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Relating Metal Particle Geometry to the Selectivity and Activity of Supported-Metal Catalysts: A Monte Carlo Study

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Monte Carlo simulations of adsorption and reaction of polyatomic molecules have been conducted on regular Euclidean shapes and on random tessellations to determine the extent to which simple geometric parameters, such as particle size and the spatial distribution of active sites, determine the selectivity and activity characteristics of supported-metal catalysts. It is observed that the influence of low coordination metal atoms at the edges and corners of metallic clusters become significant at an average particle size of approximately 5–10 nm. This is in agreement with experimental results for a range of hydrocarbon reactions catalysed by supported metals. The influence of molecule size and geometry has also been considered in these simulations, and it is demonstrated that the influence of molecule and particle geometry on the particle effectiveness factor is insignificant. By investigation of various combinations of active site distribution and particle size it has been possible to reproduce the main features observed from experimental studies relating metal particle size and catalyst performance, by consideration of geometric parameters alone. © 1998 Academic Press

1. INTRODUCTION

Despite the importance of metal particle size and geometry in applied heterogeneous catalysis, there is no quantitative theory relating metallic particle size and geometry to the activity and selectivity of supported-metal catalysts (1, 2). The principle reason for the ambiguity regarding the relationship between catalyst structure and function is the difficulty in differentiating between the relative influences of changes in the electronic structure and changes in the geometry of metallic particles, both of which are a function of particle size and crystal structure. In order to control the function of supported-metal catalysts *a priori*, the effect of both electronic structure and particle geometry on adsorption and catalytic properties needs to be adequately represented by suitable models of the surface structure. Any methodology developed for the design of more specific or active catalysts therefore needs to be able to represent these structure–property relationships.

From a consideration of the electronic structure of small particles, characterised by the spacing of the electronic energy levels, it is expected that particles above 2 nm in diameter, that is, clusters of around 400 atoms, would have electronic properties identical to those of the bulk metal (3). Further, X-ray photoelectron spectroscopy indicates that the binding energy of core electrons converges to the bulk value for particles above 1–2 nm in diameter, suggesting that a cluster of a few hundred metal atoms is required to produce bulk metal characteristics. These results are contradicted by measurements of the ionisation potential of metallic clusters which indicate a more rapid convergence to the electronic properties of the bulk metal, suggesting that the bulk metal properties are attained for clusters consisting of a few tens of atoms (4). Quantum mechanical calculations based on ideal clusters also suggest that convergence to the properties of the bulk metal occurs at these smaller cluster sizes. Although there is no definitive theory relating the electronic structure of metallic particles to particle size, it is evident from catalytic studies that in the case of many reactions considered to be sensitive to particle structure the effect of particle size becomes apparent for particles sizes significantly larger than would be predicted by consideration of their electronic structure. This observation has led to the speculative conclusion that the influence of particle geometry is the more significant factor in determining the relationship between catalyst structure and function, at least for pure metallic catalysts (5). Evidence in support of this suggestion is adequately illustrated by results reported for the hydrogenolysis of ethane over silica-supported ruthenium, where the influence of particle size on steady state activity becomes significant at a particle size of approximately 25 nm, a value far higher than would be expected from a consideration of electronic effects alone (6). Furthermore, the relationship between particle size and catalytic activity is almost identical for the same reaction over different metals of similar particle size.

Relationships between activity, selectivity, and particle size have frequently been explained in terms of the ensemble theory of catalysis by metals and alloys (7) which proposes that a connected group of metal atoms collectively

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forms the active centre. If a reaction requires a fixed number of surface atoms to form the active centre, the activity of the catalyst will decline when the particle size is reduced or if surface sites are poisoned with an inert component, thereby reducing the number of continuous groups of surface sites. The effect of ensemble size in the design of industrial catalysts is exemplified by the observation that structure insensitive reactions, which require small ensembles, are promoted by the addition of an inert species to reduce the ensemble size. The inert species inhibit reactions requiring larger ensembles and, as a consequence, increase the selectivity of the catalyst toward any structure insensitive reactions. Bimetallic alloys consisting of mixtures of active and inactive components have been used extensively for control of the active ensemble size (8). Suppression of structure sensitive hydrocarbon hydrogenolysis reactions over supported platinum/tin, platinum/indium, and platinum/gold alloys (9) in favour of the corresponding hydrogenation reaction, which requires smaller active centres, illustrates the potential for the design of selective catalysts at the molecular scale by manipulation of the catalyst morphology. Experimental evidence from these studies indicates that the geometric modification of the surface structure is frequently observed to be more significant than alteration of the electronic structure of the catalyst resulting from the interaction of the catalytically inert material with the metallic surface (10–14).

In addition to the significant influence of particle geometry on catalyst function, another reason for gaining a greater understanding of this relationship is that control of particle size and shape is also becoming possible as a result of recent developments in surface science techniques. Supported-metal catalytic materials with well defined particle size distributions have been fabricated using chemical vapour deposition and spin-coating technologies (15). Lithographic methods have recently been adapted from the fabrication of semiconductor devices in the microelectronics industry and applied to the design of catalytic materials. Optical lithography and, at higher resolution, electron lithography allow the fabrication of microstructured catalytic materials composed of arrays of active metallic particles with a predefined geometry. The kinetics of structure sensitive and structure insensitive reactions over fabricated model catalysts and conventional supported-metal materials are similar. Studies of butadiene hydrogenation, which is considered to be structure sensitive, catalysed by an array of regularly spaced square palladium clusters suggest that the geometry of the active region can have a significant influence on both the selectivity and the deactivation characteristics of the microfabricated catalyst (16). A similar study conducted with regular square platinum islands prepared by electron lithography on a silicon wafer concluded that particle geometry had little influence on the activity of platinum for the structure insensitive ethylene hydrogenation reaction (17). The results obtained from these studies were in agreement with those obtained for the hydrogenation of butadiene and ethylene over dispersed supported-metal materials.

