

# Reaction Efficiency on the Surface of a Porous Catalyst

Roberto A. Garza-López

Department of Chemistry, Pomona College, Claremont, California 91711

John J. Kozak

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received: February 25, 1999; In Final Form: April 25, 1999

The influence of geometrical factors on the efficiency of diffusion-controlled reactive processes that take place on the surface of a porous catalyst particle is studied using the theory of finite Markov processes. The reaction efficiency is monitored by calculating the mean walklength  $\langle n \rangle$  of a randomly diffusing atom/molecule before it undergoes an irreversible reaction at a specific site (reaction center) on the surface. The three cases (geometries) considered are as follows. First, we assume that the surface is free of defects and model the system as a Cartesian shell (Euler characteristic,  $\Omega = 2$ ) of integral dimension  $d = 2$  and uniform site valency  $\nu_i = 4$ . Then, we consider processes in which the diffusing reactant confronts areal defects (excluded regions on the surface); in this case, both  $d$  and  $\Omega$  remain unchanged, but there is a constriction of the reaction space, and the site valencies  $\nu_i$  are no longer uniform. Finally, the case of a catalyst with an internal pore structure is studied by modeling the system as a fractal solid, viz. the Menger sponge with fractal dimension  $d = 2.73$ . The sensitivity of the reaction efficiency to the dimensionality of the reaction space (integer vs fractal), to the local symmetry at the reaction center (as defined by the site valency  $\nu_i$ ), and to the size of the catalyst particle (as specified by the number  $N$  of lattice sites defining the system) is quantified by comparing the numerically exact values of  $\langle n \rangle$  calculated in each case.

## I. Introduction

The study of kinetic processes in microheterogeneous systems has received increasing emphasis over the past three decades,<sup>1–5</sup> with some of the most significant advances in this area reported by Professor J. Kerry Thomas and co-workers.<sup>5</sup> It is our intention in this paper to recognize the influence of Thomas on the field by examining in some detail just one of the points made in an important review<sup>6</sup> he wrote in 1993. In that work, he commented on the porous nature of many solids, an essential property for providing a large surface area for adsorption, and noted that there arise “dimensionality problems which are usually discussed in terms of fractals.” The survival probability ( $B^*$ ) of an excited donor surrounded by acceptors can be described by the equation

$$B^* = e^{\gamma[(t/\tau)(d/6) + (t/\tau)]}$$

where  $d$  is the fractal dimension of the surface containing the donor and acceptor,  $\tau$  is the fluorescence lifetime,  $t$  is the time, and  $\gamma$  is an adjustable parameter which contains the concentration of the acceptor. Citing the application of this equation to the donor rhodamine B and the acceptor malachite in porous Vycor glass,<sup>7</sup> where a fit of the data gave the values  $\gamma = 6$  and  $d = 1.74$ , he commented, “A criticism of the above treatment is that experimental data can be fitted well by many mathematical forms. Hence, often the tendency is to select a model, usually without experimental backing, and describe the data completely in terms of the suggested model.”

