Effect of Oxygen Pretreatment on Hydrogen and Carbon Monoxide Chemisorption on Zinc Oxide

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Since the treatment of an electron barrier layer was suggested for the chemisorption on semiconductors by Hauffe, Weisz, and others(1), the chemisorption and catalysis on oxide catalysts have been discussed on the basis of this model, and the relation between the catalytic activities of oxides and their properties as semiconductors have been emphasized by a number of workers(2,3). As for the catalysis by zinc oxide, Parravano and others(4) found that the activity towards hydrogen-deuterium exchange reaction increases with its electrical conductivity. On the basis of these results, Hauffe(2) emphasized the fact that the properties of oxides as semiconductors play a large part in determining the activity towards this reaction.

However, for hydrogen or carbon monoxide chemisorption on zinc oxide which belongs to a "cumulative chemisorption", the barrier is so thin that it is doubtful whether this model

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1) K. Hauffe and H. J. Engell, *Z. Elektrochem.*, **56**, 366 (1952); **57**, 763, 773 (1953); P. Aigrain and C. Dugas, ibid., **56**, 363 (1952); P. B. Weisz, *J. Chem. Phys.*, **21**, 1531 (1953).

2) K. Hauffe, *Angew. Chem.*, **67**, 189 (1955).

3) F. S. Stone, "Chemistry of the Solid State", edited by W. E. Garner, Butterworths Scientific Publications, London (1955), p. 367; T. Takaishi, *Z. Naturforsch.*, **11a**, 286, 297 (1956).

4) E. Molinari and G. Parravano, *J. Am. Chem. Soc.*, **75**, 5233 (1953); L. F. Heckelsberg, A. Clark and G. C. Bailey, *J. Phys. Chem.*, **60**, 559 (1956).

will be applicable to such systems. It appears more likely that covalent-bonding, similar to that in the chemisorption on metals determines the behavior of these systems, as pointed out by several workers[5].

It was aimed in the present work to obtain unambiguous information on the relation between the electronic state of zinc oxide and the chemisorption of hydrogen as well as carbon monoxide. For this purpose, the effect of high temperature oxygen treatment of zinc oxide was investigated, inasmuch as it is well established that such treatment markedly reduces the electrical conductivity of zinc oxide.

The present work was designed with another object in addition to that stated above. As regards hydrogen chemisorption on zinc oxide, Morrison[6] proposed a model, according to which the chemisorption means nothing but an interaction of hydrogen with adsorbed oxygen remaining after high temperature evacuation in the form of O^-_{ads} or O^{2-}_{ads}. This mechanism may be written as

$$O^-_{ads}+1/2\,H_2 \rightarrow OH^-_{ads}$$
$$O^{2-}_{ads}+1/2\,H_2 \rightarrow OH^-_{ads}+\text{electron}$$

He is of the opinion that the two types of chemisorption for this system as described by Taylor et al.[7], may be explained in terms of these two processes. According to Garner[8], however, OH_{ads} produced by the interaction of hydrogen with adsorbed oxygen is irreversible, in contradiction to Morrison's view. It may then be expected that the present study of the effect of oxygen treatment on hydrogen chemisorption would also serve to solve this problem.

Experimental

Materials.—For zinc oxide, ZnO I described in a previous paper[9] was used. Hydrogen and carbon monoxide were prepared and purified as in the previous work[9,10]. Oxygen was obtained by the electrolysis of 30% potassium hydroxide solution, and purified in the same manner as hydrogen.

Apparatus and Procedure.—The apparatus used in the present work was the same as that used in the previous work[9] except that a Pirani gauge was attached to the flask in which the gas desorbed was collected. By measuring the voltage required to balance the bridge, the composition of the desorbed gas could be calculated from the calibration curves for hydrogen and oxygen.

Results

Effect of Oxygen Pretreatment on the Amount of Hydrogen Adsorbed.—After oxygen adsorption was allowed to proceed for 3 hr. at 450°C and at a pressure of 30 mmHg, the temperature was lowered to 260°C. The system was evacuated for 30 min. at this temperature, and then the chemisorption rate measurements were carried out at room temperature (Run A). After this run, the system was evacuated for 1 hr. at 500°C and similar measurements were taken (Run B). Run B was further followed by evacuation for 15 hr. at 500°C and thereafter the chemisorption rate measurements were repeated (Run C). The results are shown in

