Study on ZnO-Cr₂O₃ Catalyst. I. Electrical Conductivity of Zinc Oxide in Oxygen and Hydrogen

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Introduction

Since the electrical conductivity of a sintered material is determined mainly by the specific boundary material existing between the grains, it is greatly affected by gases chemisorbed on the boundary surface. Therefore, the mechanism of adsorption of gases and consequently the nature of catalytic activity can be discussed from the results of measurement of the conductivity, so far as the measurement is undertaken on a working catalyst at a working temperature.

Zinc oxide is a typical *n*-type semiconductor and has been widely investigated by many workers[1~3]. Most of the investigations, except a few, have been conducted on highly sintered zinc oxides at high temperatures. Though these few investigations were indeed of considerable merit, they seemed, from the view point of electrical conductivity, to be not sufficient for a perfect understanding of ZnO-Cr₂O₃ catalyst, i.e. a catalyst for the synthesis of methanol, etc.

The measurement of conductivity in conjunction with chemisorption of oxygen and hydrogen has been conducted here, as a supplement to the investigations described above, at temperatures below 500°C on zinc oxide sintered at 600°C. Some of the present results are rather different from those reported previously and some of them are unknown. These results may be interpreted in terms of the interstitial zinc atom pair or the zinc molecule suggested by P. H. Miller.

Experimental Procedure

At varying temperatures from 45° to 500C° the conductivity of a zinc oxide pressed into a bar was measured in vacuo, and subsequently, in an atmosphere of oxygen as well as hydrogen in a range of pressure from 10^{-3} to 10^{-1} mmHg. The conductivity measurement was supplemented by the direct measurement on a separate specimen of the identical bar of both the rate of adsorption and equilibrium amount of adsorbed oxygen and hydrogen in another apparatus.

A commercial zinc oxide (chem. pure) was pressed into a bar of 8×8 mm. square and 81 mm. in length, then sintered at 600°C for two hours and allowed to cool in air. Part of the bar was subjected to the electrical measurement by direct current, and the rest was crushed into granules of 1–2 mm. diameter for the measurement of adsorption of oxygen and hydrogen.

The general technique of conductivity measurement was similar to that used by R. H. Grifith et al[4]. The specimen was placed between Pt electrodes, the upper one of which was weighted with a perforated iron cylinder. The measurement was made in vacuo and at a constant pressure of oxygen as well as hydrogen, by using a Wheatstone bridge. With capillary leaks connected to a gas reservoir it was possible to expose the specimen for prolonged periods to oxygen as well as hydrogen of well difined and reproducible pressures ranging from 10^{-3} to 10^{-1} mmHg.

The adsorption measurement was conducted in an apparatus similar to that used by R. T. D. Frankenburg[5]. The amount of adsorbed oxygen or hydrogen was evaluated from the pressure decrease in an adsorption chamber of a constant volume. The pressure was measured by means of a Pirani gauge.

Experimental Results

Electrical Conductivity for Evacuated Oxide.—The oxide sintered at 600°C in air was a poor conductor, unless it was de-oxygenated. The conductivity was, however, gradually increased by prolonged heating of the oxide in vacuo (10^{-5} mmHg) at 500°C, and then came to attain a steady value.

The temperature-dependence of resistivity at the steady state in a temperature range from 100° to 500°C was given by the usual equation,

$$R = A \cdot \exp(\varepsilon/kT) \qquad (1)$$

where R is resistivity, A, a constant, k, Boltzmann's constant, T, absolute temperature, and ε, activation energy of conductivity. The Arrhenius line for the above equation gave an apparent activation energy of about 0.025 eV. (Fig. 1). The value was nearly equal to that obtained by P. H. Miller[1] (0.02 eV.) at temperatures below room temperature. The constant A was evaluated to be approximately 2.24×10^2.

1) P.H. Miller, *Phys. Rev.*, **60**, 890 (1941).
2) H. Fritsche, *Z. Phys.*, **133**, 422 (1952).
3) E. Scharowsky, ibid., **135**, 318 (1953).

4) R.H. Grifith, P.R. Chapman et al., *Disc. Faraday Soc.*, **8**, 258 (1950).
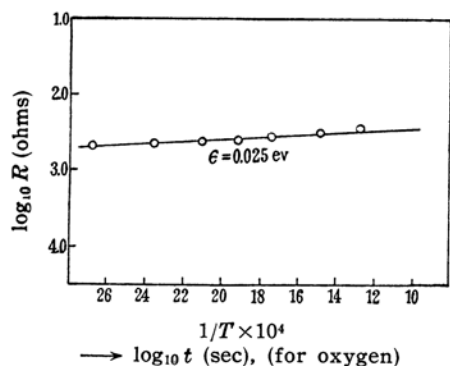5) R.T.D. Frankenburg, *J. Am. Chem. Soc.*, **66**, 1827 (1944).

