

Heterogeneous Catalyst Design Using Stochastic Optimization Algorithms

A. S. McLeod^{*,†} and L. F. Gladden[‡]

School of Chemical Engineering, University of Edinburgh, King's Buildings, Mayfield Road, Edinburgh EH9 3JL, United Kingdom, and Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, United Kingdom

Received December 2, 1999

We describe the application of two stochastic optimization algorithms to heterogeneous catalyst design. In particular, we discuss the optimal design of a two-component catalyst for the diffusion limited $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions in which each of the reactants are adsorbed specifically on one of the two distinct catalytic sites. The geometric arrangement of the catalytic sites that maximizes the catalyst activity is determined by the use of a genetic algorithm and a simulated annealing algorithm. In the case of the $A + B \rightarrow 0$ reaction, it is found that the catalyst surface with the optimal active site distribution, that of a checkerboard, is approximately 25% more active than a random site distribution. A similar increase in catalytic activity is obtained for the $A + B_2 \rightarrow 0$ reaction. While both the genetic and simulated annealing algorithms obtain identical optimal solutions for a given reaction, the simulated annealing algorithm is shown to be more efficient.

1. INTRODUCTION

Despite the increasing application of combinatorial libraries and computational chemistry in inorganic synthesis, the design of new heterogeneous catalysts remains an inexact science.^{1,2} The purpose of this paper is to present a rational methodology for catalyst design based on the use of stochastic optimization algorithms. In the present study, we discuss the application of a genetic algorithm and a simulated annealing algorithm to the design of a two-component catalyst for the diffusion limited $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions.

The aim of any rational computational approach to catalyst design first is to identify the features of the catalyst structure that are most significant in determining the catalytic characteristics of the material and then to relate these features to the catalyst synthesis procedure. There are, therefore, two principle stages in catalyst design: (i) the identification of the characteristics of the catalyst that most influence the performance of the catalyst and (ii) the development of synthesis procedures that allow for such catalysts to be manufactured. In order for any rational design methodology to be of practical use, both these aspects of catalyst design need to be addressed.

In the area of catalyst synthesis, there has recently been considerable interest in the manipulation of the microstructure of catalytic materials. Recent examples of heterogeneous catalyst synthesis at the molecular level include the fabrication of model oxide-supported metal catalysts^{3–5} and the application of microelectronics fabrication technologies to the deposition ordered metal particle arrays on inert oxide supports.⁶ In view of these developments, the technology now exists to construct catalyst surfaces with specific geometric properties at the nanometer scale. Therefore, developing numerical methodologies for determining the optimal

design of such surfaces will allow for the efficient synthesis of novel active or specific catalysts.

In this paper, we compare two stochastic optimization methods for the design of a two-component heterogeneous catalyst surface, genetic optimization, and simulated annealing. Stochastic optimization algorithms are a class of optimization algorithms that find widespread application in the area of combinatorial optimization. The current problem, determining the optimal distribution of a number of catalytic sites, is an example of a combinatorial problem. Genetic algorithms comprise a group of stochastic optimization algorithms based on Darwinian evolution.^{7,8} Drawing upon a biological metaphor, genetic algorithms are being applied increasingly in a wide range of disciplines, particularly within the engineering and physical sciences.⁹ Simulated annealing algorithms, a class of optimization algorithms based on thermodynamic principles, have also been extensively used to solve combinatorial optimization problems.^{10,11}

In the present work, the two alternative optimization algorithms have been applied to the design of a two-component catalyst for the diffusion limited $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions. These reaction mechanisms were chosen to represent the oxidation of CO by a two-component heterogeneous catalyst. In these hypothetical catalytic reactions, each of the two reactants can adsorb specifically on only one of the two types of surface site that constitute the catalyst surface. Once adsorbed, neighboring reactants may undergo a Langmuir–Hinshelwood reaction to form the reaction product, which immediately desorbs from the catalyst surface. In order to maximize the activity of the catalyst surface, both the optimal density and the optimal geometric configuration of the two types of surface site must be determined.

The remainder of this paper is structured as follows. In section 2, the optimization methodology is outlined and the details of the optimization algorithms are presented. The results of a comparative study of catalyst design using the genetic algorithm and the simulated annealing algorithm are

* Corresponding author. Phone: +44 (0)131 650 4857. E-mail: amcleod@chemeng.ed.ac.uk.

[†] University of Edinburgh.

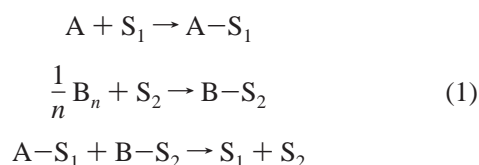
[‡] University of Cambridge.

then presented in section 3. The concluding section considers the extension of this work to more realistic catalytic systems.

