Chemisorption of Hydrogen on Zinc Oxide. III. The Effect of Additions of Foreign Ions to Zinc Oxide

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Since the electron barrier theory was suggested for the chemisorption on semiconductors by Hauffe, Weisz, and others[1], the importance of the electronic structure of oxides in catalysis has been emphasized by various workers. As an approach along this line, the following method has often been adopted. The electronic structure of a given oxide is modified by the addition of small amounts of foreign ions, and the resulting changes in catalytic activity are then studied. As regards the hydrogen-deuterium exchange reaction on zinc oxide, Parravano et al.[2] found that the addition of Al^{3+} or Ga^{3+}, which should increase its electrical conductivity, increased the activity and lowered the activation energy, while the addition of Li^+ showed a reverse effect. On the basis of these results, Hauffe[3] suggested that the rate-determining step in this case was the electron transfer from zinc oxide to adsorbed hydrogen ions to allow it to desorb, closely correlating the catalytic activity of zinc oxide with its properties as a semiconductor.

Whatever mechanism may be operative in the hydrogen-deuterium exchange reaction, it is obvious that the hydrogen chemisorption on zinc oxide samples containing these foreign ions must be studied before any conclusive explanation of the activity changes caused by such additions can be given. Apart from the exchange reaction, such a study may be of considerable interest concerning the relation between the electronic structure of oxide and its hydrogen chemisorption. At present the only work along this line seems to be that of Cimino et al.[4] In this work, as described in previous papers,[5,6] hydrogen chemisorption has been investigated by measuring the rates of adsorption and desorption, and the adsorption equilibrium, with zinc oxide modified by the addition of foreign ions such as Li^+, Al^{3+} and Ga^{3+}.

Experimental

Materials.—Zinc oxide without foreign ions was prepared by sintering at 800°C for 5 hr. of non-sintered zinc oxide, which was obtained from zinc oxalate as described previously.[5] $ZnO+1$ mole % Al_2O_3, $ZnO+1$ mole% Ga_2O_3, and $ZnO+0.5$ mole% Li_2O: Non-sintered zinc oxide was impregnated with a solution containing a desired amount of aluminum, gallium, or lithium nitrate, dried at 110°C, and sintered at 800°C for 5 hr. Hydrogen and other gases used were prepared and purified as described in the previous work[5,7].

The weight of adsorbent and the surface area determined by the B. E. T. method using nitrogen adsorption are shown in Table I.

TABLE I.

Adsorbent	Weight, g.	Surface area, m²/g.
ZnO	19.6	1.0
ZnO+1 mole% Al_2O_3	20.6	1.7
ZnO+1 mole% Ga_2O_3	22.7	3.6
ZnO+0.5 mole% Li_2O	27.5	0.40

Apparatus and Procedure. — Details of the apparatus and procedure were already described in the previous paper[5]. Prior to a series of experiments, all the adsorbents used in the present work

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) E. Molinari and G. Parravano, *J. Am. Chem. Soc.*, **75**, 5233 (1953).
3) K. Hauffe, *Angew. Chem.*, **67**, 189 (1955).

4) A. Cimino, E. Cipollini and E. Molinari, *Naturwissenschaften*, **43**, 58 (1956).
5) Y. Kubokawa, This Bulletin, **33**, 546(1960).
6) Y. Kubokawa, ibid., **33**, 550 (1960).
7) Y. Kubokawa, ibid., **33**, 555 (1960).

were subjected to repeated pretreatments with hydrogen at 450°C followed by evacuation at the same temperature.

Results

The Variation in the Adsorbed Amount on Raising Temperature During Adsorption. — Hydrogen was allowed to be chemisorbed by the adsorbent at room temperature and the temperature of the whole system was raised up to a higher temperature in stages, at each of which, in most cases, a rapid desorption followed by a slow uptake was observed. The activation energy of adsorption was determined by comparison of the rates at different temperatures corresponding to equal amount of the slow chemisorption as described in the previous paper[6]. As an example, a run between 215 and 266°C on ZnO+1 mole% Ga$_2$O$_3$ is shown in Fig. 1. The activation energies thus obtained in various temperature ranges with ZnO, ZnO+1 mole% Ga$_2$O$_3$, and ZnO+0.5 mole% Li$_2$O are shown in Table II. Here, the activation energies in similar temperature ranges are almost of the same order of magnitude throughout all the adsorbents, suggesting that the activation energy of adsorption is not affected seriously by the addition of foreign ions. However, the proportion of the amount rapidly desorbed on an abrupt temperature rise to the total amount adsorbed is clearly affected by the addition of foreign ions. The amount of such rapid desorption at each stage is shown in Figs. 2—4, together with the amount adsorbed in a certain constant time period at each temperature. Comparison between Figs. 2 and 3 shows that for ZnO+1 mole% Ga$_2$O$_3$ the rapid desorption occurs to a much less extent than for ZnO.

