Chemisorption of Hydrogen on Zinc Oxide. II. Rate of Chemisorption and Heterogeneity of the Surface of Zinc Oxide

By Yutaka KUBOKAWA

(Received September 9, 1959)

Taylor and coworkers[1], in a study of hydrogen chemisorption on zinc oxide and other catalysts, found a rapid desorption followed by a slow adsorption and explained these phenomena in terms of a heterogeneity of the surface. As pointed out by various workers[2], however, there are other possibilities leading to such phenomena, which, therefore, may not be regarded as a proof of the existence of any surface heterogeneity. As a proof in relation to this problem, it seems to be promising to investigate the behavior of desorption of the chemisorbed hydrogen in the manner described in a previous report[3], since surface heterogeneity may affect seriously its behavior. The purpose of the present work is to clarify the nature of slow chemisorption by measuring not only the rate of adsorption, but also that of desorption under various experimental conditions, and to obtain, on the basis of these results combined with those described in the previous paper[3], definite conclusions as to the heterogeneity of zinc oxide surface in hydrogen chemisorption.

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[1] H. S. Taylor and S. C. Liang, *J. Am. Chem. Soc.*, **69**, 1306 (1947); H. S. Taylor, "Advances in Catalysis", Vol. 1, Academic Press, Inc., New York (1948), p. 1.

[2] J. H. de Boer, ibid., Vol. 8, (1956), p. 18; O. Beeck, ibid., Vol. 2, (1950), p. 151.

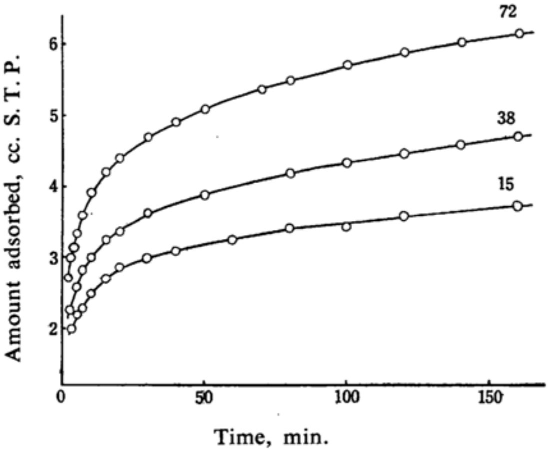
[3] Y. Kubokawa, This Bulletin, 33, 546 (1960).

Experimental

The details of materials, apparatus and procedure were described in the previous paper[3].

Results and Discussion

Dependence of Chemisorption Rate on Pressure and Temperature.—In early experiments, the rate of chemisorption was measured in the usual manner, i.e. by admitting a known amount of hydrogen to an evacuated sample and measuring the pressure change in the system at a constant volume. Some examples of the results obtained at a constant temperature and various pressures are shown in Fig. 1[4]. It might be expected that comparison of the times required for the adsorption of a certain amount, determind from such plots, would give the pressure dependence of the rate at the given temperature. However, when the rate thus obtained is represented as proportional to p^n, it is found that not only the exponent n increases with the adsorbed amount, but is also greater than unity. The explanation for such unexpected behavior will be given below, according to which experiments such as shown in Fig. 1 do not reflect the true pressure dependence of the adsorption rate. From a similar argument, it will be shown that a series of rate measurements at a constant pressure and various temperatures does not give the true temperature dependence of the rate. Consequently, in the following experiments, the dependence of the rate on pressure or temperature was determined by observing the change in rate caused by an abrupt change of pressure or temperature during adsorption.



Fig, 1. Rate of adsorption of hydrogen on zinc oxide at 140°C. Figures indicate the initial pressures in mmHg. Different samples were used in these runs.

