The Chemisorption of Hydrogen on Zinc Oxide. I. Effect of Chemisorption on the Electrical Conductivity of Zinc Oxide

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By

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Abstract

The conductivity change caused by the chemisorption of hydrogen was investigated with oxidized and reduced zinc oxide. In the former case the conductivity after hydrogen was admitted into the sorption vessel increased autocatalytically until a maximum rate was attained. The behavior was attributed to the decrease in concentration of adsorbed oxygen atom and the activation energy for this decrease was estimated to be 18 kcal. The adsorption on reduced zinc oxide revealed no significant change in conductivity below 110°C, while it produced marked increase in conductivity at higher temperatures. The results indicate that the chemisorption taking place above 110°C is of a different type from that at lower temperature.

The "activated adsorption" of hydrogen on zinc oxide was studied by H. S. Taylor et al. who found that the activation energy increased with adsorption coverage, which together with various additional experimental facts led them to the concept of the inhomogeneity of adsorbent surface.[1][2][3] As to the nature and mechanism of activated adsorption, however, little has yet been understood. Lately, on the other hand, many studies on properties of zinc oxide as an excess semiconductor have appeared. The purpose of the present work is to clarify the nature and the mechanism of chemisorption of hydrogen on zinc oxide by investigating the kinetics of adsorption as well as the effect of chemisorption on the electrical conductivity of zinc oxide. In this paper the change of electrical conductivity due to chemisorption is reported. Its relation to the kinetics of chemisorption will be given in later paper.

Experimental

Zinc oxide was prepared as follows: In solutions of zinc nitrate and sodium carbonate (both of the grade *pur analyse*) were mixed and boiled. After decantation, the precipitate of basic carbonate was washed, dried and calcinated at 350°C.

Hydrogen was obtained by the electrolysis of 30% solution of potassium hydroxide, purified by passing through heated palladium asbestos and dried on phosphorus pentoxide.

The electrical conductivity of zinc oxide was determined as follows: Zinc oxide

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powder was pressed in a mould, sintered for five hours at 500°C in air and held between platinum plates in the sorption vessel; the electrical resistance was measured by means of Wheatstone bridge or by reading directly the current at a constant voltage. In preparing zinc oxide specimen, too strong press was avoided in order to preserve the effect of adsorption on the conductivity as well as possible.
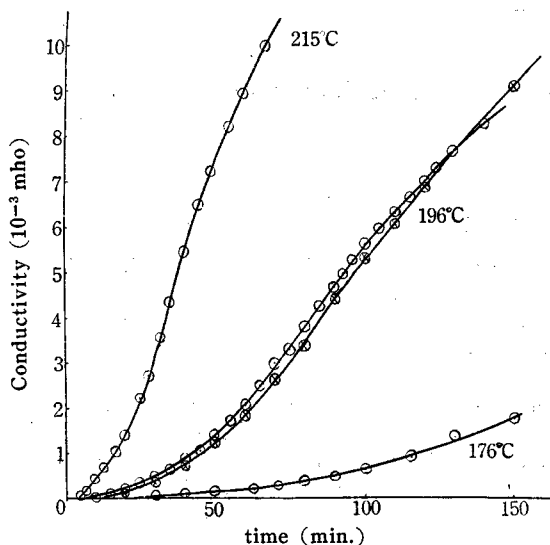

Fig. 1 Electrical conductivity change of oxidized zinc oxide
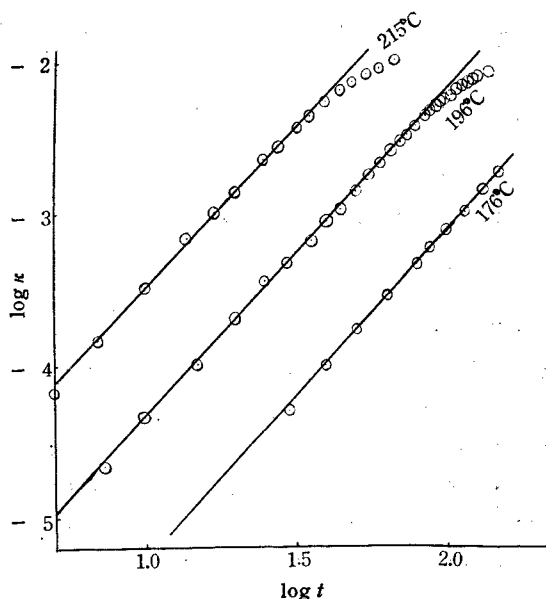
○ H₂ Press. 10–12 mm Hg
⊗ H₂ Press. 20–25 mm Hg