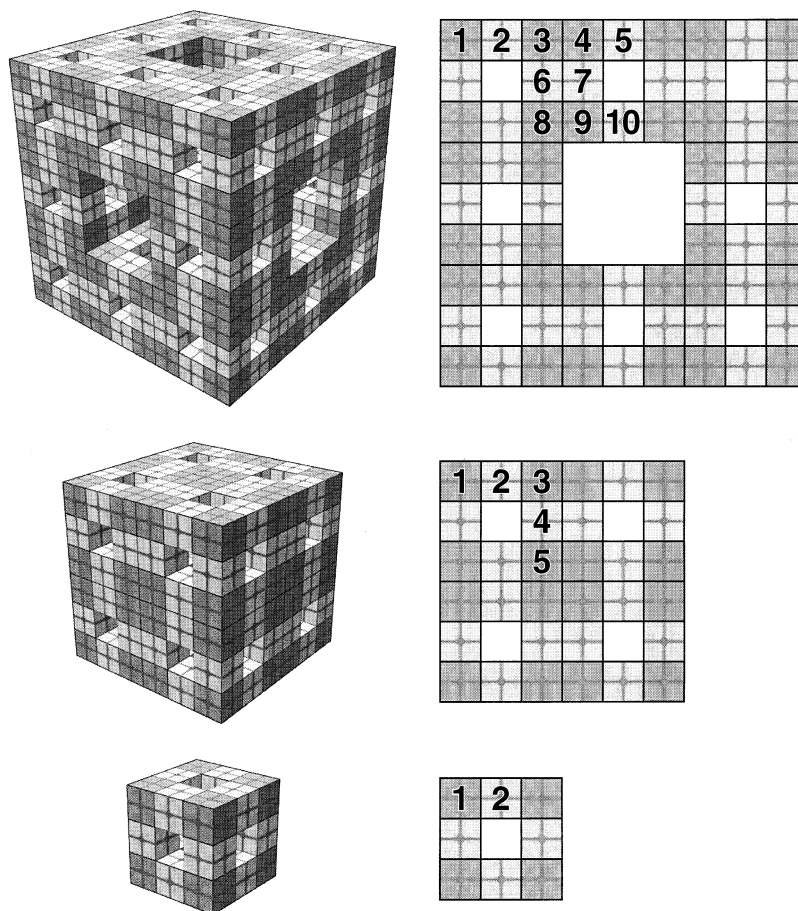
In this paper, we shall describe one possible approach for removing the arbitrariness associated with fitting such experimental data to an assumed functional form. We shall proceed

by choosing a self-similar figure of specific fractal dimension<sup>8,9</sup> and then study systematically and quantitatively the geometrical factors that influence the efficiency of reaction between a diffusing atom/molecule and a target molecule anchored on the surface. The fractal solid studied here is the Menger sponge,<sup>10–12</sup> a fractal of dimension  $d = \ln 20 / \ln 3 = 2.73\dots$  Studies of diffusion–reaction processes taking place on this fractal solid have been reported recently;<sup>13–14</sup> these studies provide the first insights on the dynamic processes taking place in a system in which the dimensionality is intermediate between the integer dimensions  $2 < d < 3$ . There is also a certain symbolism in choosing the Menger sponge as the basis for the paper presented for this issue, because the first academic appointment of the Viennese mathematician Karl Menger when he came to the United States and the first academic appointment of Kerry Thomas were at the same university, the University of Notre Dame.

In the final section, we comment on the possible relevance of this work to an experimental study of the apparent fractional dimensionality of uranyl–exchanged zeolites.<sup>15</sup>

## II. Specification of the Model

The diffusion–reaction model studied in this paper is designed to allow an evaluation of changes in the reaction efficiency when one relaxes the assumption that the surface of the catalyst particle is free of defects. We shall consider first the case where a reactant diffusing on the surface encounters regions on the surface which are inaccessible to the reactant. We shall then study the case where the reactant has access to an inner pore structure of the catalyst particle, so that it can diffuse both on and within the catalyst. As noted in the Abstract,



**Figure 1.** Representation of the three geometries considered in this paper. The figure at the bottom of the diagram is denoted I in the text, the middle figure as II, and the figure at the top as III.

the consequences of adopting these different geometries will be quantified by calculating (exactly) the mean walklength  $\langle n \rangle$  of the diffusing coreactant before it undergoes an irreversible reaction at a specific site on the surface of the catalyst. The calculations of  $\langle n \rangle$  are performed using methods based on the theory of finite Markov processes;<sup>16</sup> it can be shown that  $\langle n \rangle$  is simply related to the reciprocal of the smallest eigenvalue of the stochastic master equation describing the time evolution of the system, so that  $\langle n \rangle$ , in fact, describes the long-time behavior of the diffusion–reaction process.<sup>17–19</sup>

The specifics of the model can be described by referring to Figure 1. Consider first the figure at the bottom of the diagram. As will be developed later, the “cube with holes” is, in fact, the first generation (I) of a fractal solid with fractal dimension  $d = 2.73 \dots$ , the Menger sponge. The shading of the blocks making up the figure has no significance other than to permit an easier visualization. On this figure is “etched” a lattice, with the center of each face of each small block defining a specific lattice site; connections or pathways between lattice sites are depicted by lines or bonds, as shown. Note that the valency  $\nu_i$  of the lattice is uniform, with all  $\nu_i = 4$ . In this paper, we study the reaction efficiency in the case where the reaction center is anchored on the surface; hence, it is important to specify the symmetries of the surface sites. For example, there are sites of two distinct symmetries on the surface of I; these are noted in the diagram to the right of the cube.

