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Critical and oscillatory behavior of a dimer-monomer catalyzed reaction process

Ezequiel V. Albano*
Facultad de Ciencias Exactas, Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas,
Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

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A lattice-gas model for the catalyzed reaction $A+(1/2)B_2\rightarrow AB$ is studied. The model assumes that the catalyst's surface undergoes reactant-induced reversible phase transitions between stable and reconstructed phases, in the low and high A-coverage limits, respectively. The model exhibits a reversible transition between a regime of high reactivity and a state where reactivity is almost negligible. The structural transitions of the surface coupled with reactant coverages causes an oscillatory behavior in the high-reactivity regime of the reaction. [S1063-651X(98)03106-7]

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Since the early work of Ziff, Gulari, and Barshad [1], the interest in lattice-gas reaction systems has experienced a dramatic growth; see, e.g., [2,3] for recent reviews. Simple models aimed to account for relevant features of actual reaction systems such as the catalytic oxidation of CO [1,4], the reaction of CO and NO [5], and the oxidation of hydrogen [6], among others [2,3], have been studied extensively due to their rich and complex behavior, which includes irreversible phase transitions (IPT's), bistability, propagation of chemical waves, and chaos [1–6].

The purpose of this work is to propose and study a dimer-monomer model [namely, the dimer-monomer reaction (DMR) model] that includes adsorbate-induced surface reconstructions, as well as diffusion and desorption of A species. While the DMR is not intended to thoroughly describe any actual catalytic process, it may be considered as a substantial improvement of the early Ziff-Gulari-Barshad (ZGB) model and related lattice-gas models investigated previously [1–4].

The ZGB model [1] assumes a Langmuir-Hinshelwood mechanism, i.e.,

$$A(g)+S \underset{k_{Ade}=0}{\overset{k_{Aad}=\infty}{\rightleftharpoons}} A(a), \tag{1}$$

$$B_2(g)+2S \underset{k_{Bde}=0}{\overset{k_{Bad}=\infty}{\rightleftharpoons}} 2B(a), \tag{2}$$

$$A(a)+B(a) \underset{k_D=0}{\overset{k_R=\infty}{\rightleftharpoons}} AB(g)+2S, \tag{3}$$

where S is an empty site on the surface and (a) and (g) refer to the adsorbed and gas phases, respectively. Adsorption of A and B_2 species is very fast, i.e., $k_{Aad}=\infty$ and $k_{Bad}=\infty$, respectively, while desorption of both reactants is negligible, i.e., $k_{Ade}=k_{Bde}=0$. Also, the reaction is very fast $k_R=\infty$, but readsorption and dissociation of the product is negligible $k_D=0$. The relative impingement rates of A and B_2 species, which are proportional to their partial pressures, are normalized $(Y_A+Y_B=1)$, so the model has a single parameter, namely, Y_A. For more details on the ZGB model see, e.g., [1,3]. The ZGB model is a rough approach to the catalytic oxidation of carbon monoxide, i.e., A is CO, B_2 is O_2, and AB is CO_2. In fact, the main shortcomings of the ZGB model can be summarized as follows. (a) In the low Y_A limit, the model predicts the existence of an absorbing phase where the surface becomes fully covered by B species. This phase is not observed in actual experiments [7]. (b) Within the medium range of Y_A, the ZGB model has a reactive phase with AB production (see, e.g., Fig. 1). A smooth IPT between the reactive state and the B absorbing phase is predicted. However, such second-order IPT's, which are very well understood [8], have never been observed in actual systems. (c) In the high Y_A limit the ZGB model predicts a surface poisoned state with A species that is not observed in actual experiments due to the desorption of CO [7]. Also, an abrupt IPT between the reactive state and the A poisoned one is predicted (see Fig. 1). Actual experiments also show an abrupt decrease in the rate of CO_2 production at a certain critical pressure; however, the observed transition is reversible due to CO desorption [7]. (d) While diffusion and desorption of oxygen can be neglected [9,10], this is not the case of CO, because such molecules exhibit high surface mobility and appreciable desorption [7,9,10]. (e) The oscillatory behavior of the reactants and the product is very well documented (see, e.g., [9–11]), but is not accounted for within the framework of the ZGB model.

