

## Mechanism Discrimination in Heterogeneous Catalytic Reactions: Fractal Analysis

Farhad Khorasheh,\* Ramin Radmanesh, and Mohammad Kazemeini

Department of Chemical Engineering, Sharif University of Technology, Azadi Avenue, Tehran, Iran

Reactions on catalytic surfaces can be represented by Langmuir–Hinshelwood (LH) mechanisms and, depending on the mechanism, the reaction rate has some dependence on the total concentration of surface active sites. The concentration of these sites is proportional to the surface area of the catalyst. The irregular surface of a catalyst can be modeled as a fractal and, as such, the total available surface area depends on the size of the reactant. In this paper the concept of fractal geometry has been extended to help discriminate between mechanisms for reactions of a homologous series on fractal catalytic surfaces. In the past, differences in rates for homologous reactants have been attributed to factors such as electronuclear induction and steric effects. These factors may indeed be important; however, modeling the surface as a fractal would explain the variations in reaction rate that could arise from changes in the reactant size alone. The use of fractal analysis in this context is examined with reference to data on catalytic hydrodealkylation of alkylaromatic compounds. Simple plots used in this analysis (log initial rate versus log reactant cross-sectional area) are useful in discriminating amongst possible catalytic mechanisms. To verify the effect of reactant size on the reaction rate, a two-dimensional computer simulation is performed for catalytic reactions on fractal surfaces using reactants of different sizes. A LH mechanism is utilized where the surface reaction is rate controlling. The simulation is based on a Monte Carlo approach and considers the diffusion of reactants to a fractal catalyst surface, adsorption to and desorption from the surface, and surface reaction.

### Introduction

In recent years, the phenomena of diffusion coupled with chemical reaction in disordered media has been advanced because of new developments in the area of geometry of surfaces. The structure and geometry of a catalyst surface is an important parameter that can have a significant effect on the rate of a catalytic process. However, because of the complex nature of such irregular surfaces, it seems difficult to formulate this parameter in the analysis of catalytic processes. Solid catalysts have a highly irregular surface that can not be modeled by simple Euclidean geometry. The fractal geometry has now provided the framework to analyze physical (Feder, 1988; Sahimi, 1995) and chemical (Farin and Avnir, 1987, 1988) processes in such irregular media. Recent investigations have demonstrated that the surface of many materials that are used as catalyst supports or adsorbents, such as silica and alumina, show a self-similarity over a range of characteristic lengths and, as such, can be described as fractals (Pfeifer and Avnir, 1983; Avnir et al., 1983; 1984). On this basis, many investigators have studied diffusion and reaction in fractal objects (Sahimi et al., 1990; Gutfraind and Sheintuch, 1992; Coppens and Froment, 1994, 1995a,b, 1996) where diffusion is not described by the classical relationships, so one must implement new models that take into account the fractality of the media and its effect on the diffusion process (Orbach 1984; Giona, 1991).

In this paper, the Langmuir–Hinshelwood (LH) mechanism, in which the surface reaction is the rate-

controlling step, is considered for a catalytic reaction on a fractal surface. In this situation, the reaction rate is related to the density of the active sites on the catalyst surface, which is proportional to the catalyst surface area. In addition, the number of these sites accessible to the reactant molecules is related to the fractality of the catalyst surface. In this context, scaling laws are developed to relate the reaction rate to the fractal dimension of the catalyst surface. These scaling laws depend on the type of LH mechanism (i.e., single versus dual site) and, as such, can be utilized to discriminate among possible mechanisms. A two-dimensional computer simulation is also performed to verify the scaling laws.

### Relationship between Fractal Dimension and Catalytic Reaction Rates

The most important feature of a fractal object is the fractal dimension. There are several methods to determine the fractal dimension of a catalyst surface. Some are based on adsorption measurements (Pfeifer and Avnir, 1983; Avnir et al., 1983), and others are based on X-ray diffraction (Bale and Schmidt, 1984). In adsorption experiments, the surface is covered by a monolayer of adsorbate molecules and the relationship between the number of adsorbed molecules,  $N$ , and their size is given by eq 1:

$$N \propto r^{-D_s} \propto \sigma^{-D_s/2} \quad (1)$$

where  $D_s$  is the fractal dimension of the surface, and  $r$  and  $\sigma$  are the radius and the cross-sectional area of the adsorbate molecules, respectively. The aforementioned methodologies have been applied to a variety of surfaces

\* Author to whom correspondence should be addressed.  
Fax: 98-21-6005819. E-mail: khorashe@sharif.ac.ir.

