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2007 J. Phys.: Condens. Matter 19 065128

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Fractal pattern formation in the Ziff–Gulari–Barshad model

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Received 31 August 2006, in final form 28 September 2006

Published 22 January 2007

Online at stacks.iop.org/JPhysCM/19/065128

Abstract

The dynamics of the Ziff–Gulari–Barshad (ZGB) model is studied on three different two-dimensional (2D) lattices: square (sq) lattice, hexagonal-honeycomb (hex-hon) lattice and purely hexagonal (hex) lattice. The effects of the support geometry on the steady state and the dynamics are assessed. In all 2D lattice geometries the ZGB model is shown to exhibit non-equilibrium phase transitions of the first and second order, but the critical values of the kinetic parameters depend crucially on the substrate geometry.

Clustering and island formation are observed in all ranges of parameters, but the clusters are fractal only outside the active catalytic region. The fractal dimensions depend on the kinetic parameters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the past decades it has been demonstrated that the mean field approximation is not adequate to describe processes taking place on low-dimensional supports [1]. The problem stems from the limitations in mixing, which produce spatial and temporal inhomogeneities in low-dimensional systems. Diffusion, percolation, aggregation, chemical reactions are a few examples where the presence of a low-dimensional support induces non-trivial deviations from the mean field behaviour ([2–5] and references therein). In all these systems the mean field behaviour is approached as the dimensionality of the support increases. This is related to the fact that when the dimensionality increases, normally so does the number of nearest neighbours, or coordination number. As the coordination number increases, the system has more freedom in reacting, and mixing conditions are more easily attained, gradually approaching the mean field limit. Thus apart from the support dimensionality the geometry involved may also play

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a crucial role in the evolution of a reactive process. This is most obvious in heterogeneous catalytic systems, where the processes take place on metallic surfaces, such as Pt, Rh, Ir, Au and composite ones. The metal atoms on catalytic surfaces attain various configurations, such as square and hexagonal, and in many cases lattice phase transitions are known to take place, sometimes periodically, between different surface configurations [6–16].

The current study concentrates on the effects of the geometry on the output of heterogeneous catalytic processes, using as an example the CO oxidation on the surface of Pt. The surface of Pt(100), when catalysing CO oxidation, switches between a stable hexagonal configuration and a metastable square configuration. The metastable configuration is stabilized by the presence of CO and reconstruction between the two phases takes place depending on the partial surface coverages [10]. The dynamics on the two surfaces are different, since the geometry and the number of neighbours determines the electronic distribution between the surface atoms and thus their chemical activity. On the square lattice configuration O₂ adsorbs readily, dissociating into two atoms, while on the hexagonal lattice the sticking coefficient of oxygen is negligible. This interplay between geometry and reactivity is known to induce spatiotemporal oscillations and pattern formation in the CO oxidation system and in other heterogeneous catalytic reactions [6, 10, 14].

To address the effects of the support geometry on the dynamics of the CO oxidation system, kinetic Monte Carlo (KMC) simulations on Pt substrates with different configurations have been performed. In all cases the range of the kinetic parameters where the catalyst remains active have been studied and compared. Clustering has been explored under the different support geometries. It will be demonstrated that outside the active zone the clusters have fractal geometry, whose dimensionality relates to both kinetic parameters and support geometry.

In the next section we study the CO oxidation in three different lattice geometries, we compare the results and deduce the size of the active parametric region in relation to the coordination number of the lattice. In section 3 we study the clustering effects and we observe a scaling behaviour in the cluster size as a function of the kinetic parameters in the square lattice configuration. We compute the fractal dimension related to this clustering as a function of the kinetic parameters. In the concluding section we recapitulate our main results and we discuss open problems.

2. Modelling CO oxidation

One of the most extensively studied surface reactions is CO oxidation on the surface of Pt [10]. This reaction is of great technological importance in industry as CO is one of the most abundant and widely distributed air pollutants. From the experimental point of view it has been studied extensively because, as an out-of-equilibrium process, it presents interesting spatiotemporal evolution, producing rate oscillations, clustering and patterns.