Fig. 2 Plot of log κ–log t (m=2.1)

Preceding to chemisorption experiments, zinc oxide samples were treated in two ways: In case of "reduced" zinc oxide, a sample was treated with about 2 cm Hg hydrogen at 410°C and the vessel was evacuated for three hours at the same temperature; in case of "oxidized" zinc oxide, a sample was kept in contact with about 2 cm Hg dry air for an hour at 410°C.

Temperature of the sorption vessel was kept constant within ±1°C by regulating electrically heated oil bath.

Results and Discussion

1. Oxidized zinc oxide

The conductivity changes observed after hydrogen was admitted are shown in Fig. 1. The conductivity always increased autocatalytically in the initial stage, reached a maximum rate and thereafter the rate of increase decayed. When the vessel was pumped out after each run and dry air was admitted at 410°C, the conductivity diminished to a negligibly small value.

Though the mechanism for the conductivity increase cannot be clearly decided, the formation of excess zinc atoms in the bulk phase of zinc oxide will not be responsible for the conductivity increase, judging from the temperature range in the present

work. It seems rather probable that the decrease of oxygen atom adsorbed on the surface of zinc oxide is the cause as suggested by Hauffe and Parravano[4][5]:

$$O_{aas} + \tfrac{1}{2}H_2 \rightarrow OH_{aas} .$$
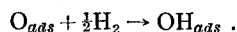
There are divergent opinions with respect to the effect of adsorbed oxygen atom on the conductivity and nothing conclusive can be said at present, especially in the case of such specimen made of pressed powder as used in the present work. As for zinc oxide, however, it is a well known fact that the temperature coefficient of the increase in conductivity falls off with increasing conductivity. The conductivity of zinc oxide, therefore, may be generally expressed by

$$\kappa = f(n) \exp. (-F(n)/RT) ,$$

or

$$\log \kappa = \log f(n) - F(n)/2.3RT , \qquad (1)$$

where n represents the concentration of adsorbed oxygen atom.

On the other hand, the experimental conductivity-time curves up to rate maxima could be fitted to the following expression as shown in Fig. 2.

$$\log \kappa = k + m \log t , \qquad (2)$$

where k and m are constants and t is time. k was found to be temperature dependent, while m was nearly independent of temperature, provided that the temperature range was not very wide.

Combining now two relations (1) and (2), we may estimate the activation energy of the rate of decrease in adsorbed oxygen atom concentration as follows: let the time when the concentration falls to a certain value n be t_1 and t_2 at temperatures T_1 and T_2 respectively. Then

$$\log f(n) - F(n)/2.3RT_1 = k_1 + m \log t_1 ,$$
$$\log f(n) - F(n)/2.3RT_2 = k_2 + m \log t_2 ,$$