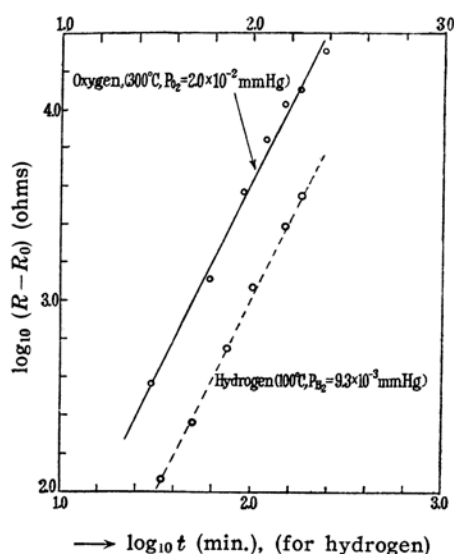Fig. 1. Temperature-dependence of resistivity of zinc oxide in vacuo.

⟶ log$_{10}$ t (min.), (for hydrogen)

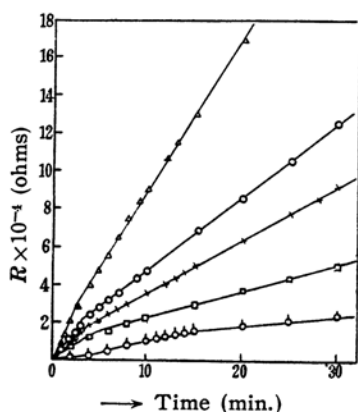Fig. 2. Relation between resistivity and time, at the earlier stage of adsorption.

⟶ Time (min.)

Fig. 3a. Relation between resistivity at 300°C and time, at various pressures;
△, $p_{o2}=5.8\times10^{-2}$ mmHg,   ○, $p_{o2}=2.8\times10^{-2}$ mmHg,   ×, $p_{o2}=2.0\times10^{-2}$ mmHg,   □, $p_{o2}=9.3\times10^{-3}$ mmHg,   ○̇, $p_{o2}=3.6\times10^{-3}$ mmHg.

Electrical Conductivity in Oxygen Atmosphere.—Fig. 2 and 3 show the adsorption
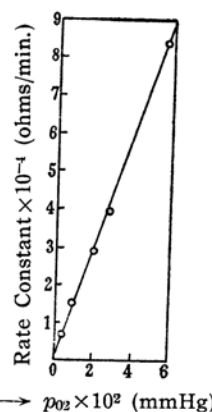

⟶ $p_{o2}\times10^2$ (mmHg)

Fig. 3b. Rate constant of the change of resistivity as a function of oxygen pressure at 300°C.

kinetics as the rate of change in resistivity of the oxide under a series of oxygen pressures at 300°C. The resistivity increased with time at an earlier stage of the adsorption, according to the relation

$$R-R_0=k'\cdot p_{o2}\cdot t^2 \qquad (2),$$
$$k'\simeq2.5\times10^5 \text{ (ohm/min. mmHg)}$$

where R_0 is the resistivity for the evacuated oxide, and then the increase was solwed down being represented by another relation, as

$$R=k''\cdot p_{o2}\cdot t+\text{Const.} \qquad (3),$$
$$k''\simeq1.5\times10^5 \text{ (ohm/min. mmHg)}$$

With prolonged period of further adsorption, it tended to increase always more slowly until an equilibrium was established between resistivity and oxygen pressure. The relationship of the resistivity in equilibrium with the oxygen pressure (Fig. 4) was given by Eq. (4)
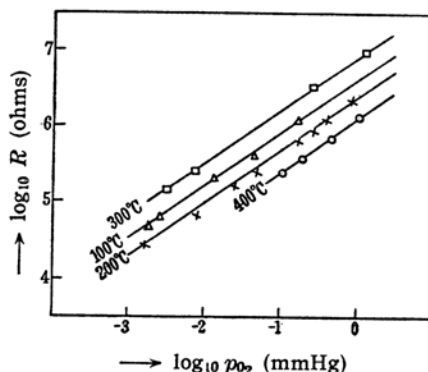

⟶ log$_{10}$ p_{o2} (mmHg)

Fig. 4. Ralation between resistivity of zinc oxide and oxygen pressure at various temperatures.

$$R = \alpha \cdot p_{O_2}^n, \quad n \simeq 2/3 \qquad (4)$$

This differs somewhat from that of $R = \alpha' \cdot p_{O_2}^{1/4} \ldots \ldots$ (5), which was usual at the higher temperature.

