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Oscillations during Carbon Monoxide Oxidation: A Monte Carlo Simulation

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Oxidation of carbon monoxide taking place on a two-dimensional catalyst surface is modeled by a Monte Carlo simulation technique. The model considers adsorption of both species from the gas phase, followed by surface migration and chemical reaction. Simulation studies indicate that islands of the two species are formed on the catalyst surface, with reaction taking place at the perimeter of the islands. The surface concentrations of the two species also oscillate with time. Fourier transformation and fractal analysis indicate that the oscillations observed are chaotic in nature, with a fractal dimention between 3.1 and 3.8. Decrease in surface mobility of the species decreases chaos (and hence the fractal dimension). If desorption of CO from the surface is considered, islands disappear and oscillations are quenched. © 1992 Academic Press, Inc.

INTRODUCTION

Several heterogeneous catalytic gas-phase reactions are now known to exhibit self-oscillations (*1*). The oldest and most thoroughly studied system among them is the oxidation of carbon monoxide on platinum as catalyst (*2*). Here a wide range of periodic and aperiodic behavior in the rate and catalyst temperature is observed. The traditional Langmuir–Hinshelwood (L.H.) model was found to be inadequate in describing the phenomena. The successful mathematical models found in the literature that describes these nonlinear phenomena either include an additional mechanistic step or modify the L.H. model. Sales *et al.* (*3*) have incorporated a slow oxidation and reduction of a surface platinum oxide, while Aluko and Chang (*4*) have included the nonisothermality of the catalyst surface due to the exothermic nature of the reaction. Mukesh *et al.* (*5*) have assumed the preexistence of islands of the reacting species, with the chemical reaction taking place along the perimeter of the islands. In this short paper it is shown by simulation studies that the oscillatory phenomena may be due to the two-dimensional spatial patterns that arise on the catalyst surface during the reaction and also to the presence of a finite number of active sites on the catalyst surface. It is also shown that islands of the two species will form on the surface as the two reactants are removed in a selective manner. The modeling studies are carried out based on Monte Carlo simulation. Araya *et al.* (*6*) and Dufour *et al.* (*7*) have also applied Monte Carlo simulation for simulating adsorption cum reaction between CO and oxygen on a surface, and then have compared the results with the well-established Langmuir–Hinshelwood model.

NOMENCLATURE

d—Dimensionality, slope of log $C(\gamma)$ vs log γ.

m—Number of gas to surface movements of species for each simulation time interval.

n—Number of chemical reactions for each simulation time interval.

p—Number of surface migrations of species for each simulation time interval.

s—Dimension of the phase space.

t_i, t_1, t_N—Time values.

x_i—Points on phase space.

τ—Time lag.

θ—Heaviside expansion.

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METHOD

The following assumptions are made in the development of the model.

1. The catalyst surface contains 40 × 40 matrix sites, with each site surrounded by 8 adjacent ones.
2. Dissociative adsorption of oxygen is assumed; hence oxygen can be adsorbed only if there are two adjacent vacant sites.
3. Product carbon dioxide is removed if one species finds another species in an adjacent site.
4. Desorption of carbon monoxide and oxygen are ignored.
5. A species can move to an adjacent vacant site.
6. The gas-phase concentration changes of both the species are ignored.

The simulation based on Monte Carlo technique between each successive time interval consists of the following steps.

1. Generation of a random number between 1 and 1600 to determine the site. (Initially the sites are filled partially in a random manner with species 1 (carbon monoxide) and species 2 (oxygen).)
2. Adsorption: Movement of a species from the gas phase to the randomly chosen surface site, if the site is vacant. If the species is oxygen then the additional condition that must be satisfied is that there be an adjacent vacant site.
3. Repeat steps 1 and 2 a specified number of times (m_1 and m_2, respectively) for both the species.
4. Generation of a random number.
5. Chemical reaction: If the chosen site is not vacant and if the other species is found at one of the eight adjacent sites (again chosen in a random manner) then the chemical reaction can take place and the product is removed from the surface.
6. Repeat steps 4 and 5 a specified number of times (n).
7. Generation of a random number.
8. Surface migration: If the chosen site contains a species and there is a vacant site adjacent to it (again chosen in a random manner), then move the species to the vacant site. There is experimental evidence (*8*, *9*) available for the surface migration of adsorbed molecules; CO in its precursor form is found to be more mobile on the surface than oxygen.
9. Repeat steps 7 and 8 a specified number of times (p).

