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Thermal analysis and self-similarity law in particle size distribution of powder samples.
Part 3

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Abstract

Based on the self-similarity law or the fractal nature in the particle size distribution of powder samples, the particle size determined by sieving is proposed as a fractal particle size which is scaled by the sieve mesh opening. A fractal specific surface area S_V is defined by a power law $S_V \propto x^{D-3}$, wherein x is the fractal particle size and D is a fractal dimension with $2 < D < 3$.

It has been shown through previous observations that the fractal nature of a powder sample can be described by thermal analysis. That is, a small portion taken from the whole sample yields TG and DTA curves quite similar to those obtained for the whole sample, provided that this sample portion maintains the fractal nature of the whole powder sample. The surface area fraction of such a sample portion is calculated by determining the fractal dimension of the particle surface, and the result is compared with the weight fraction thereof.

INTRODUCTION

In the previous papers of this series [1, 2], the authors showed that the particle size distribution of a mechanically ground powder sample is a fractal, and that the absolute size constant plays a role as the characteristic size of a powder. The result of thermal analysis for a powder sample is greatly influenced by the particle size distribution of the sample; more particularly, by whether the particle size distribution obeys a self-similarity law. With respect to two or more physicochemically equivalent powder samples, similar TG and DTA curves are obtained, at least in a

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gas-evolving decomposition reaction, if they have a self-similar particle size distribution. The absolute size constant defines the upper limit of the particle size range in which the self-similarity law is valid; hence this size is a "scale" which is valuable for defining the powder and is therefore useful in preparing a powder sample to obtain reproducible results by thermal analysis.

More specifically, the self-similarity in particle size distribution, which explains well the phenomenologically obtained Rosin–Rammler and Gaudin–Schuhmann distribution functions, can be derived theoretically by considering a stochastic process in the dynamics of grinding [1]. Furthermore, there is observed to be an upper critical size, i.e., the absolute size constant, as well as a lower critical size, i.e., ≈2–3 μm, to define the range in which the self-similarity law is valid. Based on the self-similarity or the fractal nature in particle size distribution of a powder sample, it was shown that a consistent thermoanalytical result can be obtained by taking a sample portion having a particle size distribution which inherits the fractal nature of the whole sample, and hence that this portion of the sample is useful for assuming the thermal behavior of the whole sample [1, 2].

The fact that the particle size distribution of an as-pulverized powder sample obeys a self-similarity law implicitly describes the comminution mechanism as also being fractal. This, although not positively realized by those in the field of powder technology, can be also found as a fact taken for granted if one refers to a common textbook (see, for example, refs. 3–5), since it is customary to employ a certain shape factor to derive a specific surface area from a measured particle size.

In this paper, a fractal specific surface area is derived and, as an example, the surface area of the characteristic portion of a dolomite powder which can yield a consistent TG or DTA curve is calculated.

SPECIFIC SURFACE AREA AND FRACTAL PARTICLE SIZE DISTRIBUTION

As mentioned in the introduction, the fractal nature in particle size distribution of an as-pulverized powder sample is an evidence of the presence of fractal surfaces on such particles (see Fig. 1 and the accompanying caption). The surface ruggedness and the shape of the particles which obey a self-similar particle size distribution seem to be the same, even with increasing magnification. In other words, the shape and the surface ruggedness of the particles can be regarded as being statistically fractal. Thus, the particles which are classified by sieving can be described by introducing a fractal particle size or diameter x which can be defined by the opening of a sieve [6]. Thus, a fractal surface area per unit volume, i.e., a specific surface area S_V can be expressed by

