

Effect of Hydrogen and Carbon Monoxide on the Electrical Conductivity of Zinc Oxide

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The increase in electrical conductivity of zinc oxide caused by hydrogen was investigated in previous works^{1,2)} in order to get a clue to the nature of the chemisorption of hydrogen, with the results summarized as follows: On admission of hydrogen no significant change in the conductivity is observed below 100°C, while at higher temperatures a marked increase takes place; moreover, the rate and the amount of chemisorption decrease with increasing temperature up to 110°C but increase at higher temperatures. On the basis of these results, it was suggested that two types of hydrogen chemisorption exist on zinc oxide; one is predominating at higher temperatures and responsible for the increase in conductivity, and the other is observed at lower temperatures, with little effect on conductivity. Making use of the rate of increase in conductivity, the activation energy for the chemisorption of the high temperature type was estimated as 25 kcal./mol.

However, the existence of two such types of chemisorption can not yet be regarded as established, since later studies^{3,4)} on the rate of desorption and the adsorption isotherm in addition to those on the rate of adsorption, covering wide ranges of pressure and temperature, showed that the heterogeneity of zinc oxide surface should be taken into account. The aim in the present work has been to reinvestigate the relation between the hydrogen chemisorption and the conductivity change by more extensive experiments.

Experimental

Materials.—Zinc oxide was prepared as described previously³⁾. The experiments with hydrogen were carried out with zinc oxide sintered at 800°C for 5 hr., while non-sintered zinc oxide was used for the study with carbon monoxide. Hydrogen and carbon monoxide were obtained as given in previous papers^{3,5)}.

Apparatus and Procedure.—Conductivity measure-

ments were made with a powdered specimen held between two electrodes, by means of a Wheatstone bridge. Details of the apparatus and procedure were described in the previous paper²⁾. In the measurements of the rate of conductivity decrease, an auxiliary heater of nickel wire was mounted in the reaction vessel for the purpose of changing the temperature rapidly, taking into account the slow attainment of thermal equilibrium at low pressures.

Results and Discussion

Relationship between the Rate of Conductivity Increase and that of the Formation of Donors.

There seems to be little doubt that the observed increase in conductivity of zinc oxide brought in contact with hydrogen is related to the formation of donors of a certain type. In view of the well-known difficulties, especially in the case of a powdered sample such as used in the present work, it seems questionable to discuss the kinetics of the formation of donors, from the conductivity-time curves at a constant temperature, on the assumption of a relationship between conductivity and the number of donors. However, as shown in the previous paper²⁾, the activation energy of the formation of donors may be obtained in the following way. The rate of formation of donors at the time when the number of donors present is c may be written as

$$(dn/dt)_c = (dn/d\kappa)_c (d\kappa/dt)_c$$

where κ is the conductivity and n the number of donors. The activation energy for the formation of donors, E is therefore given by $E = E_2 - E_1$, where E_1 and E_2 are the activation energies of conductivity itself and of conductivity increase, respectively, both referring to the number of donors c . Using this equation, we can obtain the value of E provided that E_1 and E_2 are known.

Temperature Coefficient of Conductivity.— E_1 decreases with increasing number of donors as described by various workers. The value for the state with a negligible number of donors was estimated from the temperature coefficient of conductivity with the specimen evacuated at about 400°C. Fig. 1 shows a typical result, which gives a value of 1.2 kcal./mol. Values

1) Y. Kubokawa and O. Toyama, *Bull. Naniwa Univ.* (at present *Bull. Univ. Osaka Prefecture*) **A2**, 103 (1954).

2) Y. Kubokawa and O. Toyama, *J. Phys. Chem.*, **60**, 833 (1956).

3) Y. Kubokawa, *This Bulletin*, **33**, 546 (1960).

4) Y. Kubokawa, *ibid.*, **33**, 550 (1960).

5) Y. Kubokawa, *ibid.*, **33**, 555 (1960).