The rate of catalysis of ethylene hydrogenolysis by nickel nanostructures has been found to be the same when using either microfabricated structures with varying characteristic length scales or dispersed particles (18). These observations contradict the view that the origin of structure sensitivity is related to the characteristics of the edges of dispersed metal crystallites (19, 20). Instead, they suggest that simple geometric considerations, such as the linear size of the metal particles, are the determining factors. Further evidence in support of a simple boundary influence is found from a study of alumina-coated platinum (21). In this study it was found that the coating of large platinum spheres with inert alumina led to a reduction in the activity of the catalyst that was significantly greater than would be expected based on the calculated reduction in platinum surface area.

The current work considers the extent to which the geometry of small metallic particles can be manipulated in order to influence the activity and selectivity characteristics of a catalyst surface. While this approach does not include details of the electronic structure of the catalyst surface, it is not implied that such influences are insignificant. Rather, the approach adopted in the current paper is in recognition of two significant factors. First, the computational limitations imposed by the use of quantum mechanical descriptions of metal-adsorbate interactions do not yet allow for reliable calculation and prediction of the influence of electronic structure on the functionality of metallic catalysts. Second, given that there is sufficient evidence to suggest that the geometry of small metal particles can play a dominant role in determining catalyst performance, it is of value to investigate the ability of numerical techniques to predict the relationship between catalyst geometry and function. In so doing one can quantify the extent to which geometric effects influence catalyst performance.

In this paper the potential for tailoring the geometric properties of dispersed metallic particles to optimise the selectivity or activity of a supported-metal catalyst is addressed through the use of Monte Carlo simulations of reaction and adsorption processes occurring on a disordered surface representative of a supported-metal catalyst. It has been demonstrated that the geometric properties of dispersed metallic particles can be utilised in the development of a rational methodology for the optimal design of catalytic materials (22). Earlier work has addressed the relationship between catalyst surface geometry and function by introducing fractal models to describe the surface geometry (23). This fractal approach is, however, arguably inappropriate for supported-metal catalysts as the metal particles themselves are Euclidean in nature (24). The present work considers adsorption and reaction on surfaces composed of regular and randomly shaped particles. A hypothetical reaction between large molecules and a monomer, representative of a typical hydrocarbon hydrogenolysis reaction, is then used as a probe of the activity and selectivity characteristics of each catalytic surface.

2. DESCRIPTION OF THE MODEL

2.1. *General Approach*

A square lattice composed of N discrete locations is used to represent the surface of a supported-metal catalyst. Each single location of the lattice may represent either the catalyst support, which is typically a refractory oxide, or a region of the catalyst surface which is occupied by the active metal component. This model neglects metal-support interactions and any other influences of the catalyst support on the reaction kinetics. The distribution of the metallic crystallites over the catalyst support is represented by a series of tessellations of the lattice which partition the surface into a number of separate regions. Both regular tessellations, consisting of a simple repeated pattern, and irregular tessellations, generated by a Voronoi tessellation of the plane, are used to represent the catalyst surface. Regular tessellations are not necessarily a realistic representation of an actual catalyst surface which may typically be composed of three-dimensional truncated polyhedral crystallites (25). Random tessellations in two dimensions are therefore used to represent a projection of the three-dimensional catalyst structure onto a two-dimensional surface.

Molecules adsorb on the metallic regions of the catalyst surface at random. Once adsorbed, neighbouring molecules may react with one another or desorb from the surface. Monte Carlo methods are used to simulate each of these processes. The possible configurations of the adsorbate on the surface are represented by means of a series of random walks over the metallic regions of the surface, the length and bias of the random walk being determined by the size and geometry of the adsorbing molecule. Once adsorbed, a molecule may react with any of its nearest neighbours, subject to the constraints imposed by the geometry of the adsorption sites.

Clearly it cannot be assumed that all the adsorption sites which comprise an individual metallic particle catalyse a given reaction at an equal rate. In particular, it is frequently observed that defect sites and low coordination sites near the edges of metallic crystallites are particularly reactive regions of the catalyst surface. To study the influence of various distributions of these sites within the boundaries of the metal particles, individual sites may be assigned as "active" sites. If a molecule adsorbs onto such an active site it may undergo reaction. In this study two distributions of active sites are considered (i) where all metal sites are active and (ii) where only the low coordination metal sites at the boundaries of metal particles facilitate reaction. The influence of particle size and geometry is studied by varying the relative sizes of the metallic regions and the support regions of the surface.

2.2. *Representing Regular and Irregular Catalyst Surfaces*

The Voronoi tessellation is commonly used to represent disordered composite media, and is used in the current context to represent the "irregular" distributions of metallic particles on a support material. The "regular" distributions were generated by tiling the surface with rectangles. A brief description of the Voronoi tessellation will be considered here, the geometric properties of the tessellation having been widely studied in the literature (26). A sweepline algorithm (27) is used to tesselate the surface into a collection of polygons using randomly distributed Poisson points as the polygon centroids, generating a division of the plane as shown in Fig. 1. Each polygon is then randomly assigned as either an active catalytic region or as an inactive region of the support material (28). By assigning a greater number fraction, ϕ, of the polygons as active regions, the average size of the regions increases due to the coalescence of the individual polygons into larger single particles. At lower values of ϕ the active polygons tend to be small and evenly distributed across the catalyst surface. These active polygons can be considered to represent dispersed metallic particles on an inactive support, each individual lattice location contained within the polygon perimeter is considered to be a single adsorption site on the surface.

