Integrated Fractal Analysis of Silica: Adsorption, Electronic Energy Transfer, and Small-Angle X-Ray Scattering

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The fractal dimension D of a mesoporous silica gel was determined by three independent approaches: (1) adsorption methods based on (a) tiling of the surface with molecules of different cross-sectional area and (b) analysis of the change in measured surface area as a function of the size of the silica particles; (2) analysis of one-step dipolar energy transfer between adsorbed rhodamine B and malachite green; (3) measurements of power-law small-angle x-ray scattering. All three techniques indicate that the surface is extremely rough and irregular, with a fractal dimension D nearly equal to 3.

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Self-similarity, or invariance to scale transformation, is quite common in a wide variety of objects and processes. Recognition of this phenomenon has evolved rapidly in recent years, mainly because of Mandelbrot's formulation of fractal geometry.[1] In virtually all domains of the natural sciences, attempts have been made, in many cases successfully, to use fractal dimensions to describe complex geometric environments and the processes in these environments. In general, one finds that experiments in this field have not kept up with the latest developments in theory and simulations. This study attempts to remedy some of this lag by testing three independent theories in a series of experiments on the same fractal object.

Common to all these theories is the general strategy in detecting fractality: performing a resolution analysis—i.e., analyzing the change in a measurable property as the yardstick size is varied. Thus, in an electronic energy transfer (ET) experiment, one studies the decrease in the rate of ET as a function of donor-acceptor separation[2]; in a small-angle scattering experiment one measures the decrease in the scattered intensity as the scattering angle increases[3,4]; and in adsorption one analyzes the decrease in apparent surface area as a function of the size of the probe molecule.[5]

This Letter summarizes an application of these three approaches to a mesoporous silica gel.[6] This investigation is one of the few cases—if not the only one—in which so many independent methods have been applied to a porous material and shown to give the same value for the fractal dimension D. An important result disclosed in this work is that the surfaces in this gel are so rough and irregular that they are nearly space filling.

In a series of adsorption experiments and analyses of published adsorption data, the fractal dimension D of the silica pore surface was always found[7] to be near 3. These studies employed two types of analysis,[8] which will be called methods 1 and 2. In method 1, the number n of moles per gram of adsorbent needed to form a monolayer is measured as a function of the cross-sectional area of the molecules. The same molecule is used for all measurements of n in method 2, but the diameter of the particles in the sample is varied. Both methods give[7] D values in the range between 2.94 and 3.05, with an uncertainty ±0.05. Thus D is essentially equal to 3, the highest value possible for a fractal surface.

Additional evidence obtained by both of these methods has shown that D is near 3 in this mesoporous silica gel. A sample of this silica[6] was sieved into seven fractions. The average particle diameters in these fractions varied from 71 to 190 Å. For each fraction, monolayer values were obtained by the N_2 Brunauer-Emmett-Teller method.[9] The surface area was essentially the same for all fractions, as expected[8] for method 2. The average area was 498 ± 6 Å^2, and D was found to be 3.00 ± 0.01. The range of self-similarity[8] of the surface extends at least from 16 to 114 Å^2 and so is sufficient to cover virtually all of chemistry in the sense that areas in this interval provide information about the surface irregularity experienced by any adsorbed molecule. Data from N_2

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Brunauer-Emmett-Teller adsorption obtained by method 1 can be combined with results from an analysis (see Farin, Volper, and Avnir[7]) by a completely different method, in which the adsorption of alcohols from solution was measured. The fractal dimensions $D=2.97\pm0.02$ and $D=3.06\pm0.05$ without and with N_2, respectively, are in good agreement. It is interesting that the adsorption behavior is largely governed by geometrical considerations, rather than by the details of the adsorbent-adsorbate physisorption interactions. In systems where chemical reactions are involved, geometrical considerations are insufficient to describe the adsorption.[10]

In a second family of experiments, Forster-type electronic energy transfer from adsorbed rhodamine B (the excited donor, RB) to adsorbed malachite green (the acceptor, MG) was studied on the silica. The application of ET for detection of fractal properties of materials has been suggested recently.[2,11] The experimental method is based on time-resolved measurements of direct long-range singlet intermolecular ET from a donor molecule to an ensemble of acceptors randomly distributed on a fractal body. The survival probability $P(t)$ of the excited donor is given by[11]

$$P(t)=\exp\{-[P_1(t/\tau)^{D/s}+(t/\tau)]\}, \qquad (1)$$

where s is the order of the multipolar ET, $P_1=\chi_A R_0^D$, R_0 is the critical transfer distance for which ET and spontaneous decay of the donor are of equal probability, and τ is the radiative lifetime of the donor in the presence of acceptors which occupy a fraction χ_A of the adsorption sites. The experiments are carried out under conditions such that $\chi_D \ll \chi_A \ll 1$, where χ_D is the fraction of sites that are occupied by donors. (For the two cases $D\to 3$ and $D=2$ considered here, separate notations for the surface and mass fractal dimensions are not necessary.) The silica was coated with RB or RB+MG, as previously described,[12] at concentrations from 2×10^{-7} to 5×10^{-7} moles of RB per gram of silica and 1.5×10^{-6} to 6×10^{-6} moles of MG per gram of silica. The one-step ET in this system is dipole-dipole induced, and therefore[13] $s=6$.

