Chemisorption of Hydrogen on Zinc Oxide. I. Rate of Desorption and Adsorption Isotherm

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(Received September 9, 1959)

The rate of adsorption and adsorption equilibrium have been measured for various chemisorption systems by many workers. As regards the rate of desorption, however, few quantitative measurements have been carried out with powdered catalysts[1]. For these catalysts the activation energy of desorption is usually taken as the sum of the activation energy of adsorption and the heat of adsorption obtained from the rate of adsorption and adsorption equilibrium, respectively. It is however frequently encountered in chemisorption that the slow attainment of equilibrium and the occurrence of bulk or surface diffusion process introduce considerable uncertainty in the values of the activation energy of adsorption and the heat of adsorption. If the activation energy of desorption is determined by direct measurements of the rate of desorption and compared with the activation energy of adsorption and the heat of adsorption, the information concerning the energy relation for a given chemisorption will be much improved. The present study was undertaken to present such an attempt for the chemisorption of hydrogen on zinc oxide. This paper reports the activation energies for desorption obtained from the rate of desorption at various temperatures, together with adsorption equilibrium data. The rate of adsorption and its relation to the results here reported, will be dealt with in a forthcoming paper.

Experimental

Materials.—For zinc oxide two samples, ZnO I and ZnO II were used. ZnO I was prepared as follows: Zinc oxalate was precipitated from the solutions of ammonium oxalate and zinc nitrate. The precipitate was washed, filtered, dried at 110°C and finally converted to the oxide by heating in air at 400°C. ZnO II was prepared from zinc nitrate and sodium carbonate by the method similar to ZnO I. The reagents were of Extra Pure grade. Hydrogen was obtained by the electrolysis of 30% solution of potassium hydroxide, purified by passing through heated palladium asbestos, phosphorus pentoxide, and finally, through a trap immersed in liquid nitrogen. Nitrogen was prepared by the thermal decomposition of sodium azide, and purified by passing through phosphorus pentoxide. Helium was obtained from commercial sources, and was used without further purification.

Apparatus and Procedure.—The adsorbed amount was determined by using a conventional constant volume apparatus, as shown in Fig. 1. The volume of the dead space was measured by the expansion of a known volume of helium over the whole range of temperatures and pressures employed. The mercury manometer M_1 and the Mcleod gauge M_2 covered a wide range of pressure from 10^{-5} to 70 mmHg.

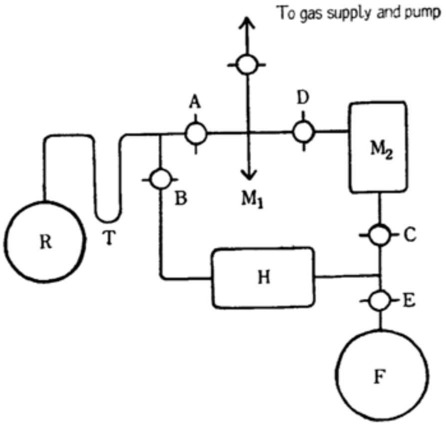

Fig. 1.

The rate of desorption was measured as follows: Before starting a measurement of desorption rate, the pressure in the adsorption vessel R was adjusted to a range of several mmHg by pumping out a known amount of gas through the Mcleod gauge M_2 and mercury manometer M_1. Then, stop-cocks A and D were closed, B and C opened, and the gas desorbed by mercury diffusion pump H was collected into M_2, whose pressure was followed at definite intervals. During a desorption experiment trap T was cooled to -78°C. By using the volume of H at its working state which was determined by an independent measurement, the rate of desorption was calculated from the pressure increase in M_2. When gas was accumulated in M_2 to such an extent that the rate of desorption might be affected by readsorption, the stopcock D was opened and C closed for a short time to pump out the gas in M_2, after which the measurement of desorption was continued. The pressure in the adsorption vessel R during the desorption experiment was measured

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[1] J. Weber and K. J. Laidler, *J. Chem. Phys.*, 19, 1089 (1951); J. J. F. Scholten and P. Zwietering, *Trans. Faraday Soc.*, 53, 1363 (1957); K. Tamaru and M. Boudart, "Advances in Catalysis", Vol. 9, Academic Press, Inc., New York (1957), p. 699.

by closing stopcock C, opening E, A and D, and leading the desorbed gas to flask F, instead of Mcleod gauge M_2.