Fig. 2. Variation in the amount adsorbed on ZnO on raising temp.; Hydrogen pressure, 80~90 mmHg; -○-, the amount adsorbed after 3 hr.; -●-, the amount rapidly desorbed.
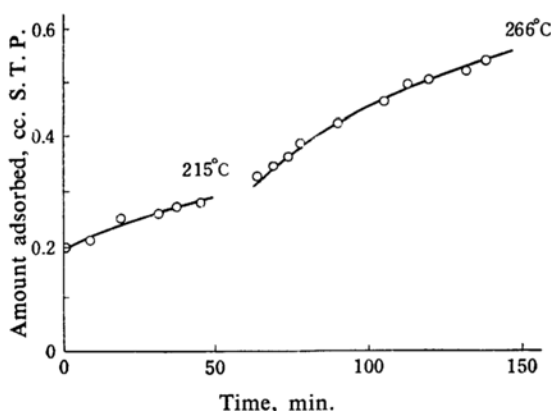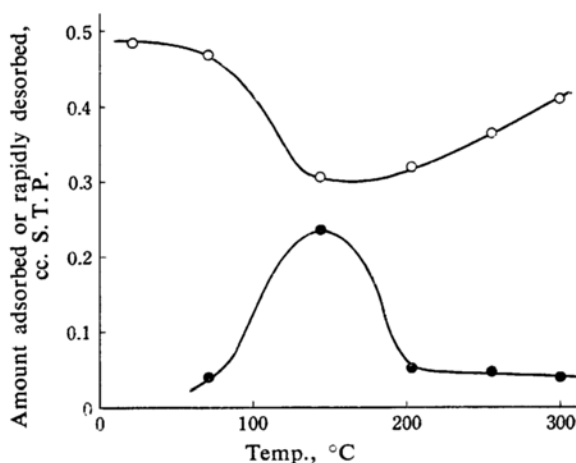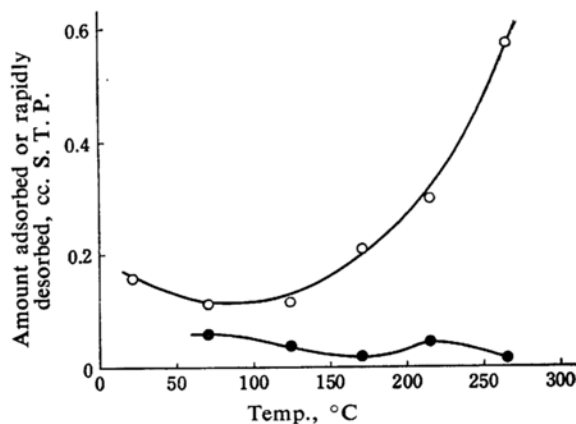

Fig. 1. Rate of hydrogen chemisorption on ZnO+1 mole% Ga$_2$O$_3$ in case of temp. change during adsorption; Pressure, 50~60 mmHg.

TABLE II. ACTIVATION ENERGY OF ADSORPTION*

Adsorbent	Temp. range, °C	Activation energy of adsorption, kcal./mole
ZnO	72~143	—
	143~203	12
	203~254	15
ZnO+0.5 mole% Li$_2$O	98~146	7.5
	146~196	11
	196~244	14.5
ZnO+1 mole% Ga$_2$O$_3$	124~171	8.5
	171~215	11.5
	215~266	16

* The upper limit of the experimental error was ±10%.