A rapid elevation of temperature, after an equilibrium between resistivity and oxygen pressure had been established at a certain temperature, produced an instantaneous fall of resistivity followed by a slower rise towards a new equilibrium value corresponding to a higher temperature (Fig. 5). The equilibrium value of the resistivity is exemplified in Fig. 6
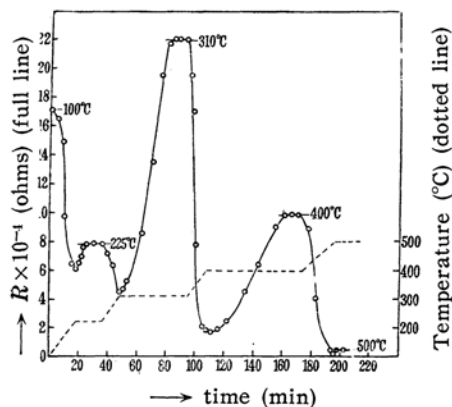
Fig. 5. Change of resistivity with rises of temperature, at an oxygen pressure of 6.9×10^{-3} mmHg.
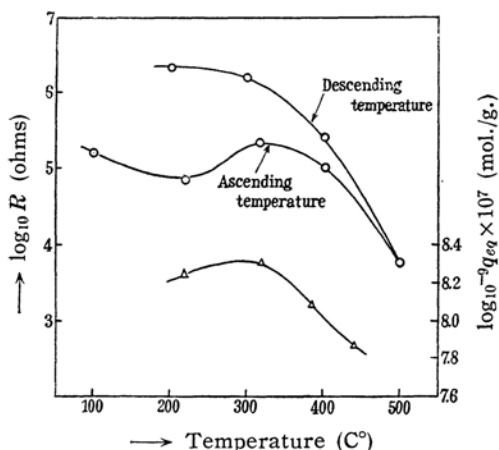
Fig. 6. Temperature-dependence of resistivity of zinc oxide at oxygen pressure of about 6.9×10^{-3} mmHg ($-\bigcirc-$), and isobar of oxygen adsorption at the pressure of 3.0×10^{-2} mmHg ($-\triangle-$).

as a function of temperature at an isobaric oxygen pressure of 6.9×10^{-3} mmHg. In this figure, a minimum as well as a maximum of resistivity is observed at about 220° and 300°C respectively with ascending temperature,

while resistivity increases rather monotonously with descending temperature from 500°C.

Adsorption of Oxygen.—The evacuated oxide could adsorb oxygen at a measureable rate at temperatures above 200°C. The equilibrium amount of the adsorbed oxygen at a range of temperature from 220° to 440°C was plotted against oxygen pressures in Fig. 7
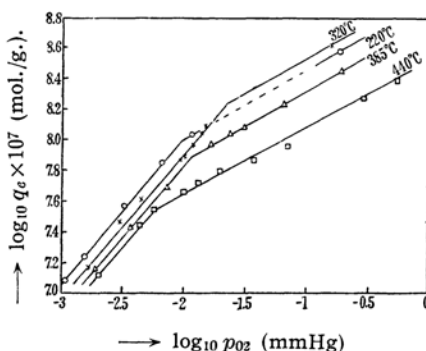
Fig. 7. Adsorption isotherms of oxygen on zinc oxide at various temperatures.

The adsorption isotherm comprised two straight lines, the one being expressed by Eq. (6) and the other by Eq. (7)

$$q_{eq} = a \cdot p_{O_2}^n, \quad n \simeq 1.0 \sim 1.2 \qquad (6)$$

$$q_{eq} = b \cdot p_{O_2}^n, \quad n \simeq 0.5 \qquad (7)$$

in a respective range of small and large adsorbed amount q_{eq}. The differential heats of the adsorption are evaluated by means of the Clausius-Clapeyron's equation to give a nearly constant value of 1.1 kcal./mol. at $p_{eq} = 1.2 \sim 4.0 \times 10^{-7}$ mol./g. and 24 kcal./mol. at $q_{eq} = 1.0 \sim 2.6 \times 10^{-6}$ mol./g. for Eq. (6) and Eq. (7) respectively.

