Surface Fractal Dimension of Small Metallic Particles

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The surface structure of small metal particles is characterized by use of electron microscopy techniques. It is found that the surface has a very extensive roughness which can be described by means of a fractal dimension. We report a new method to measure the fractal dimension by image-processing techniques, and computer measurements. Different values of the fractal dimension are found for gold, platinum, and palladium particles depending on particle preparation and surface treatment. It is found that the fractal dimension of small metallic particles changes after a methanation reaction.

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In recent years the concept of fractal has been shown to be useful to describe many physical systems.[1] In a recent work Pfeifer and co-workers[2-4] have described the fractal properties of solid surfaces. These authors have reported measurements on the fractal dimensions of a number of porous surfaces of materials which are often used as catalyst supports. Therefore, it is expected that fractal dimensions will become very useful in describing complex chemical phenomena such as catalysis. A typical catalyst is composed of metal particles with a diameter between 10 and 100 Å, such as Pt, Rh, Pd (or their alloys) supported on porous substrates such as γ alumina or zeolites. It is well established that in most chemical reactions the catalytic activity is determined not by the carrier substrates but by the small metallic particles (crystallites) supported on them. It is well known that the reaction occurs on the surface of the particles. It is then clear that in order to assess fully the usefulness of the fractal concept in catalysis, it is necessary to demonstrate that it can also be applied to the description of the surface of small metal particles.

Recently, there has been growing evidence from electron microscopy and microdiffraction studies that small metal particles do not have well defined surfaces but rather show a high degree of roughness.[5,6] In the presence of such roughness, the surface of the metal particle can be expected to have a dimension greater than two and to be described as a fractal.

Experimental evidence of particle surface roughness was obtained through electron microscope images of the particles. The weak-beam thickness fringes method[7] was used to determine the particle shape.

It is a well known fact that the electron beam intensity oscillates with specimen thickness [Eq. (4)]. Because of the roughness of the surface, the particle thickness and therefore the electron beam intensity will change erratically from point to point on the image, so that electron microscope images from small particles will consist of irregularly spaced fringes corresponding to contours of equal thickness which follow accurately the specimen shape [Fig. 1(a)]. It has been shown[8] that under the proper diffraction conditions, intensity variations will be sensitive to monatomic step changes. Then, as we will show below, electron microscope images can be used to determine experimentally the surface fractal dimensions of small metallic particles, provided one knows the fractal dimensions of the thickness contour lines.

By digitizing an electron microscope image, using a scanning microdensitometer, one can select any arbitrary intensity (or thickness) level on the computer. Plotting all points corresponding to this level will result in a topographic map of the particle. Since electron intensity oscillates with specimen thickness, there will in general be several thickness values corresponding to the same intensity value, and hence the topographic map will consist of irregularly spaced lines marking points of constant depth. The greater the rate of change of thickness, the smaller the distance between lines on the map. Figure 1(b) shows the reconstructed computer image of the particle whose image is shown in Fig. 1(a). Figure 1(c) shows the corresponding topographic map of five arbitrarily chosen intensity levels. With choice of slightly different levels, the positions of the thickness contours shift continuously to adjacent locations corresponding to the new depth. In this way one can reconstruct the whole particle surface since we already know all its cuts. The total surface area can be calculated as follows: Imagine two closely spaced contours, as depicted in Fig. 2, where each contour is approximated by yardsticks of a given length. (Thickness contours can be made arbitrarily close to each other by selecting nearly equal intensity levels.) The area of the tiles is proportional to the yardstick length, which is the base of all triangles. This is equivalent to measuring the area of a mountain by covering it with plane tiles between two given heights. The total surface area A is therefore proportional to the contour length and can be expressed as

$$A \propto \varepsilon^{1-d}, \tag{1}$$

where ε is the yardstick length used to measure the contour and d its fractal dimension.

