

Structural effects in the kinetic behavior of the monomer–dimer surface reaction over nondeterministic fractal surfaces

Joaquín Cortés* and Eliana Valencia

Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, P.O. Box 2777, Santiago, Chile

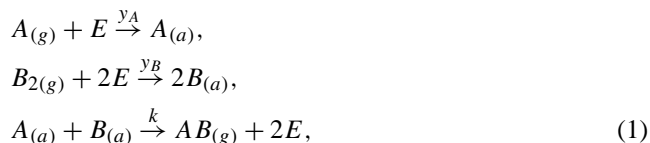
Abstract

A study is made of the segregation effect of adsorbed species related to the inner structure of two bidimensional adsorbent fractals, the incipient percolation cluster (IPC) and the backbone of the IPC, and their connection with the rate-determining step of the kinetic mechanism of the monomer–dimer (MD) surface reaction on those fractals. Production, R_{AB} , is proportional to the concentration of A in the gas phase y_A and to the fraction of vacant superficial sites x_E ($R_{AB} = y_A x_E$), and it is shown that adsorption of the monomer is the rate-controlling step of the reaction mechanism.

Keywords: Surface structure; Fractal surface; Solid–gas interfaces; Surface chemical reaction; Monte Carlo simulations; Catalysis; Computer simulations; Models of surface chemical

1. Introduction

The model proposed by Ziff, Gulari, and Barshad (ZGB) [1] in 1986 for the monomer–dimer surface reaction $2A + B_2 \rightarrow 2AB$, which mimics the oxidation reaction of CO, was the precursor of a large number of papers dealing with models for analyzing the complicated behavior of irreversible dynamics systems (oscillations, irreversible phase transitions (IPT), etc.) [2]. ZGB proposed a simplified Langmuir–Hinshelwood (LH) mechanism whose lattice-gas version is given by



where E is an empty site on the surface; (a) and (g) refer to the adsorbed phase and the gas phase, respectively; y_A is the mole fraction of A in the gas phase and $y_B = 1 - y_A$ is the mole fraction of B , since the impingement rates are normalized. The ZGB model, which assumes a square lattice of sites having nearest neighbors (nn), excludes the existence of

diffusion and desorption of the adsorbed species and considers the extreme case of an infinite reaction rate k . The results of the ZGB model have shown the existence of reactive (“reaction windows”) and nonreactive or poisoned zones separated by irreversible phase transitions. In general, two types of IPTs have been observed, one continuous, y_{A1} , and one discontinuous, y_{A2} , which have been designated, by analogy with thermally driven transitions which are reversible, as first and second order. The study of IPTs has experienced a dramatic growth since the publication of the pioneering work of the ZGB model, and it has recently been reviewed by Evans [3], Zhdanov and Kasemo [4], and Albano [5]. The reactive window undergoes alterations if additional effects are considered in the original model. Surface diffusion, for example, especially of monomer A , does not have a significant influence on y_{A1} , but y_{A2} undergoes an increase which, according to Mai et al. [6] and Lutsevich et al. [7], must reach the “stoichiometric point” of $2/3$. Evans [8], however, argues that it should tend to 0.5951 and that $2/3$ would represent the spinodal rather than the transition point. As shown by Kaukonen and Nieminen [9], the effect of desorption on the model is the randomization of the monomer distribution, and even though this stage does not affect y_{A1} , it alters the critical zone of poisoning with A . The other effect, studied by Bagnoli et al. [10] and by Satulovsky and Albano [11], is the existence of interactions between the adsorbates, which

* Corresponding author.
E-mail address: jcortes@dqb.uchile.cl (J. Cortés).

cause alterations in the phase diagram that depend on the type and magnitude of these interactions.

In general, superficial heterogeneity can be of two kinds, geometric and energetic, and these effects may also be associated with one another. Even though the study of the effects of energetic heterogeneity on the gas–solid adsorption phenomenon has been developed greatly and have been reviewed in the excellent monograph by Rudzinski and Everett [12], in which the work of our group on the subject has been considered extensively [13], in the case of complex catalytic heterogeneous systems most of the published papers assume a homogeneous surface, partly for experimental reasons and also because of the excessive complexity of the system that it is desired to model. Thus, in the present stage of the literature on the subject, theoretical and simulation studies include only the geometric factor of heterogeneity. This has happened only in relatively recent years in Monte Carlo (MC) studies of surface reactions on substrates which include degrees of geometric heterogeneity, modeling the surface by means of random fractals and percolation clusters in the studies of Albano [5,14], Casties et al. [15], Moiny and Dumont [16], Hovi et al. [17] and our group [18] or by means of deterministic fractals such as Sierpinski’s carpet and gasket [19]. Interest in these types of substrates is based on the fact that the surface of most solids at the molecular level must be considered as a microscopic fractal [20]. Such is the case, for example, of many catalysts consisting of small metallic fractal clusters dispersed on a fractal support [21] or, in some cases, on thin discontinuous metallic films [22].