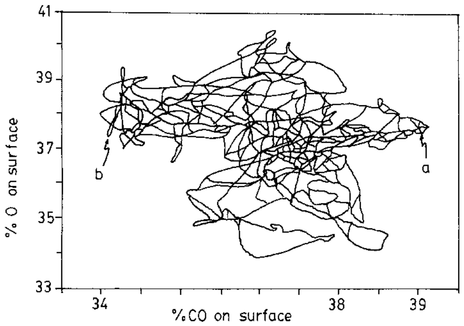

FIG. 1. Phase portrait of the two surface species. $m_1 = 74$, $m_2 = 43$, $n = 30$, $p = 7$.

RESULTS AND DISCUSSION

Carbon monoxide and oxygen can accumulate on the surface without reacting as long as they do not occupy adjacent sites. Reaction can take place only when the conditions are favorable, namely when carbon monoxide is either adsorbed or moves (due to surface motion) adjacent to an O species and vice versa. So one can imagine a buildup of the two species on the surface and then a drop in the surface concentration if it is favorable for reaction, and this process repeats again.

Simulation provides insight into the behavior of this two-species system. Phase plane projection of changes in surface concentrations of carbon monoxide and oxygen with time are shown in Fig. 1. The phase trajectory shows a nonuniform pattern. The time variation of vacant sites concentration for the same simulation is depicted in Fig. 2. The oscillations are not regular in shape and period but chaotic in nature. The time-series data is smoothed using a five-point

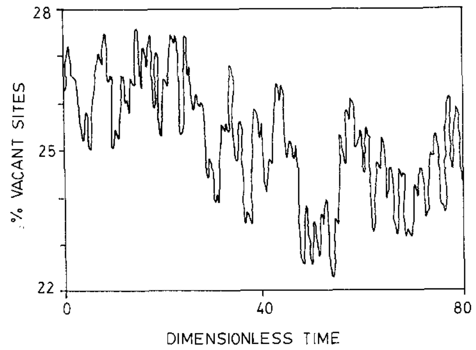

FIG. 2. Oscillations in vacant site concentration. Simulation parameters are the same as those in Fig. 1.

formula to eliminate high frequencies. Several different modeling techniques have been tried for simulating aperiodic behavior observed during CO oxidation. Multiple-peak oscillation and chaos have been simulated (*10*) by assuming nonisothermalities in conjunction with the presence of inactive species on the surface.

The distributions of the two species on the surface are shown in Figs. 3a and 3b at two different time values. One can see that islands of the two species are formed on the surface. The distribution of carbon monoxide and oxygen on the surface between these two cases is very different. Substantial evidence exists for CO and oxygen island formation in high-vacuum experiments on single crystals of platinum (*11, 12*) and palladium (*13*). Wicke *et al.* (*14*) have also simulated the formation of islands on the catalyst surface during the selective removal of reactants, but have not predicted oscillations.

For the same set of conditions if we assume that molecules do not move ($p = 0$) on the surface after adsorption then the oscillations die down and the surface becomes predominantly covered by oxygen. Surface movement of both the species hinders the adsorption of oxygen, since it requires two adjacent vacant sites. Also simulation predicts that it is more difficult to adsorb oxygen on a surface predominantly precovered by carbon monoxide than the reverse. This has also been observed by several workers (*15–17*) during experimental studies and is once again due to the fact that oxygen requires two adjacent vacant sites for adsorption. During the absence of surface movement or migration the two species are uniformly distributed on the surface and hence removed continuously as product, giving no chance for buildup of concentration on the surface. This situation leads to a steady state, with the surface predominantly covered with one of the species.

If CO desorption from the surface is considered, oscillations decrease and for very large desorption values oscillations are com-

