO at 290°K, and $M^*_{1.96}$ was determined for each spectrum. The determination of the first moment of the 2.010 line, $M^*_{2.010}$, could not be made at low oxygen coverages because of the presence of the interfering lines (g = 2.0028 and 2.0033). $M^*_{2.010}$ was evaluated only at the highest oxygen coverage in the adsorption sequence, where the contribution of the interfering lines was relatively insignificant. The other values of $M^*_{2.010}$ were calculated from the peak height of the 2.010 line on the assumption that the line shape was unchanged.

The results of the dependence of the first moments on amount of oxygen adsorbed and desorbed, N_{O_2}, are shown in Fig. 2. The residual pressure at the end of the adsorption sequence was 9×10^{-4} Torr which is mostly nitrogen due to the air leak.

Upon oxygen adsorption, $M^*_{2.010}$ and $M^*_{1.96}$ approached limiting values (Fig. 2) which then remained essentially unchanged at higher residual pressures (e.g., at 0.05 Torr O_2, see Table 1 [D]). The oxygen coverage at which the limiting value of the 1.96 line was reached is in agreement with Kokes' results (*14*), considering that slight differences of surface area may be expected from the slightly different ZnO pretreatments.

The amount of oxygen adsorbed by vacuum heated ZnO was found to be crudely twice that adsorbed by oxidized ZnO. For this measurement, vacuum heated and oxidized ZnO (e.g., Table 1 [D] and [F] were exposed to 760 Torr O_2 for at least one hour at 290°K and then evacuated for several minutes. The remaining amount of oxygen adsorbed was qualitatively measured by the pressure rise in a known volume as the ZnO was heated to 700°K (at higher temperatures and for the case of the vacuum heated ZnO alone the oxygen pressure, initially at about 5×10^{-3} Torr, decreased with time indicating that the ZnO reacted chemically with the oxygen).

Discussion

Effect of ZnO Pretreatment on Oxygen Adsorption

The ESR study of various ZnO pretreatments demonstrates that adsorbed species other than oxygen can be present and can alter the electronic and surface properties of ZnO. Indeed, it is reported to be difficult to completely remove CO_2 from ZnO (*19*). The ESR lines with g values in the range of 2.0033 to 2.04 are certainly due to adsorbed species, and not to solid state defects (e.g., holes), because only surface species would be subject to the observed pressure broadening at high oxygen pressures.

The 2.0033 line is assigned to adsorbed species other than oxygen (e.g., CO_2 and/or H_2O) which are initially present on the ZnO and can be desorbed by the vacuum heating process. This assignment is based on the observations that the 2.0033 line becomes progressively weaker after the ZnO is degassed at higher temperatures, and also that the extent of the intensity enhancement due to oxygen adsorption becomes markedly less after substantial vacuum heating of the ZnO. This enhancement suggests that the adsorbed species (CO_2 and/or H_2O) and the adsorbing oxygen interact by a process not as yet understood. It is clear that a single species cannot account entirely for the two lines, 2.0033 and 2.010, since their relative intensities vary upon adsorption and desorption. Variations of relative intensities of these lines were reported upon oxygen adsorption (*15*) and upon heating ZnO on which oxygen had been adsorbed (*20*).

The 2.010 line is assigned to an adsorbed oxygen species because this ESR line, in contrast to the 2.0033 line, still appears strongly upon oxygen adsorption after the ZnO has been extensively desorbed (Table 1 [D]).

The ESR criteria demonstrate that oxygen adsorption becomes appreciable only when solid state donor defects are present as indicated by the 1.96 line. Thus there is no ESR evidence of oxygen adsorption on thermally oxidized ZnO for which defects such as interstitial zinc or oxygen ion vacancies may be expected to have been mostly destroyed, that is, for which the 1.96 line is very weak. Likewise the volumetric adsorption–desorption results show that oxygen adsorption is much less for the thermally oxidized than for the vacuum-heated ZnO.

