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FRACTAL NATURE AND THERMAL ANALYSIS OF POWDERS

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$F(a)$ functions (where a is the rate of conversion), frequently referred to when considering non-isothermal heterogeneous processes, are reconsidered from a fractal viewpoint. This is achieved on the basis of previous studies on the fundamental properties of powders, which show that any powder obtained by mechanical size reduction yields a fractal particle-size distribution $P(X,t)$, where X is a scaled particle size, with a material-dependent power n as $P(X, t)\propto X^n$, and that the obtained powder has a specific surface area, S, expressed with the fractal particle size x as $S\propto x^{D-3}$ with the fractal dimension D. This can be interpreted to show that a powder obtained by mechanical grinding has a unique D for a specified particle-size range, and, in fact, TA results dependent on this D were obtained.

We also show that a mechanical size reduction process produces fractal surfaces. The phenomenologically known laws which relate input energy and the powder product are theoretically derived by assuming that the energy is consumed in producing fractal surfaces. The well-known *reaction functions* which relate the conversion rate with the physical and geometrical factors governing a reaction process are reconsidered from a fractal viewpoint. The validity of conventional $F(a)$ expressions based on integer dimensions are questioned.

Keywords: fractal nature, powders

Introduction

In a non-isothermal heterogeneous process such as decomposition of a solid, the rate of the process $\mathrm{d}a/\mathrm{d}t$, where a is the rate of conversion and t the time, is presumed to obey a relation expressed by

$$\mathrm{d}a/\mathrm{d}t = k \cdot F(a)$$

where k is the well-known Arrhenius equation $k = A\exp(-E/RT)$ widely accepted in homogeneous reaction kinetics, A is a constant, and E is the so-called activation energy. In this equation, $F(a)$ is a unique function of a and is dependent on the physical and geometrical relations at the boundary between the product and initial material.

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In previous papers related to dolomite decomposition, it has been found that the decomposition is greatly influenced by powder characteristics, particularly by particle-size distribution. It has also been found that a consistent result can be obtained in TA by taking a sample having a fixed particle-size distribution below a specified size; i.e. the undersieve distribution function of a powder obtained after thorough grinding obeys a power law function $P(X,t)\propto X^n$, where X is the particle size x scaled with a characteristic size constant $x_c(t)$, and t is the duration of grinding [1–3]. This power law function is valid in the particle-size range from ca. 2 μm to x_c for all kinds of powder prepared by grinding, and the power n can be obtained as a material constant [2]. On the other hand, the fact that the particle size distribution of a pulverized product obeys a power law function signifies that the surface and the shape of the particles obtained by grinding are statistically self-similar. Thus, the particle size defined by the sieve aperture can be considered a fractal particle size. Then, the specific surface area S can be expressed with the fractal particle size x as $S \propto x^{D-3}$ [3, 4], where D is the fractal surface dimension. This is essentially the same result as that verified experimentally by the Avnir group [5].

Results on dolomite decomposition can then be interpreted to show that the decomposition of a pulverized sample varies considerably with D [4]. Furthermore, it has been observed that this reaction does not increase its rate with increasing specific surface area [6]. This suggests that the reaction mechanism described by the reaction rate is a function of x^D and that $F(a)$ needs to be reconsidered from a fractal viewpoint.

Framework of the theory

Formation of fractal surfaces by taking energy, E, consumed for size reduction into consideration

Various schemes of shape analysis have been proposed, both experimentally and theoretically, to satisfactorily characterize the surface of rugged particles. It is now well established that products obtained by grinding a solid and powders synthesized or found in nature have, in general, heterogeneous surface structures which can be defined with non-integer dimensions [7]. Non-fractal surface is sometimes said to be an exception.