The mechanism attributed to this reaction is known as the Langmuir–Hinshelwood (LH) scheme, described as follows:



In this heterogeneous reaction, all species are adsorbed on the surface of Pt, which may take several configurations: square, hexagonal and more complex ones forming steps and terraces and entering the perpendicular (third) dimension. In equation (1) the index ads means species adsorbed on lattice, g means species in the gaseous phase above the lattice and * denotes

the empty lattice sites. The parameters k_1 and k_2 represent the reaction rates. Since for the lattice dynamics only the on-lattice concentrations are relevant, the lattice coverages of CO, O and vacant adsorption sites are denoted by A , B and S , respectively.

A very successful simulation model which describes the LH process was introduced by Ziff, Gulari and Barshad (ZGB) in 1986 [18, 19]. This minimal model predicts kinetic phase transitions [18, 20–22] of two kinds: a smooth second-order phase transition followed by an abrupt one of first order. The transition points in the parametric space designate borderlines between poisoning and active steady states, which are often observed in catalysis experiments [6, 10, 23]. Kinetic Monte Carlo (KMC) models in the spirit of ZGB have also been proposed for NO reduction on the surface of Pt [24, 25]. The major success of these models is that it became possible to isolate and to identify the different mechanisms responsible for the spatial structures and temporal phenomena observed experimentally. Another important feature of the ZGB model is that its behaviour is robust under various modifications of the mechanism. The general features, including the two transitions, remain unchanged, with only slight shifts of the values of the critical points.

The model used in this study is a modified version of the original ZGB model which gives more freedom to the CO₂ complex to remain on the lattice for finite times and allows for slower CO₂ desorption. This mechanism has been proposed earlier in [26] and is summarized as follows.

0. Initially the lattice of size $L \times L$ is empty.
1. At every Elementary Time Step (ETS) one random lattice site (i, j) is chosen.
2. If the chosen lattice site (i, j) is empty then
 - 2a. with probability k_1 a CO particle adsorbs;
 - 2b. with probability $1 - k_1$ one of the nearest neighbours (i_r, j_r) is selected at random and if the selected neighbour is also empty, O₂ adsorbs dissociatively on (i, j) and (i_r, j_r) ;
 - 2c. if neither of the above takes place the algorithm returns to step 1 for a new elementary step to start.
3. If the chosen lattice site (i, j) contains a CO particle and a randomly selected neighbour (i_r, j_r) contains an O particle then with probability k_2 they form a complex CO₂ and desorb, leaving two vacant sites.
4. If the chosen lattice site (i, j) contains an O particle and a randomly selected neighbour (i_r, j_r) contains a CO particle then with probability k_2 they form a CO₂ complex and desorb, leaving two vacant sites.
5. An ETS is completed and the algorithm returns to step 1.

One Monte Carlo Step (MCS) consists of L^2 ETSs and corresponds to the time where all lattice sites have been selected once on average.

The difference between the current algorithm and the original ZGB one is that, in the latter, once a particle (CO or O) has been deposited on the lattice it immediately reacts with its neighbours and if the neighbours are of the right kind (O or CO, respectively) they immediately form the CO₂ complex and desorb from the lattice. In the currently proposed version, the particles remain adsorbed on the lattice longer, until they are selected by the algorithm to react with their neighbours.

Despite the modification described above, the current ZGB variant remains closely related to the original ZGB model, as was anticipated due to the robust character of the model. As was also demonstrated in earlier studies [26] the current ZGB version on the square lattice produces critical points of the same kind but slightly shifted with respect to those of the original ZGB.

For this reason in the following we will refer to this modified version simply as the ZGB model, without making any distinction between the original and the modified model, unless otherwise stated. The value of k_2 is set to $k_2 = 1.0$ in all following computations. In all cases explored below, the kinetic parameters do not change with the lattice, only the number of bonds change from one lattice type to another.