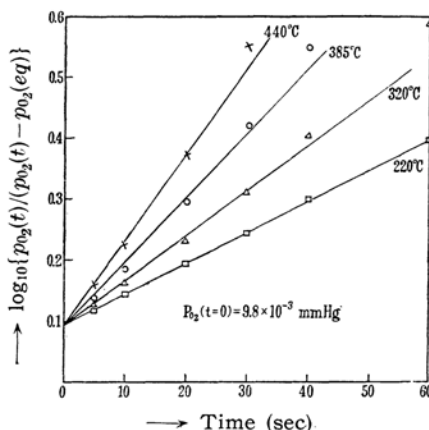The rate of decrease of the pressure is represented by Eq. (8)

Fig. 8. Relation between $\log_{10}\{p_{O_2}(t)/(p_{O_2}(t) - p_{O_2}(eq)\}$ and time at various temperatures.

$$\log_{10} p_{0_2}(t)/\{p_{0_2}(t)-p_{0_2}(eq)\}=k'''\cdot t+\text{Const.} \quad (8)$$

at the earlier stage and becomes gradually more slow with the increasing amounts, as illustrated in Fig. 8. The activation energy of the adsorption at the earlier stage was found to be 3.6 kcal./mol.

Electrical Conductivity in Hydrogen Atmosphere.—An initial steady state of conductivity was required for a series of repeated measurements in hydrogen atmosphere. On the exposure of the evacuated oxide to hydrogen, the conductivity increased more or less rapidly at temperatures above 200°C (Fig. 9a), but recovered very slowly in prolonged
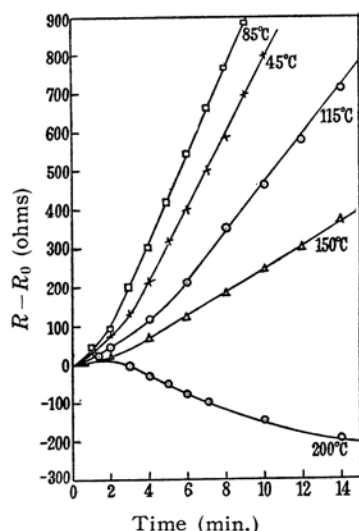
Fig. 9a. Relation between resistivity and time at a ahydrogen pressure of 9.3×10⁻³ mmHg, at various temperatures.
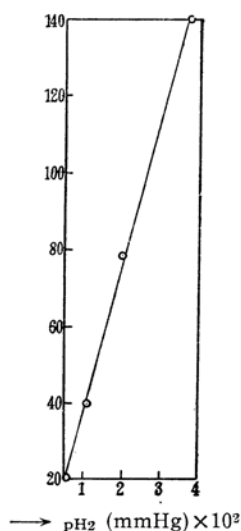
Fig. 9b. Rate constant of the change of resistivity as a function of hydrogen pressure at 150°C.

duration of evacuation at 500°C. This might probably be due to the slow evaporation of zinc metal* which was confirmed by the deposit on the cold wall of the vessel. In this respect, a steady state could be readily established by the oxidation of a specimen, which had been employed in hydrogen atmosphere, in oxygen at 500°C followed by a subsequent evacuation at the same temperature.

The decrease of conductivity accompanied by the adsorption of hydrogen took place on zinc oxide at temperatures below 200°C (Fig. 9a, 10); the matter being just the converse
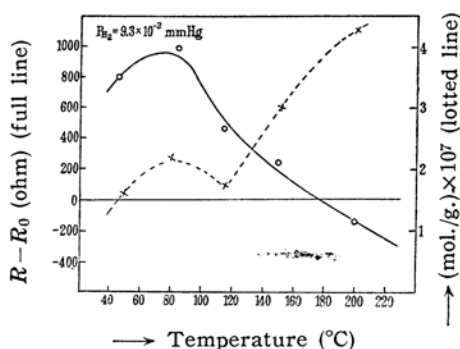
Fig. 10. Increase and decrease of resistivity (full line) accompanied by hydrogen adsorption (dotted line, indicating the amount adsorbed in 10 minutes) at various temperatures.

of the above**. The adsorption at lower temperatures was recognizable only when the specimen had been subjected to evacuation at 500°C, but scarcely so when the specimen had been oxygenated. The resistivity at a constant time interval after the beginning of adsorption being plotted against the temperature (Fig. 10, full line), a maximum appears at about 80–90°C above which it decreases monotonously with increasing temperatures, while the adsorbed amounts of hydrogen show a maximum at 80–90°C as well as a minimum at about 110°C (Fig. 10, dotted line). In contrast to two maxima expected in the adsorption*** of oxygen, no other maximum has been found in the R-T curve for the hydrogen adsorption. Whether another maximum would be present or not below 45°C could not be confirmed. The conductivity nearly paralleled the adsorbed amount of hydrogen at 45–110°C.

