Investigation of Chemisorption by Desorption Rate Measurement; CO_2 on ZnO and NiO; CO on NiO

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The importance of desorption rate measurements in the investigation of chemisorption has been emphasized in recent work¹⁾ by one of the present authors. It would seem that the most general method would be to determine the heats of adsorption from adsorption isotherms at various temperatures, but in this case the measurements are often limited to a narrow range of coverage because of a slow attainment of equilibrium, particularly at low temperatures. On the other hand, measurements of the desorption rate have no such limitations, permitting an investigation over a wide range of coverage; they also make it possible to obtain information concerning the energy relation for a given chemisorption. In addition, it has been shown that desorption measurements can lead to definite conclusions concerning the relation between the electronic state of an oxide and its chemisorption, the nature of surface heterogeneity, and also the problem of whether or not two types of chemisorption are operative. The present work describes an extension of such desorption experiments to a number of chemisorption systems.

The chemisorption of carbon dioxide on zinc oxide has been investigated by Kwan et al.²⁾, who have shown that the heat of adsorption as determined from adsorption isotherms ranges from 35 to 48 kcal./mol. On the other hand, the calorimetric measurements carried out by Garner and Veal³⁾ have shown that the heat of adsorption is only 13 kcal./mol. As for the chemisorption of carbon monoxide on nickel oxide, there seems to have been no studies made of the heat of adsorption apart from the calorimetric measurements of Dell and Stone⁴⁾. Further work is necessary to obtain a complete knowledge of all of the above systems. According to the electron barrier theory suggested by Hauffe and others⁵⁾, both systems mentioned above belong to a class characterized by anionic chemisorption on an *n*-type conductor or by cationic chemisorption on a *p*-type conductor, in which a depletion of charge carriers occurs in the boundary layer. If the formation of such a depletive layer played a large part in determining the behavior of the chemisorption, the amount adsorbed and other properties would be seriously affected by oxygen treatment at a high temperature, which would be expected to change the concentration of carriers markedly. Thus, in the present work, the energy relations of, as well as the effects of oxygen treatment

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1) Y. Kubokawa, This Bulletin, 33, 546, 550, 555, 739, 747, 936 (1960).

2) T. Kwan, T. Kinuyama and Y. Fujita, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 3, 31 (1953).

3) W. E. Garner and E. J. Veal, *J. Chem. Soc.*, **1935**, 1487.

4) R. M. Dell and F. S. Stone, *Trans. Faraday Soc.*, **50**, 501 (1954).

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

on, both of these systems have been investigated by making use of desorption measurements.

Experimental

Materials. — Nickel oxide was prepared by the thermal decomposition of nickel nitrate at 400°C and then by sintering it at 700°C for 5 hr. Zinc oxide was prepared from zinc oxalate in a method described in a previous paper[1]. The reagents were of an extra pure grade. Carbon dioxide and oxygen were obtained from the thermal decomposition of magnesium carbonate and potassium permanganate respectively. Carbon monoxide was prepared by the reaction of air-free formic acid and concentrated sulfuric acid. All the gases used were purified as usual with liquid nitrogen.

Apparatus and Procedure.—The amount adsorbed was determined by using a conventional constant volume apparatus. The method for measuring the rate of desorption has been described previously and will be repeated here only in outline. The chemisorbed gas was desorbed by means of a mercury diffusion pump, and the desorbed gas was collected in a McLeod gauge and its pressure followed at definite intervals. The activation energy of desorption was determined as follows: The temperature of desorption was lowered abruptly during the desorption experiment, and the rates before the temperature drop were extrapolated to those for the smaller amounts adsorbed when the measurements were carried out after the temperature drop. Thus, the rates at the two temperatures corresponded to the same amount adsorbed, and, hence, the activation energy of desorption could be obtained. It was found that the process of readsorption had no effect on the rates of desorption, or at least on the activation energy of the desorption or on the value of $d \ln v_{des}/dq$ (v_{des}, rate of desorption; q, adsorbed amount).

Prior to the chemisorption experiments, all the adsorbents were evacuated for five hours at 450°C. The weight of the 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	16.72	6.1
NiO I	5.49	3.1
NiO II	28.61	3.4

NiO I was used for CO_2 chemisorption and NiO II for CO chemisorption.