The three scenarios considered in this study can now be defined precisely by referring again to the geometry, I. First, imagine that all the surface holes are covered, and at the center of each “cover” is placed a lattice point; this site will be four-coordinated to its first nearest neighbors, and the surface lattice

as a whole will have  $N = 54$  sites, each of valency  $\nu_i = 4$ , accessible to the diffusing coreactant.

In the second case, we again imagine that the surface “holes” are covered but now assume that the covered regions are inaccessible to the diffusing coreactant. In this case, not all sites accessible to the coreactant will have the same valency; the site labeled “1” will have a valency  $\nu_i = 4$ , while the site labeled “2” will have valency  $\nu_i = 3$ . Moreover, consideration of the excluded surface regions leads to a constriction in the reaction space. Specifically, the problem of studying the influence of areal defects translates into the lattice-statistical problem of calculating the mean walklength  $\langle n \rangle$  on a Cartesian shell (Euler characteristic,  $\Omega = 2$ ) of dimension  $d = 2$ , but with fewer lattice sites (viz., here  $N = 48$ ) and with sites of different valency.

Finally, we wish to consider changes in the reaction efficiency when the diffusing coreactant has access to the inner pore structure of the catalyst. In this case, a particle situated at site 2 in the figure can find its way into the interior of the cube, with each lattice site (both in the interior and on the surface) characterized by a uniform valency,  $\nu_i = 4$ . The dimensionality of this figure is  $d = \ln 20 / \ln 3 = 2.73 \dots$ , and the total number of lattice sites accessible to the diffusing particle is  $N = 72$ .

Displayed in Figure 1 are three generations of lattice geometries. We denote the simplest structure (at the bottom) as I, the structure at the center as II, and the elaborated structure at the top as III. The structure III is the second, self-similar generation of the  $N = 72$  Menger sponge; the associated lattice has  $N = 1056$  total sites. The intermediate structure II was studied because, in this case, the number of internal lattice sites is exactly equal to the number of surface sites (see later text).

**TABLE 1: Values of the Mean Walklength  $\langle n \rangle$  for the Three Structures, I, II, and III**

geometry	reaction center site	$\langle n \rangle_S$	$\langle n \rangle_D$	$\langle n \rangle_M$
I		$N = 54$	$N = 48$	$N = 72$
	1	90.343	83.021	121.705
	2	86.206	99.585	116.479
II		$N = 216$	$N = 192$	$N = 384$
	1	482.136	460.684	823.861
	2	453.821	511.888	773.717
	3	441.177	413.838	738.276
	4	436.689	483.536	706.693
	5	432.876	402.161	704.485
III		$N = 486$	$N = 384$	$N = 1056$
	1	1248.687	1118.344	2542.604
	2	1180.086	1216.327	2397.092
	3	1140.343	1035.285	2270.147
	4	1119.995	1025.430	2228.183
	5	1113.686	1156.746	2236.462
	6	1129.120	1194.568	2170.784
	7	1114.203	1228.874	2152.696
	8	1115.831	1064.126	2104.022
	9	1106.322	1254.162	2090.323
	10	1102.955	1538.772	2127.889

The program of calculation can now be summarized. For each case (I, II, III), a reaction center is placed at one of the symmetry-distinct sites on the surface. The value of  $\langle n \rangle$  is then calculated for the three situations described earlier, viz., diffusion on a defect-free surface, diffusion on a surface with areal defects, and finally diffusion on/within a fractal solid. The calculations are then repeated for each of the symmetry-distinct sites on each geometry (2 cases for I, 5 cases for II, and 10 cases for III). The full set of results generated in these calculations will be discussed in the following section.

