JOURNAL OF CATALYSIS 23, 119-123 (1971)

The Effect of Crystallite Size Distribution on the Specific Activity of Supported Catalysts

DAN LUSS

Department of Chemical Engineering, University of Houston, Houston, Texas 77004

Received February 18, 1971

When the size of supported metal crystallites is dispersed about its average value the observed (average) specific activity depends on the shape of the size distribution. It is shown that information about the standard deviation of the size distribution enables an estimate of the difference between the observed specific activity and that of crystallites of the average size. A procedure is developed for determining the exact specific activity-size dependence from information about the crystallite size distribution and the corresponding average specific activity.

NOMENCLATURE

a_n	coefficient of ψ defined by Eq. (22)
C	factor defined by Eq. (19)
d	dispersion of crystallites $\sigma^2/\langle z\rangle$
$f(r)$	crystallite size density function
M_n	n-th moment defined by Eq. (16)
$P(r_i)$	fraction of surface occupied by particles such that $r_{i-1} < r < r_i$
r	dimension of crystallites
z	$r - \delta$
Γ	gamma function
δ	size of metallic atom
σ	standard deviation
ψ	specific activity
$\psi_a\langle r\rangle$	approximation to $\psi\langle r\rangle$ defined by Eq. (18)
$\langle\ \rangle$	average value

INTRODUCTION

Several techniques are now available for measuring the average size of supported metallic crystallites. These measurements have been used for correlating the specific activity (number of molecules converted per unit time per surface atom) of various reactions with the average crystallite size.

Boudart (*4*) classified catalytic reactions into two groups: facile reactions, whose specific activity is insensitive to variations in particle size; and demanding reactions, whose specific activity depends on the particle size. Bond (*1*) described the following four different types of functional dependence of the specific activity on the crystallite size:

i. Facile reactions for which the specific activity is independent of the particle size r such as found by Boreskov and Chesalova (*2*) and Boreskov *et al.* (*3*) for oxidation of sulfur dioxide or hydrogen on platinum catalysts and by Boudart and co-workers (*4*) for cyclopropane hydrogenation over platinum catalysts.

ii. Reactions with positive intrinsic factor (i.f.) for which the specific activity decreases with increasing r such as observed by Selwood and co-workers (*8*) in the hydrogenation of benzene by a nickel on silica catalyst and by Sinfelt and co-workers (*5*) for ethane hydrogenolysis by a nickel on silica–alumina catalyst.

iii. Reactions with negative intrinsic factor for which the specific activity increases with r such as observed by Hill and Selwood (*7*) for benzene hydrogenation by a nickel on alumina catalyst.

iv. Reactions for which the specific activity obtains a maximal value for some intermediate size.

The average crystallite size is a single statistic of the size distribution and many different distributions have the same average. Hence, when the reaction is demanding and the specific activity is not a linear function of r, two distributions with the same average size $\langle r \rangle$ may have different specific activities. Moreover, the average specific activity of all the crystallites $\langle \psi(r) \rangle$—which is an observed value—differs in general from $\psi\langle r \rangle$ (the specific activity of crystallites of dimension $\langle r \rangle$). Since $\langle r \rangle$ can be determined directly by X-ray diffraction line broadening measurments as well as by magnetization techniques for ferromagnetic metals,* various investigators correlated the two directly measurable quantities $\langle \psi(r) \rangle$ with $\langle r \rangle$, even though, to obtain a unique relation, one should correlate $\psi\langle r \rangle$ with $\langle r \rangle$.

In this work, we investigate the magnitude of the deviation between $\langle \psi(r) \rangle$ and $\psi\langle r \rangle$ due to the dispersion of the crystallites about the average size and relate this difference to the standard deviation of the particle size distribution. A procedure is outlined for the exact determination of $\psi(r)$ for the case that the particle size distribution is known.