2. METHOD

There are two stages in the optimization procedure: first, the calculation of the activity of the catalyst surfaces and, second, the optimization of the catalyst design using an appropriate optimization algorithm. Monte Carlo simulations of the $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions have been used to evaluate the activity of the catalyst surfaces. The turnover numbers that are obtained from the Monte Carlo simulations are then passed to the optimization algorithm as the value of the objective function. In this section, a description of the Monte Carlo reaction model is presented and the optimization algorithms are detailed.

2.1. Reaction Model. The reaction mechanism for the diffusion limited $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions can be written



where $n = 1$ for the monomer–monomer ($A + B \rightarrow 0$) reaction and $n = 2$ for the monomer–dimer ($A + B_2 \rightarrow 0$) reaction. The two distinct types of adsorption site on the catalyst surface are denoted by S_1 and S_2 .

Two-component metallic catalysts are commonly used in industrial practice.¹⁴ In two-component CO oxidation catalysts, the rate of CO oxidation is enhanced relative to that of the pure metallic catalyst by the addition of a second component that promotes the adsorption of oxygen.^{12,13} By comparison, in the single-component catalyst, the rate of reaction is inhibited by the saturation of the metallic surface by a strongly adsorbed CO overlayer. The strongly adsorbed CO overlayer poisons the catalyst surface by preventing the coadsorption of oxygen. In the two-component catalyst, the additional component partially oxidizes to form adsorption sites that are active for oxygen adsorption only. This permits molecular oxygen to adsorb at specific sites on the catalyst surface, allowing the oxidation reaction to occur. The reactive sites on the catalyst surface therefore lie at the boundaries, between the S_1 and S_2 adsorption sites.

The activity of the catalyst surfaces is evaluated by conducting Monte Carlo simulations of the reaction mechanism. There are two reasons for using Monte Carlo simulations of the reaction mechanism. First, the catalyst surface is disordered. Second, in diffusion limited reactions, reactant segregation occurs as a consequence of fluctuations in the local adsorbate density.¹⁵ Both the presence of surface disorder and the formation of ordered reactant domains imply that it is impossible to write a simple algebraic expression for the reaction rate.

The Monte Carlo method employed here follows from that described in previous Monte Carlo studies of the $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions conducted on both homogeneous surfaces^{16,17} and heterogeneous surfaces.^{18–20} The reacting system consists of a regular square lattice representing the discrete adsorption sites on the catalyst surface and of an

infinite bulk phase, composed of a mixture of the two reactants. During each step of the simulation, a reactant molecule is chosen from the bulk phase and an attempt is made to adsorb the molecule onto a randomly selected adsorption site. The probability of attempting the adsorption of an A molecule is given by p_A and that of a B molecule by $p_B = 1 - p_A$. A molecule adsorbs successfully only if the adsorption site is of the correct type and is not already occupied by another molecule. The lattice sites neighboring the adsorbed molecule are then checked for reactant molecules of the opposite species. If any AB pairs are formed by adsorption of a molecule, one of the newly formed pairs is selected at random and is removed from the surface. It is assumed that the adsorption of the reactants is irreversible and that there is no diffusion of the adsorbed reactants on the catalyst surface.

Each Monte Carlo simulation is conducted on a regular square lattice consisting of $N = 120 \times 120$ adsorption sites. Periodic boundary conditions are applied to minimize finite size effects. The simulations were typically run for 10^6 Monte Carlo steps (MCS), where 1 MCS represents N adsorption attempts. The catalyst activity, r , is expressed as a turnover frequency, $r = R/(tN)$, where R is the number of product molecules produced during t MCS. After conducting the simulation, the catalytic activity of each catalyst surface is passed to the optimization algorithm as the value of the objective function that is to be optimized.

2.2. Genetic Algorithm for Catalyst Design. The principles of genetic optimization are only briefly summarized here. A more detailed theoretical background to genetic optimization can be found elsewhere.^{7,8} Borrowing concepts from biological evolution, a genetic algorithm attempts to locate the optimal solution to an optimization problem by identifying, and then propagating, the desirable characteristics of the optimal solution throughout a population of solutions by means of selective breeding.

The genetic algorithm does not operate directly on the function that is to be optimized but on a binary representation of the function known as the *chromosome*. The actual function or object that is to be optimized, in this case the 120×120 grid representing the catalyst surface, is the corresponding *phenotype*. In the present case, the relationship between these two representations is trivial. The S_1 and S_2 sites of the phenotype can be represented by a series of 0's and 1's in the corresponding chromosome.