Fig. 3. Variation in the amount adsorbed on ZnO+1 mole% Ga$_2$O$_3$ on raising temp.; Hydrogen pressure, 50~60 mmHg; -○-, the amount adsorbed after 1.5 hr. -●-, the amount rapidly desorbed.
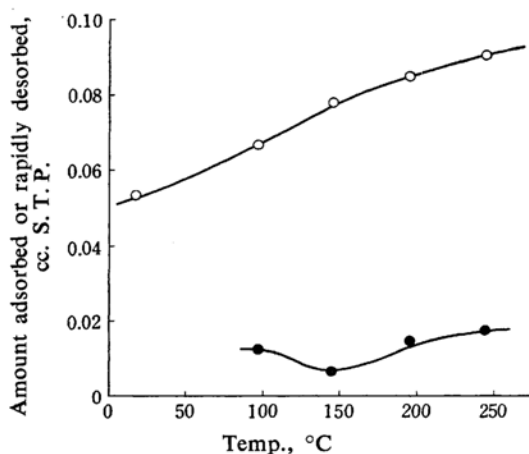
Fig. 4. Variation in the amount adsorbed on ZnO+0.5 mole% Li$_2$O; on raising temp.; Hydrogen pressure, 0.2～0.3 mmHg; -○-, the amount adsorbed after 1 hr.; -●-, the amount rapidly desorbed.
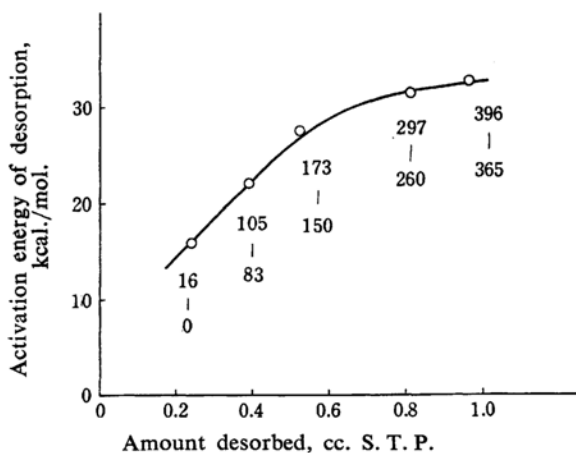

Fig. 5. Activation energies of desorption of hydrogen chemisorbed on ZnO. The amount adsorbed and equilibrium pressure at room temp. before desorption were 1.10 cc. and 42.2 mmHg, respectively. Numerical values in Figs. 5, 6, and 7 refer to the temp. interval where the activation energies were determined.

Fig. 6. Activation energies of desorption of hydrogen chemisorbed on ZnO+1 mole% Ga$_2$O$_3$. The amount adsorbed and equilibrium pressure at room temp. before desorption were 0.98 cc. and 52.3 mmHg, respectively.

Fig. 7. Activation energies of desorption of hydrogen chemisorbed on ZnO+0.5 mole% Li$_2$O. The amount adsorbed and equilibrium pressure at room temp. before desorption were 0.78 cc. and 41.0 mmHg, respectively.

The results with ZnO+0.5 mole% Li$_2$O can not be compared directly with the others owing to different pressure conditions.

The Activation Energies of Desorption at Various Coverages.—After hydrogen was allowed to be adsorbed at about 400°C, the temperature of the specimen was raised from 0 to 400°C in stages, at each of which the activation energy of desorption was determined from comparison between the rates of desorption at different temperatures corresponding to equal amounts left adsorbed as stated
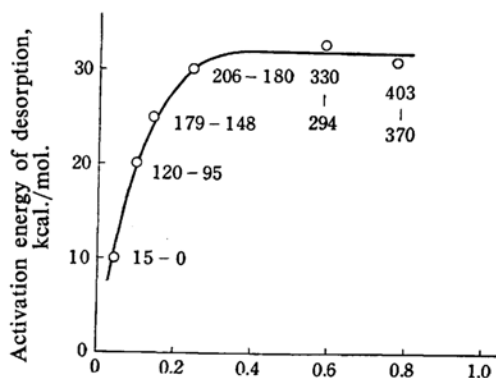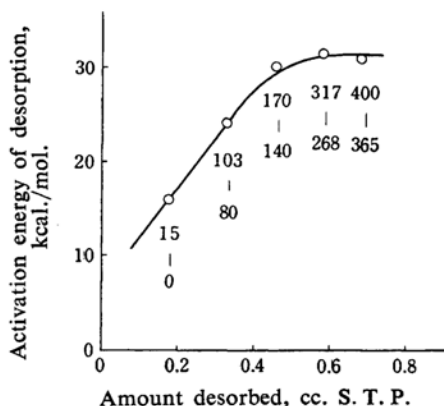
in the previous paper[5]. The results obtained with ZnO, ZnO+1 mole% Ga$_2$O$_3$ and ZnO+ 0.5 mole% Li$_2$O are shown in Figs. 5—7. Here, it was confirmed, in the same manner as described previously, that the rate of adsorption was negligible during the desorption experiment for all the adsorbents studied. From these figures the following picture would be obtained. For all the adsorbents with and without foreign ions, the activation energy increases with decreasing amount adsorbed up to almost the same value of 30～33 kcal./mol., although the proportions of the amounts desorbed with a lower activation energy (<20 kcal./mol.) to the total amount desorbed are different from one another, the smallest value being found with ZnO+1 mole% Ga$_2$O$_3$ in accordance with the results of adsorption experiment above mentioned.