or

$$k_2 - k_1 + (F(n)/2.3R)(1/T_2 - 1/T_1) = m(\log t_1 - \log t_2) . \qquad (3)$$

The activation energy $E(n)$ to be sought is given by

$$-(\log t_1 - \log t_2) = (E(n)/2.3R)(1/T_2 - 1/T_1) . \qquad (4)$$

It follows from equations (3) and (4) that

$$k_1 - k_2 = (1/2.3R)(mE(n) + F(n))(1/T_2 - 1/T_1) , \qquad (5)$$

which gives $E(n)$ if $F(n)$ is known. $F(n)$ was determined approximately by the following device: When the conductivity passed over the maximum rate position, the temperature was suddenly lowered and the conductivity corresponding to the new temperature was read; comparison between conductivities before and after the sudden temperature drop enabled to estimate $F(n)$ as seen in Fig. 3, since the concentration of adsorbed oxygen atom should have remained unaltered. $E(n)$ thus obtained finally was 18–19 kcal. (Fig. 4). It may be noted that $E(n)$ obtained naturally refers to the concentration n near
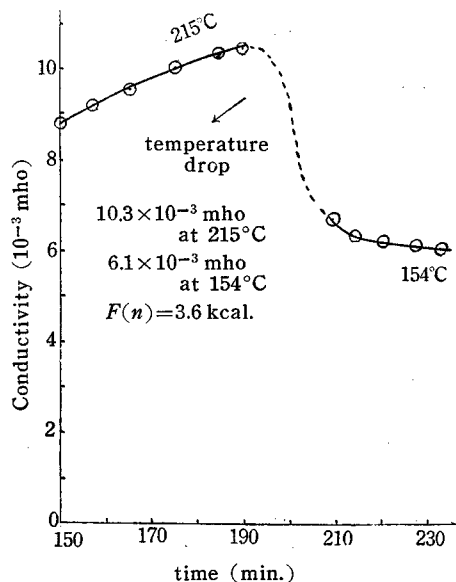
Fig. 3 Estimation of $F(n)$ by the
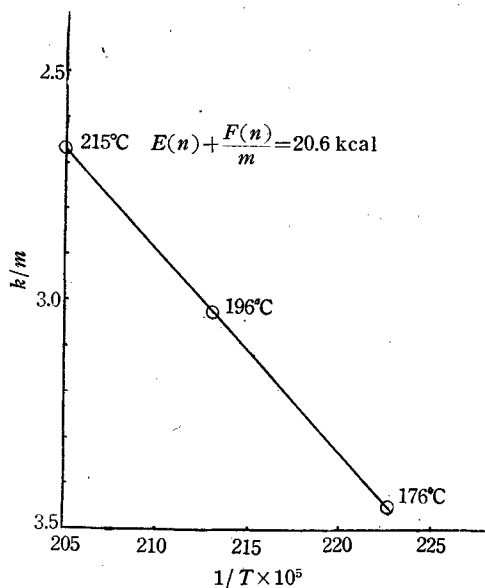sudden temperature drop

Fig. 4 Temperature dependence of k/m
(Estimation of $E(n)+F(n)/m$)

the maximum rate region in the conductivity curve, and, accordingly, is not applicable to the initial portion of the conductivity curve.

As seen in Fig. 1, the maximum rate of increase in conductivity remained nearly unchanged when the pressure of hydrogen was varied. The hydrogen pressure, therefore, appears to have little effect on the rate of conductivity increase. Whether or not the initial autocatalytic increase in conductivity is caused by a similar mechanism to that encountered generally in the solid ph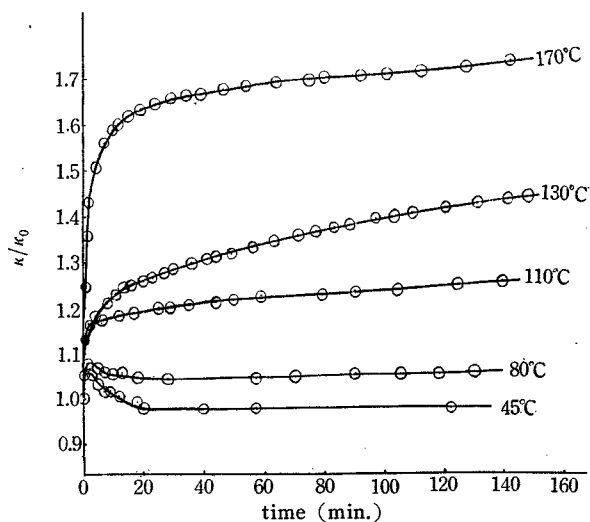ase reactions cannot be decided at present. For the rate of conductivity increase is clearly influenced by the change in $F(n)$ so that the rate of decrease in oxygen atom concentration will not necessary be itself autocatalytic. For the same reason no decisive explanation can be given to the relation (2).

A few remarks may be added as to the meaning of activation energy E. As already mentioned, E represents the activation energy of the rate of decrease in adsorbed oxygen atom concentration. It is, however, obvious that E is really the activation energy

Fig. 5 Electrical conductivity change of
reduced zinc oxide

of the rate-determining process involved. The adsorption of hydrogen may be excluded as the rate-determining process, since the rate of conductivity increase is nearly independent of hydrogen pressure. Hence there remain two possibilities: E is actually the activation energy of the migration process of adsorbed hydrogen or that of reduction process of initially adsorbed oxygen.