The oxidation of CO on Pt surfaces exhibits oscillatory behavior, within a restricted range of pressures and temperatures. Such oscillations are coupled with adsorbate-induced surface phase transitions (AISPT's) [9,10]. In their clean states the reconstructed surfaces of some crystallographic planes, e.g., Pt(100) and Pt(110), are thermodynamically stable. However, the reconstruction can be lifted by adsorbed species such as CO, NO, and O_2. So the atoms of the topmost layer move back into their 1×1 positions. The AISPT

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*FAX: 0054-21-254642. Electronic address: ealbano@isis.unlp.edu.ar

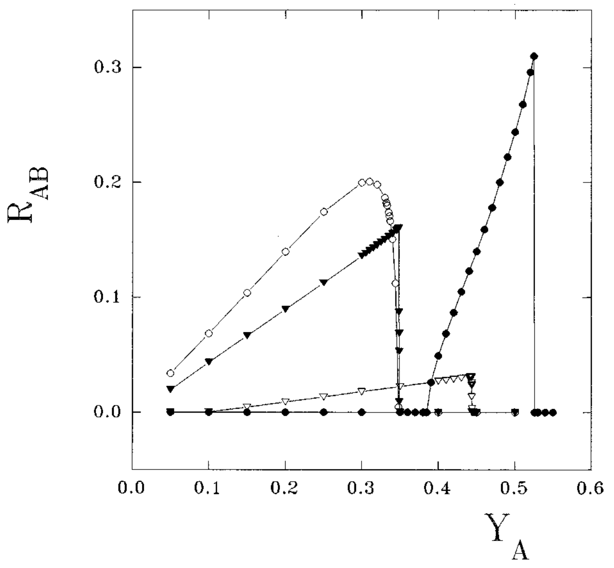

FIG. 1. Plots of the rate of AB production (R_{AB}) versus Y_A. The results of the ZGB model are denoted by ●. The results of the DMR model are obtained with $L_p = 3$ LU, $P_{De} = 0.01$, and $K_{Di} = 0$ (○), $K_{Di} = 1$ (▼), and $K_{Di} = 10$ (▽), respectively.

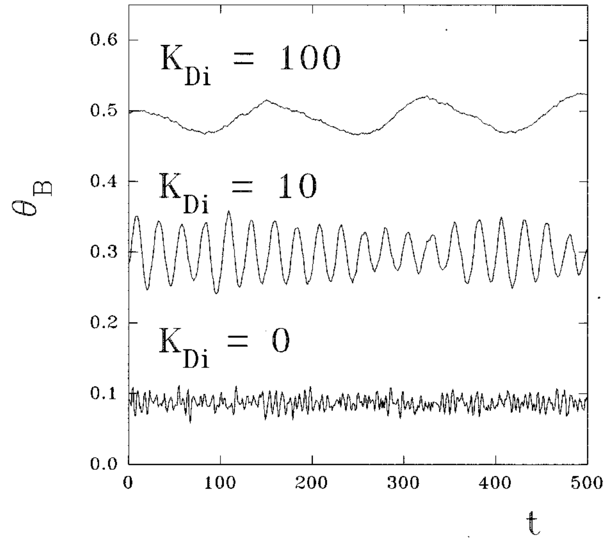

FIG. 2. Plots of θ_B versus time, measured in MCTS's, for the DMR model with $L = 528$ LU, $L_p = 8$ LU, $P_{De} = 0.01$, and the values of K_{Di} indicated in the figure. Plots corresponding to $K_{Di} = 10$ and $K_{Di} = 100$ have been shifted up by 0.20 and 0.40 for the sake of clarity, respectively.

between the reconstructed and the 1×1 phases is reversible and it can be driven by critical adsorbate coverages. For a detailed discussion of the nature of the AISPT's see [9,10]. On Pt surfaces the O_2 sticking coefficient (S_{O_2}) is highly structure dependent, and since the oscillations occur when oxygen adsorption is rate limiting, the catalytic activity is thus periodically modulated by the AISPT's. On Pt(100), one has $S_{O_2} \cong 0.1$ on the 1×1 phase, while a drastic decrease of about two to three orders of magnitude is observed for the reconstructed phase. Then a single oscillatory cycle can be described as follows (see the schema below) [9]:

CO coverage	Surface structure	O_2 adsorption	Catalytic activity
high	1×1	S_{O_2} large	high
low	reconstructed	S_{O_2} small	low

It should be noted that, recently, a different mechanism for the occurrence of oscillations has been proposed [12].