$$S_V \propto x^{D-3} \tag{1}$$

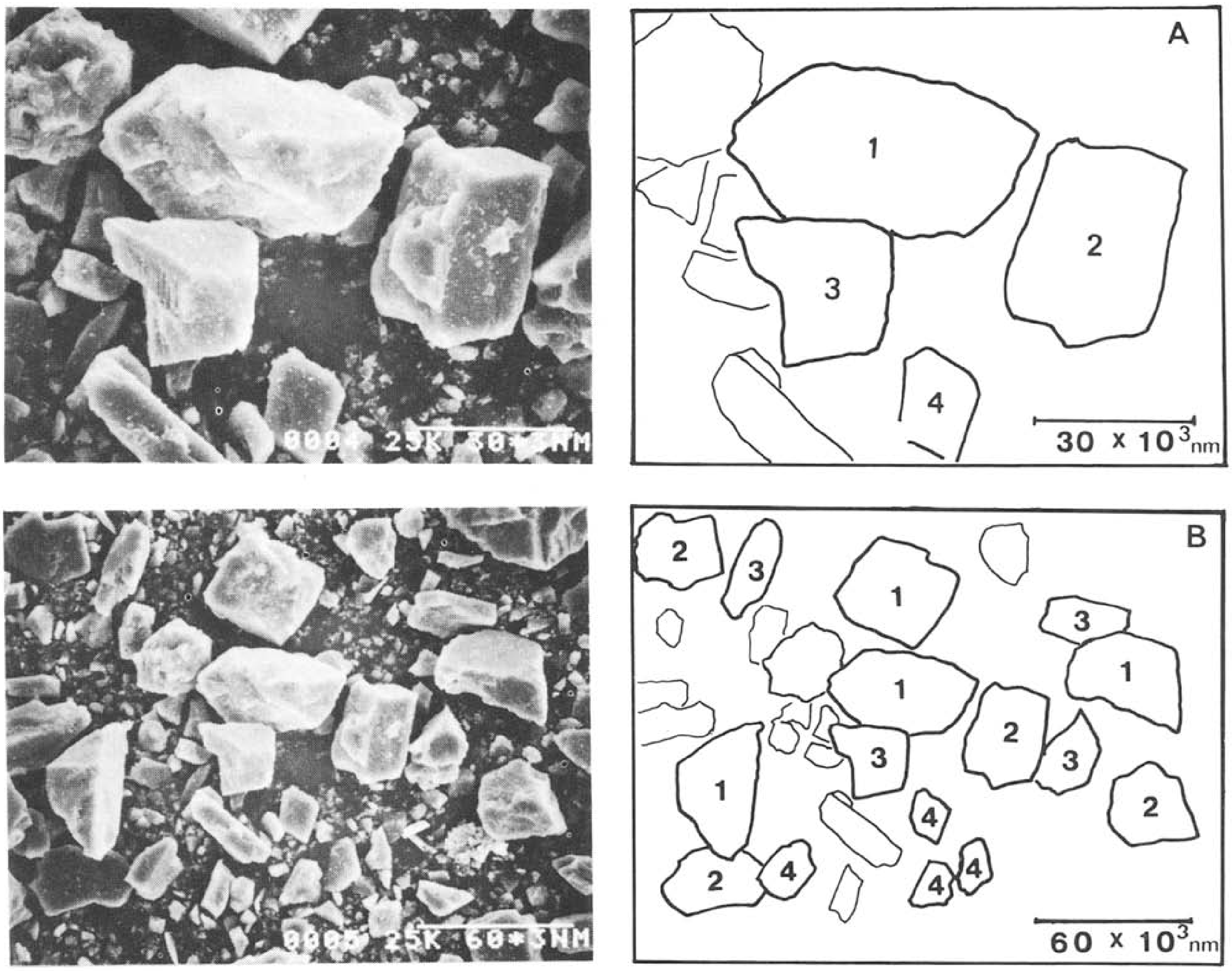

Fig. 1. Scanning electron micrographs for dolomite sample crushed and passed through a 325-mesh Tyler sieve. (A) Original magnification, $\times 10^4$. (B) The same sample. Original magnification, $\times 0.5 \times 10^4$. The particles in each of the micrographs are traced in a two-dimensional plane. Note that the population of the particles in (B) is increased four times over those in (A), with the magnification of (B) half that of (A). In (A), the largest dolomite particles having a size of approximately $2X_1$ and the second largest particles of size about $2X_2$ are distributed at populations by weight of $2\nu X_1^{\nu-1}$ and $2\nu X_2^{\nu-1}$, which are directly proportional to the volume of the particle, i.e., X_1^3 and X_2^3, respectively. In (B), the largest and the second largest particles are observed as those of size X_1 and X_2, respectively, which are distributed at $\nu X_1^{\nu-1}$ and $\nu X_2^{\nu-1}$. From $2\nu X_1^{\nu-1} = X_1^3$, $X_1^{\nu-1}$ equals $X_1^3/2\nu$. Thus, the population as observed in a two-dimensional representation in (B), i.e., $\nu X_1^{\nu-1}$, becomes $4 \times (X_1/2)^3$, which signifies that four particles of the same size are present in (B).

where D is a fractal dimension with

$$2 < D < 3$$

Then the generalized Gaudin–Schuhmann distribution function introduced previously [1] can be written using a specific surface area S_{Ve} of a particle having an absolute size constant x_e, as [6]

$$P(S, t) \approx (S_V/S_{Ve})^{-\nu(D-3)}$$

Equation (1) corresponds to the equation given by Avnir et al. [7] in their determination of the fractal dimension of surfaces by an adsorption method.