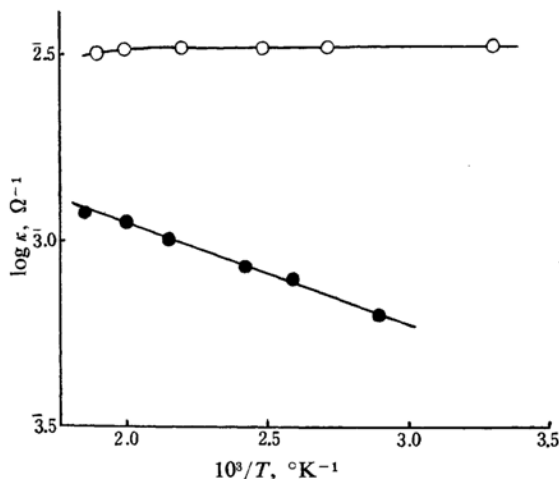


Fig. 1. Conductivity as a function of temperature.

—●—, in vacuo; —○—, in H₂.

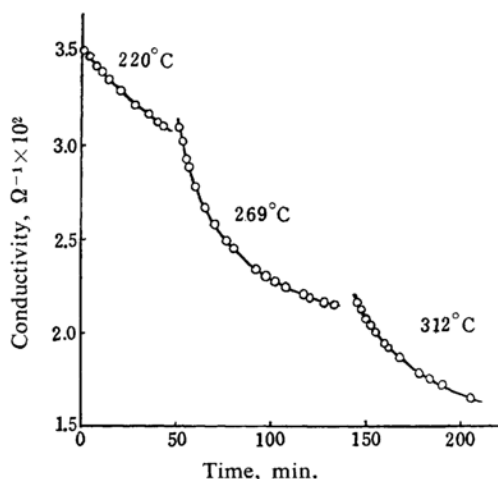


Fig. 2. Conductivity decrease by reducing pressure and the effect of a sudden temperature change.

TABLE I. VALUES OF E_1 AND THE ACTIVATION ENERGY OF CONDUCTIVITY DECREASE FOR THE DATA IN FIG. 2

Temp. range (°C)	220~269	269~312
E_1 (kcal./mol.)	0.4 ± 0.1	0.7 ± 0.2
Activation energy of cond. decrease (kcal./mol.)	31 ± 2	31 ± 2

of E_1 at an appreciable number of donors can not easily be obtained because the temperature coefficient in hydrogen such as shown in Fig. 1 does not give the true value of E_1 , since in this case the change of conductivity with temperature may arise from two factors, i. e., from the temperature coefficient of conductivity itself and from the variation of the

number of donors with temperature. However, approximate values of E_1 may be obtained as follows.

After hydrogen was introduced at about 400°C, the whole vessel was cooled down to a lower temperature, where the conductivity decrease by evacuation was followed for some time. Then the vessel was abruptly heated to a higher temperature, where the conductivity measurement was continued. The results are shown in Fig. 2. As described in a previous paper¹, by extrapolation of the $\kappa \sim t$ curves to the time of the abrupt change in temperature, the conductivities at different temperatures corresponding to equal numbers of donors were obtained. Values of E_1 thus determined are given in Table I. They are appreciably less than the value determined at the evacuated state.

Dependence of the Rate of Conductivity Increase on Temperature.—This was determined in two ways, i. e., by measuring the initial rates of conductivity increase at varied temperatures as described previously² and by observing the rate increase caused by an abrupt temperature elevation during the conductivity increase measurements. The latter method is similar in principle to that used in the adsorption rate measurements¹. By extrapolation of the rates