The results concerning the pressure dependence are shown in Figs. 2 and 3. As seen in these figures, on increasing pressure an instantaneous adsorption followed by a slow process takes place. Hence, by extrapolation of the rates to the time when a sudden pressure change occurs, the rates at different pressures corresponding

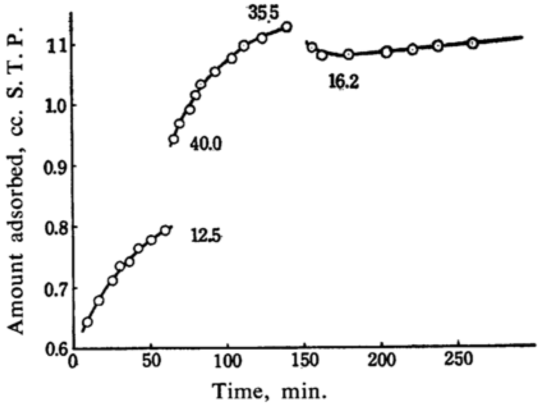


Fig. 2. Effect of the pressure change during adsorption on the rate of adsorption of hydrogen on ZnO II at 18°C. Pressure range, 10~40 mmHg. Figures indicate the pressure before and after the pressure change in mmHg.

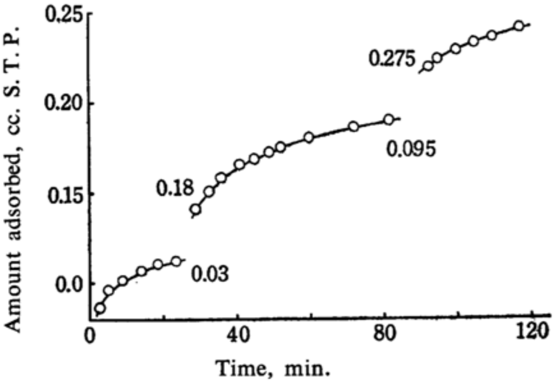


Fig. 3. Effect of the pressure change during adsorption on the rate of adsorption of hydrogen on ZnO I at 18°C. Pressure range, 0.03~0.30 mmHg. Figures indicate the pressure before and after the pressure change in mmHg.

TABLE I. VALUES OF n IN THE EXPRESSION, RATE $\propto p^n$ FOR THE DATA SHOWN IN FIGS. 2 AND 3

	Pressure before and after the pressure change	n
Fig. 2	12.5 → 40.0	1.0±0.1
	35.5 → 16.2	2.0±0.3
Fig. 3	0.03 → 0.18	1.1±0.1
	0.095→ 0.275	0.9±0.1

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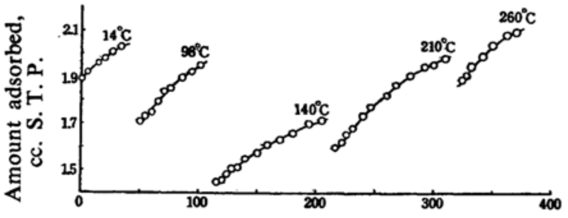
[4] The pressure decrease due to adsorption was no more than 10~20% of the initial pressure.

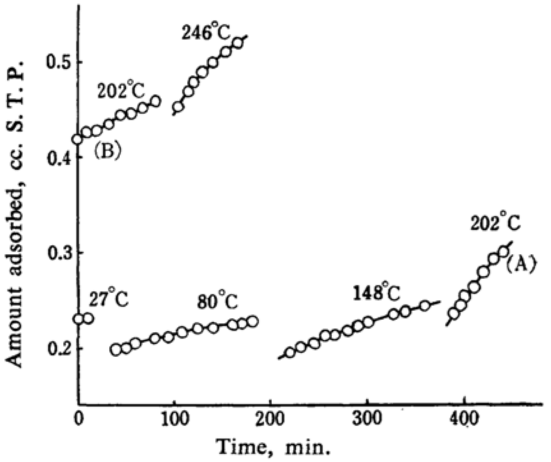
to equal amounts of slow chemisorption were evaluated. The results are shown in Table I, which shows that the rate is proportional to $p^{0.9\sim 1.1}$ on increasing pressure. This relationship was found to be applicable in the whole temperature range studied. As seen in Table I, on decreasing pressure the rate decreases more markedly than is expected from the results obtained on increasing pressure.