As the particles formed by the random tessellation are highly irregular in shape, the definition of a relevant length scale describing particle size becomes an important consideration (29). As the adsorption of molecules on the surface is simulated by a random walk from a single active site, it seems reasonable to define the relevant length scale as the average distance a molecule can walk before it reaches the boundary of the particle. The mean particle diameter, l, is therefore defined as the mean distance from each adsorption site to the boundary of the particle.

The mean particle diameter was calculated for each individual particle by taking the average of a series of diameters, $|p_j p_i|$, the distance between an adsorption site, p_j, and the edge of the lattice, p_i, for each point within the polygon. This mean diameter is defined for each tessellation as

$$l = \frac{1}{8N_p} \sum_{j=1}^{N} \sum_{i=1}^{8} \sigma_j |p_j p_i|, \qquad [1]$$

given that $\sigma = \{\sigma_1, \sigma_k, \ldots, \sigma_N\}$ is the state vector representing the distribution of active sites on the lattice; $\sigma_k = 1$ for a lattice location representing an adsorption site and $\sigma_k = 0$ for a support site, which is assumed to be catalytically inert. N_p is the total number of lattice sites occupied by the active material. An example for a random polygon is shown in Fig. 2. The choice of averaging over eight line segments

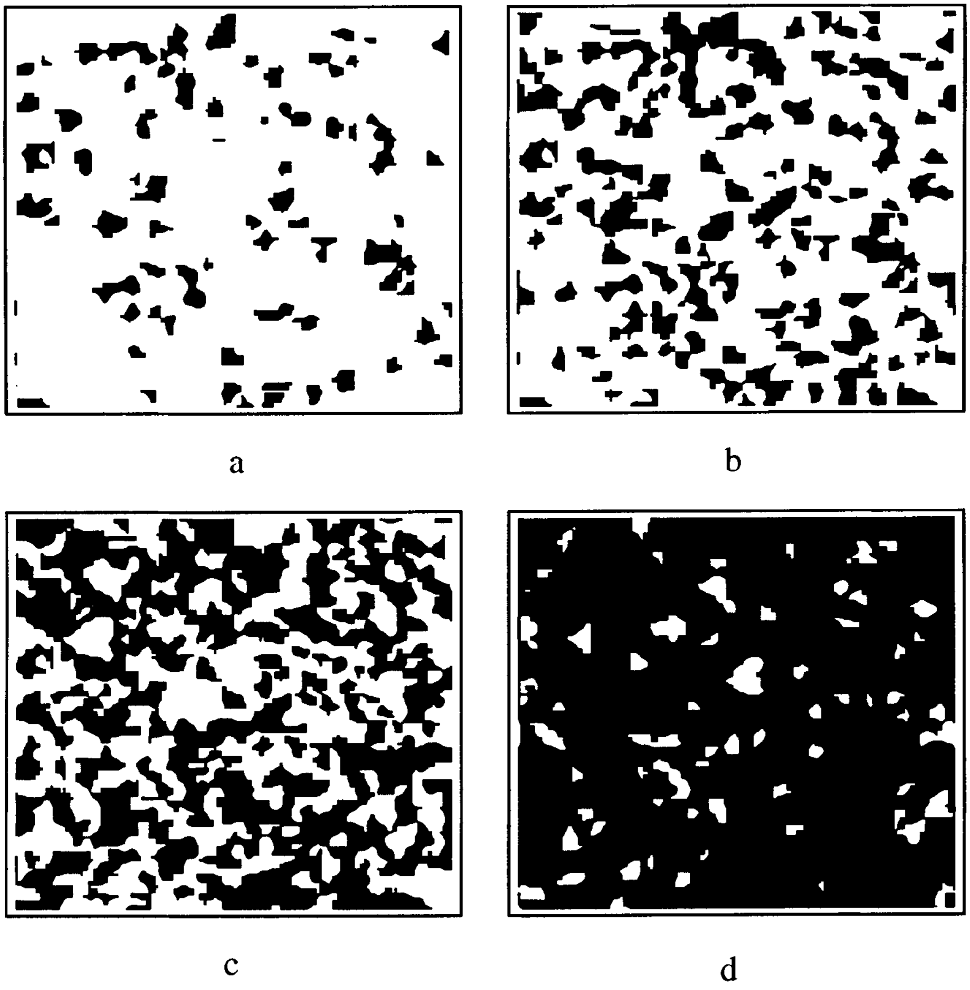

FIG. 1. A random Voronoi tessellation of the plane generated from 1000 Poisson points. The regions representing the metal distributed on an inert support are shown in black. The tessellations (a)–(d) have 100, 250, 500, and 750 active regions respectively.

linking each point to the particle perimeter, that is, four calliper diameters separated by 45°, is arbitrary. The use of yet more line segments, however, was found to have little effect on the value of l. The conversion from arbitrary lattice units to "real" units was made by assuming the side length of each adsorption site to be 0.39 nm, a typical value of the lattice constant for a noble metal. For values of ϕ below the percolation threshold, p_c, it would be expected that the relationship between θ, the fraction of lattice locations that are occupied by a metallic adsorption site, and l be linear. At higher coverages, additional polygons are more likely to join together existing polygons than form new isolated sites leading to a deviation from this linear relationship. As a result there is a rapid growth in the average size of the particles as ϕ approaches 1. Figure 3 shows the relationship between θ and l; deviation from linear growth is indeed observed above $\theta \approx 0.5$. This result is unsurprising, as for the Voronoi tessellation in two dimensions the percolation threshold occurs at $\theta = 0.5$.