Results and Discussion

Activation Energies of Desorption at Various Coverages.—*Carbon Dioxide Chemisorption on Zinc Oxide and Nickel Oxide.* — After carbon dioxide had been allowed to chemisorb at about 300°C for 2 hr., the temperature of the specimen was raised from −30 to 400°C in stages, at each of which the activation energy of the desorption was determined in the manner given above. The results are shown in Fig. 1. It is seen that in the range below room temperature the activation energy of the desorption is about 16 kcal./mol., while above room temperature it increases with the temperature of the desorption, up to 40 kcal./mol. After carbon dioxide had been adsorbed at about 400°C, the adsorption isotherms were determined by successive withdrawals of the gas by a method described in the previous paper[1]. The isotherms thus determined were reproducible on increasing or decreasing the pressure. The results are represented in Fig. 2. The heats of adsorption determined from these isotherms are represented in Fig. 1,

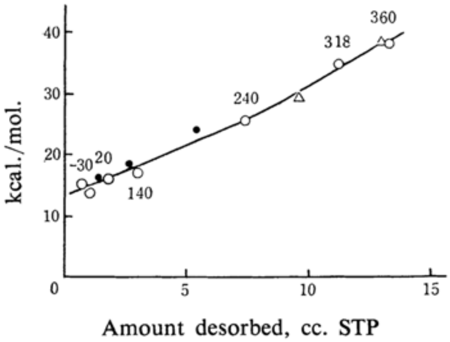

Fig. 1. Activation energies of desorption of carbon dioxide chemisorbed on zinc oxide. The amount adsorbed at room temperature before desorption was 14.33 cc. before oxygen treatment and 13.31 cc. after oxygen treatment. Figures indicate the temperature of desorption. -○-, before treatment; -●-, after treatment. The symbol △ refers to the heat of adsorption.

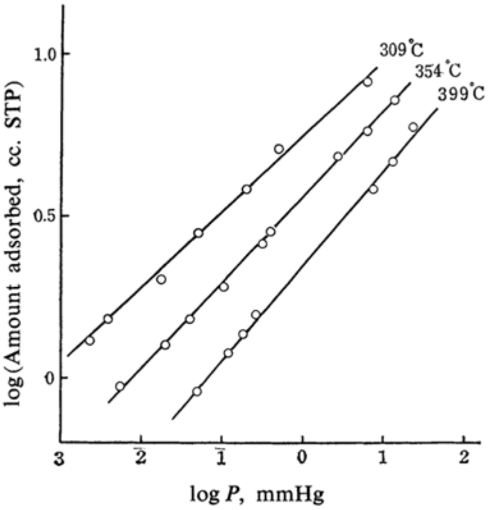

Fig. 2. Adsorption isotherms of carbon dioxide on zinc oxide.

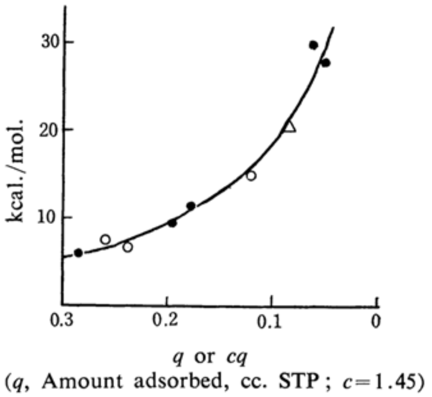

Fig. 3. Activation energies of desorption of carbon dioxide chemisorbed on nickel oxide. The amount adsorbed at room temperature before desorption was 0.357 cc. before oxygen treatment and 0.263 cc. after oxygen treatment. -○-, befor treatment ; -●-, after treatment. The symbol -△- refers to the heat of adsorption.

together with the activation energy of the desorption. It follows from this figure that, for the range with an activation energy of desorption of 40 kcal./mol., which is close to the maximum value for this system, the chemisorption involves no activation energy. Consequently, for the range with a lower activation energy of desorption, the same conclusion may also be applicable.

For carbon dioxide chemisorption on nickel oxide, the activation energies of desorption at various coverages were determined in a similar manner. The results are represented in Fig. 3. A comparison with the heats of adsorption determined from the adsorption isotherms shows that the chemisorption is also of a nonactivated type. It is evident from Figs. 1 and 3 that the activation energy of desorption, as well as the adsorbed amount per unit area, is much less on nickel oxide than on zinc oxide.