Difference Between $\langle \psi(r) \rangle$ and $\psi\langle r \rangle$

We define $f(r)dr$ as the fraction of the surface area for which the crystallites size is between r and $r + dr$ and the specific activity is $\psi(r)$. Thus, the average activity is

$$\langle \psi(r) \rangle = \int_0^\infty f(r)\psi(r)\, dr = \int_0^\infty f(z)\psi(z)\, dz, \tag{1}$$

where

$$z = r - \delta, \tag{2}$$

and δ is the diameter of a metallic atom. The dispersion of the size distribution is defined as

$$d = \frac{\sigma^2}{\langle z \rangle}, \tag{3}$$

where

$$\sigma^2 = \langle r^2 \rangle - \langle r \rangle^2 = \int_0^\infty (r - \langle r \rangle)^2 f(r)\, dr. \tag{4}$$

We will first make some qualitative observations for the rather common case that $\psi(r)$ is a monotonic function with no inflection points. Here we can use the well-established properties of convex function [Ref. (*6*), p. 150] to state that if $\psi(r)$ is convex (i.e., $\psi''(r) \geq 0$), as is likely to occur for reactions with positive i.f., then

$$\langle \psi(r) \rangle \geq \psi\langle r \rangle. \tag{5}$$

Similarly, if $\psi(r)$ in concave ($\psi''(r) \leq 0$), as is likely to occur for reactions with negative i.f., then

$$\langle \psi(r) \rangle \leq \psi\langle r \rangle. \tag{6}$$

The equality sign in Eqs. (5–6) holds only if either $\psi(r)$ is a linear function of r or that all the crystallites have the same size. Moreover, if we add the assumption that $\psi(r)$ approaches asymptotically a constant value, say ψ_∞, then it follows from Eqs. (5–6) that

$$|\langle \psi(r) \rangle - \psi_\infty| \geq |\psi\langle r \rangle - \psi_\infty|. \tag{7}$$

Thus, in both these cases the dispersion of the crystallite sizes tends to increase the deviation between the observed specific activity and ψ_∞.

To clarify this point a little further, consider an example for which the crystallite size density function can be described by the gamma density function,

$$f(z) = \frac{1}{z}\left(\frac{z}{\langle z \rangle d}\right)^{1/d} \times \exp\left(-\frac{z}{\langle z \rangle d}\right) \Big/ \Gamma\left(\frac{1}{d}\right) \quad z \geq 0. \tag{8}$$

Thus, assuming a positive convex i.f. such as

$$\psi(z) = 1 + ae^{-cz}, \tag{9}$$

we obtain that

$$\langle \psi(z) \rangle = 1 + a(1 + c\langle z \rangle d)^{-1/d}, \tag{10}$$

which is always larger than

$$\psi\langle z \rangle = 1 + ae^{-c\langle z \rangle}.$$

Similarly, assuming a negative concave i.f. such as

$$\psi(z) = 1 - we^{-cz} \tag{11}$$

we obtain that

$$\langle \psi(z) \rangle = 1 - w(1 + c\langle z \rangle d)^{1/d}, \tag{12}$$

---

* Various methods of determining average particle size yield averages which often are of different types.

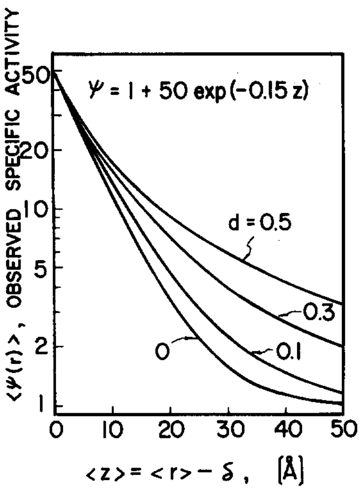

FIG. 1. The effect of the dispersion on the observed specific activity for a reaction with a positive intrinsic factor when the crystallite size is described by a gamma density function [Eq. (8)].

which is always smaller than

$$\psi\langle z\rangle = 1 - we^{-c\langle z\rangle}. \tag{13}$$

Figures 1 and 2 describe two specific examples. As shown, an increase in the dispersion d tends to increase the deviation between $\langle\psi(r)\rangle$—the observed specific activity and $\psi\langle r\rangle$. In both cases the specific activity is very close to its asymptotic value of unity for crystallites of dimension $z = 50$ Å. However, the observed specific activity may deviate by a large amount from unity for distributions with the same average crystallite size.