2.1. Results on the square lattice

In the case where the catalytic surface is represented as a square (sq) lattice, each lattice site (i, j) has four nearest neighbours, namely $(i, j + 1)$, $(i, j - 1)$, $(i + 1, j)$ and $(i - 1, j)$. When exploring the behaviour of the system for parametric values $0 \leq k_1 \leq 1$ and $k_2 = 1$, three distinct parametric regions have been identified: (a) for values $0 \leq k_1 < 0.3481$ the system is poisoned by O, (b) for values $0.3481 < k_1 < 0.3930$ the system is active and all constituents are found on the lattice, and (c) for values $0.3930 < k_1 < 1.0$ the system is poisoned by CO. The first critical point, $k_1 = 0.3481$, is described as a smooth kinetic transition and is of second order, while the second critical point, $k_1 = 0.3930$, is described as an abrupt transition and is of first order. For comparison, the critical points in the original ZGB model are $k_1 = 0.389$ for the smooth transition and $k_1 = 0.525$ for the abrupt transition.

2.2. Results on the hexagonal lattice

If the catalytic surface is in a pure hexagonal (hex) configuration each site (i, j) is in contact with six nearest neighbours, e.g., $(i, j + 1)$, $(i, j - 1)$, $(i + 1, j)$, $(i - 1, j)$, $(i + 1, j + 1)$ and $(i - 1, j - 1)$. Again, three parametric regions are observed as before. The smooth kinetic phase transition point is found at $k_1 = 0.3086$, while the second abrupt transition point is located at $k_1 = 0.3912$. The active region is more extended in the case of the hexagonal lattice due to the increased number of nearest neighbours, which allows for more efficient mixing than in the case of the square lattice.

2.3. Results on the hexagonal-honeycomb lattice

If the catalytic surface is in the hexagonal-honeycomb (hex-hon) configuration, every site (i, j) has three nearest neighbours, e.g., $(i, j + 1)$, $(i, j - 1)$ and either $(i - 1, j)$ (if j is odd) or $(i + 1, j)$ (if j is even). Also, in this case three parametric regions are observed. The smooth kinetic phase transition point is found for $k_1 = 0.3734$, while the second abrupt transition point is located at $k_1 = 0.3821$. The active region is now less extended than in the case of the square and hexagonal lattices due to the limited number of nearest neighbours, which causes less efficient mixing than in the previous two cases.

For comparison, all three cases are presented together in figure 1.

3. Clustering in the ZGB model

From the structure of the LH scheme two reactive steps, the dissociative adsorption of O_2 (1b) and the desorption of the complex CO_2 (1c), are cooperative phenomena which can lead to spontaneous clustering in the system. In particular, O_2 adsorption leads to the formation of a two-cluster of O, while CO_2 desorption leads to the formation of two-clusters of empty sites. The CO adsorption is a spontaneous, non-cooperative effect which reduces clustering. Thus, in the system, we have competitive factors: production as well as destruction of clusters. In figure 2, representative lattice configurations are depicted for $k_1 = 0.347$ in the parametric zone where the catalyst is poisoned by O. The lattice size is $L \times L = 400 \times 400$ sites. At the initial stages of evolution the system is randomly populated by the three species, while as

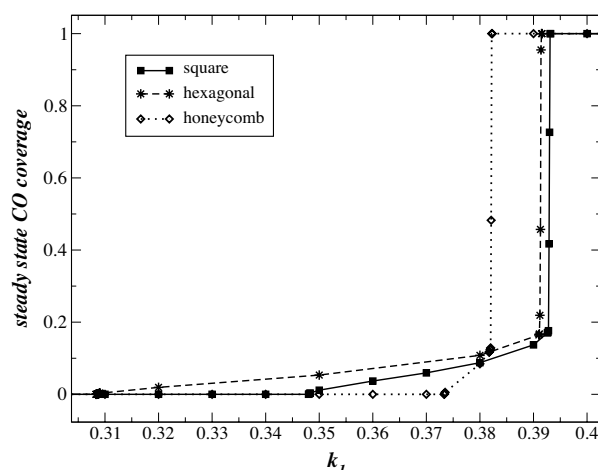


Figure 1. The CO steady state concentrations as a function of the kinetic parameter k_1 for three different lattice types: (a) square (solid line), (b) hexagonal (dashed line) and (c) hexagonal-honeycomb (dotted line).

time increases and while the system tends to the poisoning state, clustering phenomena of the CO particles and vacant sites are observed (figure 2, $t = 4, 500, 5000$ MCS). The formation of clusters is obvious and their variety of sizes and forms induces the idea of a fractal clustered structure.