The genetic algorithm is initialized by generating a number of random binary arrays that collectively represent a population of chromosomes. During optimization, the chromosome population is manipulated by the genetic algorithm using two genetic operators: (i) *crossover*, where two chromosomes mate to form two new children by swapping groups of their genes, and (ii) *mutation*, where the genes of a chromosome are flipped at random to assume the value of the alternative binary digit. The role of the crossover operator is to propagate desirable groups of genes throughout the population. The role of the mutation operator is to prevent the algorithm from becoming stuck in a local minimum. During a single iteration of the algorithm, representing a single *generation*, an attempt is made to mate each of the chromosomes in the population once on average. Evolutionary pressure is applied by selecting the chromosomes that encode the more active surfaces for crossover more often than those representing the less

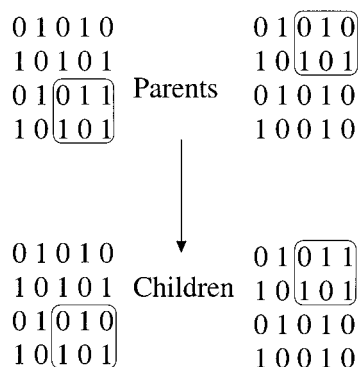


Figure 1. Two-dimensional crossover operator used to combine the chromosomes representing two catalyst surfaces.

active surfaces. By selecting the chromosomes of the more active catalyst surfaces for crossover more frequently, the traits of the active surfaces that are responsible for their higher activity are propagated throughout the population.

A two-dimensional crossover operator was incorporated into the genetic algorithm to account for the two-dimensional structure of the catalyst surface. The two-dimensional crossover operator was found to be required in order to prevent the fragmentation of desirable groups of surface sites during crossover.²¹ The result of applying the crossover operator on a pair of chromosomes is shown in Figure 1. During crossover, two gene groups of equal size are first selected from random locations in each of the two parent chromosomes. These gene groups are then swapped between the two parent chromosomes, producing two child chromosomes that are then carried forward into the next generation of chromosomes. The probability of an attempted crossover being successful is determined by the crossover probability, p_c . If an attempt at crossover fails, no children are produced.

The probability of selecting any individual member of the population for crossover is proportional to the value of the *fitness function* associated with the corresponding catalyst surface. The fitness function, $F(r)$, biases the crossover probability in favor of the more active members of the population. Although the linear function, $F(r) = r$, can be used as the fitness function, a power law function was chosen for this work, where $F(r) = r^\gamma$. The exponent γ was chosen adaptively so as to maintain the ratio $r'/\bar{r} = 3$, where $\gamma = \ln(3 - r'/\bar{r})$, where r' is the activity of the most active member of the population and where \bar{r} is the average activity of the population. The power law fitness function was required because the average activity of the population members and of the most active member did not differ sufficiently to drive the evolutionary improvement of the catalyst surfaces. Typically, the optimal catalyst surface was found to be approximately 25% more active than a randomly generated surface. Using this fitness function, a chromosome encoding the most active catalyst surface is selected for crossover three times more often than a chromosome representing a surface with average catalytic activity. After a successful crossover, an attempt is then made to mutate each gene of the two new child chromosomes. Each mutation attempt is successful with a probability p_m . In this work, a constant population size of 200 chromosomes was used, with the probabilities of crossover and mutation being 0.85 and 0.02, respectively. The parameters for the GA were selected by random search, with the parameter set minimizing the

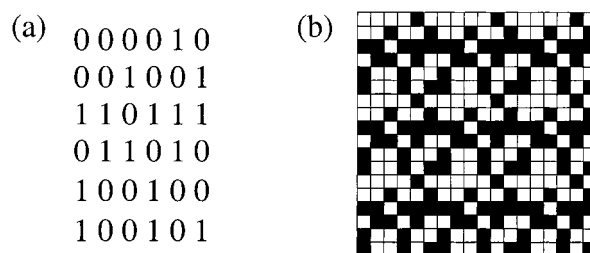


Figure 2. Relationship between the chromosome (a) used to represent a catalyst surface and a section of its corresponding phenotype (b). To generate the catalyst surface used in the Monte Carlo simulations, the 6×6 binary string representing the chromosome manipulated by the GA is tiled over a 120×120 square lattice.

time required to locate the solution to the $A + B \rightarrow 0$ problem being used for all subsequent optimization runs.

We note that, for the present optimization problem, the total number of possible solutions to the problem is $O(2^N)$. Locating the catalyst surface with the optimal catalytic activity for a lattice with $N = 14\,400$ sites will therefore require a prohibitive amount of computer time. It was not feasible, however, to reduce the number of possible solutions by reducing the size of the simulation lattice. This was because finite size effects become significant in the Monte Carlo simulations for simulation lattices with fewer than $N \approx 100 \times 100$ adsorption sites. The optimization problem was therefore simplified by describing the catalyst surface by a smaller sublattice, composed of m adsorption sites, that is tiled over a 120×120 lattice to generate the larger simulation lattice required for the Monte Carlo simulations. As the reactants only occupy one or two adsorption sites, the optimal site distribution is not expected to be described by a complex site pattern. For this reason, a sublattice of $m = 6 \times 6$ sites was used. In order to verify that this sublattice is of a sufficient size to describe the active sites for the more complex $A + B_2 \rightarrow 0$ reaction, the simulations were checked using larger subunits of $m = 8 \times 8$ and $m = 10 \times 10$ lattices. Identical solutions were obtained in each case. The relationship between the binary chromosome and the corresponding phenotype, the catalyst surface, is shown in Figure 2. The optimization problem to be addressed is, therefore, to determine the structure of the 6×6 binary array that describes the most active catalyst surface.