(Pfiefer and Avnir, 1983; Avnir et al., 1983) and  $D_S$  values were obtained in the natural range  $2 \leq D_S \leq 3$ . In general, fractal dimensions for many surfaces were the rule rather than exception.

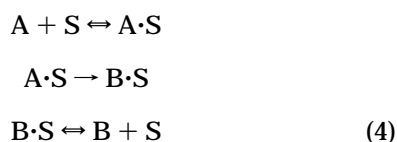
An important feature of a fractal object or phenomenon is that within a range of characteristic lengths, scaling laws of the following form can be applied:

$$\text{property} \propto (\text{scale})^\beta \quad (2)$$

In eq 2, property could represent a physical or chemical quantity, such as surface area, diffusion coefficient, reaction rate constant, etc., and the power  $\beta$  is related to the fractal dimension. One can develop scaling laws for catalytic reaction rates that utilize a characteristic length (radius of the reactant) and the surface fractal dimension. The rate of a catalytic reaction depends on the number of active sites on the catalyst surface. However, accessibility to these sites and, hence, the reaction rate is influenced by the surface structure. Smaller molecules can see more details of a fractal catalytic surface and, thus, larger reaction rates are expected compared with larger molecules to which much of the surface is not accessible. It is therefore possible to relate the catalytic reaction rate to the fractal dimension of the catalyst surface. For this purpose, the LH mechanism is considered for the following simple reaction:



One may propose a single-site or a dual-site mechanism for the overall reaction where a different scaling law may be obtained for each case. The single-site mechanism for the above reaction is as follows:



If the surface reaction is rate controlling, the overall reaction rate is given by

$$\text{rate} = \frac{dN_B}{dt} = kN_{A \cdot S} \quad (5)$$

where  $N_{A \cdot S}$  is the number of adsorbed species A,  $N_B$  is the number of product particle B, and  $k$  is surface reaction rate constant.  $N_{A \cdot S}$  can be obtained from the Langmuir adsorption isotherm as follows:

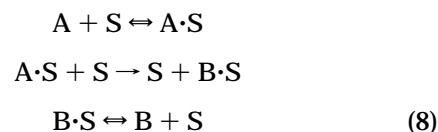
$$N_{A \cdot S} = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} N_{A \cdot m} \quad (6)$$

where  $K_A$  and  $K_B$  are adsorption equilibrium constants for species A and B, respectively, and  $N_{A \cdot m}$  is the number of adsorbed molecules A needed for monolayer surface coverage. Hence

$$\text{rate} \propto N_{A \cdot m} \propto r^{-D_S} \propto \sigma^{-D_S/2} \quad (7)$$

For a homologous series of reactants, assuming that the adsorption equilibrium constants for different homologues are not significantly different, the reaction rate decreases with increasing reactant size according to

eq 7. The dual-site mechanism for reaction 3 is as follows:



If the surface reaction is rate controlling, the reaction rate is then given by

$$\text{rate} = kC_S N_{A \cdot S} \quad (9)$$

where  $C_S$  is the concentration of vacant sites. From the Langmuir adsorption isotherm, one obtains the following expression:

$$\text{rate} = \frac{kK_A P_A N_{A \cdot m}^2}{(1 + K_A P_A + K_B P_B)^2} \quad (10)$$