### III. Results

Listed in Table 1 are the values calculated for the mean walklength  $\langle n \rangle$  for each of the cases considered. The location of the reaction center is specified in column 2, with  $\{1, 2, \dots\}$  in each case referring to the sites coded in the diagrams accompanying the structures I, II, III. The entries  $\langle n \rangle_S$ ,  $\langle n \rangle_D$ , and  $\langle n \rangle_M$  then denote, respectively, the  $\langle n \rangle$  values for the case of coreactant trajectories confined to the surface (only) of the respective geometry, for the case where the diffusing particle confronts areal defects, and for the case where the reactant has access to the interior of the catalyst particle.

Before proceeding, we note that there is a very sensitive test of the accuracy of these calculations. Montroll<sup>20</sup> showed that the mean walklength initiated from each of  $m$  sites nearest-neighbor to the trap, when summed and then divided by the valency of the lattice, equals the integer  $N - 1$  exactly, provided that all sites of the lattice are characterized by the same value of the valency; that is, he showed that

$$(\langle n \rangle_{i,1} + \langle n \rangle_{i,2} + \dots + \langle n \rangle_{i,m})/m = N - 1$$

exactly. In the present study, this quantity was calculated for all cases reported under  $\langle n \rangle_S$  and  $\langle n \rangle_M$  (where the uniform valency condition is satisfied), and the associated integer value,  $N - 1$ , was confirmed numerically to the number of significant figures reported in Table 1.

When placed within the context of theoretical results obtained by Montroll, some remarkable conclusions can be drawn from the data presented in Table 1. Montroll<sup>21</sup> showed that the mean walklength  $\langle n \rangle$  could be calculated exactly in dimension  $d = 1$ ,

**TABLE 2: Values of the Mean Walklength  $\langle n \rangle$  for Lattices of Integer Dimension**

$N$	$d = 2; \nu = 4$	$d = 3; \nu = 4$
48	69.859	65.800
54	80.481	74.991
72	113.525	102.831
192	360.530	293.212
216	413.510	331.794
384	804.236	604.003
384	804.236	604.003
486	1053.851	770.410
1056	2548.538	1707.341

and that asymptotic analytic results could be obtained in the integer dimensions  $d = 2, 3$ . In particular, he showed that

$$\langle n \rangle = \frac{N(N+1)}{6} \quad d = 1 \quad (1)$$

$$\langle n \rangle = \frac{N}{N-1} \{A_1 N \ln N + A_2/N + A_3 + A_4/N\} \quad d = 2 \quad (2)$$

with the coefficients  $\{A_1, A_2, A_3, A_4\}$  dependent on the valency of the  $d = 2$  lattice, and

$$\langle n \rangle = 1.516\,386\,0591N + O(N^{1/2}) \quad d = 3 \quad (3)$$

for the simple cubic lattice ( $\nu = 6$ ).

Two critical conclusions can be drawn from his work. First, for a given number  $N$  of lattice sites, the quantity  $\langle n \rangle$  behaves like  $\langle n \rangle \sim N^2$  in  $d = 1$ , like  $\langle n \rangle \sim N \ln N$  in  $d = 2$ , and like  $\langle n \rangle \sim N$  in  $d = 3$ . Thus, for given  $N$ , the mean walklength  $\langle n \rangle$  decreases with increase in the dimensionality of the lattice. Second, Montroll found that for a given dimension  $d$ , the value of  $\langle n \rangle$  is dependent on the valency of the lattice. For example, in  $d = 2$ , the lead coefficient in the representation, eq 2, is  $A_1 = 3^{1/2}/2\pi$  for  $\nu = 6$ ,  $A_1 = 1/\pi$  for  $\nu = 4$ , and  $A_1 = (3^{1/2})/4\pi$  for  $\nu = 3$ . Thus, for a given dimension (here,  $d = 2$ ) and fixed lattice size  $N$ , the value of  $\langle n \rangle$  decreases with increase in the (uniform) valency of the lattice.

Listed in Table 2 are values of  $\langle n \rangle$  calculated for lattices of integer dimensionality and specified (uniform) valency, corresponding to the  $N$  values reported in Table 1. The results in Table 2 were determined either from Montroll's analytic expressions, eqs. (2, 3), as refined by den Hollander and Kasteleyn<sup>22</sup> or from previously reported polynomial representations<sup>23</sup> of results calculated numerically for  $\langle n \rangle$  on lattices with various values of  $N$ ,  $d$ , and  $\nu$ .