The DMR model is formulated on a square lattice of side L, measured in lattice units (LU), which represents the catalytic surface. We first describe the model that assumes the global reconstruction of the surface. Let θ_{1A} and θ_{2A} be the critical coverages at which the AISPT's take place and S_{1B_2} and S_{2B_2} the corresponding sticking probabilities of B_2 species. The Monte Carlo algorithm for the simulation is as follows. (i) A or B_2 molecules are selected randomly with relative probabilities Y_A and $Y_B = 1 - Y_A$, respectively. If the selected species is A, one surface site is selected at random; if that site is vacant, A is adsorbed on it [Eq. (1)]. Otherwise, if that site is occupied, the trial ends and a new molecule is selected. If the selected species is B_2, a pair of nearest-neighbor sites is selected at random. Only if they are both vacant adsorption proceeds according to Eq. (2), but with probabilities S_{1B_2} or S_{2B_2} depending on the local structure of the surface. (ii) After each adsorption event, the nearest-neighbor sites of the added molecule are examined in order to account for the reaction given by Eq. (3). If more than one $[B(a),A(a)]$ pair is identified, a single one is selected at random and removed from the surface. Also, it is assumed that A desorption proceeds with probability P_{De}, while the rate of A diffusion relative to the total rate of adsorption is given by K_{Di}.

In order to account for *local reconstructions* of the surface, the lattice of size $L \times L$ is due to the addition of small patches of size $L_p \times L_p$, such as $L = nL_p$, where n is an integer with $n \gg 1$. Each atom of a dimer can adsorb on adjacent patches and also neighboring A and B species adsorbed on different patches are allowed to react. The reconstruction of the individual patches are now triggered by local coverages of A species. It should be noted that other reaction models including AISPT's have also been proposed [13].

The Monte Carlo time step (MCTS) involves L^2 trials. The first 10^4 MCTS's are disregarded and then the subsequent 8×10^4 MCTS's are used to compute stationary quan-