Carbon Monoxide Chemisorption on Nickel Oxide. — After carbon monoxide had been chemisorbed at room temperature, the activation energies of desorption were determined in a similar manner in the range below room temperature. The results are represented in Fig. 4. Figure 5 shows similar results obtained with a specimen on which carbon monoxide chemisorption had been carried out at about 260°C. The carbon dioxide content of the desorbed gas was examined by immersing the trap attached to the McLeod gauge in liquid nitrogen. As is seen in Fig. 6, the content is negligibly small below room temperature, but it increases steadily with the increasing temperature of the desorption. At 250°C, most of the desorbed gas consists of carbon dioxide.

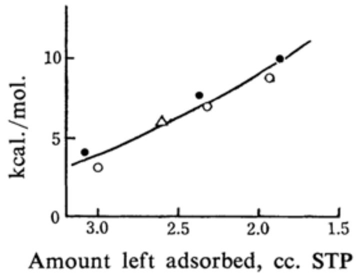

Fig. 4. Activation energies of desorption of carbon monoxide chemisorbed on nickel oxide. The amount adsorbed at room temperature before desorption was 2.82 cc. before oxygen treatment and 2.64 cc. after oxygen treatment. -○-, before treatment ; -●-, after treatment. The symbol -△- refers to the heat of adsorption.

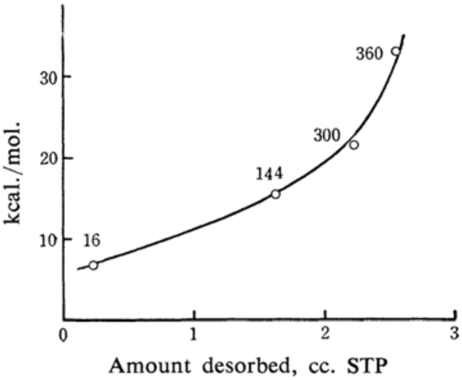

Fig. 5. Activation energies of desorption of carbon monoxide chemisorbed on nickel oxide. Carbon monoxide was chemisorbed at about 260°C. Figures indicate the temperature of desorption. The amount adsorbed at room temperature before desorption was 2.69 cc.

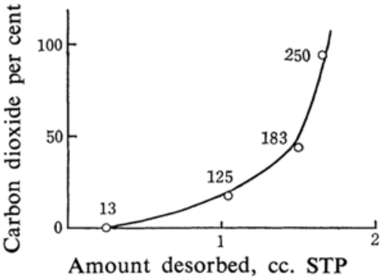

Fig. 6. Carbon dioxide content of the desorbed gas. Figures indicate the temperature of desorption.

Such behavior indicates the existence of two types of chemisorption, one being reversible, the other, irreversible. As is seen in Fig. 6, most of the carbon monoxide reversibly adsorbed can be desorbed below 200°C, suggesting that the upper limit of the activation energy of the desorption for the reversible type is about 16∼20 kcal./mol. (Fig. 5).

The adsorption isotherms were determined to be between 0°C and −22°C in a manner similar to that described above. The heat of adsorption determined from these isotherms is represented in Fig. 4. It follows from this figure that the reversible chemisorption is of a non-activated type. On the other hand, it was found that the adsorption isobar obtained on increasing the temperature of the specimen, which had chemisorbed carbon monoxide at room temperature, showed a maximum at about 250°C, suggesting that some part of the irreversible chemisorption involves an activation energy.