An interesting subset of the IPC is the backbone that is obtained by removing the dangling bonds from the IPC [23]. Both substrates constitute fractal lattices having dimensions $d_f = 91/48$ for the IPC [24] and 1.6432 for the backbone [25]. An important question about these percolation clusters refers to their “texture” or internal structure, which is, as we shall see, of direct importance in the behavior of these substrates in models of surface reactions. Three distinct pictures have been proposed for describing the structure of these clusters [26,27]. The first one suggests a superlattice of nodes joined by links or macrobonds of various unidimensional “cutting bonds” (like large fishing nets). At the opposite end of this “nodes and links” model, the cluster has been replaced by a Sierpinski gasket, which assumes a structure of interconnected loops and so has no singly connected links, but does have multiply connected “blobs” of all length scales. A third model which seems to have more advantages considers a “nodes, links and blobs” picture of the cluster. However, since these structures are self-similar, the blobs are “volatile” fractals in Herrmann and Stanley’s terminology [27], in the sense that if the size, L , of the lattice is increased, smaller blobs can become part of larger blobs.

The fractal nature of the substrate introduces interesting new effects on the reactive zone, in addition to those related to the introduction of new mechanism stages or adsorbate interactions. This paper studies the behavior of the surface

monomer–dimer (MD) reaction over the IPC and a substrate formed by the backbone of the IPC. The phase diagrams (critical concentrations and reactive window) of both fractals and the influence of the inner structure of the fractal on the kinetic behavior (rate-controlling step of the mechanism) of the surface reaction are compared.

2. Simulations and results

The MD reaction was studied by means of Monte Carlo (MC) simulations according to the mechanism shown in Eq. (1), simulated over two fractals: the incipient percolation cluster (IPC) and the backbone generated from the IPC. In the case of the IPC, the substrate sites were generated operationally on a square lattice of sites of size $L \times L$ by blocking a fraction $r = 1 - p_c$ of the sites (impurities) with $p_c = 0.592746$. The spanning cluster was chosen by means of Kopelman’s algorithm [28], applied without periodic boundary conditions and requiring the larger cluster to percolate in both directions. To build the backbone, Herrmann et al.’s burning algorithm [27,29] was applied to the already generated IPC starting from two points located near two opposite corners, separated by a distance greater than L . The results are the average of 400 experiments carried out, two for each of the 200 substrates previously generated independently, considering two different initial sites using different random numbers for each value of L , both for the IPC and for the respective backbone. We have considered that a value of $L = 70$ as the lower limit for the size of the lattice is sufficient for the paper’s objectives. This is in agreement with the literature [5] as well as with some of our recent papers [18] in which we have been concerned very particularly to ensure that the description of the fractal, given its statistical character, guarantees sufficiently the reproducibility of the results.

The steps involved in the simulation procedure are as follows. In the adsorption stage, monomer A is adsorbed with probability y_A on a random site of the lattice if it is vacant. If it is already occupied, is blocked, or does not belong to the spanning cluster, the event is rejected and the trial ends. In the case of dimer B_2 , it is adsorbed with probability $1 - y_A$ if two randomly chosen nn lattice sites are vacant. If both sites are vacant, the dimer is adsorbed; otherwise, the event is rejected and the trial ends. In the reaction step and after a successful adsorption, one has to scan randomly the nn sites of the A or B atoms that have just been adsorbed. Atoms A and B sitting next to each other form AB that desorbs from the surface, leaving behind two vacant sites. The time unit is one Monte Carlo step (MCS), defined as a number of MC attempts equal to the number of sites, $L \times L$, in the lattice. The results were obtained using in general 4×10^4 MCS for the backbone and 3×10^4 MCS for the IPC.