To explore the possibility of scaling behaviour in the cluster structure the standard box counting method is used. One of the three constituents (CO in this case) is assumed to be the covering (or distributed) species, while the other two (O and empty sites in this case) are assumed to be the support. The entire lattice is covered by boxes of size s . Denote by $N(s)$ the number of boxes of size s needed to cover all the distributed (CO) species on the lattice. If the number of boxes $N(s)$ scales as

$$N(s) \sim s^{-d_f} \quad (2)$$

then d_f is the fractal dimension of the distributed species. In the case where $d_f = 2$ on a 2D support then the distributed species does not have a fractal structure but it covers the support randomly and homogeneously. If $d_f = 0$ there is complete absence or spurious presence of the distributed species. In all other cases, the distributed species covers the support fractally. In figure 3, the values of $N(s)$ of CO as a function of s is depicted for different times (MCS) in a double logarithmic scale. It is observed that the slope of the line starts curving for early times and later acquires a linear part for about two orders of magnitude, dictating a unique spatial scaling. This scaling behaviour persists for intermediate temporal scales and the values of the fractal dimensions reported have been calculated for consistency when the system has reached 75% of its lifetime before poisoning is attained. Only near the steady state, where the system is populated by O, do the number of CO particles and the fractal dimensions vanish.

In figure 4, representative lattice configurations are depicted for $k_1 = 0.37$ in the parametric zone where the catalyst is active. Simple inspection of the particle distributions shows that all particles are more or less homogeneously distributed on the lattice.

Similarly to figure 3, in figure 5 the values of $N(s)$ as a function of s are depicted for different times (MCS) and for the parametric value $k_1 = 0.37$ where the catalyst is active. It is observed that the slope of the line remains constant, equal to 2, indicating a uniform non-fractal coverage of the support.

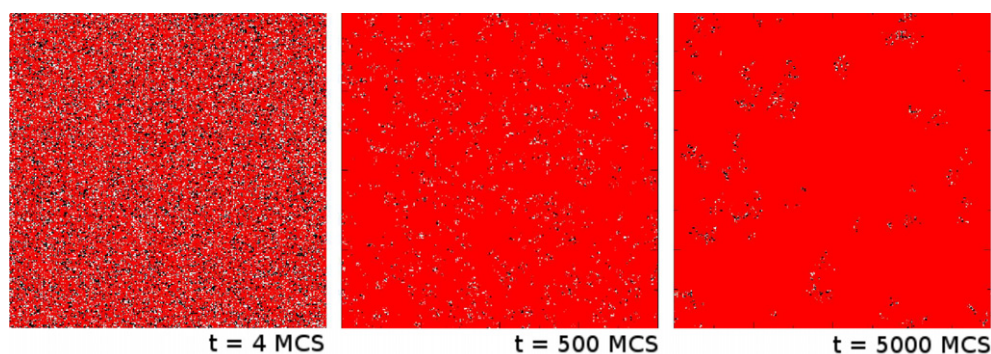


Figure 2. Representative square lattice configurations at three different time steps, for parameter values $k_1 = 0.347$, $k_2 = 1.0$, located outside the active zone. Black points correspond to Co, grey (red) correspond to O and white points correspond to vacant sites.