Two Types of Chemisorption and their Behavior in Desorption.—According to previous work by one of the present authors(1), there seems little doubt that, at least in the case of the chemisorption on oxides, the heat of the adsorption or the activation energy of the desorption increases with the adsorbed amount mainly as a result of an a priori heterogeneity of the surface rather than an induced heterogeneity(6) or interaction between the adsorbed species. For such a heterogeneous surface the rate of desorption can be derived by introducing the following method, first given in a previous work(7). The surface may be divided into a number of sets of identical sites, each of which has a particular activation energy of desorption. At any moment during the desorption experiments, there exists a certain set of sites, S_{m}, for which the rate of desorption passes through a maximum. Such a maximum rate may be assumed to be approximately proportional to the rate for the whole surface. The rate expression thus derived is given as

$$\mathrm{d}\ln v_{\mathrm{des}}/\mathrm{d}q = -(\mathrm{e}^{\beta}/\boldsymbol{RT}N\theta)$$

where θ and N are the coverage at equilibrium and the distribution function of the sites respectively, both referring to the set of sites, S_{m}, mentioned above, and β is a constant associated with the distribution of sites. As was described in a previous work, the term of e^{β} is of secondary importance in determining the value of $\mathrm{d}\ln v_{\mathrm{des}}/\mathrm{d}q$. It may therefore be expected that the value of $\mathrm{d}q/\mathrm{d}\ln v_{\mathrm{des}}$ will increase with the increasing value of $N\theta$ and vice versa.

In the desorption rate measurements, if the temperature of the specimen is raised in stages, as has been described above, the set of sites, S_{m}, will be shifted in the direction of a higher activation energy of desorption, that is, of a higher value of θ, with the increasing temperature of the desorption. The variation of N, accompanied by such a shift of S_{m}, depends upon the distribution of sites; without any information about this, however, a quantitative discussion of it does not seem feasible. However, at least for the case in which only one type of adsorption is operative, it would not be expected that the value of N, and hence the product $N\theta$, would pass through a minimum with the progress of the desorption, since θ is increased with the increasing temperature of the desorption. Thus, the occurrence of such a minimum in $N\theta$, i. e., $\mathrm{d}q/\mathrm{d}\ln v_{\mathrm{des}}$, suggests that the adsorption sites are divided into two groups, which is to be expected for two types of chemisorption. As an illustration, we can mention the results of the chemisorption of carbon monoxide on nickel oxide, for which the existence of two types of chemisorption has been confirmed. From the plots of $\log v_{\mathrm{des}}-q$ at various temperatures for this system, the values of $\mathrm{d}q/\mathrm{d}\log v_{\mathrm{des}}$ at different amounts adsorbed were determined to be as shown in Fig. 7. It is seen that this value shows a minimum at 150∼170°C, below which temperature most of the carbon monoxide reversibly chemisorbed can be desorbed (Fig. 6), thus confirming the above conclusion.

Similar treatments were carried out using

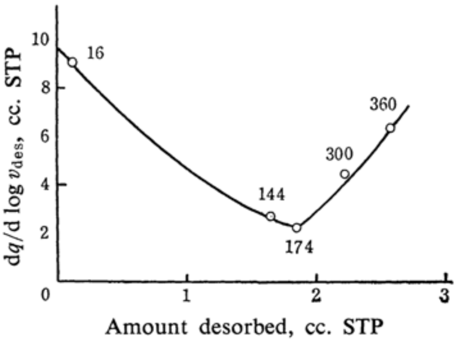

Fig. 7. Values of $\mathrm{d}q/\mathrm{d}\log v_{\mathrm{des}}$ for carbon monoxide chemisorption on nickel oxide. Figures indicate the temperature of desorption.

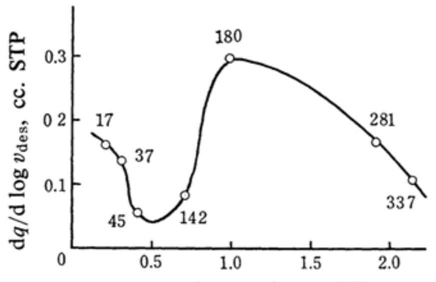

Fig. 8. Values of $\mathrm{d}q/\mathrm{d}\log v_{\mathrm{des}}$ for carbon dioxide chemisorption on zinc oxide. The weight of adsorbent used in these runs was 3.51 g. Figures indicate the temperature of desorption.