The IPT values were obtained following the procedure of Albano [14,30] who, using finite-size scaling analysis, determined for the MD reaction on IPC the values $y_{A1} = 0.314$

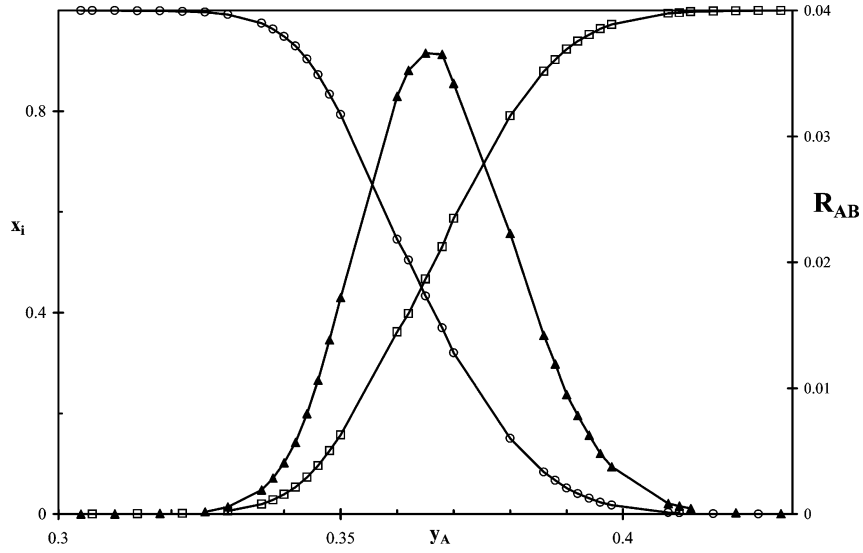


Fig. 1. Phase diagram of the monomer-dimer reaction on the backbone obtained by MC. Average coverage x_A (\square), x_B (\circ), and production R_{AB} (\blacktriangle) versus y_A . R_{AB} (AB number/site MCS); $y_{A1} = 0.323$; $y_{A2} = 0.418$.

