Carbon Monoxide Chemisorption on Zinc Oxide

By Yutaka Kubokawa

(Received September 9, 1959)

Carbon monoxide chemisorption on zinc oxide at room temperature has been investigated by Garner and coworker[1] who reported that the heat of adsorption obtained from the adsorption isotherms is 10~14 kcal./mol., and that the chemisorption is instantaneous and completely reversible at room temperature. Few studies[2] have hitherto been reported on the carbon monoxide chemisorption at high temperatures, which appears to play an important role in the reaction of carbon monoxide, e. g. the oxidation of carbon monoxide. The present work has therefore been undertaken to obtain quantitative information concerning this chemisorption over a wide temperature range by measuring the rate of adsorption and adsorption equilibrium as well as the rate of desorption in the manner described in previous papers[3,4]. Moreover, in this paper, the nature of surface heterogeneity in this system is discussed on the basis of the results obtained, and especially those of the desorption under various experimental conditions which proved to be useful in clarifying the nature of the heterogeneity of zinc oxide surface in the hydrogen chemisorption[4].

Experimental

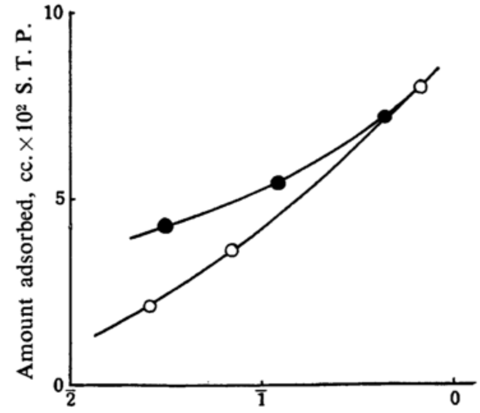
Materials.—Zinc oxide was prepared from zinc oxalate in a manner similar to that described in the previous paper[3]. The weight of adsorbent was 16.72 g. and the surface area determined by the B. E. T. method was 6.1 m²/g. Carbon monoxide was prepared by the reaction of air-free formic acid and concentrated sulfuric acid, purified by passing through soda lime and phosphorus pentoxide, and finally through a trap immersed in liquid nitrogen.

Apparatus and Procedure. — Details of the apparatus and procedure were described in the previous paper[3]. Before a series of experiments, the pretreatment of the sample with carbon monoxide at 400°C followed by evacuation at this temperature were repeated several times.

Results and Discussion

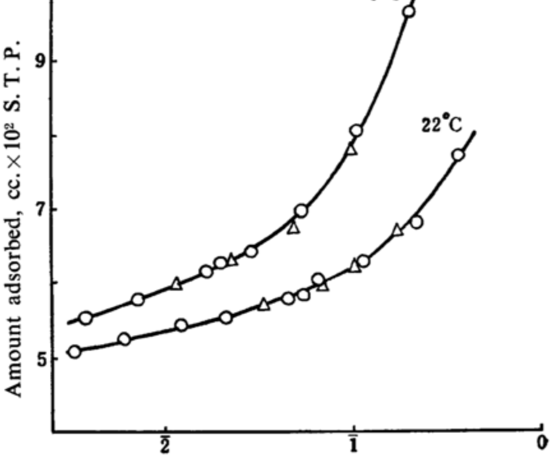
Adsorption Isotherms at About Room Temperature.

—According to the investigations by Garner et al.[1], carbon monoxide chemisorption at room temperature is instantaneous and involves no appreciable activation energy. The results obtained in the present study were similar to their results except for the occurrence of a slow uptake even at room temperature, though its amount was very small. The adsorption isotherm obtained by successive



log *P*, mmHg

Fig. 1. Adsorption isotherms on the adsorption and desorption branches for the chemisorption of CO on ZnO at 22°C. -○-, on adsorption ; -●-, on desorption.



log *P*, mmHg

Fig. 2. Adsorption isotherms of CO on ZnO at 0 and 22°C. -○-, on decreasing pressure ; -△-, on increasing pressure.