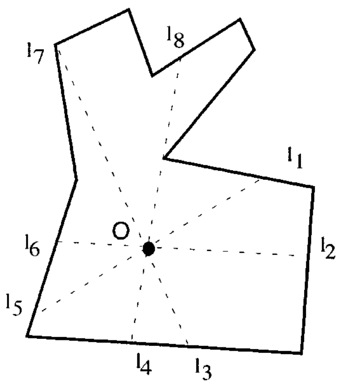

FIG. 2. Calculation of the mean particle diameter scale for an irregular polygon.

2.3. Simulation of Adsorption and Reaction

Possible configurations of each reactant molecule adsorbing onto the catalyst surface are represented by random

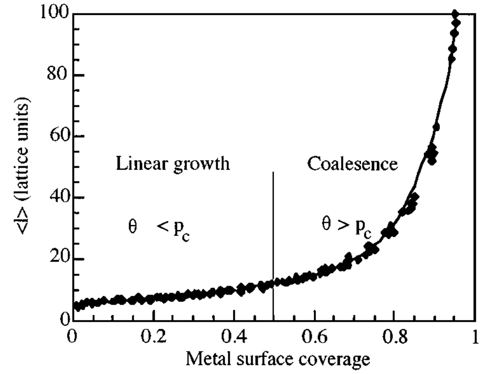

FIG. 3. Growth of the mean particle length scale as a function of metal surface coverage. Linear growth occurs below p_c, the percolation threshold. Coalescence of the growing particles leads to more rapid growth above p_c.

walks along a path of a particular length in the x–y plane. The geometry of the adsorbed molecule is determined both by the length of this walk and by a parameter $\gamma = \Pr(\mathbf{x})/\Pr(\mathbf{y})$, where $\Pr(\mathbf{x})$ is the probability that the random walker will move along the unit vector in the x direction and $\Pr(\mathbf{y})$ is the corresponding probability for the y direction. The value of γ is, therefore, a measure of the extent to which the random walk is biased along a particular axis. With $\gamma = 0$ the molecule can be represented by a vertical line, while as $\gamma \rightarrow 1$ the molecule resembles the path traced by an unbiased random walker. Representing a molecule by a single random walk does not allow for the fact that the molecule can hit the surface in any arbitrary configuration. For this reason each molecule is represented by a population of such walks; 10 configurations were typically used to represent a single molecule. One of these random walks will then be selected at random to represent the configuration of the adsorbed molecule.

The adsorption of a pure component of size n, that is, comprising n monomer units, from the bulk phase onto the catalyst surface is represented by

$$A_{\gamma,n} + n^* \rightarrow A^*_{\gamma,n}, \qquad [2]$$

where $A_{\gamma,n}$ is a species of size n with an adsorbed state configuration characterised by a bias γ. A vacant adsorption site is denoted by $*$ and the corresponding adsorbed species by $A^*_{\gamma,n}$. The probability of an attempted adsorption being successful is proportional to the adsorption rate constant, k_{ads}.

The simulation begins by selecting a site on the lattice at random. If the lattice site lies within a region assigned as a section of the catalyst support, the adsorption attempt fails. Another site is then chosen and the procedure repeated again. If an occupied site is selected, then the molecule occupying that lattice location is desorbed with probability proportional to the desorption rate constant, k_{des}. If the selected site is a vacant adsorption site, then a configuration of the molecule is selected at random from the population of all possible random walks representing the molecule. The random walk is then attempted with probability of success equal to k_{ads}. The walk starts at the selected site and traces out a path on the surface. The adsorption is considered successful if the whole walk can be completed without the random walker colliding either with the particle boundary or with another adsorbed molecule. The possible outcomes from an attempt at adsorbing a number of molecules on a section of the lattice are shown in Fig. 4. The random walk is not self-avoiding, in that it is possible for the walker to cross over itself. The walk will, however, always occupy exactly n locations on the surface so any site occupied by the adsorbing molecule that is crossed over by the random walk is not counted twice. Periodic boundary conditions are applied to minimise the influence of boundary effects.

As many hydrocarbon reactions catalysed by a supported-metal catalyst involve the reaction of a hydrocarbon with hydrogen, a hypothetical reaction between a large molecule and a smaller molecule was chosen as a probe reaction in this study. The reaction scheme involved the irreversible adsorption of an n-mer, A, and a monomer, B, from the bulk phase followed by subsequent reaction steps.

$$\begin{aligned}
&\text{(a)}\quad A_{\gamma,n} + n^* \xrightarrow{k_a} A^*_{\gamma,n}\\
&\text{(b)}\quad B + * \xrightarrow{k_b} B^*\\
&\text{(c)}\quad A^*_{\gamma,n} + A^*_{\gamma,n} \xrightarrow{k_c} C \qquad [3]\\
&\text{(d)}\quad A^*_{\gamma,n} + B^* \xrightarrow{k_d} D\\
&\text{(e)}\quad B^* + B^* \xrightarrow{k_e} E
\end{aligned}$$