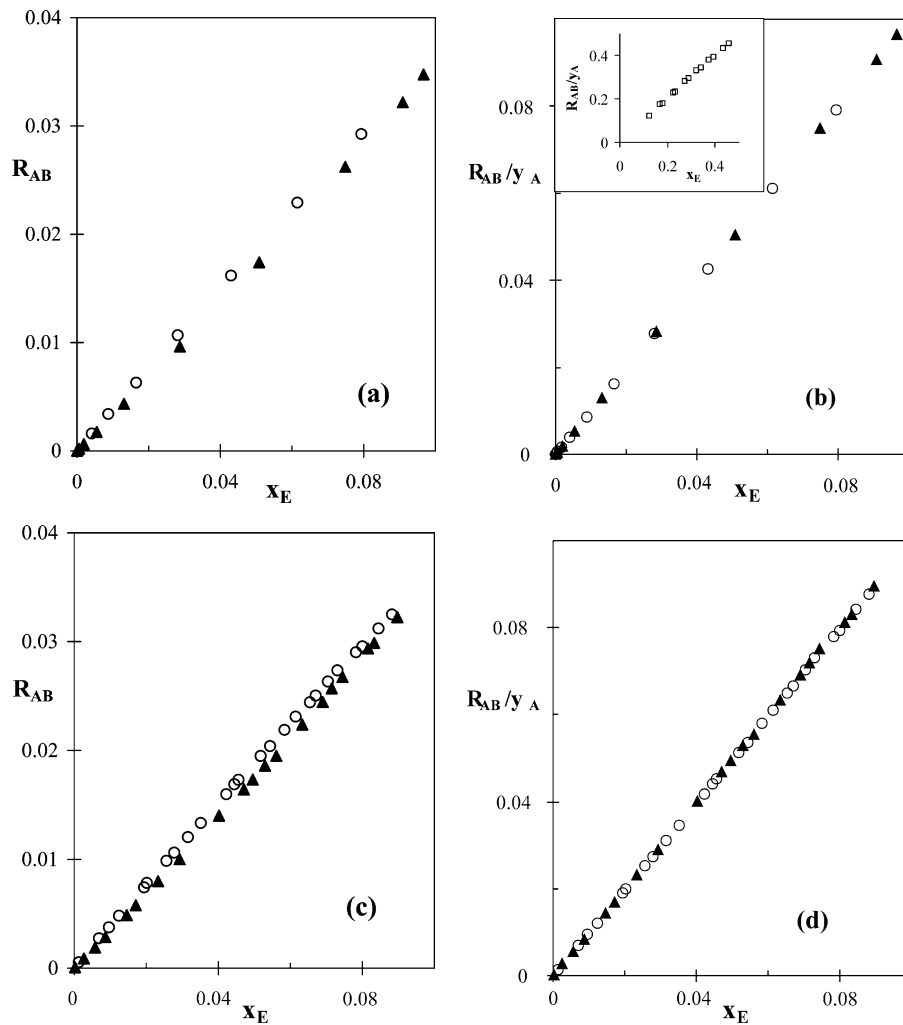


Fig. 2. (a), (b) Plots of R_{AB} and R_{AB}/y_A versus x_E , respectively, for the monomer-dimer reaction on the IPC; $y_A < y_A(R_{AB} \text{ peak})$ (\blacktriangle); $y_A > y_A(R_{AB} \text{ peak})$ (\circ). The insert shows the case of a uniform substrate, $L = 100$, 10^7 MCS. (c), (d) The same on the backbone.

and $y_{A2} = 0.408$. Values of $y_{A1} = 0.323$ and $y_{A2} = 0.418$ were obtained for the MD reaction on the backbone.

Figure 1 shows, in the phase diagram for the MD reaction on the backbone, the concentrations of the superficial species x_i ($i = A, B$), defined with respect to the sites of the active substrate, and the production R_{AB} , defined as the number of AB particles per site and per MCS, versus the concentration of A in the gas phase y_A .

Figure 2 shows the results of the production R_{AB} versus x_E for the MD reaction on the backbone corresponding to $L = 70$ – 400 , and on the IPC we have applied the same value used by Albano, $L = 150$ [14]. Considering that for the ZGB model on the IPC Albano [30] reports that R_{AB} is proportional to the fraction of empty sites x_E on the substrate in the whole reactive zone, we have plotted R_{AB} versus x_E in Figs. 2a and 2c, showing an approximately straight line, even though a separation is seen between the points on different sides of the peak of the R_{AB} curve of the phase diagram. However, if R_{AB}/y_A is plotted versus x_A , a straight line with an excellent correlation better than 0.9999 results for both substrates over the whole range of x_E , showing a perfect coincidence between the data obtained from both sides of the R_{AB} peak. This shows that the following expression, which will be discussed below, is followed for the production:

$$R_{AB} = y_A x_E. \quad (2)$$

This differs from Albano's finding [30] since he suggests a behavior of type $R_{AB} \propto x_E^{1.5}$.

3. Discussion

The phase diagram of Fig. 1 shows for the MD reaction on the backbone a behavior similar to the IPC case previously studied by Albano [14], with two continuous phase transitions, in contrast to results from the same model applied to homogeneous media, leading to a curve for R_{AB} having a rather symmetric peak, roughly at the center of the reaction window, which coincides with the minimum of $x_A + x_B$. An active steady state regime (the reactive window) is seen only for $y_{A1} < y_A < y_{A2}$, where y_{Ai} ($i = 1, 2$) are the critical concentrations, beyond which only nondegenerate absorbing states exist in which the surface is poisoned by species A or species B . It is also seen that the effect of removing the dangling bonds causes a slight shift of the critical concentrations to higher values, retaining, however, the width of the reactive window.

The snapshots in Fig. 3 illustrate the conformation of the superficial species for various situations of the systems, typically explaining the behavior of a surface reaction over the studied fractals. With the purpose of quantifying the picture provided by the snapshots, we have determined $x_i(k)$, the fraction of sites with species i ($i = A, B, E$) such that they have k neighbors belonging to the substrate. After inspection of a set of snapshots like those in Fig. 3, and of the corresponding $x_i(k)$ values, some interesting conclusions may be

obtained in relation to the structure of the system, while at the same time the behavior of the kinetic mechanism corresponding to Eq. (2) can be explained.

In the first place, a segregation of the superficial species is seen in regions poisoned alternatively by A and B , which are the result of the self-poisoning of finite samples [14] and are also the cause of the fluctuations commonly seen in simulations. Just as rather large B islands and a negligible A coverage dominate the kinetics of the ZGB model in the reactive zone on homogeneous media, in the case of these disordered substrates there are regions covered by either pure A or pure B species, forming islands of relatively high stability since their existence is related to the structure of the substrate [30].