Adsorption Isotherms. — Adsorption equilibrium measurements were carried out only with ZnO and ZnO+1 mole% Al₂O₃ in the same manner as described previously[5]: After hydrogen was allowed to be adsorbed at about 350°C, the isotherms were determined by successive withdrawals of the gas. The isotherms thus obtained were found to be reproduced on increasing or decreasing pressure subsequently. For both systems the Langmuir plot was applicable in the pressure range
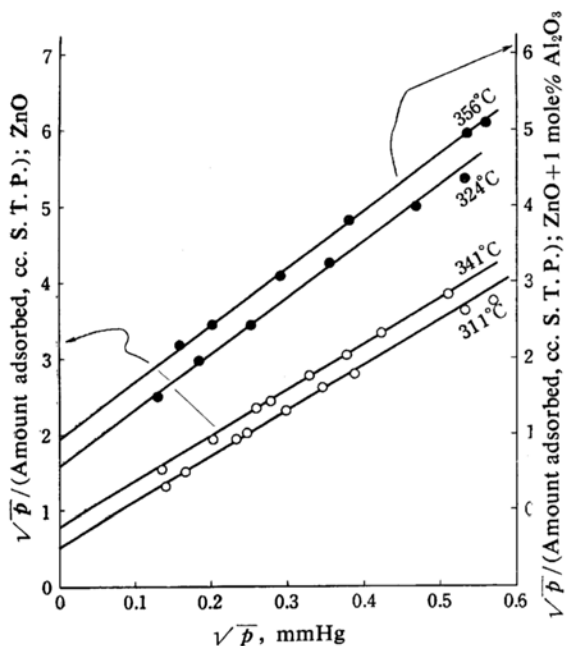

Fig. 8. Langmuir plots for ZnO and ZnO +1 mole% Al₂O₃; -○-, ZnO; -●-, ZnO+1 mole% Al₂O₃.

studied as seen in Fig. 8. It follows from this figure that the heat of adsorption is unaffected by the addition and is equal to 18 kcal./mol. Although such applicability of the Langmuir plot probably results from a limited range of coverage, the slopes of the lines in Fig. 8 may be utilized to estimate the magnitude of the surface available for the chemisorption under the given experimental conditions; (Reciprocal of the slope per unit area) is 0.0039 cc. for ZnO+1 mole% Al₂O₃ and 0.0085 cc. for ZnO.

The Effect of Additions of Foreign Ions on Carbon Monoxide Chemisorption. — According to the previous work[7] on carbon monoxide chemisorption on zinc oxide, there are two types of chemisorption, one predominating at low and the other at high temperatures. The effect of foreign ions was studied only for the adsorption of the former type. Because of a small amount adsorbed on ZnO+0.5 mole% Li₂O, the adsorption isotherms were

determined only with ZnO and ZnO+1 mole% Al₂O₃ in similar way to that given previously. The heats of adsorption thus obtained for the two adsorbents proved to be almost the same, i. e., 10～12 kcal./mol.

Discussion

In view of the low temperature used in preparing the samples, it seems unlikely that the added foreign ions are distributed uniformly throughout. As seen in Table I, however, surface area of the adsorbents is increased by the addition of Ga₂O₃ or Al₂O₃ and decreased by that of Li₂O. According to Hauffe[8] and Parravano[3], such variation in surface area suggests a decrease in the concentration of interstitial zinc ions, i. e., an increase in the concentration of free electrons in the former case, and the reverse change in the latter case. It may therefore be supposed that at least in a qualitative sense the electronic structure of the adsorbents in this work has been modified by such addition in the manner predicted by the theory of Hauffe and others.