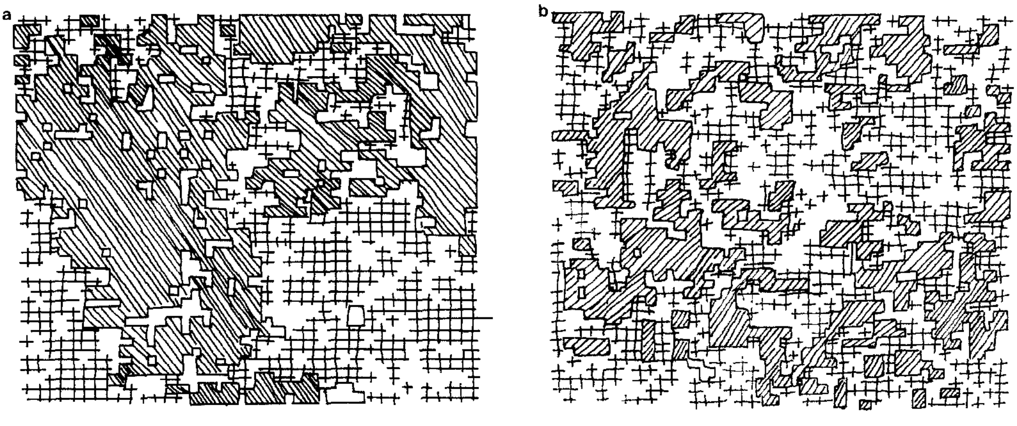

FIG. 3. Surface species distribution at two time values. Figures 3a and 3b correspond to points a and b, respectively, in Fig. 1. (▨) CO, (+) O, (☐) vacant site.

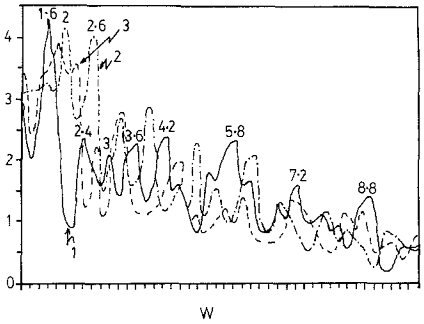

FIG. 4. Fourier transform of time variation of surface oxygen species. Simulations carried out with total number of sites; (1) 1600, (2) 2500, (3) 900.

pletely quenched. Large islands disappear,and CO is found well spread out on the surface, allowing oxygen to be adsorbed.

Araya *et al.* (*6*) have also predicted, based on Monte Carlo simulation, disappearance of CO clusters at high CO desorption rates. They found that results from Monte Carlo simulation matched with that from Langmuir–Hinshelwood predictions only during the absence of CO clusters. The Langmuir–Hinshelwood model does not presume any island formation, and the surface reaction rate is assumed to be directly proportional to the surface concentration of both the species. On the other hand, the surface reaction in the Monte Carlo simulation depends only on the presence of CO and oxygen in adjacent sites, which leads to low rate of reaction during the presence of large CO clusters. This leads to discrepancy between the two models during the presence of CO clusters.

The Fourier transform of the time-domain data for the surface oxygen species is given in Fig. 4 (solid line) for the same set of simulation conditions. The presence of several frequencies and broadbands in the spectrum is an indication of chaotic oscillations (*18*). In order to verify whether the chaotic oscillations observed is an artifact, arising due to the size of the matrix (40 × 40), the Monte Carlo simulation is carried out by varying the matrix size. Figure 4 also plots the Fourier transform of the time-domain data for the surface oxygen species for a matrix size of 50 × 50 (dotted line) and 30 × 30 (double dotted line). It is seen that in all cases the observed oscillations are chaotic in nature.

FRACTAL ATTRACTOR THEORY

The nature of attractors in phase space provides extensive information on the time-series behavior of the variables and on the nature of their coupling. Thus a point attractor of zero dimension ($d = 0$) implies that the behavior of the system will be time independent and can be represented by one variable ($s = 1$). An attractor in the form of a closed curve linear attractor ($d = 1$) implies that the system will perform sustained oscillations. The simplest quasi-periodic phenomenon needs a two-dimensional torus ($d = 2$). A fractal attractor (d nonintegral and larger than 2) indicates a chaotic regime, characterized by a marked unpredictable behavior.

Hence existence of a fractal attractor of dimensionality greater than two is an indication that the system under consideration exhibits chaotic behavior.

Procedure for Determining the Dimensionality of the Attractor (*19*)

Consider a set of N points on an attractor embedded in a phase space of s dimensions obtained from

$$\begin{array}{l} x(t_1), \ldots, x(t_N) \\ x(t_1 + \tau), \ldots, x(t_1 + \tau) \\ \ldots \\ \ldots \\ x(t_1 + (s - 1)\tau), \ldots, x(t_N + (s - 1)\tau) \end{array}$$

τ is the time lag. The integral correlation function of the attractor can be calculated from the data as

$$C(\gamma) = (1/N^2) \Sigma\, \Theta\, (\gamma - |x_i - x_j|)$$
$$i, j = 1, \ldots, N$$
$$i \neq j,$$

where Θ is the Heaviside function, $\Theta(x) = 0$ if $x \leq 0$, $\Theta(x) = 1$ if $x > 0$. x_i stands for a

