JOURNAL OF CATALYSIS 76, 294–299 (1982)

A Mathematical Model for Characterization of a Catalyst Having a Skewed Unimodal Acid Strength Distribution

KERRY C. PRATT

CSIRO, Division of Materials Science, Catalysis and Surface Science Laboratory, University of Melbourne, Parkville, Victoria 3052, Australia

Received June 2, 1981; revised December 29, 1981

The distribution of acid strength on a catalyst was described in terms of a log normal distribution. Equations are developed which allow the standard deviation and geometric mean heat of adsorption to be calculated from the raw data of a calorimetric titration. Catalysts can then be directly compared in terms of these two parameters which completely specify the distribution. This work may find application in quality control or in catalyst specification. Other useful calculations can be made by an extension of the theory, and it is suggested that the use of the log normal distribution to describe the site energy distribution could overcome some of the conceptual difficulties involved in earlier attempts to derive adsorption isotherms on the basis of a specified site energy distribution.

INTRODUCTION

Solid acids are used in a wide variety of catalytic processes including dehydration, isomerization, reforming, polymerization, and catalytic cracking (*1*). The most common catalysts or supports of this nature are alumina, silica–alumina, and synthetic zeolites. In the case of catalytic cracking, the zeolite is usually contained within a silica-alumina matrix. The relationship between activity and total acidity of such catalysts is long established (e.g., (*2*)).

The acid characteristics of catalysts are an important property, and various techniques have been devised for their measurement (*3*, *4*). The simplest technique for measuring total acidity is to follow the weight change consequent upon the adsorption of a base such as ammonia or pyridine. The acid sites on catalysts are not homogeneous, however, and a spread of acid strengths among the various sites exists. In many cases, a particular reaction only occurs on acid sites falling within a particular range of acid strengths. It is therefore often necessary to determine the distribution of acid strengths, in addition to the total acidity. This is commonly achieved by titration of the catalyst acidity by an organic base in a nonaqueous medium. The endpoint is indicated by an adsorbed indicator. By repeating the titration with various indicators having differing p*K*a values, it is possible to establish the amount of acidity within each range (*3*–*5*). This method is tedious and suffers from the disadvantage that the color change of the indicator frequently occurs over a period of 2 or 3 days. A more satisfactory method is to carry out the titration in a calorimeter (*5*, *6*). Measurement of the temperature rise during the course of the titration allows the calculation of the heat of neutralization of the acid sites as a function of the amount of base added. The use of the heat of adsorption (neutralization) of a base as a measure of acid strength seems more readily identifiable with reaction parameters than do other measures of acid strength. Differentiation of the temperature rise data (either graphically or numerically) gives a cumulative distribution of acid strength versus coverage, a second differentiation provides the distribution function of the acid strengths. However, the graphical or numerical differentiation is tedious and notoriously inaccurate. This paper describes a simple method whereby the acid-

0021-9517/82/080294-06$02.00/0

ity distribution function can be obtained from the temperature rise versus titer data of the calorimetric titration, by assuming a form of the acid strength distribution function.

THE DISTRIBUTION FUNCTION MODEL

The acidity distribution of many catalysts is effectively a unimodal type, skewed toward the weak acid strengths. A similar distribution occurs in mixtures of solid particles, where the particle size distribution is commonly skewed toward the smaller particle sizes. Such a distribution is described by the log normal distribution function (*7*). We assume that a function of this form can describe a skewed unimodal acidity distribution.

For our purposes we can write the distribution function in terms of the acid strength *H*, here taken as the heat of adsorption (neutralization) of a base, i.e.,

$$G(H) = \frac{1}{\sigma H(2\pi)^{1/2}} \cdot e^{-(\ln H - \ln H_{\mathrm{gm}})^2/2\sigma^2}, \quad (1)$$

where σ is the standard deviation of the distribution, and H_{gm} is the geometric mean acid strength. The specification of σ and H_{gm} completely defines the acid strength distribution.