EXPERIMENTAL

The dolomite sample used was the same as those reported in the previous papers [1, 2]. The micrographs were obtained using a Hitachi S-415 scanning electron microscope (SEM). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method on classified dolomite powder samples using a Digisorb 2600 surface-area, pore-volume analyzer (Micromeritics Instrument Corp.), with argon as the adsorption gas. The dolomite powder samples subjected to the measurement of specific surface area were (1) a powder composed of particles between 105 and 90 μm (−150 mesh and +170 mesh Tyler sieves), (2) a powder composed of grains between 44 and 38 μm (−325 mesh and +400 mesh Tyler sieves), and (3) one that was ground for a sufficiently long period of time. The last sample was confirmed as retaining the dolomite structure by X-ray diffraction (XRD), and was observed by SEM to be composed dominantly of particles about 3 μm in size.

RESULTS AND DISCUSSION

The specific surface areas obtained for the above samples are summarized in Table 1. By plotting the observed specific surface area values against the fractal size in a log–log diagram, as in Fig. 2, there is obtained a fractal dimension D of 2.33. Considering that a well crystallized dolomite sample was used in the present study, the result is in fair agreement with the values reported by Avnir et al. [7]; for example, $D = 2.58 \pm 0.01$ for a Niagara dolomite.

In the previous paper [2], the authors showed that a portion of a pulverized dolomite sample represents quite well the thermal behavior, i.e., the thermal decomposition in this case, of the whole sample. In the powder system under consideration, the gas-evolving reaction of the sample having a fractal particle size distribution with x_e (absolute size constant; for details, see [1]) of 74 μm can be represented by a sample portion composed of particles with $x_e = 74$ μm or smaller and 44 μm or larger in size. This signifies that a sample portion of about 30% by weight can indicate the thermal reaction characteristics of the whole dolomite sample having a self-similar particle size distribution.

TABLE 1

Specific surface area for classified dolomite samples

Tyler sieve range (mesh)	Fractal particle size (μm)	Specific surface area ($m^2 g^{-1}$)
150–170	105–90	0.51
325–400	44–38	1.05
–	≈3	7.05