2.3. Simulated Annealing Algorithm for Catalyst Design. Simulated annealing algorithms are a group of optimization algorithms based on thermodynamic principles^{10,11} that exploit the concept of energy minimization by slow cooling. The principle of simulated annealing can be illustrated by analogy with the phase transition undergone by a material as it is cooled. If a material cools slowly, or anneals, the resulting solid phase that is formed is often stable and crystalline. If, however, the same material is quickly quenched, the rate of cooling will be too great to allow the material to form a stable crystalline structure, and a metastable amorphous phase of higher energy will form.

In simulated annealing, the solution to an optimization problem is located by conducting a random walk through the set of all feasible solutions to the problem. In the present optimization problem, the set of feasible solutions consists of all the possible configurations of the 6×6 grid describing the two-component catalyst surfaces.

A number of functions need to be specified to define the annealing algorithm. The cost function, $C(R)$, defines the relationship between the catalyst activity and the value of the function that is to be minimized by the annealing algorithm. In the present example, the cost function was simply taken to be the negative value of the catalytic activity. In simulated annealing, the value of the cost function is analogous to the free energy of a thermodynamic system. The order in which the set of feasible solutions is to be searched is determined by a stochastic generating function, g_k . The generating function defines the probability that a specific solution will be selected as the next step in the search from the set of feasible solutions. The acceptance criterion, P , defines the probability of accepting each new solution selected by the generating function. The initial temperature of the system and the rate at which the system cools are defined by the annealing schedule, T_k .

During each iteration of the algorithm, a new trial solution is generated and its cost function is compared to that of the best previous solution. Improved solutions, i.e., those with lower cost functions than the current best solution, are always accepted. Inferior solutions can also be accepted, but the probability of accepting a solution with a higher cost function is a strong function of the system temperature. Inferior solutions are occasionally accepted in order to prevent the algorithm from converging too quickly to a local minimum. Initially, at high temperature, most of the new solutions that are generated during the search are accepted. This allows for large regions of the parameter space to be searched efficiently. As the optimization progresses, and the system cools, the acceptance criterion becomes more difficult to satisfy, and only successive improvements in the cost function are accepted.

Annealing algorithms differ in the choice of the cooling schedule and of the generating function. In the original Boltzmann annealing algorithm, a logarithmic cooling schedule is used where the temperature of the system after k iterations of the algorithm is given by $T_k = T_0/(\ln k)$, where T_0 is the initial temperature.¹⁰ The choice of the generating function, g_k , is not arbitrary but is determined by the cooling schedule. In order to locate the globally optimal solution, it must be possible to sample each solution infinitely often during annealing. The generating function must therefore satisfy the condition $\sum_{k=0}^{k=\infty} g_k = \infty$. It is prudent to note, however, that this condition does not prove that the search is ergodic but only that each solution is statistically certain to be visited by the algorithm.

Several more efficient alternatives to Boltzmann annealing, that allow for a more rapid cooling of the system, have been proposed.²² In this study, the very fast simulated reannealing (VFSR) algorithm²³ has been used in place of the conventional Boltzmann algorithm because of the high computational cost of evaluating the catalyst activity by Monte Carlo simulation. While the VFSR algorithm is more efficient than Boltzmann annealing, the disadvantage of using VFSR is that there is no known proof of global convergence. The governing equations of the VFSR algorithm are briefly reviewed below.

The VFSR algorithm is initiated by choosing, at random, a feasible solution to the optimization problem. The cost function corresponding to this solution is then evaluated by

conducting a Monte Carlo simulation of the catalytic reaction. A new solution is then generated from the initial solution. The probability of accepting this trial solution as the next step in the search is given by the generating function

$$g_k = \prod_{i=1}^m \frac{1}{2(|y_i| + T_k) \ln(1 + 1/T_k)} \quad (2)$$

The parameter $|y_i|$ is a measure of the similarity of the new trial solution and the previous solution. In the present example, $|y_i|$ is equal to the total number of differences between the sites of the two surfaces. Small steps through the set of possible solutions are therefore more likely to be attempted than large leaps. Once the next trial solution has been selected, the cost function associated with the surface is then calculated. The probability, P , of accepting the new trial solution in place of the current best solution is given by

$$P = \begin{cases} \frac{\exp(\Delta C/T_k)}{1 + \exp(\Delta C/T_k)} & \text{if } \Delta C < 0 \\ 1 & \text{otherwise} \end{cases} \quad (3)$$

where $\Delta C = C^* - C$ is the difference in the cost function between the new trial solution, C , and the current best solution, C^* .