---

[1] W. E. Garner and J. Maggs, *Trans. Faraday Soc.*, 32, 1744 (1936).

[2] R. L. Burwell and H. S. Taylor, *J. Am. Chem. Soc.*, 59, 697 (1937); E. R. S. Winter, "Chemisorption", edited by W. E. Garner, Butterworths Scientific Publications, London (1957), p. 189.

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

[4] Y. Kubokawa, ibid., 33, 550 (1960).

additions of the gas in the usual manner was found to be different from that obtained in the reverse way, i. e., by successive withdrawals of the gas, as shown in Fig. 1. However, the isotherms determined by the latter method were reproducible on increasing or decreasing pressure as found for the hydrogen chemisorption described in the previous paper³⁾. Fig. 2 shows the results obtained, which give the heat of adsorption as 10∼12 kcal./mol.

Dependence of the Rate of Adsorption on Pressure and Temperature.—Carbon monoxide was introduced at room temperature and its adsorption followed, the temperature being raised in stages up to about 300°C. The results obtained are shown in Fig. 3, which shows that the rate of slow uptake increases markedly with temperature, and that above 100°C only a slight rapid desorption takes place on raising the temperature, in contrast with the case of hydrogen chemisorption previously reported⁴⁾. The pressure dependence of the slow process was obtained in a manner similar to that for hydrogen chemisorption, i. e. by comparison of the rates at equal amounts of slow chemisorption between before and after a rapid pressure change during the adsorption rate measurements. A typical result is shown in Fig. 4 and Table I. The rate is proportional to $p^{0.8\sim0.9}$ on both increasing and decreasing pressures, indicating that desorption is negligible during adsorption.

The temperature dependence of the slow process was obtained by a comparison of the rates corresponding to the equal amounts of slow chemisorption at different temperatures. The results evaluated from Fig. 3 are shown

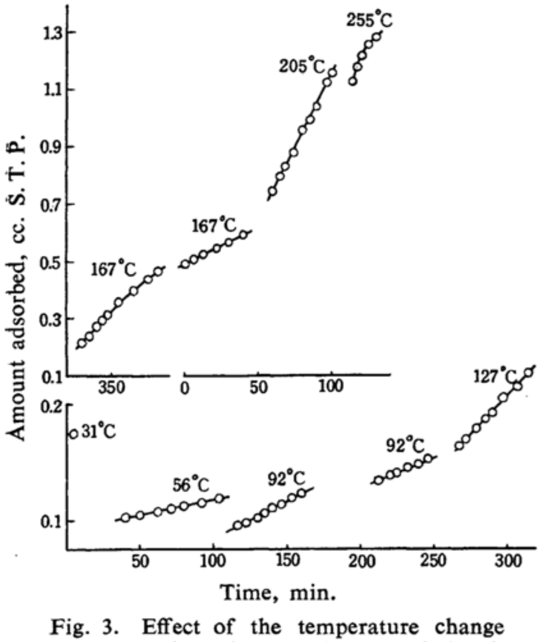


Fig. 3. Effect of the temperature change during adsorption on the rate of chemisorption of CO on ZnO. Pressure, 0.2∼0.4 mmHg. Runs at 92 and 167°C were interrupted by reducing pressure or temperature.

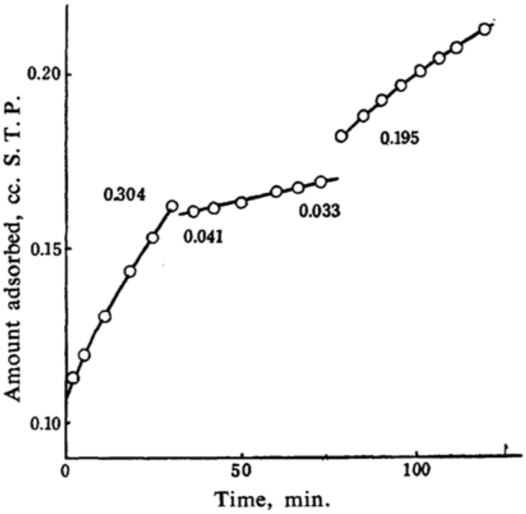


Fig. 4. Effect of the pressure change during adsorption on the rate of chemisorption of CO on ZnO. Temp., 120°C. Figures indicate the pressure before and after the pressure change in mmHg.