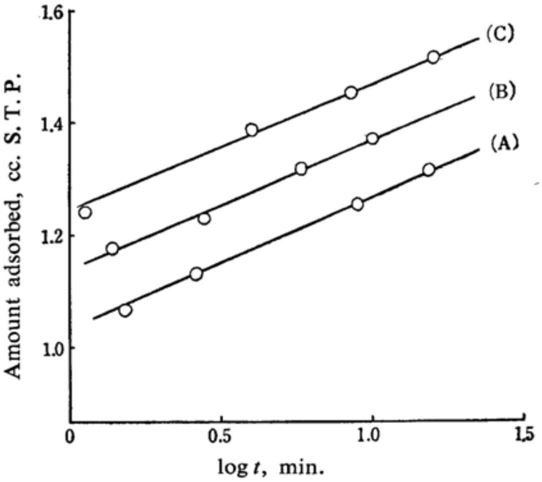

Fig. 1. Effect of oxygen pretreatment on the amount of hydrogen adsorbed at 14°C. Pressure, 20~25 mmHg.

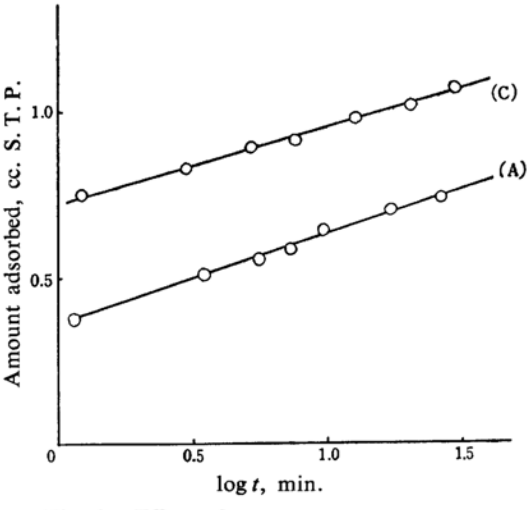

Fig. 2. Effect of oxygen pretreatment on the amount of hydrogen adsorbed at 189°C. Pressure, 20~25 mmHg.

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[5] D. A. Dowden, N. Mackenzie and B. M. W. Trapnell, *Proc. Roy. Soc.* **A237**, 245 (1956); F. S. Stone, loc. cit.

[6] S. R. Morrion, "Advances in Catalysis", Vol, 7, Academic Press Inc., New York (1955), p. 259.

[7] H. S. Taylor and C. O. Strother, *J. Am. Chem. Soc.*, **56**, 586 (1934); H. S. Taylor and S. C. Liang, ibid., **69**, 1306 (1947).

[8] W. E. Garner, *J. Chem. Soc.*, **1947**, 1239.

[9] Y. Kubokawa, This Bulletin, **33**, 546, 550 (1960).

[10] Y. Kubokawa, This Bulletin, **33**, 555 (1960).

Fig. 1. In these runs the order of the amounts of oxygen adsorbed is expected to be A>B>C. As seen in this figure, the amount adsorbed at a particular time also increases in this order. The amount adsorbed after 16 hr. was 1.95 cc. in run A and 2.21 cc. in run C, showing a slight difference. Fig. 2 represents the results obtained at a higher temperature. It follows from the figure that, in this case too, the decrease in the amount adsorbed after oxygen treatment will become unmarked in a later stage of adsorption.

Effect of Oxygen Pretreatment on the Rate of Desorption of Hydrogen.—After hydrogen was allowed to be chemisorbed at room temperature on the specimen pretreated with oxygen at 450°C followed by evacuation at 260°C, the activation energies of desorption at various coverages were determined in the manner described previously⁹⁾. For comparison, similar measurements were carried out with the specimen before such pretreatment. Allowing for the different amounts initially adsorbed on these specimens, the activation energy of desorption was plotted in each case against the ratio of the amount desorbed to that initially adsorbed. As seen in Fig. 3, the results obtained with the two specimens were essentially indentical. Moreover, the comparison at various temperatures between the amount desorbed from the two specimens before the rates of desorption fell to a particular value shows, as seen in Table I, that there is no marked difference between the rates of desorption from these specimens. It may therefore be concluded that the rate of desorption as well as its activation energy is scarcely affected at all by oxygen treatment of the adsorbent at a temperature as high as 450°C.

