Hydrogen Chemisorption on $ZnO \cdot Cr_2O_3$, $ZnO \cdot MoO_3$ and Cr_2O_3

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(Received September 9, 1959)

In previous papers[1] hydrogen chemisorption on zinc oxide was studied by measuring the rate of adsorption, adsorption equilibrium and the rate of desorption, which made it possible to obtain quantitative information on the energy relation for this system. The behavior of desorption under various experimental conditions suggested the existence of a heterogeneity of the surface, the nature of which was such that the activation energy of adsorption and the heat of adrorption varied in the same direction, in contrast with carbon monoxide chemisorption on zinc oxide where these quantities varied in the reverse direction to each other.

It seemed then desirable to ascertain whether the conclusion obtained with zinc oxide is generally applicable to hydrogen chemisorption on oxides or not. As a first step in such an investigation, the hydrogen chemisorption was measured with $ZnO \cdot Cr_2O_3$, $ZnO \cdot MoO_3$ and Cr_2O_3, in the same manner as with zinc oxide and the results obtained are reported in this paper.

Experimental

Materials. — $ZnO \cdot Cr_2O_3$ and $ZnO \cdot MoO_3$ were prepared in the same way as described in the previous work[2]. Cr_2O_3 was prepared by controlled

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

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

ignition of CrO_3 of extra pure grade in a stream of dry air at 450°C as described by Bevan et al.[3] The gases were obtained as described in the previous papers[1]. The weight of the adsorbent and surface area determined by the B. E. T. method using nitrogen adsorption were as follows: $ZnO\cdot Cr_2O_3$, 6.71 g., 28m²/g.; $ZnO\cdot MoO_3$, 8.83 g., 13 m²/g.; Cr_2O_3, 14.13 g., 17 m²/g.

Apparatus and Procedure.—Details of the apparatus and procedure were described in the previous papers[1]. Before a series of experiments, all the adsorbents were subjected to repeated pretreatments with hydrogen at 450°C followed by evacuation at this temperature.

Results and Discussion

Dependence of Chemisorption Rate on Temperature.—The problem was investigated in two ways, one comparing, as usual, the rate at varied temperatures after admission of a known amount of hydrogen to a degassed sample and the other observing the rate increase caused by an abrupt temperature elevation during an adsorption rate measurement as previously applied to hydrogen chemisorption on zinc oxide. Measurements making use of the former method were already carried out in the previous work[2] with the following results: With $ZnO\cdot Cr_2O_3$ an instantaneous chemisorption followed by a slow process occurred and apparent activation energies of adsorption in the low and high temperature ranges were 7 and 13~16 kcal./mol., respectively, while with $ZnO\cdot MoO_3$, only a slow chemisorption with an activation energy of 28 kcal./mol. was observed.

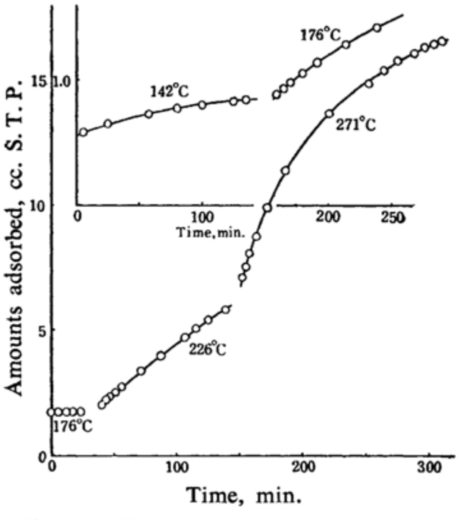

Fig. 1. Effect of temperature change during adsorption on the rate of hydrogen chemisorption on $ZnO\cdot MoO_3$. Pressure, 60~80 mmHg. Run at 176°C was interrupted by cooling the adsorbent to room temperature.