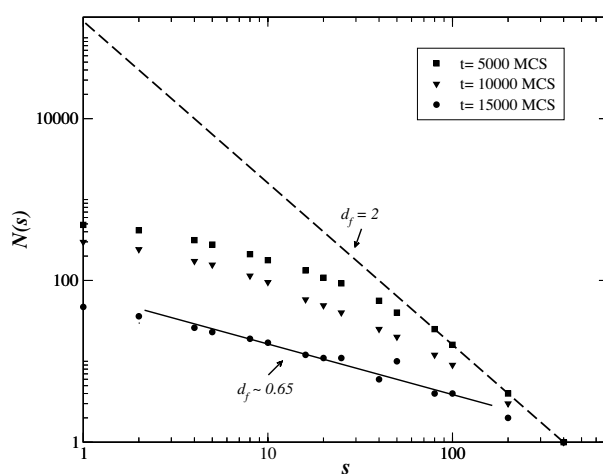


Figure 3. The scaling of $N(s)$ for the CO species at different time steps on a square lattice support. The kinetic parameters are $k_1 = 0.347$ and $k_2 = 1.0$.

Similarly to figures 2 and 4, in figure 6 representative lattice configurations are depicted for $k_1 = 0.394$ within the parametric zone where the catalyst is poisoned by O. Simple inspection shows clear non-trivial scaling behaviour and fractality for intermediate timescales, before the CO poisoning state is attained.

In figure 7, similarly to figures 3 and 5, the value of $N(s)$ as a function of s is depicted for different times (MCS) and for $k_1 = 0.394$. It is observed that even from early time steps linear slopes are formed for almost two spatial scales. The fractal dimension of the oxygen clusters is calculated when the system has reached 75% of its lifetime before poisoning.

As a concluding remark in this section, it is noted that when the oxidation of CO takes place on low-dimensional supports, numerical simulations indicate that clusters are formed whose spatial distribution presents non-trivial, fractal scaling. In particular, the ZGB realization of the CO oxidation demonstrates that non-trivial clustering is observed for intermediate times and for kinetic parameters away from the active zone, while within the active zone the three species are distributed randomly, but homogeneously, on the lattice. Qualitatively similar results are

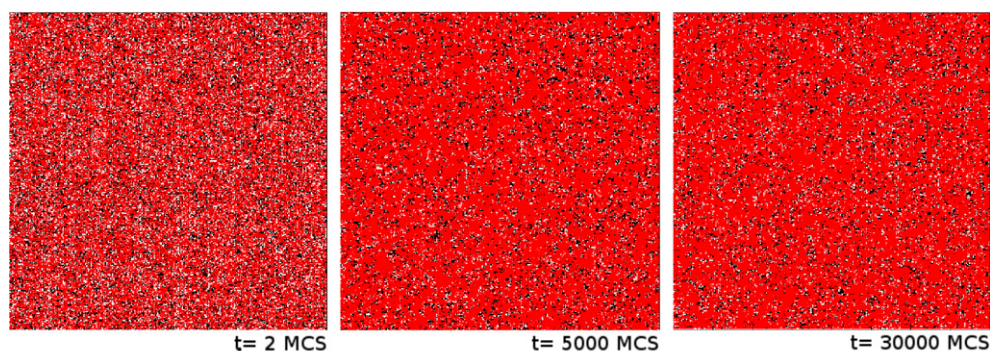


Figure 4. Representative square lattice configurations in different time steps, for $k_1 = 0.37$, $k_2 = 1.0$, parametric region where the catalyst is active. The lattice size is $L \times L = 400 \times 400$ sites. Colours as in figure 2.

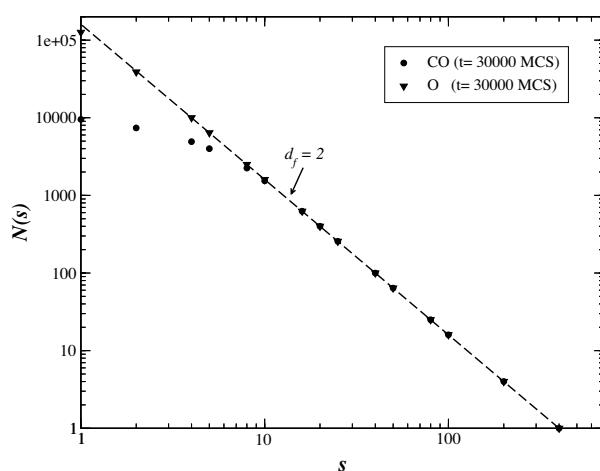


Figure 5. The scaling of $N(s)$ for CO and O clusters, at different time steps on a square lattice support. The lattice size is $L = 400$ and the kinetic parameters are $k_1 = 0.37$ and $k_2 = 1.0$, within the parametric range where the catalyst is active.

also observed for the hexagonal and hexagonal-honeycomb lattices, but the value of the fractal dimensions depends on the lattice type.

