Rate of Desorption from a Heterogeneous Surface

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The previous studies of chemisorption of hydrogen and carbon monoxide on zinc oxide and other catalysts[1], particularly of the rates of desorption at a constant temperature, showed that, although the Elovich equation was approximately obeyed in a limited range of coverage, a slight decrease in the adsorbed amount caused a marked increase in the value of $\mathrm{d}\ln R_{\mathrm{dep}}/\mathrm{d}q$ where R_{dep} is the rate of desorption and q the adsorbed amount. A typical example is shown in Fig. 1. As was pointed out previously, such a phenomenon cannot be explained in terms of the concept that the decrease in the heat of adsorption is due to interaction between adsorbed species or to the induction effect emphasized by Boudart[2]. The concept of an a priort heterogeneity alone seems therefore to offer a satisfactory explanation of the experimental results.

Rate expressions for adsorption on such a heterogeneous surface were already derived in the previous work[3], whereby the physical meaning of $\mathrm{d}\ln R_{\mathrm{adp}}/\mathrm{d}q$ (R_{adp} = rate of adsorption) was also given. This paper presents an attempt to formulate the rate of desorption from a heterogeneous surface in a similar manner, and to explain the variation in $\mathrm{d}\ln R_{\mathrm{dep}}/\mathrm{d}q$ mentioned above on the basis of the surface heterogeneity.

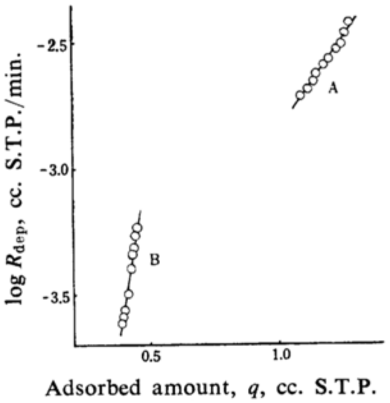

Fig. 1. Rates of desorption of carbon monoxide chemisorbed on zinc oxide. (Reproduced from "Carbon Monoxide Chemisorption on Zinc oxide" by the present author.) Temp., 192°C; The adsorbed amount at saturation is about 10 cc.; the time allowed for adsorption in run A is different from that in run B.

As described previously, the measured rate of desorption is, in most cases, unaffected by the reverse reaction, i. e., the re-adsorption. Consequently, the rate of desorption from any set of sites of the same kind on a heterogeneous surface may be

$$R = N\theta_i k\mathrm{e}^{-kt} = \alpha k\mathrm{e}^{-kt},\ \alpha = N\theta_i$$

where θ_i is the coverage at $t=0$ and N is the distribution function of sites, both of which may usually have different values for a different set of sites. At any moment during a desorption experiment, as was found for adsorption, there is always a certain set of sites for which the rate passes through a maximum. The condition for the maximum, can be written as

$$\mathrm{d}R/\mathrm{d}k = \alpha\mathrm{e}^{-kt}(1+\beta-kt) = 0,\ \beta = \mathrm{d}\ln\alpha/\mathrm{d}\ln k$$

or

$$kt = 1+\beta \tag{1}$$

Thus the maximum rate is

$$R_m = \alpha k\mathrm{e}^{-(1+\beta)} \tag{2}$$

Such a maximum rate may be assumed, as a first approximation, to be proportional to the overall rate on a similar ground to that given previously. Then, from the same argument as that given for the rate of adsorption, the following expression can be derived for the overall rate of desorption R_{dep} by using Eqs. 1 and 2:

$$\mathrm{d}\ln R_{\mathrm{dep}}/\mathrm{d}q = -(\mathrm{e}^{\beta}/RT\alpha) \tag{3}$$

In the course of desorption, k and α will vary as the set of sites for which the rate passes through a maximum is replaced by others successively. Hence, the left-hand side of Eq. 3 will generally vary as the desorption proceeds. In a limited range of coverage, however, an approximately constant value of $\mathrm{d}\ln R_{\mathrm{dep}}/\mathrm{d}q$ will be expected. The behavior of desorption such as that shown in Fig. 1 is thus in agreement with what would be expected on a heterogenous surface, although its quantitative discussion is not feasible without complete information on the site distribution function etc.

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

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

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