TABLE I. VALUES OF n IN THE EXPRESSION, RATE ∝ P^n FOR THE DATA IN FIG. 4

Pressure before and after the pressure change, mmHg	n
0.304 → 0.041	0.89±0.06
0.033 → 0.195	0.86±0.06

TABLE II. ACTIVATION ENERGIES OF ADSORPTION FOR THE DATA IN FIG. 3

Temp. range, °C	Activation energy kcal./mol.
56∼ 92	5.5±1.0
92∼127	7.5±1.0
127∼167	11.5±0.7
167∼205	16.5±0.7

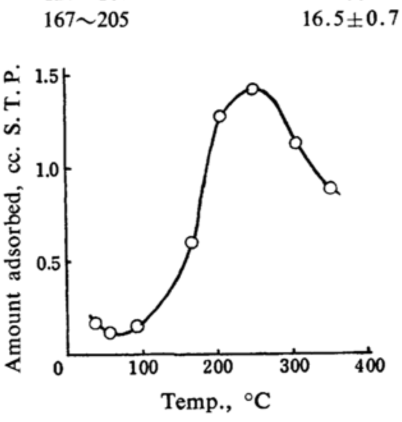


Fig. 5. Adsorption isobar of CO on ZnO at 0.2∼0.4 mmHg.

in Table II, which indicates that the activation energy of the slow process increases as the temperature range becomes higher.

The adsorption isobar at approximately constant pressure 0.2∼0.4 mmHg was obtained from the amount adsorbed after 1 hour at each temperature. Fig. 5 illustrates this isobar which shows a minimum at about 70°C and a maximum at about 250°C.

Activation Energies of Desorption at Various Coverages.—The temperature of the adsorbent which had already adsorbed carbon monoxide at about 300°C was raised from -72 to about 400°C in stages, at each of which the activation energy of desorption was determined in the manner described in the previous paper[3]. The variation of the activation energy for desorption with the amount desorbed is shown in Fig. 6. As seen in this figure, the curve of activation energy of desorption against the desorbed amount is composed of two parts, one corresponding to the desorption below room temperature with the activation energy of 2.5 kcal./mol., and the other to that above 200°C with the activation energy of approximately 40 kcal./mol. The former value is essentially the same as the heat of adsorption derived from the isotherms around room temperature, indicating that the chemisorption at room temperature involves no activation energy, as may be expected. In the latter case, the activation energy of desorption increases somewhat with decreasing coverage.

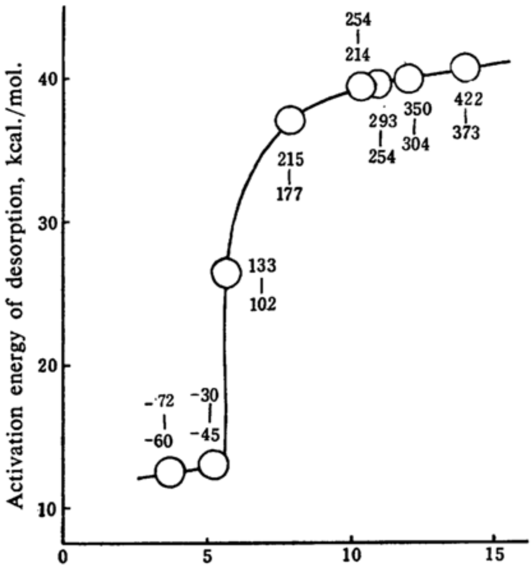


Fig. 6. Activation energies of desorption of CO chemisorbed on ZnO. Figures indicate the temperature interval where the activation energy was determined. The amount adsorbed at room temperature before desorption was 15.81 cc.