Figs. 1 and 2 represent the results obtained by the latter method: After hydrogen was allowed to be adsorbed at room temperature, the temperature was raised up in stages. As seen in Fig. 1, in the case of $ZnO\cdot MoO_3$ the amount of rapid desorption due to the abrupt temperature raise is negligibly small, and the rate of slow uptake increases steadily with temperature as in the carbon monoxide chemisorption on zinc oxide described previously[4]. Similar behavior was observed on Cr_2O_3. On the other hand, the result obtained with $ZnO\cdot Cr_2O_3$ is similar to that for hydrogen chemisorption on zinc oxide, as seen in Fig. 2. Here on increasing the temperature a rapid desorption was followed by the occurrence of a slow

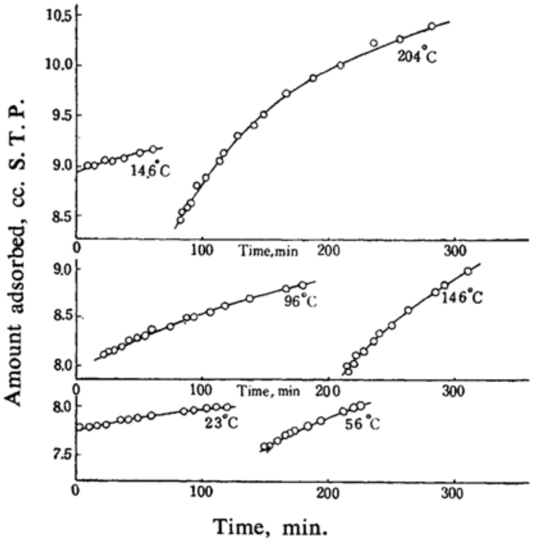

Fig. 2. Effect of temperature change during adsorption on the rate of hydrogen chemisorption on $ZnO\cdot Cr_2O_3$. Pressure, 60~80 mmHg. Both after the run at 56°C and during that at 146°C, the rate measurement was interrupted by cooling the adsorbent to room temperature.

TABLE I. ACTIVATION ENERGIES OF ADSORPTION

Adsorbent	Temp. range °C	Activation energy of adsorption kcal./mol.
$ZnO\cdot MoO_3$ (Fig. 1)	142~176	14.5±1.0
	176~226	23 ±1.5
	226~271	25 ±1.5
Cr_2O_3	160~205	13 ±1.5
$ZnO\cdot Cr_2O_3$ (Fig. 2)	23~56	8.0±1.0
	96~146	9.5±1.0
	146~204	12 ±1.0

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[3] J. M. Bevan, J. P. Shelton and J. S. Anderson, *J. Chem. Soc.*, **1948**, 1729.

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

uptake. Apparent activation energies were determined by a method similar to that described in the previous papers[1], i. e., by comparison of the rates at different temperatures, corresponding to equal amounts of the slow chemisorption. The results obtained are shown in Table I.

Although a rapid desorption on an abrupt temperature raise is observed with $ZnO\cdot Cr_2O_3$, which shows, on the whole, a normal pattern of an activated adsorption according to the previous work[2], i. e., except in the temperature range 80∼110°C, the rate of adsorption increases steadily with temperature. In addition, both methods of obtaining the dependence of rate on temperature give similar values of activation energy, contrary to the results for zinc oxide. This may be attributed to a much smaller proportion of the amount desorbed rapidly on raising the temperature to the amount adsorbed before the temperature rise.

Dependence of Chemisorption Rate on Pressure.—As described in previous papers[1,4], the pressure dependence was determined by observing the rate change caused by an abrupt pressure change during adsorption. As an example, the results obtained with $ZnO\cdot MoO_3$ are shown in Fig. 3. The comparison of the rates at different pressures corresponding to equal amounts of slow uptake gives the pressure dependence, with the results listed in Table II.