The specific surface area S of a ground particle can be given [8] in the form

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

where D represents a fractal dimension. It has been found experimentally that a characteristic size x_0 which gives the fractal specific surface area S_0 appears with progressive grinding. It is naturally assumed that the energy E consumed for breakage is used to generate a new fractal surface and is shown by

$$dS \propto (S_0 - S)dE \tag{2}$$

Using Eq. (1), we can obtain the following relation

$$dE \propto x^{D-4}\,dx \tag{3}$$

Equation (3) is what the Lewis' law states. From Eq. (3) we can obtain the other three experimentally known equations as follows by putting particular values for D:
with $D = 2$, the Rittinger's law

$$E = C\left(\frac{1}{x_2} - \frac{1}{x_1}\right)$$

where x_1:represents the particle size of the feed; and x_2, the particle size of the size-reduced product, with $D = 2.5$, the Bond's Law:

$$E = C\left(\frac{1}{\sqrt{x_2}} - \frac{1}{\sqrt{x_1}}\right)$$

with $D = 3$, the Kick's Law:

$$E = C\log\left(\frac{x_1}{x_2}\right)$$

where C is a constant. Thus, it can be seen that the conventionally accepted empirical laws for the energy of comminution are each a part of the generalized fractal energy law expressed by Eq. (3), with a specific value for D. It is also known, that Bond's law among the energy laws above describes fairly well the experimental results. This also supports the assumption of forming a fractal surface on powder particles produced by grinding.

Based on our previous reports and the newly interpreted energy laws for comminution, the functions which describe the mechanisms in solid reactions are reconsidered below.

General description of heterogeneous reaction

We describe a heterogeneous reaction in terms of a degree of conversion, a, as

$$a = V/V_0 \tag{4}$$

where the volume V of the reacted portion is selected as the changing property which can be monitored during the reaction, and V_0 is the initial volume of the system. Thus, the same relation noted in the Introduction can be obtained, viz:

$$da/dt \propto F(a) \tag{5}$$

Then, the conventionally accepted equations $F(a)$ as shown in Table 1 [9] are reconsidered.

Surface-controlled reactions

Table 1 Reaction function forms (Sharp *et al.* [9])

Symbol	Function form $F(a)$	
D_1	a^{-1}	
D_2	$[-\ln(1-a)]^{-1}$	[10]
D_3	$(1-a)^{1/3}[(1-a)^{-1/3}-1]^{-1}$	[11]
D_4	$[(1-a)^{-1/3}-1]^{-1}$	[12]
R_2	$(1-a)^{1/2}$	[13]
R_3	$(1-a)^{2/3}$	[13]
A_2	$(1-a)[-\ln(1-a)]^{1/2}$	[14]
A_3	$(1-a)[-\ln(1-a)]^{2/3}$	[14]

We assume that the reaction rate is proportional to the surface area A of the reacting boundary:

$$\mathrm{d}V/\mathrm{d}t = k\cdot A \tag{6}$$

where k is a constant, and with Eq. (6),

$$\mathrm{d}a/\mathrm{d}t = k/V_0 \cdot A \tag{7}$$

If the morphology of the reacting particle does not change markedly during the reaction, the initial volume V_0 and the unreacted or remaining volume V' can be written as

$$V_0 = C\cdot r_0^D$$

$$V' = C\cdot r'^D$$

where r' is the fractal size of the unreacted particle. Then, by adopting Mandelbrot's theory of co-dimension, the area A of the reaction boundary can be expressed by $A = C'\cdot r^{D-1}$. By simple substitution and $V = V_0 - V'$, from Eq. (4), we can rewrite Eq. (7) as

$$\mathrm{d}a/\mathrm{d}t \propto (1-a)^{(D-1)/D}$$

with D = fractal dimension of $2 \leq D \leq 3$.

Diffusion-controlled reaction

In this reaction, the rate of diffusion of a substance within a thin boundary layer between the unreacted material and the reacted product corresponds to the reaction rate. Here, the reacting volume is assumed to be proportional to the diffused amount, expressed by:

$$dV/dt = K \cdot dN/dt \tag{8}$$

where N is the quantity of the diffusing material, and K is a constant. By assuming a simple one-dimensional diffusion, we obtain $d^2N/dr^2 = 0$ according to Fick's second law: ; and by further assuming the concentration gradient along the direction of the diffusion to be constant, we obtain dN/dr = constant.

$$dV/dt = K \cdot dN/dt = -D' \cdot K \cdot A \cdot dN/dr \tag{9}$$

where D' is diffusion constant, and A represents the cross-sectional area of the reaction system.