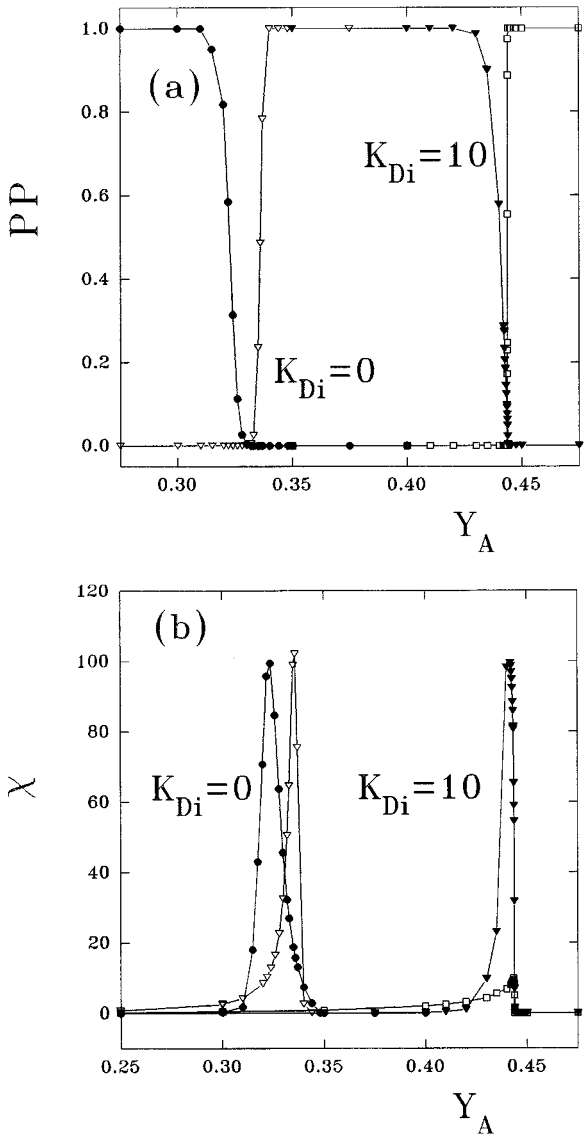

FIG. 3. Plots of (a) the percolation probability (PP) and (b) the susceptibility χ, versus Y_A, for the DMR model with $L_p=3$ LU and $P_{De}=0.01$. The plots of the left (right) correspond to $K_{Di}=0$ ($K_{Di}=10$), respectively. ● and ▽ are the PP's of patches of the nonreconstructed surface, while ▼ and □ are the PP's of patches of the reconstructed surface.

tities, i.e., the coverages with A and B species given by θ_A and θ_B, and the rate of AB production R_{AB}, respectively. Simulations are performed assuming $S_{1B_2}=1.0$, $S_{2B_2}=0.0$, $\theta_{1A}=0.10$, and $\theta_{2A}=0.485$. It is found that variations of these parameters cause only qualitative changes in the results. Most simulations are performed with lattices of side $L=258$ LU (close to critical thresholds $L=516$ LU are also used) and patches of side $L_p=3$ LU.

Figure 1 shows plots of R_{AB} vs Y_A for both the ZGB and the DMR models. The ZGB model exhibits IPT's between the reactive regime and poisoned states at the critical points $Y_{1A}\cong 0.3905$ and $Y_{2A}\cong 0.525$. Such IPT's are of second and first order, respectively. In contrast, for the DMR model, the introduction of AISPT's inhibits the B poisoned state. Also, this model shows a transition from the reactive regime to an almost A poisoned state. Such a transition is reversible due to A desorption, as previously pointed out [14], also in agreement with experiments [7]. The transition is rounded-off when A diffusion is neglected ($K_{Di}=0$) and it takes place close to $Y_{2A}\cong 0.346\pm 0.002$. However, transitions become abrupt for $K_{Di}\geqslant 1$ (see Fig. 1), taking place close to $Y_{2A}\cong 0.3495\pm 0.0005$ and $Y_{2A}\cong 0.443\,85\pm 0.000\,15$ for $K_{Di}=1$ and $K_{Di}=10$, respectively. For $K_{Di}=0$, the patches of the surface are almost uncorrelated, except for adsorption and reaction events at the boundary between neighboring patches. So the output of the product is due to the contribution of many independent regions of the surface, which may be in different reconstructed phases and consequently the averaged value of R_{AB} is smoothed close to the transition. This behavior is no longer observed when A diffusion introduces long-range correlations and the state of the surface becomes more homogeneous on a global scale. These statements are supported by plots of the time dependence of θ_B shown in Fig. 2 (θ_A and R_{AB} exhibit similar behavior). For $K_{Di}=0$, the uncorrelated contribution of the patches gives a strongly irregular ''oscillatory'' behavior. For $K_{Di}=10$, the pattern becomes clearly oscillatory, but both the amplitude and the period of the oscillation remain irregular. For $K_{Di}=100$, due to the high mobility of A species, the oscillatory behavior is quite regular, suggesting the cooperative behavior of the patches on a global scale. In this case, results are similar to those of the DMR model with global reconstruction. These findings are also in qualitative agreement with experiments [9–11].