With $ZnO\cdot MoO_3$, the rate was found to be proportional to $P^{0.8}$ on both increasing and decreasing pressure, indicating that desorption is negligible during adsorption. The results obtained with Cr_2O_3 were similar. In the case of $ZnO\cdot Cr_2O_3$, it is clear that desorption can not be neglected, since on decreasing pressure the exponent n in the expression Rate $\propto P^n$ is, markedly larger than the value when desorption is negligible, namely 0.8, and on increasing pressure too, a value somewhat greater than 0.8 was obtained, as seen in Table II.

Activation Energies of Desorption at Various Coverages.—The temperature of the adsorbent which had already adsorbed hydrogen at about

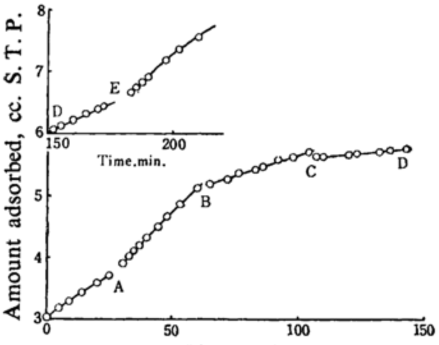

Fig. 3. Effect of pressure change during adsorption on the rate of hydrogen chemisorption on $ZnO\cdot MoO_3$. Temp., 228°C. Pressures before and after the pressure change are shown in Table II.

TABLE II. VALUES OF n IN THE EXPRESSION, RATE $\propto P^n$

Adsorbent		Pressure before and after the pressure change, mmHg	n
$ZnO\cdot MoO_3$*	(A)	27.0→73.2	0.77
(Fig. 3)	(B)	64.8→19.0	0.80
	(C)	15.4→ 4.6	0.81
	(D)	3.7→27.7	0.83
	(E)	24.2→67.5	0.79
$ZnO\cdot Cr_2O_3$		20.5→86.5	0.95±0.1
		77.1→49.2	2.5 ±0.5

* An upper limit of the error was ±7%.

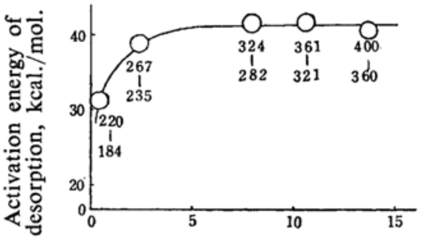

Fig. 4. Activation energies of desorption of hydrogen chemisorbed on $ZnO\cdot MoO_3$. The amount adsorbed and equilibrium pressure at room temperature before desorption were 15.42 cc. and 22.0 mmHg, respectively. Figures indicate the temperature interval where the activation energy was determined.

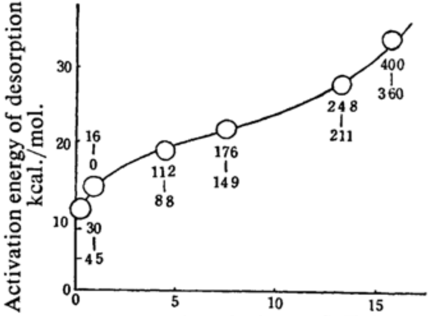

Fig. 5. Activation energies of desorption of hydrogen chemisorbed on $ZnO\cdot Cr_2O_3$. The amount adsorbed and equilibrium pressure at room temperature before desorption were 16.82 cc. and 42.3 mmHg respectively. Figures indicate the temperature interval where the activation energy was determined.

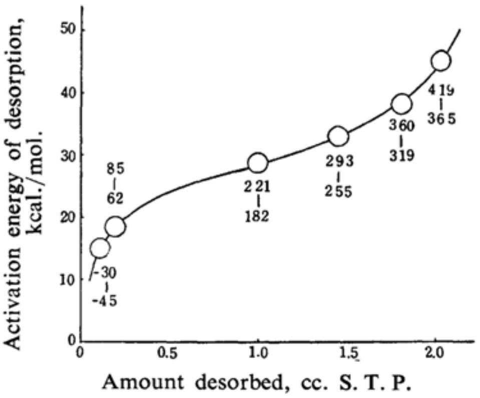

Fig. 6. Activation energies of desorption of hydrogen chemisorbed on Cr_2O_3. The amount adsorbed and equilibrium pressure at room temperature before desorption were 2.18 cc. and 36.4 mmHg respectively. Figures indicate the temperature interval where the activation energy was determined.