The data displayed in Table 1 can most easily be analyzed by constructing ratios and then comparing the consequent values with respect to lattice size  $N$ , lattice valency  $\nu_i$  and lattice dimensionality (integer or fractal). In particular, we define the quantities

$$R_D = \frac{\langle n \rangle_D}{\langle n \rangle_S}$$

and

$$R_M = \frac{\langle n \rangle_M}{\langle n \rangle_S}$$

i.e., we calibrate for each structure the results calculated for  $\langle n \rangle$  relative to the value of the mean walklength for a particle diffusing on the surface of a defect-free Cartesian shell (Euler characteristic,  $\Omega = 2$ ),  $d = 2$ , and uniform valency  $\nu = 4$ .



On the basis of Montroll's work on lattices of integer dimension, one would anticipate that the calculated walklength should correlate with  $N$ , viz., the larger the lattice, the longer the walklength. Considering first the case of a catalyst particle with areal defects ( $\Omega = 2$ ,  $d = 2$ ), we find that the behavior of  $\langle n \rangle_D$  relative to  $\langle n \rangle_S$  is more subtle. If the reaction center is anchored at a site of valency  $\nu_i = 4$ , the  $N$ -dependence is as expected, i.e.,  $\langle n \rangle_D < \langle n \rangle_S$ ; however, positioning the reaction center at a site of valency  $\nu_i = 3$  or  $\nu_i = 2$  results in a calculated  $\langle n \rangle$  value for the defect case that is greater than that calculated for the defect-free Cartesian shell, even though, on the basis of the theoretical  $N$  dependence, one would expect exactly the opposite behavior. This result, which pertains to all three structures (I, II, III), demonstrates the extraordinary sensitivity of the reaction efficiency to the number of nearest-neighbor pathways leading from the surrounding lattice to the reaction center.

Turning next to the case of the fractal solid, we find at first glance that the values of  $\langle n \rangle_M$  and related ratios  $R_M$  for the porous catalyst are systematically in accord with the results of Montroll, viz.,

$$\langle n \rangle_M > \langle n \rangle_S$$

for all three cases, I–III. However, Montroll's results were obtained for lattices of integer dimension, and so the important question is whether the calculated values of  $\langle n \rangle$  for the Menger sponge, a fractal of dimension  $d = 2.73$ , lie between the corresponding values calculated for  $\langle n \rangle$  in  $d = 2$  and  $d = 3$ . In earlier work,<sup>13,14</sup> we showed that this expectation is strictly satisfied for the Menger sponge when one performs calculations in which all symmetry-distinct sites, both internal and external in the geometries represented in the structures I and III, are taken into account; specifically, one constructs the overall mean walklength  $\langle \bar{n} \rangle$  by averaging over all sites of the lattice and then compares the resultant  $\langle \bar{n} \rangle$  with values corresponding to those in Table 2. The results reported here show that this correlation holds even if one restricts consideration to surface-only locations of the reaction center except for a few special site locations (viz., the corner sites in all cases and the additional site 2 in I).

As is seen from Table 3, for each of the Menger geometries, the ratios  $R_M$  are in approximate accord with the ratio of sites, i.e.,

$$R_M \sim \frac{N_M}{N_S} \quad (4)$$

where, again,  $N_M$  is the total number of sites accessible to the diffusing coreactant (exterior and interior), and  $N_S$  is the number of surface-only sites. Thus, for the case of unbiased, nearest-neighbor random walks, this ratio provides a useful, first-order estimate of the dilation in time scale when a diffusion-controlled reactive process takes place on the surface of a solid with an internal pore structure. The relation 4 may be thought of as a counterpart to the kind of power-law scaling relation

$$\text{interaction property} \sim r^d \quad (5)$$

(where  $r$  is the size of the object and  $d$  is an empirical exponent related to a "fractal dimension") often used in the interpretation of phenomena<sup>24–29</sup> in problems as diverse as physisorption, chemisorption, thermal decomposition, noncatalytic reactions,