* The appearance of zinc metal had already been reported by L. Yang (*J. Amer. Electrochem. Soc.*, **97**, 910 (1950).

** Y. Kubokawa and O. Toyama (*Bull. Naniwa Univ.*, **2**, 103 (1954)) have recently observed the decrease at 45°C, but the increases at temperatures higher than 80°C. Their results are somewhat different from ours.

** In the R-T curve of oxygen adsorption at an atmos- pheric pressure, two maxima were found at 150° and 350°C respectively.

The adsorption on hydrogen on oxide at temperatures below 200°C is similar in rate to the oxygen adsorption. The rate of increase of resistivity could be again represented by Eq. (2) at the earlier stage and by Eq. (3) at the subsequent stage respectively (Figs. 2 and 9).

Discussion

Zinc Atom Pair and its Ionized State.— The straight line relation between $\log R$ and $1/T$ as well as the small activation energy of the conductivity (0.02 eV.), which for the case below room temperature had already been reported by P. H. Miller, was also found in the intermediate range between 100° and 500°C. The value of the activation energy which was considerably lesser than that (0.5 eV.) obtainable normally above 500°C, was attributed by P. H. Miller to the presence of interstitial zinc atom pairs, while the greater value was generally believed to be due to interstitial zinc atoms.

With respect to ionization of the interstitial zinc atoms, Zn^{++} was estimated by C. Wagner et al[6] and K. Hauffe et al[7] and Zn^+ by F. Seitz[8] and E. Scharowsky[9]. E. Scharowsky conducted his experiments at temperatures nearly the same as that of the present experiments, and suggested the presence of Zn^+ from his experimental results. It seems to be reasonable to assume that Zn^+, consequently, $Zn^+ \cdot Zn^+$ or $Zn^+ \cdot Zn$ in conjunction with the atom pairs, may confer the conductivity at temperatures below 500°C.

Equilibrium of Conductivity and Rate of Conductivity Change in Oxygen.— The observed isotherms of oxygen adsorption given by Eqs. (6) and (7) are suggestive of a molecular adsorption and an adsorption with dissociation occurring at a small and a large q_{eq} respectively. According to T. Iijima[10], the rate equation given by Eq. (8) can be derived from the postulate of a molecular adsorption. However, even the adsorption at the earlier stage has been shown to be always associated with change of the conductivity, and any adsorption with dissociation may therefore take place consecutively at a stage where the molecular adsorption may be predominant. In this respect, an interpretation of the results will be given in terms of the zinc atom pair under the following assumptions.

6) H. H. von Baumbach and C. Wagner. *Z. Phys. Chem.*, **22**, 199 (1933).
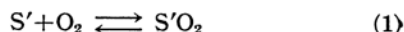7) H. J. Engell and K. Hauffe. *Z. Elektrochem.*, **56**, 366 (1952).
8) F. Seitz, "Modern Theory of Solids", p. 466 (1940).
9) E. Scharowsky. *Z. Phys.*, **135**, 318 (1953).
10) T. Iijima, *Riken Iho (Bull. Phys. Chem. Res. Inst.*, Tokyo), **17**, 286 (1937) (in Japanese).

1. A molecular adsorption takes place between oxygen in gas phase and S' site on the oxide surface according to expression (1),
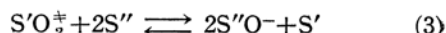
$$S' + O_2 \rightleftarrows S'O_2 \qquad (1)$$

S' may be any one of the sites, Zn, Zn·Zn, cation Zn^{++}, and anion O^{--} of the surface of the stoichiometric crystal.
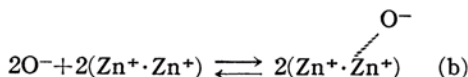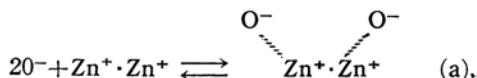
2. An activated complex $S'O_2^{\pm}$ is produced by a reaction of quasi-free electrons on the surface with $S'O_2$, and the reaction rate determines the rate of the conductivity change.