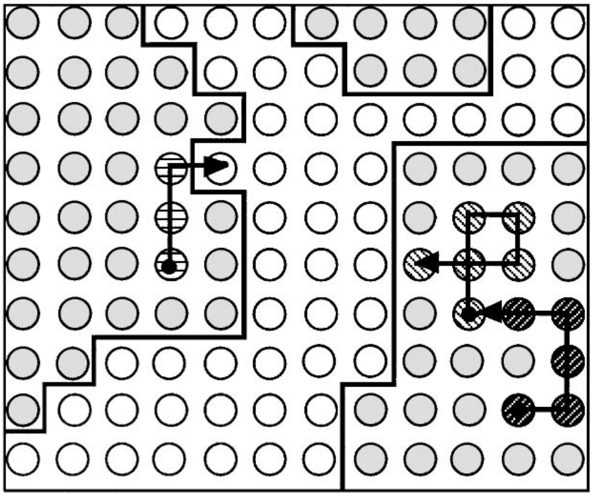

FIG. 4. Adsorption onto a random surface by a series of attempted random walks, of length $n = 6$, on a surface composed of metal sites, ◍, and support sites, ○. Adsorption of the molecule ⊘ is successful, the random walk being successfully completed on a particle. Adsorption of the molecule ⊖ fails as an attempt is made to walk off the edge of a particle and adsorption of the molecule ● fails due to the obstruction of an adsorption site by the molecule ⊘.

The n-mer is represented by the adsorption of a random walker as discussed in the previous section. The monomer is assumed to occupy a single lattice site, and k_i is defined as the rate constant for step i. The above mechanism can be taken to represent a reaction, such as the hydrogenolysis of ethane, which requires a large continuous ensemble of surface atoms, the polyatomic molecule representing the required ensemble of continuous free surface sites.

The activity and selectivity of the catalyst surface toward each reaction were investigated as a function of the mean particle diameter of the active regions. In the reaction simulations considered, adsorption was assumed to be irreversible, the adsorbed particles being removed from the surface only by reaction. The bulk gas-phase mixture above the catalyst was considered to be an infinite reservoir of a binary mixture of A and B, the mole fraction of A in this mixture taking a constant value y_a. The events to be described in the adsorption/reaction processes are represented by the algorithm as follows:

1. *Species selection.* A random number, r, uniformly distributed between 0 and 1 is chosen. Adsorption of A is attempted if $r < y_a$. Otherwise an attempt is made to adsorb the monomer.

2. *Site selection.* A site on the catalyst surface is selected at random. If the site is vacant an adsorption is attempted (step 3), otherwise a reaction is attempted (step 4).

3. *Adsorption.* The molecule chosen by step 1 is then adsorbed according to the algorithm detailed previously.

4. *Reaction.* All molecules that neighbour the selected molecule are then identified and one is chosen to react with the newly adsorbed molecule. The probability of a reaction between a molecule and one of its neighbours is given by the normalised product of the number of neighbouring pairs and the rate constant for each pair. For example, the probability of reaction between two A molecules is given by

$$\Pr(AA) = \frac{z_{AA}k_c}{z_{AA}k_c + z_{AB}k_d + z_{BB}k_e}, \qquad [4]$$

where z_{ij} is the number of nearest neighbour pairs of molecules of type i and j. After a reaction is chosen both molecules are removed from the surface and the procedure begun again by selecting, at random, another lattice site.

A lattice consisting of 128×128 locations with periodic boundary conditions was found to be sufficient to eliminate edge effects for the simulations of both adsorption and reaction. Simulations were run for 5×10^4 Monte Carlo steps (MCS). A single MCS is defined as one attempted adsorption per site (16384 adsorption attempts in this case; a typical simulation would therefore consist of $\approx 1 \times 10^9$ adsorption attempts). This was found to be a simulation time sufficient to avoid any transient effects resulting from the choice of initial conditions.

2.4. Definition of an Effectiveness Factor for Surface Reactions

In order to quantify the influence of particle size on the reaction rate a surface effectiveness factor, η, is introduced where

$$\eta = \frac{r}{r_\infty}, \qquad [5]$$

where r_∞ is the rate on a surface which is uniform and active at all locations and r is the corresponding rate of reaction on a disordered surface. Hence, by performing Monte Carlo simulations of the reaction of interest on both heterogeneous and uniformly active surfaces, the surface effectiveness factor can be evaluated.

An approximate analytical analysis of the relationship between particle size and activity and selectivity can also be made once assumptions regarding the molecule and particle geometry are made. If it is assumed that the surface reaction can be approximated by the reaction of pairs of rectangular ensembles on rectangular islands, then simple analytical expressions can be obtained for the rate of reaction on a disordered surface relative to that on a homogeneous surface (30). The number of square ensembles, n_e, of side length, n_s, that can be accommodated by a square island of side length L is given as

$$n_e = 2(L - n_s + 1)^2. \qquad [6]$$

For sufficiently large ensembles the reaction will be limited by the number of vacant ensembles that can form on the surface. This leads to the assumption that the adsorption of a large molecule will be the rate limiting step. The turnover number, r, can then be approximated as

$$r \propto (L - n + 1)^2, \qquad [7]$$

where n is the size of the molecule. The ratio of rates for the reaction on the disordered surface compared to the homogeneous surfaces defines η, an effectiveness factor for the surface reaction. For a homogeneous surface $L \to \infty$, giving

$$\eta = \frac{r_l}{r_\infty} = \frac{(L - n)^2}{L^2}, \qquad [8]$$

where r_l is the rate of reaction. The above analysis makes the additional assumption that L is real and n integer. It is useful to generalise Eq. [8] by introducing a dimensionless