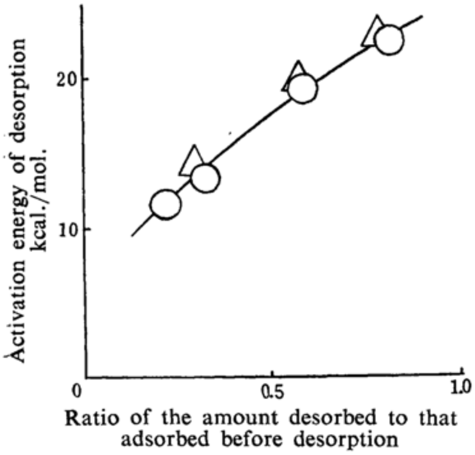

Fig. 3. Effect of oxygen pretreatment on the activation energy of desorption of hydrogen.
-○-, before oxygen pretreatment; -△-, after oxygen pretreatment. The amount of hydrogen adsorbed before desorption was 2.15 cc. before pretreatment and 1.82 cc. after pretreatment.

TABLE I. RATIO OF THE AMOUNT DESORBED BEFORE THE RATE OF DESORPTION FELL TO 3.73×10^{-3} cc. S. T. P./min. TO THE AMOUNT ADSORBED BEFORE DESORPTION

Temp. of desorption (°C)	−30	20	71
Before oxygen pretreatment	0.323	0.572	0.759
After oxygen pretreatment	0.295	0.582	0.741

Interaction of Hydrogen with Adsorbed Oxygen.—After hydrogen was allowed to be chemisorbed at room temperature, the temperature of the system was raised up to 400°C, and after several hours it was again lowered to room temperature. Then the amount of gas desorbed during the temperature elevation up to 400°C was measured and its composition was analyzed by means of the Pirani gauge. These measurements were carried out with a specimen which had been subjected to the same oxygen treatment as that used in the experiment shown in Fig. 1. The results are shown in Table II. In the Runs A and B the gas desorbed below 400°C consisted solely of hydrogen, while above 400°C a considerable amount of water was detected in the gas desorbed and its uncondensable fraction was found to be almost entirely oxygen. This indicates the occurrence of an irreversible chemisorption of hydrogen, the extent of which may be estimated from the amounts not removed by pumping out at 400°C. As seen in Table II, the amount of irreversible chemisorption increases with that of the oxygen adsorbed. On the other hand, in Run C where little or no oxygen remained adsorbed, no water vapor was detected even above 400°C, suggesting that hydrogen chemisorption was completely reversible in this case.

TABLE II

	Amount absorbed at room temp. before desorption (1)	Amount desorbed below 400°C (2)	Residual amount adsorbed (1)—(2)
Run A	3.94	3.48	0.46
Run B	3.85	3.54	0.31
Run C	4.10	3.96	0.14

Amount adsorbed is in cc. S. T. P. The order of the amounts of oxygen adsorbed is A>B>C.

Effect of Oxygen Pretreatment on Carbon Monoxide Chemisorption.—As described in the

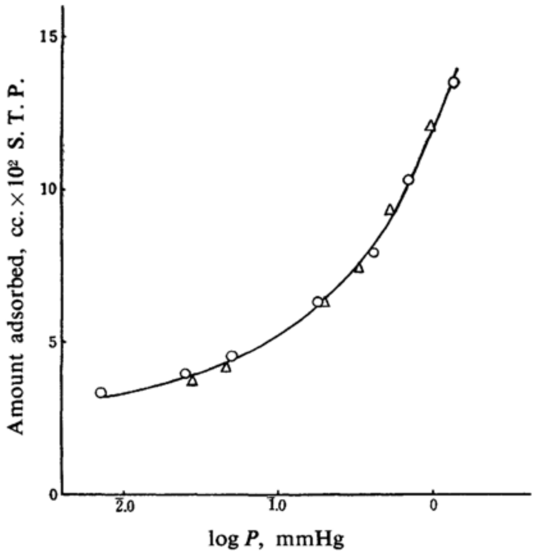

Fig. 4. Effect of oxygen pretreatment on carbon monoxide chemisorption at 15°C. -○-, before oxygen pretreatment; -△-, after oxygen pretreatment.

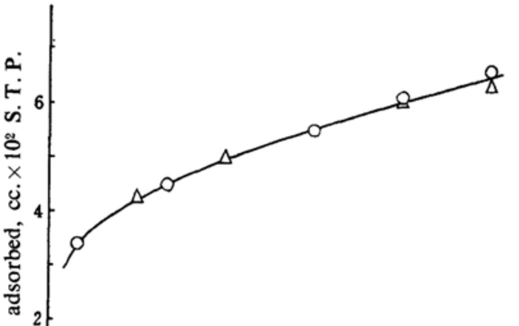

Fig. 5. Effect of oxygen pretreatment on carbon monoxide chemisorption at 90°C. -○-, before oxygen pretreatment; -△-, after oxygen pretreatment. Pressure, 0.1 ~0.2 mmHg.

previous paper10), there are two types of chemisorption for carbon monoxide, one of them being a non-activated adsorption at low temperature, and the other an activated absorption at high temperature. The effect of oxygen treatment was therefore investigated in the following two ways. Fig. 4 shows the effect on the adsorption isotherm at room temperature obtained on a desorption branch, such as was described previously. It follows from this figure that the oxygen treatment has no effect on the chemisorption of low temperature type, in agreement with the results obtained by Garner et al.11) For the chemisorption of high temperature type, similar results were obtained, as shown in Fig. 5. Oxygen treatment in this case was conducted at 450°C, followed by evacuation at 260°C.

