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Fractal clustering of reactants on a catalyst surface

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The islands of adsorbed molecules in an $A+B\rightarrow AB$ reaction model on a two-dimensional catalyst surface (with no surface diffusion) are found to be fractal with dimension $D=1.90\pm0.03$.

When catalytic reaction occurs on a plane surface, clusters or islands of unreacted adsorbed species may form. Such islands have been seen, for example, in the catalysis of $CO+\frac{1}{2}\,O_2\rightarrow CO_2$ on palladium and platinum crystal surfaces.[1] Recently, a dynamical computer simulation of a simplified model for this reaction was found to produce such islands,[2] and an obvious and practically important question is whether these clusters are fractal in nature. This question is important because the shape and, especially, the perimeter of the clusters determines the turnover frequency (the rate of the reaction).

Here we investigate the cluster properties in the reaction model[2] of $A+B\rightarrow AB$. This model has the virtues that its transition point is known exactly and the dynamics are somewhat simpler than those of the CO system. In this model, the catalyst surface is represented by a two-dimensional lattice of reactive sites, and a trial is composed of the following steps: (1) A molecule from the gas phase impinges on a randomly chosen site. That molecule is randomly chosen to be A with P_A and B with probability $P_B=1-P_A$. (2) If the site is already occupied by an adsorbed molecule, the impinging molecule bounces off and the trial ends. (3) Otherwise, the molecule adsorbs, and immediately the four nearest neighbors are checked. (4) If any of the neighbors is of the opposite kind as the newly adsorbed molecule, a reaction occurs and the AB product desorbs immediately (the two sites are made blank). If more than one neighbor can react, then one is chosen randomly. If no reaction neighbors are found, then the impinging molecule remains adsorbed at the site, and a new trial is started.

After many of these trials are carried out on the lattice, clusters of A and B molecules appear, separated from each other by at least a perimeter of blank sites. The clusters fluctuate in size, disappear, and reform. For $P_A<0.5$, the surface eventually is covered with B, while for $P_A>0.5$, it is covered with A. Exactly at $P_A=\frac{1}{2}$, an apparently steady-state, reactive configuration develops, with clusters in a range of sizes as shown in Fig. 1.

It is natural to suppose that at this critical point, the clusters form a hyperbolic distribution

$$n_s\sim s^{-\tau} \tag{1}$$

on an infinite lattice, where n_s is the number of clusters (per site) of size s of either A or B molecules. Equation (1) implies that for a finite lattice, a cluster as big as the lattice will eventually appear and completely cover the surface. Indeed, this phenomenon was seen in our previous studies of this model on a fairly small lattice (128×256 sites). Therefore, to study the behavior for large times, a larger lattice is needed.

We thus carried out a simulation on a square lattice of 1024×1024 sites, using periodic boundary conditions. The simulation was carried out for 6500 time steps, where a unit of time is defined as $2^{20}=1\,048\,576$ trials, or one visit