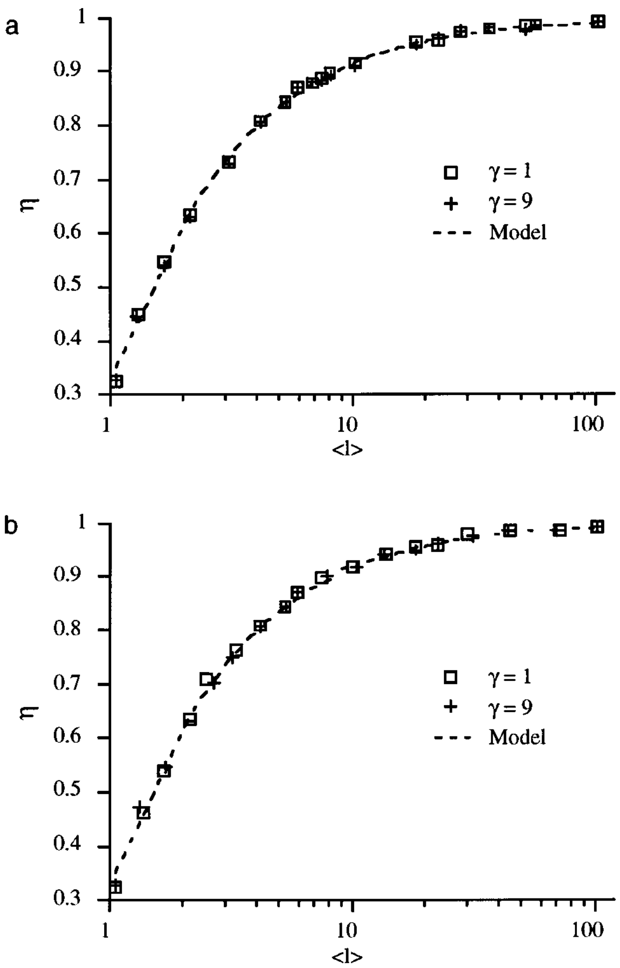

FIG. 5. A comparison of the particle effectiveness factors obtained by Monte Carlo simulation and predicted by Eq. [11] for the case where $k_a = k_b = 1$, $k_d = 1$, and $k_c = k_e = 0$. The effectiveness factor is given as a function of scaled particle size for $\gamma = 1$ and $\gamma = 9$. Plots (a) and (b) correspond to the results obtained for irregular and regular tessellations respectively. Both the bias of the random walk, γ, representative of the geometry of the adsorbed molecule, and the geometry of the metal particles have little influence on the adsorption characteristics.

particle length scale, $\langle l\rangle$, defined as the ratio of the mean particle diameter to the size of the reactant, where

$$\langle l\rangle = \frac{l}{n}. \qquad [9]$$

Applying the definition of the mean particle diameter, as given by Eq. [1], to a square particle of side length L, it can be shown that

$$\begin{aligned}\langle l\rangle &= \frac{1}{4Ln}\int_0^L (L + \sqrt{2}x)\,dx \\ &= \frac{1 + 1/\sqrt{2}}{4n}L. \qquad [10]\end{aligned}$$

Thus, by substituting the mean particle diameter into [8], the effectiveness factor for the reaction is obtained as a function of the dimensionless particle length scale.

$$\eta = \frac{\left(\frac{4}{1+1/\sqrt{2}}\langle l\rangle - 1\right)^2}{\left(\frac{4}{1+1/\sqrt{2}}\langle l\rangle\right)^2}. \qquad [11]$$

This approximation holds if the reaction is limited by the availability of large ensembles. Results for $k_a = k_b = 1$, $k_d = 1$, and $k_c = k_e = 0$ are given in Fig. 5. This represents a general form of the widely studied $A + B \rightarrow 0$ reaction (31). The approximate model given by Eq. [11] is found to accurately represent the relation between effectiveness factor and scaled particle size, provided the rate limiting step is the adsorption of the larger molecule on to the surface.

The agreement between the analytical solution, which contains no information describing either the metal particle or the adsorbate shape, and Monte Carlo simulation demonstrates that the shapes of both the metal particle and the adsorbing molecule are less important than their relative sizes in determining the adsorption characteristics of a tessellated surface. The use of Eq. [11] to determine the surface effectiveness factor is, however, limited in application to the case where the distribution of the active sites of the metal crystallites is not dependent on the crystallite geometry. Equation [11] will not apply if, for example, the active sites of the metal crystallites were principally located at the edges of the crystallites.

3. RESULTS

This section discusses the influence of particle size and of the geometry of active sites on the turnover number of a simple surface reaction. The hypothetical reaction between two particles A and B is considered, following the reaction scheme detailed previously. The effect of molecule geometry on the effectiveness of random catalyst surfaces is investigated by considering linear and unbiased random walks. The influence of surface structure on the activity and selectivity characteristics of the catalyst surface are investigated by considering random and regular tessellations of the plane.