As for the interpretation of the effect of the addition of foreign ions in the present work, it should be taken into consideration that such addition will change the heterogeneity of the surface as well as the electronic state of zinc oxide, both affecting the features of its hydrogen chemisorption. Although it is difficult to separate these two effects, the results obtained in this work, however, may be interpreted as follows: The identical heat of adsorption of 18 kcal./mol. for ZnO and ZnO +1 mole% Al₂O₃ is in agreement with the maximum heat of adsorption for non-sintered zinc oxide given in the previous work[5], suggesting that the maximum heat of adsorption is probably unaffected by the additions of foreign ions. This result together with the identical maximum activation energy of desorption throughout all the adsorbents with and without foreign ions would be unexpected, if the electronic state of zinc oxide played a large part in determining the features of hydrogen chemisorption. In addition, the activation energies of adsorption in similar temperature ranges are almost the same throughout all the adsorbents. Moreover, as described in the previous paper[9], the oxygen pretreatment at a high temperature which should change the electronic state of zinc oxide, gives little effect on its hydrogen chemisorption. Thus, taking account of the existence of surface heterogeneity in this system, the following tentative conclusion may be drawn:

8) K. Hauffe and A. L. Vierk, *Z. physik. Chem.*, **196**, 160 (1950).
9) Y. Kubokawa, This Bulletin, **33**, 743 (1960).

The heat of adsorption and the activation energy of adsorption associated with each set of sites may not be affected seriously by the addition of foreign ions; the variation in the features of the hydrogen chemisorption caused by such addition can probably be attributed to the change in the distribution function of sites rather than to that in the electronic structure of the adsorbents.

According to Cimino et al.[4], the adsorption isobars obtained with ZnO and ZnO+0.5 mole% Li_2O show one or two maxima, while on ZnO+0.3 mole% Ga_2O_3 the amount adsorbed increases steadily with temperature, in qualitative agreement with the results mentioned above; the addition of Ga_2O_3 reduces the amount adsorbed over the whole range of temperature in an analogous way to that of Al_2O_3 (Fig. 8). This is reflected in the change of the amount adsorbed before desorption experiments (Figs. 5—7); the amount adsorbed on unit surface area is 0.056 cc. for ZnO, 0.012 cc. for ZnO+1 mol% Ga_2O_3, and 0.071 cc. for ZnO+0.5 mole% Li_2O. Although the true nature of such change in the amount adsorbed is not yet clear, there seems to be little or no doubt that such behavior can not be explained in terms of the change in the electronic structure of zinc oxide alone.

As regards the change in activity towards the hydrogen-deuterium exchange reaction caused by the addition of foreign ions, the considerations given above seem to indicate that it is doubtful that such an effect is attributed to the change in the electronic structure of zinc oxide. In fact, according to Heckelsberg et al.[10], although the activity is higher on ZnO+1 mole% Al_2O_3 than on ZnO, the activation energy is essentially the same for the two adsorbents, in contradiction with

the results of Parravano. Such an identical activation energy is, however, what would rather be expected from the results in the present work. Further study of the hydrogen chemisorption and the exchange reaction with one and the same specimen of zinc oxide will probably lead us to a more consistent picture of all the related phenomena.

Summary

The hydrogen chemisorption on zinc oxide samples modified by the addition of foreign ions such as Li^+, Al^{3+}, and Ga^{3+} was investigated by measuring the rates of adsorption and desorption, and the adsorption equilibrium. The addition of foreign ions gave little or no effect on the maximum values of the activation energy for desorption and of the heat of adsorption, and the activation energies of adsorption in similar temperature ranges. On the basis of these results combined with the effect of oxygen treatment on this chemisorption on zinc oxide described previously, it was tentatively concluded that the variation in the features of hydrogen chemisorption caused by the addition of foreign ions is probably attributable to the change in a heterogeneity of the surface rather than that in the electronic state of zinc oxide. Finally, it was mentioned that the heat of adsorption of carbon monoxide at room temperature was also unaffected by such additions.

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10) L. F. Heckelsberg, A. Clark and G. C. Bailey, J. Phys. Chem., 60, 559 (1956).