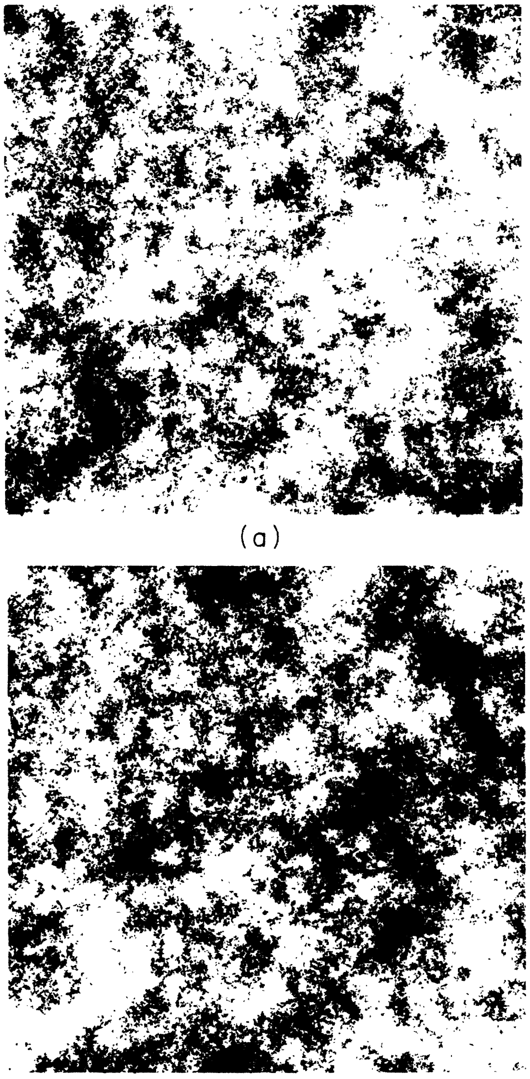

FIG. 1. A representation of the adsorbed A (a) and B (b) molecules on a 1024×1024 catalyst surface after 6.8×10^9 trials or 6500 time steps at $P_A=\frac{1}{2}$.

per site, on the average. For one side of the lattice to communicate with the other 1024 sites away, one would expect about 1024 time steps would be needed, and our simulation was about 6.3 times this amount. After each time step, the lattice was scanned for the size and radius of gyration of each cluster. Those clusters spanning the boundaries of the system were also included, and a check was made to see if the maximum extent of a cluster was greater than half the size of the lattice, which would imply a violation of the periodic boundary conditions and a possible communication of a single cluster in two opposite directions. This violation never occurred during the 6500 time steps.

The resulting clusters of A and B adsorbed molecules at $t = 6500$ are shown in Fig. 1. In Fig. 2, we show the size distribution plotted as a function of the size on a log-log plot, averaged over the time steps in the range 0–1000, 4000–4250, and 6250–6500. On the ordinate we plot N_s, the number of clusters with sizes between s and $2s-1$, and the scale is shifted for each time to make the curves more visible. It can be seen that the average cluster size increases as time progresses, and a hyperbolic distribution develops, as evidenced by a straight line on this plot. The slope of that line should be $1-\tau$, and mass conservation requires that $\tau > 2$, so the slope must be less than -1. The dotted line in Fig. 1 is of slope -1, and it can be seen that a value of τ slightly greater than 2 is developing for smaller cluster sizes ($s < 128$) as time is progressing. It seems possible that τ is close to the percolation value 2.05. However, the determination of τ on a lattice of this size is very difficult because of the boundary effects, and here it is further complicated by the fact that the system is not really in equilibrium and the clusters are still growing. We stopped the simulation at 6500 time steps because we did not want to run the system to the point where clusters spanning half the lattice were formed.

The clusters appear quite solid (see Fig. 1), with few holes or inclusions, but the boundary is rather ramified and suggests fractal geometry. For such compact clusters, the correlation function method of determining the fractal dimension D of a single large cluster is inaccurate even for the large clusters considered here, and the radius-of-gyration method for an ensemble of clusters is preferred. Here, D is defined by

$$R_g \sim s^{1/D} . \tag{2}$$

In Fig. 3 we plot the average R_g as a function of s, in each bin, averaged over the 250 steps $t = 6250$–6500. There was no tendency for this value to increase of decrease monotonically as time progressed, and only fluctuations seemed to occur. Averaging the slope over this and earlier time periods, and leaving out the endpoints, we find $D = 1.90 \pm 0.03$. The value $D = 2$ seemed to be ruled out. Note that this value of D implies a value of $\tau = 2.05 \pm 0.02$ according to the formula $\tau - 1 = 2/D$.[3-6] These values of τ are consistent with the observations in Fig. 1.

The value of D is similar to that of percolation clusters which, however, do not show the solidity of these clusters (at least on a small length scale). The D is also similar to the value found by Grest and Srolovitz for quenched Ising clusters.[7] However, for Ising clusters this value of D is really a reflection of the percolation initial condition, and when one waits long enough, the value of D changes on all length scales.[4] In contrast, in our model, the value of 1.9 appears to represent the steady-state, long-time behavior of D.