It is understandable that donor defects are required for oxygen adsorption to occur with electron transfer from bulk to surface. However, in order to account for the substantial molecular oxygen adsorption occurring without electron transfer (e.g., associated with the ESR line at $g = 2.04$, see below), it is proposed that neutral oxygen molecules are attracted to surface defects by electric-field–induced dipole forces. The slow equilibration of the 2.04 line (when a vacuum-heated ZnO is exposed to 760 Torr O_2) suggests that surface ordering of the adsorbing oxygen molecules is required. The amount of this type of adsorption is decreased by thermal oxidation presumably because the surface defects are altered so that the local electric fields are reduced. The concept of electric-field–induced dipole interactions between adsorbate molecules and surface ion defects of the adsorbent has been developed by King and Benson to account for the separation of hydrogen isotopes on chromatographic columns (*21*).

Adsorption–Desorption Processes

Insight into the oxygen adsorption–desorption processes, with and without electron transfer, can be developed from the concurrent measurements of (1) the behavior of the lines with g values in the range of 2.0033 to 2.04 attributed to adsorbed species; (2) the behavior of the 1.96 line attributed to mobile bulk electrons which can be transferred to the surface during adsorption; and (3) the amount of oxygen adsorbed or desorbed. It will be shown that the interrelationship among the parameters $M^*_{1.96}$, $M^*_{2.010}$, and N_{O_2} demonstrates that oxygen is adsorbed on ZnO by two mechanisms—with electron transfer, which is complete for small surface coverages, and without electron transfer, which dominates at large surface coverages.

The essentially reciprocal relationships between $M^*_{1.96}$ and N_{O_2} and between $M^*_{2.010}$ and $M^*_{1.96}$ upon oxygen adsorption (Fig. 2A) indicate that the adsorbing oxygen decreases the concentration of solid state mobile electrons and results in formation of negative oxygen ion radicals at the surface.

Adsorption without electron transfer is indicated partly by the increase of the amount of oxygen adsorbed (i.e., N_{O_2}) as $M^*_{2.010}$ and $M^*_{1.96}$ approach constant values (Fig. 2A). This type of oxygen adsorption becomes inappreciable for values of $N_{O_2} > 20 \times 10^{15}$ O_2/g ZnO. Adsorption without electron transfer is also indicated by the 2.04 line which will be shown to be due to a molecular species.

The following reactions are proposed as a basis, not intended to be complete in detail, to discuss the adsorption–desorption results. The reactions are divided into those which occur with and without electron transfer between the bulk and the surface. Unless otherwise indicated the species are surface-adsorbed.

ADSORPTION → DESORPTION ←

Without Electron Transfer

$$O_2(\text{gas}) \leftrightarrow O_2 \quad (1)$$

$$O_2 + O_x^- \leftrightarrow O_{x+2}^- \quad (2)$$

$$O_2 + 2O^- \leftrightarrow 2O_2^- \quad (3)$$

With Electron Transfer

$$O_2(\text{gas}) + e \leftrightarrow O_2^- \quad (4)$$

$$O_2(\text{gas}) + 2e \leftrightarrow 2O^- \quad (5)$$

$$O_2(\text{gas}) + 2e \leftrightarrow O_2^{2-} \quad (6)$$

$$O_2(\text{gas}) + 4e \leftrightarrow 2O^{2-}(\text{lattice}) \quad (7)$$

The tentative identifications of the adsorbed oxygen species and assignments of their resonance signals are indicated below, and the basis of selection will be discussed subsequently.

Species A = O_2 (2.04)
Species B = O_2^- (NR)
Species C = O^- (2.010)

The g value of the resonance is in parenthesis, and NR signifies that no resonance was observed.