In order to investigate the ET process, the samples were excited with the second-harmonic pulse of a Nd^{3+}-doped yttrium aluminum garnet laser (25 psec FWHM and 1 Hz repetition rate). With this experimental setup,[14] the fluorescence was imaged onto the entrance slit of a C939 Hamamatsu streak camera whose output was recorded and digitized by means of a PAR 1205D optical multichannel analyzer interfaced to a microcomputer for data processing. Each fluorescence curve represents the signal average of thirty separate laser shots. The fluorescence of RB was separated from residual MG by means of optical filters. The time-resolved decay of RB was simulated by the convolution of the excitation pulse and the function $e^{-t/\tau}$. The decay profile for RB on the silica was found to be a simple exponential with $\tau_0=4.8\pm0.1$ nsec. This value is somewhat higher than the result $\tau_0=2.5$ nsec found in methanol. The increase in lifetime is probably due to inner-field effects[15] exerted by the adsorbate-adsorbent interactions and not to an increase in the fluorescence quantum yield, which already is 0.9 to 1 in solution and thus is near its maximum value.

The decay of the RB+MG system was simulated by the convolution of the survival probability [Eq. (1)] and the exciting pulse. With the use of the τ value for RB decay, the best values of P_1 and D were extracted by a least-squares fit for a number of χ_A coverages (Table I and Fig. 1). The resulting fractal dimension, $D=3.0\pm0.1$, persists from the contact radius (~ 5 Å) out to at least the critical transfer distance[13] ($R_0=90$ Å). As predicted,[11] P_1 varies linearly with χ_A. These parameters are insensitive to χ_D within the range indicated above. This result indicates that donor-donor ET is not significant.

The third set of experiments was a small-angle x-ray scattering study of the silica sample. This technique,[3] like the scattering of other wavelengths of electromagnetic radiation,[4,16] is a powerful tool in structural characterization of irregular objects. The scattering data were recorded and corrected as in previous work.[17]

The outer portion of the corrected scattering curve is linear in the logarithmic plot shown in Fig. 2. The slope of the linear part was determined by a least-squares fit and corresponds to an intensity which is proportional to $q^{-3.95\pm0.06}$, where $q=4\pi\lambda^{-1}\sin(\theta/2)$, λ is the x-ray wavelength (1.54 Å), and θ is the scattering angle.

Equation (8) of Ref. 3 cannot be used for analysis of the scattering data from samples in which D approaches 3, because the prefactor in this equation is zero when $D=3$. A higher-order approximation is necessary for scattering curves from samples in which D is near 3, as the adsorption and ET data indicate is the case for mesoporous silica.

This equation was obtained by replacing the fractal pair correlation function[3] $g_{\text{fr}}(r)$ by the pair correlation

TABLE I. Energy transfer data. The values of χ_A were calculated by the method of Ref. 12. The letters following the acceptor concentrations indicate curves in Fig. 1.

Acceptor concentration (mole/g)	χ_A (%)	P_1	D
2×10^{-6} (a)	0.6	2.0	3.0
4×10^{-6} (b)	1.2	3.8	3.0
6×10^{-6} (c)	1.9	5.7	2.9

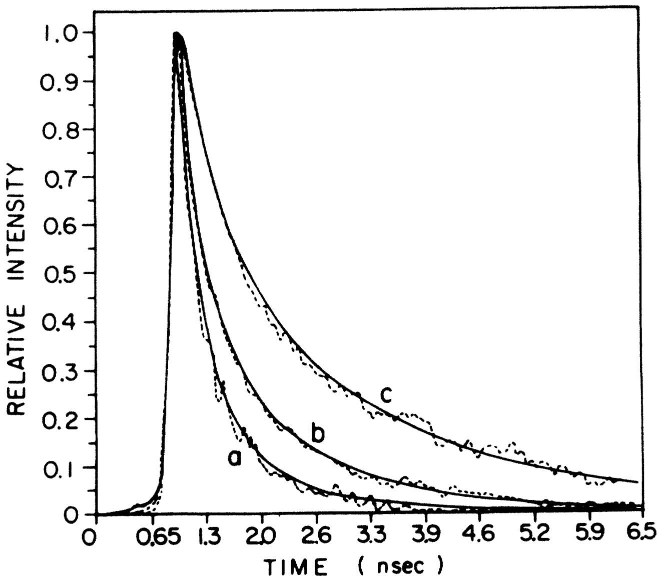

FIG. 1. Resolution analysis by energy-transfer measurements. Emission intensity of rhodamine B in the presence of three different concentrations (see Table I) of malachite green on silica is plotted as a function of time. Full and broken lines show simulations and experimental data, respectively. *a*, *b*, and *c* show curves for the concentrations corresponding to these letters in Table I.

function

$$g(r)=g_{\mathrm{fr}}(r)g_d(r/\xi). \tag{2}$$

In (2), $g_{\mathrm{fr}}(r)$, which is the correlation function given by Eq. (6) of Ref. 3, is multiplied by a function $g_d(r/\xi)$ which expresses the effects of the size of the pores in terms of the average pore size ξ. Equation (2) is based on the assumption, which is reasonable in a random porous material, that the pore size and the pore-boundary surfaces exert independent effects on $I(q)$. Similar arguments[18,19] have been used to obtain equations for the scattering from fractal aggregates.