At an arbitrary position r in the product layer of a particle of dimension D, the diffusion flux per unit time becomes constant irrespective of r. Thus, by integration, Eq. (9) becomes

$$dN/dt \int_{r_0}^{r} \left[-r^{-(D-1)}\right] dr \propto \int_{N_0}^{N} dN \tag{10}$$

where $1 \le D \le 3$.
Thus from Eq. (10) and $\Delta N = N - N_0 > 0$ we obtain:
when $1 \le D < 2$

$$dN/dt \propto \Delta N\,[-r^{(2-D)} + r_0^{(2-D)}]^{-1} \tag{11}$$

when $D = 2$

$$dN/dt \propto \Delta N\,[-\ln(r/r_0)]^{-1} \tag{12}$$

when $2 < D \le 3$

$$dN/dt \propto \Delta N\,[r^{(2-D)} - r_0^{(2-D)}]^{-1} \tag{13}$$

By substituting $r/r_0 = (1-a)^{1/D}$

$$D_D\,(1 \le D < 2) \quad da/dt \propto [-(1-a)^{(2-D)/D} + 1]^{-1}$$

$$D_D\,(2 < D \le 3) \quad da/dt \propto [(1-a)^{(2-D)/D} - 1]^{-1}$$

$$D_D\,(D = 2) \quad da/dt \propto [-\ln(1-a)]^{-1}$$

Nucleation-dependent process

With respect to a process controlled by the nucleation–growth mechanism, the basic concept follows that established by Avrami [14], which describes a process involving intergrowth of the nuclei during their rapid growth. Here it is assumed that the rate of formation of the germ nuclei and that of the growth of the grains are both constant. Hence

$$\mathrm{d}N/\mathrm{d}t = k \cdot N_o \qquad (14)$$

$$v = K \cdot (k' \cdot t)^{\mathrm{D}} \qquad (15)$$

where N represents the number of grains; v the volume of a grain or nucleus; D, the fractal dimension of the direction of growth; k and k' each rate constants of the formation of nuclei and of the growth of grains, respectively. N_o is the number of sites suitable for nucleus formation, and K is a volume conversion factor.

The total volume, V, for nuclei having formed in the initial stage can be obtained by

$$V = K \cdot k'^{\mathrm{D}} \int_0^{\tau} (t-\tau)^{\mathrm{D}} \frac{\mathrm{d}N}{\mathrm{d}t} \mathrm{d}\tau = \frac{1}{(D+1)} K \cdot N_o \cdot k \cdot k'^{\mathrm{D}} \cdot t^{(\mathrm{D}+1)} \qquad (16)$$

By differentiation and substitution, we obtain

$$\mathrm{d}a/\mathrm{d}t \propto a^{\mathrm{D}/(D+1)} \qquad (17)$$

If the nucleation is complete in the initial stage, the total volume V after time t becomes

$$V = k \cdot N \cdot k'^{\mathrm{D}} \cdot t^{\mathrm{D}}$$

thus

$$\mathrm{d}a/\mathrm{d}t \propto a^{(\mathrm{D}-1)/\mathrm{D}} \qquad (18)$$

If the grains grow sufficiently large as to impinge on one another, the actual amount reacted, $\propto$ is related to the theoretical a' as

$$a' = -\ln(1-a)$$

Thus we obtain

$$\mathrm{d}a/\mathrm{d}t = (1-a)\,\mathrm{d}a'/\mathrm{d}t \qquad (19)$$

If the nucleation proceeds at a constant rate, from Eqs (17) and (19) we obtain

$$\mathrm{d}a/\mathrm{d}t \propto (1-a) \cdot [-\ln(1-a)]^{\mathrm{D}/(\mathrm{D}+1)} \qquad (20)$$

If nucleation completes at the initial stage of reaction, from Eqs (19) and (20) we obtain

$$\mathrm{d}a/\mathrm{d}t \propto (1-a)\cdot[-\ln(1-a)]^{(D-1)/D} \tag{21}$$

where $1 \le D \le 3$.