Equation (1) and the fact that the thickness contours

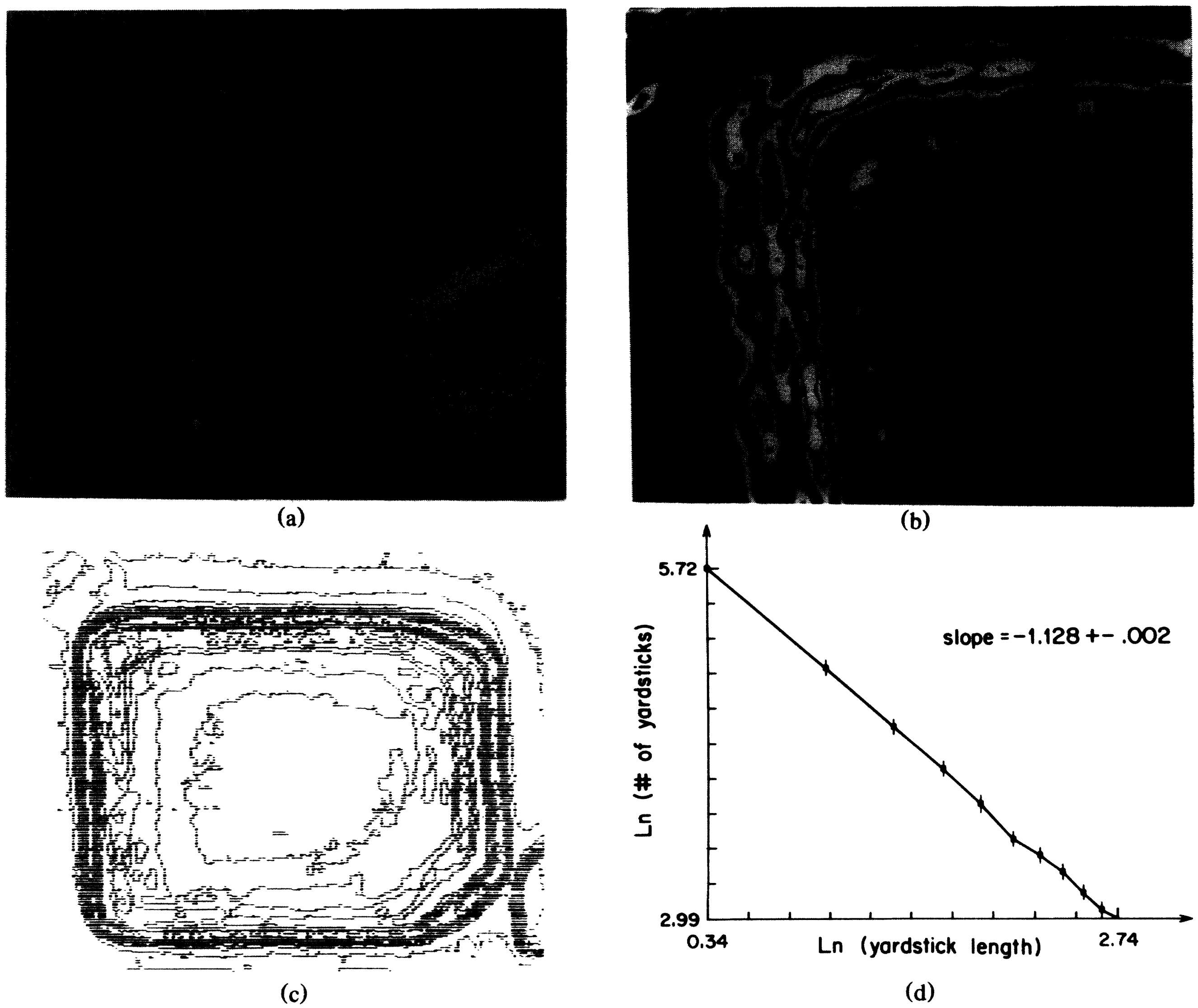

FIG. 1. (a) Transmission electron microscopy image of a small gold particle in the weak-beam mode showing thickness fringes. (b) The same image of the particle in (a) but after computer processing. The gray levels indicate variations in thickness. (c) Computer-reconstructed contour levels of the same particle. (d) Plot obtained from the contour in (c) by the compass method. The fractal dimension corresponds to 2.13 ± 0.002 in this case. The size of the particle is 250 Å.

are continuously defined across the particle imply that if these are fractal quantities, so is the area.

If the surface is characterized by a fractal dimension D, then the area can be expressed as

$$A \propto \varepsilon^{2-D}. \tag{2}$$

By comparison of Eqs. (1) and (2) it follows that

$$D = d + 1. \tag{3}$$

To determine the fractal nature of contours, their total lengths were measured with successively shorter yardstick lengths following the original method of Mandelbrot.[1] A log-log plot of the contour length was obtained as shown in Fig. 1(d), in which a straight line was fitted to the first five points to obtain the value of d. Since the slope of the straight part of the log-log plot is 1.13 ± 0.002 (here the error quoted refers to the estimated error in the measurement of a single contour), the surface fractal dimension is 2.13, in accordance with Eq. (3).

