A New-Type Adsorption Isotherm of CO on Transition Metal Surfaces with Adsorption-Assisted Processes

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A new adsorption isotherm is proposed, taking the adsorption-assisted desorption into consideration for the first time. The new adsorption isotherm is in reasonable agreement with the experimental data.

The adsorption and desorption of gases at solid surfaces have been studied for many years. The most famous theory of kinetics of adsorption and desorption was proposed by Langmuir: It appears in most of the textbooks of surface sciences. According to the theory, the rate of adsorption (r_a) and that of desorption (r_d) can be expressed by the following equations, where P and θ are the pressure of the ambient adsorbing gas and its coverage, respectively, and k_a and k_d are the rate constants.

$$r_a = k_a P(1-\theta), \tag{1}$$

$$r_d = k_d \theta. \tag{2}$$

At adsorption equilibrium, r_a is equal to r_d, and the following adsorption isotherm may be obtained, assuming that Eqs. 1 and 2 are both applicable in its adsorption equilibrium:

$$\theta = bP/(1+bP), \tag{3}$$

where b is equal to k_a/k_d.

It is generally accepted that the properties of solid surfaces, such as for instance, work function, change as the coverage (θ) changes, and, simultaneously, the rate constants, k_a and k_d, change accordingly. Under those circumstances, many varieties of kinetic equations as well as adsorption isotherms have been proposed. For example, Freundlich adsorption isotherm and Zeldovich kinetic equation appear in many textbooks.[1] However, the rate of desorption is always considered to be a function of coverage of the adsorbed gases only, and this is the reason why the rate of desorption is generally measured by TPD (temperature-programmed desorption) experiments, in which the rate of desorption is estimated under vacuum, and it is generally assumed that the rate is equal to that in the adsorption equilibrium.

Yamada, Tamaru, and their co-workers measured the absolute rates of adsorption and desorption of carbon monoxide on transition metal surfaces in the presence of ambient CO gas, by means of the isotope jump method which one of the authors proposed previously.[2] It was very interesting to note that the rate of desorption, for instance, is markedly dependent upon the pressure of ambient CO gas (Fig. 1).[3] In other words, the rate of desorption of adsorbed CO in the presence of CO is considerably faster than that under vacuum, which was called "adsorption-assisted desorption". The absolute rates of adsorption and desorption of CO on transition metals were given as follows:

$$r_a = k_+ P/[1+K\theta/(1-\theta)], \tag{4}$$

$$r_d = k_- \theta(1+BP^n), \tag{5}$$

where K and n are constants which are approximately 0.2 and 0.8, respectively, and k_+ and k_- are the rate constants. The BP^n term in Eq. 5 corresponds to the adsorption-assisted desorption. These rate equations were treated theoretically by Lombardo and Bell.[4] Kawai and her co-workers recently confirmed such behavior by experiments using time-resolved infrared reflection absorption spectroscopy.[5]

In adsorption equilibrium, by putting r_a equal to r_d, an adsorption isotherm of CO on transition metals may be obtained:

$$k_+ P/[1+\theta K/(1-\theta)] = k_- \theta(1+BP^n), \tag{6}$$

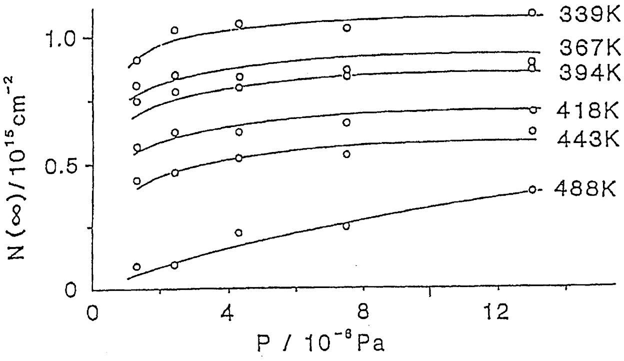

Fig. 1. Adsorption isotherms of CO on Rh polycrystalline surface.
P: gas-phase pressure of CO. $N(\infty)$: equilibrium surface concentration of CO. Gas-phase temperature T_0=298 K. The temperature of the surface T is shown in the figure.