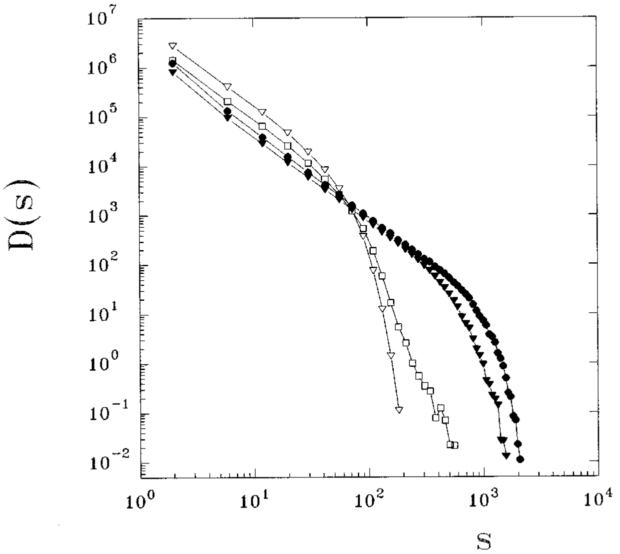

FIG. 4. Plots of the cluster size distribution [$D(s)$ versus s] for the DMR model with $L_p=3$ LU, $P_{De}=0.01$, and $K_{Di}=10$. ● and ▼ correspond to clusters of patches of the nonreconstructed and reconstructed surfaces measured at criticality, respectively. □ and ▽ correspond to clusters of patches of the nonreconstructed and reconstructed surfaces measured off criticality, respectively.

From the theoretical questions of view, however, some interesting points remain unanswered and would merit further investigation, e.g., will globally coherent oscillations persist in the thermodynamic limit with K_{Di} finite or will the reaction proceed essentially independent in widely separated regions. We expect that a finite-size analysis, using larger lattices (beyond our capability, i.e., $L=256$ and 518 LU), would be useful to clarify this topic. This subject is also related to the possible propagation of chemical waves, as experimentally observed [9,10]. Also, the study of the power spectra for long-time series would provide valuable information on the oscillatory regime [15].

Based on analogies between the oxidation of CO and a forest-fire model with spontaneous lightning [16], it has been conjectured [17] that the surface of the catalyst may be in a self-organized-critical (SOC) [18] state in the sense that one may expect clusters of patches, in the same reconstructed state, spanning over all sizes, i.e., extended over all length scales. So relevant properties of clusters formed by neighboring patches at the same reconstructed state have been evaluated. Figure 3(a) shows of the probability of a cluster spanning the whole lattice, i.e., the so-called percolation probability (PP) [19], vs Y_A. Clusters of both types of reconstructed surfaces pass through critical edges where the PP changes from 1 to 0 and vice versa. The existence of these critical points is also well documented in Fig. 3(b), which shows plots of the fluctuations of clusters sizes, i.e., the so-called susceptibility in the terminology of percolation theory and magnetic critical phenomena [19]. The critical percolation edges are close to $Y_A \cong 0.324 \pm 0.001$ and $Y_A \cong 0.3336 \pm 0.001$ for $K_{Di} = 1$ for the unreconstructed and stable phases, respectively. These figures are shifted towards $Y_A \cong 0.442 \pm 0.001$ and $Y_A \cong 0.4435 \pm 0.0002$ for $K_{Di} = 10$, respectively. So the results shown in Fig. 3 suggest that criticality may occur only for certain critical values of the external parameter Y_A, in contrast to the SOC hypothesis, which requires scale invariance independently of any externally tunable parameter [18]. The cluster size distribution $D(s)$ has also been evaluated, where $D(s)$ gives the normalized number of clusters of size s disregarding the biggest cluster [19]. Figure 4 shows that scale invariance is observed only at the critical thresholds determined earlier (see Fig. 3). Figure 4 also suggests the validity of the standard power-law behavior $D(s) \propto s^{-\tau}$, which holds at criticality [19], where τ is an exponent. Results for $K_{Di} = 1$, 10, and 100 are consistent with $\tau \simeq 2.04 \pm 0.03$. Furthermore, plots of the cluster radii of gyration versus cluster size (not shown here for the sake of space) are consistent with fractal clusters of dimension $D_F \simeq 1.90 \pm 0.03$. These figures are in agreement with the exponents of standard percolation in two dimensions, which are exactly known [19], namely, $\tau = 187/91 \cong 2.055$ and $D_F = 91/48 \cong 1.895$ [20], suggesting that clusters of patches at the critical edges are percolating clusters.

Summing up, a dimer-monomer lattice-gas reaction model that generalizes the well-known ZGB model, in order to account for AISPT's in the structure of the catalyst, as well as surface diffusion and desorption of A species, is introduced and studied. The results obtained have many points of qualitative agreement with the experimentally observed behavior of the catalytic oxidation of CO. It is suggested that the model exhibits self-organized collective behavior, but it cannot be claimed to be SOC.

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[20] Notice the validity, within error bars, of the scaling relationship $\tau - 1 = 2/D_F$.