If the new solution satisfies the acceptance criterion, then the new solution is retained in the computer memory and the old one is rejected. The temperature of the system is then reduced. In the VFSR algorithm, an exponential cooling schedule is used where

$$T_k = T_0 \exp(-\beta k^{1/m}) \quad (4)$$

The parameter β determines the rate of cooling of the system. Increasing β increases the rate at which the algorithm converges but also increases the probability of the algorithm becoming frozen in a local minimum. The only two parameters that must be specified are the initial system temperature, T_0 , and the cooling rate, β . As with the genetic algorithm, the choice of the parameters for simulated annealing is arbitrary. Since there exists no algorithm to determine a unique set of optimal parameters, a random search was used to obtain the values of β and T_0 . In this work, parameter values of $T_0 = 5.0$ and $\beta = 1 \times 10^{-3}$ were used.

3. RESULTS AND DISCUSSION

3.1. Application of a Genetic Algorithm to Catalyst Design. The evolution of the optimal solution to the $A + B \rightarrow 0$ problem for a $p_A:p_B$ ratio of 1:1 using the genetic algorithm is shown in Figure 3. The A adsorption sites are shown in white in the figures, or as the "0" sites in the matrix notation. The optimal catalyst design, a checkerboard site distribution, is located after 50 generations. The propagation of the highly reactive $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ group, which maximizes the mixing of the reactants on the surface, illustrates the ability of the genetic algorithm to identify and propagate the desirable characteristics of the solution through the population. The corresponding activity of the most active surface in the population and the average activity of the population

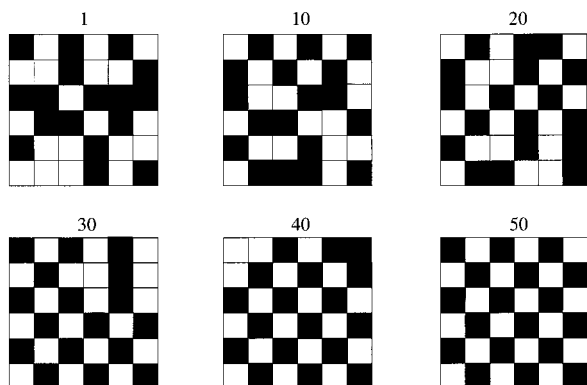


Figure 3. Evolution of the optimal solution to the $A + B \rightarrow 0$ problem with $p_A = p_B$ using the genetic algorithm. The panels show the most active surface from the population. The A adsorption sites are shown in white.

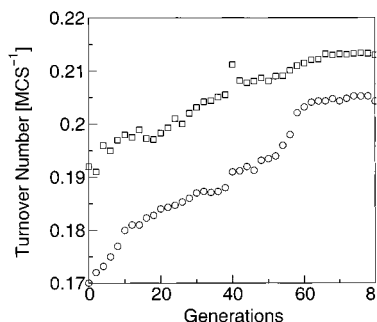


Figure 4. Evolution of the catalytic activity of the most active surface (\square) and population average (\circ) for the $A + B \rightarrow 0$ reaction with $p_A = p_B$ obtained using the genetic algorithm.

are shown in Figure 4. There also exists an equivalent symmetrical solution with transposed black and white sites.

Although it may have been possible to predict the checkerboard solution, the solution for other bulk-phase compositions is not as intuitive. As a further test of the methodology, the design of a catalyst surface for the $A + B \rightarrow 0$ reaction was repeated using a range of bulk-phase compositions. A very different solution is yielded by altering the bulk-phase composition so that the A species is twice as likely to make an adsorption attempt than B. The most active surface in this case is given by a tiling of the

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$$

group. The site density is thus modified to increase the probability of adsorbing the component that is deficient in the bulk phase. This diagonal pattern was maintained for increased $p_A:p_B$ ratios of 3:1 and 4:1.

The results for the optimization of a catalyst surface for the $A + B_2 \rightarrow 0$ reaction are shown in Figures 5 and 6. The reacting mixture is again assumed to consist of equal quantities of the A and B_2 molecules. For this reaction, the genetic algorithm is found to converge to a locally optimal solution in 55 generations. This solution is a tiling of the $\begin{bmatrix} 0 & 0 & 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 1 & 1 \end{bmatrix}$ group. In the $A + B_2 \rightarrow 0$ reaction, the adsorption of an A molecule is more probable than that of the B_2 molecule because an A molecule requires only a single vacant adsorption site. Therefore, as the A molecules are more abundant on the catalyst surface than the B_2 molecules, each successful

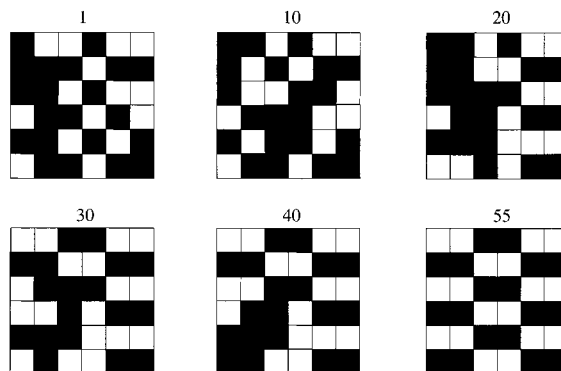


Figure 5. Evolution of the optimal solution to the $A + B_2 \rightarrow 0$ problem with $p_A = p_B$ using the genetic algorithm. The panels show the most active surface from the population. The A adsorption sites are shown in white.