The adsorption vessel was maintained at various required temperatures in the following manner; for the range above room temperature an electric furnace was used, with the constancy of ±1°C; for the range below room temperature, solid carbon dioxide in ethanol and melting chlorobenzene and bromobenzene were used; a bath for −60°C was obtained by cooling acetone by the addition of a small amount of dry ice from time to time.

Preceding to the chemisorption experiment, the adsorbent was subjected to alternating evacuation and exposure to hydrogen at 400°C several times, and then evacuated for five hours at 420°C. The surface area of the adsorbents was determined by the B. E. T. method using nitrogen as an adsorbate with the following results; ZnO I, 6.6 m²/g.; ZnO II, 5.2 m²/g. The weight of the adsorbent was 14.64 g. (ZnO I) or 11.60 g. (ZnO II).

Results and Discussion

Rates and Activation Energies of Desorption at Various Coverages.—Since the observed rate of desorption is that substracted by the rate of the reverse process, i. e. readsorption, the activation energy of desorption can not be determined from the observed rates unless the rate of readsorption is negligible. As a test to decide whether this condition is satisfied, the following experiment was carried out. After measuring the pressure in adsorption vessel during desorption rate measurements, the pressure increase caused by isolating the adsorption vessel from the mercury diffusion pump was observed. Fig. 2 represents a typical experiment carried out at room temperature. Although adsorption equilibrium was not easily attained, the rapid pressure increase observed suggests that the pressure in the adsorption vessel at the moment when the diffusion pump was cut off would have been negligible compared with the equilibrium pressure corresponding to the adsorbed amount at that moment, and hence that the rate of readsorption was negligible compared with that of desorption. The same was also found to be the case for desorption under other experimental conditions.

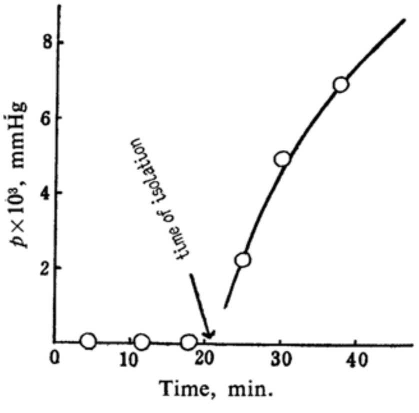

Fig. 2. Pressure increase on isolating the adsorption vessel from the mercury diffusion pump. Pressure in the adsorption vessel before the isolation was 1.3×10^{-4} mmHg.

After hydrogen was allowed to be adsorbed at about 300°C and 20∼25 mmHg, the system was cooled down to 209 or 22°C, at which temperature the rate of desorption was measured with the results shown in Fig. 3. Fig. 4 represents the same results as the plots of the logarithm of desorption rate $\log R_{\text{dep}}$ against desorbed amount q. As to the data given in Fig. 3 a simple unimolecular or bimolecular rate law was found to be inapplicable. This results, together with the fact that the plot of $\log R_{\text{dep}}$ against q in Fig. 4 is nearly linear, will be explained by the increase of activation energy for desorption with decreasing amount

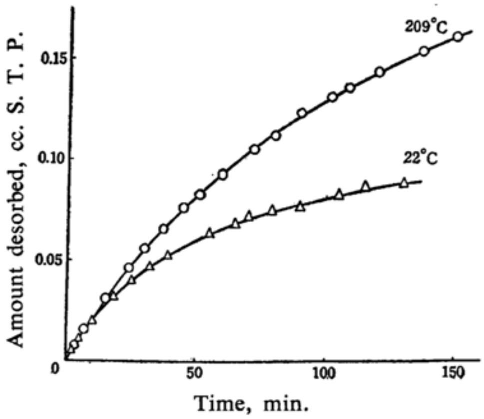

Fig. 3. Rates of desorption of hydrogen chemisorbed on ZnO II. The amount adsorbed at $t=0$ was 0.51 cc. at 209°C and 1.12 cc. at 22°C.