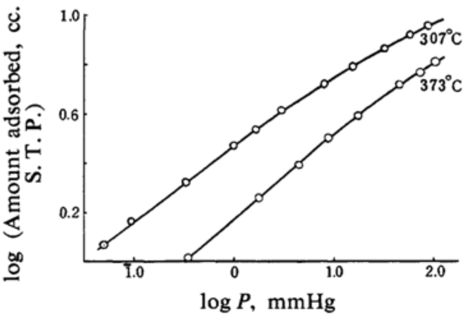

Fig. 7. Adsorption isotherms of hydrogen on $ZnO\cdot Cr_2O_3$ at 307 and 373°C.

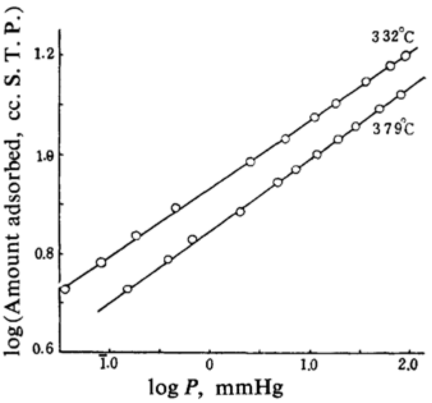

Fig. 8. Adsorption isotherms of hydrogen on $ZnO\cdot MoO_3$.

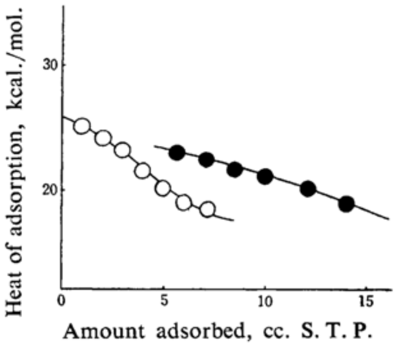

Fig. 9. Heats of adsorption of hydrogen on $ZnO\cdot Cr_2O_3$ and $ZnO\cdot MoO_3$. -○-, $ZnO\cdot Cr_2O_3$; -●-, $ZnO\cdot MoO_3$.

400°C was raised up from −72 to about 400°C in stages at each of which the activation energy of desorption was determined in the same manner as described previously[1]. The results obtained are shown in Figs. 4, 5 and 6. For all the systems studied in the present work, it was confirmed that adsorption could be neglected during desorption rate measurement as in the case of hydrogen chemisorption on zinc oxide. In the case of $ZnO\cdot MoO_3$, the amount desorbed with an activation energy less than 30 kcal./mol. is a negligible fraction of the total amount desorbed. In addition, the greater part of the chemisorbed hydrogen desorbs with an approximately constant activation energy of 41 kcal./mol. On the other hand, for the other systems, the activation energy of desorption varies considerably with the amount desorbed, i. e., for $ZnO\cdot Cr_2O_3$ from 10 to 35 kcal./mol. and for Cr_2O_3 from 15 to 45 kcal./mol. Moreover, in the former case a considerable fraction of chemisorbed hydrogen desorbs with a low activation energy of desorption (<20 kcal./mol.), while in the latter, this fraction is negligibly small.

Adsorption Isotherms. — After hydrogen was allowed to be adsorbed at a high temperature, the adsorption isotherm was determined by successive withdrawals of the gas. The isotherm thus determined on the desorption branch was, as in the case of hydrogen chemisorption on zinc oxide, reproducible at increasing as well as decreasing pressure. The results obtained with $ZnO\cdot Cr_2O_3$ and $ZnO\cdot MoO_3$ are shown in Figs. 7 and 8[5]. The variations of the heat of adsorption determined from these isotherms with the amount adsorbed are represented in Fig. 9.