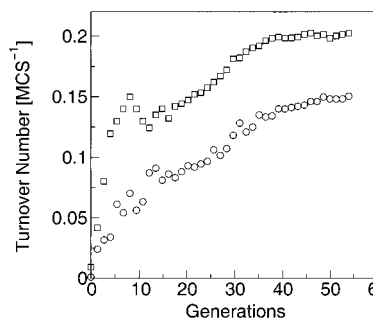


Figure 6. Evolution of the catalytic activity of the most active surface (\square) and population average (\circ) for the $A + B_2 \rightarrow 0$ reaction with $p_A = p_B$ as obtained by the genetic algorithm.

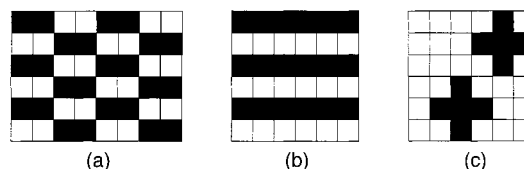


Figure 7. Alternative active catalyst surfaces for the $A + B_2 \rightarrow 0$ reaction that include the active connected $[1\ 1]$ groups.

B_2 adsorption is likely to result in a reaction with a neighboring A molecule. The optimization problem is, therefore, to determine the optimal way in which to distribute the B_2 adsorption sites on a surface that is saturated with A molecules.

Unlike the elementary $A + B \rightarrow 0$ reaction, the solution to the $A + B_2 \rightarrow 0$ problem is not intuitive. If a similar line of argument were followed for the $A + B_2 \rightarrow 0$ reaction as for the $A + B \rightarrow 0$ reaction, one would expect the optimal solution to be a checkerboard distribution of dimer adsorption sites, i.e., a tiling of the $\begin{bmatrix} 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 \end{bmatrix}$ element. This surface is shown in Figure 7a. Although this surface appears to be similar to the optimal solution, it is found to be relatively inactive, with a turnover frequency of only 0.120 MCS^{-1} , as compared to an activity of 0.209 MCS^{-1} for the most active surface obtained. Note that the only difference between the most active surface and that shown in Figure 7a is the presence of connected $[1\ 1]$ groups on the more active catalyst surface. The low activity of the checkerboard pattern for this reaction occurs because the isolated $[1\ 1]$ groups only permit the adsorption of a B_2 molecule in a single configuration.

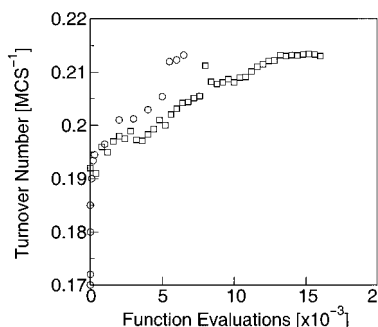


Figure 8. Comparison of the efficiency of the genetic algorithm (\square) and the simulated annealing algorithm (\circ) in obtaining the solution to the $A + B \rightarrow 0$ problem with $p_A = p_B$. The final point shown for each data set represents the activity of the optimal checkerboard surface.

It may, therefore, be expected that surfaces composed of connected $[1\ 1]$ groups would lead to highly active catalyst surfaces. Two alternative surfaces based on this group are shown in Figure 7b,c. The surface composed of alternate layers of 1 and 0 sites is expected to be active due to the presence of the connected $[1\ 1]$ groups. The activity of this surface is indeed found to be higher than that of the dimer checkerboard, at $0.202\ \text{MCS}^{-1}$. The activity of this surface is, however, limited due to the low number of active $[0\ 1]$ boundary sites. Another surface that may be expected to be active would be the cross-structure shown in Figure 7c. The cross-structure, based on the

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

element, is also found to be less active than the optimal solution with an activity of $0.187\ \text{MCS}^{-1}$. In this case, the activity is low as the density of the "0" sites is too low to allow for an adequate supply of A molecules.

3.2. Application of Simulated Annealing to Catalyst Design. Comparison with the Genetic Algorithm. Genetic optimization has been shown to be effective in determining the optimal structure of a two-component catalyst surface. In order to assess the efficiency of the genetic algorithm, the optimization problems outlined in the previous section are again considered using the VFSR algorithm.