It is convenient first to consider the nature of the adsorbed species which gives rise to the 2.04 line. The 2.04 line is assigned to a neutral molecular species (species A) because its surface concentration is much larger than that possible for a charged species. For example, at 760 Torr O_2 the surface concentration of this species, considered to be O_2 molecules, is calculated to be about 4×10^{17} O_2/g ZnO or 1.4×10^{13} O_2/cm^2 [i.e., $M^*_{2.04} = 700$; spin conversion factor, $S = 1.2 \times 10^{15}$ spins/g ZnO·M^*; 2 spins/O_2; and surface area[15] 3×10^4 cm^2/g ZnO]. The corresponding fractional surface coverage $\theta = 0.02$—assuming 6×10^{14} surface sites/cm^2 ZnO (*22*)—is larger by a factor of about 10^2 than the amount of electron transfer permissible from theoretical considerations of the space-charge layer (*23*) and also from experimentally considerations of the maximum value of $M^*_{1.96} \sim 8$. The assignment is supported by the fact that for ZnO at 100°K the broad 2.04 line exhibits unresolved structure which resembles the ESR of oxygen adsorbed on porous glass at 77°K (*24*). Atomic oxygen is an alternative neutral species, but it is unlikely to be produced by adsorption because its formation from the molecule is 5.1 eV endothermic, and it is difficult to imagine a surface-binding mechanism which could provide this amount of energy for neutral atoms. The neutral adsorbed species assigned to the 2.04 line is probably the same species which has been postulated to account for reversible oxygen adsorption without changes of electrical conductivity (*25*).

Neutral oxygen adsorption also occurs in the adsorption sequence (Fig. 2A), but it seems unlikely that this adsorption can be accounted for by species A (i.e., the 2.04 line). For example, at 0.05 Torr O_2 when $M^*_{2.04} = 1$ (Table 1 [D2]), the amount of species A is estimated to be about 1×10^{15} O_2/g ZnO or 1/20 of the total oxygen adsorbed in the adsorption sequence. This fraction will be much less at the residual pressure (10^{-3} Torr) after the adsorption sequence. It may be possible to account for adsorption of some neutral species by a polymerization of the type indicated by reaction (2). For example, the species O_4^- has been postulated to account for isotopic exchange reactions on ZnO (*26*).

In the following discussion of the adsorption–desorption results shown in Fig. 2, the magnitude of $\Delta M^*_{1.96}$ will be used to measure the number of electrons transferred between the bulk and the surface.

The initial oxygen adsorption of 0.1×10^{15} O_2/g ZnO produced an increase of $\Delta M^*_{1.96} = 2$ (from 3.3 to 5.3) which is unexpected both in sign and magnitude. In Kokes' adsorption data (*14*) an analogous maximum is indicated at 400°C, but not at 25°C probably because, according to the present results, the maximum would have occurred at very small surface coverages. This value of $\Delta M^*_{1.96}$ is equivalent to the transfer of 25 electrons from surface to bulk per oxygen molecule adsorbed. It is possible to account for the sign (but not the magnitude) of this initial electron transfer by postulating that adsorbing oxygen reacts with surface acceptor states and releases to the bulk those electrons which were trapped at the surface states; such a mechanism was found for initial oxygen adsorption on germanium (*27*). In order to account for the magnitude as well as the sign of the effect it is proposed that the microwave skin depth of the ZnO, and hence the sample volume examined by ESR, was initially limited by a relatively high intergranular electrical conductivity of the ZnO (after vacuum heating). Then upon oxygen adsorption, with oxygen acting as an electron acceptor, a slight increase in the surface potential of each grain would result in a substantial decrease of the intergranular electrical conductivity and an increase of the skin depth. The skin depth in ZnO for donor densities of 10^{17} to 10^{18} cm^{-3} and at X-band frequencies is estimated to be 10^{-1} to 10^{-2} cm (*28, 29*), which values are large relative to the grain diameter ($\sim 10^{-4}$ cm) but small relative to the diameter of the quartz tube containing the ZnO. Therefore, according to the above argument, the initial value of $M^*_{1.96}$, prior to adsorption, will be assumed to be ≥ 5.3. Skin depth effects are probably less significant in the desorption sequence because a pressure of at least 10^{-3} Torr O_2 was present over the hot ZnO, and readsorption of this oxygen upon cooling the ZnO would tend to minimize intergranular electrical conductivity. The reason for the difference between the values of $M^*_{1.96}$ at the beginning (5.3) and the end (7.9) of the adsorption–desorption cycle is obscure. In order to understand this difference, it appears necessary to consider the influence of various factors, for example, the microwave skin effect, the extent of thermal decomposition of the ZnO during desorption, and peculiar effects on the ESR sensitivity due to changes in electrical conductivity of ZnO.