This conclusion is based on the assumption that the measured rate of desorption is not affected by the reverse reaction. This was confirmed in the manner previously described[3], i. e., by observing the pressure increase caused by isolating the adsorption vessel from the mercury diffusion pump. In the temperature range above room temperature the observed behavior was almost the some as that of the hydrogen chemisorption previously[3] described, indicating that adsorption is negligible during the desorption rate measurement. Whilst in the temperature range below room temperature, somewhat different behavior was observed as represented in Fig. 7. This shows that an equilibrium pressure P_e is here easily attained, and moreover that the pressure in the adsorption vessel during the desorption experiment P, is now comparable to P_e. However, the ratio P_e/P was found not to vary seriously by an abrupt change of temperature. From the data given in Fig. 7 this ratio was estimated to be 3.5 at -30°C, while the similar measurements at -45°C following these experiments gave the value of 2.6. The error introduced in the activation energy of desorption by this difference in P_e/P was estimated to be at most 1 kcal./mol. It may therefore be concluded that the activation energy of desorption obtained below room temperature is also nearly equal to the true value.

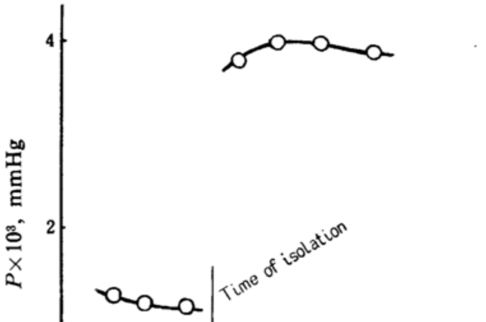


Fig. 7. Results obtained by isolating the adsorption vessel from the mercury diffusion pump. Temp., -30°C.

In order to confirm the reversibility of chemisorption the content of carbon dioxide in the desorbed gas was examined by immersing the trap attached to the MacLeod gauge in liquid nitrogen. The absence of carbon dioxide was confirmed below 350°C, while above this temperature its content amounted to the fraction 1/3∼1/2 of the desorbed gas.

Adsorption Isotherms at Higher Temperature⁵⁾. —The adsorption isotherms in temperature 300~370°C were determined by successive withdrawals of the gas as described for low temperature isotherms. These isotherms are strictly reproduced on increasing or decreasing pressure, as shown in Fig. 8. Fig. 9 represents the fact that the heat of adsorption derived from these isotherms decreases with the increasing amount adsorbed from 38 to 25 kcal./mol.

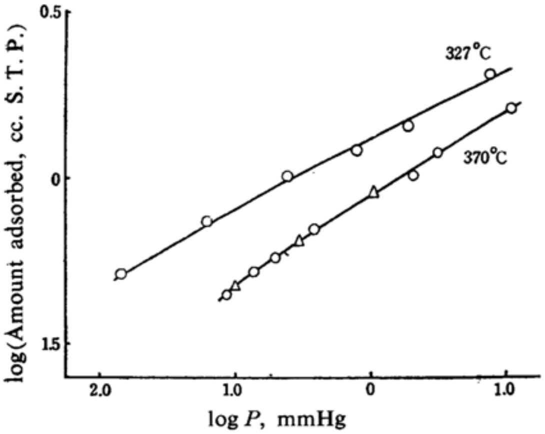


Fig. 8. Adsorption isotherms of CO on ZnO at 327 and 370°C. -○-, on decreasing pressure; -△-, on increasing pressure.

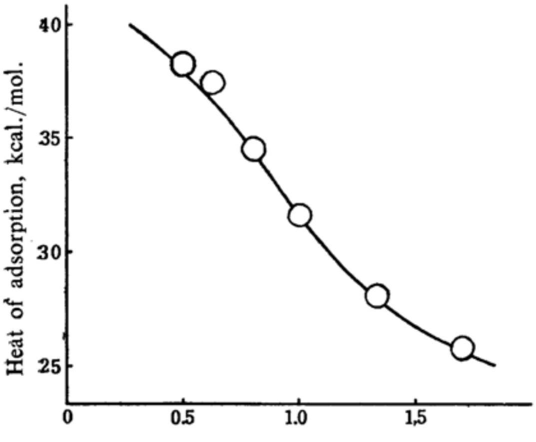


Fig. 9. Heats of adsorption of CO on ZnO.