Figure 8 presents a comparison of the results obtained for the $A + B \rightarrow 0$ reaction with $p_A = p_B$ using the genetic algorithm and the simulated annealing algorithm. In order to compare the efficiency of the two algorithms, the activity of the most active catalyst surface is plotted against the number of calls to the Monte Carlo simulation routine. As the Monte Carlo simulation requires far more computer processor time than any other aspect of the optimization, the number of function calls is proportional to the total time required to complete each iteration of the optimization algorithm. In Figure 8, the best solution from each generation is shown for the genetic algorithm. For the simulated annealing data, each point represents a sequential improvement over the previous solution. The corresponding data for the $A + B_2 \rightarrow 0$ reaction, also shown for $p_A = p_B$, are presented in Figure 9. In both examples the same solution to the optimization problem was obtained using either algorithm.

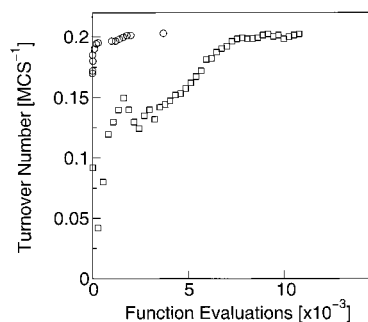


Figure 9. Comparison of the efficiency of the genetic algorithm (\square) and the simulated annealing algorithm (\circ) in obtaining the solution to the $A + B_2 \rightarrow 0$ problem with $p_A = p_B$.

The comparison of the two algorithms demonstrates that, for both reactions, simulated annealing is the more efficient optimization method. For the $A + B \rightarrow 0$ reaction, the first occurrence of the optimal solution required approximately 5×10^3 function evaluations, as compared to 1×10^4 evaluations for the genetic algorithm. The same checkerboard solution was obtained using both algorithms. For the $A + B_2 \rightarrow 0$ reaction, the simulated annealing algorithm was again found to be more efficient than the genetic algorithm, the genetic algorithm requiring 1.1×10^4 function evaluations as compared to the 2.7×10^3 function evaluations required by the annealing algorithm.

The relative inefficiency of the genetic algorithm as compared to the annealing algorithm has been attributed to the difficulty in determining the optimal values for the parameters of the genetic algorithm.²⁴ In the case of the genetic algorithm, the parameters chosen for the mutation and crossover probabilities, as well as the rules used for describing the crossover operator, are arbitrary. Furthermore, there is no clear relationship between the choice of these parameters and the performance of the algorithm. In contrast, the influence of the cooling rate, β , on the performance of a simulated annealing algorithm is more obvious. Too rapid a cooling rate leads the algorithm to become stuck in a local minimum, while slow cooling results in a random search with no apparent improvement in the solution as the optimization proceeds.

Despite the efficiency of the simulated annealing algorithm, there is, however, a compelling reason for using the genetic algorithm for practical design problems where the catalyst surfaces are more complex than the model surfaces discussed here. The advantage of using the genetic algorithm is that the algorithm does not seek out a single optimal solution directly but, instead, aims to propagate the gene groups associated with active site configurations throughout the solution population. These groups correspond to the desirable traits of the catalyst surface. Therefore, even if a single optimal solution is not obtained for a complex problem, the aspects of the catalyst surface that most influence the catalytic activity or selectivity may be identified. In the $A + B \rightarrow 0$ reaction, for example, 50 generations are required to find the optimal site distribution. Examination of the population after only a few generations reveals, however, that the majority of solutions in the population had an $S_1:S_2$ ratio of 1:1. Thus, the principle influence on the catalyst activity is the proportion of $S_1:S_2$ sites rather than their geometric distribution on the surface.

4. CONCLUSIONS

A rational methodology for the optimal design of simple catalyst surfaces at the molecular level has been detailed. The method has been applied to the design of two-component catalysts for the $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions. For the $A + B \rightarrow 0$ reaction, where the bulk phase is a mixture of equal amounts of the two components, the surface yielding the highest catalytic activity is found to be a checkerboard distribution of the two active sites. Deviations from this configuration are observed for cases in which the bulk phase is not composed of an equal mixture of the reactants. As the relative proportion of one of the species increases, the number of adsorption sites for that species tends to a ratio of 2:1 in favor of the species that is deficient in the bulk phase. Extension to the more complex $A + B_2 \rightarrow 0$ reaction with equal amounts of each component in the bulk phase produces a displaced checkerboard pattern consisting of a tiling of pairs of adjacent B_2 adsorption sites.

For both the $A + B \rightarrow 0$ and $A + B_2 \rightarrow 0$ reactions, the very fast simulated re-annealing algorithm has been found to be more efficient than the genetics algorithm. In all the reactions considered, the same solutions to the optimization problems were consistently obtained by the annealing algorithm and the genetic algorithm. In spite of the efficiency of the annealing algorithm, the genetic algorithm is expected to be more suited to practical catalyst design problems. The advantage of the genetic algorithm is that the genetic algorithm identifies the desirable characteristics common to a large population of solutions. For complex optimization problems, where qualitative trends are of more practical importance than locating unique optimal solutions, the genetic algorithm will be preferable to the annealing algorithm.