The arrangement of the various superficial species in the different structural sectors of the fractal substrate naturally depend on the value of y_A . We shall first analyze extreme situations in which the superficial concentration of one of the adsorbates is small. For example, if we consider only the average of the nonpoisoned configurations, for a value of $y_A = 0.335$, located in the neighborhood of y_{A1} , we have that for the backbone only approximately 30% of the A particles occupy sites having three or four neighbors ($x_A(3) + x_A(4) \approx 0.3$), showing that the particles of A for this value of y_A are located basically on the links of the fractal, as seen in Fig. 3a, since we have approximately 70% of the A particles occupying sites with only one and two neighbors. This is different from what happens at the other end of the phase diagram. For example, for $y_A = 0.39$, located in the neighborhood of y_{A2} , approximately 70% of B occupy sites having three or four neighbors belonging to the substrate ($x_B(3) + x_B(4) \approx 0.7$) so that the B particles occupy mostly the blobs, in view of the natural difficulty for occupying the links because of the requirement of two nn sites for the adsorption of B_2 to occur, as seen in Fig. 3c.

The region of greatest interest is, however, the active zone where the reaction takes place, and therefore the distribution of the empty species E there is of fundamental importance. For example, for $y_A = 0.36$, located in the neighborhood of the peak of the R_{AB} production curve, approximately 65% of the vacant sites are sites with three or four neighbors ($x_E(3) + x_E(4) \approx 0.65$) for both substrates, showing that the empty sites are found on blobs rather than on the links, as seen in Figs. 3b and 3d. With respect to the superficial clusters of A and B , there are empty sites, as expected, in the boundary zone located between both kinds of clusters. However, most of them are inserted within the B clusters and almost no empty sites can be found within the A clusters. This observation is of interest in relation to the kinetics of the system described by Eq. (2). The productive situations occur when a particle of A reaches an empty site and reacts with a neighboring one of B . This happens within the B clusters and in the boundary zone between the A and B clusters and explains Eq. (2), which shows that the production of R_{AB} is proportional to the empty sites and to y_A , the

concentration of A in the gas phase. In other words, the kinetics is thus controlled by the adsorption of A , which is the first step in the LH mechanism of Eq. (1). The adsorption of B_2 particles, on the other hand, is not productive in the active zone because two conditions are needed: the existence of two nn empty sites, and that around them there must be particles of A . The latter condition is not fulfilled within the B clusters, where most of the E sites are located, and the former is very improbable in the narrow boundary zone between the A and B clusters where the rest of the E sites are found.

Equation (2) is also followed by the model in a homogeneous system, as seen in the insert of Fig. 2b. Although it is completely different from the case of a fractal substrate, it is interesting to note that the explanation of the phenomenon at the microscopic level is the same as the one given in this paper for the fractal surface since for homogeneous media in the active zone the substrate is mainly covered with B particles and x_A is negligible, except when y_A is very close to y_{A2} , and therefore the empty sites are in a similar situ-

ation, yet for different reasons, as in the case of a fractal substrate.

4. Conclusions

Simple kinetic behavior in which monomer adsorption is the rate-controlling step in the mechanism of the superficial monomer–dimer reaction is seen in the systems studied. In the case of the incipient percolation cluster and backbone fractals, this is explained by the segregation of the A and B species and by the distribution of the vacant sites on the substrate structure.

The phase diagram of the monomer–dimer reaction on the backbone shows a behavior qualitatively similar to that of the same reaction over the incipient percolation cluster, which differs from the previous one in the dangling bonds, showing two continuous phase transitions, the same reactive window width, and a slight shift of the critical values to higher concentrations of A in the backbone with respect to the IPC.