In figure 8, cumulative results of the cluster fractal dimensions on the square lattice are depicted as a function of the kinetic parameter k . The kinetic phase transitions which were first observed in terms of the particle concentrations are also mirrored here in terms of the fractal dimensions of the corresponding covering species.

4. Conclusions

In the current study the influence of the substrate geometry (as opposed to dimensionality) on reactive dynamics is explored, using the Ziff–Gulari–Barshad model of CO oxidation on the surface of Pt. For the modelling three types of lattices are employed, having different geometry (coordination number): square lattice (four nearest neighbours), hexagonal lattice (six nearest neighbours) and hexagonal-honeycomb lattice (three nearest neighbours).

The main geometry effect is the shifting of both critical transition points and the modification on the size of the parametric zone where the catalyst is active. From the numerical

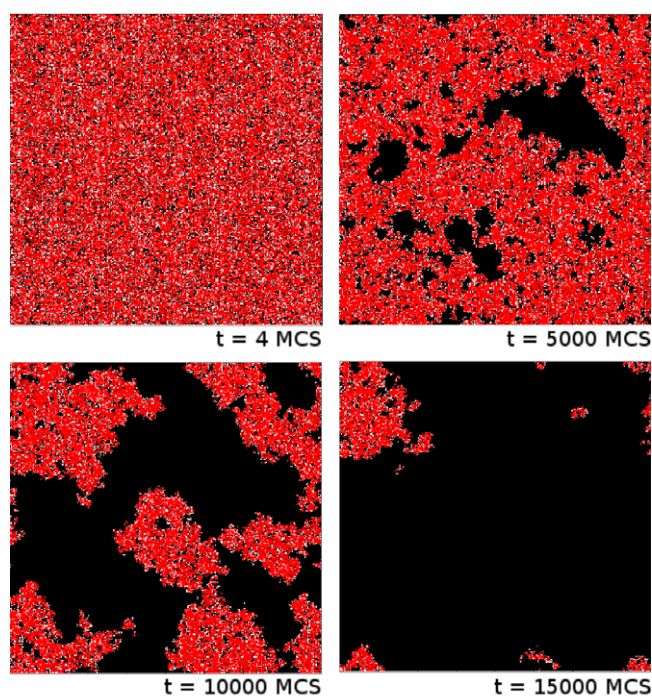


Figure 6. Representative square lattice configurations at different time steps, for parameter values $k_1 = 0.394$, $k_2 = 1.0$, outside the active zone. Colours as in figure 2.

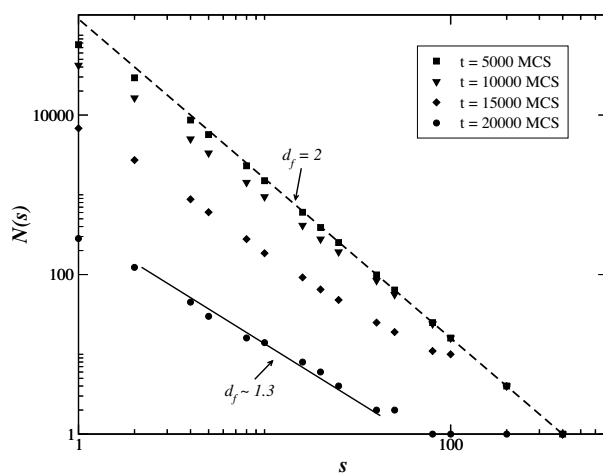


Figure 7. The scaling of $N(s)$ for the species O at different time steps on a square lattice support. The kinetic parameters are $k_1 = 0.394$ and $k_2 = 1.0$, within the parametric range where the catalyst is finally poisoned by CO.

simulations it is deduced that the higher the coordination number of the lattice, the larger the parametric zone where the catalyst remains active. This is attributed to the larger number of possibilities for reaction and thus higher possibility for the catalyst to remain active.

