Rate of Adsorption on a Heterogeneous Surface. Determination of the Distribution Function of Sites from Adsorption Rate Curves

By Yutaka KUBOKAWA

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In view of the importance of surface heterogeneity in the chemisorption on oxide catalysts as revealed by desorption experiments[1], the present author has derived in a recent paper[2] the rate of adsorption on a heterogeneous surface for the cases where the distribution function of sites is variable and/or desorption can not be neglected. The rate formula thus obtained has led to an interpretation of the Elovich equation

$$\mathrm{d}q/\mathrm{d}t = a\mathrm{e}^{-bq}$$

where q is the adsorbed amount and a and b are constants. Thus, explicit expressions and hence a physical meaning have been given to the constant b in the Elovich equation on the basis of the surface heterogeneity. The frequently observed variation in the constant b with pressure or temperature has been shown to be explained since the Elovich equation is usually applied only in a limited range of coverage. It is rather customary to use the integrated form of the Elovich equation for its actual application. Nevertheless, as has been pointed out in the previous paper, the constant b obtained from the integrated form of the equation, in most cases, can not be given any such physical meaning as that mentioned above, and consequently can not be related to the surface heterogeneity in a quantitative way. It has therefore been undertaken in the present work to devise a method of obtaining quantitative information on the surface heterogeneity, i. e, the distribution function of sites, directly from the adsorption rate curves.

Analysis of Adsorption Rate Curves. — As described in the previous work[2], the rate of adsorption on a heterogeneous surface can be represented by the following equation when desorption is negligibly small during the adsorption rate measurement:

$$v = Kf(p)\boldsymbol{RTN}\mathrm{e}^{-\beta} \tag{1}$$

where K and N are the rate constant of adsorption and the distribution function of sites respectively, both referring to the set of sites mainly responsible for adsorption at a given time; the value of K in Eq. 1 varies with time according to

$$Kf(p)t = 1+\beta \tag{2}$$

where $\beta = \mathrm{d}\ln N/\mathrm{d}\ln K$. Thus the rate as a function of time becomes

$$v = (\boldsymbol{RTN}/t)(1+\beta)\mathrm{e}^{-\beta} \tag{3}$$

Using Eq. 1—3, the constant b of the Elovich equation, $\mathrm{d}\ln v/\mathrm{d}q$, is given by[3]

$$\mathrm{d}\ln v/\mathrm{d}q = -(1/\boldsymbol{RTN})\mathrm{e}^{\beta} \tag{4}$$

Transposing Eq. 3,

$$\mathrm{d}\ln t/\mathrm{d}q = (1/\boldsymbol{RTN})(1/1+\beta)\mathrm{e}^{\beta} \tag{5}$$

Combining Eq. 4 and 5,

$$1+\beta = -(\mathrm{d}\ln v/\mathrm{d}q)/(\mathrm{d}\ln t/\mathrm{d}q) \tag{6}$$

The right hand side of Eq. 6 is determined from the adsorption rate curves by graphical differentiation, and consequently the value of β at a given adsorbed amount, q, is obtained. Substituting β thus obtained into Eq. 1 and 4, the values of N and K are determined as a function of the adsorbed amount.

As described previously[3], the chemisorption of hydrogen on chromic oxide gel investigated by Burwell and Taylor[4] belongs to the case where desorption is negligibly small above 457°K. The data at 457°K and 1 atm. have been treated in the manner mentioned above

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1) Y. Kubokawa, This Bulletin, 33, 546, 550, 555, 739, 743, 747 (1960).

2) Y. Kubokawa, This Bulletin, 33, 734 (1960).

3) The pressure term in the rate expression, $f(p)$, is assumed to be constant during adsorption.

4) R. L. Burwell and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 697 (1936).