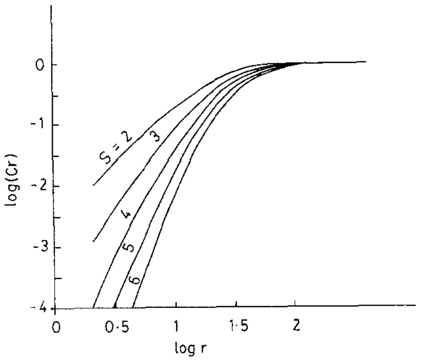

FIG. 5. Log $C(\gamma)$ vs log γ ($\tau = 3$, $N = 500$) for the time-series data obtained from Monte Carlo simulation.

point of phase space whose coordinates are $\{x(t_i), \ldots, x(t_i + (s - 1)\tau)\}$. The nonvanishing of $C(\gamma)$ measures the extent to which the presence of a data point x_i affects the position of the other points. For various values of γ, $C(\gamma)$ could be estimated and the dimensionality, d, of the attractor is given by the slope of the log $C(\gamma)$ versus log γ for a given phase space dimension s. If d reaches a saturation limit beyond some relatively small s, the system should possess an attractor. If this saturation value is fractional, the system is assumed to be chaotic in nature.

Carbon Monoxide Oxidation

The above-mentioned procedure is followed to determine the dimensionality of the present carbon monoxide oxidation system. For the study, only the time-series data of carbon monoxide concentration on the surface is considered. For $\tau = 3$ and $N = 500$ Fig. 5 gives the relationship between log $C(\gamma)$ and log γ for s ranging from 2 to 6. The plot of the slopes (d) of the individual curves against s shows that saturation is reached for a value of $d = 3.3$ (Fig. 6), which indicates that the time-series data are chaotic in nature embedded in a five-dimensional state space ($s = 5$). If the data are only noise then there will not be any tendency for d to saturate and d will follow the 45° line (d will be equal to s).

The fractal dimension, d, estimated during the absence of surface mobility of the two species, decreases to 1.8, indicating the absence of any chaotic oscillation and the decrease in complexity of the system. The fractal dimension varies beween 3.1 and 3.8 for different values of surface adsorption in the presence of mobility of the two species on the surface. Ziff and Fichthorn (*20*) have found from Monte Carlo simulation that islands of adsorbed molecules in a two-species reaction model on a two-dimensional catalyst surface (with no surface diffusion) are fractal with a fractal dimension of 1.9. As mentioned in the previous section a fractal dimension of 1.9 indicates absence of chaos.

CONCLUSIONS

Mukesh *et al.* (*5*) have shown that when reactant islands are assumed to be already present on the catalyst surface, it is possible to simulate periodic and aperiodic oscillations. In this communication it is demonstrated by Monte Carlo simulation, Fourier transform, and fractal analysis of the ensuing time-domain data that if one considers (a) the possibility of reaction only if two different species are present adjacent to each other, (b) adsorption of carbon monoxide and oxygen from the gas phase on vacant sites with dissociative adsorption of oxygen, and (c) migration of the two species on the surface, then the surface concentrations of the two species oscillate with time in a chaotic manner and also islands of the two spe-

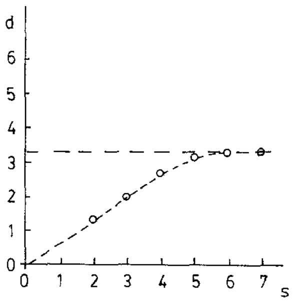

FIG. 6. s vs d. d-values are slopes of curves log $C(\gamma)$ vs log γ obtained from Fig. 5.

cies are formed and destroyed during the course of the simulation time. Fractal analysis also indicates that the time-series data is chaotic in nature embedded in a five-dimensional space phase. Hence the chaotic oscillation seen by many workers during the oxidation of carbon monoxide could be purely a molecular phenomenon arising due to the movement and reaction of the two species on the catalyst surface. Razon and Schmitz (*18*) in their review on the oxidation of carbon monoxide on platinum also conclude on the basis of a thorough study of the literature that even if the surface itself is physically or chemically uniform, in a real situation the movement of an adsorbate is hindered by the presence of other adsorbate in its vicinity and is possible only in a two-dimensional matrix. Hence, it is reasonable to expect that spatial patterns will arise spontaneously. It should be emphasized that the analysis described in the note applies only to single crystals and not to dispersed crystallites, where models must explain synchronization of oscillations, probably coupled through adsorption–desorption effects from the gas phase. The main drawback of the Monte Carlo simulation technique is that the probability parameters used in the simulation cannot be directly translated into absolute rate constants for different elementary steps. However, the ratio of the probability parameters used in the Monte Carlo simulation can be compared with the appropriate ratio of the kinetic constants obtained from kinetic data.

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