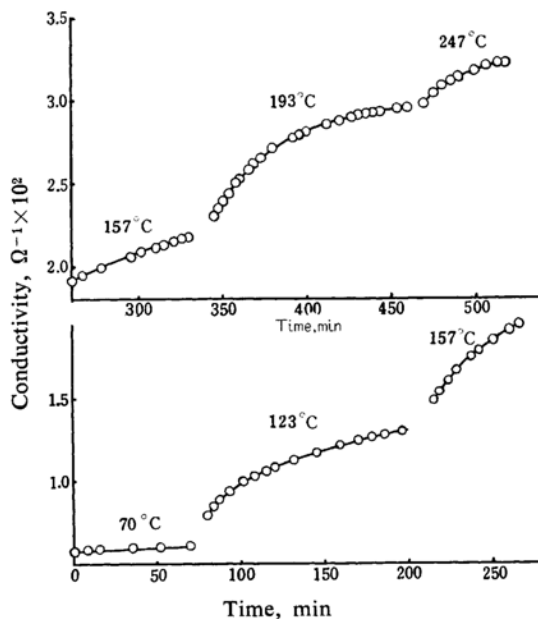


Fig. 3. Conductivity increase by hydrogen and the effect of a sudden temperature change. Pressure, 56 mmHg.

TABLE II. VALUES OF E_2 FOR THE DATA IN FIG. 3

Temp. range (°C)	70~123	123~157	157~193
E_2 (kcal./mol.)	18 ± 1.5	21.7 ± 1.5	20.5 ± 1.5

to the time of the abrupt change, the rate at the two different temperatures corresponding to equal numbers of donors and consequently E_2 for that number of donors were obtained. In a typical example shown in Fig. 3, the temperature was raised in stages up to about 300°C after hydrogen was admitted at room temperature. The value of E_2 found here was about 21 kcal./mol., being roughly constant in the temperature range 120–200°C (Table II). E_2 is therefore of much greater magnitude compared with E_1 described above, indicating that the activation energy of the formation of donors is almost equal to that of conductivity increase.

The initial rate measurements, i. e., the other one of the two methods mentioned above, gave a value of 20 kcal./mol. for E_2 , in agreement with that obtained by a rapid temperature elevation. The conductivity-time curves obtained were similar to those described in the previous paper².

Dependence of the Rate of Conductivity Increase on Pressure.—This was determined in two ways similar to those used for the tempera-

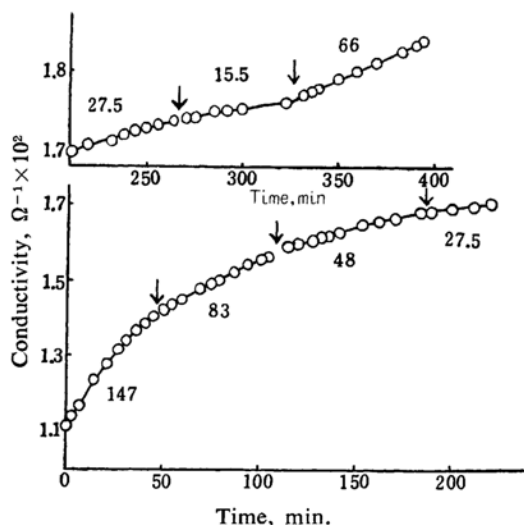


Fig. 4. Conductivity increase by hydrogen at 130°C and the effect of a sudden pressure change. Figures indicate the pressure in mmHg.

TABLE III. VALUES OF n IN THE EXPRESSION, $\text{RATE} \propto p^n$ FOR THE DATA IN FIG. 4

Pressure before and after the pressure change (mmHg)	n
147 → 83	0.82
83 → 48	0.85
48 → 27.5	0.85
27.5 → 15.5	0.88
15.5 → 66	0.93

An upper limit of the experimental error was $\pm 10\%$.

ture dependence. Fig. 4 shows the results obtained by a rapid pressure change during the measurements of conductivity increase. The pressure dependence was supposed to take the form p^n and the values of the exponent n were determined from this figure, as given in Table III. It is seen that the rate of conductivity increase is proportional to $p^{0.85}$ at increasing as well as decreasing pressure. The measurements of the initial rates of conductivity increase gave a similar pressure dependence.

Dependence of the Rate of Conductivity Decrease by Reducing Pressure on Temperature.

—This may be estimated by the comparison of the rates at different temperatures corresponding to equal numbers of donors. For this purpose we may utilize the results described in Fig. 2, which were used for the determination of E_1 . In the same manner as described above, the activation energy of conductivity decrease was estimated as 31 kcal./mol. (Table I).