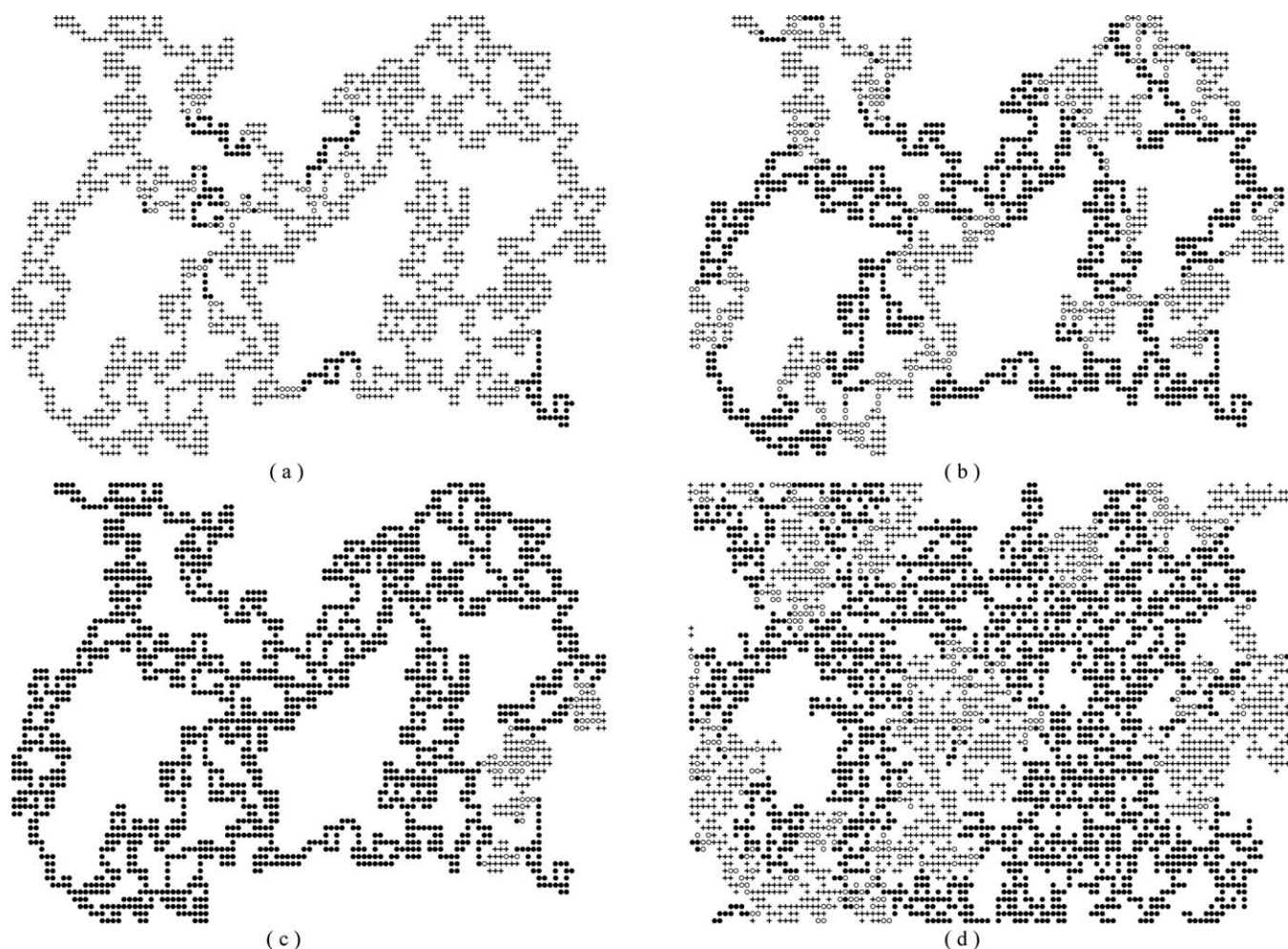


Fig. 3. Snapshots of one part of the substrate surface under steady-state conditions after 4×10^4 MCS of a lattice of size $L = 300$ for the monomer–dimer reaction. B (+), A (●), and E (○). (a) On the backbone at $y_A = 0.335$ in the neighborhood of y_{A1} . (b) The same at $y_A = 0.36$ in the neighborhood of the peak of R_{AB} . (c) The same at $y_A = 0.39$ in the neighborhood of y_{A2} . (d) On the IPC corresponding to $y_A = 0.36$.

Acknowledgment

The authors thank Fondecyt N 8.000.015 for financial support of this work.