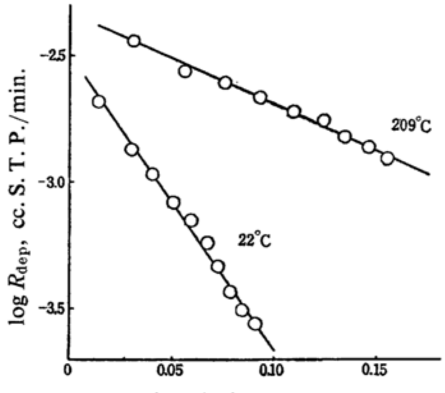

Fig. 4. Plots of $\log R_{\text{dep}}$ against the amount desorbed q for the data in Fig. 3.

adsorbed, and its quantitative relationship will also be shown later.

The activation energy of desorption was determined as a function of adsorbed amount by the following procedure: The temperature of desorption was lowered abruptly during the rate measurement, as shown in Fig. 5 (hydrogen chemisorption before the desorption experiment was carried out in a similar manner to that in Fig. 3); the plot of $\log R_{\mathrm{dep}}$ against q for the curve before the temperature drop, such as shown in the figure, was extrapolated to a smaller amount adsorbed where the rate measurements after the temperature drop were carried out. Thus, the rates at the two different temperatures corresponding to the same amount adsorbed and, consequently, the activation energy of desorption were obtained.

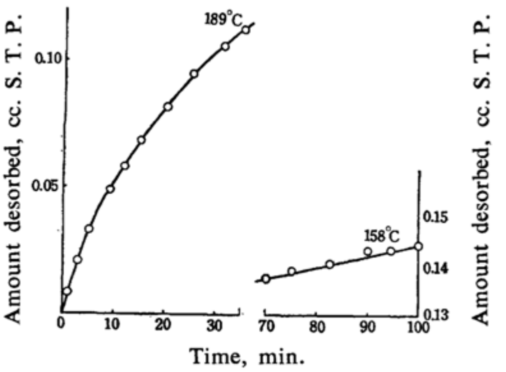

Fig. 5. Determination of the activation energy of desorption. The amount adsorbed at $t=0$ was 0.72 cc. The activation energy was estimated as 23.5 kcal./mol.

The initial admission of hydrogen was usually made at about 300°C and 30∼40 mmHg, after which the temperature of the system was lowered to room temperature, and after about 10 hr. it was raised up to 400°C in stages, at each of which the activation energy of desorption was determined in the above mentioned manner. The results obtained with ZnO II are shown in Fig. 6. Fig. 7 shows similar results obtained with ZnO I[2] for a range of higher coverage where desorption was measurable at lower temperatures. It follows from the two figures that the activation energy of desorption increases with decreasing amount adsorbed, up to 31 kcal./mol., and thereafter remains nearly constant[3].

It may be noted that such behavior of the activation energy toward coverage is responsible for the fact that the slope of the plot $\log R_{\mathrm{dep}}-q$ is smaller in the higher temperature range, as seen in Fig. 4.

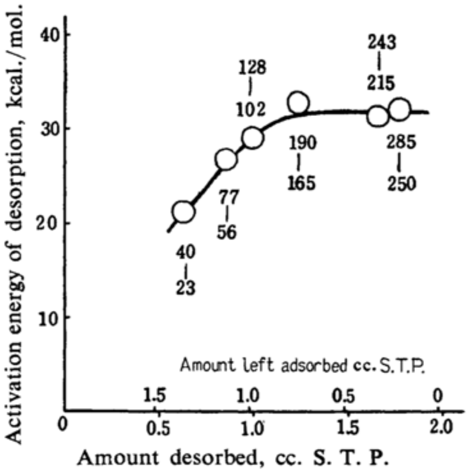

Fig. 6. Activation energies of desorption of hydrogen chemisorbed on ZnO II. The amount adsorbed before desorption at room temperature was 1.98 cc. Figures indicate the temperature interval where the activation energy was determined.