By the technique described above, the fractal dimensions of different small metallic systems were measured: (a) gold, palladium, and platinum particles grown by evaporation on a NaCl substrate; (b) platinum particles grown by H reduction of a chemically deposited salt, with the standard procedures for catalyst preparation,[9] on an amorphous carbon substrate or on graphite; (c) platinum particles prepared as in (b) and then subjected

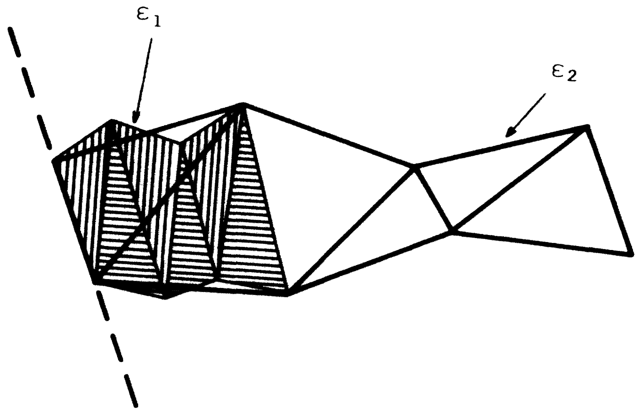

FIG. 2. Schematic representation of the geometry involved in the particle structure.

to a very strong chemical reaction in a H flow at 700 °C (for a detailed description of the reaction procedure see Ref. 9). Table I shows the results for the different particles studied. The values reported are the average of at least five different measurements on particles of each kind. Several contours were considered for each particle. It appears that indeed the particles have a surface dimension greater than two. An interesting result is that surface roughness increased after the particle acted as a catalyst in a chemical reaction. This clearly shows the usefulness of the fractal dimension to describe changes on a surface before and after a reaction.

The observed changes in surface dimension are not due to noise in the micrographs. The most important source of noise in high-resolution images is the so called "quantum" or "shot" noise that is known to be distributed according to Poisson statistics, so that if n is the number of electrons arriving (to a given pixel) then the standard deviation in the number of counts will be $\sqrt{n}$. In our experiments, with some 500 electrons arriving at a typical pixel (an area of 20 μ on film), the standard deviation will be of about 22 electrons, or 5%. Now, the kinematical diffraction expression (that is, a first Born approximation to the problem of the scattering of electrons by solids) gives

$$I = \sin^2(\pi t s)/\zeta^2 s^2, \tag{4}$$

where I is the intensity (proportional to the number of electrons reaching the photographic plate), t is the sample thickness, ζ is a parameter ("extinction distance") specifying the strength of the electron-sample interaction, and s is a measure of deviation from exact Bragg diffracting conditions. A change of 5% in I corresponds to a 1.44-Å "error" in position (a value of s of $\frac{1}{20}$ Å^{-1} was estimated from fringe spacing in the micrographs). Hence shot noise is not noticeable in our case, and the image profile represents real roughness and not just noise. Other sources of noise such as microdensitometer thermal noise and computer-generated noise have also been found to be small compared to the detail observed on the micrographs. In addition, if the changes in a dimension were due to noise in the pictures, we would not expect changes with the type of preparation and surface condition as observed in Table I.

TABLE I. Average values of the surface fractal dimension for different metal particles with different treatments.

Metal	Type of growth and substrate	Surface fractal dimension D
Au	Evaporation on NaCl crystal in a 10-Pa vacuum.	2.130 ± 0.039
Pd	Same	2.132 ± 0.027
Pt	Same	2.146 ± 0.038
Pt	Chemical reduction in H_2 of a salt deposited in amorphous carbon or graphite (Ref. 8).	2.103 ± 0.039
Pd	Same	2.072 ± 0.042
Pt	Chemical reduction in H_2 of a salt deposited on carbon. A heavy methanation reaction at 700 °C was performed.	2.330 ± 0.087

Although here the power law of Eq. (2) can be asserted for a narrow yardstick range only, such a range carries all attributes of a fractal surface because it can support several similarity iterations consistent with the observed value of the fractal dimension. For instance, in Fig. 1(d) it is clear that there were four iterations consistent with the value of 2.13 (i.e., that the log-log plot of length versus yardstick was straight for a range of yardsticks that goes from the smallest yardstick used to four times this yardstick). On the other hand, it is clear from the results shown in Table I that the fractal concept is useful in describing chemical reactions. In most cases very few changes in particle structure after a reaction can be observed by the standard characterization methods. The fractal concept, on the other hand, provides a clear cut distinction between the surface structures before and after the reaction. We can understand the results in Table I as saying that the chemical reaction increased the surface roughness from $D = 2.146$ to $D = 2.33$. It can be expected that the use of fractals will produce a lot of interesting information on the nature of catalytic reactions.