The results concerning the temperature dependence obtained with ZnO I in the pressure range 50∼70 mm Hg are represented in Fig. 4. It is seen in this figure that on an abrupt temperature change⁵⁾, as suggested by Taylor and Liang¹⁾, a rapid desorption followed by a slow adsorption takes place. The activation energy for the slow process was determined in the same manner as for the pressure dependence, with the results shown in Table II. The activation energy increases steadily as the temperature becomes higher. As shown in Fig. 5 and Table II, the results obtained in the pressure range 0.1∼0.2 mmHg are similar except for the smaller amount of rapid desorption on raising temperature.



Time, min.

Fig. 4. Effect of the temperature elevation during adsorption on the rate of adsorption of hydrogen on ZnO I. Pressure range, 50∼70 mmHg.



Time, min.

Fig. 5. Effect of the temperature elevation during adsorption on the rate of adsorption of hydrogen on ZnO I. Pressure range, 0.1∼0.2 mmHg. Between the runs A and B, the sample was kept at room temperature for 10 hours.

TABLE II. ACTIVATION ENERGIES OF ADSORPTION FOR THE DATA SHOWN IN FIGS. 4 AND 5

Pressure	Temp.	Activation energy
50∼70 (Fig. 4)	14∼ 98	5.5±1.5
	98∼140	7.5±1.0
	140∼210	11.0±1.5
	210∼260	14.5±1.5
0.1∼0.2 (Fig. 5)	80∼148	6.3±1.0
	148∼202	13.0±1.0
	202∼246	15.0±1.0

In view of the occurrence of hydrogen-deuterium exchange reaction on zinc oxide and, in addition, from a comparison of the energy values for the system of hydrogen on zinc oxide described previously³⁾ with the information concerning the hydrogen chemisorption on metals given by Gomer and other workers⁶⁾, hydrogen chemisorption on zinc oxide at room temperature or above may be assumed to be a dissociative adsorption. Hence, if the rate-determining step of the slow process were a surface migration of the adsorbate, the exponent n in the rate expression Rate $\propto p^n$ would be lower than 0.5. Such expectation is evidently inconsistent with what was observed. It may therefore be concluded that the rate-determining step is not a sort of surface migration, but an adsorption.

As described above, the pressure dependence obtained by increasing pressure differs markedly from that by decreasing pressure. This suggests that desorption can not be neglected during adsorption⁷⁾. Because of this effect, the pressure dependence obtained by increasing pressure, may be somewhat larger than the true value, although the difference may be small compared with that in the case of decreasing pressure.

Heterogeneity of the Surface of Zinc Oxide in Hydrogen Chemisorption.—The considerations given above indicate that the slow process is a chemisorption with an appreciable activation energy which increases with adsorbed amount, judged from the considerable change of the activation energy of desorption as described in

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5) A blank experiment carried out with helium in place of hydrogen showed that on such an abrupt temperature change the temperature equilibrium was attained in less than three minutes.

6) R. Gomer et al., *J. Chem. Phys.*, **26**, 1147 (1957); **27**, 1099 (1957); O. Beeck, loc. cit., etc.

7) Taking into account of desorption, the rate of dissociative adsoption on a homogeneous surface will be

$$kp(1-\theta)^2[1-(p_e/p)]$$

where p_e is the equilibrium pressure corresponding to a coverage θ. The term $1-(p_e/p)$ is a correction for desorption. This equation predicts such behavior as observed on an abrupt pressure change during the adsorption rate measurements: In the case where desorption takes place considerably during adsorption, the decrease in the value of $1-(p_e/p)$ on decreasing pressure will be markedly larger than its increase on increasing pressure.