The above reaction functions are summarized in Table 2.

Discussion

In $\mathrm{d}a/\mathrm{d}t \propto (1-a)^{(D-1)/D}$, with D being the fractal dimension of $2 \le D \le 3$ simple substitutions with $D = 2$ and $D = 3$ give $F(a)\,\alpha\,(1-a)^{1/2}$ and $F(a) \propto (1-a)^{1/3}$, correspoding to R_2 and R_3 functions in Table 1, respectively. Similarly, in diffusion-

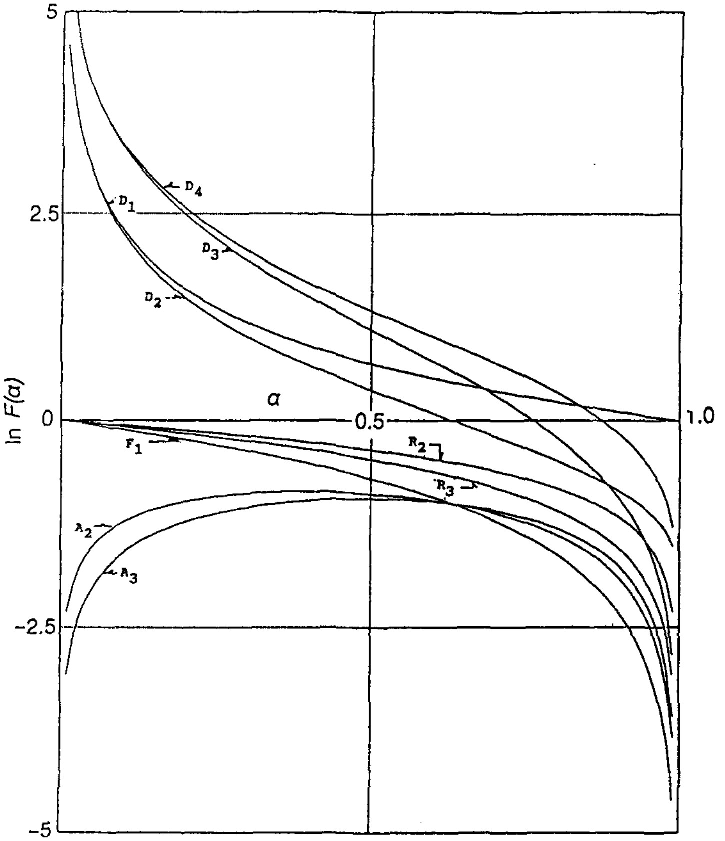

Fig. 1 a *vs.* ln$F(a)$ plots corresponding to the $F(a)$ values in Table 1, according to the classification of Sharp *et al.* [9]

controlled reactions, the conventional forms can be obtained by inserting specific values for D as 1, 2 and 3, as $F(a) \propto 1/a$, $F(a) \propto [-\ln(1-a)]^{-1}$ and $F(a) \propto 1/[(1-a)^{-1/3}-1]$, respectively, corresponding to D_1 to D_3 functions in Table 1. Similar results can be obtained for nucleation–growth processes by inserting $D = 2$ and $D = 3$, to obtain A_2 and A_3 functions, respectively, as $F(a) \propto (1-a) \cdot [-\ln(1-a)]^{1/2}$ and $F(a) \propto (1-a) \cdot [-\ln(1-a)]^{2/3}$.