From the observation of the lattice configuration during the evolution of the reactive system, it becomes apparent that clustering of different species may be observed. In particular,

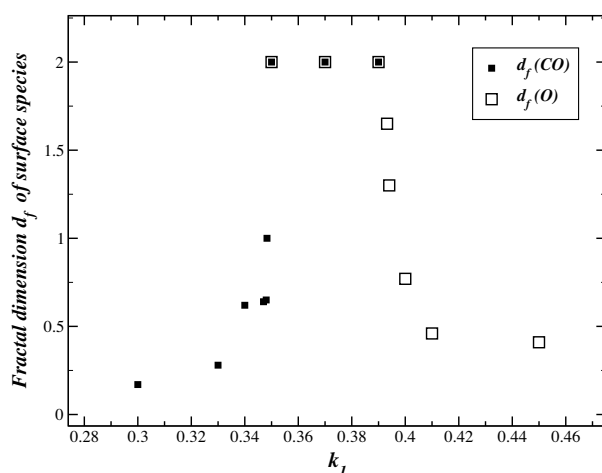


Figure 8. The values of d_f as a function of the kinetic parameter k_1 ($k_2 = 1.0$) for the square lattice configuration.

the clusters are distributed in a random fractal manner on the lattice, when the parameter k_1 is in the range where the catalyst attains a poisoning state. Alternatively, the clusters cover the 2D lattice in a random but uniform way, when the parameter k_1 is within the range where the catalyst remains active. The numerical investigations were conducted on the square lattice configuration, but preliminary results on the hexagonal and hexagonal-honeycomb lattices indicate that this effect holds qualitatively, independently of the lattice type.

In real physical surface processes, the formation of clusters of homologous particles with fractal local properties is one way through which the system attains a poisoning state. If a system maintains a uniform distribution then all components have equal opportunity to react and the system (catalyst in this case) remains in an active state. Alternatively, when segregation and clustering of the species dominate on the surface the reactivity is limited only between the species at cluster interfaces. As the number of cluster interfaces and/or their sizes decrease, larger and larger clusters are created, leading to poisoning. Note that fractal clusters have extended interfaces and designate an intermediate state between a completely random system, where the size of cluster interfaces attains a maximum, and a poisoned system, where the size of cluster interfaces is zero. If, on the other hand, a mixing process is added (e.g., diffusion of some species) making the local particle distributions uniform, local fractality is destroyed and higher reactivity may be attained.

The ZGB model is a minimal model describing the complex CO oxidation process, which is known to develop very special characteristics, such as spatiotemporal oscillations, chaos, and various dynamical patterns depending on the reaction conditions. This minimal model does not account for such features because it does not take into account processes such as surface diffusion of the species (mainly CO), surface reconstruction, possibility of desorption of the reactants, and terrace and edge effects. (It is known, for example, that if different sticking coefficients of some of the reactants are considered, the range of active catalytic states may increase [27].) It would be interesting to add at least some of the above processes and explore the persistence of fractality and clustering under these modifications.

As a final conclusion, we would like to add that this work indicates further that clustering and fractality emerge spontaneously in nonlinear dynamical systems, when they are constrained on low-dimensional surfaces. It remains an open problem, to be confirmed in other cases of reactive dynamical systems, if the fractal behaviour is always consistent with the poisoning of

the catalyst, whereas homogeneously distributed systems are consistent with the active states of the catalyst.

Acknowledgments

VKN acknowledges financial support through the NCSR ‘Demokritos’ fellowships program. The authors would like to thank Professors G Nicolis, R Imbihl and A S Mikhailov and Drs G A Tsekouras and O Chichigina for helpful discussions.

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