Influence of reactant geometry. A comparison of the effectiveness factor obtained for the case of a molecule represented by an unbiased random walk, for which $\gamma = 1$, and a linear configuration, for which $\gamma = 9$, is given in Fig. 5. The results obtained for $\gamma = 1$ and $\gamma = 9$ are identical to within the accuracy of the simulation, demonstrating that the influence of molecule geometry on the surface effectiveness factor is insignificant. A study of the adsorption behaviour of molecules of various configurations and sizes suggests that the reason for this is that the sticking probability, characterising adsorption from the gas phase, is unaffected by molecule geometry. In Fig. 6 the equilibrium surface

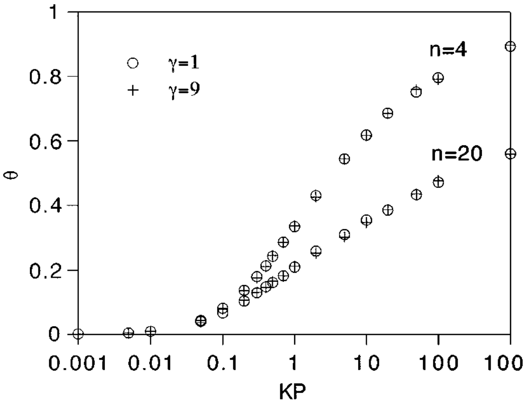

FIG. 6. Adsorption of molecules of random walk length n and bias γ onto a homogeneous surface. The equilibrium surface coverage, θ, is given as a function of the product of the adsorption equilibrium constant, K, and the adsorbate pressure P.

coverage is shown as a function of the adsorption equilibrium constant for a homogeneous surface. While increasing the size of the molecule is found to reduce the equilibrium surface coverage, as would be expected, the molecule geometry is shown to have no influence on the equilibrium surface coverage.

Influence of surface structure. The results shown in Fig. 5a were obtained by conducting simulations on random Voronoi tessellations, while the results shown in Fig. 5b were obtained from the use of a rectangular tessellation. There was no observable difference in the effectiveness factor obtained between surfaces composed of irregular tessellations and those constructed from regular tessellations of rectangles. This result demonstrates that, provided the density of the active sites of the metal crystallite are independent of crystallite geometry, an arbitrary representation

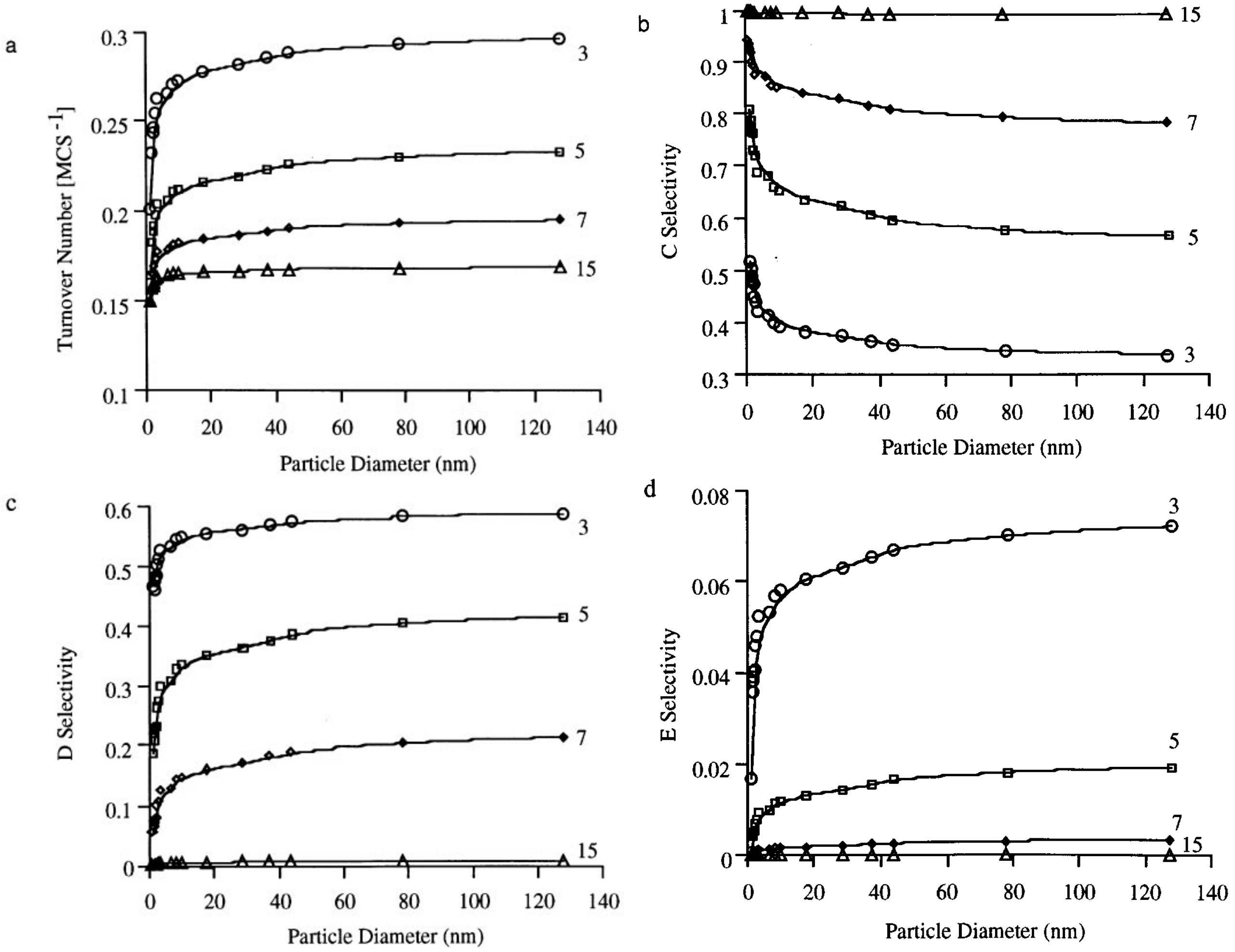

FIG. 7. The overall rate of the $A_n + B$ reaction as a function of particle size is shown in (a). It is found that a critical particle size of approximately 10 nm exists, below which the low coordination sites begin to inhibit adsorption. This finding is compatible with experimental results for structure insensitive hydrocarbon hydrogenation reactions. The selectivity to each of the possible products of the reaction mechanism (Eq. [3]) is shown in (b)–(d). As the particle size declines the adsorption of B is inhibited, thus the selectivity toward the $A_n + A_n$ reaction increases and that of the $B + B$ reaction declines. In each figure the size of the n-mer is indicated on the appropriate plot.

of a disordered catalytic material may be replaced by a simpler geometric representation with an equal particle diameter, defined by Eq. [1]. This finding is consistent with the effectiveness factors predicted by Monte Carlo simulation being the same as those predicted by the analytical result given by Eq. [11]; hence the Monte Carlo simulation provides a justification for modelling the disordered surface as a collection of regular rectangles, as required by Eq. [11].

