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NOTES

Application of Metallurgical Theory in the Estimate of Optimal Metal-Particle Size in Supported Catalysts

The purpose of this paper is to examine the general tendency of the variation in catalytic activity with metal-particle size in a supported catalyst, using the theoretical equation and the metallurgical, physicochemical constants. The relative concentration of point defects has been calculated. It has been found that the curve of concentration vs particle diameter (d) for each metal has a maximum in the diameter region of 10 to 200 Å, and that this region agrees with that of the optimal diameter in most of the supported metal catalysts.

Fujita (*1*) gave the following equation:

$$n_r/n_b = N^{-1/6} \exp(E_f/2kT), \qquad (1)$$

where n_r is the number of point defects in a fine metal particle with a radius of r; n_b is that of the bulk crystal; E_f is the energy required for the formation of a vacancy, and k is the Boltzman constant. N is the total number of lattice sites. Then

$$N = (4/3)\pi r^3/V, \qquad (2)$$

where V is the atomic volume. Equation (1) is derived from Eqs. (3), (4) and (5):

$$n_b = N \exp(-E_f/kT), \qquad (3)$$

$$n_r = (NN')^{1/2} \exp(-E_f/2kT), \qquad (4)$$

$$N' = \alpha N^{2/3}, \qquad (5)$$

where N' is the number of step kinks which are produced on the surface corresponding to the formation of point defects; α is a constant which depends on the shape of the crystal. Equations (3) and (4) are derived from Eqs. (6) and (7), respectively, with Eq. (8):

$$\Delta S = k\log[(N + n_b)!/(N!n_b!)], \qquad (6)$$

$$\Delta S = k\log[N!N'!/(N - n_r)!(N' - n_r)!n_r!n_r!], \qquad (7)$$

$$\Delta F = nE_f - T\Delta S \cdots (n = n_b \text{ or } n_r), \qquad (8)$$

under the following conditions: $N! = N^N \times \exp(-N)$ (Stirling's formula) $n_b \ll N$, $n_r \ll N$, N', $[\partial(\Delta F)/\partial n]_T = 0$ at thermal equilibrium. The 2/3 in Eq. (5) arises from the fact that N is proportional to the volume of a particle and N' is proportional to its surface area. Here, it is assumed that α is 1. Since E_f and V are metallurgical and physicochemical constants, $\log(n_r/n_b)$ must be linear with r. However, Fujita also introduced a correction for the surface tension, γ, of the small particle, yielding Eq. (9).

$$n_r/n_b = N^{-1/6} \exp[(E_f - 2V\gamma/r)/2kT]. \qquad (9)$$

Equation (9) is derived as follows; when the atomic vacancies (point defects), the number of which are n, are pulled out from the inside of a small sphere with a radius of r and put on its surface, the increase in the volume is $4\pi r^2\delta r = nV$ and that of the surface area is $\delta s = 8\pi r\delta r$, where δr is the increment of r; the increase in the surface energy is $\gamma\delta s = 2V\gamma n/r$. Consequently, the increase in free energy for the sphere is:

$$\Delta F = nE_f + 2nV\gamma/r - T\Delta S. \quad (10)$$

By using Eq. (10) instead of Eq. (8), Eq. (9) is derived. Since γ is also a physicochemical constant, introducing this dependence on $(1/r)$ in the exponential function leads to a maximum in a plot of $\log(n_r/n_b)$ vs d, as Fujita showed. According to Fujita's report, the value of n_r/n_b has no absolute meaning, because there is a statistical uncertainty about N'.

Here, we would like to propose another equation; one which represents the effect of the catalyst-support and which is fully consistent with Eq. (9) also. When the interaction between the catalyst-support and the metal particle is taken into account, the surface tension, γ, decreases as a result of the interfacial tension, which acts in the opposite direction, and the energy for formation of a point defect, E_f, also changes. The decrease in γ causes the maximum in $\log(n_r/n_b)$ to occur in a smaller radius, but little is known concerning the experimental data of the interfacial tension between metal and inorganic compounds. Therefore, the intact value of γ for an unsupported metal particle was used for convenience; a correction was made on only E_f.

Here, the binding energy, E_o, between the metal atom and the oxygen atom on the surface of catalyst-supports was adopted in order to correct E_f. Since the fine metal particle is stabilized by the existence of a support, it seems natural that E_f increases upon the participation of E_o. We assumed the corrected E_f (E_f') as follows, using a parameter f:

$$E_f' = E_f + E_o f N_o/N, \quad (11)$$

where N_o is the number of surface atoms and where f is the proportion of N_o which exists at the interface between the metal and the catalyst-supports. From this definition:

$$N_o = 4\pi r^2\beta/V, \quad (12)$$

where β is the interatomic distance of the metal. From Eqs. (2), (11) and (12), Eq. (13) is derived:

$$E_f' = E_f + 3fE_o(\beta/r). \quad (13)$$

Instead of E_f in Eq. (9), E_f' is used; then,

$$n_r/n_b = N^{-1/6} \times \exp[(E_f + 3E_o f\beta/r - 2V\gamma/r)/2kT]. \quad (14)$$

When the parameter, f, is 0, Eq. (14) is equal to Eq. (9). As a first approximation, E_o was calculated tentatively from the heat of formation of metal oxide and the heat of dissociation of the oxygen molecule according to Pauling's method. The values of E_f, β, V, and γ were cited from various handbooks and the literature.