Table 2 Functional forms with non-integer D values

Symbol	Function form $F(a)$
D_D ($D = 1 - 2$; $\neq 2$)	$[-(1-a)^{(-D+2)/D}+1]^{-1}$
D_D ($D = 2 - 3$; $\neq 2$)	$[(1-a)^{(-D+2)/D}-1]^{-1}$
D_2	$[-\ln(1-a)]^{-1}$
R_D ($D = 2 - 3$)	$(1-a)^{(D-1)/D}$
A_D ($D = 1 - 3$)	$(1-a)[-\ln(1-a)]^{(D-1)/D}$

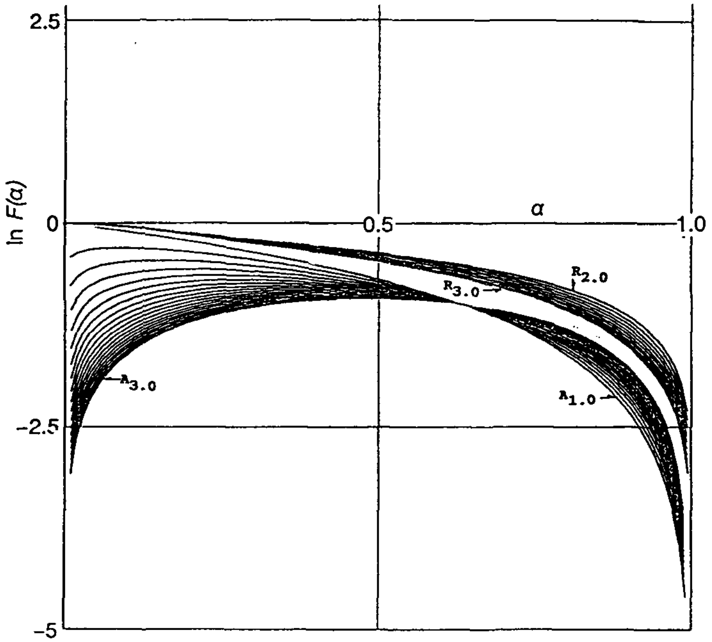

Fig. 2 *a vs. F(a)* plot curves of surface-controlled reactions, indicated by R_D, and for the nucleation–growth process A_D, where D is increased from 1 or 2 to 3 in 0.1 steps. Note that the *a vs.* ln*F(a)* plots fall within the area defined between the conventional R_2 and R_3 curves and between A_1 and A_3 curves in Fig. 1, where A_1 corresponds to the F_1 curve in the conventional description

The generalized reaction functions with non-integer D values listed in Table 2 above are shown graphically in Figs 2 and 3. In Fig. 1 are given the a–ln $F(a)$ plots corresponding to the $F(a)$ values in Table 1.

Figure 2 shows the $a - \ln F(a)$ plot curves for surface-controlled reactions, i.e., those indicated with symbol R_D, and for nucleation–growth reactions indicated by A_D, where D is increased from 1 or 2 to 3 at 0.1 steps. Thus we can see that any sample which undergoes a reaction with its $a - \ln F(a)$ plot falling within the area between the R_2 and R_3 curves may possibly obey a surface-controlled reaction. The same discussion may be applied to those between the A_1 and A_3 curves, showing a nucleation–growth reaction.