As seen in Fig. 5, with $ZnO\cdot Cr_2O_3$, the chemisorption with a low activation energy of desorption occurs to a considerable extent. The heat of adsorption for such chemisorption was estimated from the adsorption isotherms at 115 and 85°C, determined in desorption branch with the specimen which had chemisorbed hydrogen at about 300°C. The result

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[5] The isotherm for Cr_2O_3 was not determined.

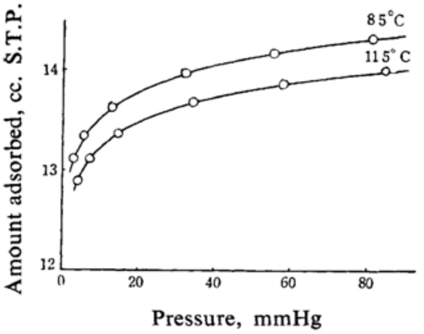

Fig. 10. Adsorption isotherms of hydrogen on $ZnO\cdot Cr_2O_3$ at 85 and 115°C.

obtained is shown in Fig. 10, from which the heat of adsorption is estimated as 7~8 kcal./mol.

Nature of Heterogeneity of the Surface.—The problem was dealt with as described in the previous papers[1,4]: At a particular temperature, hydrogen was left in contact with the adsorbent for some time; then, by pumping a known amount of gas from the system, the desorption rate was measured. The measurement was conducted with various times for each adsorbent. The results obtained with $ZnO\cdot MoO_3$, as shown in Fig. 11, are similar to those for carbon monoxide chemisorption on zinc oxide: The rate of desorption is greater on the surface with a larger amount adsorbed and there is a marked difference between the value of d log R_{dep}/dq for the runs of different times of contact with hydrogen. This suggests the existence of a heterogeneity of the surface where the heat of adsorption and the activation energy of adsorption vary inversely to each other as described in the previous paper[4].

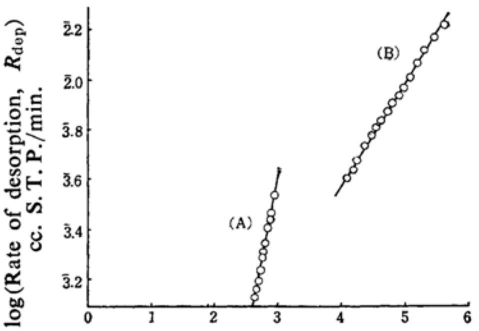

Fig. 11. Rate of desorption of hydrogen chemisorbed on $ZnO\cdot MoO_3$ as a function of the amount left adsorbed. Temp., 266°C. The weight of adsorbent used in these runs was 3.81 g. The amount adsorbed at room temperature before desorption was 3.54 cc. in Run A and 6.41 cc. in Run B. (A) After 30 min.; (B) After 3 hr.

In contrast to the case with $ZnO\cdot MoO_3$, the behavior observed on $ZnO\cdot Cr_2O_3$ was almost identical with that of hydrogen chemisorption on zinc oxide, i. e., a marked difference between the rates of desorption at equal amounts adsorbed after different contact times. Such behavior together with a rapid desorption observed on raising temperature suggests that the existence of an a priori heterogeneity of the surface where the activation energy of adsorption and the heat of adsorption vary in the same direction as was concluded in the previous work[1].