The processes occurring during the adsorption–desorption cycle and the nature of the adsorbed oxygen species can now be discussed in a quantitative way. The $M^*_{1.96}$ curve indicates that electron transfer occurs efficiently upon initial oxygen adsorption but then occurs less so as a limiting value of $M^*_{1.96}$ is reached. The limiting value is presumed to be determined by such factors as the surface potential, donor density, and particle size of the ZnO. The lower limit of $M^*_{1.96}$ is related to the concentration of mobile electrons remaining in the bulk after the surface space-charge region is exhausted of electrons. The decreasing slope of the $M^*_{1.96}$ curve upon adsorption indicates an increasing importance of neutral species, that is, of adsorption without electron transfer.

At least two oxygen surface species are believed to be involved as acceptors in the electron transfer process accompanying adsorption. The essentially reciprocal behavior of $M^*_{1.96}$ and $M^*_{2.010}$ suggests that the 2.010 line is due to an oxygen surface species, species C, which adsorbs with electron transfer to form a negatively charged surface species; that is, both these parameters change rapidly initially and ultimately approach limiting values at about the same surface coverage.

There is indirect evidence of a second acceptor species, species B, with no observable resonance, from the threefold greater number of electrons transferred from the bulk to the surface than can be accounted for by the 2.010 line (species C). For example, during the adsorption sequence $\Delta M^*_{1.96} = 4.4$ while $\Delta M^*_{2.010} = 1.4$, and this difference is not complicated by microwave power saturation effects. Thus of the total number of electrons transferred from bulk to surface about two-thirds are accepted by species B and one-third by species C.

Useful information concerning the identity of the surface oxygen species which adsorb or desorb with electron transfer can in principle be deduced from the slope $\Delta M^*_{1.96}/\Delta N_{O2}$. The absolute magnitudes of this slope are about 1.2×10^{-15} for initial adsorption and 0.9×10^{-15} $M^* \cdot$ g ZnO/O_2 for final desorption. The virtual equivalence of these slopes suggests qualitatively that a given surface oxygen species (species B with no observable resonance) is predominantly the first to be adsorbed and the last to be desorbed. The charge of species B can be calculated from the product of the above slopes and the spin intensity calibration factor, S. Although the charge cannot be unequivocally specified because of the uncertainty in the determination of S, this approach provides a consistent and satisfactory interpretation of the results. The product $(S)(\Delta M^*_{1.96}/\Delta N_{O_2})$ for the initial adsorption and the final desorption leads to the results: 1.4 and 1.0 spin/O_2, respectively; the changes of $M^*_{1.96}$ corresponding to 1 spin/O_2 molecule adsorbed or desorbed are indicated by the dotted lines in Fig. 2. These experimental data for adsorption are in agreement with those reported by Kokes (*14*) for oxygen adsorption under comparable conditions; however, the interpretations of the results differ.