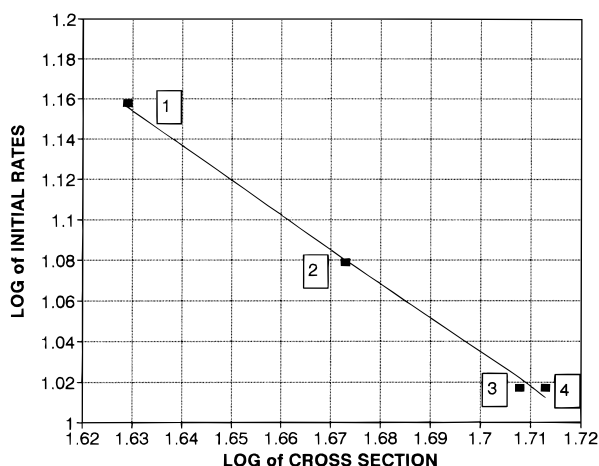
and hence

$$\text{rate} \propto N_{A \cdot m}^2 \propto \sigma^{-D_S} \quad (11)$$

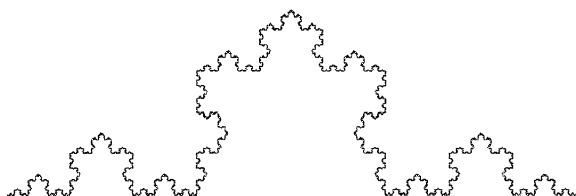
To analyze catalytic rate data in terms of the scaling laws represented by eqs 7 and 11, one needs to perform experiments with a homologous series of reactants of different sizes. The reactants should be geometrically similar so that the proportionality constant in eqs 7 and 11 will be the same for all reactants. If the fractal dimension of the catalyst surface is independently measured from experimental methods described earlier, the governing mechanism can be deduced from the log-log plot of the reaction rate versus reactant cross-sectional area in which a slope of  $-D_S/2$  would indicate a single-site and that of  $-D_S$  demonstrates a dual-site mechanism. To illustrate the utility of eqs 7 and 11, reference is made to an experimental study.

Beranek and Kraus (1966) and Machacek et al. (1966) studied the hydrodealkylation of alkylbenzenes at 350 °C and 1 atm over a nickel/alumina catalyst. The reaction involved the cleavage of the terminal bond in the alkyl group to give methane and a product that was one carbon atom shorter. They measured the initial reaction rates at low overall conversions, interpreted the data by means of LH mechanisms, and found that the surface reaction was rate controlling with adsorbed alkylaromatics reacting with gas phase hydrogen in a single site mechanism. They also found no marked difference between the adsorption equilibrium constants of homologous alkylbenzenes, and attributed changes in the initial rates (Figure 1) to changes in the rate constant for the surface reaction because of the inductive effect of the aromatic nucleus; that is, the further away the reaction center from the aromatic ring, the less the inductive effect and subsequently smaller reaction rates. They also found that if there is branching at the reaction center, then steric effects become important and branched alkyl chains showed lower reactivity than their  $n$ -alkyl counterparts.

To interpret the data in terms of eq 7 or 11, one must determine the cross-sectional area,  $\sigma$ , for various reactants. These values were obtained from the two-dimensional van der Waal's constant  $b$  (Hill, 1949). Figure 1 is the log-log plot of the initial rates versus  $\sigma$  for a number of alkylbenzenes, which results in a straight line with slope of about  $-1.6$ . This value is in



**Figure 1.** Log of initial rates versus log of reactant cross-sectional area for catalytic hydrodealkylation of alkylbenzenes. Key: (1) ethylbenzene; (2) *n*-propylbenzene; (3) *sec*-butylbenzene; (4) *n*-butylbenzene.



**Figure 2.** A Koch curve with five iterations as the catalyst surface.

agreement with the expected value for the single-site mechanism, eq 7, and indicates a highly irregular surface with fractal dimension close to 3. Monte Carlo simulations were performed for LH mechanisms with surface reaction being rate controlling. Simulated reactions of reactants of different sizes over a fractal surface served to verify the scaling laws of eqs 7 and 11.

### Details of the Computer Simulation

The first step in the computer simulation was to generate a fractal to serve as the catalyst surface. Different fractal objects have been used to represent the fractal surface of a catalyst. These include the Koch Curve (KC), Devil's Staircase (DS), Cantor Set (CS), and Diffusion-Limited Aggregate (DLA). DS and its parent structure CS, are often used where there is a distribution of active sites on the catalyst surface. For example, only the edges on metal catalysts have an important role in the cleavage of stable bonds such as C–C, C–H, and H–H bonds. DS and CS are suitable fractals for modeling such surfaces (Gutfraind et al., 1990, 1991). KC has been used for cases where all the surface sites are active (Seri-Levy and Avnir, 1991), whereas DLA is used in situations where the diffusion of the reactant particles is important (Tambe et al., 1990; Meakin, 1986; Yang et al., 1987). In this study a KC with five iterations (Figure 2) with a fractal dimension of 1.22 and a straight line of dimension 1 were used to represent the catalyst surface in a two-dimensional simulation. The fractal dimension of the generated KC was obtained by the box-counting method (Mandelbrot, 1982) and was only slightly lower than its theoretical value of 1.26.

Once the fractal surface was generated, reactant molecules A (spherical particles) were placed within a

region above the surface using random numbers with a uniform distribution; 1000 reactant particles were used in the simulation. To perform the random walking of the reactant particles in the region above the surface, a two-dimensional square lattice was used. Each particle could move to any of the adjacent sites with equal probability. To use more reactant particles and reduce the run time of the simulation, it was assumed that the particles were transparent with respect to each other so that a given site in the region above the surface could be occupied with more than one particle at a time. Furthermore, when a particle had moved outside the region above the surface, it was immediately replaced back in the region.