A more complex situation arises where there is the possibility of competitive reaction, as the surface structure can now influence the selectivity of the catalyst. As an example, the case where $k_c = k_e = 0.5$ is considered, the other parameters taking the same values as for the $A_n + B \rightarrow 0$ reaction. As the particle size declines, it would be expected that the overall activity of the catalyst will also decline and the influence of low coordination sites at the particle edges will become significant. Low coordination sites limit the adsorption of large molecules near the metal particle boundaries, leading to a reduction in the selectivity toward reactions involving the A_n molecule. Experimental observations for a range of hydrocarbon reactions over supported metal catalysts report a critical particle diameter of around 5–20 nm, at which size effects become significant (5). The results of the Monte Carlo simulations are given in Fig. 7 as a function of absolute particle size. The activity of the catalyst surface is found to decline sharply below 10 nm; this value is approximately independent of the size of the reactant molecule. The conversion between the arbitrary lattice units used in the Monte Carlo simulations and realistic units is approximate, being based on the lattice constant for platinum, hence the critical value of particle diameter of 10 nm should not be taken as an absolute value for all reactions over supported-metal catalysts. However, the simulations do demonstrate that the size of the supported metal crystallites alone can account for observed catalytic behaviour in the size range 5–20 nm.

Particle structure has a particularly significant influence on the selectivity of the material; small particles inhibit the adsorption of larger molecules and so favour reactions in which smaller molecules are reactants. The selectivity of the catalyst surface toward each of the possible reaction products is given in Fig. 7. The location of the active sites is also a significant factor in the activity and selectivity characteristics of the catalyst. Figure 8 illustrates the case where the active sites of each particle are limited to the edge and corner sites on the particle boundary. The figure gives the rate of reaction between a pair of n-mers for $n = 10$. This model is based on the observation that for hydrocarbon reactions the sites at the edges of metal crystallites and at the boundary between the supported metal and support exhibit different catalytic characteristics compared to sites some distance from the particle edge (21). It is also the general case that defect sites and low coordination sites tend to be more active than those of the bulk. The results given here are of some interest as it is demonstrated that the influence of particle size is dependent on the size of the adsorbing molecule. For small molecules, the activity is found to be simply proportional to the fraction of the active sites that lie on particle edges, as steric hindrance in adsorbing small molecules is negligible. For larger molecules, such as is the case illustrated in Fig. 8, there is a trade off between having a high proportion of active sites, as will occur for small metal particles, and a reduction in the adsorption rate due to the influence of the particle boundary. The example given here demonstrates the existence of an optimal particle size, with a clear maximum in the turnover number at around 8 nm.

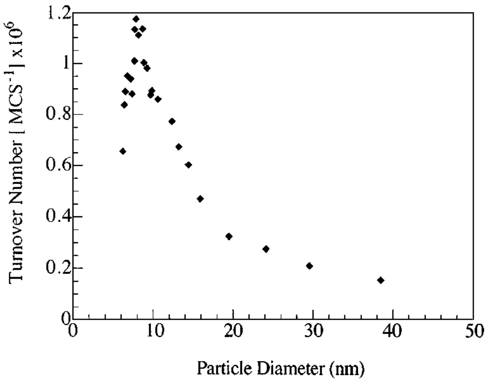

FIG. 8. The activity of the $B + B$ reaction with active site boundaries only, for the case of $n = 10$. The rate at first increases as particle size declines, as the total fraction of metal sites that are active increases with decreasing particle size. As the particle size drops below 10 nm the rate of adsorption of B declines rapidly.

4. CONCLUSIONS

A Monte Carlo model has been developed to study reaction and adsorption of polyatomic molecules and monomers on regular and irregular surfaces. The surfaces studied are regular tessellations of rectangles, an irregular surface constructed from a Voronoi tessellation of the plane and a homogeneous surface. It has been demonstrated that the results obtained on regular and irregular tessellations of the plane are identical. Furthermore, it has been shown that the configuration of the ensemble of continuous free sites required for reaction does not influence the selectivity or activity of the reaction.

An analytical model based on the results obtained from Monte Carlo simulations has been developed to relate the surface effectiveness factor to the structure of a disordered catalyst surface. The good agreement obtained between the analytical model and Monte Carlo simulation provides evidence that the activity and selectivity of a catalyst surface are independent of the metal particle or molecule shape, being dependent only on the relative size of the metal particles and the reactant molecules.

Where the adsorption of the polyatomic molecule onto the surface is the rate-limiting step, an approximate analytical relationship can be found between the scaled particle size and an effectiveness factor based on the geometry of the active catalytic sites. This simple relationship does not hold for competitive reactions as the presence of a second component effectively modifies the surface structure. The simulations of catalytic activity and selectivity have quantitatively reproduced experimental results in which it is observed that the influence of particle size and geometry become significant below a particle size of approximately 10 nm.

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