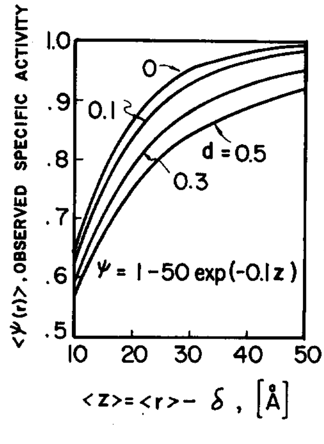

FIG. 2. The effect of the dispersion on the observed specific activity for a reaction with a negative intrinsic factor when the crystallite size is described by a gamma density function [Eq. (8)].

In order to obtain a quantitative estimate about the deviation between $\langle\psi(r)\rangle$ and $\psi\langle r\rangle$ we will use the Taylor series expansion

$$\psi(r) = \psi\langle r\rangle + \sum_{n=1}^{\infty} \frac{\psi^{(n)}\langle r\rangle}{n!}(r - \langle r\rangle)^n. \tag{14}$$

Averaging Eq. (14) yields

$$\langle\psi(r)\rangle - \psi\langle r\rangle = \sum_{n=1}^{\infty} \frac{\psi^{(n)}\langle r\rangle}{n!} M_n(\langle r\rangle), \tag{15}$$

where

$$M_n(\langle r\rangle) = \int_0^{\infty} (r - \langle r\rangle)^n f(r)\, dr. \tag{16}$$

Hence, if $\psi(r)$ is a linear function or when all the particles have the same size, the right side of Eq. (15) vanishes. If $\psi(r)$ is sufficiently smooth around its average, we obtain, retaining the first term in the summation

$$\langle\psi(r)\rangle - \psi\langle r\rangle \simeq \psi''\langle r\rangle\sigma^2/2. \tag{17}$$

Thus, the magnitude of the difference between $\langle\psi(r)\rangle$ and $\psi\langle r\rangle$ is a linear function of the standard deviation of the crystallite size distribution. The exact value of $\psi''\langle r\rangle$ cannot be determined from the measured values of $\langle\psi(r)\rangle$. However, as a first order approximation its value can be replaced by $\langle\psi(r)\rangle''$—the second derivative of the observed specific activity to yield

$$\psi\langle r\rangle \simeq \langle\psi(r)\rangle - \langle\psi(r)\rangle''\sigma^2/2 = \psi_a\langle r\rangle. \tag{18}$$

In order to check the accuracy of the above approximation the value of the correction ratio,

$$C = \frac{\psi_a\langle r\rangle - \psi\langle r\rangle}{\langle\psi(r)\rangle - \psi\langle r\rangle}, \tag{19}$$

was computed for the example described in Fig. 1, and the results are shown in Fig. 3. As shown, the absolute value of C is always smaller than one indicating that $\psi_a\langle r\rangle$ is a much better approximation to $\psi\langle r\rangle$ than is $\langle\psi(r)\rangle$.

Now we will consider the case that two catalysts have different size density func-

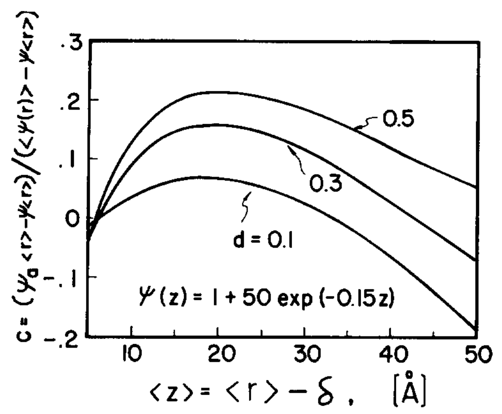

FIG. 3. The effect of the average crystallite size and the dispersion of C for the case shown in Fig. 1.

tions, say $f_1(r)$ and $f_2(r)$, both of which have the same average and second moment, and examine the magnitude of the difference in the corresponding specific activity. Defining

$$\langle\psi_1(r)\rangle = \int_0^\infty f_1(r)\psi(r)\,dr, \tag{20}$$

$$\langle\psi_2(r)\rangle = \int_0^\infty f_2(r)\psi(r)\,dr, \tag{21}$$

$$\psi(r) = \sum_{n=0}^{N} a_n r^n, \tag{22}$$

we obtain

$$\langle\psi_1(r)\rangle - \langle\psi_2(r)\rangle = \sum_{n=3}^{N} a_n \Delta M_n, \tag{23}$$

where

$$\Delta M_n = \int_0^\infty r^n(f_1(r) - f_2(r))\,dr. \tag{24}$$

Hence, if $\psi(r)$ can be described by a polynomial of order two or less, both catalysts will have an identical specific activity. However, when $\psi(r)$ has to be described by a polynomial of degree $N \geq 3$ the two catalysts may not have the same specific activity, the difference depending on the moments of the two density functions and the magnitude of a_n $(3 \leq n \leq N)$.