2. Reduced zinc oxide.

The effect of hydrogen adsorption on the electrical conductivity is shown in Fig. 5, where κ and κ_0 are conductivity after and before hydrogen admission respectively. κ_0 was of the magnitude of 0.07–0.09 mho and the initial hydrogen pressure was 20–25 mm Hg. As seen in the figure, apart from initial insignificant changes, the conductivity below 80°C remained practically constant, unaffected by the progress of adsorption, while above 110°C the conductivity clearly increased with adsorption and the increase was greater, the higher the temperature was. The conductivity change was reversible; by evacuating the adsorption vessel at 410°C after each run, the conductivity was brought to the original initial value within about 10%.

The results in Fig. 5 indicate that the adsorption above 110°C is of a different type from that at lower temperatures. In order to confirm this, measurements were repeated with another sample of zinc oxide prepared and treated in the same way as the first. Though the second sample gave different magnitudes of conductivity change and different values of ratio (conductivity change)/(the initial conductivity) from those obtained with the first sample probably owing to the different contact conditions in both samples, the general feature as to temperature effect was found to be unaltered. The appearance of conductivity increase with adsorption above 110°C was thus established.

Such analysis of the conductivity curves as carried out in the case of oxidized zinc oxide was abandoned in this case. For the initial parts of the conductivity curves, as seen in Fig. 5, appear to be influenced by the initial rapid adsorption which is to be discriminated from the secondary slow adsorption.

The results obtained may be compared with previous studies on hydrogen chemisorption on zinc oxide. H. S. Taylor et al. observed that the adsorption attained the maximum amount at 80°C, decreased at higher temperature and again began to increase at 110°C. Lately[3] they carried out experiments in which hydrogen was adsorbed on zinc oxide and the temperature of the system was raised and lowered repeatedly. As shown in Fig. 6, they found
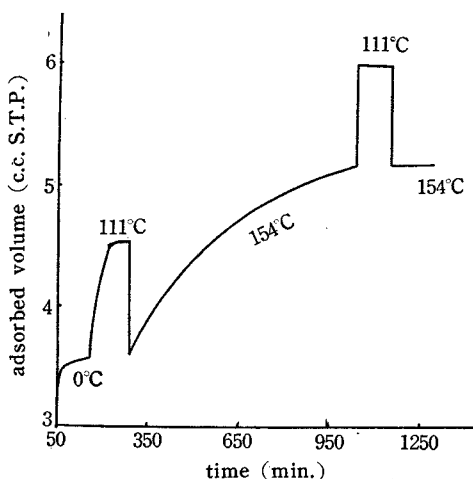

Fig. 6 Adsorption rate curve on raising and lowering temperature
(Taylor and Liang)

that on raising the temperature higher than 110°C, desorption and subsequently rapid readsorption of even a greater amount than before took place; when the temperature was lowered again, the adsorption recovered the original amount; the adsorption increased, however, monotonously as the temperature of zinc oxide which adsorbed hydrogen at a high temperature was lowered successively. They explained these results assuming the heterogeneous structure of zinc oxide surface, while E. Wicke[6], on the other hand, sug-gested an interpretation that hydrogen is adsorbed in the form of hydride below 100°C, but at higher temperatures it forms hydroxylic bond.

The results in this paper appear to support Wicke's interpretation. For it is quite probable that conductivity increases above 110°C, if hydroxylic bond formation takes place above that temperature. The argument, however, cannot be made decisive when another experimental fact is taken into consideration, that chemisorption of hydrogen on zinc oxide in this temperature range is reversible as reported by Taylor: Hydrogen once adsorbed can be almost completely pumped out again as hydrogen, while one may expect recovering as water if hydroxylic bond is formed on zinc oxide surface. The hydrox-ylic bond in this case, therefore, may be one of unstable intermediate type, or the situa-tion may correspond to such an intermediate step in the course of hydroxylic bond forma-tion in which only electron·donation from hydrogen to zinc takes place as predicted by Wicke. Although at present it seems impossible to clarify this point further, it may be concluded at least that the type of hydrogen adsorption on zinc oxide changes at about 100°C.

References

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