Two Types of Carbon Monoxide Chemisorption on Zinc Oxide.—The plots of the activation energy for desorption against the amount adsorbed shown in **Fig.** 6, together with the adsorption isobar shown in **Fig.** 5, suggest that the two types of chemisorption are operating, one being a non-activated type predominating at a lower temperature, and the other an activated type occurring at a higher temperature. Moreover, not only the former, but also a considerable fraction of the latter is reversible, i. e. desorbed as such. Such behavior of the high temperature chemisorption appears to be inconsistent with the investigations by Garner and coworkers⁶⁾, who report that on a number of oxide catalysts the high temperature chemisorption takes place on the oxygen ion and the desorbed gas consists of carbon dioxide. However, the exchange reaction of the oxygen atom between carbon monoxide and the oxide surfaces have recently been investigated by Winter²⁾, who shows that the high temperature chemisorption does not necessarily lead to the desorption of carbon dioxide, in agreement with the results in the present work.

On the other hand, as described above, there is a slow uptake at room temperature which seems to imply that the chemisorption with the lower activation energy occurs even at room temperature. The phenomena of hysteresis observed at room temperature may then be accounted for, since the high temperature type is considered to be irreversible at this temperature.

Nature of Heterogeneity of the Surface.—The problem was dealt with in the same manner as previously reported for the hydrogen chemisorption⁴⁾: At 192°C a known amount of carbon monoxide was left in contact with the adsorbent for fifteen minutes in one case and for fifteen hours in the other case; then, by pumping out a known amount of the gas from the system, the desorption rates in the two cases were compared with the results shown in Fig. 10, where curves A and B represent desorption rates after fifteen minute and fifteen hour contacts, respectively. After desorption B a certain amount of carbon monoxide was further pumped out at a higher temperature until the remaining amount adsorbed became comparable to that left after desorption A; thereupon, the temperature was lowered down to 192°C, and desorption rate measurements were carried out. Their results, denoted by C, are also shown in Fig. 10. It follows from this figure that the rate of desorption is greater on the surface where the larger amount is adsorbed, and is determined by the remaining amount adsorbed alone, independent of the conditions employed for the adsorption, in contrast with the behavior of hydrogen described in the previous paper⁴⁾.

These results might be explained in terms of the concept that the increase of the activation

---

5) During the adsorption isotherm measurements, the formation of carbon dioxide was negligibly small and darkening of zinc oxide was not observed, suggesting that the reaction $2CO \rightarrow C+CO_2$ scarcely takes place at all, in disagreement with the results obtained by Taylor and Burwell²⁾. Such discrepancy appears to be explained by the severe carbon monoxide treatment in the present work, since the authors cited above reported a marked decrease in the activity toward this reaction after the carbon monoxide treatment.

6) W. E. Garner, *J. Chem. Soc.*, **1947**, 1239.

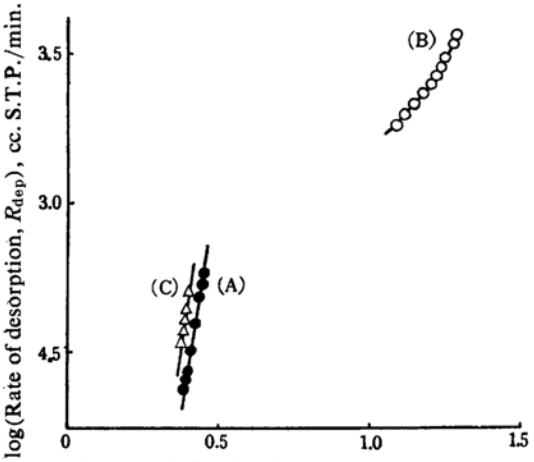


Fig. 10. Rate of desorption as a function of the amount left adsorbed. Temp, 192°C.