Exact Determination of $\psi(r)$

We will now describe a technique for extracting the correct value of $\psi(r)$ from experimental data when the complete size distribution is known. [This information may be obtained from electron (scan) micrographs.] This determination of $\psi(r)$ requires solving the integral equation,

$$\langle\psi(r)\rangle = \int_0^\infty f(r)\psi(r)\,dr. \tag{25}$$

While it may be tempting to solve for $\psi(r)$ from the results of a single experiment, this procedure usually leads to large errors since integral equations of the above form are rather insensitive to the correct form of $\psi(r)$ and moreover the value of $f(r)$ and $\psi(r)$ can be determined only within a certain experimental accuracy. Thus, it would be necessary to conduct several experiments for catalysts with different crystallite size distributions and the resulting set of integral equations should be solved simultaneously for $\psi(r)$.

In practice, $f(r)$ is determined by counting the number of crystallites within a prescribed size range. We will consider the case that the size distribution is composed of N intervals and define by $P(r_i)$ the fraction of the metallic surface area occupied by particles for which $r_{i-1} \leq r \leq r_i$. Here Eq. (25) reduces to

$$\sum_{i=1}^{N} P(r_i)\langle\psi(r_i)\rangle = \langle\psi(r)\rangle, \tag{26}$$

where $\langle\psi(r_i)\rangle$ is the average specific activity of all the crystallites in the i-th size interval. In order to determine each of the N values of $\langle\psi(r_i)\rangle$ we need to conduct at least N experiments with catalysts of different size distributions. Writing down Eq. (26) for each one of the experiments, a set of linear equations is obtained, which can be solved for the N values of $\langle\psi(r_i)\rangle$. It should be noted that this procedure assumes that the value of $\langle\psi(r_i)\rangle$ is invariant in all the experiments. This should be a rather good approximation when the size intervals are small. The validity of the assumption can be tested by performing additional experiments and comparing the observed and predicted value of $\langle\psi(r)\rangle$.

CONCLUSIONS

This work indicates that the experimentally observed specific activity may differ from $\psi(r)$—the deviation depending on the crystallite size distribution and on the form of $\psi(r)$. To obtain the exact dependence of $\psi(r)$, it is necessary to measure, in addition to the average specific activity, the complete size distribution. Lack of information about this size distribution will introduce a certain uncertainty into the correlation—the magnitude of which can be estimated using the equations presented above. This work points out the desirability of determining, in addition to the average size, at least the standard deviation of the crystallite size distribution when an accurate correlation is sought, since this information enables an estimate of the effect of the dispersion on the observed specific activity.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. T. Richardson for helpful discussions and to Mr. S. Golikeri for help in the numerical computations.

REFERENCES

1. BOND, G. C., *Int. Congr. Catal., 4th, Moscow, 1968*, Prep. No. 67.
2. BORESKOV, G. K., AND CHESALOVA, V. S., *Zh. Fiz. Khim.* **30**, 2560 (1956).
3. BORESKOV, G. K., SLINKO, M. G., AND CHESALOVA, V. S., *Zh. Fiz. Khim.* **30**, 2787 (1956).
4. BOUDART, M., ALDAG, A., BENSON, J. E., DOUGHERTY, N. A., AND HARKINS, C. G., *J. Catal.* **6**, 92 (1966).
5. CARTER, J. L., CUSUMANO, J. A., AND SINFELT, J. H., *J. Phys. Chem.* **70**, 2257 (1966).
6. HARDY, G. H., LITTLEWOOD, J. E., AND POLYA, G., "Inequalities." Cambridge Univ. Press, London/New York, 1934.
7. HILL, F. N., AND SELWOOD, P. W., *J. Amer. Chem. Soc.* **71**, 2522 (1949).
8. SELWOOD, P. W., ADLER, S., AND PHILLIPS, T. R., *J. Amer. Chem. Soc.* **77**, 1462 (1955).