When (2) is substituted into Eq. (2) of Ref. 3, the asymptotic approximation[20] for the scattered intensity $I(q)$ is

$$I(q)=A_d(D)q^{-4}+A_{\mathrm{fr}}(D)q^{-(6-D)}, \tag{3}$$

for $q\xi >> 1$, where δ is the electron density or the scattering-length density (for x-ray or neutron scattering, respectively), I_e is the intensity scattered by a single electron,

$$A_d(D)=-8\pi\delta^2 I_e c(1-c)\xi^{-1}Vg_d^{(1)}(0),$$

V is the volume of the sample, c is the fraction of this volume which is occupied by matter, $g_d^{(1)}(x)=dg_d/dx$,

$$A_{\mathrm{fr}}(D)=\pi\delta^2 I_e N_0\Gamma(5-D)\sin[(D-1)(\pi/2)],$$

N_0 is the parameter defined in Eq. (3) of Ref. 3, and $\Gamma(5-D)$ is the gamma function. Since $g_d(r/\xi)$ is a correlation function, $g_d^{(1)}(0)$ will be negative.[21]

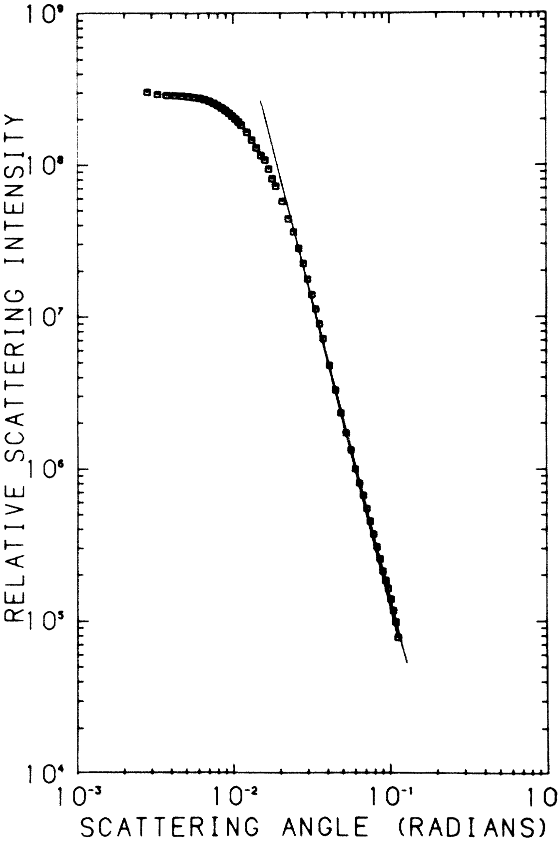

FIG. 2. Resolution analysis from small-angle x-ray scattering data.

Since $A_{\mathrm{fr}}(3)=0$ in Eq. (3), $I(q)$ is proportional to q^{-4} for $D=3$. Thus $I(q)$ is proportional to q^{-4} for $q\xi >> 1$ *both* for $D=3$ and also[3] for $D=2$. As the absorption and ET results rule out the possibility that D can be 2, it must equal 3. Many other studies[22] provide additional evidence that the surface of mesoporous silica is not smooth.

The slope of the line in Fig. 2, which was determined by a least-squares fit of a power-law scattering curve to the data points for scattering angles between 0.024 and 0.113 rad, corresponds to fractal dimension $D=3.0\pm0.1$ after allowance is made for possible systematic errors in the measurements. The distances associated with first-order Bragg reflections at the scattering angles 0.024 and 0.113 rad were used to estimate the interval of dimensions within which this fractal dimension governs the scattering. This calculation suggests that the pore boundaries are fractal for distances from at least 14 to 63 Å. The dimensions probed by the scattering measurements thus lie in the interval of distances for which adsorption and ET show that $D=3$.

The conclusion that $D=3$ is supported and given special emphasis by a comparison with Aerosil silica gel, which is nonporous and is composed of spherical beads with smooth boundary surfaces. The beads have diameters of about 1.25 Å and form long chainlike aggregates with a low coordination number.[23] According to fractal geometry, such a surface is smooth and featureless.[24] All three of the methods which have been discussed indicate that $D = 2$ in this silica. On a scale below about 100 Å (i.e., on a scale smaller than the size of the surface structure), the surface in Aerosil is locally smooth. On this scale, N_2 adsorption data, when analyzed with method 2, yield[25] $D = 2.02 \pm 0.06$ for distances under 100 Å. Small-angle x-ray scattering measurements[26] give the same fractal dimension on scales below 100 Å. Also, according to ET studies[27] like those used in the study of mesoporous silica, $D = 2.0 \pm 0.2$.

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