energy of adsorption with the adsorbed amount is due to the decrease of the heat of adsorption with coverage, without the concept of an *a priori* heterogeneity. However, the fact that the value of $d \log R_{dep}/dq$ differs markedly between the two runs, A and B, as shown in Fig. 10, can not be explained in terms of the induced heterogeneity[7] above mentioned, because there is no marked difference in the coverage θ between these two runs, considering that the adsorbed amount at $\theta=1$ estimated from Fig. 8 is about 10 cc. With respect to this problem, the following experimental results may be mentioned. From the plots of $\log R_{dep}-q$ at varied temperatures which were determined for the purpose of determining the activation energy of desorption at various coverages, the values of $d \log R_{dep}/dq$ at different adsorbed amount were estimated as shown in Fig. 11. This considerable change[8] can not be expected from the concept of induced heterogeneity. It may therefore be concluded that in this system again the variation of the heat of adsorption with the adsorbed amount will arise mainly from *a priori* heterogeneity, the nature of which is such that the activation energy of adsorption and the heat of adsorption varies conversely to each other, in contrast with hydrogen chemisorption. Such a correlation between the activation energy of adsorption and the heat of adsorption requires that the maximum activation energy of adsorption 16 kcal./mol. should correspond to the minimum activation energy of desorption 37 kcal./mol. and the minimum of the former 5 kcal./mol. to the maximum of the latter 41 kcal./mol. This gives as the heats of adsorption 36 and 21 kcal./mol. in fair agreement with the values directly obtained from the adsorption isotherms[9].

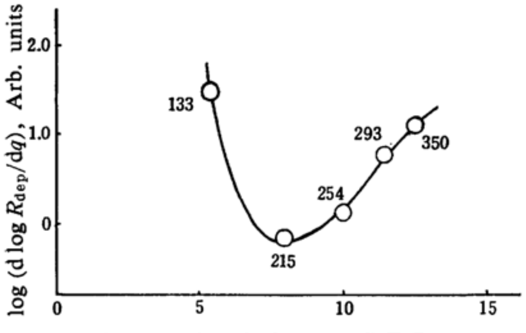


Fig. 11. Values of $d(\log R_{dep})/dq$ at various amounts adsorbed. Figures indicate the temperature in °C where the rate of desorption was measured.

Summary

The rates of adsorption and desorption, and the adsorption equilibrium for carbon monoxide chemisorption on zinc oxide were measured over a wide range of temperatures as in the previous study of hydrogen chemisorption on zinc oxide. The behavior of desorption indicated the existence of two types of chemisorption; the non-activated type and the activated type. For the former type the heat of adsorption was estimated as 10~12 kcal./mol. from the adsorption isotherms, in agreement with the activation energy of desorption. The considerable fraction of the latter type was reversible, i.e. desorbed as such. For this type, the activation energy of adsorption increased with the adsorbed amount from 5 to 16 kcal./mol., and the rate was proportional to $P^{0.8\sim0.9}$. Moreover, the heat of adsorption obtained from the adsorption isotherms ranged from 25 to 38 kcal./mol., in fair agreement with those estimated from the activation energy of adsorption and desorption. The behavior of desorption suggested the predominance of surface heterogeneity, the nature of which was such that the activation energy of adsorption and the heat of adsorption varied conversely to each other.

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

---

[7] M. Boudart, *J. Am. Chem. Soc.*, 74, 3556 (1952).

[8] It will be shown in a forthcoming paper that this considerable change inevitably arises on a surface where *a priori* heterogeneity is predominating.

[9] In Figs. 3, 6 and 9, the states of the carbon monoxide adsorbed to an equal amount can not be be compared, since the surface has a heterogeneous character, and moreover the observed amount of adsorption includes the irreversible one, the extent of which varies with the experimental conditions.