$$S'O_2 + 2e \rightleftarrows S'O_2^{\pm} \qquad (2)$$
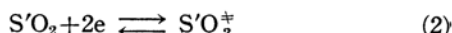
3. S'O reacts with other site S″ to produce S″O$^-$ and S'

$$S'O_2^{\pm} + 2S'' \rightleftarrows 2S''O^- + S' \qquad (3)$$

Interaction between the oxygen molecule and the electron may take place in either of the following, $O_2 + 2e \rightleftarrows 2O^-$ or $O_2 + e \rightleftarrows O^- + O$. In this respect, the latter proves, however, inadequate for teh interpretation of the results. S″ may be any one of the sites, $Zn^+ \cdot Zn$, and $Zn^+ \cdot Zn^+$. Oxygen is adsorbed on either of the sites in two different manners, say, on $Zn^+ \cdot Zn^+$

$$2O^- + Zn^+ \cdot Zn^+ \rightleftarrows \quad \overset{O^-}{\underset{}{Zn^+}} \overset{O^-}{\cdot \underset{}{Zn^+}} \qquad (a),$$

$$2O^- + 2(Zn^+ \cdot Zn^+) \rightleftarrows 2(Zn^+ \cdot \overset{O^-}{\underset{}{Zn^+}}) \qquad (b)$$

Among the above, (a) proves inadequate for the interpretation of the results.

(A) *Rate at the Later Stage of Adsoption.* The rate of adsorption is given by Eq. (4), the equilibrium being established in (1)

$$V_{ads} = [S'O_2]_{eq} \cdot [e]^2 \frac{kT}{h} \cdot \frac{f_{\pm}}{f_{S'O_2} \cdot f_e^2} \cdot \exp(-\epsilon_1/kT) \qquad (4)$$

where f is a partition function with respect to the subscripts. As the rate of the disappearance of the electron is equal to tiwice the above rate, one obtaines

$$-\frac{d[e]}{dt} = k_1 \cdot [S'O_2]_{eq} \cdot [e]^2 \qquad (5),$$

$$k_1 \equiv 2 \frac{kT}{h} \cdot \frac{f_{\pm}}{f_{S'O_2} \cdot f_e^2} \cdot \exp(-\epsilon_1/kT).$$

From (1), in equilibrium, $[S'O_2]_{eq} = K_1 \cdot p_{O_2} \cdot [S']_{eq}$, is obtained, where K_1 is the equilibrium constant at a constant temperature. The substitution of this relation in Eq. (5) gives

$$-\frac{d[e]}{dt} = k_1 \cdot K_1 \cdot [S']_{eq} \cdot p_{O_2} \cdot [e]^2 \qquad (6).$$

Integrating Eq. (6), one obtaines

$$[e]^{-1} = A \cdot p_{O_2} \cdot t + \text{const.}, \quad A \equiv k_1 \cdot K_1 \cdot [S']_{eq} \qquad (7)$$

When combined with the relation $[e] = B\kappa = BR^{-1}$, where κ is electrical conductivity, B, a constant, Eq. (7) results in Eq. (8)

$$R = A \cdot B \cdot P_{O_2} \cdot t + \text{const.} \qquad (8)$$

which agrees well with the experimental equation (2) in the preceding chapter.

(B) *Rate at the Earlier Stage of Absorption.* At the sarlier stage of the adsorption before the equilibrium in (1) is established, the rate of disappearance of $S'O_2$ according to Eq. (2) $\left(\text{denoted by} -\dfrac{d[S'O_2]_{(2)}}{dt}\right)$ depends upon the rate of appearance of $S'O_2$ according to (1) $\left(\text{denoted by} \dfrac{d[S'O_2]_{(1)}}{dt}\right)$. The respective rate is given by the following equation (9) and (10).

$$\frac{d[S'O_2]_{(1)}}{dt} = k_2 \cdot p_{O_2} \cdot \{[S']_0 - [S'O_2]_{(1)}\} \qquad (9)$$

$[S']_0$, concentration of S' on the surface of the evacuated oxide.

$$-\frac{d[S'O_2]_{(2)}}{dt} = \frac{k_1}{2} \cdot \{[S'O_2]_{(1)} - [S'O_2]_2\} \cdot [e]^2 \quad (10)$$