Of the possible surface species only O_2^- can adsorb and desorb with the transfer of 1 electron/O_2, as expressed by reaction (4), and the O_2^- species is favored as species B for other reasons. Of all the reactions involving electron transfer, reaction (4) is the most favored since it is probably the most exothermic, based on the energetics of the gas-phase reactions. Also it seems likely that the O_2^- species would not have an observable resonance by analogy to O_2^- in KCl, for which the ESR signal is not observed because of line-broadening for temperatures above 35°K (*30*). Species C and the 2.010 line should probably be identified with O^-. The formation of O^- from O_2 (or from O_2^-)

is probably less energetically favored than the formation of O_2^- from O_2, for example for the gas phase, reaction (5) is about 2 eV endothermic and reaction (4) is 0.15 eV exothermic; this is consistent with the observation that the number of electrons transferred is less to form species C (O^-) than species B (O_2^-). Further support of the assignment of these species is provided by the observation that the value of the number of spins transferred per O_2 molecule for initial adsorption is somewhat greater than unity, as is expected for adsorption occurring mostly by O_2^- and partly by O^-.

Measurements are planned by which it may be possible to make a more positive identification of species C if hyperfine splittings of the 2.010 line can be resolved when O_2^{17} is used in the adsorption study.

This interpretation differs from that of Kokes, who, for comparable data, postulated that oxygen adsorption at 300°K occurs by formation of the O^- species, and that this chemisorption depends upon an equilibrium of the solid state electrons between the conduction band and donors which are assumed to be largely un-ionized (*14*). However the donors of ZnO are thought to be nearly completely ionized at 300°K (*31*) and therefore the equilibrium of electrons between the conduction band and the donors will not significantly influence chemisorption. Accordingly, the number of electrons transferred from bulk to surface upon adsorption is indicated directly by $\Delta M^*_{1.96}$ assuming that the 1.96 line is due to conduction electrons (*14*).

The possibility exists that species B, with no observable resonance, should be identified with the nonparamagnetic charged species O_2^{2-} or O^{2-}. However, the formation of these species upon adsorption by reaction (6) or (7) is less energetically favored than formation of O_2^- and O^-. Certainly O^{2-} (lattice) would be formed only at high temperatures.

In about the first half of the desorption sequence, the oxygen is desorbed without electron transfer as indicated by the essentially constant value of $M^*_{1.96}$. Therefore this desorption process is primarily due to neutral surface oxygen species. Also, in this part of the desorption species C is destroyed since $M^*_{2.010}$ decreases to zero. In order to account for the destruction of a charged surface species without electron transfer to the bulk, it is proposed that at the higher temperatures required for desorption a charge exchange occurs on the surface between O_2 and O^- to form O_2^- according to the forward reaction (3), which in the gas phase is exothermic by about 2.3 eV. This reaction may be significant only at temperatures high enough to provide surface mobility.

The second half of the desorption sequence occurs primarily with electron transfer and with nearly a linear dependence between $M^*_{1.96}$ and N_{O_2}. As discussed above, this desorption is attributed to O_2^- surface species, desorbing according to reaction (4).

The total amount of electron transfer occurring during adsorption can be calculated from the product of $\Delta M^*_{1.96} = 4.4$ and the spin intensity calibration factor to yield 5.3×10^{13} electrons/g ZnO. It is thereby estimated that the surface charge density is about 2×10^{11} cm^{-3} and the fractional surface coverage of electrons is $\theta \sim 3 \times 10^{-4}$. This estimate is consistent with theoretical expectations (*23*) of the maximum number of chemisorbable molecules on ZnO assuming a donor density of 10^{17} cm^{-3}. The donor density is estimated to be about 3×10^{16} cm^{-3}, assuming that the 1.96 line represents all the donors uniformly distributed in the volume of the ZnO.

According to the above calculation, 5.3×10^{15} O_2/g ZnO is the maximum amount of oxygen molecules which can adsorb with electron transfer to form O_2^-, and the amount adsorbed will be lower to the extent that O^- is formed. This amount is in substantial agreement with the experimental results in Fig. 2 from which it can be seen that about 90% of the electron transfer is complete ($M^*_{1.96}$ changes from 5.3 to 1.3) upon adsorption of about 6×10^{15} O_2/g ZnO some of which adsorbs without electron transfer.