the previous paper[3]. With respect to the behavior observed on raising temperature during adsorption, there are apparently two possible explanations, as the rate-determining step of the slow process is confined to adsorption; one is a heterogeneity of the surface emphasized by Taylor et al. and the other is the coexistence of two types of bonding on a homogeneous surface as frequently proposed by various workers[8] (Fig. 6). In the latter case the increase of activation energy of adsorption is attributed to the decrease of heat of adsorption with coverage. According to this model the chemisorption of type A has a low heat of adsorption and negligible activation energy, and hence the adsorption equilibrium is nearly realized throughout the course of slow adsorption, while that of type B involves an appreciable activation energy increasing with coverage and is responsible for the slow process. The behavior observed in this work on raising temperature might be explained by this model in terms of the rapid desorption of the A-type adsorbate followed by the slow adsorption of type B. On the other hand, as regards the rate of desorption, the observed slow process would solely be the desorption of the B-type adsorbate, since that of type A would be probably rapid; the rate of slow desorption would thus be determined only by the adsorbed amount at a given time, irrespective of other experimental conditions.

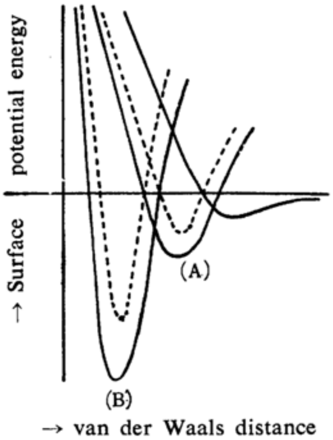

Fig. 6. Energy relation for the two types of chemisorption. Full line, for bared surface; broken line, for covered surface.

In order to examine if such a prediction is realized, the following experiments were carried out: At room temperature hydrogen was allowed to be left in contact with the adsorbent for 15 min. in one experiment and 16 hr. in the other one; after which, pumping out a known amount of hydrogen from the system, the rate of desorption was measured in the manner described in the previous paper[3]. The results are shown in Fig. 7, where, contrary to what has been predicted above, the desorption rates corresponding to equal amounts adsorbed differ markedly from each other, indicating that the postulate of two types of chemisorption can not be applied to this system. Similar results were obtained by the experiments at higher temperatures, an example at 188°C being given in Fig. 8.

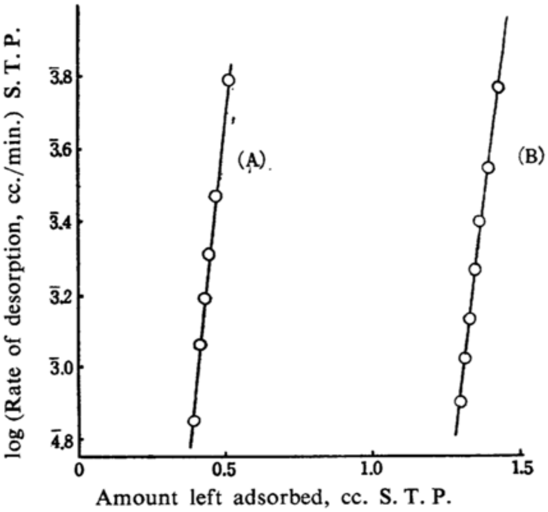

Fig. 7. Rate of desorption as a function of the amount left adorbed. Temp., 16°C.

	Time of contact	Amount adsorbed before desorption in cc.
Run A	15 min.	1.67
Run B	16 hr.	2.65

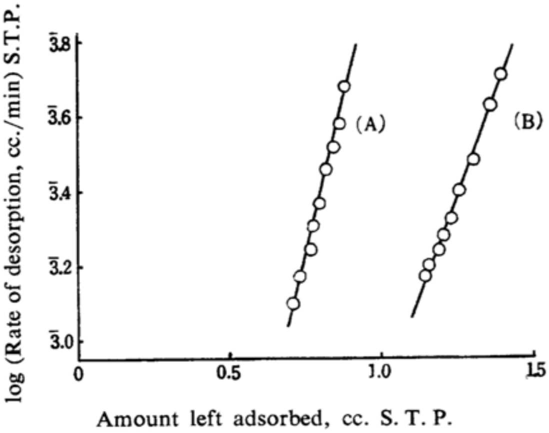

Fig. 8. Rate of desorption as a function of the amount left adsorbed. Temp., 188°C

	Time of contact	Amount adsorbed before desorption in cc.
Run A	15 min.	1.38
Run B	16 hr.	1.85

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[8] E. Wicke, *Z. Elektrochem.*, 53, 279 (1949); J. H. de Boer, loc. cit.; P. M. Gundry and F. C. Tompkins., *Trans. Faraday Soc.*, 52, 1609 (1956); etc.