Variation of the Conductivity with Hydrogen Pressure.—Above 300°C, the rate of conductivity increase on admitting hydrogen was found to be very great, suggesting that in this temperature range the conductivity increased to an equilibrium value may be obtained as a function of pressure in a manner similar to the adsorption equilibrium measurements. Thus hydrogen was introduced at 350°C, and the conductivity was measured at various pressures and a constant temperature by decreasing pressure successively. The results were reproducible when pressure was inversely increased as shown in Fig. 5.

Conductivity Increase by Carbon Monoxide.—Using carbon monoxide, in place of hydrogen, similar measurements were performed. Fig. 6 shows the $\kappa \sim t$ curves at varied temperatures and an approximately constant initial pressure, which gives a value of 25 kcal./mol. for the activation energy of conductivity increase. This

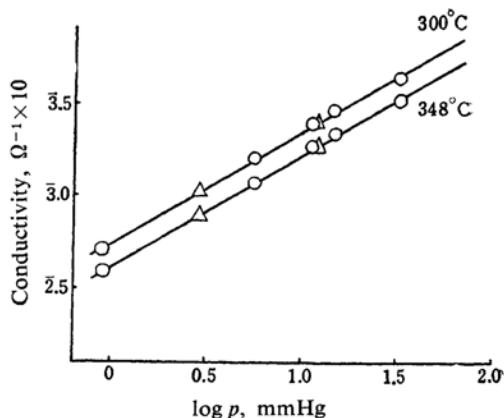


Fig. 5. Conductivity as a function of hydrogen pressure. —○—, on decreasing pressure; —△—, on increasing pressure.

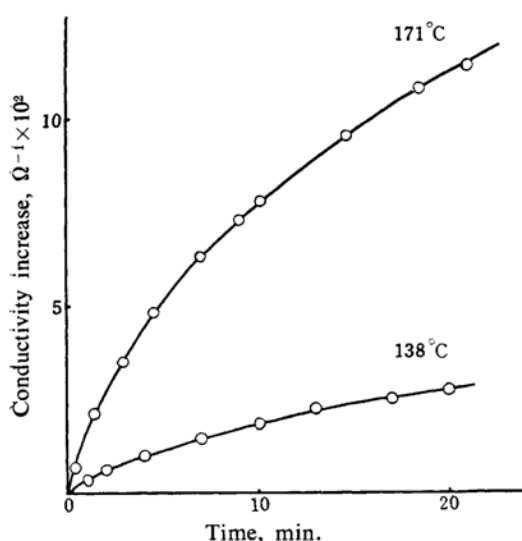


Fig. 6. Conductivity increase by carbon monoxide. Pressure, 1.4 mmHg. The activation energy was estimated as 25 kcal./mol.

may be regarded approximately as that of the formation of donors because of the negligible value of E_1 . Almost the same value of activation energy was obtained in the method of a rapid temperature elevation. The conductivity increase was reversible as with hydrogen: by evacuation at 400°C the original conductivity was restored.

Relation between the Hydrogen Chemisorption and the Conductivity Increase.—As described in the previous paper²³, the conductivity enhanced by hydrogen was restored nearly to the original value by pumping out at 400°C. In addition, the conductivity increased to an equilibrium value varies reproducibly on increasing as well as decreasing pressure. These results, together with the fact that the amount of hydrogen adsorbed is almost completely desorbed as such, appear to indicate that this conductivity increase may not arise from the reduction of zinc oxide, but from the hydrogen adsorption of a certain type.

However, from the results obtained in this work, the assumption that the conductivity increase is due to a sort of chemisorption leads to the heat of chemisorption of 10 kcal./mol. and the activation energy of 21 kcal./mol. Relative magnitudes of these values are quite unusual for a chemisorption. Moreover, the activation energy of hydrogen chemisorption obtained from adsorption measurements⁴⁾ is 7~10 kcal./mol. in the comparable temperature range 100~140°C, and hence markedly less than the above value of 21 kcal./mol. These considerations suggest that the conductivity increase is not directly related to the hydrogen chemisorption of any type, and that the hydrogen

uptake associated with the conductivity increase, if any, is only a negligible portion of the total uptake. It seems therefore necessary to modify the conclusion drawn from the earlier conductivity measurements²⁾ that two types of chemisorption exist, one of them being responsible for the conductivity increase while the other is not.