Discussion

If the electronic state of zinc oxide had played a large part in determining the behavior of hydrogen chemisorption, the amount adsorbed as well as the rate of desorption of hydrogen would have been seriously affected by oxygen treatment at high temperature, in contradiction to what was found actually in this work. It may therefore be concluded that the change of the electronic state of zinc oxide has little or no effect on hydrogen chemisorption.

This conclusion in turn suggests that a slight decrease in the amount adsorbed caused by the oxygen treatment is not due to the change of the concentrations of electrons. In view of the existence of surface heterogeneity in this system as revealed in a previous work9), this decrease may probably be ascribed to the variation of the distribution function of sites, although details of the variation are unknown at present.

According to Parravano et al.4), the activity of zinc oxide towards hydrogen-deuterium exchange reaction decreases markedly after oxygen treatment. On the basis of the considerations given above, it seems unlikely that this decrease in the catalytic activity is attributed to the change of the concentrations of free electrons. In addition, the extent of decrease in the activity after oxygen treatment as reported by these authors appears to be markedly greater than that in the amount of hydrogen adsorbed in the present work, although there may be more or less uncertainty in such comparisons, as no measurements with the same specimen of zinc oxide were carried out. Such a marked difference, if it is real, suggests that only a negligible portion of the total amount of hydrogen adsorbed is responsible for the exchange reaction, in agreement with what may be expected from the surface heterogeneity established for this system.

Various workers12) have emphasized the fact that hydrogen chemisorption on zinc oxide is confined to interstitial zinc atoms or F-centers which probably exist after evacuation at high temperature. The observation in this work

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11) W. E. Garner and J. Maggs, *Trans. Faraday Soc.*, 32, 1744 (1936).

12) J. H. de Boer, " Advances in Catalysis ", Vol. 8 (1956), p. 18; W. E. Garner, " Advances in Catalyss ", Vol. 9 (1957), p. 169.

that the amount adsorbed is not seriously affected by the oxygen treatment indicates that such interpretation is unjustifiable.

The decrease in the amount of hydrogen adsorbed after oxygen treatment and the increase of the extent of irreversible adsorption with the increasing amount of oxygen adsorbed suggest that Morrison's mechanism is unjustifiable and that OH_{ads}, produced by the interaction of hydrogen with adsorbed oxygen, is irreversible and desorbed as water above 400°C, in accordance with Garner's view.

As for carbon monoxide chemisorption, the results obtained in the present work indicate again and still more clearly that this chemisorption is not affected by the electronic state of zinc oxide. Moreover, these results together with the fact that the amount adsorbed at $\theta=1$, estimated from the isotherms, amount to about a half of the amount of nitrogen adsorbed in a monolayer determined by the B. E. T. method as previously described[10] suggest that carbon monoxide chemisorption is not confined to special active sites, e. g., interstitial zinc atoms or F-centers, but the entire surface of zinc oxide participates in the chemisorption.

Finally, with respect to the change of the catalytic activity of zinc oxide caused by the addition of small amounts of Li_2O or Al_2O_3 as shown by a number of workers, the results presented here, seem to indicate that it is doubtful in some cases that this effect can be attributed to the change of the electronic state of zinc oxide caused by the addition.

Summary

The effect of oxygen treatment at about 500°C of zinc oxide upon the chemisorption of hydrogen as well as of carbon monoxide was investigated in order to clarify the relation between the electronic state of the adsorbent and the chemisorption. In the case of hydrogen chemisorption, the amount adsorbed was reduced only slightly and the rate of desorption remained practically unaltered after oxygen treatment. On carbon monoxide chemisorption the oxygen treatment gave no effect. It was concluded from these results that both the chemisorption of hydrogen and that of carbon monoxide are essentially independent of the electronic state of zinc oxide. On the basis of such a conclusion combined with other results, the inapplicability of the model of hydrogen chemisorption proposed by Morrison was pointed out.

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