It is convenient to write

$$\ln H/H_{\mathrm{gm}} = x\sigma \quad (2)$$

or

$$H = H_{\mathrm{gm}}\, e^{x\sigma}. \quad (3)$$

Thus

$$G(H) = \frac{1}{\sigma H_{\mathrm{gm}}\,(2\pi)^{1/2}} \cdot e^{(-x^2/2 - x\sigma)} \quad (4)$$

and so

$$\phi = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{x} e^{-x^2/2} dx, \quad (5)$$

where ϕ is the fraction of acid sites having an acid strength less than H ($=H_{\mathrm{gm}}e^{x\sigma}$), and $G(H) = d\phi/\mathrm{d}H$. (Note that the lower limit of integration $x = -\infty$ corresponds to $H = 0$.)

Integration of Eq. (5) yields

$$\phi_x = \frac{1}{2}\left[1 + \mathrm{erf}\,\frac{x}{2^{1/2}}\right]. \quad (6)$$

We note, however, that during the course of the titration the strongest acid sites are neutralized first, and hence

$$\theta_x = 1 - \phi_x, \quad (7)$$

where θ_x is the fraction of acid sites titrated (referred to below as coverage). Therefore

$$\theta_x = \frac{1}{2}\left[1 - \mathrm{erf}\,\frac{x}{2^{1/2}}\right]. \quad (8)$$

Equation (8) represents a relation between coverage of acid sites and acid strength.

We now need to derive a relationship between the experimental temperature rise and the titer of base added.

The heat of neutralization at a particular coverage is obtained from the temperature rise versus titer curve according to

$$H = \frac{1}{K}\frac{d\Delta T}{d\theta}, \quad (9)$$

or

$$d\theta = \frac{1}{KH} d\Delta T, \quad (10)$$

where *K* is a constant which, as we shall see, includes the thermal equivalent of the calorimeter and contents, the molarity of the titrant, and the final titer, when the analysis refers to a liquid phase titration.

Using Eqs. (1) and (7),

$$\frac{1}{-KH} d\Delta T = \frac{1}{\sigma H(2\pi)^{1/2}} \cdot e^{-(\ln H - \ln H_{\mathrm{gm}})^2/2\sigma^2} dH \quad (11)$$

and so substituting as before

$$-d\Delta T = \frac{K\,H_{\mathrm{gm}}}{(2\pi)^{1/2}}\, e^{(x^2/2 + x\sigma)} dx. \quad (12)$$

Inserting the appropriate limits after some manipulation, we find

$$-\int_0^{\Delta T_x} d\Delta T = \frac{K\,H_{\mathrm{gm}}}{(2\pi)^{1/2}} \cdot e^{\sigma 2/2} \int_\infty^x e^{(x/2^{1/2}-\sigma/2^{1/2})^2}\,dx. \quad (13)$$

Integration of Eq. (13) yields

$$\Delta T_x = \frac{K \cdot H_{\mathrm{gm}}}{2} \cdot e^{\sigma^2/2} \left[1 - \mathrm{erf}\left(\frac{x-\sigma}{2^{1/2}}\right)\right]. \quad (14)$$

Now when $x = -\infty$ ($H = 0$), $\Delta T_x = \Delta T_{\max}$, and hence

$$\Delta T_{\max} = K \cdot H_{\mathrm{gm}}\, e^{\sigma^2/2}. \quad (15)$$

And again, if $x = \sigma$ then

$$\Delta T_{x=\sigma} = \frac{K \cdot H_{\mathrm{gm}}}{2} \cdot e^{\sigma^2/2}, \quad (16)$$

that is,

$$\Delta T_{x=\sigma} = (1/2)\Delta T_{\max}, \quad (17)$$

Hence, from Eq. (8),

$$\theta_{(1/2)\Delta T_{\max}} = (1/2)[1 - \mathrm{erf}^{\sigma/2^{1/2}}]. \quad (18)$$

Hence determination of the ultimate temperature increase, and the coverage of titrant at half the maximum temperature increase allows the calculation of H_{gm} and σ via Eqs. (15) and (18). Therefore the acidity distribution function can be entirely specified.