The plot of $\log(n_r/n_b)$ vs $\log d$ from Eq. (1) represents a straight line, while those from Eq. (14) for various choices of the parameter, f, represent curves. The results are shown in Fig. 1 in the cases of Ni, Pd, and Pt. One should call attention to the position of the maximum on the abscissa

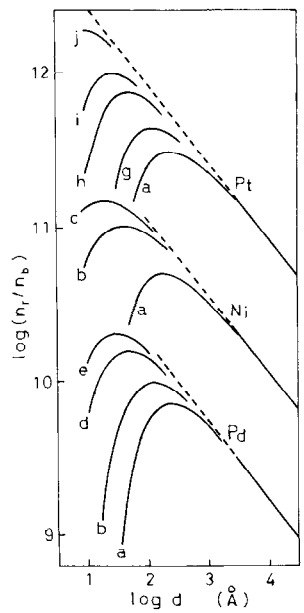

FIG. 1. The log (n_r/n_b) vs log d. The values of f: (a) 0; (b) 0.05; (c) 0.056; (d) 0.083; (e) 0.091; (g) 0.10; (h) 0.167; (i) 0.182; (j) 0.20; other constants for each metal are shown in Table 1.

TABLE 1
THE METALLURGICAL, PHYSICOCHEMICAL CONSTANTS AND THE OPTIMAL DIAMETERS WHICH WERE CALCULATED

metal	E_f (eV/atom)	E_0	γ^a (dyn/cm)	$V^b \times 10^{23}$ (cm³/atom)	β^c (Å)	d (Å)	f
Ni	1.4	5.10	1735	1.102	2.49	20	0.056
Pd	1.3	3.45	1600	1.470	2.75	50	0.083
Pt	1.5	1.92	1740	1.515	2.78	20	0.18
Ru	1.86[d]	3.69	2250	1.362	2.67	20	0.10
Ag	1.09	—	940	1.71	—	100	0

[a] The values in the vicinity of melting point cited from "Gmelins Handbuch."
[b] The values in the vicinity of room temperature.
[c] The values obtained from atomic radius in crystal.
[d] The value estimated from the heat of sublimation 156 kcal/mol.

and the decrease in n_r/n_b in the region of smaller d values. The calculated particle diameter, d, at which the n_r/n_b has a maximum, and the experimental values of the optimal particle size for activity in the various reactions, are summarized in Tables 1 and 2, respectively. The optimal diameter, d, which takes a maximum activity was selected from among several data which had been measured by means of H_2 adsorption, CO adsorption, or an electron microscope. Here, of course, the mean particle diameter is adopted.

The values calculated for each metal by using physicochemical and metallurgical constants agreed well with the experimental data. The n_r/n_b corresponds to the step kinks, and hence these step kinks which consist of low coordinate atoms, may be active sites for catalytic reactions. In the region of diameters smaller than 10 Å, metal particles will be strongly influenced by catalyst-supports and will begin to lose their metallic character, and then V, β, γ, etc., will probably take different values from those which

TABLE 2
THE OPTIMAL METAL-PARTICLE SIZE OF THE SUPPORTED CATALYSTS FOR VARIOUS REACTIONS

Catalyst	Reaction	Temp (°C)	Measured activity	Optimal d (Å)	Ref.
Ni-silica	Benzene hydrogenation	25	Entropy factor (μmol/min m²)	12	(2)
Pd-charcoal	*cis*-1.4-dimethylcyclohexane epimerization	73	Entropy factor (mol/min cm²)	45	(3)
Pt-alumina	Benzene hydrogenation	50	Reaction rate (mg-mol/g-atom)	14[a]	(4)
Ru-silica	Cyclohexene formation in cyclohexane dehydrogenation	500	Rate constant (mol/hr mg-atom)	24[b]	(5)
Ag-silica -alumina	Ethylene oxide formation in ethylene oxidation	200 190	Reaction rate (mol/hr g-cat)	50 150	(6)

[a] The value was estimated from the H_2 adsorption data, by using Gruber's report (7).
[b] The value was estimated from the CO adsorption data (8) using the model of crystal by reference to the studies of Hardeveld and Hartog (9).

have been described in handbooks. This range is not the subject of the present study. Moreover, when the variation in these constants, V, β, γ, etc., with the radius is taken into account, their effects may be very complicated; at any rate, no appropriate function of these parameters has been found. Therefore, these parameters were used as constants in the present work.

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M. KOBAYASHI
T. SHIRASAKI

Tokyo Institute of Technology
Research Laboratory of Resources Utilization
O-okayama, Meguro-ku, Tokyo 152 Japan
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