Combining $-\dfrac{d[e]}{dt} = -2\dfrac{d[S'O_2]_{(2)}}{dt}$ with Eq. (10) and rearranging, one obtaines

$$-\frac{d[e]}{dt} = k_1 \cdot [S'O_2]_{(1)} \cdot \left\{1 - \frac{[S'O_2]_{(2)}}{[S'O_2]_{(1)}}\right\} \cdot [e]^2 \qquad (11)$$

At the earlier stage there may be $\dfrac{[S'O_2]_{(2)}}{[S'O_2]_{(1)}} \ll 1$, and therefore

$$-\frac{d[e]}{dt} = k_1 \cdot [S'O_2]_{(1)} \cdot [e]^2 \qquad (12)$$

By integrating Eq. (9) and substituting the integrated equation (13) in Eq. (12), Eq. (14) is obtained.

$$[S'O_2]_{(1)} = [S']_0 \cdot \{1 - \exp(-k_2 \cdot p_{O_2} \cdot t)\} \qquad (13)$$

$$-\frac{d[e]}{dt} = k_1 \cdot [S']_0 \cdot \{1 - \exp(-k_2 \cdot p_{O_2} \cdot t)\} \cdot [e]^2 \qquad (14)$$

The second term in the bracket can be simplified by neglecting the terms including higher powers of t in the expanded series of $\exp(-k_2 p_{O_2} \cdot t)$ and Eq. (15) results

$$-\frac{d[e]}{dt} = k_1 \cdot [S']_0 \cdot (-k_2 \cdot p_{O_2} \cdot t) \cdot [e]^2 \qquad (15)$$

Integration of Eq. (15) gives Eq. (16)

$$[e]^{-1} - [e]_0^{-1} = k_1 \cdot k_2 \cdot [S']_0 \cdot p_{O_2} \cdot t^2 \qquad (16)$$

where $[e]_0$ is concentration of quasi-free electrons on the evacuated oxide. Eq. (16) may be expressed in terms of resistivity as follows.

$$R - R_0 = B \cdot k_1 \cdot k_2 \cdot [S']_0 \cdot p_{O_2} \cdot t^2 \qquad (17)$$

Eq. (17) is consistent with the experimental equation (2) at the earlier stage of the adsorption*.

(C) *Equilibrium Conductivity in Varying Pressures of Oxygen.* The rate of desorption is expressed by Eq. (18) according to (2).

$$V_{des} = \frac{[S''O^-]^2 \cdot [S']}{[S'']^2} \cdot \frac{kT}{h} \cdot \frac{f_* \cdot f_{S''}^2}{f_{S''O^-}^2 \cdot f_{S'}}$$
$$\exp(-\epsilon_2/kT) \qquad (18)$$

By taking into account the relation, $\dfrac{d[e]}{dt} = 2V_{des}$, Eq. (18) may be rearrnaged to Eq. (19)

$$\frac{d[e]}{dt} = k_3 \cdot \frac{[S''O^-]^2 \cdot [S']}{[S'']^2} \qquad (19),$$

$$k_3 \equiv 2\frac{kT}{h} \cdot \frac{f_* \cdot f_{S''}^2}{f_{S''O}^2 \cdot f_{S'}} \cdot \exp(-\epsilon_2/kT)$$

When the adsorption equilibrium is reached, the net rate of adsorption becomes zero, which results in Eq. (20)

$$\frac{[S'']_{eq}^2 [e]_{eq}^2}{[S''O^-]_{eq}^2} = \frac{k_3}{k_1 \cdot K_1} \cdot p_{O_2}^{-1} \equiv D \cdot p_{O_2}^{-1} \qquad (20)$$

On the other hand, $[e]_{eq}$ is given by $[e]_{eq} = [e]_0 - [e]'_{eq}$, where $[e]'_{eq}$ is concentration of quasi-free electrons occupied by oxygen atoms at equilibrium. By combining Eq. (20) with the following relation, Eq. (21) can be obtained

$$[S'']_{eq} = [S'']_0 - [S''O]_{eq} = [S'']_0 - [e]'_{eq}$$
$$= [S'']_0 - [e]_0 + [e]_{eq}$$

$$\{[S'']_0 - [e]_0 + [e]_{eq}\}^2 \cdot [e]_{eq}^2 / \{[e]_0 - [e]_{eq}\}^2$$
$$= D \cdot p_{O_2}^{-1} \qquad (21)$$

When $[S'']_0/[e]_0 \ll 1$, and $[e]_{eq}/[e]_0 \ll 1$, Eq. (21) reduces to Eq. (22).

$$[e]_{eq}^2 \simeq D \cdot p_{O_2}^{-1} \qquad (22)$$

i.e. $\kappa \propto p_{O_2}^{-1/2}$ or $R \propto p_{O_2}^{1/2}$

The relation is approximate to the experimental relation of $R \propto p_{O_2}^{2/3}$, but does not attain to a complete agreement.