or

$$\theta[1+\theta K/(1-\theta)] = (k_+/k_-)P/(1+BP^n). \tag{7}$$

The adsorption isotherm (6) or (7) is the isotherm in which the adsorption-assisted desorption is taken into consideration for the first time. The isotherm (6) or (7) is not a simple equation to treat, but it demonstrates qualitatively the following relation between CO pressure and its coverage:

Case 1. At Lower Coverages. When θ is less than 1/3, the following adsorption isotherm may be obtained, since $\theta K/(1-\theta)$, which will be named α hereafter, is less than 0.1, provided K is 0.2:

$$\theta = (k_+/k_-)P/(1+BP^n). \tag{8}$$

This adsorption isotherm resembles the Langmuir adsorption isotherm given by Eq. 3, but, since n is smaller than unity, θ increases more rapidly than in Langmuir adsorption isotherm, as the pressure gets higher. Since the value of k_+/k_- is smaller at higher temperatures, the gradient $\mathrm{d}\theta/\mathrm{d}P$ at the beginning of the isotherm curve for $\theta \Rightarrow 0$ and $P \Rightarrow 0$ is also smaller at higher temperatures.

Case 2. At Higher Coverages. According to Eq. 6 or Eq. 7, the following conclusions may be derived:

(a) As the pressure becomes higher, θ increases correspondingly.

(b) The rate of increase in θ with pressure increase (or $\mathrm{d}\theta/\mathrm{d}P$), however, becomes less as the pressure becomes higher (or as θ increases), not only because the value of the right hand side of Eq. 7 increases less rapidly as the pressure becomes higher, but also because the value of α increases more prominently as θ gets closer to unity, finally approaching an apparent saturation.

In the Langmuir adsorption isotherm (Eq. 3) the saturation corresponds always to the full coverage, or $\theta=1$, for all the curves at different temperatures. However, in the adsorption isotherms given in Eq. 6 or Eq. 7, the desorption is accelerated by the presence of ambient gas molecules, in particular, under higher pressures and coverages, such that the apparent saturation appears at some coverage which depends upon the temperature. Such are the characteristic features of the adsorption isotherm (6) or (7) which are different from those of the Langmuir adsorption isotherm (3).

(c) The value of k_+/k_- decreases, while B increases, at higher temperatures: Consequently, the apparent saturation value becomes smaller. At lower temperatures, on the contrary, k_+/k_-, is bigger, and B is smaller, and the apparent saturation value becomes higher.

(d) As to the rate to approach the apparent saturation point with the pressure increase, at higher temperatures θ approaches more slowly than at lower temperatures, since B is comparatively bigger and θ, smaller at higher temperatures.

These characteristic features derived from Eq. 6 or Eq. 7 are in complete agreement with the adsorption isotherms obtained experimentally, which is given, for example, in the figure.[6)]

Case 3. At Extremely High Pressures. Under extremely high pressures θ increases and BP^n and α are both considerably bigger than unity and the adsorption isotherm (7) becomes as follows:

$$1-\theta = K(k_-/k_+)B\theta^2/P^{1-n}, \tag{9}$$

which indicates that under extremely high pressures the coverage approaches unity, that is, the full coverage.

The chemisorption of carbon monoxide is frequently used to estimate the surface area of transition metals highly dispersed on high surface area supports. It is easily concluded that for such purposes, the pressure of carbon monoxide should not be in the range which corresponds to the Case 2, but to the Case 3, otherwise the saturation point obtained does not correspond to the full coverage. In most cases, however, the pressure of carbon monoxide is high enough to get to the Case 3.

In conclusion, Eq. 6 or Eq. 7 is the adsorption isotherm derived directly, for the first time, from the kinetics of adsorption-assisted desorption obtained experimentally. The isotherm thus obtained, taking the adsorption-assisted desorption into consideration is in reasonable agreement with the adsorption isotherm obtained experimentally.

References

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