When a reactant particle reached an empty site on the surface, it was adsorbed with a probability  $P_a$  and was removed from the random walking loop. All the reactant particles that were adsorbed on the surface, could be desorbed from the surface with a probability  $P_d$  and thus restart its random walking. This setup would allow an equilibrium to be established between adsorption and desorption of reactant particles. In this simulation,  $P_a$  and  $P_d$  were chosen as 100 and 0.2%, respectively. The choice of these values were arbitrary and they were intended merely to develop an equilibrium between reactant particles adsorbed on the surface and those in the region above the surface. It was also assumed that each surface site could only be accommodated by one adsorbed particle. To implement this assumption, a repulsion was included between particles that were adsorbed on the surface and those that were random walking in the region above the surface.

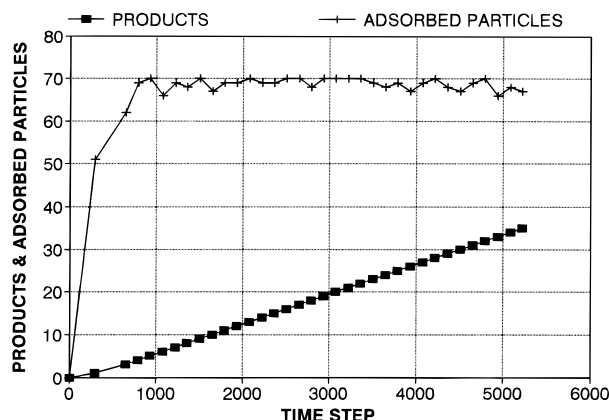
Time in this simulation was fictitious and was set to zero before the start of the random walking of the particles. Each time that all the particles had moved a single random step, one time step was added to the fictitious time. Using this definition, the rate equations for the single- and the double-site mechanisms could be discretized and expressed by simple algebraic equations. These equations would allow the calculation of the number of product particles at the end of each time step. For the time step  $n$ , the rate equation for the single-site mechanism, (eq 5), can be written as follows:

$$\frac{(N_{B|n} - N_{B|n-1})}{(n) - (n-1)} = kN_{A \cdot S|n} \quad (12)$$

or

$$N_{B|n} = N_{B|n-1} + kN_{A \cdot S|n} \quad (13)$$

where  $N_{A \cdot S|n}$  is the number of reactant particles A adsorbed on the surface at time step  $n$ . Equation 13 provides a means to calculate the number of product particles B formed during time step  $n$ . The number of product molecules formed up to time step  $n$ ,  $N_{B|n-1}$ , was incremented by an amount equal to  $(kN_{A \cdot S|n})$  after time step  $n$  and when its value exceeded one (or an integer number more than one), one (or an integer number more than one) of the adsorbed particles A was selected at random and converted to a product. Product molecules were not allowed to occupy surface sites and were immediately desorbed from the surface once they were formed. To maintain a uniform concentration of particles A within the region above the surface, once an adsorbed particle A was converted to product, another reactant particle A was placed at random in the region above the surface.



**Figure 3.** Number of adsorbed reactant particles A and product particles B formed after time step  $n$  (single-site mechanism on KC with  $k = 10^{-4}$  and particles A with radius of 5 pixels).

For the dual-site mechanism, the equation for the number of product particles formed during time step  $n$  is given by

$$N_{B|n} = N_{B|n-1} + k(N_{A-S|n})(C_t - N_{A-S|n}) \quad (14)$$

where  $C_t$  is the total number of surface sites that depends on the size of the reactant particles. From eqs 13 and 14, the number of products formed after time step  $n$ , and hence the reaction rate, can be determined for the single- and the dual-site mechanisms, respectively.

### Results of the Simulation

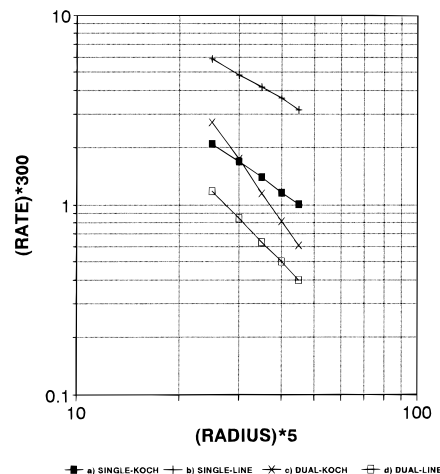
To study the effect of surface irregularities on the reaction rates, simulations were performed for the single- and the dual-site mechanisms using reactants (spherical particles) of different diameters. For this purpose, it was assumed that the surface reaction rate constant was the same for all reactants. The following scaling laws could be examined by plotting rate versus reactant diameters on a log-log scale:

$$\text{single site mechanism: rate} \propto d^{-D_s} \propto \sigma^{-D_s/2} \quad (15)$$

$$\text{dual site mechanism: rate} \propto d^{-2D_s} \propto \sigma^{-D_s} \quad (16)$$

where  $d$  is the diameter of the reacting particle.