We now need to evaluate the constant K. The heat Δh released when an amount of titrant Δt is added is given by

$$\Delta h = \Delta(\Delta T) \cdot M, \quad (19)$$

where M is the thermal equivalent of the calorimeter and contents.

The number of moles, n, added is

$$n = \frac{\Delta t \cdot m}{1000}, \quad (20)$$

where m is the molarity of base.

Therefore the differential heat of adsorption is

$$H = \frac{M}{m} \cdot \frac{\Delta(\Delta T)}{\Delta t}. \quad (21)$$

In the limit

$$H = \frac{M}{mQ} \cdot \frac{d\Delta T}{d\theta} \quad (22)$$

and hence

$$K = mQ/M. \quad (23)$$

Therefore Eq. (15) becomes

$$\Delta T_{\max} = \frac{mQ}{M} \cdot H_{\mathrm{gm}} \cdot e^{\sigma^2/2}. \quad (24)$$

The use of the simple equations developed above is best illustrated by an experimental example.

EXPERIMENTAL

The basic technique of the calorimetric titration is outlined by Tanabe (*5*). Although the example below is based on a titration carried out in a nonaqueous liquid phase, the theory developed above applies equally well to vapor-phase titrations, with modification of the constant K. A quantity of a zeolite-containing fluid cracking catalyst was calcined for 4 h at 500°C, and cooled in a desiccator. The catalyst (2.499 g) was added to 110 ml of dry benzene in a stirred Dewar flask. The temperature was measured with a platinum resistance thermometer. The thermal equivalent of the calorimeter and contents was measured electrically using a heated filament as 56.73 cal/°C. The catalyst was titrated with a 1 M solution of *n*-butylamine in dry benzene, using a microburette to which was attached a hypodermic needle. After allowing for viscous dissipation and cooling corrections, the ΔT versus titer curve was as shown in Fig. 1. From Fig. 1, the maximum temperature rise is 0.92°C, corresponding to a titer of 4.0 ml. Hence from Fig. 1

$$\theta_{1/2\Delta T_{\max}} = \frac{1.0}{4.0} = 0.25.$$

Values of the Error Function are available from standard tables (e.g., (*8*)). Using Eq. (18), we find that $\sigma = 0.672$. Substituting in

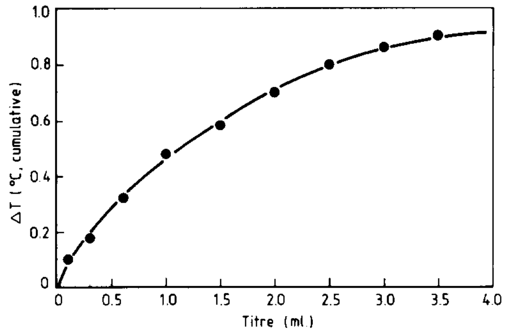

FIG. 1. Raw data from the calorimetric titration. The size of the data points indicates the maximum errors involved.

Eq. (24), we obtain H_{gm} from

$$0.92 = \frac{1 \times 4}{56.73} \cdot H_{gm} \cdot e^{0.226},$$

which gives $H_{gm} = 10.40$ Kcal/mole. Hence the acidity distribution of the catalyst is completely specified by a log normal distribution having a standard deviation of 0.672 and a geometric mean acid strength of 10.40 Kcal/mole of *n*-butylamine.