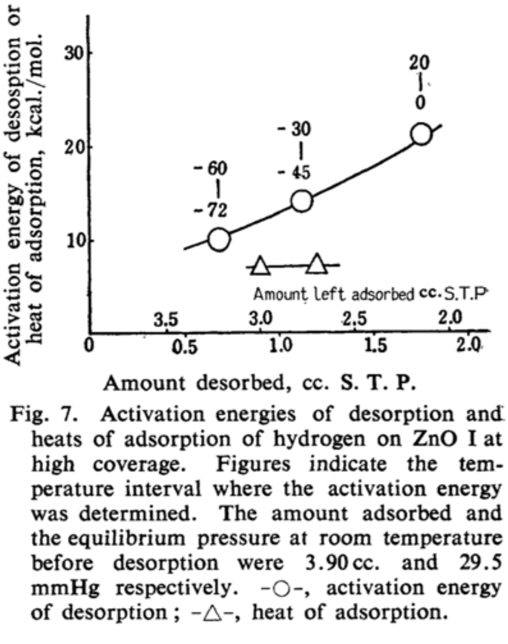

Fig. 7. Activation energies of desorption and heats of adsorption of hydrogen on ZnO I at high coverage. Figures indicate the temperature interval where the activation energy was determined. The amount adsorbed and the equilibrium pressure at room temperature before desorption were 3.90 cc. and 29.5 mmHg respectively. -○-, activation energy of desorption; -△-, heat of adsorption.

Adsorption Isotherms at Various Temperatures.—An adsorption isotherm obtained in the usual manner, i. e. by admitting a small amount of gas to an evacuated sample successively, was found to be different from that obtained in the reverse way, i. e. by successive withdrawals of the gas. These may be called the adsorption and the desorption branches of the isotherm, respectively. An example at 370°C is given in Fig. 8. This result was obtained with ZnO II

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[2] Results with ZnO II were similar.

[3] The fact that a simple unimolecular or bimolecular rate law was not applicable to the data above 200°C, where the approximately constant activation energy was observed, appears to have resulted from a slight change of the activation energy with the amount desorbed, within the experimental error, ±2 kcal./mol.

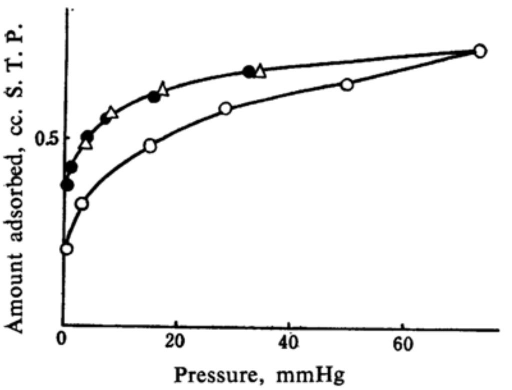

Fig. 8. Adsorption isotherms on the adsorption and desorption branch for the hydrogen chemisorption on ZnO II at 370°C. -○-, initial adsorption; -●-, desorption; -△-, readsorption.

which had been evacuated for five hours at 420°C. On the desorption branch the adsorption equilibrium was rapidly established and reproduced on decreasing or increasing pressure in the pressure range lower than the maximum pressure employed on the adsorption branch. It may therefore be concluded that the isotherm obtained on the desorption branch represents a true equilibrium. The isotherm at varied temperatures was obtained in the following way. After recording the equilibrium pressure at a particular temperature, the temperature was lowered and the new equilibrium pressure at a lower temperature was obtained; a certain amount of hydrogen was then pumped out and the measurements were repeated. The results obtained with ZnO II are shown in Fig. 9. It follows from this figure that the heat of adsorption is nearly constant and equal to 18 kcal./mol. The same value of the heat of adsorption was obtained with ZnO I.

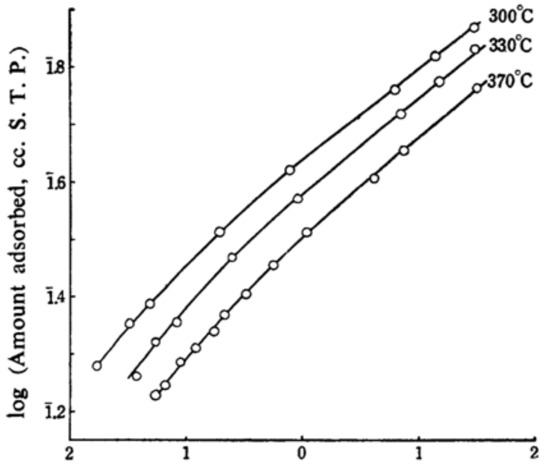

Fig. 9. Adsorption isotherms for hydrogen on ZnO II.