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6) M. Boudart, *J. Am. Chem. Soc.*, **74**, 3556 (1952).
7) Y. Kubokawa, This Bulletin, **33**, 734, 1226, 1227 (1960).

the results of desorption experiments on other systems. For carbon dioxide chemisorption on zinc oxide, a similar minimum is observed, as may be seen in Fig. 8. This suggests the existence of two types of chemisorption, the existence of which has been recently supported by the work of Matsushita[8)] on the infrared spectrum of carbon dioxide chemisorbed on zinc oxide. On the other hand, for the carbon dioxide-nickel oxide system, somewhat different results were obtained, the value of $dq/d \log v_{des}$ decreasing steadily with the increasing temperature of the desorption. Such behavior is inconsistent with that expected for the two types of chemisorption. Further study, therefore, seems necessary before we can understand the difference between the nickel oxide and zinc oxide systems and clarify the true nature of the two types of chemisorption on zinc oxide.

Effect of Oxygen Treatment on the Chemisorption.—This problem was investigated in the following way. All the adsorbents were treated with oxygen at about 450°C, followed by evacuation at 260°C for carbon dioxide and at 100°C for carbon monoxide chemisorption. The activation energies of the desorption at various coverages were then determined in a similar manner. As may be seen in Figs. 1 and 4, for carbon monoxide on nickel oxide and for carbon dioxide on zinc oxide such an oxygen treatment has little or no effect on either the adsorbed amount or on the activation energy of the desorption. This indicates that both chemisorptions are essentially independent of the electronic state of the adsorbents. It may, therefore, be concluded that the formation of an electrical double layer at the interface, which has been emphasized by Hauffe and others, probably plays no significant role in determining the features of the chemisorption already mentioned, although some contribution by ionic binding to the adsorption bond is undeniable. It seems likely that the above-mentioned marked change in the activation energy of the desorption with the change in coverage is mainly to be attributed to a heterogeneity of the surface, as was concluded in a previous work. Such a conclusion is supported by a marked variation in the value of $dq/d \log v_{des}$ with a slight change in the coverage, examples being given in Figs. 7 and 8. As has been described previously, such a phenomenon seems very difficult to explain in terms of the concept of induced heterogeneity.

For carbon dioxide on nickel oxide, somewhat different results were obtained, the amount adsorbed being appreciably reduced after the oxygen treatment. However, if q is replaced by cq (c, constant) in the plots of the activation energy of the desorption against q, then the resulting plots before and after the oxygen treatment lie on the same curve, as may be seen in Fig. 3. This slight effect on the activation energy of the desorption and the results obtained with zinc oxide suggest that the decrease of the adsorbed amount is not closely associated with a change in the electronic state.

Carbon dioxide chemisorption on doped zinc oxide has been investigated by Hart and Sebba[9)]. According to their work, the doping with aluminum oxide, which increases the electrical conductivity of zinc oxide, increased the heat of the adsorption, while the doping with lithium oxide had a reverse effect; they have discussed such effects in terms of the change in the Fermi level of zinc oxide. As has been suggested by various workers, however, it should be taken into consideration that such doping will change the surface heterogeneity as well as the electronic state of zinc oxide, both changes affecting the features of the chemisorption. It seems questionable, therefore, to attribute the effect of doping to only the change in the electronic state, as these workers have done. In fact, rather unusual behavior is observed in their work, since they show that the adsorbed amount per unit area is the largest on lithium-doped zinc oxide, which shows the lowest heat of adsorption.

Summary

As an extension of previous work, the study of chemisorption by desorption rate measurement was carried out for carbon dioxide adsorbed on zinc oxide and nickel oxide, and also for carbon monoxide adsorbed on nickel oxide. For the chemisorption of carbon dioxide, the activation energy of the desorption was increased with the decreasing amount adsorbed from 16 to 40 kcal./mol. on zinc oxide and from 7 to 30 kcal./mol. on nickel oxide. In the case of the chemisorption of carbon monoxide, where the two types of chemisorption are seemingly operating, the activation energy of the desorption for the reversible type ranged from 5 to 18 kcal./mol. A method of distinguishing these two types of chemisorption from the behavior on desorption has been proposed, for it has been found that there are two types of chemisorption for the carbon dioxide-zinc oxide system. From the effect of oxygen treatment at high temperatures on the chemisorption, it was concluded that the effect

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[8)] S. Matsushita and T. Nakata, *J. Chem. Phys.*, **36**, 665 (1962).

[9)] P. M. G. Hart and F. Sebba, *Trans. Faraday Soc.*, **56**, 551 (1961).

of the surface barrier, emphasized by Hauffe and others, seems to be only of secondary importance in the above system.

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