In the case of Cr_2O_3, although the result obtained at 162°C was similar to that with $ZnO\cdot MoO_3$ mentioned above (Fig. 11), at 206°C, somewhat different behavior was observed, as seen in Fig. 12 and Table III. Here in an early stage of adsorption, the proportion of the amount desorbed rapidly to the total amount adsorbed increases as adsorption proceeds, while after one hour since the admission of hydrogen, the situation is reversed, i. e., this proportion is now smaller on the surface with a larger amount adsorbed, indicating that the sites with a higher heat of adsorption are covered in a later stage. This behavior may be explained by assuming that the sites

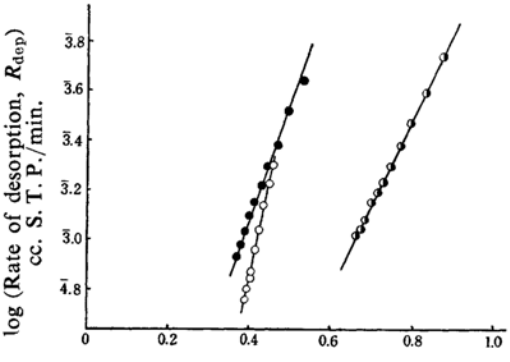

Fig. 12. Rate of desorption of hydrogen chemisorbed on Cr_2O_3 as a function of the amount left adsorbed. Temp., 206°C. Time of contact: -○-, 15 min.; -●-, 50 min.; -◑-, 15 hr.

TABLE III.

Time of contact	Amount desorbed rapidly* cc.	Amount adsorbed at room temp. before desorption cc.
15 min.	0.04	0.55
50 min.	0.27	0.77
15 hr.	0.21	1.05

* This amount was estimated by the amount desorbed before log R_{dep} fell to $\bar{3}.64$. (cc. S. T. P./min.)

with the highest heat of adsorption are not accessible to the gas phase, but can be reached by a surface or bulk diffusion process from the sites with a lower heat of adsorption. Such an explanation may be more plausible than one assuming that the relationship between the heat of adsorption and the activation energy of adsorption changes abruptly in the final stage of adsorption. Irrespective of the explanation for this phenomenon, it may be concluded that the nature of surface heterogeneity in this system is, in principle, such that the heat of adsorption varies inversely to the activation energy of adsorption, since the desorbed amount in question is only a small fraction of the total amount desorbed.

On the basis of the relationship between the heat of adsorption and the activation energy of adsorption described above, we can estimate the activation energy of adsorption indirectly from the heat of adsorption and the activation energy of desorption. In the case of $ZnO \cdot MoO_3$, from the maximum value of heat of adsorption, 26 kcal./mol., and that of the activation energy of desorption, 41 kcal./mol., the minimum value of the activation energy of adsorption can be estimated as 15 kcal./mol., in agreement with that obtained directly from adsorption measurements. Similar estimation with $ZnO \cdot Cr_2O_3$ yields 10 kcal./mol. as the maximum activation energy of adsorption, in approximate agreement with that directly determined. Considering that for the latter system the minimum activation energy of desorption is 10 kcal./mol. and the minimum heat of adsorption will be below 7 kcal./mol., it may be concluded, as in the case of hydrogen chemisorption on zinc oxide, that almost the whole process of chemisorption involves activation energy.

It may be noted that the following correlation is obtained from the results described above and in previous papers(1,4): When desorption can not be neglected during adsorption, a rapid desorption on an abrupt temperature raise always takes place. Moreover, the presence of the fraction with a low activation energy of desorption is always associated with a rapid desorption on raising the temperature. Such correlation can be expected for the surface heterogeneity, the pattern of which is characterized by a continuous distribution function of sites with the heats of adsorption varying in the same direction with the activation energy of adsorption.

Hydrogen Chemisorption on Oxides. — From the results presented here, combined with those described in previous papers(1), the following common features for hydrogen chemisorption on oxides may be mentioned:

1) On oxides of reduced state, hydrogen chemisorption is reversible, in the sense that hydrogen is desorbed as such. For zinc oxide, this was already described in the previous work(6). For $ZnO \cdot Cr_2O_3$, $ZnO \cdot MoO_3$ and CrO_3, essentially the same conclusion was obtained although the complete desorption requires a very long time.