References

- [1] R.M. Ziff, E. Gulari, Y. Barshad, *Phys. Rev. Lett.* 56 (1986) 2553.
- [2] G. Nicolis, I. Prigogine, *Self-Organization in Nonequilibrium Systems*, Wiley-Interscience, New York, 1977; H. Haken, *Synergetics*, Springer-Verlag, New York, 1977.
- [3] J.W. Evans, *Langmuir* 7 (1991) 2514.
- [4] V.P. Zhdanov, B. Kasemo, *Surf. Sci. Rep.* 20 (1994) 111; V.P. Zhdanov, *Surf. Sci. Rep.* 45 (2002) 231.
- [5] E.V. Albano, *Heterog. Chem. Rev.* 3 (1996) 389; E.V. Albano, in: M. Borówko (Ed.), *Computational Methods in Surface and Colloid Science*, Marcel & Dekker, New York, 2000, pp. 387–437, Chap. 8.
- [6] J. Mai, W. von Niessen, A. Blumen, *J. Chem. Phys.* 93 (1990) 3685.
- [7] L.V. Lutsevich, V.I. Elokhin, A.V. Myshlyavtsev, A.G. Usov, G.S. Yablonskij, *J. Catal.* 132 (1991) 302.
- [8] J.W. Evans, *J. Chem. Phys.* 98 (1993) 2463.
- [9] H.P. Kaukonen, R.M. Nieminen, *J. Chem. Phys.* 91 (1989) 4380.
- [10] F. Bagnoli, B. Sente, M. Dumont, R. Dagonnier, *J. Chem. Phys.* 94 (1991) 777.
- [11] J. Satulovsky, E.V. Albano, *J. Chem. Phys.* 97 (1992) 9440.
- [12] W. Rudzinski, D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.
- [13] J. Cortés, *J. Chem. Phys.* 88 (1988) 8081; J. Cortés, *J. Chem. Phys.* 91 (1989) 1932; J. Cortés, *Langmuir* 9 (1992) 2583.
- [14] E.V. Albano, *Phys. Rev. B* 42 (1990) 10818; E.V. Albano, *Phys. Rev. A* 46 (1992) 5020.
- [15] A. Casties, J. Mai, W. von Niessen, *J. Chem. Phys.* 99 (1993) 3082.
- [16] F. Moiny, M. Dumont, *J. Chem. Phys.* 111 (1999) 4743.
- [17] J.P. Hovi, J. Vaari, H.P. Kaukonen, R.M. Nieminen, *Comp. Mater. Sci.* 1 (1992) 33.
- [18] E. Valencia, J. Cortés, H. Puschmann, *Surf. Sci.* 470 (2000) L109; J. Cortés, E. Valencia, *Physica A* 309 (2002) 628; J. Cortés, E. Valencia, *J. Colloid Interface Sci.* 252 (2002) 256.
- [19] J. Mai, A. Casties, W. von Niessen, *Chem. Phys. Lett.* 196 (1992) 358; A.Y. Tretyakov, H. Takayasu, *Phys. Rev. A* 44 (1991) 8388; Z. Gao, R. Yang, *Phys. Rev. E* 60 (1999) 2741; I. Jensen, *J. Phys. A Math. Gen.* 24 (1991) L1111.
- [20] D. Avnir, D. Farin, P. Pfeifer, *Nature* 308 (1984) 261; P. Pfeifer, D. Avnir, *J. Chem. Phys.* 79 (1983) 3558; D. Avnir, D. Farin, P. Pfeifer, *J. Chem. Phys.* 79 (1983) 3566.
- [21] D. Romen, A. Gómez, J.G. Pérez-Ramírez, R. Silva, O.L. Pérez, A.E. González, M. José-Yacamán, *Phys. Rev. Lett.* 57 (1986) 2552.
- [22] F. Voss, R.B. Laibowitz, E.I. Alessandrini, *Phys. Rev. Lett.* 49 (1982) 1441; A. Kapitulnik, G. Deutscher, *Phys. Rev. Lett.* 49 (1982) 1444.
- [23] G. Schlifer, W. Klein, P.J. Reynolds, H.E. Stanley, *J. Phys. A Math. Gen.* 12 (1979) L169.
- [24] A. Bunde, S. Havlin (Eds.), *Fractals and Disordered Systems*, Springer-Verlag, Berlin, 1996, and references therein; D. Stauffer, *Introduction to the Percolation Theory*, Taylor & Francis, London, 1985.
- [25] P. Grassberger, *Physica A* 262 (1999) 251.
- [26] A. Coniglio, *J. Phys. A Math. Gen.* 15 (1982) 3829.
- [27] H.J. Herrmann, H.E. Stanley, *Phys. Rev. Lett.* 53 (1984) 1121.
- [28] R. Kopelman, *J. Stat. Phys.* 42 (1986) 185.
- [29] H.J. Herrmann, D.C. Hong, H.E. Stanley, *J. Phys. A Math. Gen.* 17 (1984) L261.
- [30] E.V. Albano, *Surf. Sci.* 235 (1990) 351.