As described in the previous paper²³, the rate of adsorption and the adsorbed amount decrease with any increase in temperature up to 110°C, but increase at higher temperatures. Although such behavior, apparently, is adequately explainable in terms of the two types of chemisorption, this can not be the only explanation. Now that the heterogeneity of zinc oxide surface is undeniable through desorption measurements, the concept of single type chemisorption on a heterogeneous surface seems to present a more probable explanation. In addition, as previously described²³, the change in the activation energy of desorption is continuous, in contrast with that of carbon monoxide for which the presence of the two types of chemisorption was confirmed⁵⁾. This again appears to favor the concept of single type chemisorption on a heterogeneous surface.

Nature of the Conductivity Increase by Hydrogen.—As regards the nature of the conductivity increase, an interpretation is that hydrogen atoms diffuse as protons into the lattice close to the surface, as suggested by various workers⁶⁾. However, such an interpretation may not easily be reconciled with the following results obtained: The rate of conductivity increase is proportional to $p^{0.85}$; essentially the same behavior is observed with carbon monoxide on zinc oxide where there is no possibility of dissolution into crystals; in addition, this conductivity increase is an exothermic phenomenon, in contrast with hydrogen dissolution into a crystal of zinc oxide which is an endothermic phenomenon, as reported by Mollwo and others⁷⁾.

At present, the most plausible interpretation of the conductivity increase seems to be that proposed by Thomas et al.⁸⁾, who attributed it to the surface reduction of zinc oxide. This possibility was excluded previously on the basis of the fact that no water vapor was detected on desorption and that the conductivity increase was reversible. However, the amount of hydrogen uptake is a negligible portion of the total uptake as shown above. Hence such a

6) e.g., F. S. Stone, "Chemisorption", edited by W. E. Garner, Butterworths Scientific Publications, London (1957), p. 181.

7) E. Mollwo, *Z. Physik.*, **138**, 478 (1954); D. G. Thomas and J. J. Lander, *J. Chem. Phys.*, **25**, 1136 (1956).

8) D. G. Thomas and J. J. Lander, *J. Phys. Chem. Solids*, **2**, 318 (1957).

small amount of water vapor will not be detectable. Moreover, the recovery of the original conductivity by pumping out at high temperature and the reproduction of the conductivity on increasing and decreasing pressure may be explained on the assumption that zinc atoms produced by reduction evaporate rapidly at high temperature. This seems to be a plausible assumption, since the reduction is probably confined to the surface layer^{9,10}.

This interpretation may be applied in the temperature range above 100°C, but a slight conductivity change observed below this temperature described in the previous paper² probably arises from the chemisorption of hydrogen, although this behavior has not been studied in detail.

Summary

The rate of increase in conductivity of zinc oxide caused by hydrogen was found to be

9) The conductivity increase observed on the oxidized state described in a previous paper¹⁾ may also be attributed to the surface reduction of zinc oxide.

10) According to the previous work²⁾, the activation energy of the conductivity increase is 25 kcal./mol., being somewhat different from the value of 21 kcal./mol. found in the present work. Considering that this activation energy is a composite quantity including the activation energy of adsorption and that of the surface reduction, this difference may be explained by different proportions of the contributions of the two processes.

proportional to $p^{0.85}$ and to have an activation energy of 21 kcal./mol. For this system the activation energy of the increase of donors was shown to be almost the same as that of the conductivity increase. The activation energy of the decrease of donors by evacuation was 31 kcal./mol. A similar conductivity increase was observed with carbon monoxide. On the basis of these results together with those of adsorption measurements reported previously, it was concluded that the conductivity increase was scarcely related at all to the hydrogen chemisorption, indicating that it is untenable to postulate two such types of hydrogen chemisorption as was believed in the previous work, i. e., one responsible for the conductivity increase and the other without such effect. As for the cause of the conductivity increase, the surface reduction of zinc oxide was suggested.

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