ACKNOWLEDGMENT

A.S.M. thanks Peterhouse, Cambridge, for the award of the Rolls Royce Frank Whittle research fellowship.

REFERENCES AND NOTES

- (1) Moates, F. C.; Sumani, M.; Annamalai, J.; Richardson, J. T.; Luss, D.; Willson, R. C. Infra-Red Screening of Combinatorial Libraries of Heterogeneous Catalysts. *Ind. Eng. Chem.* **1996**, *35*, 4801–4803.
- (2) Schultz, P. G.; Xiang, X. D. Combinatorial Approach to Materials Science. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 153–158.
- (3) Gunter, P. L. J.; Niemantsverdriet, J. W.; Ribeiro, F. H.; Somorjai, G. A. Surface Science Approach to Modelling Supported Catalysts. *Catal. Rev.—Sci. Eng.* **1997**, *39*, 77–168.
- (4) Henry, C. R. Surface Studies of Supported Metal Catalysts. *Surf. Sci. Rep.* **1998**, *31*, 231–325.
- (5) Baumer, M.; Freund, H. J. Metal Deposits on Well Ordered Films. *Prog. Surf. Sci.* **1999**, *61*, 127–198.
- (6) Krauth, A. C.; Lee, K. H.; Bernstein, G. H.; Wolf, E. E. A Novel Microfabricated Pd/SiO₂ Catalyst for the Hydrogenation of 1,2-Butadiene. *Catal. Lett.* **1994**, *27*, 43–51.
- (7) Holland, J. H. *Adaptation in Natural and Artificial Systems*; MIT Press: Cambridge, MA, 1994.
- (8) Goldberg, D. E. *Generic Algorithms in Search, Optimisation, and Machine Learning*; Addison-Wesley: New York, 1989.
- (9) Davis, L. *Generic Algorithms and Simulated Annealing*; Pitman: London, 1987.
- (10) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. Optimization by Simulated Annealing. *Science* **1983**, *220*, 671–680.
- (11) Kirkpatrick, S. Optimization by Simulated Annealing—Quantitative Studies. *J. Stat. Phys.* **1983**, *34*, 975–986.
- (12) Szanyi, J.; Goodman, D. W. Kinetics of CO Oxidation on Cu/Rh(100) Model Bi-Metallic Catalysts. *J. Catal.* **1994**, *145*, 508–515.
- (13) Logan, A. D.; Paffett, M. T. Steady State CO Oxidation Kinetics Over the Pd(100) Single Crystal Surface and the C(2×2) Sn/Pd(100) Bi-Metallic Surface Alloy. *J. Catal.* **1992**, *133*, 179–190.
- (14) Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts and Applications*; Wiley: New York, 1983.
- (15) Kang, K.; Redner, S. L. Fluctuation Dominated Kinetics in Diffusion Controlled Reactions. *Phys. Rev. A* **1985**, *32*, 435–447.
- (16) Wicke, E.; Kumman, P.; Keil, W.; Scheifler, J. Unstable and Oscillatory Behaviour in Heterogeneous Catalysis. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *4*, 315–323.
- (17) Ziff, R. M.; Gulari, E.; Barshard, Y. Kinetic Phase Transitions in an Irreversible Surface Reaction Model. *Phys. Rev. Lett.* **1986**, *56*, 2553–2556.
- (18) McLeod, A. S.; Gladden, L. F. Relating Metal Particle Geometry to the Selectivity and Activity of Supported-Metal Catalysts: A Monte Carlo Study. *J. Catal.* **1998**, *173*, 43–52.
- (19) Frachebourg, L.; Krapivsky, P. L.; Redner, S. L. Heterogeneous Catalysis on a Disordered Surface. *Phys. Rev. Lett.* **1995**, *75*, 2891–2894.
- (20) Head, D. A.; Rogers, G. J. Kinetics of Catalysis with Surface Disorder. *Phys. Rev. E* **1996**, *54*, 1101–1105.
- (21) McLeod, A. S.; Johnston, M. E.; Gladden, L. F. A Genetic Algorithm for Molecular Scale Catalyst Design. *J. Catal.* **1997**, *167*, 279–295.
- (22) Szu, H.; Hartley, R. Fast Simulated Annealing. *Phys. Lett. A* **1987**, *122*, 157–162.
- (23) Ingber, A. L. Very Fast Simulated Re-Annealing. *Math. Comput. Model.* **1989**, *12*, 967–973.
- (24) Ingber, A. L.; Ronsen, B. Genetic Algorithms and Very Fast Simulated Re-Annealing—A Comparison. *Math. Comput. Model.* **1992**, *16*, 87–100.

CI990277M