Temperature-dependence of Conductivity in Oxygen Atmosphere.—The temperature-

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* Without simplification, Eq. (14) results in the following equation.
$R - R_0 = B \cdot k_1 \cdot [S']_0 \cdot t + B \cdot k_1 \cdot k_2$ $[S']_0 \cdot p_{O_2} \cdot \exp(-k_2 \cdot p_{O_2} \cdot t)$
The equation is rather inconvenient for comparison with the experiments.

dependence of conductivity at a constant pressure of oxygen (the shape of the isobar as well as the change caused by a rapid rise of temperature) is similar to that obtained by H. S. Taylor with the adsorption of hydrogen on zinc oxide. H. S. Taylor[11] explained his results in terms of the heterogeneity of active sites on the surface. A similar consideration being employed, two kinds of impurity centers associating with the conductivity should be assumed. In this respect, the heat of adsorption would probably be different, irrespective of the nearly equal activation energy of adsorption, for the adsorption on either the $Zn^+ \cdot Zn^+$ or the $Zn^+ \cdot Zn$ site suggested in the foregoing chapter, but no decisive explanation is available at this time.

Adsorption of Hydrogen.—H. S. Taylor[12] as well as E. Wicke[13] has already found two maximum amounts of the adsorbed hydrogen, the one at a temperature below 100°C and the other at a temperature between 250-300°C respectively. H. S. Taylor explained his results as was described, but gave no concept of the structure of the sites. E. Wicke attributed the adsorption predominant at temperatures below 100°C to the adsorption with dissociation on the oxide cation Zn^{++} of the surface of stoichiometric crystal of zinc oxide, and the other at higher temperatures to the formation of surface hydroxides.

In the light of the present results, the adsorption at the lower temperature may be estimated to take place predominantly on zinc atom pairs of the surface. The evidence is given by the facts that the adsorption at the lower temperature can take place on the evacuated oxide with relatively high conductivity, but not on the oxygenated one with negligibly small conductivity, and that the rate of the adsorption is closely relevant to the change of the conductivity. Zn^{++} in the normal lattice of zinc oxide suggested by E. Wicke seems not to participate in the adsorption, as it can hardly confer the conductivity. The parallel relation observed between the conductivity and the adsorbed amount in the range of temperature is also an evidence in favour of the above estimation.

The expression for the rate of hydrogen

adsorption at lower temperatures similar to that for the oxygen adsorption is suggestive of a molecular adsorption taking place predominantly at the earlier stage of adsorption as well as the adsorption with dissociation at the subsequent stage.

The hydroxyl formation between the adsorbed hydrogen and O^{--} in the oxide above 200°C as is suggested by E. Wicke may probably be expected from the view point of the facts for the higher temperatures, that the conductivity increases markedly on the exposure of the oxide to hydrogen and that the specimen subjected to the hydrogen treatment evaporates zinc metal which may be produced as the result of loss of OH radical combined previously with zinc metal.

Summary

With the evacuated zinc oxide, there has been found, in an intermediate range of temperatures from 100° to 500°C, a linear relation between $\log R$ and $1/T$, from which an activation energy of 0.025 eV. has been evaluated.

From the results of the measurement of adsorption a molecular adsorption and an adsorption with dissociation seemed to take place on the evacuated oxide at an earlier and a subsequent stage of oxygen adsorption respectively. The more detailed results from the conductivity measurements revealed that the adsorption with dissociation took place consecutively in the earlier stage in which the molecular adsorption was predominant.

At temperatures below 200°C, the conductivity decreases accompanied by hydrogen adsorption, while it increases at higher temperatures. The adsorption kinetics as the rate of change of the conductivity is given by expressions similar to those in the oxygen adsorption.

The adsorption of oxygen as well as hydrogen accompanied by the conductivity decrease may be explained in terms of two different kinds of sites, on which the molecular adsorption and the adsorption with dissociation take place respectively. The interstitial zinc atom pair suggested by P. H. Miller being employed for the site of the latter adsorption, a quantitative interpretation is available for the rate and the equilibrium of the adsorption associating with the conductivity.

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