ACKNOWLEDGMENTS

The author gratefully acknowledges the helpful and stimulating discussions with his colleagues, Drs. T. Freund, S. R. Morrison, and S. Benson. He also acknowledges the generosity of the New Jersey Zinc Co. for the indium-doped ZnO and its analysis.

REFERENCES

1. OKUDA, M., AND TACHIBANA, T., *Bull. Chem. Soc. Japan* **33**, 863 (1960).
2. ROONEY, J. J., AND PINK, R. C., *Proc. Chem. Soc.*, p. 70 (1961).
3. BROUWER, D. M., *Chem. and Ind.*, p. 177 (1961).
4. LEFTIN, H. P., HOBSON, M. C., AND LEIGH, J. S., *J. Phys. Chem.* **66**, 1214 (1962).
5. FOGO, J. K., *J. Phys. Chem.* **65**, 1919 (1961).
6. STAMIRES, D. N., AND TURKEVICH, J., *J. Am. Chem. Soc.* **86**, 749 (1964).
7. ROONEY, J. J., AND PINK, R. C., *Proc. Chem. Soc.*, p. 142 (1961).
8. HIROTA, K., AND KUWATA, K., *Bull. Chem. Soc. Japan* **36**, 229 (1963).
9. BUKANAEVA, F. M., PECHERSKAYA, Y. I., KAZASKII, V. B., AND DZISKO, V. A., *Kinetics Catalysis (USSR) (Engl. Transl.)* **3**, 315 (1962).
10. TURKEVICH, J., NOZAKI, F., AND STAMIRES, D., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964.*
11. LANSFORD, J. H., *J. Phys. Chem.* **68**, 2312 (1964).
12. SANCIER, K. M., AND FREUND, T., *J. Catalysis* **3**, 293 (1964).
13. BARANOV, E. V., KHOLMOGOROV, V. E., AND TERENIN, A. N., *Dokl. Phys. Chem.* **146**, 125 (1962).
14. KOKES, R. J., *J. Phys. Chem.* **66**, 99 (1962).
15. KOKES, R. J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964.*
16. FUJITA, Y., AND KWAN, T., *Shokubai (Tokyo)* **5**, 206 (1963).
17. KASAI, P. H., *Phys. Rev.* **130**, 989 (1963).
18. MULLER, K. A., AND SCHNEIDER, J., *Phys. Letters* **4**, 288 (1963).
19. KESAVULU, K., AND TAYLOR, H. A., *J. Phys. Chem.* **64**, 1124 (1960).
20. SEDAKA, M., AND KWAN, T., *Bull. Chem. Soc. Japan* **38**, 1414 (1965).
21. KING, J., JR., AND BENSON, S., private communication.
22. BARRY, T. I., AND STONE, F. S., *Proc. Roy. Soc. (London)* **A255**, 124 (1960).
23. WEISZ, P. B., *J. Chem. Phys.* **21**, 1531 (1953).
24. ARMSTRONG, R. A., Natl. Res. Council, Ottawa, Canada, private communication.
25. BARRY, T. I., AND KLIER, K., *Disc. Faraday Soc.* **31**, 219 (1961).
26. HIROTA, K., AND CHONO, M., *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* **58**, 115 (1965).
27. PALMER, D. R., MORRISON, S. R., AND DAUENBAUGH, C. E., *Phys. Rev.* **129**, 608 (1963).
28. GINZTON, E. L., "Microwave Measurements," p. 493. McGraw-Hill, New York, 1957.
29. BOGNER, G., AND MOLLWO, E., *Solid State Phys.* **8**, 265 (1959).
30. BURCH, D. S., SMITH, S. J., AND BRANSCOMB, L. M., *Phys. Rev.* **112**, 171 (1958).
31. HOBSTETTER, J. N., *in* "Semiconductors" (N. B. Hannay, ed.), p. 581. Reinhold, New York, 1959.