2) When desorption is negligible, the rate of chemisorption is proportional to $P^{0.8}$ over a wide range of temperatures, indicating that the rate-determining step is not a sort of surface migration but an adsorption.

3) Almost the whole process of hydrogen chemisorption on oxides involves activation energy which becomes higher as the adsorption proceeds, although its magnitude varies from one oxide to another.

4) There is no evidence to support the existence of two types of hydrogen chemisorption which was believed to exist previously(2). Although extensive conductivity measurements were not made with $ZnO \cdot Cr_2O_3$ and $ZnO \cdot MoO_3$ as in the case of zinc oxide, the concept of two types chemisorption is not required for these systems either, since all the results can be explained by the concept of single type chemisorption on a heterogeneous surface. The fact that the variation of activation energy of desorption is continuous over the whole range of the amount adsorbed appears to favour this concept.

5) The change of activation energy of adsorption with the amount adsorbed mainly arises from an a priori heterogeneity of the surface and not from the induced heterogeneity or the formation of electrical double layer owing to charge transfer between the gas adsorbed and the surface. At present the reason for the fact that the relation between the heat of adsorption and the activation energy of adsorption varies from one oxide to another is unknown. As regards the chemisorption of hydrogen on oxides other than those studied by the present author, the results obtained in this work may serve to make some prediction. In the cases of MnO and $MnO \cdot Cr_2O_3$ investigated by Taylor et al.(7), the activation energy of adsorption and the heat of adsorption will vary inversely to each other, since a rapid desorption on raising temperature is not observed. The situation with V_2O_3 studied by Tarama and Teranishi(8), may be similar, since the general features of the chemisorption are similar to those with $ZnO \cdot MoO_3$, i. e., the chemisorption measurement is possible

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6) Y. Kubokawa, This Bulletin, 33, 743 (1960).

7) H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, 53, 2168 (1931).

8) K. Tarama and S. Teranishi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagagu Zasshi*), 55, 376 (1952).

only above 200°C, and the rate increases steadily with increasing temperature. It may be concluded that the variation of the activation energy and the heat of adsorption in the reverse direction is more frequently encountered in hydrogen chemisorption on oxides.

Summary

For hydrogen chemisorption on $ZnO \cdot Cr_2O_3$, $ZnO \cdot MoO_3$ and Cr_2O_3, the rates of adsorption and desorption, and adsorption equilibrium were investigated. The activation energy of adsorption ranged from 8 to 12 kcal./mol. for $ZnO \cdot Cr_2O_3$, and from 15 to 25 kcal./mol. for $ZnO \cdot MoO_3$. The value for Cr_2O_3 was about 13 kcal./mol. In the cases of $ZnO \cdot MoO_3$ and Cr_2O_3, where desorption is negligible during adsorption, the rate of adsorption was proportional to $P^{0.8}$, while with $ZnO \cdot Cr_2O_3$ desorption was found to occur appreciably. The activation energy of desorption increased with a decreasing amount adsorbed from 10 to 35 kcal./mol. for $ZnO \cdot Cr_2O_3$, and from 15 to 45 kcal./mol. for Cr_2O_3, while an approximately constant value of 41 kcal./mol. was obtained with $ZnO \cdot MoO_3$ except in the initial stage of desorption. The maximum heat of adsorption estimated from adsorption isotherms was about 25 kcal./mol. for both $ZnO \cdot Cr_2O_3$ and $ZnO \cdot MoO_3$. For all the systems studied, desorption experiments suggested the existence of surface heterogeneity with the activation energy of adsorption and heat of adsorption varying inversely in the cases of $ZnO \cdot MoO_3$ and Cr_2O_3, while with $ZnO \cdot Cr_2O_3$ the variation in the same direction was observed. On the basis of the results hitherto obtained, the general characteristics of hydrogen chemisorption on oxides were discussed.

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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