The smoothed cumulative distribution and the distribution function curves obtained by successive graphical differentiation of the data in Fig. 1 are shown in Fig. 2. A heat of adsorption versus coverage curve derived from Fig. 2 is given in Fig. 3. The similarity between the distribution function predicted using the derived parameters H_{gm} and σ in Eq. (1), and that derived from double differentiation of the raw data is good. Though it is necessary to emphasize again the inaccuracy of the latter procedure, which may produce errors estimated at around ±20%. Examination of Fig. 3 shows that the heat of adsorption at 50% coverage 12.5 Kcal/mole, is close to the value of 10.40 Kcal/mole obtained for H_{gm}. In fact this should be expected if the distribution of acid strengths is indeed approximated by a log normal distribution, since it is a property of the log normal distribution that the geometric mean is equal to the median, i.e., H_{gm} is simply the heat of adsorption at 50% coverage of base. It appears therefore that this particular catalyst is quite well described by a log normal distribution. In fact it might have been expected that zeolite contained in a silica–alumina matrix would have shown a bimodal distribution of acid strength. It is likely, however, that the acidity due to the silica–alumina would be of much lower strength than the zeolite, and that the titration technique employed here is not sufficiently sensitive to produce a bimodal plot.

The main use for the analysis described above would appear to be for cases where multiple tests are being made on the same catalyst type, e.g., in quality control work. Once it has been established that the acidity distribution of the particular catalyst can be satisfactorily described by a log normal distribution, then different samples of the same catalyst type can be directly compared or specified in terms of the two unique parameters, i.e., σ and H_{gm}. It would of course be possible to perform the differentiation of the data numerically using a computer. However, accuracy is still lost in this procedure, and no unique parameters for characterizing the distribution are obtained.

There are other useful calculations that can be made utilizing the theory and data obtained above. For example, suppose that for a given reaction, it was required to esti-

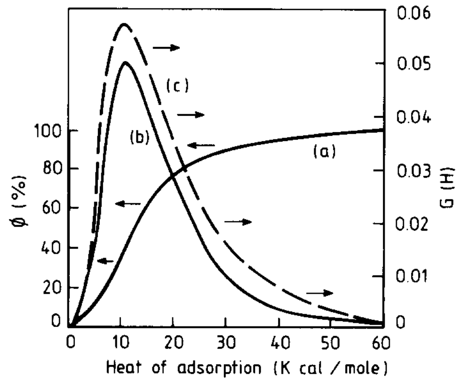

FIG. 2. Cumulative distribution of acid site strength (a), and acid strength distribution function as derived by differentiation (b), and by the prediction of Eq. 1 (c).

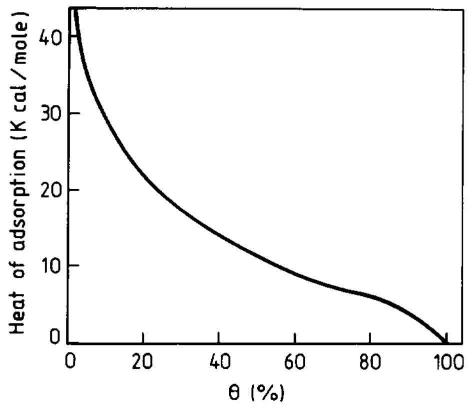

FIG. 3. Acid site strength (heat of adsorption) versus coverage of base.

mate the fraction of sites having acid strengths greater than a particular value, H_1, say.

This is just the coverage θ, at $H = H_1$, and can be obtained from Eq. (8) as

$$\theta_{>H_1} = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{\ln H_1/H_{\mathrm{gm}}}{\sigma 2^{1/2}}\right)\right]. \quad (25)$$

The fraction of sites having acid strengths lying between H_1 and H_2 ($H_1 < H_2$) is simply

$$\theta_{H_1H_2} = \frac{1}{2}\left[\mathrm{erf}\left(\frac{\ln H_2/H_{\mathrm{gm}}}{\sigma 2^{1/2}}\right) - \mathrm{erf}\left(\frac{\ln H_1/H_{\mathrm{gm}}}{\sigma 2^{1/2}}\right)\right]. \quad (26)$$

For example, what fractions of acid sites for the catalyst analyzed above have acid strengths greater than (i) 7 Kcal/mole, and (ii) 20 Kcal/mole? Use of Eq. (25) gives the results as 72.35 and 14.95%, respectively. The fraction of acid sites having strengths between 7 and 20 Kcal/mole is 57.4%.