To make the surface reaction (and not diffusion) the rate-controlling step in the reaction mechanism, a very small value for the surface reaction rate constant was utilized for both the single- and the dual-site mechanism. Figure 3 illustrates a typical simulation result for the single-site mechanism where the number of the product particles and the number of reactant particles adsorbed on the surface are plotted against the time step for a reactant diameter of 5 pixels and a surface reaction rate constant of  $10^{-4}$  1/time. During the initial period of the simulation, there were only a few adsorbed reactant particles adsorbed on the surface and, hence, the rate of desorption from the surface was much lower than the rate of adsorption. As time increased, the number of adsorbed reactant particles on the surface reached a maximum and an equilibrium was established between adsorption and desorption. Once this equilibrium was reached, the number of adsorbed reactant particles (and, hence, the reaction rate) showed only a slight fluctuation about the maximum. This pattern



**Figure 4.** Reaction rates versus particle diameters for the following: (a) the single-site mechanism on KC with  $k = 10^{-4}$ ; (b) the single-site mechanism on straight line with  $k = 5 \times 10^{-4}$ ; (c) the dual-site mechanism on KC with  $k = 10^{-6}$ ; (d) the dual-site mechanism on straight line with  $k = 5 \times 10^{-6}$ .

was consistent for reactants of different sizes for both mechanisms. This maximum rate that represented the reaction rate at steady state was used to compare the reaction rates for reactants of different sizes and examine the scaling laws.

The final simulation results for the single-site mechanism (reaction rate versus particle diameter) are presented on a log-log plot in Figure 4 (plots a and b) for KC ( $k = 10^{-4}$ ) and straight line ( $k = 5 \times 10^{-4}$ ), respectively. The slope of the resulting line for KC was  $-1.26$ , whereas that for the straight line was  $-1.04$ . These values showed only slight deviations from the expected values (eq 15) of  $-1.22$  and  $-1$ , respectively. The results for the dual-site mechanism are presented in Figure 4 (plots c and d) for KC ( $k = 10^{-6}$ ) and straight line ( $k = 5 \times 10^{-6}$ ), respectively. The slope of the resulting lines were  $-2.57$  for KC and  $-1.84$  for the straight line, which were only slightly different from the expected values of  $-2.44$  and  $-2$  (eq 16), respectively. By examining Figure 4, it can be seen that the behavior of reaction rate versus reactant size was different for the single-site versus the dual-site mechanism. Such differences can be used to discriminate between the two mechanisms using experimental rate data for homologous reactants.

### Conclusions

The geometry of a solid medium is a major parameter in determining the reaction rate in catalytic systems. In this context, fractal geometry provides an appropriate mathematical tool to describe the surface irregularities. In this paper, through LH mechanisms, the reaction rate was related to the fractality of the catalyst surface by means of scaling laws for the case where the surface reaction was rate controlling. Ultimately, with information on reaction rate for reactants of different sizes, one may determine the reaction mechanism. The scaling laws were verified using a two-dimensional computer simulation.

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## Nomenclature

$b$  = two-dimensional van der Waal's constant  
 $C_S$  = concentration of vacant surface sites  
 $C_t$  = total number of surface sites  
 $d$  = diameter of the reacting particle  
 $D_S$  = surface fractal dimension  
 $k$  = surface reaction rate constant  
 $K_i$  = adsorption equilibrium constant for species  $i$   
 $n$  = counter for time step  
 $N$  = number of adsorbed molecules  
 $N_{A-m}$  = number of adsorbed species A on the surface for monolayer coverage  
 $N_{A-S}$  = number of adsorbed species A on the surface  
 $N_B$  = number of product particles B formed  
 $P_a$  = adsorption probability  
 $P_d$  = desorption probability  
 $P_i$  = partial pressure of species  $i$   
 $r$  = radius of the adsorbing molecule  
 $b$  = scaling law parameter  
 $s$  = cross-sectional area of the adsorbing molecule

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