TABLE 3: Ratios  $R_D$  and  $R_M$

geometry	reaction center site	$N_D/N_S$	$\nu_D$	$R_D$	$N_M/N_S$	$\nu_M$	$R_M$
I		0.888			1.333		
	1		4	0.919		4	1.347
	2		3	1.155		4	1.351
II		0.888			1.753		
	1		4	0.956		4	1.709
	2		3	1.128		4	1.705
	3		4	0.938		4	1.673
	4		3	1.107		4	1.618
	5		4	0.929		4	1.627
III		0.790			2.173		
	1		4	0.896		4	2.036
	2		3	1.031		4	2.031
	3		4	0.908		4	1.991
	4		4	0.916		4	1.989
	5		3	1.039		4	2.008
	6		3	1.058		4	1.923
	7		3	1.103		4	1.932
	8		4	0.954		4	1.886
	9		3	1.134		4	1.889
	10		2	1.395		4	1.929

catalytic reactions with supported metal catalysts, and photochemical reactions with semiconductors.

#### IV. Concluding Remarks

As indicated in the Introduction, our intention in this paper was to examine the geometrical factors which influence dynamic processes in a porous solid media. As a counter point to the more usual procedure of fitting experimental data to an assumed functional form to extract the fractal dimension of the solid, the approach taken here is exactly the opposite. We start by choosing a well-defined, self-similar figure and then calculate for this fractal (numerically exact) values of the mean walklength  $\langle n \rangle$  of a diffusing coreactant on the surface before trapping. The  $\langle n \rangle$  is a sensitive signature of the underlying dynamical process and, as we have shown here, is clearly dependent on the dimensionality of the system (integral vs fractal), the number of nearest-neighbor pathways to the active site, and the extent of the reaction space. It is important to emphasize that, once the model was defined, no further assumptions were made or approximations introduced in elaborating the dynamical consequences of changes in ( $N$ ,  $d$ ,  $\nu$ ) values; the results reported for  $\langle n \rangle$  are numerically exact.

It is of interest to relate the present work to experimental studies on one class of porous catalysts that has received much attention in the literature, both for their intrinsic interest and for their commercial importance, viz., the set of aluminosilicate structures known as zeolites. These lattice systems are characterized by translational symmetry (with excluded volumes), in contrast to fractal systems (such as the Menger sponge) which have dilation symmetry (and, in the  $n$ th generation, holes of different sizes).

In an earlier study, Yang et al.<sup>15</sup> used the Klafter–Blumen (KB) theory<sup>27</sup> for one-step energy transfer processes on fractal structures to suggest a corresponding theoretical relationship for energy-transfer on zeolite systems. In particular, an equation similar to the KB equation was used to determine the "apparent fractional" dimension of four uranyl-exchanged zeolites for the observed decay of the uranyl ion (donor) emission in the presence of europium ion as acceptor. These authors showed that the "apparent fractional" dimensions of the zeolites A, Y, mordenite, and ZMS-5, assuming a dipolar exchange mechanism, were 2.43, 2.47, 2.66, and 1.30, respectively. The first

three values are close to the (exact) fractal dimension of the Menger sponge (viz., 2.73), suggesting that the fractal lattice studied here might serve as a model for reactive processes in certain zeolite systems. For example, Turro<sup>30</sup> and colleagues studied the size/shape selectivity of *o*-methyldibenzyl ketone (o-ACOB) absorbed on ZSM zeolites. At room temperature, on photolysis of o-ACOB, fragments o- $\dot{A}$  and  $\dot{B}$  are formed and can recombine; owing to steric effects, the products o-A-o-A and o-A-B are formed on the external zeolite surface (only) whereas the product B-B is found on the internal surface. It was noted that the B-B product can result by recombination of  $\dot{B}$  fragments either on a surface within the zeolite or on the external surface, followed by sieving of B-B into the zeolite. The B-B reaction is found to exhibit a pronounced temperature effect, with the percentage of B-B formed on the external surface increasing as the temperature decreases. Turro argues that this experimental effect can be understood if there is "a relatively high activation energy for sieving of  $\dot{B}$  radicals from the external to the internal surface."