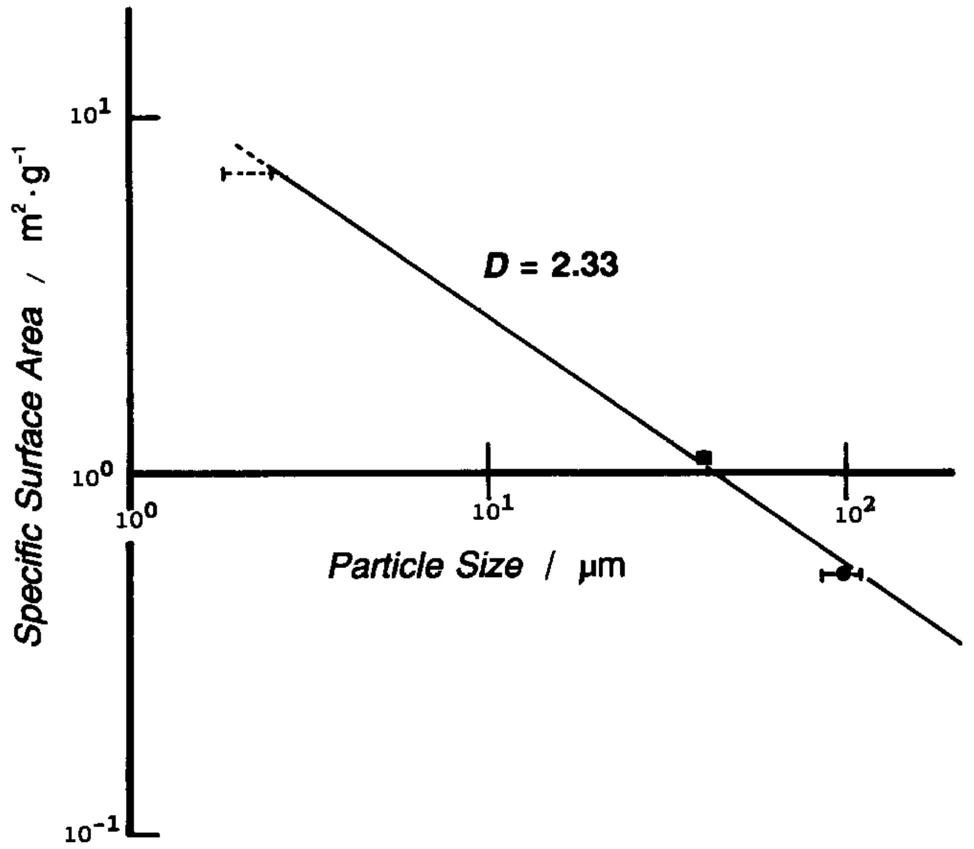

Fig. 2. Determination of the fractal surface dimension D of the dolomite sample by plotting specific surface area by BET (Ar gas adsorption) against particle size in a log–log diagram.

Then the fraction of the whole surface area which can represent the thermal behavior of the whole sample is calculated. From the undersieve distribution function by weight $P_w(X) = KK^\nu$, where K is a constant and X is a scaled particle size given by $X = x/x_e$, we obtain the weight fraction of particles of size X

$$\frac{d}{dX}P_w(X) = \nu KX^{\nu-1} \tag{2}$$

which can be readily converted into an equation using a volume fraction $P_v(X)$ of particles of size X

$$\frac{d}{dX}P_v(X) = \rho^{-1}\nu KX^{\nu-1} \tag{3}$$

where ρ is the density of dolomite.

Thus, the surface area for particles having the scaled particle size X can be obtained by multiplying the volume fraction of eqn. (3) by the specific surface area by volume S_V. By introducing the specific surface area of eqn. (1), we obtain

$$\frac{d}{dX}P_v(X)S_V = \rho^{-1}\nu KX^{\nu-1}K'X^{D-3} \tag{4}$$

where K' is a constant.

Because the powder system under consideration is the same as that reported previously [1], the particle size distribution can be described by $P(X) = X^{\nu}$, where $\nu = 0.95$ and $x_e = 74\ \mu m$. Thus, the total surface area for a sample portion obtained between 325-mesh and 200-mesh sieves ($x = 44$–$74\ \mu m$) can be calculated by integrating eqn. (4)

$$\int_{0.6}^{1} \frac{d}{dX} P_{\nu}(X) S_V \, dX = A \int_{0.6}^{1} X^{\nu + D - 4} \, dX \tag{5}$$

where $A = \nu KK'$. Hence, by putting $\nu \approx 1$ and $D = 2.33$ with $A' = A/0.32$, there is obtained $A(\nu + D - 3)^{-1}[X^{\nu+D-3}]_{0.6}^{1} = 0.15A'$. This signifies that the surface area of the particles having particle size 44–74 μm accounts for about 15% in the total surface area of the particles 74 μm or less in fractal particle size.

Referring to the TG–DTA curves of the decomposition of dolomite in the previous report [2], it can be seen that the well accepted discussion of surface activation (see, for example, ref. 8) ascribed to the particle size reduction and the corresponding increase in the specific surface area is no longer valid in this case. A sample consisting of particles 74 μm or smaller in size has a larger total surface area as compared with a sample of the same weight but consisting of particles in the size range 44–74 μm. However, the initial temperature as well as the whole TG–DTA curve for the decomposition reaction is approximately the same for those two samples. This indicates that further considerations should be made taking the packing properties of the powder into account.

CONCLUSIONS

The particle size determined by the openings of sieves is, in a sense, a fractal particle size which is scaled with the mesh opening. Then a fractal specific surface area S_V can be defined accordingly with the fractal particle size x by a power law as $S_V \propto x^{D-3}$, where D is a fractal dimension with $2 < D < 3$.

Based on the previous papers stating the validity of thermal analysis in describing the fractal or the self-similar nature of powder samples, the surface area of the portion of a sample which is necessary to provide information for the whole sample, at least in a gas-evolving thermal decomposition, is estimated to be approximately 15% of that for the whole sample. It is noted, however, that the generally accepted activation of a powder ascribed to the increase in specific surface area does not hold for a powder consisting of particles below a certain size, and hence the matter requires further consideration.

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