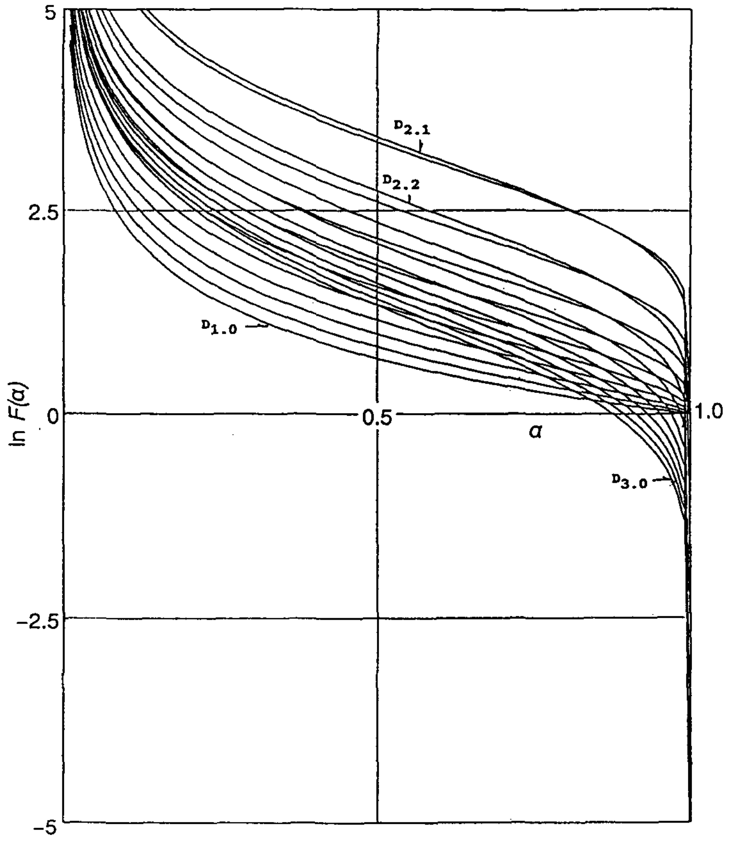

Fig. 3 a *vs.* ln$F(a)$ plots for diffusion-controlled reactions indicated by D_D with $D = 1.0$ to 1.9 and $D = 2.1$ to 3.0 in steps of 0.1. The curves with $D = 2$ coincide with the D_2 curve in Fig. 1. Note that the curves shift to the upper part of the graph with increasing D values to 1.9, and then shift downward from $D = 2.1$ to 3.0 to cover an area defined between the conventional D_2 and D_4 curves

Clearly, a deviation in the $a - \ln F(a)$ plots from the conventionally known curves is observed in the D_D series. If the fractal viewpoint is again applicable to the theoretical base for the diffusion-controlled reactions, it can be seen that there may be numerous reactions with their $a - \ln F(a)$ plots deviating from conventionally proposed ones.

Though there appears no firm basis at present concerning the applicability of the starting Arrhenius equation [15], it seems meaningless to limit the reaction functions to only those related to the specific integer dimensions, 1, 2 and 3.

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Zusammenfassung — Die bei Betrachtungen an nichtisothermen heterogenen Prozessen oft eingesetzten Funktionen $F(a)$ (wobei der Konversionsgrad ist), wurden unter "fractalen" Aspekten neu überdacht. Dies erfolgte auf der Grundlage vorangehender Untersuchungen über die grundlegenden Eigenschaften von Pulvern, welche zeigen, daß alle durch mechanische Herabsetzung der Größe erhaltenen Pulver eine fractale Korngrößenverteilung $P(X,t)$ mit einem stoffabhängigen Exponenten D gemäß $P(X,t) \propto X^n$ aufweisen und daß die erhaltenen Pulver eine spezifische Oberfläche S besitzen, die mit Hilfe der fractalen Korngröße x und der fractalen Dimension D als $S \propto x^{D-3}$ ausgedrückt werden kann. Dies kann dahingehend interpretiert werden, daß ein durch mechanisches Zerkleinern erhaltenes Pulver für ein bestimmtes Korngrößenintervall ein eindeutiges D besitzt und daß man TA-Ergebnisse erhält, die eigentlich von diesem D abhängen.

Außerdem wird gezeigt, daß eine mechanische Herabsetzung der Größe fractale Oberflächen ergibt. Phänomenologisch bekannte Gesetze zwischen zugeführter Energie und dem Pulverprodukt werden theoretisch unter der Annahme abgeleitet, daß die Energie zur Erzeugung fractaler Oberflächen verbraucht wird. Unter einem "fractalen" Gesichtspunkt werden auch die gutbekannten Reaktionsfunktionen zwischen Umsetzungsgrad und den die Reaktion beherrschenden physikalischen und geometrischen Faktoren überdacht. Die Gültigkeit der üblichen Ausdrücke $F(a)$ mit ganzzahligen Dimensionen wird bezweifelt.