TABLE I. HYDROGEN CHEMISORPTION ON Cr_2O_3 GEL AT 457°K AND 1 atm.

q	$-\mathrm{d}\ln v/\mathrm{d}q$	$\mathrm{d}\ln t/\mathrm{d}q$	$-\beta$	$-\ln N$	$-\ln K$
3	0.163	0.495	0.67	5.66	2.02
5	0.131	0.333	0.61	5.38	2.51
7	0.092	0.244	0.62	5.04	3.06
10	0.072	0.172	0.58	4.74	3.55
12	0.064	0.142	0.55	4.60	3.79
15	0.059	0.115	0.49	4.46	4.07
20	0.053	0.092	0.43	4.30	4.45
25	0.051	0.082	0.38	4.21	4.75
30	0.047	0.075	0.37	4.12	5.07

q is in cc. (S. T. P.), v in cc./min., N in cc./cal., and K in min^{-1}.

with the results listed in Table I[5]. Here, as adsorption proceeds, the value of $\ln N$ increases with decreasing value of $\ln K$. The relationship of $\ln N$ against $\ln K$ is also obtained from a similar treatment for the data at other pressures at 457°K; the plots $\ln N - \ln K$ at different pressures at 457°K thus obtained were found to lie on the same curve, as would be expected.

By assuming that the variation in $\ln K$ arises only from that in activation energy of adsorption E, the following expression results:

$$RT\ln K = RT\ln C - E$$

where C is a constant. Plots of $\ln N$ against $\ln K$ at various temperatures combined with the above expression give those of $\ln N$ against E all of which should lie on the same curve since N has been assumed to be a function of E alone. This requirement is fulfilled by adjusting the parameter C as shown in Fig. 1 where $\ln C = 20.1$. The figure shows that, as adsorption proceeds, the value of E increases with that of $\ln N$ from 20 to 23 kcal./mol. Values of E in this range seem to be reasonable, judging by the temperature dependence of the rate.

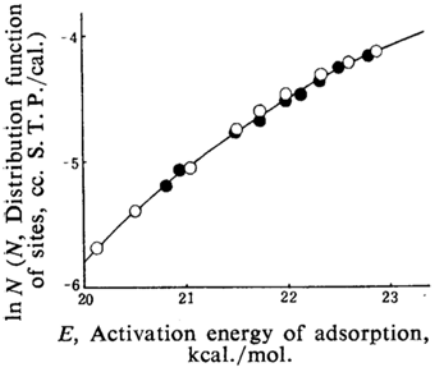

Fig. 1. Hydrogen chemisorption on Cr_2O_3 gel (Burwell and Taylor).
-○-, 457°K; -●-, 491°K; $\ln C = 20.1$.

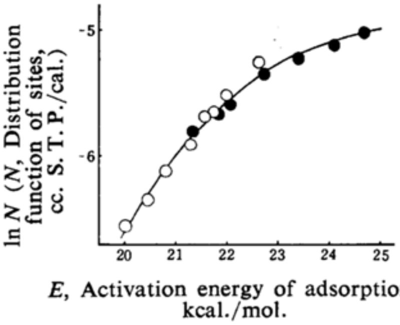

Fig. 2. Hydrogen chemisorption on $ZnO\cdot MoO_3$ (Taylor and Ogden).
-○-, 527°K; -●-, 577°K; $\ln C = 15.5$.

Fig. 2 represents the result of a similar treatment of the data of Taylor and Ogden[6] on the chemisorption of hydrogen on $ZnO\cdot MoO_3$, where desorption is negligible as described in the previous paper[1]. It is seen that the sites with a lower value of E are mainly occupied at a lower temperature.

Summary

A device to obtain the distribution function of sites from adsorption rate curves was worked out for the chemisorption for which desorption is negligible. It was then applied to the rate data of hydrogen chemisorption on chromic oxide gel and on $ZnO\cdot MoO_3$ with reasonable results.

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

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[5] $f(p) = p^{0.8}$ (p in atm.) was used, since Burwell and Taylor state that the rate of adsorption is proportional to $p^{0.8}$.

[6] G. Ogden and H. S. Taylor, *Trans. Faraday Soc.*, **30**, 1178 (1934).