Of the two alternatives given above, there remains now the postulate of heterogeneity of the surface to be accepted[9,10]. In view of the continuous variation of the activation energy of desorption with adsorbed amount, the pattern of this heterogeneity seems to be characterized by a continuous distribution function of sites with the heats of adsorption and the activation energies of adsorption varying in the same direction as proposed by Halsey[11]. According to this model, on the sites with a low activation energy, the heat of adsorption is also low and adsorption equilibrium will immediately be established after admission of hydrogen. Whilst, those with a high activation energy are covered by a slow process and the activation energy becomes higher as the adsorption proceeds. On raising the temperature during adsorption, a rapid desorption takes place on the sites with a low activation energy, but on the sites with a high activation energy the slow adsorption continues. In this way this model can explain the phenomena found by Taylor and Liang[1]. Furthermore, the observation such as the marked difference in the rates of desorption corresponding to equal amounts adsorbed in the two experiments with different times of contact with hydrogen and the unexpected pressure dependence of the rate of adsorption obtained in the usual manner may be explained as follows: under different experimental conditions, e.g. different times for adsorption or different initial pressures, different sets of sites may be covered to different extents. Hence, the states of equal amounts adsorbed are not necessarily comparable.

Activation Energy of Adsorption.—The temperature dependence of slow chemisorption given in Table II will give the true activation energy of adsorption, if desorption is negligible. As described above, this condition is not satisfied in this system. However, in view of the nature of surface heterogeneity given above, the situation before and after a temperature raise may be supposed as follows. Before the temperature raise adsorption proceeds mainly on the sites with a particular value of activation energy, since on those with a lower activation energy the adsorption equilibrium must be almost established, while those with a higher activation energy must be nearly bare. On raising temperature, coverage on these sites may become close to the equilibrium value. Hence, adsorption now proceeds mainly on those with a higher activation energy. Since the heat of adsorption changes in parallel with the activation energy, it seems unlikely that the effect of desorption is markedly altered on raising temperature. Thus, the temperature dependence obtained by extrapolating these rates to the time of a rapid temperature change will give the activation energy not greatly in error. In fact, as described in the previous report[3], the maximum value of the activation energy of adsorption estimated from the activation energy of desorption and the heat of adsorption is 13 kcal./mol., in agreement with 15 kcal./mol. obtained directly from the adsorption rate measurements.

Summary

With respect to hydrogen chemisorption on zinc oxide, the dependence of adsorption rate on pressure and temperature was determined by an abrupt change of pressure or temperature during adsorption. The pressure dependence obtained on increasing pressure differed markedly from that on decreasing pressure, indicating that desorption can not be neglected. The apparent activation energy of slow chemisorption increased from 6 to 15 kcal./mol. as the temperature range becomes higher. Marked differences were found between the rates corresponding to equal amounts adsorbed in the two experiments where the times of contact with hydrogen were different. On the basis of these results, combined with the variation of activation energy of desorption with the amount adsorbed previously, it was shown that for this system the concept of the two types of chemisorption on a uniform surface can not be applied. Instead a postulate of a heterogeneous surface where the activation energy of adsorption and the heat of adsorption varies in the same direction was found to be able to explain all the results obtained.

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

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai-shi Osaka

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[9] An assumption of the coexistence of three or more types of bonding on a homogeneous surface in a limited temperature range might explain the observed behavior. It is, however, difficult to work out plausible physical models for such various types of bonding.

[10] The experiments described above, of course, can not decide between the two possibilities, one-type and two-type chemisorption on a heterogeneous surface. As will be shown in a later paper, there is no convincing evidence to support the latter at present.

[11] G. D. Halsey, *J. Phys. Chem.*, 55, 21 (1951).