Our calculations would apply to the situation in which a  $\dot{B}$  fragment formed on the surface in the photolysis event can either recombine with another  $\dot{B}$  fragment on the surface or, upon entering and diffusing through the internal pore structure of the catalyst, return to the surface and react there to form B-B. As gauged by our determination of  $\langle n \rangle_M$  versus  $\langle n \rangle_S$  or  $\langle n \rangle_D$ , it is clear that the latter process is considerably less efficient than surface-only recombination events, a difference which would be further enhanced if the mean displacement time for migration through the catalyst was longer than for surface-only diffusion-reaction events.

## References and Notes

- (1) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.
- (2) Gratzel, M.; Kalyanasundaram, K. *Kinetics and Catalysis in Microheterogeneous Systems*; Marcel Dekker: New York, 1991.

- (3) *Photochemistry in Organized and Constrained Media*, Ramamurthy, V., Ed.; VCH: New York, 1991.
- (4) Bard, A. J. *Integrated Chemical Systems: A Chemical Approach to Nanotechnology*; Wiley: New York, 1994.
- (5) Thomas, J. K. *Chemistry of Excitation at Interfaces*; ACS Monograph 191; American Chemical Society: Washington, DC, 1983.
- (6) Thomas, J. K. *Chem. Rev.* **1993**, 93, 301.
- (7) Pines, D.; Huppert, D.; Avenir, D. *J. Chem. Phys.* **1988**, 89, 1177.
- (8) Mandelbrot, B. B. *The Fractal Geometry of Nature*; Freeman: San Francisco, 1983.
- (9) Peitgen, H.-O.; Jürgens, H.; Sape, D. *Chaos and Fractals*; Springer: New York, 1992.
- (10) Menger, K. *Dimensionstheorie*; B. G. Teubner: Leipzig, 1928.
- (11) Blumental, L.; Menger, K. *Studies in Geometry*; Freeman: San Francisco, 1970.
- (12) Menger, K. *J. Graph. Theory* **1981**, 5, 341.
- (13) Kozak, J. J. *Chem. Phys. Lett.* **1997**, 275, 199.
- (14) Garza-Lopez, R. A.; Ngo, M.; Delgado, E.; Kozak, J. J. *Chem. Phys. Lett.*, in press.
- (15) Yang, C.-I.; El-Sayed, M. A.; Suib, S. L. *J. Phys. Chem.* **1987**, 91, 4440.
- (16) Walsh, C. A.; Kozak, J. J. *Phys. Rev. Lett.* **1981**, 47, 1500. Walsh, C. A.; Kozak, J. J. *Phys. Rev. B* **1982**, 26, 4166. Politowicz, P. A.; Kozak, J. J. *Phys. Rev. B* **1983**, 28, 5549.
- (17) Montroll, E. N.; Shuler, K. E. *Adv. Chem. Phys.* **1958**, 1, 361.
- (18) Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; Wiley: New York, 1977.
- (19) Haken, H. *Synergetics*; Springer-Verlag: Heidelberg, 1977.
- (20) Montroll, E. W. *Proc. Symp. Appl. Math.*; Am. Math. Soc. **1964**, 16, 193.
- (21) Montroll, E. W. *J. Math. Phys.* **1969**, 10, 753.
- (22) den Hollander, W. Th. F.; Kasteleyn, P. W. *Physica A* **1982**, 112A, 523.
- (23) Politowicz, P. A.; Kozak, J. J. *Mol. Phys.* **1987**, 62, 939.
- (24) *Molecular Dynamics in Restricted Geometries*; Klafter, J., Deake, J. M., Eds.; Wiley: New York, 1989.
- (25) *The Fractal Approach to Heterogeneous Catalysis*; Avnir, D., Ed.; Wiley: Chichester, 1989.
- (26) Klafter, J.; Deake, J. M.; Blumen, A. *Lumin.* **1984**, 31, 642.
- (27) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1985**, 80, 874.
- (28) *Fractal and Disordered Systems*; Bunde, A., Havlin, S., Eds.; Springer-Verlag: Heidelberg, 1991.
- (29) Avenier, D.; Carberry, J. J.; Citri, O.; Farin, D.; Grätzel, M.; McEvoy, A. J. *Chaos* **1991**, 1, 397.
- (30) Turro, N. J. *Pure Appl. Chem.* **1986**, 58, 1219.