By assuming a form of the distribution function for site energies, it is possible to derive adsorption isotherms for a catalyst. For example, Halsey and Taylor (9) assumed an exponential type of distribution, which when integrated between the limits for heat of adsorption of $-\infty$ to $+\infty$ gave a result equivalent to the Freundlich isotherm. This work has been criticized on the grounds that integration limits of $-\infty$ to $+\infty$ involve the untenable concept of negative heats of adsorption (*10*). The procedure was, however, necessary for mathematical expediency.

It is worth noting that in the distribution function employed in this work, integration of the variable x between the limits of $-\infty$ and $+\infty$ corresponds to values of H of 0 to $+\infty$, and hence overcomes the problem. Rudnitsky and Alexeyev (*11*) have also proposed an asymmetric distribution function, but that used in the present work seems simpler. It may be possible therefore to derive realistic adsorption isotherms for solids using the log normal distribution function to describe the site energy distribution.

CONCLUSIONS

By assuming that the distribution of acid strengths of a catalyst can be described by a log normal distribution, a simple mathematical procedure has been developed which allows the distribution to be completely specified using only the raw data of a calorimetric titration. This technique would be appropriate for catalysts whose characteristic distribution of acid strengths is of a skewed unimodal type.

Specification of two unique parameters of the distribution, the standard deviation and the geometric mean heat of adsorption (or the heat of adsorption at 50% coverage of base) is sufficient to completely define the distribution. This technique avoids the need to perform two consecutive graphical or numerical differentiations of the calorimetric data, and allows quantitative comparisons of catalysts in terms of the distribution parameters. This may find use in quality control applications, or in catalyst specification. The use of the technique was illustrated by an example, and it was shown that the fractions of the acid sites falling within given ranges of acid strength could be simply calculated by using extensions of the theory. To be really useful, this technique should be able to discriminate between catalysts whose activity–selectivity patterns display small but significant differences. It is hoped that future work may establish this. It was also suggested that the log normal distribution function may be a useful starting point for the derivation of adsorption isotherms.

APPENDIX: NOTATION

$G(H)$ = distribution function of acid site strengths.
H = heat of adsorption (neutralization) of acid sites, Kcal/mole of base.
H_{gm} = geometric mean value of heat of adsorption (= heat of adsorption at 50% coverage of base).
K = constant (Eq. (23)).
m = molarity of base titrant, mole/liter.
M = thermal equivalent of calorimeter and contents, cal/°C.
Q = final titer of base, ml.
Δt = incremental quantity of base added, ml.
ΔT = temperature rise of calorimeter and contents, °C.
x = variable defined by Eq. (2).

Greek letters

θ = fractional coverage of acid sites by base titrant.
σ = standard deviation of the distribution.
ϕ = fraction of acid sites, defined by Eq. (5).

REFERENCES

1. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.
2. Tamele, M. W., *Discuss. Faraday Soc.* **8,** 270 (1950).
3. Forni, L., *Catal. Rev. Sci. Eng.* **8,** 65 (1973).
4. Benesi, H. A., and Winquist, B. H. C., *Advan. Catal.* **27,** 97 (1978).
5. Tanabe, K., "Solid Acids and Bases: Their Catalytic Properties." Kodansha, Tokyo, 1970.
6. Gravelle, P. C., *Catal. Rev. Sci. Eng.* **16,** 37 (1977).
7. Allen, T., "Particle Size Measurement." Chapman & Hall, London, 1968.
8. Abramowitz, M., and Stegun, I. A., "Handbook of Mathematical Functions." Dover, New York, 1972.
9. Halsey, G. D., and Taylor, H. S., *J. Chem. Phys.* **15,** 624 (1947).
10. Young, D. M., and Crowell, A. D., "Physical Adsorption of Gases," p. 253. Butterworths, London, 1961.
11. Rudnitsky, L. A., and Alexyev, A. M., *J. Catal.* **37,** 232 (1975).