Could the A and B clusters be essentially Eden clusters for which $D = 2$? In the Eden model, cluster growth occurs at a randomly chosen perimeter site, producing solid, nonfractal clusters. Likewise, in the AB model, the next point of growth of a given cluster is "chosen" by the impinging molecule at a random place on the perimeter. However, in contrast to the Eden model which concerns only a single cluster, the AB model contains a collection of

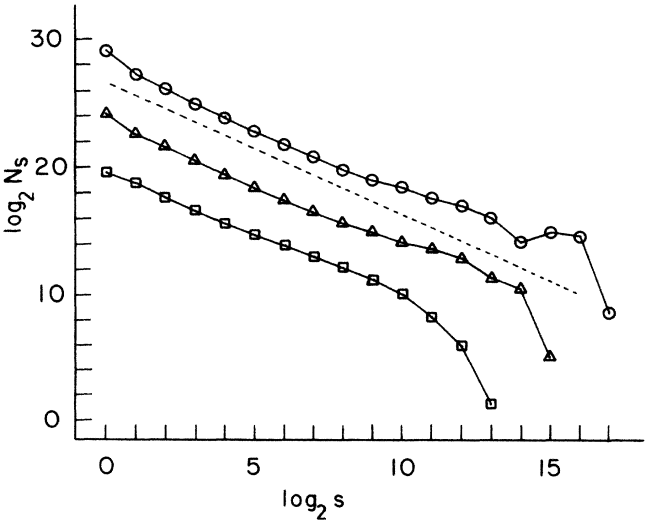

FIG. 2. A plot of the number of clusters in the range s to $(2s-1)$, for $t = 0-1000$ (□), 4000−4250 (△), and 6250 −6500 (○) time steps. The dotted line has slope equal to -1, and shows that τ is close to 2.

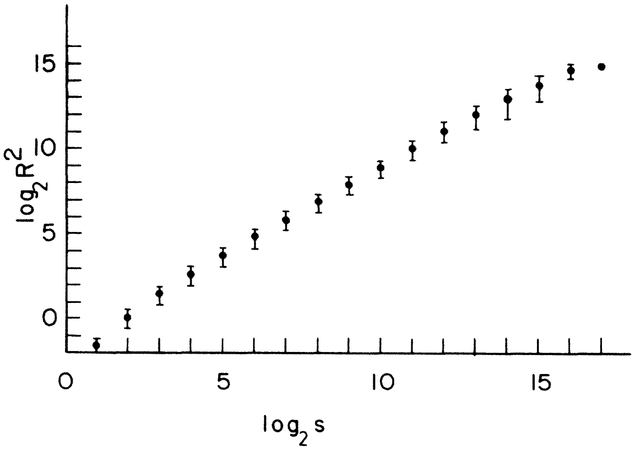

FIG. 3. A plot of the radius of gyration for the clusters in the 6250–6500 time interval, showing the standard deviation of the data. The last point has no error bars since it represented a single cluster of $> 2^{17}$ sites. A linear least-squares fit of the slope (excluding the endpoints), averaged with previous time intervals, gives $D = 1.90 \pm 0.03$.

clusters of all sizes which can link together (or break apart). This "cascading of scales" can lead to fractal structure, even though the point of growth is chosen randomly.

In fact, for an Eden-type model with a large number of growing sites randomly distributed in space, the fractal dimension of the large clusters produced when many islands link together must be $D_{\text{percolation}}$, since this is essentially a percolation process. In the AB model, this argument is somewhat complicated by the reversible nature of the mechanism. However, if one believes that the clusters formed here are essentially blobs randomly linked together, then D should also equal $D_{\text{percolation}}$ for the AB model.

We note that a related model was considered by Wicke, Kummann, Keil, and Scheifler[8] in which the reaction was also $A+B \rightarrow AB$, but with the limiting step being determined by the reaction rather than the impingement rate. Thus, the lattice is always covered by A and B molecules which are randomly chosen to react and desorb, and the vacated sites are immediately replaced by new A's and B's. As in our model, a state where the surface is not covered by one species occurs only for $P_A = \frac{1}{2}$. We would expect that this model would give clusters with a morphology and fractal dimension very similar to that of the model presented here.