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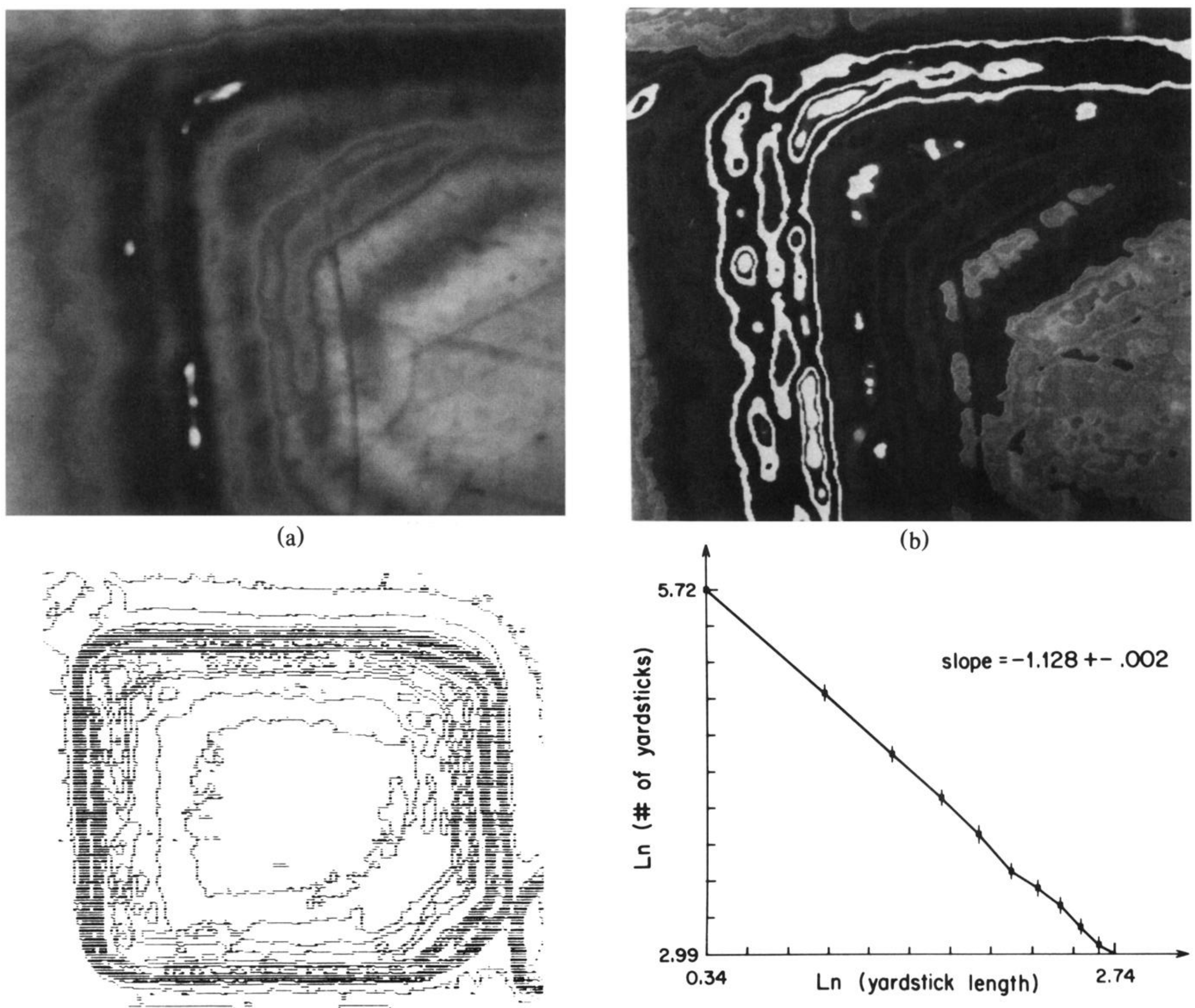

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