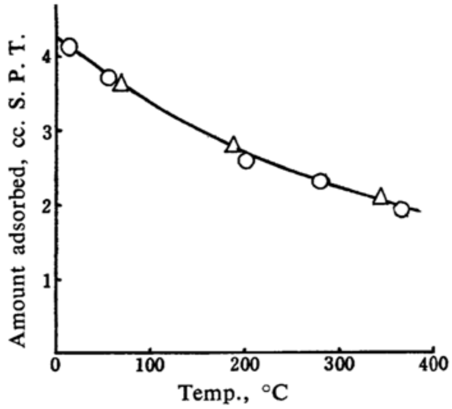

Fig. 10. Adsorption isobar for hydrogen on ZnO I in the pressure range 40~70 mmHg. -△-, on raising temperature; -○-, on lowering temperature.

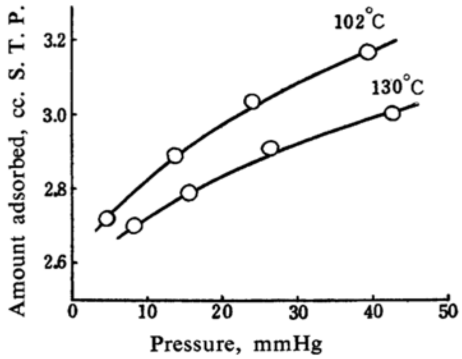

Fig. 11. Adsorption isotherms for hydrogen on ZnO I at 102 and 130°C. The amount adsorbed and the equilibrium pressure at room temperature were 3.76 cc. and 32.8 mmHg respectively.

The adsorption isobar for this system was obtained in the following way: After hydrogen was allowed to be adsorbed at about 350°C, the temperature was lowered in stages down to room temperature and then raised again to 350°C. The results obtained with ZnO I are shown in Fig. 10. It is seen in the figure that the isobars obtained by lowering and raising the temperature nearly coincide, indicating that, once hydrogen is adsorbed at a high temperature, adsorption equilibrium is nearly attained even at considerably lower temperatures, and hence that approximate adsorption isotherms can also be obtained at such low temperatures. Fig. 11 represents such isotherms at 102 and 130°C obtained with ZnO I after hydrogen adsorption at about 300°C, determined in the manner already described for the higher temperature range. Though these low temperature isotherms may be less accurate, the heat of adsorption is estimated from these as 6∼8 kcal./mol.

The activation energy of adsorption may be estimated by combining the activation energy of desorption and the heat of adsorption. As described above, the maximum value of activation energy for desorption and the heat of adsorption are 31 and 18 kcal./mol., respectively. The maximum activation energy of adsorption is, therefore, estimated as 13 kcal./mol.

For the range where the activation energy of adsorption or desorption varies with the amount adsorbed, it seems necessary to take into account the fact that on a heterogeneous surface equal amounts adsorbed do not necessarily mean identical states of adsorption. As described in Figs. 7 and 11, however, adsorbed amount and equilibrium pressure at room temperature differs a little between these two runs, suggesting that in this case the states of hydrogen adsorbed to an equal amount may be compared. Thus, in Fig. 7, the values of the heat of adsorption in the low temperature range described above were shown as a function of the adsorbed amount, together with the activation energy of desorption. It follows from this figure that the activation energy of adsorption in this range is about 5∼7 kcal./mol. This figure also suggests that most part of hydrogen chemisorption on zinc oxide is an activated adsorption, although it is doubtful whether the same argument is valid for the fraction which desorbs rapidly below −72°C.

Summary

The rate of desorption of hydrogen chemisorbed on zinc oxide was measured over a wide range of temperatures. The rate at a constant temperature was found to obey approximately the kinetics of the Elovich type. The activation energy of desorption was determined at various coverages, with the result that it increased with decreasing amount from at least about 10∼31 kcal./mol. and then remained constant. The heat of adsorption obtained from adsorption isotherms in the temperature range 300∼370°C was found to be 18 kcal./mol., being roughly constant. Meanwhile, from the isotherms at about 100°C, a heat of adsorption of 6∼8 kcal./mol. was obtained. Comparison between the activation energy of desorption and the heat of adsorption suggests that most part of hydrogen chemisorption on zinc oxide involves an activation energy, its highest value being estimated as 13 kcal./mol.

The author wishes to express his sincere thanks to Professor O. Toyama for his guidance and encouragement throughout the course of this study.

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