Practical systems usually involve substantial diffusion and spontaneous desorption, so in a realistic model, these processes would have to be taken into account. Still, we find it interesting that in a simple caricature of that system, fractal islands are found. In a recent study, Silverberg, Ben-Shaul, and Rebentrost[9] have studied a Monte Carlo model of A-B reaction on a catalyst, in which surface hopping and interactions between the molecules was included. Indeed, their model also shows solid islands with ramified perimeters like those in Fig. 1.

Further work is being carried out to study the perimeter of these clusters, to compare those perimeters to those of percolation clusters,[6,10] and especially to study the relation between the properties of the perimeters and the activity of the catalyst.

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[1] T. Engel and G. Ertl, *Advances in Catalysis* (Academic, New York, 1979), Vol. 28, pp. 1–78.

[2] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).

[3] S. Kirkpatrick, in *Ill-Condensed Matter,* edited by R. Balian, R. Maynard, and G. Toulouse, Proceedings of the Les Houches Summer School, Session 31 (North-Holland, New York, 1983), p. 372.

[4] R. J. Harrison, G. J. Bishop, and G. P. Quinn, J. Stat. Phys. **19**, 53 (1978).

[5] B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, New York, 1983).

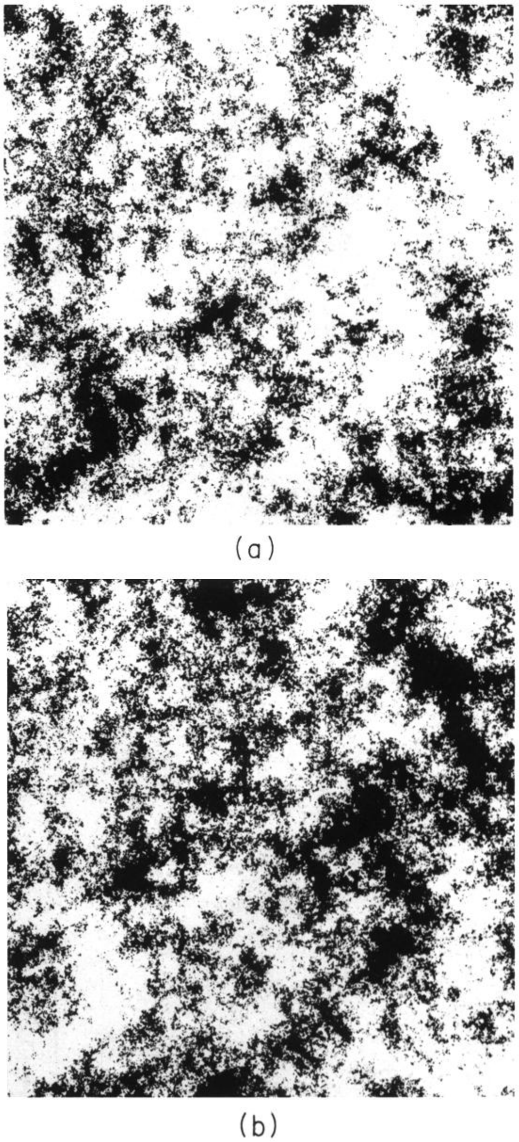
[6] R. F. Voss, J. Phys. A **17**, L373 (1984).

[7] G. S. Grest and D. J. Srolovitz, Phys. Rev. B **30**, 5150 (1984). See also P. S. Sahni and J. D. Gunton, Phys. Rev. Lett. **47**, 17545 (1981).

[8] E. Wicke, P. Kummann, W. Keil, and J. Scheifler, Ber. Bunsengese. Phys. Chem. **84**, 315 (1980).

[9] M. Silverberg, A. Ben-Shaul, and F. Rebentrost, J. Chem. Phys. **83**, 6501 (1986).

[10] R. M. Ziff, Phys. Rev. Lett. **56**, 545 (1986).


(a)

(b)

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